

GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen
Universiteit Utrecht

No. 171

**Geochemistry of trace metals
in the Scheldt estuary**



Gertjan Zwolsman

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Geochemistry of trace metals in the Scheldt estuary

Geochemisch gedrag van zware metalen in het Schelde-estuarium

(met een samenvatting in het Nederlands en het Frans)

Proefschrift

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Promotor: Prof. Dr. C.H. van der Weijden

Co-promotor: Dr. G.Th.M. van Eck

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*For what are we
Without hope in our hearts
That someday we'll drink from God's blessed waters
And eat the fruit from the vine
I know love and fortune will be mine
Somewhere across the border*

Bruce Springsteen

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Samenvatting

Inleiding

Dit proefschrift behandelt het geochemische gedrag van zware metalen in het Schelde estuarium. Het studiegebied is gelegen tussen Rupelmonde (15 km bovenstrooms van Antwerpen) en Vlissingen, een traject van ca. 100 km. Het gedrag van zware metalen is onderzocht in de waterfase, het zwevende stof, de waterbodem (sediment) en in intergetijdegebieden (platen en schorren). De waterkolom is bemonsterd tussen februari 1987 en februari 1988. De schorren zijn bemonsterd in september 1987; gedetailleerde sediment- en poriewaterprofielen zijn opgenomen tussen maart en juni 1989. Voor de waterbodem was een grote dataset beschikbaar over de periode 1959-1990. Een tweede monstercampagne voor water en zwevend stof heeft plaatsgevonden tussen mei 1995 en juni 1996. De resultaten van deze campagne worden eveneens (summier) besproken en vergeleken met de resultaten van de campagne uit 1987-1988.

In het Schelde estuarium wordt het zoete rivierwater geleidelijk vermengd met (schoon) zeeewater. Deze menging zorgt voor een autonome verbetering van de waterkwaliteit. Andere fysische processen die een belangrijke rol in het estuarium spelen zijn sedimentatie (bezinking) van zwevend stof en resuspensie (opwerveling) van bodemslib. Daarnaast treedt een groot aantal geochemische processen op in het estuarium, waaronder afbraak van organisch materiaal (mineralisatie), omzetting van ammonium in nitraat (nitrificatie) en beluchting (re-aeratie). Deze processen zijn van invloed op het (geochemische) gedrag van zware metalen. De geochemie van zware metalen is bestudeerd in relatie tot het zoutgehalte van het water (de saliniteit, S). Specifieke zones die kunnen worden onderscheiden in het Schelde estuarium zijn het instromende rivierwater ($S < 0.5$), de laag-saliene zone ($1 < S < 5$), de brakwaterzone ($5 < S < 20$) en de mariene zone ($20 < S < 30$). Zeeewater heeft een saliniteit van 35.

Gedrag van opgeloste metalen (cadmium, koper, zink)

Het gedrag van opgeloste zware metalen in het estuarium wordt in sterke mate bepaald door de zuurstofconcentratie van het instromende rivierwater. In het zomerhalfjaar (april t/m september) is het rivierwater vaak zuurstofloos en bevat het sporen aan opgelost sulfide. Dit heeft tot gevolg dat de concentraties aan opgeloste metalen in het rivierwater vaak zeer laag zijn gedurende het zomerhalfjaar, vanwege vorming van slecht oplosbare metaalsulfides. Gedurende de winter is de Schelde niet geheel zuurstofloos, zodat vorming van metaalsulfides in de waterkolom niet optreedt. De opgeloste metaalconcentraties in het rivierwater zijn daarom relatief hoog in de winter.

In de laag-saliene zone, die meestal rond Antwerpen ligt, wordt vaak een concentratie-minimum gevonden voor opgelost koper en zink. Dit kan worden verklaard door adsorptie aan opgewerveld bodemslib (rijk aan sulfides) en adsorptie aan ijzer- en mangaanoxides. Deze laatste worden gevormd in de waterkolom door oxidatie van gereduceerde ijzer en mangaanverbindingen. Ijzer- en mangaanoxides staan bekend om hun grote vermogen tot adsorptie van zware metalen.

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Na passage van de laag-saliene zone nemen de concentraties aan opgelost cadmium, koper en zink weer toe. Maximale concentraties worden bereikt in de brakwaterzone, bij een saliniteit van 6-9 (zink) en 9-21 (cadmium en koper). Deze pieken kunnen niet worden verklaard door industriële lozingen, maar wel door geochemische processen. Het zwevende stof in de waterkolom bevat metaalsulfides, afkomstig uit het zuurstofloze rivierwater en/of uit de waterbodem. Deze sulfides kunnen alleen maar bestaan in afwezigheid van zuurstof. Tijdens het transport door de brakwaterzone neemt het zuurstofgehalte van de waterkolom snel toe, waardoor de metaalsulfides worden geoxideerd. Hierbij komen de gebonden zware metalen weer vrij (mobilisatie). Een tweede bron van opgeloste zware metalen zijn de schorren en de platen in de brakwaterzone, waar ook mobilisatie van zware metalen is gevonden. In de mariene zone nemen de concentraties aan opgeloste zware metalen weer af. Mobilisatie van zware metalen speelt hier geen grote rol meer, zodat de concentraties slechts worden bepaald door continue verdunning met zeewater.

In de mariene zone kan het fytoplankton zich sterk ontwikkelen tussen april en juni. Deze zgn. voorjaarsbloeï is van invloed op de concentraties aan opgelost cadmium en zink, die dan bijzonder laag zijn. Dit kan worden verklaard door opname van cadmium en zink door het fytoplankton, maar ook door adsorptie van cadmium en zink aan zwevend stof. Deze adsorptie is het gevolg van de stijging van de zuurgraad (pH), die wordt veroorzaakt door de ontwikkeling van het fytoplankton (fotosynthese).

Gedrag van zware metalen in zwevend stof

De gehalten aan zware metalen in het zwevende stof nemen continu af in zeewaartse richting. Hetzelfde geldt voor de gehalten in de waterbodem, indien wordt gecorrigeerd voor verschillen in korrelgrootte. Dit patroon kan eenvoudig worden verklaard door menging van rivierslib en zeeslib in het estuarium. Het effect van mobilisatie op de samenstelling van het zwevende stof is betrekkelijk gering. Dit kan worden verklaard door het feit, dat de bijdrage van opgeloste metalen aan de totale concentratie relatief gering is in de brakwaterzone (voor cadmium, koper en zink).

Geochemische processen die de samenstelling van het zwevende stof sterk beïnvloeden zijn opwerveling van bodemslib in de laag-saliene zone, de vorming van ijzer- en mangaanoxides, en planktonbloeï in de mariene zone. Opwerveling van bodemslib komt tot uiting in een verhoogd sulfide-gehalte van het zwevende stof in de laag-saliene zone. De waterbodem in de laag-saliene zone lijkt een belangrijke bron te zijn van opgelost (gereduceerd) ijzer en mangaan. Bij het vrijkomen in de waterkolom wordt opgelost ijzer ter plekke geoxideerd, terwijl oxidatie van opgelost mangaan later plaatsvindt, in de brakwaterzone. De hierbij gevormde mangaanoxides verwijderen nikkel en kobalt uit de waterfase (coprecipitatie). Planktonbloeï leidt tot een verhoging van het gehalte aan biogene elementen in het zwevende stof (zoals koolstof en stikstof), ten koste van lithogene elementen (zoals aluminium en ijzer). Ook de gehalten aan zware metalen in zwevend stof zijn relatief laag tijdens een planktonbloeï, met uitzondering van cadmium. Dit betekent dat het metaalgehalte van fytoplankton lager is dan dat van het minerale deel van het zwevende stof.

De gehalten aan zware metalen in het zwevende stof zijn sterk afgenomen tussen 1980 en 1995. Het huidige cadmium gehalte in zwevend stof uit de rivier de Schelde is acht maal zo laag als dat van eind jaren zeventig; de gehalten aan koper en zink zijn ca. twee maal zo laag

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als die van eind jaren zeventig. Ook voor andere metalen is een afname van de vervuiling te constateren na 1980. Het mangaangehalte van het rivierslib is nu ruim twee maal zo hoog als dat in 1974, hetgeen kan worden verklaard door de verbetering van de zuurstofhuishouding van het Scheldewater.

Gedrag van zware metalen in sediment en poriewater

Het metaalgehalte van de waterbodem wordt in sterke mate bepaald door de korrelgrootte van het sediment, en door menging van rivierslib en zeeslib. De invloed van processen op de samenstelling van de waterbodem is relatief gering, behalve voor cadmium, dat vrijkomt uit het sediment in de brakwaterzone. De geringe reactiviteit van zware metalen in sediment uit de laag-saliene zone hangt samen met het feit, dat deze sedimenten sterk reducerend zijn. Dit wordt veroorzaakt door het hoge organisch-stofgehalte van deze sedimenten en het lage zuurstofgehalte van het bovenliggende water. Door de reducerende condities worden zware metalen effectief vastgelegd, met name als metaalsulfides. De concentraties aan zware metalen in het poriewater zijn dan ook zeer laag. Ook in de mariene sedimenten lijkt de reactiviteit van zware metalen minder groot te zijn, wat mogelijk kan worden verklaard door het feit dat het hier recent afgezette sedimenten betreft.

In de intergetijdegebieden van de brakwaterzone is de invloed van processen veel groter. Dit wordt veroorzaakt door de periodieke beluchting van deze sedimenten, die droogvallen bij laag water. Als gevolg hiervan is de toplaag van intergetijde-sedimenten niet gereduceerd, zoals het geval is met sedimenten die permanent onder water staan, maar relatief oxiderend. De redox-potentiaal van deze sedimenten verschuift van oxiderend in de toplaag naar reducerend in de diepere lagen (beneden 10 cm diepte). Deze gradiënt in de redox-potentiaal is van grote invloed op het gedrag van zware metalen. In de oxiderende toplaag van het sediment komen zware metalen vrij door afbraak van organisch materiaal en oxidatie van sulfides. Dit blijkt uit een sterke concentratiepiek van cadmium, koper en zink in het poriewater van de toplaag van het sediment. Dieper in het sediment, waar sulfaat reductie optreedt, slaan de metalen vermoedelijk neer als sulfides. Dit blijkt uit de zeer lage concentraties aan metalen in het poriewater in de gereduceerde zone.

Gedrag van zware metalen in schorren

In twee schorren van de brakwaterzone zijn gedetailleerde diepte-profielen van zware metalen bepaald. Het doel hiervan was om de vervuiling van het estuarium met zware metalen te reconstrueren. Al snel bleek echter, dat de reactiviteit van zware metalen in schorren zeer groot is. Na afzetting van zwevend stof op een schor treedt mobilisatie van zware metalen op, analoog aan wat is beschreven voor sedimenten in intergetijdegebieden. Deze mobilisatie houdt verband met de zuurstofhoudende toplaag in schorren, die wel 40 cm diep kan zijn. Zo wordt ca. 50% van de cadmium aanvoer via het zwevende stof gemobiliseerd. Gelet op het grote areaal aan schorren in de brakwaterzone, kan worden verondersteld dat schorren een aanzienlijke bron kunnen zijn van opgeloste metalen in het Schelde estuarium.

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Ondanks de sterke beïnvloeding van de metaalprofielen door geochemische processen (diagenese), was het mogelijk om een reconstructie uit te voeren van de vervuilingshistorie van het estuarium. Twee periodes kunnen worden onderscheiden waarin de belasting met metalen zeer groot was, nl. rondom 1965 en aan het eind van de jaren zeventig. Na 1980 is de metaalbelasting sterk verminderd, wat eveneens blijkt uit de ontwikkeling van de kwaliteit van het zwevende stof.

Modellering van het gedrag van zware metalen

De kennis over het gedrag van zware metalen in het Schelde estuarium is gebruikt voor het opstellen van een wiskundig model, waarmee het effect van beleidsopties (zoals vermindering van lozingen) op de waterkwaliteit kan worden voorspeld. De mobilisatie van zware metalen wordt modelmatig beschreven door oxidatie van metaalsulfides als functie van het zuurstofgehalte en de temperatuur. Overige processen die in het model zijn opgenomen zijn adsorptie-desorptie reacties en menging van rivierslib en zeeslib. Met het model konden de meetgegevens uit 1987 redelijk tot goed worden gereproduceerd. Tevens bleek het mogelijk om met het model historische meetgegevens voor opgelost cadmium (kwalitatief) en zink (kwantitatief) te reproduceren. Het model lijkt dus geschikt om een rol te spelen bij het toekomstige beleid en beheer van het Schelde estuarium.

Een blik op de toekomst

Uit dit onderzoek blijkt dat het gedrag van zware metalen in het Schelde estuarium in sterke mate wordt bepaald door de zuurstofhuishouding. In de jaren negentig is de zuurstofhuishouding van de Schelde geleidelijk verbeterd. Tegelijkertijd is ook de belasting met zware metalen verminderd, hetgeen blijkt uit de verbetering van de kwaliteit van het zwevende stof. Deze verbetering is echter in het algemeen niet terug te vinden in de concentraties aan opgeloste metalen in het Schelde estuarium. Zo is de concentratie aan opgelost zink onveranderd (hoog) gebleven en is de concentratie aan opgelost koper zelfs gestegen. Dit kan worden verklaard door de toename van zuurstof in het water, waardoor de oxydatie van metaalsulfides in het zwevende stof is toegenomen. Ook de nalevering van zware metalen uit de (gereduceerde) waterbodem van de laag-saliene zone zal toenemen indien zuurstof weer terugkeert in de waterkolom. Deze mobilisatie is nadelig voor het ecosysteem, omdat opgeloste metalen in het algemeen beter kunnen worden opgenomen door organismen dan aan zwevend stof gebonden metalen.

Herstel van de zuurstofhuishouding is één van de belangrijkste doelstellingen van het huidige beheer van het Schelde estuarium. Uit dit proefschrift blijkt nu dat realisatie van deze doelstelling, wat overigens een zaak van lange adem is, leidt tot ongewenste neveneffecten, zoals mobilisatie van zware metalen. Het is dus gevaarlijk om het waterkwaliteitsbeheer te baseren op simpele doelstellingen. Naast herstel van de zuurstofhuishouding is blijvende aandacht gewenst voor vermindering van lozingen en sanering van de verontreinigde waterbodems in het stroomgebied van de Schelde. Hierdoor zal de kwaliteit van het zwevende stof verbeteren, waardoor de mobilisatie van zware metalen in het estuarium, en daarmee het risico voor organismen, zal afnemen.

Résumé

La distribution des métaux traces a été étudiée dans les compartiments abiotiques de l'estuaire de l'Escaut (colonne d'eau et sédiment). Des campagnes saisonnières, menées en 1987 et 1988, indiquent que la géochimie des métaux traces dissouts (Cd, Cu, Zn) est déterminée par le statut redox dans l'estuaire supérieur et par la production primaire dans l'estuaire inférieur. Durant les mois les plus chauds (printemps à automne), l'eau de rivière entrante est anoxique et induit de faibles concentrations en métaux dues à leur précipitation sous forme de sulphides. En hiver, bien que fortement sous-saturée, l'eau de rivière n'est généralement pas entièrement dépourvue d'oxygène, ce qui prévient la précipitation des métaux par les sulphides. En conséquence, les concentrations en métaux dissouts dans l'eau de rivière entrante sont les plus élevées en hiver.

Dans *l'estuaire supérieur* durant l'hiver, les métaux traces dissouts disparaissent de la phase dissoute sous l'effet par exemple de l'adsorption sur des oxyhydroxydes de fer et de manganèse formés dans la colonne d'eau. Le manganèse et le fer dissouts introduits dans la colonne d'eau sont issus d'eaux interstitielles réduites. Après leur rejet depuis le sédiment, le fer dissout est immédiatement oxydé alors qu'une fraction du manganèse réduit est transporté tel quel vers l'estuaire inférieur. La matière en suspension d'origine fluviale (riche en métaux traces) est mélangée au matériel d'origine marine pauvre en métaux et transporté vers l'estuaire supérieur sous l'action de la circulation estuarienne. Une grande partie de la matière en suspension exogène se dépose au niveau du maximum de turbidité situé aux alentours de la ville d'Anvers. La resuspension sédimentaire est importante dans la zone de turbidité maximum en raison des activités de dragage ininterrompues et des courants de marée. En raison des conditions sub-anoxiques de la colonne d'eau, les métaux traces précipitent sous forme de sulphides dans les sédiments superficiels. En conséquence, la mobilité des métaux traces après leur déposition dans les sédiments est probablement insignifiante.

Dans la *partie orientale de l'estuaire inférieur* (saumâtre), les ions manganèse sont oxydés sous l'effet de l'accroissement des concentrations en oxygène dans la colonne d'eau. Des précipitations de nickel et de cobalt associées à la formation des oxydes de manganèse sont également observées dans la colonne d'eau et au niveau des marais salés. Les sulphides de métaux traces dans la matière en suspension, importés depuis l'estuaire supérieur, sont oxydés dans la zone saumâtre conduisant à un maximum de concentration pour le zinc dissout pour des salinités de 6 à 9 ‰ alors qu'un maximum de concentration pour le cadmium et le cuivre dissouts est mesuré en aval pour des salinités comprises entre 9 et 21 ‰. Les eaux interstitielles de la zone saumâtre est à l'origine d'un flux additionnel (non quantifié à ce jour) de métaux traces dissouts vers la colonne d'eau. Un autre flux de métaux traces dirigé vers la colonne d'eau est issu des marais salés qui ne retiennent que partiellement leurs apports particuliers en métaux traces (par exemple, 50% du cadmium capté par les marais salés est relargué). La matière en suspension, transportée de l'estuaire supérieur vers l'estuaire inférieur est progressivement diluée avec du matériel d'origine marine conduisant à une décroissance continue des concentrations en métaux traces dans la matière en suspension (et également

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dans les sédiments) accompagnant l'accroissement des salinités. Les profils de métaux traces dans les sédiments intertidaux de la zone saumâtre semblent être en grande partie déterminés par des processus de dégradation précoces dont l'intensité est à mettre en relation avec la claire zonation des zones redox dans ces sédiments. La mobilité des métaux traces après déposition, est particulièrement prononcée dans les marais salés de l'estuaire inférieur en raison de l'épaisseur de la couche oxygène présente dans ces sédiments (20 à 40 cm).

Dans la *partie occidentale de l'estuaire inférieur* (marine), les métaux traces présentent généralement un caractère conservatif, à l'exception des périodes de blooms phytoplanctoniques. Ce caractère conservatif est principalement dû au fait que la remobilisation des métaux traces à partir de la matière en suspension est achevée (les sulfures de métaux traces ont été entièrement oxydés). D'autre part les échanges entre les sédiments et la colonne d'eau sont également réduits en raison de la granulométrie grossière des sédiments marins (sables moyens et grossiers) et donc de leur faible teneur en métaux traces. Dans les sédiments plus vaseux des zones intertidales, les métaux traces sont partiellement mobilisables, mais ils sont piégés lors de la précipitation des oxyhydroxydes de fer à proximité de l'interface eau-sédiment. Une partie du manganèse s'échappe vers la colonne d'eau, accroissant ainsi de manière sensible les concentrations en manganèse dissout. Le faible impact des processus de dégradation précoce de la matière organique sur la distribution des métaux traces dans les sédiments marins est illustré par le fait que les concentrations sédimentaires en métaux traces sont exclusivement déterminées par la teneur en pélites des sédiments. Les blooms phytoplanctoniques se développant dans l'estuaire inférieur du printemps au début de l'été contribuent à la disparition du cadmium et du zinc de la colonne d'eau. Ces derniers sont, soit directement assimilés par des processus biologiques soit adsorbés sur la matière en suspension sous l'effet promoteur de l'accroissement du pH. La teneur en métaux traces de la matière en suspension a tendance à diminuer durant les blooms phytoplanctoniques, illustrant la dilution des minéraux contaminés par la matière organique produite *in situ*.

Ces caractéristiques du comportement des métaux traces dans l'estuaire de l'Escaut se sont graduellement modifiées au cours des dernières décennies du fait d'un changement des conditions redox. Ces dernières sont en effet déterminantes pour la distribution des métaux traces entre les phases particulaires et dissoutes. Il est suggéré que l'oxydation des sulfures métalliques contenus dans la matière en suspension avait lieu aux cours des années 60 à 70 pour des salinités relativement élevées du fait de la localisation plus en aval (comparée à la situation présente) de la zone de restauration des concentrations en oxygène. De plus, les concentrations en métaux traces (dans les phases particulaires et dissoutes) étaient bien plus élevées dans les années 70 que maintenant en raison de l'importance des rejets à cette époque. Cette idée est supportée par deux campagnes de terrain menées en octobre 1978 et septembre 1979. Dans ces études, de très importants pics de concentrations en cadmium, cuivre et zinc dissouts étaient observés pour des salinités relativement élevées. Après 1980, les conditions d'oxydo-réduction de l'estuaire commencèrent à s'améliorer tandis que les émissions en métaux traces amorçaient leur décroissance. Ces deux évolutions conduisirent à une réduction

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des maxima en métaux traces dans l'estuaire intermédiaire et à leur déplacement en amont vers des zones à salinité plus réduite.

Les caractéristiques majeures de la distribution des métaux traces dans l'estuaire de l'Escaut ont pu être reproduites par un modèle dynamique compartimenté à une dimension. Les processus-clés introduits dans le modèle sont, l'oxydation des sulfures de métaux traces, la complexation par des ligands (les ions chlore par exemple) et le mélange des particules fluviales et marines. Le rôle de l'estuaire de l'Escaut en tant que filtre biogéochimique pour les métaux traces est évalué à l'aide du modèle. Le filtre estuarien tend en général à transformer les émissions particulières de métaux traces au niveau de l'estuaire supérieur en flux de métaux dissouts quittant l'estuaire (à l'exception du manganèse pour lequel l'inverse est observé). L'impact du filtre estuarien a pu être quantifié. Par exemple, pour l'année 1987, il a pu être calculé que la rétention dans l'estuaire pour le cadmium, le cuivre et le zinc était comprise entre 40 et 50%. Ce chiffre correspond à une situation d'équilibre dans laquelle la teneur en métaux traces dans le sédiment est en équilibre avec les apports en métaux traces externes à l'estuaire. Cet état de chose ne correspond cependant pas à la situation présente puisque les teneurs sédimentaires actuelles reflètent des contaminations passées dont le niveau a fortement décliné après 1980.

Dans les années 90, plusieurs évolutions d'importance pour la qualité de l'eau de l'estuaire se sont développées. Il s'agit principalement de la poursuite de la décroissance des émissions de métaux traces, une amélioration graduelle des conditions redox dans l'estuaire supérieur et l'extraction de sédiments pollués de l'estuaire supérieur. Des données récentes sur la qualité générale de l'eau et les concentrations en métaux traces dans l'estuaire de l'Escaut ont pu être recueillies au cours de dix campagnes de prélèvements en 1995/96. Ces résultats ont été comparés à ceux collectés au cours des campagnes 1987/88; la comparaison s'est effectuée au niveau saisonnier (Février, Mai et Août). Cette étude a conduit aux observations suivantes: Au printemps et en été, la rivière est toujours anoxique en 1995/96. Cependant la restauration des concentrations en oxygène se produit plus en amont (pour des salinités plus faibles donc) en 1995 comparé à 1987, ce qui est à mettre en relation avec la diminution du rapport ammonium / nitrate dans l'eau de rivière entrant dans l'estuaire. La meilleure oxygénation de l'estuaire de l'Escaut a également conduit au développement massif d'un phytoplancton d'origine fluviale, plus particulièrement en été. La géochimie du cadmium, cuivre et zinc dissouts présente les mêmes caractéristiques en 1987 et 1995: faibles concentrations en métaux traces dans l'eau de rivière au printemps et en été, s'accroissant en hiver. Dans l'estuaire lui même, le cadmium, cuivre et zinc sont mobilisés vers la phase dissoute. Ce processus a lieu cependant plus en amont (pour des salinités plus faibles donc) en 1995 qu'en 1987 et ce principalement en raison de l'amélioration du potentiel d'oxydo-réduction dans l'estuaire supérieur. En conséquence, la réduction des émissions en métaux traces observée entre 1987 et 1995 (40 à 50% diminution de Cd, Cu et Zn dans la matière en suspension fluviale), ne donne pas lieu à une diminution des concentrations en métaux dissouts dans l'estuaire supérieur. Les concentrations en zinc dissout sont restées inchangées alors que les concentrations estivales en cadmium dissout se sont accrues. Quant au cuivre dissout, ses concentrations sont plus élevées en 1995 qu'en 1987 tout au long de l'année.

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Dans l'avenir, la charge organique de l'estuaire continuera à décroître et les concentrations en oxygène dissout devrait être en voie de restauration partielle ou totale dans l'estuaire supérieur et la zone fluviale du bassin versant. Ces processus sont importants pour la capacité de filtration de l'estuaire en ce qui concerne les métaux traces. La restauration des concentrations en oxygène devrait induire un accroissement des flux de cadmium, cuivre et zinc dissouts depuis les sédiments en raison de la baisse d'intensité de la précipitation des sulphides métalliques à l'interface eau-sédiment. Ce phénomène concerne non seulement les sédiments de l'estuaire supérieur mais également ceux de la rivière Escaut elle-même et de ses affluents (par exemple le Rupel et la Dendre). De plus le piégeage des métaux traces dans la zone de turbidité maximum par les oxyhydroxydes de fer et manganèse devrait décroître en raison de la diminution du flux des ions Fe et Mn réduits depuis le sédiment elle même induite par la meilleure oxygénation de la colonne d'eau sus-jacente. Ainsi, la restauration des concentrations en oxygène dissout dans la rivière Escaut et son estuaire devrait, pour une certaine période, conduire à une augmentation des flux de cadmium, cuivre et zinc vers la zone côtière. Cette tendance sera également maintenue dans le cas d'une poursuite de la diminution des émissions de métaux traces comme c'est le cas aujourd'hui. Les présentes observations ont pour conséquence directe concernant la gestion de l'estuaire que toute poursuite de la restauration des concentrations en oxygène devraient être précédée par le retrait préalable des sédiments contaminés par des métaux de la rivière Escaut, de ses affluents et de l'estuaire supérieur.

Summary

The distribution of trace metals has been studied in abiotic compartments of the Scheldt estuary (water column and sediments). Seasonal surveys, carried out in 1987-1988, indicate that the geochemistry of dissolved trace metals (Cd, Cu, Zn) is determined by the redox status of the upper estuary, and by primary production in the lower estuary. During the warmer period (spring till autumn), the incoming *river water* is anoxic, leading to very low dissolved metal concentrations due to precipitation of metal sulphides. During winter, the river water is usually not completely devoid of oxygen (although highly undersaturated), precluding metal sulphide precipitation. Therefore, the dissolved metal concentrations in the incoming river water are much higher during winter.

In the *upper estuary*, during winter, dissolved trace metals are removed from solution, e.g. by adsorption onto Fe and Mn oxyhydroxides, formed in the water column. Dissolved Mn and Fe are introduced into the water column by inflow of reducing pore-waters. After their release from the sediments, dissolved Fe is immediately oxidised, but part of the dissolved Mn escapes from oxidation and is transported to the lower estuary. The fluvial suspended matter (rich in trace metals) is mixed with metal-poor marine material, transported to the upper estuary by the estuarine circulation. A major part of the suspended matter input is deposited in the high-turbidity zone, around the city of Antwerp. Sediment resuspension is important in the high-turbidity zone, because of continuous dredging and tidal disturbance. Due to the suboxic condition of the water column, trace metals are precipitated as sulphides in the sediments close to the sediment-water interface. This means that post-depositional mobility of trace metals in the sediments is probably insignificant.

In the *eastern* (brackish) part of the *lower estuary*, the incoming dissolved Mn is oxidised, because of the increasing oxygen concentration in the water column. Coprecipitation of Ni and Co with the Mn oxides formed is observed, both in the suspended matter and in the salt marshes. Trace metal sulphides in the suspended matter, imported from the upper estuary, are oxidised in the brackish water zone, leading to a dissolved Zn maximum at relatively low salinity (6-9), whereas the maxima of Cd and Cu occur more seawards in the salinity range 9-21. The pore-waters in the brackish water zone cause an additional (but yet unknown) flux of dissolved trace metals to the water column. Another flux of dissolved trace metals to the brackish water zone comes from the salt marshes, which only partially retain their particulate metal inputs (e.g. 50% of the particulate Cd flux to the marshes is mobilised). The suspended matter, transported from the upper to the lower estuary, is progressively diluted with marine material, leading to continuously decreasing trace metal contents in the suspended matter (and also in the sediments) with increasing salinity. Trace metal profiles in the intertidal sediments of the brackish water zone appear to be significantly influenced by early diagenetic reactions, which is related to the well-resolved spacing of the redox zones in these sediments. Post-depositional mobility of trace metals is even more important in the salt marshes of the lower estuary, because of the thick oxic top layer present in salt marsh sediments (20 to 40 cm).

Summary

In the *western* (marine) part of the *lower estuary*, conservative behaviour of dissolved trace metals is generally observed, except during phytoplankton blooms. The reason for this is that the mobilisation of trace metals from the suspended matter has been terminated (trace metal sulphides have become completely oxidised), whilst sediment-water exchanges are also small because the marine sediments are typically medium to coarse sands, i.e. low in trace metals. In more silty sediments (intertidal flats), trace metals are mobilised to some extent, but they are trapped during precipitation of Fe oxyhydroxides near the sediment-water interface. Some Mn escapes to the water column, increasing the dissolved Mn concentration to a measurable extent. The low impact of early diagenetic processes on the distribution of trace metals in the marine sediments is illustrated by the fact that the sediment trace metal contents are exclusively determined by the amount of silt present in the sediments. Phytoplankton blooms, occurring in the lower estuary from spring to early summer, remove dissolved Cd and Zn from the water column, due to direct biological uptake or enhanced adsorption onto suspended matter, driven by a major increase in pH. The trace metal content of the suspended matter tends to decrease during algae blooms, reflecting dilution of contaminated mineral particles with autochthonous organic matter.

This general picture of trace metal behaviour in the Scheldt estuary has changed gradually in time because the redox conditions, which control the distribution of trace metals among the dissolved and particulate phases, have changed over the years. It is suggested that oxidation of metal sulphides in the suspended matter occurred at relatively high salinities in the sixties and seventies, since the restoration of dissolved oxygen occurred more seawards at that time. Moreover, the concentration levels of dissolved (and particulate) trace metals in the estuary were much higher in the seventies, because of the higher metal inputs. This general view is supported by two historic field surveys, carried out in October 1978 and September 1979. In these surveys, peaks of dissolved Cd, Cu, and Zn were observed at relatively high salinities, with very high concentrations. After 1980, the redox status of the estuary started to improve and the metal inputs began to decrease, reducing the mid-estuary maxima of dissolved trace metals and shifting them to lower salinities.

The major features of trace metal behaviour in the Scheldt estuary could be reproduced by a one-dimensional dynamical box-model. Key processes included in the model are oxidation of trace metal sulphides, complexation with dissolved ligands (e.g. chloride), and mixing of fluvial and marine particulates. The role of the Scheldt estuary as a biogeochemical filter for trace metals was evaluated by the model. In general, the estuarine filter tends to transform the particulate metal inputs entering the upper estuary into dissolved metal fluxes leaving the estuary (except for Mn, for which the opposite is true). The impact of the estuarine filter was quantified. For instance, in the year 1987, it was calculated that the retention of Cd, Cu, and Zn in the estuary was on the order of 40-50%. This figure is applicable to an equilibrium situation, in which the trace metal content in the sediments is in equilibrium with the external trace metal loading of the estuary. At present, however, this is not the case, because the sediments still reflect the history of trace metal contamination of the estuary, which decreased strongly after 1980.

Summary

In the nineties, several developments relevant to the water quality of the estuary have taken place. These are the ongoing reduction of trace metal inputs, a gradual improvement in the redox condition of the upper estuary, and the removal of polluted sediments in the upper estuary. Recent data on general water quality and trace metal concentrations in the Scheldt estuary have been collected during ten surveys in 1995/96. The results of the 1995/96 campaign were compared to the results of the 1987/88 campaign on a seasonal basis (February, May, and August surveys). This comparison leads to the following observations. During spring and summer, the river water is still anoxic (1995/96). However, restoration of dissolved oxygen takes place faster (i.e. at lower salinity) in 1995 than in 1987, which is in keeping with the observed shift from ammonium to nitrate in the incoming river water. The increasing oxygenation of the Scheldt river has also led to a massive development of fresh water phytoplankton, especially during the summer. The geochemistry of dissolved Cd, Cu, and Zn shows similar features in 1987 and 1995, i.e. low dissolved trace metal concentrations in the river water during spring and summer and higher concentrations during the winter. In the estuary, mobilisation of Cd, Cu, and Zn to the dissolved phase occurs. In 1995, however, mobilisation of Cd and Cu takes place faster (at lower salinity) than in 1987, which is related to the improved redox potential of the upper estuary. Therefore, the reduction in trace metal inputs which has taken place between 1987 and 1995 (40-50% for Cd, Cu, and Zn, based on the change in fluvial suspended matter composition), is not reflected by the dissolved trace metal concentrations in the upper estuary. The dissolved Zn concentration has remained the same, dissolved Cd tends to increase during the summer, and dissolved Cu levels have increased over the year in the upper estuary between 1987 and 1995.

In the future, the organic loading of the estuary will further decrease and the dissolved oxygen concentration will be partially or completely restored in the upper estuary and the fluvial part of the drainage basin. This has important consequences for the role played by the estuary as a filter for trace metals. Restoration of dissolved oxygen is expected to increase the outflow of dissolved Cd, Cu, and Zn from the sediments, because metal sulphide precipitation at the sediment-water interface would become less important than it is today. This holds true not only for the sediments of the upper estuary, but also for the sediments of the Scheldt river and its oxygen-depleted tributaries (e.g. the Rupel and the Dender). Moreover, scavenging of trace metals in the high-turbidity zone by Fe and Mn oxyhydroxides will decrease, because the outflow of reduced Fe and Mn from the sediments will be limited if the overlying water column is aerobic. Thus, restoration of dissolved oxygen in the Scheldt river and its estuary may, for a certain period of time, lead to an increase in the flux of dissolved Cd, Cu, and Zn to the coastal zone. This is even so in a situation of decreasing metal inputs, as is the case today. An obvious implication of these findings for the management of the estuary is that restoration of dissolved oxygen should be preceded by removal of the metal-contaminated sediments in the Scheldt river, its tributaries, and in the upper estuary.

Chapter 1

General introduction

1.1. Introduction - The SAWES project

The Scheldt river and its estuary, in ecological respect one of the most important tidal river systems in Europe, is still heavily contaminated by domestic, industrial and agricultural waste loads. Although the situation is less dramatic nowadays than in the sixties and seventies, water quality problems are still manifold. Decomposition of the organic load results in an anoxic water column in the river and upper estuary from spring to late autumn (Somville and De Pauw, 1982). This situation was already manifest in the early fifties (Van Meel, 1958), but in the sixties and seventies the situation deteriorated even further. Without exaggeration, it can be stated that the Scheldt river and its major tributaries were merely an open sewer in the sixties and early seventies. A prime example is provided by the evolution of the dissolved oxygen concentration at the Dutch-Belgian border (Fig. 1.1), reaching an all-time low of 1 mg/l in 1973. In 1971, however, the growing awareness of environmental problems prompted legislation in Belgium (and Holland), aiming to reduce the industrial and domestic waste water discharges. As a result, the water quality of the Scheldt estuary started to improve slowly in the seventies, and this improvement is still going on in the nineties (Van Damme *et al.*, 1995; Van Eck *et al.*, 1998).

The gradual improvement in water quality of the Scheldt estuary during the last two decades is very important because of its high ecological potential (Boeije, 1992). It is generally recognised, both in Holland and Belgium, that ecological recovery of the estuary must be achieved in the framework of integrated water management (Internationaal Schelde-symposium, 1991; 1995). Integrated water management seeks for the optimal balance between the different functions of the estuary, which are transport of water and sediments, navigation, dilution and purification of effluents, ecology, and recreation. Since these functions can be conflicting (e.g. dredging versus ecology), one of the key factors for integrated management of the Scheldt estuary is a sound scientific understanding of its physical, ecological, and geochemical structure. It is for this reason that the Dutch Institute for Marine and Coastal Management (RIKZ) started the SAWES project (System Analysis Western Scheldt) in 1987. The main goals of the SAWES project were to acquire fundamental knowledge with respect to pollution problems of the estuary and to apply this knowledge on an operational level. Insight into the relation between contaminant inputs and their effects on the ecosystem should provide a rational basis for integrated water management and policy development. The knowledge obtained in the SAWES project was implemented in a mathematical water quality model, described in detail by Van Gils *et al.* (1993) and Ouboter *et al.* (1998).

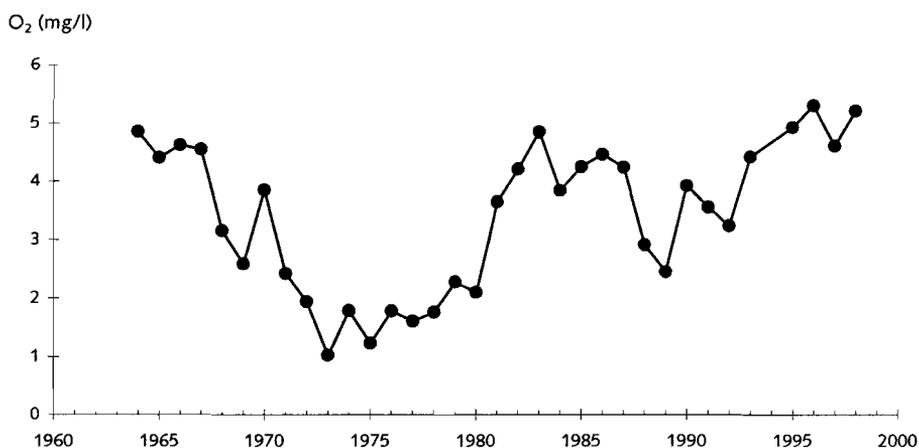


Fig. 1.1. Evolution of the mean annual dissolved oxygen concentration at the Dutch-Belgian border between 1964 and 1998. Data from the water quality monitoring programme of the Netherlands.

1.2. Hydrodynamics of the Scheldt estuary

The hydrographic basin of the river Scheldt covers an area of 21600 km² in northwest France, west Belgium and the southwest Netherlands. The drainage basin is composed of the catchments of numerous small streams, feeding larger tributaries such as the rivers Leie, Dender, and Rupel. The brackish water zone is situated between the confluence of the rivers Scheldt and Rupel and the city of Vlissingen, covering a distance of 100 km (Fig. 1.2). The average annual discharge of the Scheldt river amounted 104 m³/s in the period 1949-1986; the actual river flow varies considerably through the year with a minimum during the summer (up to 20 m³/s) and a maximum during winter (up to 600 m³/s). The hydrodynamical features of the Scheldt estuary can be summarised as follows (Wollast, 1988). The residence time of the water masses in the brackish water zone ranges from one to three months, depending on the river discharge. The estuary is well-mixed (except during peak discharges), which means that vertical salinity gradients are small or negligible. The tidal range increases from 4 m at the mouth to 5 m at the city of Antwerp; downstream from Antwerp the tidal range decreases till 2 m at the city of Ghent. The water depth is 10 m on the average, with a maximum of 40 m in the tidal channels. The estuary can be divided into three zones (Fig. 1.2).

General introduction

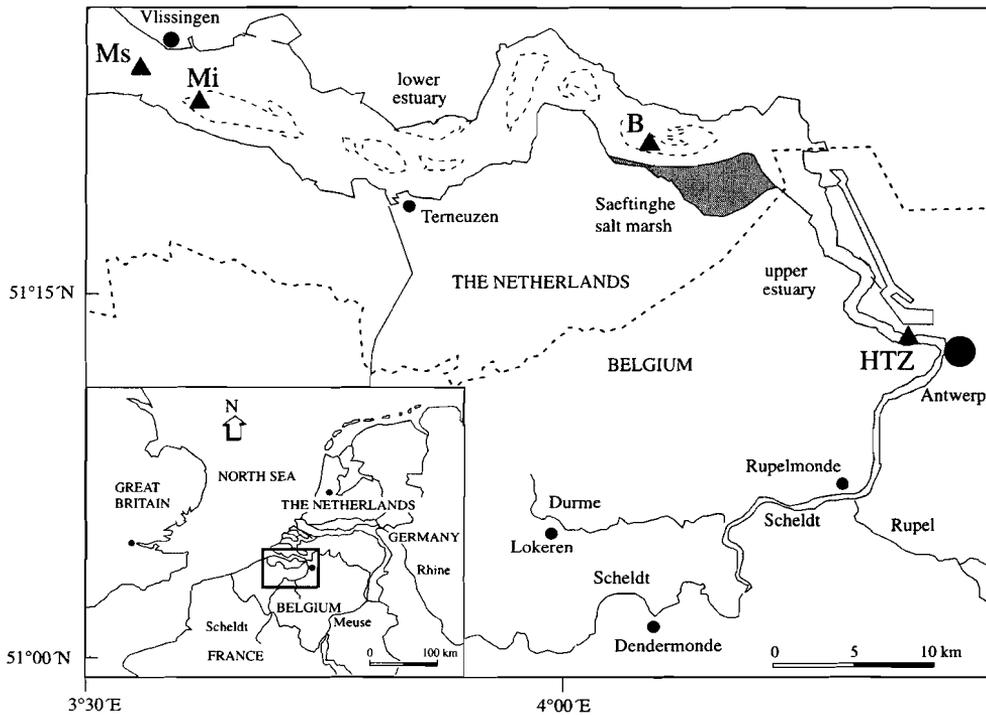


Fig. 1.2. Map of the Scheldt estuary. The upper estuary is situated between the confluence of the Scheldt and Rupel rivers (km 0) and the Dutch-Belgian border (km 40). The lower estuary stretches from the border up to the city of Vlissingen (km 100). Sampling points for sediment cores are indicated by solid triangles (see chapter 6).

- (1) The fluvial estuary, upstream from the confluence of the Scheldt and Rupel rivers, is the freshwater zone subject to tidal influence. This zone was not covered by the present study and will not be considered further.
- (2) The upper estuary, located entirely in Belgium, is heavily polluted by domestic, industrial and agricultural waste loads (Wollast, 1982; Billen *et al.*, 1985). Due to its high organic loading, the water column in the low-salinity zone is frequently anoxic. The length of the anoxic zone depends on temperature and river flow (Somville and De Pauw, 1982). Under unfavourable conditions, i.e. high temperatures and low river flows, the entire upper estuary could be anoxic in the late seventies (Salomons *et al.*, 1981; Duinker *et al.*, 1982^a). The sediments of the upper estuary consist of sands, sandy muds and clayey muds (Wartel, 1977). The finest sediments occur in the so-called high-turbidity zone, situated between the city of Antwerp and the Dutch-Belgian border. Being a major sedimentation area, the high-turbidity zone is dredged intensively in order to keep the port of Antwerp accessible for shipping (Claessens *et al.*, 1991).

- (3) The lower estuary, situated between the Dutch-Belgian border and the North Sea, has a complex morphology with flood and ebb channels surrounded by intertidal sand- and mudflats. The water column is partially oxygenated at the border and fully oxygenated at the mouth. The bottom sediments of the lower estuary consist mainly of medium to coarse sands; mud deposits occur exceptionally (Wartel, 1977). Much finer sediments are found in the salt marshes of the lower estuary (Beeftink *et al.*, 1977). The Saeftinge marsh near the Dutch-Belgian border is an important sedimentation zone. The lower estuary is continuously dredged for navigational purposes (Claessens *et al.*, 1991).

1.3. Previous studies in the Scheldt estuary

Because of its severe contamination, the Scheldt river and its estuary have received much scientific attention in the past (De Pauw, 1971; Bruyneel and Wauters, 1981; Van der Kooij, 1982; De Brabander *et al.*; 1983; Ringele and De Brabander, 1986; Van Loon, 1987; Goethals, 1988; Van Eck *et al.*, 1991). Extensive research programmes have been carried out in Belgium, on behalf of the Belgian Ministry of Science Policy (Programmatie van het Wetenschapsbeleid). These programmes, entitled 'Project Zee' (11 reports in 1976), 'Geconcerteerde onderzoeksacties oceanologie' (reports in 1979 and 1982), and 'Progress in Belgian Oceanographic Research' (reports in 1985 and 1989), were executed by the universities of Brussels, Ghent, Antwerp, and Liège. The focus of the Belgian research was on organic matter decomposition, redox chemistry (Billen *et al.*, 1976; Wollast *et al.*, 1979; Somville and De Pauw, 1982) and nutrient cycling (e.g. Wollast and De Broeu, 1971; Billen, 1975; Wollast, 1982; Billen *et al.*, 1986). In addition, the composition of the suspended matter and the sediments was investigated (Wollast *et al.*, 1973; Wartel, 1977; Wollast and Marijns, 1981; Van Alsenoy *et al.*, 1989). Moreover, several water quality models of the estuary were developed, the first one already in the early seventies (Wollast, 1973; 1976; Baeyens *et al.*, 1981; Billen *et al.*, 1983).

One group of contaminants, which has a long history of contamination in the Scheldt estuary, are trace metals. In spite of this, information on the geochemistry of trace metals in the Scheldt estuary was rather scarce and fragmentary at the beginning of the SAWES project. This was especially the case for dissolved trace metals. Moreover, it should be realised that historic data for dissolved trace metals are generally unreliable, because of serious contamination problems and insufficient sampling and analytical techniques (Shiller and Boyle, 1987; Bowers and Yeats, 1989; Windom *et al.*, 1991^a). Contamination may arise from the materials used in the filtration procedure (filters, filtration block, storage bottles), which should be thoroughly acid-cleaned, or from dust particles entering the water samples (clean-room conditions are necessary). Insufficient sampling techniques are incomplete separation of the dissolved and the particulate phase (settling instead of filtration), and delay in the filtration of the water samples (shipboard filtration is recommended). For these reasons, all the historic monitoring data on dissolved trace metals in the Scheldt estuary should be regarded as

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unreliable (both the Belgian and the Dutch monitoring data). However, some projects have been carried out in which sufficient analytical precautions seem to have been taken. These are the studies of Salomons *et al.* (1981) and Duinker *et al.* (1982^a) on the axial distribution of dissolved and particulate trace metals in the estuary, the study of Valenta *et al.* (1986) on seasonal variation of trace metal partitioning in the lower estuary, and the study of Baeyens *et al.* (1987) on trace metal cycling in the Belgian coastal zone (i.e. the mouth of the estuary).

Contamination problems are less serious for solid-phase analyses of trace metals (suspended matter and sediments). Reliable historic information on trace metal distributions in the suspended matter of the Scheldt estuary was available at the start of the SAWES project (Hoening, 1976; Salomons *et al.*, 1981; Duinker *et al.*, 1982^a; Baeyens *et al.*, 1982). Many studies on the distribution of trace metals in the sediments were also available. However, information on trace metals in the salt marshes of the estuary was scarce (Beefink *et al.*, 1982; Oenema *et al.*, 1988), and information on the pore-water chemistry of trace metals was virtually absent at the start of the SAWES project (Baeyens *et al.*, 1986).

Several studies should be mentioned which were reported after completion of the SAWES project. Comprehensive studies on dissolved and particulate trace metals were carried out in 1981-1983 and 1995 by Baeyens *et al.* (1998^{a,b}) and in 1991-1994 by Paucot and Wollast (1997). The composition of the suspended matter was studied in 1987-1988 by Van Alsenoy *et al.* (1993) and in 1988-1989 by Regnier and Wollast (1993). The trace metal distribution in the pore-waters of the fluvial estuary was studied by Monteny (in prep.). The dynamics of suspended matter transport were studied by Van Maldegem *et al.* (1993) and Verlaan (1998).

1.4. Aim and outline of the present study

In order to obtain the input data for the SAWES model, various sampling campaigns were carried out between 1987 and 1989. Data were collected on the distribution of nutrients, organic contaminants, and trace metals in the abiotic compartments of the estuary (water, suspended matter, sediments). This thesis deals with the results with respect to trace metals. Results for nutrients and trace organic contaminants (PAH, PCB, etc.) are discussed elsewhere (Boderie *et al.*, 1993; Zwolsman, 1994; Van Zoest and Van Eck, 1990; 1991; 1993). The global aim of this work was to investigate the biogeochemistry of trace metals in the Scheldt estuary. The leading research question was: What are the processes controlling the distribution of trace metals among the dissolved and particulate phases, in the water column and in the sediments? Can these processes be translated into model formulations? In the next five chapters, these questions will be addressed, for each abiotic compartment of the Scheldt estuary separately. *Chapter 2* deals with the geochemistry of dissolved Cd, Cu, and Zn, based on eight sampling cruises in 1987-1988. It is shown that the redox gradient in the estuary controls the distribution of these metals among the dissolved and particulate phase, as suggested before by Salomons *et al.* (1981) and Duinker *et al.* (1982^a). In addition, phytoplankton blooms appear to alter the distribution of trace metals in the lower estuary, as

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noted before by Valenta *et al.* (1986). The geochemistry of the suspended matter, based on the same sampling campaign (1987-1988), is discussed in *chapter 3*. The trace metal composition of the suspended matter is primarily controlled by particle mixing processes. The trace metal composition of the sediments is described in *chapter 4*, based on a dataset of three decades (1959-1990). Again, particle mixing processes appear to control the spatial distribution of trace metals in the sediments. *Chapter 5* deals with trace metal profiles in radiodated sediment cores from two salt marshes, sampled in September 1987. Although these profiles have been modified by diagenetic processes to a great extent, they partly reflect the history of trace metal pollution of the Scheldt estuary. The composition of the pore waters in the estuary is discussed in *chapter 6*, based on eight sediment cores collected in 1989. The redox zonation of the sediments appears to control both the dissolved trace metal concentrations at the sediment-water interface, and the impact of diagenetic processes on the solid-phase composition of the sediments. An outline of the water quality model for the Scheldt estuary is presented in *chapter 7*. The model is able to reproduce the redox chemistry and the dissolved and particulate trace metal profiles in the estuary fairly well. In *chapter 8*, recent data on dissolved and particulate trace metals in the Scheldt estuary (1995/96) are summarised and compared to the data used in this study (1987/88). In the time span considered, the general water quality has improved, due to the ongoing purification of effluents and the removal of contaminated sediments in the upper estuary. However, this improvement is not reflected by the dissolved Cd, Cu, and Zn profiles, due to enhanced mobilisation of these metals in the upper estuary, related to the improved redox condition of the water column.

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Geochemistry of dissolved trace metals (Cd, Cu, Zn) in the Scheldt estuary

J.J.G. Zwolsman, G.T.M. Van Eck and C.H. Van der Weijden

Abstract - The distribution of dissolved Cd, Cu, and Zn in the Scheldt estuary has been studied during eight axial surveys, carried out between February 1987 and February 1988. The observed metal-salinity profiles depend on the season. During spring and summer, when the river water is anoxic (containing traces of dissolved sulphide), the dissolved metal concentrations in the riverine end-member are extremely low. This observation is ascribed to formation of sparingly soluble metal sulphides in the water column. During winter, when the river water is not totally devoid of oxygen, the dissolved Cu and Zn concentrations in the riverine end-member are an order of magnitude higher, but rapid removal is apparent in the very low-salinity zone. Flocculation (of organometal complexes) or coagulation (of colloid-associated metals), sediment resuspension and formation of particulate Fe and Mn oxyhydroxides are likely to be involved in the removal process. At higher salinities, maxima of dissolved Cd, Cu, and Zn are consistently found over the year. These maxima are ascribed to dissolution and desorption of particulate metal forms with increasing salinity. Reoxidation of trace metal sulphides during transport from the anoxic (or suboxic) upper estuary to the fully oxygenated lower estuary is suggested as the first step in the mobilisation process. During phytoplankton blooms, desorption of Cd and Zn (but not Cu) is suppressed, which is attributed to the pH increase related to primary production, and to biological uptake. The impact of mobilisation processes in the Scheldt estuary is reflected by effective dissolved Cd and Cu concentrations which are much higher than the observed metal concentrations in the river water. Based on these findings, it is expected that restoration of the dissolved oxygen concentration, which is a major goal of the present-day management of the Scheldt estuary, will lead to an increase in the dissolved metal transport to the North Sea.

2.1. Introduction

The distribution of trace metals in estuaries has been studied extensively during the last two decades for reasons of environmental concern (e.g. Klinkhammer and Bender, 1981; Apte *et al.*, 1990^a) and the development of realistic oceanic mass balances (Boyle *et al.*, 1982; Edmond *et al.*, 1985). Today, many of the older studies on dissolved trace metals are regarded to be unreliable, due to the major improvement in sampling procedures and analytical techniques that was made during the eighties (Shiller and Boyle, 1987; Bowers and Yeats, 1989; Windom *et al.*, 1991^a). The growing awareness of possible analytical problems has led to a renewed interest in dissolved metal distributions in estuaries and their controlling mechanisms (Salomons and Förstner, 1984; Bourg, 1988). The estuarine geochemistry of dissolved trace metals is controlled by a complex interplay of hydrodynamic factors, industrial and municipal waste water discharges, and biogeochemical processes. Geochemical reactivity of trace metals in estuaries is commonly ascribed to changes in metal adsorption-desorption equilibria along the salinity gradient. The assumption of chemical equilibrium may not always be correct, however, depending on the estuarine residence time (Morris, 1990). For instance, Millward *et al.* (1992) successfully used a kinetic framework to explain the distribution of dissolved Cu and Zn in the Tamar estuary, involving trace metal adsorption rates and residence time in the low-salinity zone. Biological control on trace metal distributions in estuaries is related to primary production and degradation of organic matter (Church, 1986; Mart and Nürnberg, 1986; Flegal *et al.*, 1991; Windom *et al.*, 1991^b). In moderate climates, biological reactivity is highly dependent on the season, which is generally much less the case for geochemical reactivity (e.g. Edmond *et al.*, 1985; Church, 1986).

The estuarine chemistry of Cd has been resolved more satisfactorily than that of other trace metals. Laboratory experiments and a large number of field studies have shown unambiguously that Cd, bound to suspended matter, is desorbed when river water mixes with sea water (Edmond *et al.*, 1985; Elbaz-Poulichet *et al.*, 1987; Shiller and Boyle, 1991; Boutier *et al.*, 1993). Speciation calculations suggest that the desorption process is due to formation of Cd-chlorocomplexes during estuarine mixing (Turner *et al.*, 1981; Comans and Van Dijk, 1988). Competition with Ca for sorption sites has been proposed as another major desorption mechanism (Paalman *et al.*, 1994). Contrary to the picture for Cd, there is no general distribution pattern of dissolved Cu and Zn in estuaries. All types of distributions of dissolved Cu and Zn have been found in estuaries, involving either removal or addition or both, as well as conservative distributions (Danielsson *et al.*, 1983; Windom *et al.*, 1983; Edmond *et al.*, 1985; Ackroyd *et al.*, 1986; Shiller and Boyle, 1991; Flegal *et al.*, 1991). These contrasting patterns appear to be a reflection of each estuary's physical and biogeochemical characteristics. Moreover, within a particular estuary the dissolved metal distributions may vary from season to season (e.g. Church, 1986; Flegal *et al.*, 1991).

Most of the studies on trace metal reactivity in estuaries are based on a single or small number of surveys. Moreover, determination of potentially important parameters other than salinity has often been ignored. It is not the purpose of this paper to discuss another example

of (non-)conservative behaviour of trace metals in a particular estuary. Instead, we intend to demonstrate that a better understanding of the estuarine geochemistry of trace metals can only be obtained by a seasonal sampling strategy, taking into account the variability in environmental conditions throughout the year. The research presented here was carried out in the highly polluted Scheldt estuary, in order to support the development of an estuarine water quality model (Van Gils *et al.*, 1993). Previous surveys on the behaviour of trace metals in the Scheldt estuary, carried out in October 1978 (Duinker *et al.*, 1982^a) and September 1979 (Salomons *et al.*, 1981), have shown that Cd, Cu, and Zn are mobilised to the dissolved phase within the mid-estuary, whereas Mn is mobilised in the low-salinity zone and precipitated later. These observations, which were related to the presence of a longitudinal redox gradient, may not be representative of the behaviour of these metals in other seasons, because redox distributions in the Scheldt estuary depend highly on the season (Somville and De Pauw, 1982). The objective of this study was to obtain a comprehensive view of the distributions of dissolved Cd, Cu, and Zn in the Scheldt estuary throughout the year, and identify the physico-chemical and biological processes controlling these distributions.

Our research was restricted to Cd, Cu, and Zn, because these are the metals considered to be most problematic in the Scheldt estuary. Distributions of other (dissolved) trace metals in the Scheldt estuary can be found in the literature, namely As (Andreae *et al.*, 1989) and other metalloids (Van der Sloot *et al.*, 1985), Hg (Temmerman *et al.*, 1989; Leermakers *et al.*, 1995), Mn (Duinker *et al.*, 1979; Wollast *et al.*, 1979), and Fe (Zwolsman, 1994). A comprehensive study on dissolved and particulate trace metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Zn), encompassing eight surveys in 1991-1994, was recently completed by Paucot and Wollast (1997).

2.2. Sampling and analysis

Eight surveys were carried out at regular intervals between February 1987 and February 1988. Two surveys each season allowed us to investigate the distribution of trace metals over a wide range of environmental conditions. Water samples were collected from the main shipping channel during axial cruises from the mouth of the estuary (salinity 22-29) up to the Rupel confluence (salinity 0.3-1.0). Sampling was focused on the low-salinity zone because of its strong geochemical gradients. During each survey, six samples were taken within the salinity range 0.5-6; further downstream six additional samples were taken at regular salinity intervals. Since the water column in the Scheldt estuary is generally well-mixed, we decided to take surface water samples only. Each survey was completed within two days. Supplementary data on the composition of the Scheldt river plume (salinity 30-35) were available from regular monitoring cruises of the 'Appelzak' transect, comprising three stations in the southern North Sea (2, 20, and 70 km off the mouth of the Scheldt estuary). Seawater samples were handled and analysed according to the same procedures as the estuarine samples. For cruises 3 and 5, supplementary data were available for nutrients only. The time-

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span between the estuarine surveys and the routine seawater monitoring campaigns was 1-2 days for cruises 1, 2, 3, 5, and 8, one week for cruises 4 and 7, and two weeks for cruise 6. These time-spans were considered to be acceptable in view of the long residence time in the Scheldt estuary (two to three months).

The research vessel was equipped with a sensor system which allowed in-situ monitoring of the salinity, pH, dissolved oxygen and water temperature. At appropriate salinities, water was pumped from 1 meter below the surface and sampled for analysis of trace metals and general water quality parameters. Suspended matter was collected by continuous flow centrifugation ($1 \text{ m}^3/\text{h}$). Samples for general water quality parameters were filtered immediately after collection, stored at 4°C in the dark, and analysed within one or two days according to standard seawater methods (Grasshoff *et al.*, 1983). Nutrients were determined colorimetrically, dissolved sulphide was analysed according to the methylene-blue method, and chlorophyll-a was determined by reversed-phase HPLC. Suspended matter was analysed by ICP-AES, after total digestion in a mixture of $\text{HF-HClO}_4\text{-HNO}_3$ (see chapter 3).

Special care was taken to avoid contamination during sampling for dissolved trace metals. All materials (flasks, filters, filtration block) were acid-cleaned prior to use, and the ship's pumping line was continuously flushed with ambient water. Water samples for trace metal analyses were pressure-filtered through $0.45\text{-}\mu\text{m}$ membrane filters (Sartorius) within 30-60 minutes after collection. The filtration was carried out under nitrogen pressure in an all-teflon filtration block, placed in a laminar-flow hood. The first 100 ml of the filtrate was rejected to minimise contamination. The next 250 ml was collected in a polypropylene flask and adjusted to $\text{pH} \approx 1$ with ultra-pure HNO_3 . These flasks were sealed inside plastic bags and stored at 4°C in the dark. All metal concentrations were determined by atomic absorption spectroscopy after preconcentration (Dornemann and Kleist, 1979). Metals were complexed with hexamethylenammonium/hexamethylenedithiocarbamate and extracted in di-isopropyl-ketone/xylene. Dissolved Zn was measured by flame AAS (Perkin-Elmer 430), while Cd and Cu were measured by graphite furnace AAS (Perkin-Elmer 5000). Detection limits were 0.09 nM for Cd, 1.5 nM for Cu, and 3 nM for Zn (but 15 nM for Zn in the seawater samples, because of a less favourable water/organic matrix ratio during preconcentration). Blank concentrations, estimated by passing distilled water through the filtration block, were lower than the limits of detection. Variability in water column composition in time was checked for three times by sampling water bodies of similar salinity within a 15-hour time span (i.e. overnight). In general, these water bodies were found to have very similar compositions in terms of dissolved nutrient and trace metal concentrations (not shown).

At the start of our sampling program, we investigated whether the research vessel influenced the ambient dissolved trace metal concentrations, e.g. due to contamination from the pumping line. Coastal seawater was sampled in duplicate from a rubber boat, floating some 200 m upstream from the vessel, and by the vessel itself in triplicate. All samples were pressure-filtered immediately and analysed for Cd, Cu, and Zn. No differences were observed for Cu, but samples taken by the vessel appeared to have slightly higher dissolved Cd and Zn concentrations, the average increase being 0.12 nM for Cd and 8 nM for Zn (at ambient

concentrations of 0.53 nM for Cd and 65 nM for Zn). Based on prior information on dissolved Cd and Zn concentrations in the estuary, we judged these differences to be acceptable within the goal of this study, i.e. recording of trace metal profiles under a wide range of environmental conditions. Given the concentration ranges recorded in the estuary (0.09-1.2 nM for dissolved Cd and 9-350 nM for dissolved Zn), it is clear that slight contamination by the research vessel will not affect the dissolved metal profiles to a significant extent.

Regarding possible analytical problems in dissolved trace metal analysis, our laboratory participated in two intercomparison exercises on dissolved trace metals in coastal waters of the North Sea, organised by the Marine Chemistry Working Group of the International Council for the Exploration of the Sea (Berman *et al.*, 1988). Our laboratory was judged to have performed satisfactorily at all concentrations of Cd, Cu, and Zn examined in the two intercomparison exercises (the highest ranking in the test). For this and other reasons (discussed later), we are confident that the dissolved metal data presented here are reliable.

2.3. Results

2.3.1. River water composition

The discharge of the Scheldt river during the sampling campaign is shown in Fig. 2.1.

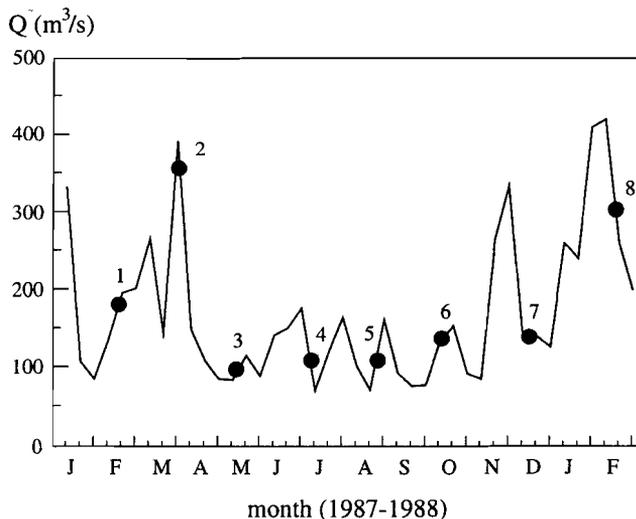


Fig. 2.1. Freshwater discharge of the Scheldt river during the sampling campaign. Numbers 1-8 refer to sampling cruise numbers.

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The mean quarterly river flows were 207, 123, 106 and 163 m³/s in 1987, and 330 m³/s in the first quarter of 1988. These river flows are quite high, especially during the summer period, reflecting the fact that 1987 was a very wet year.

Prior to a discussion of estuarine profiles, it is necessary to consider the composition of the river water which enters the estuary (the freshwater end-member). There appears to be a strong seasonal variation in the composition of the freshwater end-member, both for general water quality parameters and dissolved trace metal concentrations (Table 2.1). During the colder period (cruises 1, 2, 7, 8), the river water is highly undersaturated in dissolved oxygen, but not anoxic (except cruise 7), and has a low pH. During the warmer period, the river water is truly anoxic and partially (cruises 4 and 6) or completely (cruises 3 and 5) depleted in nitrate as well, while traces of dissolved sulphide are present in the water column. Dissolved Cu and Zn in the river water show a seasonal pattern similar to nitrate, with relatively high concentrations in the colder period and very low concentrations in the warmer period. The pattern of dissolved Cd is less conclusive due to detection limit problems, but dissolved Cd is always present in the river water during the colder period (0.09-0.27 nM), whereas dissolved Cd is usually below the detection limit during the warmer period.

Table 2.1. General water quality and dissolved metal concentrations in the Scheldt river at the beginning of the salinity gradient (fluvial end-member composition).

Nr	Date of sampling	Salinity	T °C	SPM mg/l	Chl-a* µg/l	pH	O ₂ µM	NO ₃ µM	HS ⁻ µM	Cd nM	Cu nM	Zn nM
1	18 Feb 87	0.60	4.2	101	2.6	7.13	81	285	n.a.	0.18	31	352
2	1 Apr 87	0.50	8.2	67	15.8	7.11	97	360	n.a.	0.18	35	269
3	13 May 87	0.89	14.3	222	30.6	7.65	5	4	0.94	<0.09	6	44
4	7 Jul 87	0.98	21.4	80	53.1	7.60	5	81	n.a.	0.27	17	69
5	25 Aug 87	0.55	20.1	36	7.1	7.45	3	1	0.20	<0.09	5	9
6	14 Oct 87	0.42	12.8	96	11.1	7.56	6	51	0.21	<0.09	13	58
7	15 Dec 87	0.44	3.8	76	0.4	7.30	3	180	n.a.	0.27	22	274
8	17 Feb 88	0.32	5.6	116	1.8	7.12	129	361	n.a.	0.09	28	271

* Chl-a = chlorophyll-a; n.a. = not analysed.

Compared to the variation in dissolved metal concentrations, the trace metal content of the riverine suspended matter shows relatively little variation over the year (Table 2.2). Particulate metal concentrations in the freshwater end-member were calculated from the trace metal content of the suspended matter and the ambient suspended matter concentration during sampling (as listed in Table 2.1). The results, expressed as percentage of total metal concentration, are listed in Table 2.2. The particulate state appears to be far more important than the dissolved state, averaging 98% of total Cd, 93% of total Cu and 90% of total Zn. This extreme preference of trace metals for the particulate state in the anoxic (or suboxic) Scheldt river is also illustrated by distribution coefficients (K_d 's). Compared to typical K_d 's for (oxic) branches of the Rhine River in the Netherlands, i.e. 130 ± 20 l/g for Cd, 40 ± 5 l/g for Cu, and

Geochemistry of dissolved Cd, Cu and Zn in the Scheldt estuary

100 ± 10 l/g for Zn (Van der Kooij *et al.*, 1991), the K_d 's in the Scheldt river are up to an order of magnitude higher, except for Zn during the colder period (Table 2.2).

Table 2.2. Trace metal content of the suspended matter, particulate metal concentrations (relative to total metal concentrations) and trace metal distribution coefficients (K_d 's) in the Scheldt river at the beginning of the salinity gradient.

Cruise Nr	Metal content (µmol/g)			Particulate metal (%)			K_d (l/g)		
	Cd	Cu	Zn	Cd	Cu	Zn	Cd	Cu	Zn
1	0.097	3.11	17.5	98	91	83	550	100	50
2	0.109	3.04	16.3	98	85	80	610	90	60
3	0.107	3.37	14.1	>99	99	99	>1200	540	320
4	0.108	2.85	13.1	97	93	94	400	170	190
5	0.116	3.23	14.3	>98	96	98	>1300	680	1560
6	0.118	4.54	18.0	>99	97	97	>1300	360	310
7	0.124	4.11	18.3	97	93	84	460	190	70
8	0.091	2.57	15.4	99	91	87	1020	90	60

2.3.2. Seasonal estuarine geochemistry

Estuarine profiles of general water quality parameters and nutrients are given in Fig. 2.2, showing strong seasonal behaviour for all the variables studied. The most important features of these profiles are briefly summarised in this section, discriminating between 'winter' (cruises 1, 2, 7, 8), 'spring' (cruise 3), and 'summer' (cruises 4-6) conditions. Seasons are defined here for conceptual reasons; the actual time spans considered are December till March (winter), May (spring), and July till October (summer).

Winter profiles (cruises 1, 2, 7, 8)

Typical winter conditions are low water temperatures (Table 2.1) and high river discharges (Fig. 2.1). Under these conditions, there is no anoxic zone in the upper estuary, although the water column is highly undersaturated in dissolved oxygen at low salinities. Differences among the dissolved oxygen profiles during winter are related to river flow variations (Somville and De Pauw, 1982), i.e. oxygen depletion in the upper estuary is less dramatic during periods of high river flow (cruises 2 and 8). The dissolved oxygen concentration increases with increasing salinity, due to reaeration and dilution with sea water. A temporary dip in dissolved oxygen may occur in the low-salinity zone (cruises 1 and 2), reflecting resuspension of bottom sediments. A turbidity maximum, with suspended matter concentrations up to 250 mg/l, is present in the low-salinity zone. The pH increases from 7.1-7.3 in the river to 8.0 at the mouth of the estuary, and increases further offshore to 8.5.

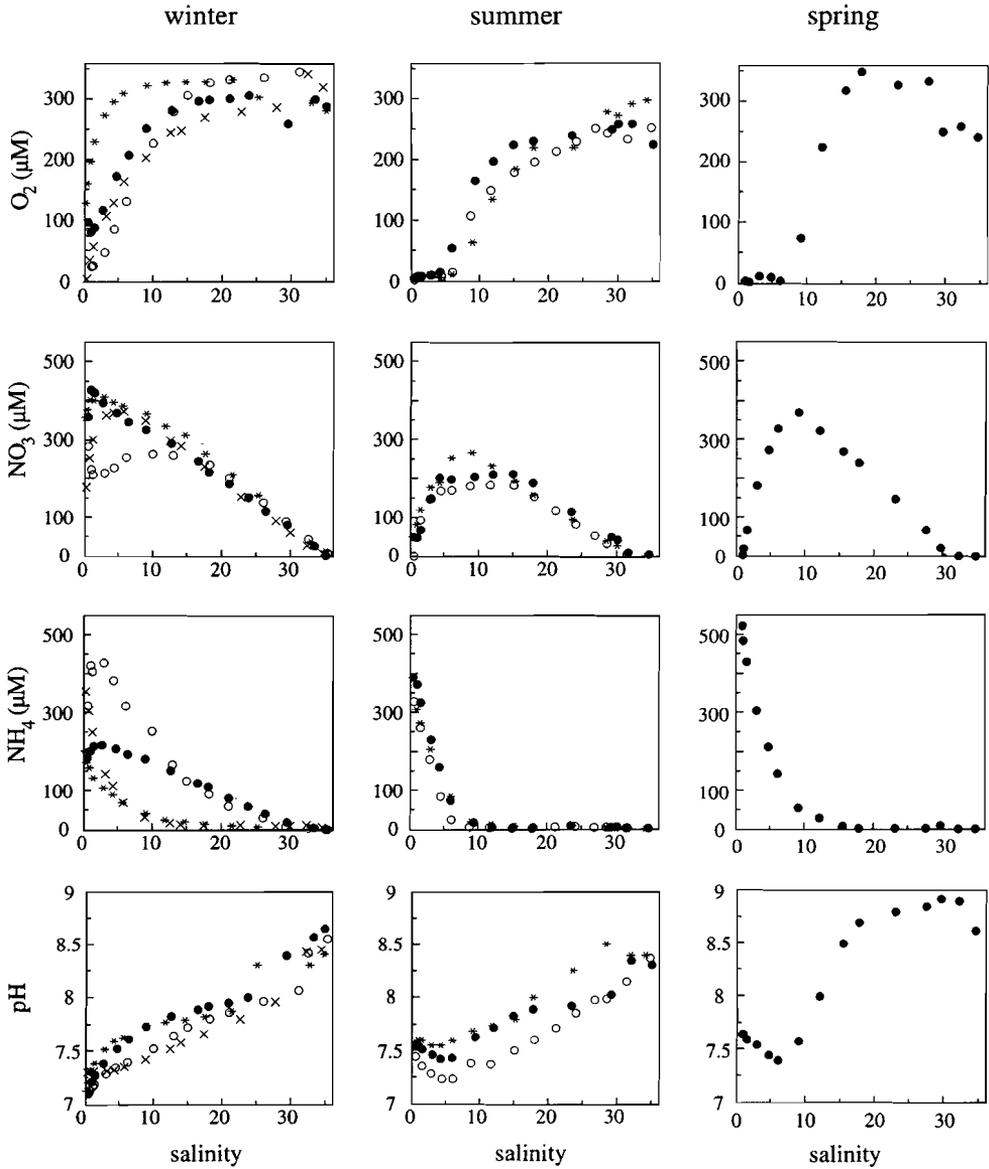


Fig. 2.2. Seasonal profiles of oxygen, nitrate, ammonium, pH, suspended matter, chlorophyll-a, and dissolved silicon in the Scheldt estuary. Note the similarity among winter profiles (nrs. 1, 2, 7, 8) and among summer profiles (nrs. 4-6). The spring profiles (nr. 3) show the impact of an algae bloom in the lower estuary.

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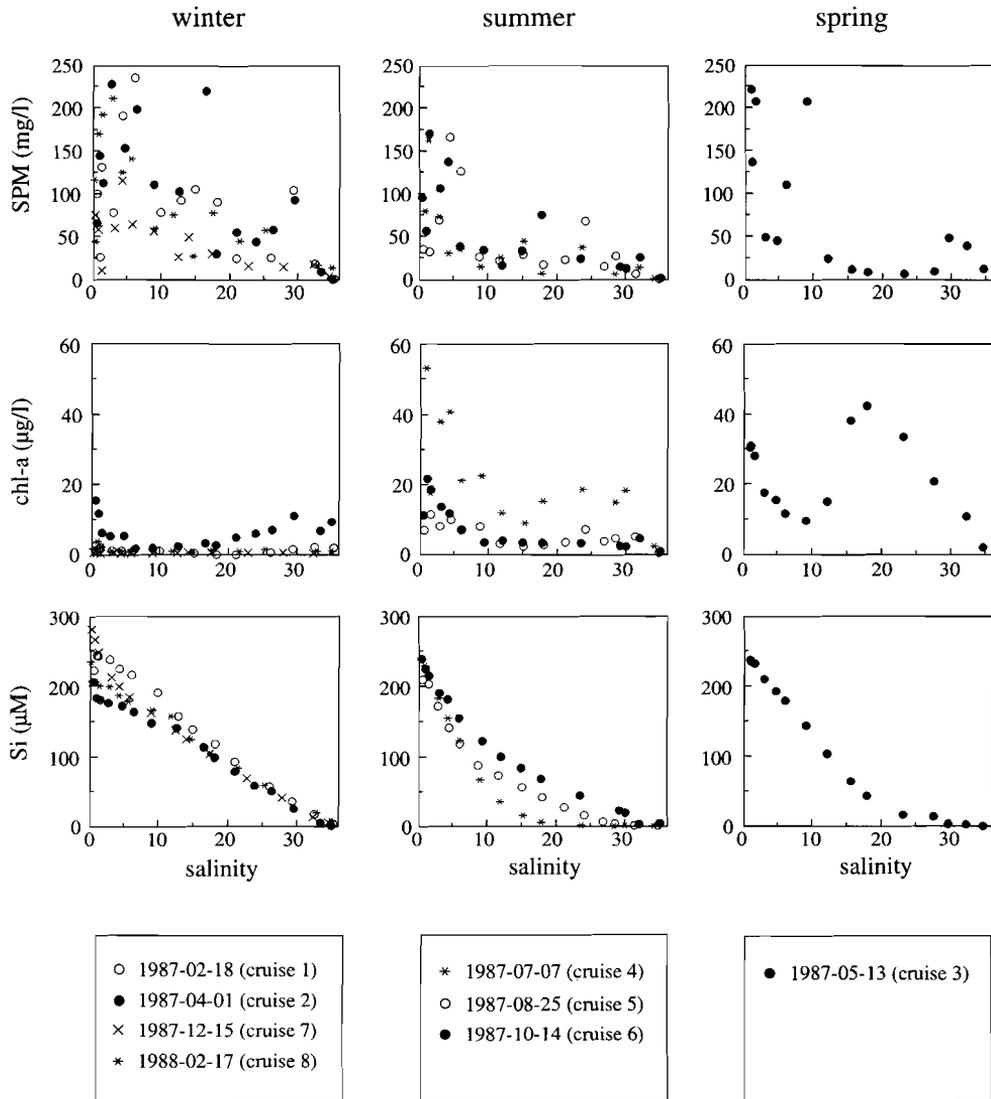


Fig. 2.2. (continued)

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During the winter, the chlorophyll-a concentrations are extremely low in the entire estuary (except for cruise 2), indicating that primary production is negligible. The conservative behaviour of dissolved Si, seaward from the low-salinity zone, supports this observation.

Summer profiles (cruises 4-6)

During summer, the river flow is quite small, while the temperature reaches a maximum. As a consequence, an anoxic zone develops in the upper estuary, due to intense nitrification and organic matter decomposition in the low-salinity zone (Somville and De Pauw, 1982; Billen *et al.*, 1988). In the lower estuary, where ammonium is almost completely oxidised to nitrate, dissolved oxygen is restored. The pH shows a minimum in the upper estuary, together with a pronounced nitrate maximum, suggesting nitrification to be involved. The absence of a pH minimum during winter, when the nitrification rate is much lower, supports this hypothesis, and rules out the alternative explanation (Mook and Koene, 1975) that the pH minimum is caused by a shift in the dissociation constant of carbonic acid with increasing salinity. The suspended matter profiles show a turbidity maximum in the upper estuary, similar to the winter profiles, but generally at lower concentrations. The chlorophyll-a concentration in the river water is quite high during summer but decreases rapidly in the upper estuary, reflecting decay of freshwater phytoplankton with increasing salinity (Billen *et al.*, 1988). During cruise 4, however, primary production seems to be occurring in the upper estuary, in view of the high chlorophyll-a concentrations observed there ($> 20 \mu\text{g/l}$). A second zone of primary production is located in the lower estuary, in the salinity range 15-30. These observations are supported by the dissolved Si profile of cruise 4, showing large-scale removal from solution starting in the low-salinity zone, and even total Si depletion in the lower estuary. Seasonal removal of Si in the Scheldt estuary is attributed to uptake by brackish and marine diatoms (Wollast and De Broeu, 1971; Zwolsman, 1994). Obviously, primary production is more important during cruise 4 than during the cruises 5 and 6.

Spring profiles (cruise 3)

The profiles of the spring cruise (May) are for the major part similar to the summer profiles discussed above. Thus, the basic features of the upper estuary are the presence of an anoxic zone; a pH minimum, coinciding with a nitrate maximum; and a turbidity maximum. The difference between spring and summer conditions is related to phytoplankton activity, as reflected by the chlorophyll-a profiles. The spring profile of chlorophyll-a reflects decay of freshwater phytoplankton in the upper estuary and production in the lower estuary, on a much larger scale than during summer. Other effects of the spring phytoplankton bloom are supersaturation of dissolved oxygen and a major pH increase in the lower estuary by almost one unit (cf. the spring and summer profiles). Moreover, removal of dissolved Si is apparent during spring (and summer), as is the case for orthophosphate (Zwolsman, 1994).

2.3.3. Profiles of dissolved Cd, Cu, and Zn

The profiles of dissolved Cd, Cu, and Zn in the Scheldt estuary are given in Fig. 2.3. Similar to the seasonal variability in estuarine geochemistry, the dissolved metal distributions depend strongly on the season. It should be noted that differences between dissolved metal distributions recorded during the same season (e.g. 4 winter cruises) are only minor compared to the differences among profiles recorded during different seasons. This high degree of seasonal reproducibility is one of the arguments for the quality of the dissolved metal data.

Winter profiles (cruises 1, 2, 7, 8)

The basic features of the dissolved metal-salinity plots recorded during winter can be summarised as follows. High concentrations of Cu and Zn are found in the incoming river water; dissolved Cd concentrations in the river water are well above the detection limit. A sudden decline of the dissolved Cu and Zn concentrations is apparent in the low-salinity zone (Table 2.3), which is usually located around the city of Antwerp. Seaward from the low-salinity zone, all dissolved metal concentrations show a gradual increase with increasing salinity, leading to a well-defined peak for Zn at relatively low salinity (6-9), a broad maximum for Cu within the salinity range 9-18 and one for Cd at salinity 12-21. The dissolved Zn peak is located around the Dutch-Belgian border, whereas the dissolved Cu and Cd maxima are always located in the lower estuary. Seaward from the mid-estuarine maxima, the dissolved metal concentrations decrease due to dilution with sea water. The dissolved Cu profiles show a plateau near the mouth (salinity 25-30), which may have been caused by local inputs (e.g. from shipping). The dissolved Cu and Cd concentrations found in offshore North Sea water (70 km off the Dutch coast) are comparable to winter values reported by Burton *et al.* (1993) for the central southern North Sea and by Fileman *et al.* (1991) for the southern Dogger Bank.

Table 2.3. Magnitude and salinity of the dissolved Cu and Zn minima in the low-salinity zone.

Cruise nr	Cu (nM) river	Cu (nM) minimum	Salinity Cu min.	Zn (nM) river	Zn (nM) minimum	Salinity Zn min.
1	31.5	12.6-14.2	1.3-6.1	352	214	2.9-4.3
2	34.6	22.0	0.9-4.6	269	153	0.9
4	17.3	6.3-7.9	3.0-6.0	69	41-43	3.0-4.3
6	12.6	7.9-9.4	1.0-4.2	58	-	-
7	22.0	14.2-15.7	0.9-1.4	274	148	3.3
8	28.3	15.7-17.3	0.5-1.0	271	93	1.0

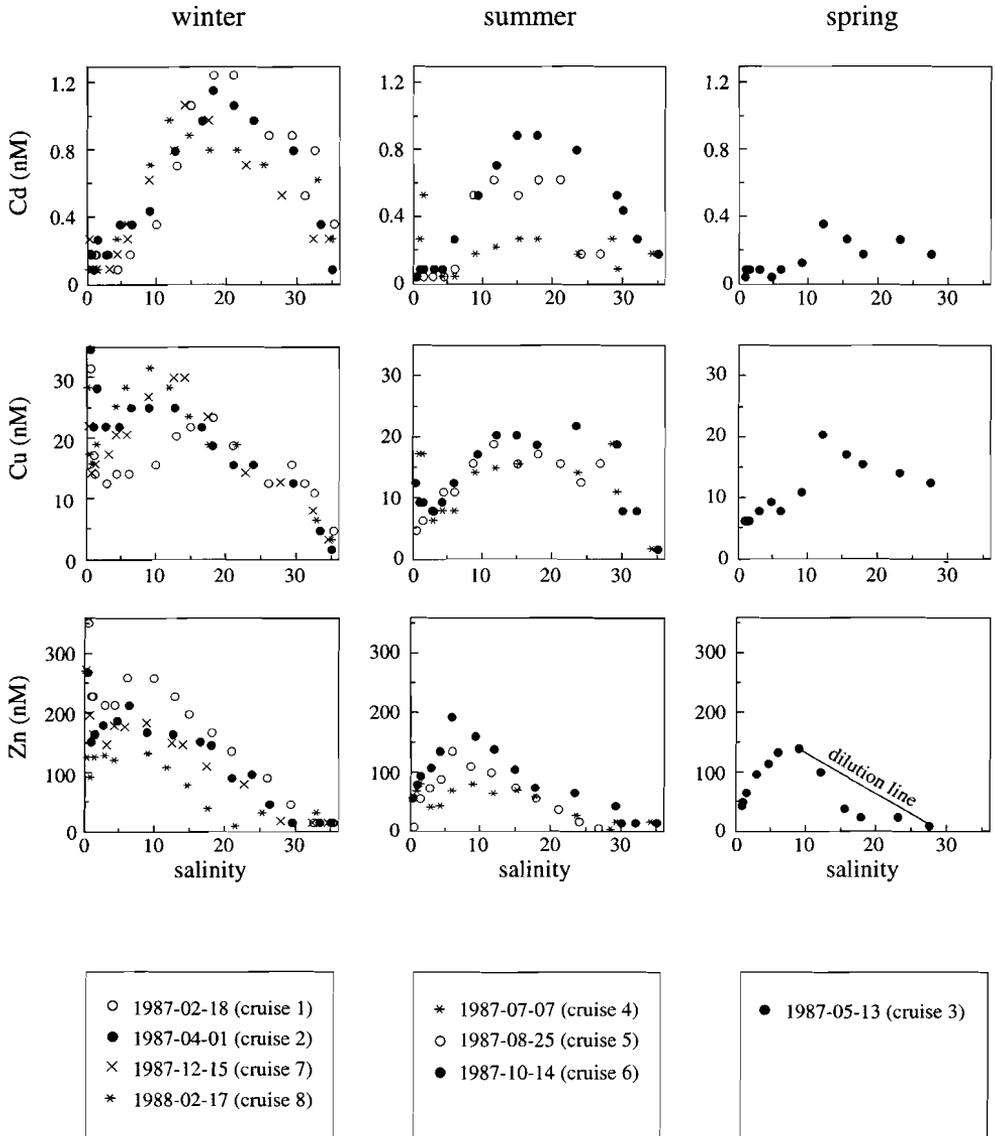


Fig. 2.3. Seasonal distributions of dissolved Cd, Cu, and Zn in the Scheldt estuary. The theoretical dilution line is indicated in the spring profile of dissolved Zn to show a removal process operating in the lower estuary.

Geochemistry of dissolved Cd, Cu and Zn in the Scheldt estuary

Summer profiles (cruises 4-6)

The characteristics of the metal-salinity plots recorded during summer are fundamentally different from the winter profiles. The most remarkable feature of the summer profiles is the very low dissolved metal concentration in the incoming river water (see also Table 2.1). A decrease of dissolved Cd, Cu, and Zn is observed in the low-salinity zone during cruise 4, similar to the winter profiles (and also during cruise 6 for Cu). During cruises 5 and 6, the dissolved Cu and Zn concentrations increase rapidly with increasing salinity, whereas the dissolved Cd concentration increases only at higher salinities (note the plateau for dissolved Cd up to salinity 6). Mid-estuarine maxima for dissolved Cd, Cu, and Zn are observed at approximately the same salinity ranges as those during winter. Considering the concentration levels, there is a major difference between the Cd and Zn profiles (not Cu) of cruise 4 on the one hand, and those of cruises 5 and 6 on the other. It is obvious that the dissolved Cd and Zn concentrations are relatively low during cruise 4.

Spring profiles (cruise 3)

Comparison of the dissolved metal profiles recorded during spring (cruise 3) with those recorded during summer (cruises 5 and 6) shows that the Cu distributions are basically similar. For Cd and Zn, however, this is not the case. Similar features are only observed in the upper estuary, namely (1) the very low dissolved Cd and Zn concentrations in the incoming river water, (2) the rapid increase in dissolved Zn concentrations in the upper estuary, and (3) the slight increase in dissolved Cd at somewhat higher salinities. The most striking feature of the dissolved Cd and Zn profiles of cruise 3 (and cruise 4) are the low concentrations found in the lower estuary. Moreover, the dissolved Zn profile of cruise 3 is indicative of removal in the lower estuary (note the concave shape seaward from the Zn maximum).

2.4. Discussion

Four features of the trace metal profiles need to be discussed in order to understand the behaviour of dissolved Cd, Cu, and Zn in the Scheldt estuary. These are (1) the pronounced seasonal variability in dissolved trace metal concentrations in the freshwater end-member; (2) the decrease in dissolved Cu and Zn concentrations in the low-salinity zone, as observed during winter; (3) the concentration maxima of dissolved Cd, Cu, and Zn in the mid-estuary; (4) the very low concentrations of dissolved Cd and Zn in the lower estuary during spring and early summer (cruises 3 and 4). The impact of biogeochemical processes on the dissolved metal transport through the Scheldt estuary is assessed in the last section.

2.4.1. Seasonal variability in river water composition

The concentrations of dissolved Cu and Zn in the Scheldt river display a seasonal pattern similar to nitrate, with relatively high concentrations during winter and very low concentrations during spring and summer (Table 2.1, Fig. 2.4). Since nitrate is a fair measure of the redox condition in the (anoxic) water column, this observation suggests that the dissolved metal behaviour in the Scheldt river is influenced by redox chemistry.

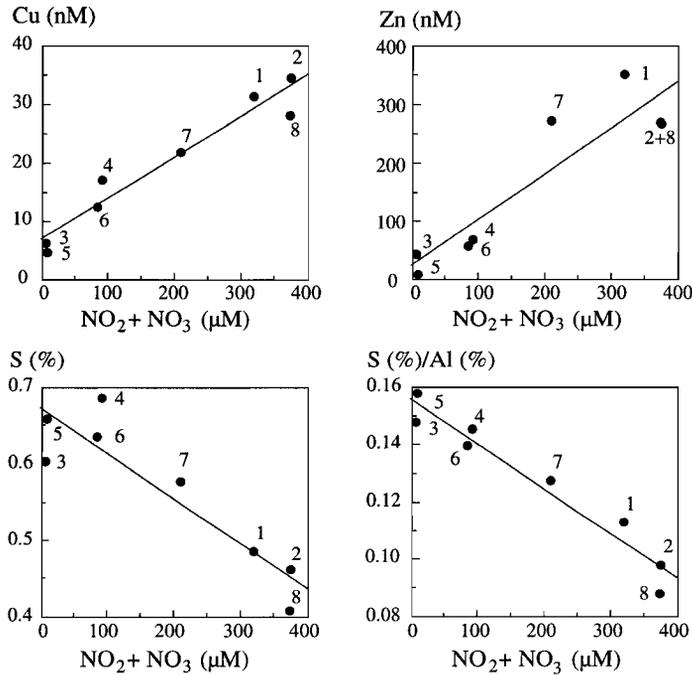


Fig. 2.4. Relationship between nitrate (plus nitrite) in the freshwater end-member, and (a) dissolved Cu; (b) dissolved Zn; (c) particulate sulphide in the suspended matter; (d) particulate sulphide divided by Al content (normalisation for grain-size effects). Sampling cruise numbers are indicated in the figures. Linear regression equations:

$$\begin{aligned}
 \text{Cu (nM)} &= 6.9 + 0.070 \times \text{NO}_{2+3} (\mu\text{M}) && n = 8, r^2 = 0.939 \\
 \text{Zn (nM)} &= 24 + 0.79 \times \text{NO}_{2+3} (\mu\text{M}) && n = 8, r^2 = 0.842 \\
 \text{S (\%)} &= 0.673 - 0.00059 \times \text{NO}_{2+3} (\mu\text{M}) && n = 8, r^2 = 0.835 \\
 \text{S (\%)/Al (\%)} &= 0.156 - 0.00016 \times \text{NO}_{2+3} (\mu\text{M}) && n = 8, r^2 = 0.944
 \end{aligned}$$

Salomons *et al.* (1981) and Duinker *et al.* (1982^a) have previously suggested that the anoxic nature of the Scheldt river leads to formation of metal sulphides within the water column, giving rise to very low dissolved trace metal concentrations. This explanation is indeed corroborated by the presence of dissolved sulphide in anoxic river water samples (Table 2.1), and by the extraordinary preference of trace metals for the particulate state in the Scheldt river (Table 2.2). Since sulphate reduction in the water column is unlikely to occur (presence of nitrate), the origin of the sulphide lies probably in a small leak from the highly reducing fluvial sediments, where sulphate reduction is abundant (see chapter 6). Chemical control of sulphide on dissolved trace metal concentrations is a well-known feature of anoxic marine basins (e.g. Jacobs *et al.*, 1985; Haraldsson and Westerlund, 1988) but applies to anoxic lacustrine environments as well (Balistrieri *et al.*, 1992).

During winter months, when the river water is not totally devoid of oxygen and rich in nitrate, precipitation of trace metal sulphides is unlikely to occur in the water column. Furthermore, if metal sulphides are introduced in the slightly oxic water column, e.g. by resuspension of reduced sediments, they will slowly oxidise and dissolve. The relatively low sulphide content of the fluvial suspended matter during winter (Table 2.4, Fig. 2.4) supports this view. Moreover, trace metal adsorption onto suspended matter will be reduced due to the low pH of the river water (7.1 to 7.3) during winter (Bourg, 1983; Johnson, 1986). This interplay between favourable redox conditions and low pH values may well explain the high concentrations of dissolved Cu, Zn, and (less obviously) Cd in the river water during winter.

2.4.2. Trace metal removal in the low-salinity zone

Concentration minima of dissolved Cu and Zn are always present in the low-salinity zone during winter, when the dissolved metal concentration in the river water is relatively high (Table 2.3). Before one can attribute these minima to removal processes, the influence of variability in the riverine concentration on the dissolved metal profiles needs to be considered. It is well-known that when the time-scale for river concentration variability is similar to or less than the residence time of water in the estuary, this will result in apparent non-conservative profiles (Officer and Lynch, 1981; Kaul and Froehlich, 1984; Cifuentes *et al.*, 1990). A prime example of this phenomenon is probably offered by the dissolved Si profiles during winter, showing either apparent addition (cruise 1) or removal (cruises 2, 7, 8) in the very low-salinity zone (Fig. 2.2). However, these effects are relatively small compared to the decrease in dissolved Cu and Zn concentrations in the low-salinity zone. Moreover, if short-term variations in river composition would influence the dissolved metal profiles (during winter), a relation between river flow and dissolved metal concentrations would be expected. For instance, apparent non-conservative distributions of total dissolved As in the upper Scheldt estuary have been related to an inverse relationship between dissolved As and river discharge (Andreae and Andreae, 1989). But, our data do not show any relation between river flow (Fig. 2.1) and dissolved metal concentrations (Table 2.1) during winter, although both

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high-flow (cruises 2 and 8) and low-flow periods (cruises 1 and 7) are covered. In addition, the dissolved metal minima are observed both during periods of increasing river flow (cruises 1 and 2) and decreasing river flow (cruises 7 and 8). For these reasons, the possibility that the sudden decrease in dissolved Cu and Zn concentrations in the low-salinity zone is caused by fluctuations in freshwater end-member composition is highly unlikely. Thus, geochemical removal processes must be involved, such as (1) flocculation or coagulation, (2) adsorption onto suspended matter, and (3) adsorption onto resuspended sediments.

- (1) Kramer and Duinker (1984) have shown previously that the complexation capacity of Scheldt river water decreases rapidly during the first stages of estuarine mixing, which was attributed to flocculation of large organic molecules or coagulation of colloids. Flocculation of humic acids may lead to removal of trace metals from solution (Sholkovitz, 1978), especially Cu because its freshwater speciation is dominated by organic complexes (Hart and Davies, 1981; Paulson *et al.*, 1984; Kuwabara *et al.*, 1989; Apte *et al.*, 1990^b). However, the concentrations of dissolved Cd and Zn will be less affected, because these metals appear to exist predominantly as inorganic forms in river water (Turner *et al.*, 1981; Hart and Davies, 1981; Bourg, 1983; Kuwabara *et al.*, 1989).
- (2) Adsorption of trace metals onto suspended matter in the low-salinity, high-turbidity zone has been reported for many estuaries (e.g. Bowers and Yeats, 1978; Duinker *et al.*, 1982^b; Ackroyd *et al.*, 1986; Morris, 1986). In the upper Scheldt estuary, adsorption of trace metals is especially favoured during winter due to the high suspended matter concentrations and the rapid increase in pH with increasing salinity (Fig. 2.2). Trace metal adsorption in the Scheldt estuary is supported by the phenomenon of tidal pumping, which creates an upstream transport of suspended matter from the lower estuary to the high-turbidity zone (Wollast, 1988; Martin *et al.*, 1994). In this way, the adsorbing particle population in the high-turbidity zone is continuously replaced by less contaminated (marine) material, which is a necessary requirement to maintain trace metal adsorption (Morris, 1986).
- (3) The high-turbidity zone of the Scheldt estuary is underlain by muddy (weakly consolidated) sediments which are subject to repeated cycles of erosion and sedimentation under tidal influence (Wartel, 1977; Duinker *et al.*, 1982^a). Pore water profiles reveal that the sediments are highly reduced, with sulphate depletion within the top 5-10 cm, and high concentrations of dissolved Fe (see chapter 6). The sulphide content of the sediments may reach up to 1% by weight. Dispersion of highly reduced sediments into the water column will, on the short term, lead to adsorption of trace metals by (iron) sulphides (Jean and Bancroft, 1986; Morse and Arakaki, 1993). Though the metal sulphides are unstable in the water column, their oxidation kinetics will be relatively slow during winter because of low temperatures and the low oxygen concentration in the low-salinity zone (Fig. 2.2). Another effect of sediment resuspension is pore water infusion, which is a major source of Mn and Fe to the water column in the high-turbidity zone. Once released into the water column, dissolved Fe is rapidly oxidised and precipitated (Zwolsman, 1994). Dissolved Mn, which is oxidised

more slowly, precipitates in the lower estuary, but particulate Mn is returned to the low-salinity zone through tidal pumping (Duinker *et al.*, 1979). The in-situ formation of Fe and Mn (oxy-)hydroxides, which are effective scavengers of dissolved trace metals (e.g. Laxen, 1984; Tessier *et al.*, 1985; Johnson, 1986), will lead to removal of dissolved Cd, Cu, and Zn in the low-salinity zone. The suspended matter composition in the low-salinity zone offers evidence for these processes (see Table 2.4). Sediment resuspension is clearly shown by the enrichment of total sulphide, increasing from a mean value of 0.48% in the river water to 0.75% in the low-salinity zone (during winter). The suspended matter from the low-salinity zone is also enriched in Fe and Mn, as reported previously by Duinker *et al.* (1979), Salomons and Eysink (1981) and Baeyens *et al.* (1987). Electron microprobe analyses show that most of the sulphide in the suspended matter belongs to some Fe-S type (23% Fe, 61 % S; Van Alsenoy *et al.*, 1989).

Table 2.4. Major element composition of the suspended matter at the beginning of the salinity gradient (riverine end-member, REM), the low-salinity zone (LSZ, salinity 1-4), and the mouth of the Scheldt estuary (marine end-member, MEM).

Nr	Al (%)			Fe (%)			Mn (µg/g)			S (%)		
	REM	LSZ	MEM	REM	LSZ	MEM	REM	LSZ	MEM	REM	LSZ	MEM
1	4.28	4.93	5.16	4.33	4.99	3.49	742	1052	1347	0.49	0.78	0.56
2	4.71	4.84	4.84	4.36	4.59	3.31	804	1223	1206	0.46	0.75	0.54
3	4.08	4.40	3.33	4.17	4.37	2.12	855	969	918	0.60	0.68	0.66
4	4.71	4.98	4.79	4.93	5.17	3.23	1205	1064	1709	0.69	0.83	0.63
5	4.17	5.12	4.26	4.44	5.01	2.68	748	939	1066	0.66	0.78	0.38
6	4.55	5.63	5.37	4.83	5.50	3.27	839	1156	1043	0.64	0.89	0.37
7	4.52	5.33	5.20	5.09	5.37	3.36	863	1096	1099	0.58	0.75	0.43
8	4.63	5.18	5.15	4.40	5.17	3.34	872	1207	939	0.41	0.70	0.44

Number of samples: REM = 1, LSZ = 4, MEM = 1.

2.4.3. Trace metal mobilisation

Concentration maxima of dissolved Cd, Cu, and Zn in the mid-estuary are a typical feature of the Scheldt estuary during the year (Fig. 2.3; Paucot and Wollast, 1997). These maxima can either be caused by waste water discharges or desorption of particulate metals, or both. Discharges of industrial and domestic effluents into the upper estuary account for a major increase in the Cd load (41% of the total load in 1991), but make up a rather modest contribution to the load of Cu (12% in 1991) and Zn (9% in 1991; Lefèvre, 1992). However, dissolved Cd maxima were always found in the lower estuary, where direct inputs of Cd are insignificant (Lefèvre, 1992). Therefore, the profiles of dissolved Cd, Cu, and Zn cannot be ascribed to local industrial inputs. Mobilisation of particulate-bound metals to the dissolved phase must explain the dissolved metal maxima.

Several observations indicate that trace metal mobilisation in the Scheldt estuary is related to reoxidation processes. The position (salinity) of the dissolved metal maxima, recorded under various conditions of oxygen depletion, is shown in Table 2.5, including results from two historic cruises with extreme oxygen depletion. According to Table 2.5, the position of the dissolved trace metal maxima is inversely related to the length (i.e. salinity range) of the anoxic zone. This is a clear indication that reoxidation causes mobilisation of Cd, Cu, and Zn in the Scheldt estuary. The role of reoxidation is further supported by apparent relations between dissolved Cd and Cu and the dissolved oxygen concentration in the brackish water zone (Fig. 2.5). Another hint as to the importance of reoxidation is given by the salinity where mobilisation of Cd begins. Under oxygenated conditions (cruise 8), mobilisation of Cd starts at low salinities (1.5-3), in agreement with thermodynamic predictions (Comans and Van Dijk, 1988). In the absence of dissolved oxygen (cruises 3-6), mobilisation of Cd is not observed at low salinities (note the plateau in the dissolved Cd profiles up to salinity 6). Similarly, Duinker *et al.* (1982^a) found that dissolved Cd concentrations did not increase in the anoxic zone (up to salinity 13), but increased rapidly when oxygen returned in the water column at higher salinities.

Table 2.5. Influence of the length of the anoxic zone ($O_2 < 15 \mu M$) on the position (salinity) of the dissolved trace metal maxima in the Scheldt estuary.

Date	Salinity range anoxic zone	Salinity (maximum)			Reference
		Cd	Cu	Zn	
Oct 1978	0-13	18-22	no data	16-18	Duinker <i>et al.</i> (1982 ^a)
Sep 1979	0-12	17-21	18-24	12-16	Salomons <i>et al.</i> (1981)
Aug 1987	0-6	12-20	10-14	5-7	this work (cruise 5)
Oct 1987	0-4	14-18	11-15	5-7	this work (cruise 6)
Feb 1988	oxic	10-14	7-11	3-9	this work (cruise 8)

The apparent role of reoxidation in the mobilisation of Cd, Cu, and Zn in the Scheldt estuary has been related to the presence of metal sulphides in the suspended matter (Salomons *et al.*, 1981; Duinker *et al.*, 1982^a; Paucot and Wollast, 1997). This hypothesis was confirmed by electron microprobe analysis of a suspended matter sample, taken in the low-salinity zone during June 1986 (method described in Bernard *et al.*, 1986). Of the 250 particles studied, 47 were identified as iron sulphides (Fe = $30 \pm 4\%$, S = $54 \pm 11\%$) and two as discrete zinc sulphides (S = 34-46%, Zn = 33%, Cu = 2-4%, Pb = 3%, Fe = 3-4%). CdS was not detected, which is not surprising in view of the relatively low Cd content of the suspended matter (compared to Zn, see Table 2.2). The metal sulphides are derived from precipitation in the Scheldt river during the anoxic period, and also from resuspension of reduced sediments within the high-turbidity zone (which is their only source during winter).

Geochemistry of dissolved Cd, Cu and Zn in the Scheldt estuary

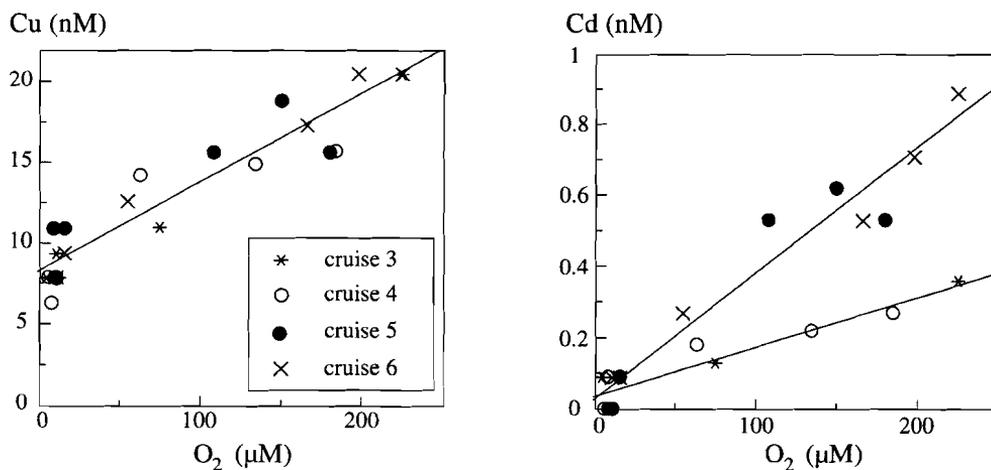


Fig. 2.5. Relationship between dissolved Cd or Cu and dissolved oxygen in the brackish water zone (salinity 3-15) during spring and summer (cruises 3-6). Linear regression equations:

$$\begin{aligned}
 \text{cruises 3 + 4: Cd (nM) = } & 0.038 + 0.0014 \times \text{O}_2 (\mu\text{M}) \quad ; \quad n = 11, r^2 = 0.881 \\
 \text{cruises 5 + 6: Cd (nM) = } & 0.024 + 0.0036 \times \text{O}_2 (\mu\text{M}) \quad ; \quad n = 12, r^2 = 0.945 \\
 \text{cruises 3-6 : Cu (nM) = } & 8.3 + 0.054 \times \text{O}_2 (\mu\text{M}) \quad ; \quad n = 23, r^2 = 0.892
 \end{aligned}$$

In this context it should be noted that the sediments of the upper estuary are rich in acid-volatile sulphide (AVS), and that a major fraction of the metals in the sediments exists in weakly bound forms (Table 2.6). The metal sulphides, present in the suspended matter, will be oxidised during transport to the oxygenated lower estuary, leading to mobilisation of trace metals to the dissolved phase (Holmes, 1986; Moore *et al.*, 1988; Förstner *et al.*, 1989; Gerringa, 1991; Kerner and Wallmann, 1992). Although the released metals may be re-adsorbed, this process is less efficient in estuaries because of chloride complexation and competition with major ions (Comans and Van Dijk, 1988; Paalman *et al.*, 1994). The net effect of this oxidation-complexation process is, therefore, desorption. The fact that Zn is more rapidly mobilised than Cd and Cu (Fig. 2.3, Table 2.5) is in keeping with the relatively low stability of ZnS compared to the much higher stabilities of CuS and CdS (Dyrssen, 1988; Di Toro *et al.*, 1992).

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Table 2.6. Contents of acid-volatile sulphide (AVS) and simultaneously extracted metals (Fe, Cd, Cu, Zn) in silty surface sediments of the upper Scheldt estuary, taken in January 1993 (Kerdijk *et al.*, 1993). Extracted metals are given in absolute contents and in percentage of their total content in the sediments.

Nr	< 63 μm		AVS $\mu\text{mol/g}$	Fe		Cd		Cu		Zn	
	%	%		$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%	$\mu\text{mol/g}$	%
1	96.5	8.39	21.2	391	44	0.066	81	0.42	25	6.97	85
2	92.9	8.43	20.0	368	37	0.063	76	0.34	23	7.27	80
3	91.0	8.81	18.4	364	43	0.063	77	0.53	34	7.84	74

2.4.4. Removal of dissolved Cd and Zn in the lower estuary

During spring and early summer (cruises 3 and 4), there are indications that the mobilisation of Cd and Zn is suppressed, as suggested by the low dissolved metal concentrations compared to those observed in late summer (cruises 5 and 6). On the other hand, the dissolved Cu profiles of cruises 3-6 show comparable concentration levels (Figs. 2.3 and 2.5), indicating that removal of dissolved Cu is insignificant during spring and early summer. More direct proof for removal of dissolved Zn is offered by the concave shape of the dissolved Zn profile in the lower estuary during spring. The low dissolved Cd and Zn concentrations during spring and early summer might be explained by a removal process, counteracting the effect of trace metal mobilisation through sulphide oxidation. Since phytoplankton is blooming during this period (Fig. 2.2), it is tempting to ascribe the removal of dissolved Cd and Zn during spring and early summer to biological uptake. The involvement of trace metals in biological cycles is a well-established fact for the open ocean (e.g. Bruland *et al.*, 1991), but similar processes have been reported to operate in estuaries as well (Church, 1986; Mart and Nürnberg, 1986; Hunter and Tyler, 1987; Kuwabara *et al.*, 1989; Shiller and Boyle, 1991). Additional evidence for biological uptake can be obtained from metal-nutrient relationships, but these relations can be obscured by geochemical processes. For instance, buffering of phosphate occurs in the Scheldt estuary (Zwolsman, 1994), masking the possible relationship with dissolved trace metals. However, a good relation between dissolved Si and dissolved Cd and Zn is apparent in the lower Scheldt estuary over the year (not shown). Although the evidence is circumstantial, biological uptake of Cd and Zn in the Scheldt estuary during phytoplankton blooms seems likely, given the analogy to other systems. Apart from direct uptake, phytoplankton growth may also affect trace metal concentrations indirectly by increasing the pH, which favours adsorption onto suspended matter. The pH in the lower estuary during the spring phytoplankton bloom is a full unit higher than pH levels observed during the rest of the year (Fig. 2.2). The apparent lack of Cu removal might be related to the strong association between dissolved Cu and humic acids, which can prevent biological uptake (Gerringa *et al.*, 1996).

2.4.5. Quantitative assessment of trace metal mobilisation

The net impact of mobilisation and removal processes on the transport of dissolved metals through an estuary can be evaluated by comparing observed trace metal concentrations in the freshwater end-member with 'effective' river water concentrations, which can be obtained by extrapolation of the tangent to the seaward end of the metal-salinity curve to zero salinity. This approach, introduced by Boyle *et al.* (1974), is used frequently by geochemists in order to construct realistic mass balances for estuaries (Windom *et al.*, 1983; Edmond *et al.*, 1985; Bowers and Yeats, 1989; Flegal *et al.*, 1991; Boutier *et al.*; 1993). We used this extrapolation method to calculate effective dissolved metal concentrations for each survey where sea water data were available. In general, reasonable regression coefficients were obtained, except for Cd in cruise 4 and Zn in cruise 8 (see Table 2.7).

Table 2.7. Observed and effective dissolved trace metal concentrations in the Scheldt estuary.

Cruise	Salinity ^a	Statistics		c _{eff} (nM)	c _{obs} (nM)	c _{eff} / c _{obs}
		n	r ²			
<u>Cd</u>						
1	18-35	7	0.854	2.21	0.18	12
2	18-35	7	0.835	2.38	0.18	13
4	15-34	6	0.339	0.35	0.27	1
6	15-35	7	0.907	1.55	<0.09	>17
7	14-35	6	0.989	1.68	0.27	6
8	12-35	7	0.832	1.27	0.09	14
<u>Cu</u>						
1	29-35	4	0.985	69	31	2.2
2	26-35	4	0.996	66	35	1.9
4	18-34	4 ^b	0.930	38	17	2.2
6	18-35	4 ^c	0.961	36	13	2.8
7	28-35	3	0.987	59	22	2.7
8	22-35	4	0.993	45	28	1.6
<u>Zn</u>						
1	10-35	10	0.976	349	352	1.0
2	6-35	11	0.942	255	269	0.9
4	9-34	8	0.890	106	69	1.5
6	6-35	10	0.952	213	58	3.7
7	9-35	8	0.966	241	274	0.9
8	9-35	8	0.665	138	271	0.5

(a) Salinity range for extrapolation to zero salinity; (b) one outlier deleted; (c) two outliers deleted.

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Comparison of the effective dissolved trace metal concentrations with those actually observed shows that the effective dissolved Cd concentrations are an order of magnitude higher during winter (Table 2.7). During phytoplankton blooms, however, the effective dissolved Cd concentration appears to be very low (cruise 4). The effective dissolved Cu concentrations are about two to three times as high as those measured in the river water. The observed and effective dissolved Zn concentrations are similar during winter (except cruise 8), but during summer the effective Zn concentrations are two to four times higher. The effective dissolved metal concentrations typically make up 10-20% of the total metal concentration in the riverine end-member, indicating that the particulate metal concentration is sufficiently high to sustain the mobilisation of Cd, Cu, and Zn within the estuary.

2.5. Conclusions

The major mechanisms which control the distribution of dissolved Cd, Cu, and Zn in the Scheldt estuary are (1) precipitation of trace metal sulphides in the tidal river stretch during the anoxic period (spring and summer), (2) removal of dissolved Cu and Zn in the low-salinity zone, mainly during winter, (3) mobilisation of Cd, Cu, and Zn upon (further) estuarine mixing, and (4) removal of dissolved Cd and Zn, mainly in the lower estuary, during phytoplankton blooms. Because both redox status and phytoplankton activity within the estuary are prone to seasonal variability, such is also the case for the dissolved metal profiles. For instance, Cd mobilisation is evident during winter, when biological processes are suppressed, but can be masked completely during phytoplankton blooms. Seasonal sampling has proved to be an essential tool to improve our understanding of trace metal reactivity in the Scheldt estuary.

The Scheldt estuary is unique in that the behaviour of trace metals can be studied along a full redox gradient. However, measures are now being taken to reduce the organic load of the estuary, aiming to restore the dissolved oxygen concentration. According to this study, such a management strategy might increase the output of dissolved Cd, Cu, and Zn to the North Sea, especially during spring and summer, because precipitation of trace metal sulphides in the tidal river would be precluded. This unintended effect of water quality improvement can be lifted by additional measures, such as removal of the highly polluted sediments in the high-turbidity zone, and reduction of the metal burden of the Scheldt river and its tributaries.

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Chapter 3

Geochemistry of major elements and trace metals in suspended matter of the Scheldt estuary

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Abstract - The geochemistry of suspended matter from the Scheldt estuary has been studied during 8 surveys in 1987-1988. Samples were analysed for major elements (Al, Ca, Fe, K, Mg, Na, Si, Ti, POC, N, P, S) and trace metals (Ag, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sn, Sr, V, Zn). Physical mixing of fluvial and marine particulates leads to a continuous decrease in the trace metal content of the suspended matter with increasing salinity. Principal component analysis shows that the effect of desorption processes (e.g. of Cd, Cu, and Zn) on the suspended matter composition is relatively minor compared to that of particle mixing. A particulate S maximum is present in the upper estuary, reflecting resuspension of reduced sediments. Pore water infusion into the (suboxic) upper estuary is a major source of Fe and Mn to the suspended matter. Due to differences in oxidation kinetics, precipitation of dissolved Mn occurs later (in the lower estuary) than that of Fe (in the upper estuary). Coprecipitation with Mn (hydr)oxides is observed for Ni and Co, but not for the other metals studied. Phytoplankton activity leads to a seasonal shift in the suspended matter composition in the lower estuary. During the spring bloom, the contents of trace metals and lithogenic elements are decreased, in favour of biogenic elements (POC, N, P). This observation is attributed to dilution of mineral particles by phytoplankton which, apparently, has lower trace metal levels. However, the Ba content of the suspended matter is increased during the bloom, which is ascribed to biological formation of barite. Another effect of the spring bloom is depletion of dissolved Cd and Zn (but not of Cu), leading to an increase in their distribution coefficients in the lower estuary. Phytoplankton may both directly (through biological uptake) and indirectly (by increasing the pH) be involved in the seasonal shift of Cd and Zn from the dissolved to the particulate phase. Comparison of recent data on suspended matter composition with historical data shows that the trace metal burden of the Scheldt river has decreased considerably between 1980 and 1995. The decrease in trace metal levels of the fluvial suspended matter amounts to 88% for Cd, 85% for Hg, 74% for As, 59% for Cu, and 50-54% for Cr, Ni, Pb and Zn over the time span considered. However, the Mn content of the fluvial suspended matter has doubled from the early 1970's till the mid 1990's, reflecting the increase in the dissolved oxygen concentration of the river water over the last 20 years.

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3.1. Introduction

It is well known that estuaries can be efficient traps for suspended matter and associated trace metals (e.g. Kennedy, 1984; Bowers and Yeats, 1989). The river input of trace metals to the sea is significantly affected by sedimentation processes in estuaries. Other processes relevant to the geochemistry of particulate trace metals in estuaries are (1) mixing of (contaminated) riverine suspended matter and particles of marine origin (Turner *et al.*, 1991; Mulholland and Olsen, 1992); (2) resuspension of sediments due to dredging, tidal action or storms (Tramontano and Bohlen, 1984; Balls, 1990); (3) mobilisation of Fe and Mn in reducing sediments and subsequent precipitation in the water column (Feely *et al.*, 1986; Paulson *et al.*, 1988); (4) flocculation and coagulation of colloidal material (Sigleo and Helz, 1981; Li *et al.*, 1984); (5) adsorption onto suspended matter in the low-salinity, high-turbidity zone (Morris, 1986; see also chapter 2); (6) desorption from suspended matter or decomposition of labile compounds such as organic matter and sulphides (Jouanneau *et al.*, 1983; see also chapter 2); (7) industrial and domestic waste water discharges (Luther *et al.*, 1986; Campbell *et al.*, 1988); (8) production of organic matter by phytoplankton (Kuwabara *et al.*, 1989; Windom *et al.*, 1989^a; Balls, 1990). Studies on (particulate) trace metal concentrations in estuaries are usually based on a small number of field surveys. This is a serious drawback, hampering the study of seasonal influences related to variation in river flow, storm events, algae blooms, etc. (Helz and Sinex, 1986; Balls, 1990). In addition, few studies deal with the geochemistry of particulate trace metals along a complete salinity gradient. Therefore, our knowledge of the behaviour of particulate (and dissolved) trace metals in estuaries is still fragmentary.

This work deals with the composition of suspended matter, in particular the trace metal geochemistry, of the highly polluted Scheldt estuary. The major objectives were to investigate seasonal changes in suspended matter composition and to identify the processes which control the trace metal content of the suspended matter. Particulate trace metals in the Scheldt estuary have been studied before, but never as part of a time series suitable for identifying seasonal effects (Salomons *et al.*, 1981; Duinker *et al.*, 1982^a; Baeyens *et al.*, 1982; Regnier and Wollast, 1993; Van Alsenoy *et al.*, 1993). The mineralogy of the estuarine suspended matter has been studied fairly well in the past (Wollast *et al.*, 1973; Wartel, 1977; Van Alsenoy *et al.*, 1989). The major components are quartz, calcite, clay minerals (illite, montmorillonite, kaolinite and chlorite), organic matter and iron oxyhydroxides. Minor components include feldspars, dolomite and aragonite, glauconite, rutile, and iron sulphides.

A cohesive sediment balance for the Scheldt estuary for the period 1975-1985 has been constructed by Van Maldegem *et al.* (1993). The balance is based on recorded sedimentation rates, dredging figures, and other data. The input of riverine suspended matter into the estuary was estimated at 400 kton/yr, and the input of marine suspended matter at 200 kton/yr. Most of the suspended matter input is deposited in the sediments between Antwerp and the Dutch-Belgian border (the high-turbidity zone), and in the salt marshes of the lower estuary. Model

calculations indicate that $85 \pm 8\%$ of the fluvial suspended matter input is trapped within the estuary (Verlaan, 1998).

3.2. Sampling and analysis

Suspended matter and water column samples were collected during eight field cruises, carried out regularly between February 1987 and February 1988. All samples were taken at fixed salinities (1 meter below the water surface), irrespective of geographical location or tidal phase. The research vessel was equipped with a sensor system for *in-situ* monitoring of the salinity, pH, dissolved oxygen, and water temperature. Six samples were taken in the low-salinity zone (salinity 0.5-6) where the geochemical gradients are strongest. Further downstream, six additional samples were taken at regular salinity intervals up to the mouth. Suspended matter was collected by flow-through centrifugation (1000 l/h) during 30-45 minutes. The interior of the centrifuge was covered with teflon sheets, which could be removed in order to collect the sample. The suspended matter samples were frozen at $-20\text{ }^{\circ}\text{C}$ and freeze-dried within two days.

Suspended matter was digested according to the method of Nakashima *et al.* (1988), which was slightly modified. A mixture of HClO_4 (9 ml) and HNO_3 (6 ml) was added to powdered aliquots (500 mg) of the suspended matter samples in 100-ml Teflon reaction vessels. A concentrated HF solution (40%, 15 ml) was added, the vessels were closed with a Teflon screw-cap and the samples were decomposed overnight at $90\text{ }^{\circ}\text{C}$. Visual inspection indicated that the digestion of the samples was complete. The open vessels were placed on a sand-bath and the solutions were evaporated nearly to dryness at $180\text{ }^{\circ}\text{C}$ during 4-5 hours, in order to remove excess HF and HClO_4 . The residues were redissolved in diluted HNO_3 (15%, 15 ml) at $90\text{ }^{\circ}\text{C}$. The resulting solutions were transferred into 25-ml calibrated flasks, and diluted to volume with doubly distilled water. For the analysis of Si, an alternative digestion method was used. Aliquots (100 mg) of the suspended matter samples were mixed with LiBO_2 (600 mg) in carbon crucibles. Samples were decomposed at $900\text{ }^{\circ}\text{C}$ during one hour. The crucibles were slowly swung in order to collect the entire melt. After cooling to room temperature, the resulting beads were dissolved completely in diluted HCl (0.2 M, 1 l).

All solutions and reagent blanks were analysed for major elements and trace metals by Inductively Coupled Plasma Atomic Emission Spectrometry. The reliability of the analytical techniques was assessed by analysis of three internal laboratory standards and four Standard Reference Materials: SGR and MAG1 (NBS, Washington), and MESS1 and BCSS1 (NRC, Canada). The contents of each element matched the certified values within 10%, except for Cr. The Cr contents appeared to be underestimated by 20-30%, which might be caused by evaporation of Cr-oxychloride (B.P. $117\text{ }^{\circ}\text{C}$) during the sand-bath drying. Using the certified values as reference data, the analytical results were corrected for incomplete recoveries (typically 5-10% correction but 25% for Cr). The reproducibility of the major element (and Zn) analyses was tested by comparing the contents found after the strong acid digestion with

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those determined after fusion with LiBO_2 . Although the dilution factor (solution volume/sample weight) in these determinations differs by a factor of 200, consistent results were obtained ($r^2 > 0.90$, $n = 102$). We also reanalysed 24 acid-digested samples for Cd and Cu by Atomic Absorption Spectrometry, and found excellent agreement ($r^2 > 0.98$). For these reasons, and also because similar metal contents were found by Regnier and Wollast (1993) one year later, we are confident that the trace metal data presented in this work are reliable.

Particulate organic carbon (POC) was determined in HCl-treated samples by combustion and CO_2 analysis. The carbonate content was determined by CO_2 analysis after acidification. Comparison between the carbonate and the Ca content of the samples showed that virtually all Ca (> 95 %) is present as carbonate. This has also been observed in sediments of the Scheldt estuary (Gaspard, 1984). Particulate nitrogen was determined as ammonium after destruction with concentrated H_2SO_4 (1.5 h at 400 °C).

All elemental contents were corrected for the presence of sea salt, which precipitates during drying of the samples. Washing the dried samples with distilled water to remove the salt was found to cause some loss of K, S, Cu, Ni, and Zn (5-20% of their total contents), and major loss of P and Ba (10-50%), especially in algae-rich samples. These losses are probably related to destruction of cellular material during sampling and/or drying, as noted before by Collier and Edmond (1984). We therefore decided not to wash the dried samples, but to correct for the presence of salt after total analysis. The salt content of the dried samples (0.1-7.0%) was calculated from the ambient salinity of the water during sampling and the water content of the freshly collected suspended matter, determined by gravimetry (55-77%). The salt correction appeared to be very important for Na (up to 80% of the total Na content of the samples is derived from salt) and, to a lesser extent, also for Mg and S (up to 30% of total Mg and S comes from salt). The correction for Ca, K, and Sr was minor (up to 5% of their total element content). For all other elements, a small correction was performed to account for the dilution effect of salt in the samples (maximum 7%).

Water samples for nutrient analyses were filtered on board, stored at 4 °C in the dark, and analysed within two days by standard seawater techniques (Grasshoff *et al.*, 1983). Chlorophyll-a and pheophytin were determined by reversed-phase HPLC. Water samples for trace metal analyses were pressure-filtered through 0.45- μm membrane filters (Sartorius) within 30-60 minutes after collection. The filtration was performed under nitrogen pressure in a laminar-flow hood. The filtrate was adjusted to $\text{pH} \approx 1$ with ultra-pure HNO_3 and stored at 4 °C. Dissolved metals were determined by atomic absorption spectroscopy after preconcentration (Dornemann and Kleist, 1979). Dissolved Zn was measured by flame AAS (Perkin-Elmer 430); Cd and Cu were measured by graphite furnace AAS (Perkin-Elmer 5000). Detection limits were 0.09 nM for Cd, 1.5 nM for Cu, and 3 nM for Zn. Further analytical details are given in chapter 2.

3.3. Results and discussion

3.3.1. Seasonal profiles of general water quality variables

Profiles of the basic water quality variables of the estuary (pH, dissolved oxygen, chlorophyll-a and suspended matter concentration) for four selected cruises are shown in Fig. 3.1. It is not necessary to show all the profiles because of the internal similarity among winter profiles (December-March; cruises 1, 2, 7, 8) and spring-summer profiles (May-October, cruises 3-6). These profiles, which are discussed in detail in chapter 2, are presented here in order to facilitate the discussion on the suspended matter composition.

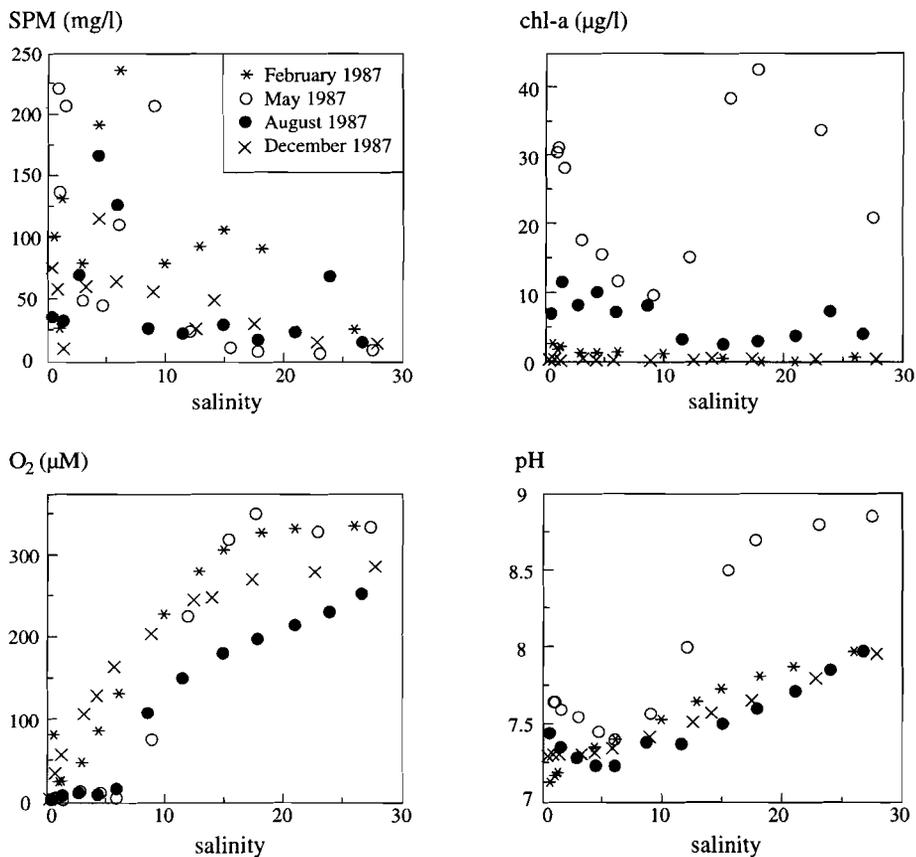


Fig. 3.1. Seasonal profiles of dissolved oxygen, pH, chlorophyll-a and suspended matter concentration in the Scheldt estuary.

The most important features of these profiles are the high-turbidity zone in the upper estuary, the presence of an anoxic water column at low salinities during spring and summer, and the increase in pH and dissolved oxygen with increasing salinity. The chlorophyll-a profiles indicate that primary production is important within the estuary during cruise 3 (the spring bloom) and, to a lesser extent, cruise 4 (not shown). The spring phytoplankton bloom was dominated by mesohaline diatoms in the mid-estuary and by marine diatoms and flagellates near the mouth (Zwolsman, 1994). During late summer and fall (cruises 5 and 6), primary production is much lower and during winter it appears to be negligible (cruises 1, 2, 7, 8).

3.3.2. Fluvial and marine end-member compositions

The average composition of the suspended matter at the fresh-brackish interface and at the mouth of the Scheldt estuary is shown in Table 3.1. Although suspended matter collected at the mouth is not completely of marine origin (80-90% according to Verlaan *et al.*, 1998), we will refer to this material as the marine end-member. The trace metal content of the fluvial suspended matter is high compared to natural background values (see Table 4.4), whilst the marine end-member is relatively uncontaminated. In general, the composition of suspended matter within the estuary lies between these end-member compositions, except for Fe, S, and Mn, which show a maximum in the estuary itself. The trace metal content of the fluvial end-member is relatively constant over the sampling period (see also Table 2.2), whereas the suspended matter concentration varies by almost an order of magnitude (36-222 mg/l; see Table 2.1). This variation in suspended matter concentration is related to differences in river flow and tidal stage during sampling.

Table 3.1. Average composition of the suspended matter at the beginning of the salinity gradient and at the mouth of the Scheldt estuary (1987/88).

		fluvial SPM	marine SPM			fluvial SPM	marine SPM
CaCO ₃	%	11.0 ± 5.4	27.6 ± 3.5	Ag	µg/g	5.5 ± 1.2	2.3 ± 0.7
POC	%	7.1 ± 1.7	5.0 ± 3.4	Ba	µg/g	461 ± 29	235 ± 34
Si	%	24.9 ± 2.2	20.3 ± 2.7	Be	µg/g	1.5 ± 0.1	1.4 ± 0.3
Al	%	4.5 ± 0.2	4.5 ± 0.9	Cd	µg/g	12.2 ± 1.2	1.2 ± 0.5
Ca	%	4.1 ± 0.5	9.9 ± 1.5	Co	µg/g	16.1 ± 1.3	9.5 ± 2.1
Fe	%	4.6 ± 0.3	2.9 ± 0.6	Cr	µg/g	285 ± 24	110 ± 22
K	%	1.56 ± 0.10	1.64 ± 0.12	Cu	µg/g	213 ± 42	29 ± 10
Mg	%	0.66 ± 0.05	0.98 ± 0.15	Li	µg/g	33 ± 3	43 ± 11
N	%	0.48 ± 0.11	0.51 ± 0.41	Mn	µg/g	866 ± 146	1047 ± 182
Na	%	0.40 ± 0.04	0.59 ± 0.08	Ni	µg/g	62 ± 3	35 ± 6
P	%	0.74 ± 0.09	0.21 ± 0.09	Pb	µg/g	207 ± 40	63 ± 13
S	%	0.56 ± 0.10	0.48 ± 0.10	Sn	µg/g	14 ± 6	2 ± 1
Ti	%	0.34 ± 0.02	0.30 ± 0.05	Sr	µg/g	226 ± 28	411 ± 19
				V	µg/g	89 ± 4	95 ± 20
				Zn	µg/g	1039 ± 128	196 ± 35

3.3.3. Interelement relationships

Principal component analysis was performed on the entire dataset in order to identify elements with similar behaviour. The results, listed in Table 3.2, can be summarised as follows. About 90% of the variance in the dataset is explained by four factors, viz. (1) a trace metal group, comprised of Ag, Ba, Cd, Co, Cr, Cu, Ni, Pb, Sn, Zn, but also P and Fe; (2) a detrital element group, consisting of Al, Mg, Ti, Be, Li, and V; (3) a biogenic element group, consisting of chlorophyll-a, POC, and N; and (4) a carbonate group, comprised of Ca and Sr. Elements which cannot be readily classified are K, Mn, Na, S, and Si. The poor relation between K and Al is related to the fact that K is only partially present in the clay fraction (as illite); the rest is in the form of glauconite (Fe-K silicate), as concluded before by Gaspard (1984). Some typical examples of interelement relationships are shown in Fig. 3.2.

Table 3.2. Results of principal component analysis on the entire dataset (n = 98). For each factor, the percentage of variance explained and the individual component loadings are shown.

Factor	1	2	3	4
% variance	45.5	27.8	10.8	5.2
Cr	0.979	0.051	-0.045	0.069
Cd	0.967	-0.141	0.033	0.051
Cu	0.966	-0.168	-0.044	0.136
Pb	0.965	-0.094	0.013	0.167
Zn	0.964	-0.164	-0.059	0.089
Ni	0.942	0.130	0.162	-0.078
Sn	0.880	-0.230	0.000	0.255
Co	0.878	0.369	0.039	-0.104
P	0.866	-0.394	0.254	0.072
Ag	0.847	-0.195	0.106	0.215
Fe	0.830	0.487	0.030	-0.026
Ba	0.759	-0.450	0.148	-0.058
Li	-0.021	0.930	0.107	0.140
Al	0.274	0.924	0.036	0.056
Mg	-0.259	0.903	0.262	0.084
V	0.353	0.872	0.262	0.104
Be	0.502	0.770	0.150	-0.041
Ti	0.537	0.750	-0.164	0.015
POC	0.119	-0.636	0.705	-0.028
Chl-a	-0.347	-0.624	0.643	-0.041
N	-0.158	-0.707	0.630	0.078
Ca	-0.673	0.508	-0.017	0.495
Sr	-0.673	0.308	0.341	0.428
K	0.041	0.551	0.581	-0.355
Mn	-0.363	0.596	0.194	-0.436
Na	-0.796	-0.018	0.196	-0.046
S	0.463	0.254	0.508	-0.496
Si	0.168	-0.227	-0.773	-0.452

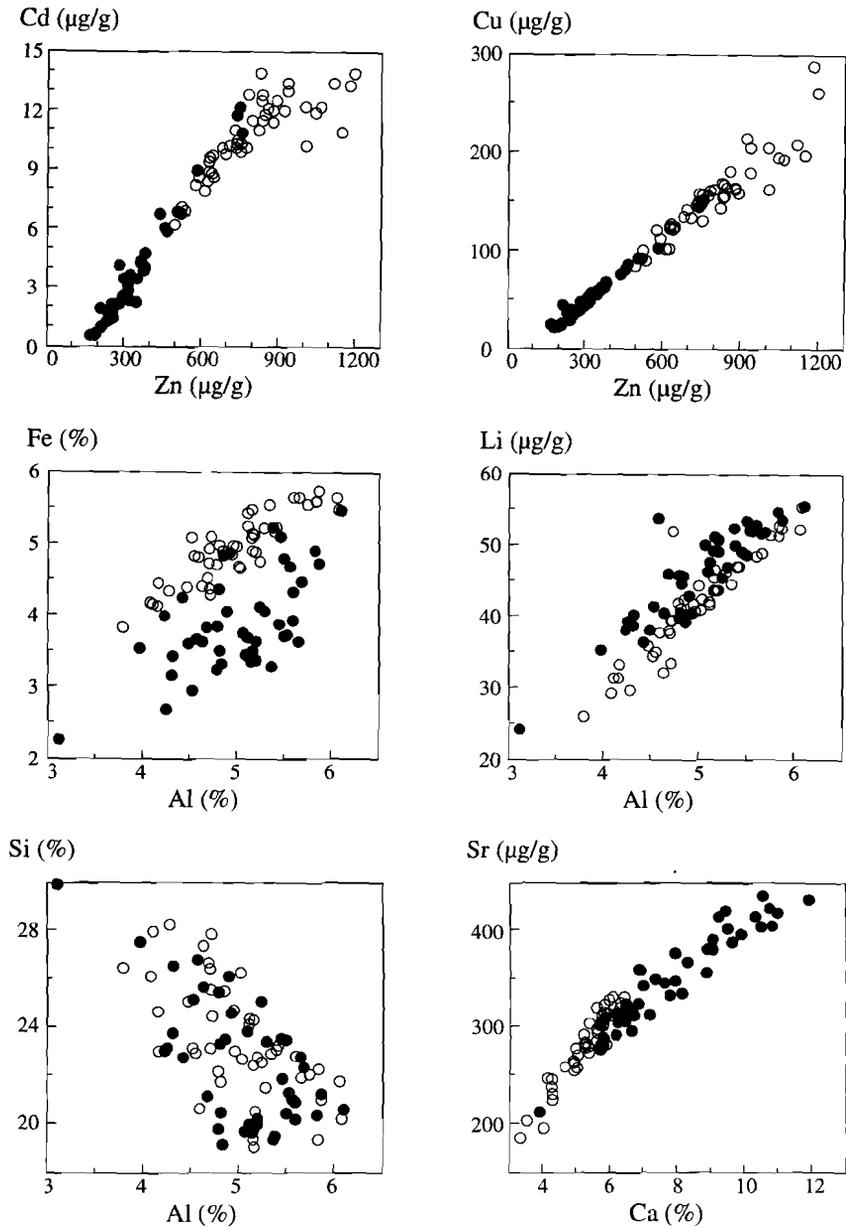


Fig. 3.2. Interelement relationships in suspended matter from the upper estuary (o; salinity < 6) and the lower estuary (•; salinity > 9). Eight algae-rich samples (chlorophyll-a > 1 mg/g) were excluded from the data set.

3.3.4. Estuarine suspended matter composition

The composition of the suspended matter is plotted as a function of salinity in Fig. 3.3 (a-d). Since many elements are strongly interrelated, it is not necessary to show the salinity diagrams for each individual element. The salinity diagrams for the four winter cruises appeared to be so similar, that it is sufficient to show only two winter diagrams (cruises 1 and 7). For similar reasons, only one summer diagram (cruise 5) and one spring diagram (cruise 3) are presented. Information on the other cruises and elements not shown in Fig. 3.3 is included in the tables, however. The geochemistry of the suspended matter is discussed along the following lines: (1) the clay fraction, (2) the carbonate system, (3) Na and Mg, (4) redox-related elements, (5) trace metals, and (6) biogenic elements.

The clay fraction: Al and related elements

In the absence of primary production, the Al content of the suspended matter is more or less independent of salinity (Fig. 3.3a), as is the case for Si, K, Ti, Li, V and Be (not shown). Outside the productive period (i.e. disregarding cruises 3 and 4), the Al content of the suspended matter averages $5.1 \pm 0.5\%$. This narrow range in particulate Al contents implies that grain-size effects on the suspended matter composition will be relatively small. For that reason, the impact of differences in grain-size on the trace metal content of the suspended matter is not regarded in this work. During phytoplankton blooms, the Al content of the suspended matter is significantly lower, especially in the lower estuary (minimum 2.3%).

Suspended matter from the low-salinity zone (salinity 1 to 5) has a slightly higher Al content ($5.1 \pm 0.1\%$, $n=31$) than the fluvial end-member ($4.5 \pm 0.2\%$, $n=8$). This apparent enrichment of Al in the low-salinity zone can be explained by preferential settling of coarse particulates upstream from Antwerp, where the current velocity is relatively high (Wartel, 1977). Similar observations on preferential settling of coarse particulates were made in the high-turbidity zone of the Saint-Lawrence estuary (Gobeil *et al.*, 1981).

The carbonate system: Ca and Sr

The particulate Ca and Sr contents show a major increase with increasing salinity (Fig. 3.3a). Similarly, the calcium carbonate content of the suspended matter increases from 11% in the fluvial end-member to 28% in the marine end-member. The distribution of particulate Ca within the estuary may be explained by physical mixing of fluvial and marine particulates, as concluded by Van Alsenoy *et al.* (1989). However, it can not be ruled out that carbonates are actively precipitating within the estuary, because the water column is highly supersaturated with respect to calcite (Wollast *et al.*, 1973). The close relationship between Ca and Sr (Fig. 3.2) can be explained by incorporation of Sr in the carbonate fraction. Similar Sr-Ca relationships have been observed in salt marshes of the Scheldt estuary (see chapter 5).

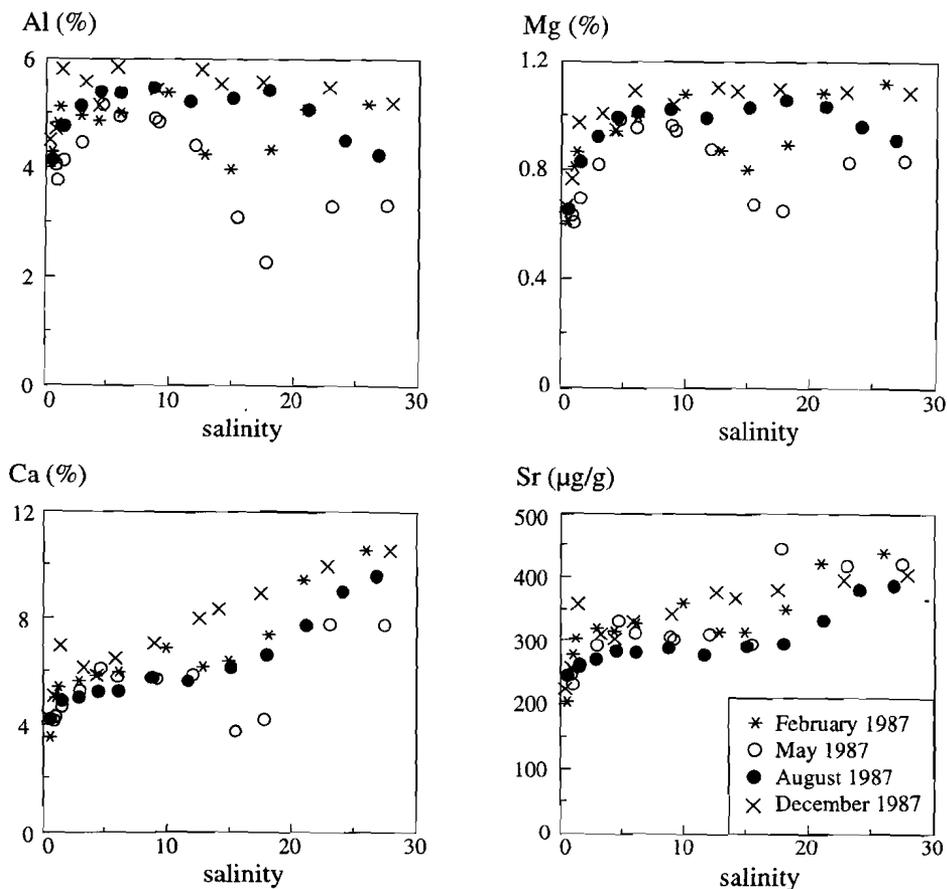


Fig. 3.3a. Suspended matter composition versus salinity: clay-related (Al, Mg) and carbonate-related (Ca, Sr) elements.

Na and Mg

A slight increase with increasing salinity is observed for particulate Na (Table 3.1) and Mg (Fig. 3.3a). The increase in Na may be explained by cation exchange reactions (substitution) on the surface of clay minerals (Sayles and Mangelsdorff, 1977; Sholkovitz and Price, 1980). The seaward increase in particulate Mg is probably related to the (partial) presence of Mg in the carbonate fraction. Gaspard (1984) found that a significant part of Mg in the sediments of the Scheldt estuary is dissolved in diluted acetic acid. He concluded that part of the Mg in the sediments is present as low-Mg calcite, the rest being present in the clay fraction (as chlorite).

Trace metal geochemistry in suspended matter of the Scheldt estuary

Redox elements: Fe, Mn, and S

Maximum contents at intermediate salinities are observed for Fe, Mn, and (total) S (Fig. 3.3b). Particulate Fe and S peak in the upper estuary, whereas the Mn peak is found far more downstream. Van Alsenoy *et al.* (1989) also found an increased abundance of sulphide-rich particles (23% Fe, 61% S) in the upper estuary. The enrichment of S in the suspended matter can be explained by resuspension of sulphidic sediments. The sediments in the upper estuary are highly reducing, with sulphate reduction occurring closely to the sediment-water interface (Fig. 3.4). As a result, the sediments are rich in sulphide, with total S contents up to 1% (Wollast *et al.*, 1973). Due to their weak degree of consolidation, the sediments are easily resuspended, e.g. under the influence of tidal currents (Wartel, 1977; Duinker *et al.*, 1982^a) or dredging operations.

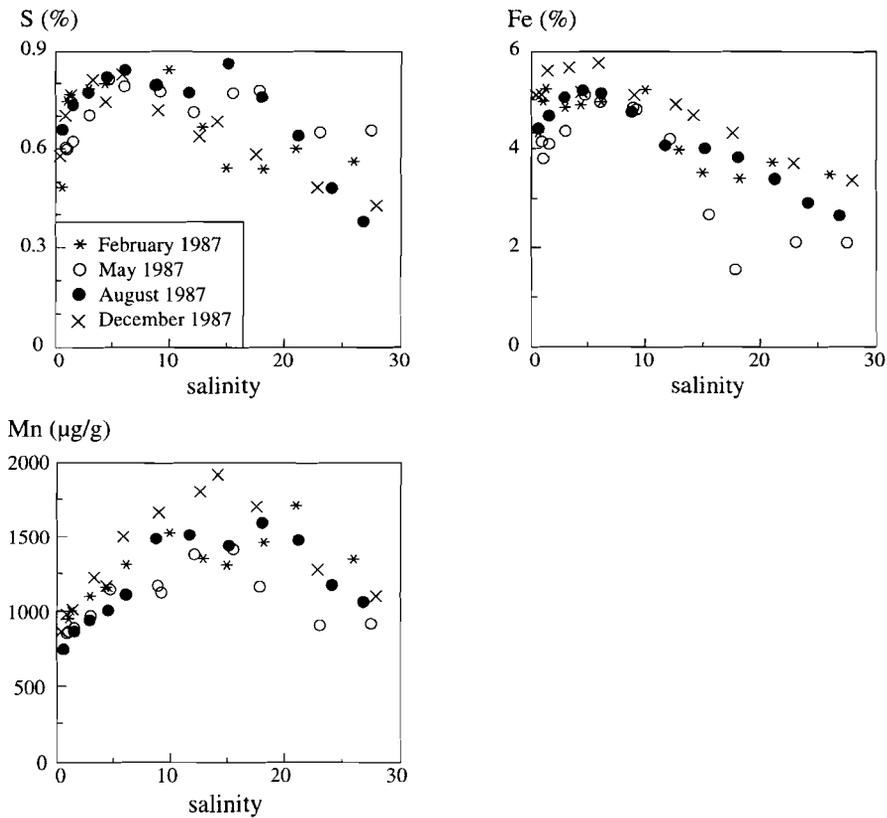


Fig. 3.3b. Suspended matter composition versus salinity: redox-related elements (total S, Fe, Mn).

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Sediment resuspension also promotes injection of pore water species into the water column (Tramontano and Bohlen, 1984). Pore water profiles from the high-turbidity zone were recorded under strictly anaerobic conditions in April 1989 and June 1989, by pressure-filtration of sediment sections under nitrogen atmosphere (details are given in chapter 6). The profiles suggest that release of Mn and Fe from the sediments to the water column takes place in the upper estuary (Fig. 3.4). After release to the water column, dissolved Fe is immediately oxidised and precipitated (Zwolsman, 1994). Dissolved Mn, which is oxidised more slowly, precipitates in the lower estuary, but particulate Mn is returned to the upper estuary through tidal pumping (Duinker *et al.*, 1979; 1982^a). Based on Fick's first law, dissolved Fe and Mn fluxes were estimated for the sediment core taken in June 1989, which was sampled in detail near the sediment-water interface. Assuming a linear profile in the top 1 cm of the sediments, concentration gradients of $2.5 \mu\text{g}/\text{cm}^4$ for Mn and $24 \mu\text{g}/\text{cm}^4$ for Fe are obtained. The diffusion coefficient for these muddy sediments has been estimated by Baeyens *et al.* (1986) to be $10^{-4} \text{ cm}^2/\text{s}$; the sediment porosity is about 0.8. Assuming the obtained fluxes to be typical for all the muddy sediments in the upper estuary (surface area 10 km^2), the outflow of dissolved Mn and Fe from the sediments in the upper estuary is estimated at 20 g/s and 190 g/s , respectively. Given a total suspended matter inflow (fluvial and marine) into the upper estuary of 500 kton/yr (Van Maldegem *et al.*, 1993), these fluxes would result in a significant increase in the Mn and Fe content of the suspended matter ($1260 \mu\text{g/g}$ for Mn and 1.2% for Fe). This calculation should be considered as indicative, because it is based on one sediment core, and also because of the uncertainty in the concentration gradients at the sediment-water interface. Nevertheless, it is clear that diagenetic mobilisation can be a major source of Fe and Mn to the suspended matter of the Scheldt estuary. The role of pore water outflow as a source of Fe and Mn enrichment in the suspended matter is widely recognised in the literature (e.g. Feely *et al.*, 1986; Sundby *et al.*, 1986; Paulson *et al.*, 1988; Dehairs *et al.*, 1989).

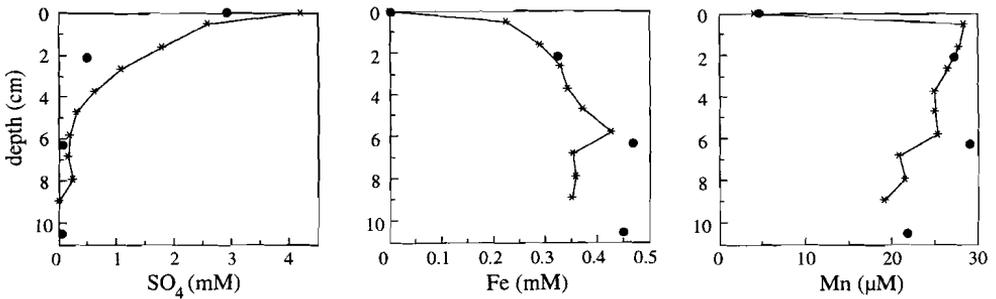


Fig. 3.4. Pore water profiles of Mn, Fe, and sulphate in the low-salinity, high-turbidity zone, sampled in April (●) and June (*) 1989. Average pore water salinities in the top 10 cm were 1.9 (April) and 5.0 (June).

Trace metal geochemistry in suspended matter of the Scheldt estuary

It should be noted that the chemical speciation of Fe in the suspended matter is relatively complex. Electron microprobe analyses have revealed the presence of various Fe-rich particle types, viz. Fe-aluminosilicates (chlorites and smectites), Fe-K silicates (glauconite), Fe oxyhydroxides, and Fe sulphides (Van Alsenoy *et al.*, 1989). Sequential extractions on two suspended matter samples, collected near the Dutch-Belgian border in May 1986 (salinity 9-14), were performed by Saager and Reynders (1986) using the method of Calmano and Förstner (1983). The contribution of Fe oxides (amorphous and crystalline) to the total Fe content of the suspended matter was found to be $37 \pm 2\%$; the oxidisable fraction (e.g. Fe sulphides) contributed only 4%, and the residual fraction $57 \pm 2\%$. Thus, 40% of the total Fe content is not in the form of aluminosilicates (at that location). Considering the speciation of particulate Mn, it was found that $15 \pm 2\%$ of the Mn was present in readily exchangeable forms, $28 \pm 3\%$ was in the form of carbonates, $48 \pm 5\%$ was present as oxides (predominantly in the easily reducible fraction) and $7 \pm 1\%$ was in the residual fraction. This means that almost half of the Mn in the suspended matter is present in reduced forms (Mn^{2+}), halfway down the estuary.

Trace metals

A somewhat exponential decrease with increasing salinity is observed for particulate Ag, Cd, Cr, Cu, Pb, Sn, and Zn (only shown for Cd, Cu, and Zn; see Fig. 3.3c). A less dramatic decrease with increasing salinity is observed for Ni and Co (Fig. 3.3c). Similar particulate trace metal distributions have been observed before in the Scheldt (Salomons *et al.*, 1981; Duinker *et al.*, 1982^a; Regnier and Wollast, 1993), as well as in many other estuaries, both in Europe and in the U.S.A. (e.g. Olsen *et al.*, 1989; Schoer, 1990; Turner *et al.*, 1991; Paalman and Van der Weijden, 1992). It is well-known that these distributions are primarily related to physical mixing of fluvial and marine particulates. Studies with stable carbon isotopes, stable nitrogen isotopes, and radionuclides have provided convincing evidence of particle mixing processes in the Scheldt estuary (Mariotti *et al.*, 1984; Laane *et al.*, 1990; Martin *et al.*, 1994). The decrease in trace metal content of the suspended matter with increasing salinity simply reflects the increase in the (relatively uncontaminated) marine component of the suspended matter. It might be argued that the decrease in particulate metal contents is also caused by desorption processes, which have been demonstrated in the Scheldt estuary for Cd, Cu, and Zn (see chapter 2). However, the principal component analysis indicates that all trace metals show common geochemical behaviour, since they cluster together into one group (factor 1 in Table 3.2). Since desorption of Cr and Pb is insignificant in the estuary (Salomons and Eysink, 1981; Zwolsman and van Eck, 1993), it follows that the decrease in particulate, Cr, Pb, and other trace metals with increasing salinity is primarily caused by mixing of fluvial and marine particulates. Simple calculations show that this is due to mass-balance constraints.

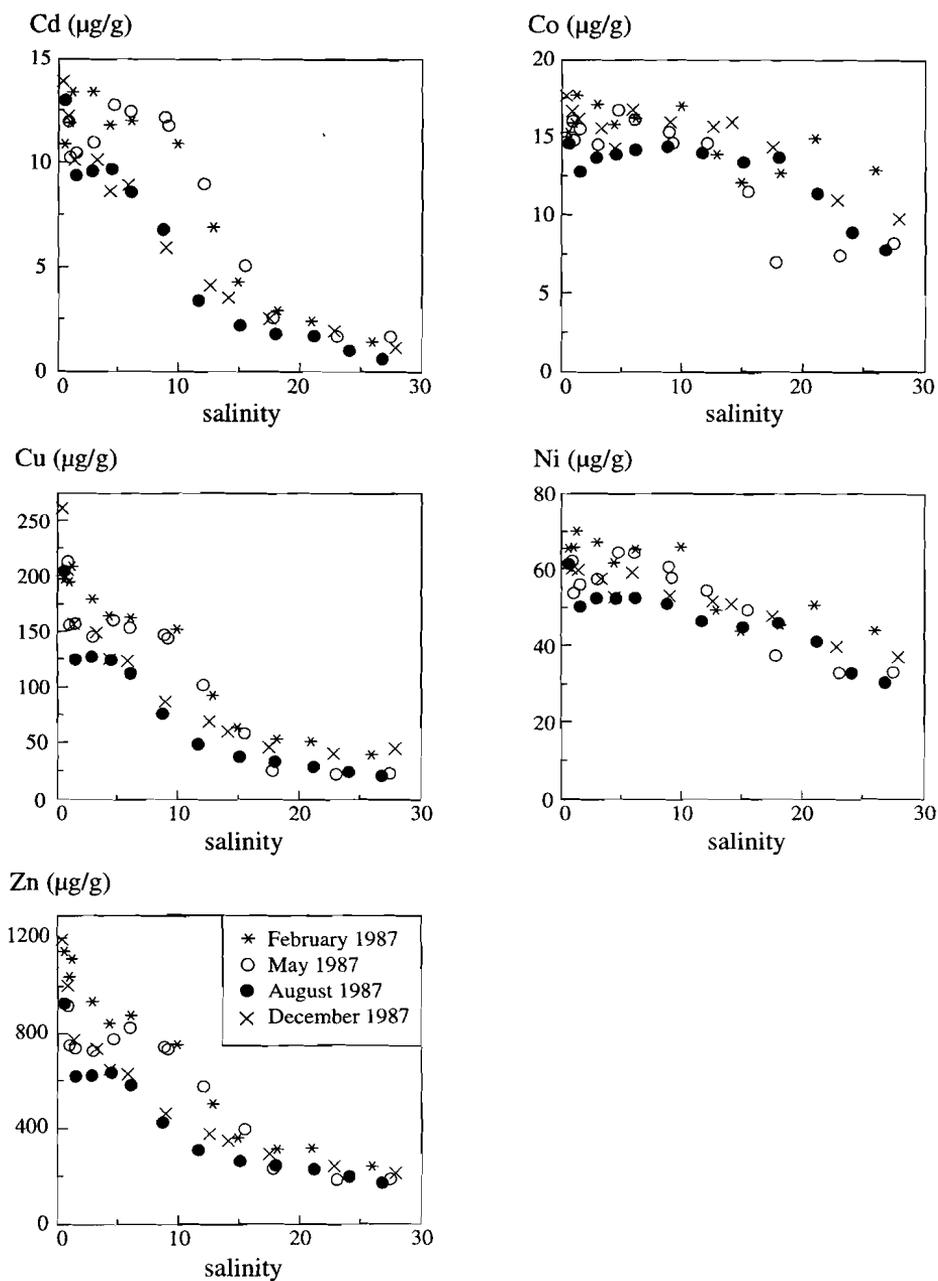


Fig. 3.3c. Suspended matter composition versus salinity: trace metals (Cd, Co, Cu, Ni, Zn).

Typically, desorption processes increase the dissolved trace metal concentration in the mid-estuary by 0.5-1.0 nM for Cd, 10-15 nM for Cu and 50-100 nM for Zn (Fig. 2.3). Given a typical suspended matter concentration of 50 mg/l in the brackish water zone, this increase in dissolved trace metals is equivalent to a decrease in the particulate trace metal content of 1.1-2.2 µg/g for Cd, 13-19 µg/g for Cu, and 65-130 µg/g for Zn. These are maximum estimates, because other sources of dissolved trace metals to the mid-estuary, i.e. metal inputs from the salt marshes (see chapter 5) and from the sediments (see chapter 6), are not considered. Thus, the calculated losses due to desorption processes are second-order compared to the observed decrease in particulate trace metal contents over the salinity gradient, amounting on the average 11 µg/g for Cd, 184 µg/g for Cu, and 843 µg/g for Zn (Table 3.1).

In the heavily industrialised area around Antwerp, there are indications that the suspended matter composition is somewhat modified by industrial effluents. This is especially clear for the Cd content of the suspended matter, which frequently shows a maximum in the low-salinity zone (cruises 1, 3, 4 and 8). An obvious example is provided by the salinity diagrams of cruise 1 (Fig. 3.3c), featuring particulate Cd levels of 10.9 µg/g in the fluvial end-member, increasing to 13.4 µg/g near Antwerp, whereas particulate Zn levels decrease from 1147 µg/g to 936 µg/g in that same section (due to particle mixing processes). Such obvious impacts of direct inputs are restricted to Cd, however. Smaller impacts were observed for Ni (cruises 1, 3, 4, 8) and, incidentally, for Cr (cruise 3) and Pb (cruise 1).

The behaviour of particulate Ni and Co deserves special attention here. In the upper estuary, the Ni and Co contents of the suspended matter are not related to Mn, but in the lower estuary a good relationship between Ni, Co, and Mn is found (Fig. 3.5). This observation can be explained by considering the precipitation dynamics of Mn oxides. In the (suboxic) upper estuary, particulate Mn is predominantly present as MnCO₃. Ni and Co, on the other hand, may be partially associated with sulphides, as suggested before for Cd, Cu, and Zn (see chapter 2). These metal sulphides are gradually oxidised during restoration of dissolved oxygen with increasing salinity (Fig. 3.1), resulting in release of trace metals to the dissolved phase. At the same time, Mn (hydr)oxides are being formed, which are very effective scavengers of trace metals. The close relationship between Ni, Co, and Mn in the suspended matter of the lower estuary indicates that Ni and Co are mobilised from the suspended matter but then scavenged back by Mn oxides. The distribution of dissolved Co confirms the presence of a removal process in the lower estuary, where aerobic conditions are restored (Martin *et al.*, 1994). Coprecipitation of Ni and Co with Mn oxides was also found near the oxic-suboxic interface in salt marshes of the Scheldt estuary (see Fig. 5.4). Considering other trace metals (Cd, Cr, Cu, Pb, Zn), only weak correlations with Mn were observed in the lower estuary ($r^2 = 0.3$ to 0.4 , as opposed to 0.78 for Co and 0.82 for Ni). Although these metals may be scavenged by Mn oxides too (e.g. Feely *et al.*, 1986; Paulson *et al.*, 1988), this process seems to be of minor importance in the Scheldt estuary.

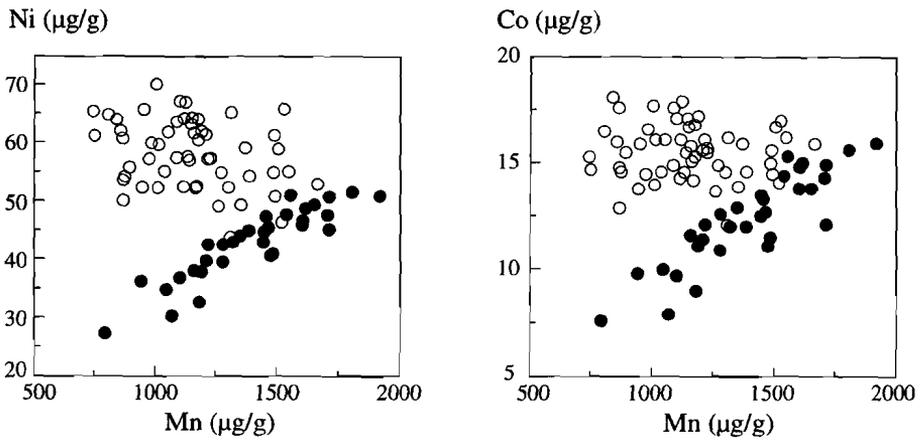


Fig. 3.5 Ni-Mn and Co-Mn relationships in suspended matter from the upper estuary (o) and the lower estuary (•). Eight algae-rich samples were excluded.

Biogenic elements: POC, N, P, and Ba

Outside the productive period, the POC, N, P, and Ba contents of the suspended matter show a decrease with increasing salinity (Fig. 3.3d). Very different salinity diagrams are obtained during the spring bloom (cruise 3), when a sudden increase in the POC, N, P, and Ba contents is observed in the lower estuary. At the same time, the contents of lithogenic elements such as Al and Fe are relatively low (Fig. 3.3a). This shift towards biogenic elements in the lower estuary reflects the presence of a major planktonic component in the suspended matter. This conclusion is corroborated for POC, N, and P, by their linear relationships with the chlorophyll-a content in the lower estuary over the year (Fig. 3.6). From the slope of these equations, the elemental composition of the phytoplankton can be calculated as $C_{106} N_{10} P_{1.1}$, which seems quite reasonable.

Trace metal geochemistry in suspended matter of the Scheldt estuary

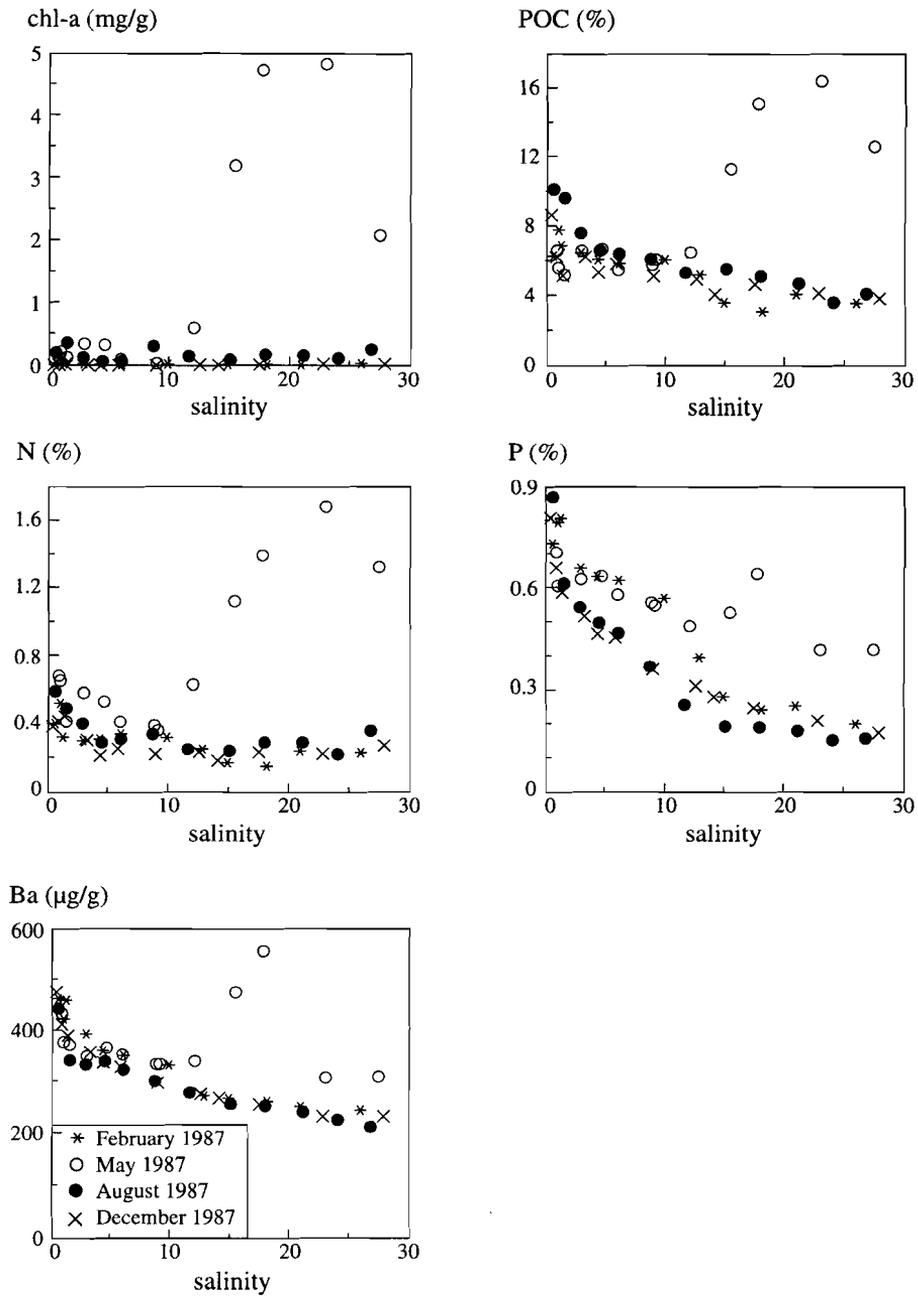


Fig. 3.3d. Suspended matter composition versus salinity: chlorophyll-a and biogenic elements (POC, N, P, Ba).

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The impact of primary production on the suspended matter composition in the lower estuary is shown in Table 3.3. For some trace metals (Co, Cr), dilution of mineral particles by phytoplankton leads to lower concentration levels in the suspended matter. This dilution effect of primary production on suspended matter composition has been reported in other estuaries (Valenta *et al.*, 1986; Windom *et al.*, 1989^a; Balls, 1990) and also in freshwater basins fed by the Rhine (Salomons and Mook, 1980; Van de Meent *et al.*, 1985). The observed enrichment of Ba in the suspended matter during the spring bloom is probably related to biological formation of barite. It is generally accepted that primary productivity and barite formation are closely associated, although the geochemical mechanism of barite formation remains controversial (Dehairs *et al.*, 1987; Bishop, 1988). Biologically produced barite may contain minor amounts of Sr (Bishop, 1988), which could explain the high Sr/Ca ratio of the suspended matter during the bloom (Table 3.3).

Table 3.3. Seasonal evolution of suspended matter composition in the lower Scheldt estuary (salinity > 15; n = 4 for each cruise).

Season		Winter	Spring	Early summer	Summer/fall
Cruise		1, 2, 7, 8	3	4	5, 6
Salinity		20 ± 4	21 ± 5	21 ± 5	21 ± 5
Chl-a	mg/g	0.03 ± 0.04	3.7 ± 1.1	1.3 ± 1.0	0.1 ± 0.1
POC	%	3.6 ± 0.8	13.9 ± 2.0	7.3 ± 2.5	3.9 ± 0.9
N	%	0.24 ± 0.07	1.38 ± 0.20	0.67 ± 0.26	0.28 ± 0.04
P	%	0.23 ± 0.03	0.50 ± 0.09	0.28 ± 0.08	0.19 ± 0.03
S	%	0.57 ± 0.09	0.71 ± 0.06	0.62 ± 0.12	0.63 ± 0.18
K	%	1.71 ± 0.08	1.69 ± 0.09	1.72 ± 0.19	1.70 ± 0.10
Si	%	22.1 ± 4.5	18.3 ± 3.1	21.8 ± 2.7	22.8 ± 1.6
Ca	%	9.4 ± 1.5	5.8 ± 1.9	7.3 ± 1.3	8.2 ± 1.4
Al	%	5.0 ± 0.5	3.0 ± 0.4	4.0 ± 0.7	5.2 ± 0.5
Fe	%	3.7 ± 0.4	2.1 ± 0.4	2.7 ± 0.6	3.6 ± 0.5
Mg	%	1.03 ± 0.10	0.75 ± 0.08	0.88 ± 0.15	1.05 ± 0.06
Ti	%	0.33 ± 0.02	0.21 ± 0.03	0.27 ± 0.05	0.35 ± 0.02
Mn	µg/g	1398 ± 259	1104 ± 209	1422 ± 399	1386 ± 217
Ba	µg/g	246 ± 19	415 ± 107	226 ± 14	243 ± 18
Sr	µg/g	392 ± 37	394 ± 59	357 ± 44	344 ± 39
Zn	µg/g	283 ± 50	254 ± 87	222 ± 54	240 ± 41
Cr	µg/g	136 ± 19	96 ± 24	100 ± 15	127 ± 18
V	µg/g	107 ± 9	70 ± 9	86 ± 17	101 ± 12
Pb	µg/g	80 ± 8	62 ± 17	64 ± 15	63 ± 7
Ni	µg/g	44 ± 5	38 ± 7	39 ± 9	41 ± 6
Cu	µg/g	47 ± 10	33 ± 15	30 ± 9	32 ± 8
Li	µg/g	48 ± 5	26 ± 4	37 ± 8	48 ± 5
Co	µg/g	13 ± 2	9 ± 2	10 ± 2	12 ± 2
Cd	µg/g	2.4 ± 0.9	2.8 ± 1.4	1.7 ± 0.2	1.9 ± 1.1
Ag	µg/g	2.8 ± 0.9	2.6 ± 0.6	2.4 ± 0.6	1.4 ± 0.4

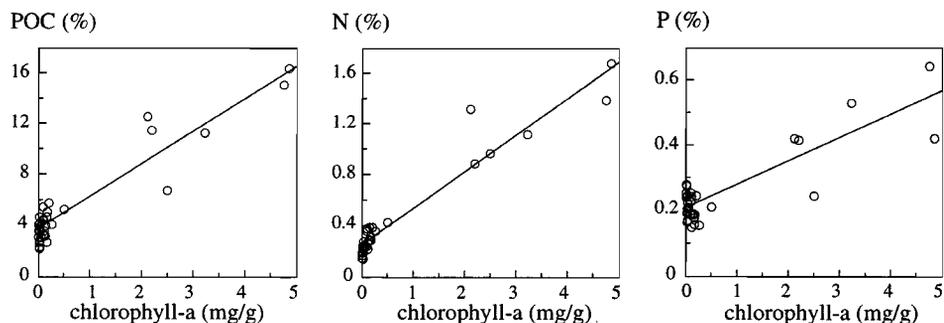


Fig. 3.6. Relation between POC, N, P, and chlorophyll-a content of the suspended matter in the lower estuary (salinity > 15, n = 4 for each cruise). Linear regression equations:

$$\text{POC (\%)} = 3.67 + 2.572 \times \text{chlorophyll-a (mg/g)}; r^2 = 0.886, n = 32$$

$$\text{N (\%)} = 0.25 + 0.287 \times \text{chlorophyll-a (mg/g)}; r^2 = 0.930, n = 32$$

$$\text{P (\%)} = 0.21 + 0.071 \times \text{chlorophyll-a (mg/g)}; r^2 = 0.736, n = 32$$

3.3.5. Impact of primary production on trace metal partitioning

In the previous section, it was shown that phytoplankton activity leads to a seasonal shift in the suspended matter composition in the lower estuary. During the spring bloom, the suspended matter is made up of lithogenic and biogenic particles, whereas during winter the phytoplankton component of the suspended matter is negligible. This seasonal difference in suspended matter composition may affect the distribution of bioactive trace metals between the dissolved and the particulate phase (Tappin *et al.*, 1995). In Table 3.4, the seasonal evolution of dissolved and particulate Cd, Cu, and Zn within a narrow salinity range of the lower estuary is presented, together with data on general water quality variables and dissolved nutrients. The spring diatom bloom (cruise 3) is reflected by supersaturation of dissolved oxygen, a major pH increase (almost a full pH unit), and a decrease in the concentrations of orthophosphate and dissolved silicate (i.e. compared to the previous winter situation). In addition, a major decrease of dissolved Cd and Zn accompanies the bloom, whereas dissolved Cu is much less affected (cf. cruise 3 with cruises 1 and 2). A concomitant decrease in particulate Cu and (less obvious) Zn occurs, but particulate Cd levels remain constant. As a result, the distribution coefficients (K_d = particulate/dissolved metal ratio) of Cd and Zn increase, whilst the K_d of Cu decreases during the phytoplankton bloom. These results suggest that, in the lower Scheldt estuary, the affinity of phytoplankton for Cd and Zn is greater than that of lithogenic particles. The association between Cd and phytoplankton is frequently reported in the literature (e.g. Valenta *et al.*, 1986; Kuwabara *et al.*, 1989; Balls, 1990).

Table 3.4 Seasonal evolution of water column chemistry and trace metal partitioning in the lower Scheldt estuary (salinity range 15-23, n = 3 for each cruise). Note the increase in the K_d 's for Cd and Zn during the productive period (cruise 3 and 4).

Cruise nr. date (1987)		1 February 18	2 April 1	3 May 13	4 July 7	5 August 25	6 October 14	7 December 15
Salinity		18.0 ± 2.5	18.5 ± 1.9	18.7 ± 3.2	18.9 ± 3.5	18.0 ± 2.5	18.6 ± 3.5	18.1 ± 3.6
T	°C	2.3 ± 0.1	5.2 ± 0.1	11.5 ± 0.3	19.4 ± 0.5	19.4 ± 0.1	13.3 ± 0.2	4.7 ± 0.3
SPM	mg/l	74 ± 35	103 ± 84	9 ± 2	30 ± 17	24 ± 5	45 ± 22	32 ± 14
Chlorophyll-a	µg/l	0.1 ± 0.2	3.7 ± 0.9	38 ± 4	14 ± 4	3.1 ± 0.5	3.3 ± 0.1	0.4 ± 0.1
Pheophytin	µg/l	0.1 ± 0.1	0.3 ± 0.1	0.5 ± 0.1	1.4 ± 0.6	0.2 ± 0.2	0.1 ± 0.1	0.1 ± 0.1
pH		7.8 ± 0.1	7.9 ± 0.1	8.7 ± 0.1	8.0 ± 0.2	7.6 ± 0.1	7.9 ± 0.1	7.7 ± 0.1
O ₂	µM	323 ± 11	299 ± 2	332 ± 13	207 ± 16	197 ± 14	232 ± 6	265 ± 13
PO ₄	µM	9.7 ± 0.8	7.0 ± 0.6	5.3 ± 1.8	8.4 ± 2.0	10.4 ± 1.5	10.5 ± 1.6	7.7 ± 1.0
Si	µM	118 ± 18	98 ± 14	42 ± 20	7 ± 6	42 ± 12	68 ± 17	99 ± 23
d-Cd	nM	1.2 ± 0.1	1.1 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.6 ± 0.1	0.9 ± 0.1	0.9 ± 0.2
d-Cu	nM	22 ± 2	19 ± 3	16 ± 1	16 ± 2	16 ± 1	20 ± 1	23 ± 6
d-Zn	nM	168 ± 25	131 ± 28	29 ± 6	51 ± 18	57 ± 15	84 ± 17	114 ± 28
p-Cd	µg/g	3.2 ± 0.8	2.7 ± 0.7	3.1 ± 1.4	1.7 ± 0.2	1.9 ± 0.2	3.0 ± 1.1	2.6 ± 0.7
p-Cu	µg/g	56 ± 5	53 ± 4	37 ± 16	35 ± 3	34 ± 4	39 ± 7	49 ± 8
p-Zn	µg/g	331 ± 22	315 ± 27	275 ± 91	253 ± 1	253 ± 14	277 ± 28	293 ± 44
K_d -Cd	l/g	24 ± 8	23 ± 7	118 ± 46	66 ± 14	28 ± 5	31 ± 10	25 ± 3
K_d -Cu	l/g	41 ± 4	45 ± 3	36 ± 13	35 ± 6	33 ± 4	30 ± 6	36 ± 6
K_d -Zn	l/g	31 ± 3	38 ± 6	142 ± 18	90 ± 41	73 ± 16	52 ± 5	40 ± 4

PO₄ = orthophosphate, Si = dissolved silicate, d-Cd = dissolved Cd concentration, p-Cd = particulate Cd content, K_d -Cd = distribution coefficient for Cd.

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The uptake of dissolved Zn may be related to incorporation in the opaline exoskeleta of the diatom community (Hunter and Tyler, 1987). An alternative explanation is increased adsorption onto suspended matter, driven by the increase in pH (Shiller and Boyle, 1985) which is an indirect effect of the bloom. The biological uptake of Cu is possibly limited due to the strong association between dissolved Cu and humic acids or organic colloids (Valenta *et al.*, 1986; Gerringa *et al.*, 1996).

3.3.6. Metal pollution history

An historic overview of the trace metal content of the suspended matter at the beginning of the salinity gradient is presented in Table 3.5. Data from 10 recent sampling cruises (1995-96; see chapter 8) are included. It is justified to compare the data obtained in 1987-88 and 1995-96 (total digestion) to those determined in the 1970's (strong acid digestion), because the difference in extraction efficiency is small for all the trace metals considered here, except for Cr. Table 3.5 indicates that the trace metal content of the fluvial suspended matter was very high at the end of the 1970's, as confirmed by other surveys carried out in 1978 (Duinker *et al.*, 1982a) and 1981 (Baeyens *et al.*, 1982). Trace metal profiles in radiodated sediment cores also indicate the presence of a pollution maximum around 1980 (see chapter 5). However, the suspended matter quality has significantly improved over the last two decades. Compared to the situation in 1979, the present-day (1996) trace metal levels in the fluvial suspended matter have decreased by 88% for Cd, 74% for As, 59% for Cu, and 50-54% for Cr, Ni, Pb, and Zn (Table 3.5). The particulate Hg content of the fluvial suspended matter has decreased by 85%, from 10 µg/g in 1981-83 to 1.5 µg/g in 1991-94 (Leermakers *et al.*, 1995).

Table 3.5. Trace metal content of the suspended matter in the fluvial end-member between 1974 and 1996. Samples were analysed by AAS after strong acid extraction (refs. a, b) or ICP-AES after total digestion (refs. c, d). Particulate As was analysed by neutron activation analysis (ref. b) or hydride generation AAS (ref. d).

		April 1974 ^a n = 2	Sept. 1979 ^b n = 25	1987-1988 ^c n = 8	1995-1996 ^d n = 10
As	µg/g	-	141 ± 13 ^e	-	37 ± 5
Cd	µg/g	-	52 ± 7	12.2 ± 1.2	6.5 ± 1.2
Cr	µg/g	311 ± 2	336 ± 57	285 ± 24	155 ± 21
Cu	µg/g	220 ± 2	271 ± 67	213 ± 42	112 ± 18
Mn	µg/g	484 ± 49	787 ± 86	866 ± 146	1073 ± 296
Ni	µg/g	-	83 ± 13	62 ± 3	42 ± 5
Pb	µg/g	234 ± 13	334 ± 50	207 ± 40	157 ± 22
Zn	µg/g	1225 ± 39	1341 ± 262	1039 ± 128	644 ± 69

(a) Hoenig (1976); (b) Salomons *et al.* (1981); (c) this work; (d) see chapter 8; (e) n = 10.

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Opposite to the trend in particulate trace metal levels, the Mn content of the fluvial suspended matter has doubled over the last 20 years (Table 3.5). This observation is probably related to variations in the dissolved oxygen concentration over time. In the early 1970's, the dissolved oxygen concentration in the Scheldt river was dramatically low, resulting in reductive dissolution of Mn from the suspended matter (Wollast *et al.*, 1979). The low Mn content of the fluvial suspended matter in the early 1970's, which is confirmed by other surveys (e.g. 420 µg/g in October 1973 and 550 µg/g in April 1974; Duinker *et al.*, 1979), may well be explained by this process. However, the dissolved oxygen concentration of the Scheldt river increased gradually in the 1980's due to waste water purification measures, and this improvement is still going on in the 1990's (see Fig. 1.1). Consequently, reductive dissolution of particle-bound Mn becomes less favourable and may eventually be prevented. The increasing Mn content of the fluvial suspended matter thus reflects the increasing redox potential of the river water over the last 20 years.

3.4. Conclusions

This study has shown that the suspended matter composition in the Scheldt estuary is controlled by various processes. The most important process is obviously physical mixing of fluvial and marine particulates, which leads to a continuous decrease in the trace metal content of the suspended matter with increasing salinity. The effect of desorption processes on the suspended matter composition is relatively small compared to that of particle mixing. Processes which affect specific elements in the suspended matter are resuspension of muddy sediments in the upper estuary (S), release of Mn²⁺ and Fe²⁺ from the pore waters, followed by oxidative precipitation, coprecipitation with Mn oxides (Co and Ni), and metal inputs into the upper estuary (Cd and Ni). The suspended matter composition in the lower estuary is significantly altered by phytoplankton blooms, resulting in an increase in biogenic element contents at the expense of lithogenic element contents. In the upper estuary, where the suspended matter concentrations are much higher, the impact of phytoplankton on the suspended matter composition is negligible.

Acknowledgements - Thanks are due to the crews of the research vessels 'Argus' and 'Delta', and to C. Buurman for technical assistance during sampling and analysis. We gratefully acknowledge T. Van Zessen, P. Anten and B. Djie-Kwee for their help in the ICP-AES measurements and interpretations. We also thank W. Schreurs and his laboratory staff for analysis of POC, carbonate and nitrogen in the suspended matter, and for the analyses of the water samples.

Chapter 4

Spatial and temporal distribution of trace metals in sediments of the Scheldt estuary

J.J.G. Zwolsman, G.T.M. Van Eck and G. Burger

Abstract - The spatial and temporal distribution of trace metals in sediments of the Scheldt estuary has been studied, in order to identify trends in space and time. Sediment trace metal data, obtained by 11 laboratories, were considered for the period 1959 to 1990. It was found that trace metal data obtained by complete sample digestion (e.g. $\text{HClO}_4\text{-HF}$) were incomparable to those obtained by strong acid leaching (e.g. $\text{HNO}_3\text{-HCl}$). However, various strong acid leaches were found to yield comparable results for sediment trace metals, except for chromium. Hence, trace metal data obtained by strong acid digestion could be merged into a comprehensive database (except for chromium), which was analysed by an ANOVA procedure. Sediment trace metal contents were normalised on a common standard, based on grain-size fraction $< 16 \mu\text{m}$ and organic matter content. Spatial variations were investigated for four areas, encompassing the entire Scheldt estuary, within the periods 1978-1985 and 1986-1990. For one specific area, halfway down the estuary, trace metal data were studied from 1959 to 1987. For each area and period considered, the sediment trace metal content was calculated at the average percentage $< 16 \mu\text{m}$ and organic matter content of the whole data-set. The results showed that: (1) The upper Scheldt estuary is strongly polluted by trace metals, especially cadmium; (2) Viewed in historic perspective, pollution of the Scheldt estuary by trace metals was maximal at the end of the 1950's but decreased considerably through the 1970's and again in the 1980's. (3) The trace metal content of the sediments decreases going from the upper estuary to the lower estuary, due to mixing of metal-rich fluvial sediments and metal-poor marine sediments; (4) Though physical mixing is the most important process that controls the trace metal content of the sediments, evidence is presented for mobilisation of cadmium with increasing salinity, whilst this is suggested for arsenic.

4.1. Introduction

Pollution of the natural environment by trace metals is a world-wide problem (e.g. Nriagu and Pacyna, 1988). The impact of anthropogenic perturbation is most strongly felt by rivers draining densely populated and industrialised areas, and their estuaries. Once released into the environment, trace metals are transferred to the sediments through adsorption onto suspended matter and subsequent sedimentation (Hart, 1982). Therefore, the deterioration of the aquatic environment is clearly reflected by the composition of the sediments (e.g. Taylor, 1986; Mudroch *et al.*, 1988). From an environmental point of view, there are three major reasons for studying the distribution of trace metals in sediments.

- (1) An important fraction of trace metals in polluted sediments exists in relatively unstable forms, making them available to benthic fauna (Loring, 1981; Luoma and Bryan, 1982; Tessier *et al.*, 1984; Luoma, 1989). Though there is no general relationship between the trace metal content of a sediment and its biological effects (Bryan and Langston, 1992; Long, 1992), thresholds can be identified above which effects frequently or always occur (Long, 1992).
- (2) The surface layer of the sediments can be assumed to be in some state of equilibrium with the overlying water column. Sediment-bound trace metals may, therefore, become a source of pollution to the water column if anthropogenic metal loads are reduced (Salomons *et al.*, 1987; Santschi *et al.*, 1990).
- (3) The history of trace metal pollution in the aquatic environment over the last 50 years is not well-documented, mainly because of analytical problems. The role trace metals have played in the deterioration of aquatic ecosystems is, therefore, difficult to evaluate. Sediment trace metal data can best be used for such an evaluation, since they are usually more widely available and generally more reliable than dissolved metal concentrations in a water system (Santschi *et al.*, 1984; Finney and Huh, 1989; Gearing *et al.*, 1991).

This study deals with the spatial and temporal distribution of trace metals in sediments of the Scheldt estuary, which is severely polluted by trace metals. The main objectives of the study were:

- (1) To summarise the results obtained from regular monitoring surveys and from individual sampling campaigns, carried out between 1959 and 1990 on behalf of Rijkswaterstaat, the Dutch authority responsible for the management of the estuary;
- (2) To assess the spatial and temporal changes of the trace metal content of the sediments in a statistically reliable way;
- (3) To identify the processes controlling the spatial distribution of trace metals in the sediments.

4.2. Study area

The geological substratum of the Scheldt estuary consists of Oligocene to Pliocene and Quaternary sands, clayey sands and clays, covered by a 2 m thick Holocene peat layer overlain by clays (Dunkerque transgressions). Between Rupelmonde and Hoboken (see Fig. 4.1) a very cohesive clay layer (Boom clay) is present with a continuous Quaternary gravel deposit on top. The grain-size distribution and the mineralogy of the surface sediments has been described in detail by Wartel (1977). The major constituents of the silt and clay fractions are quartz, clay minerals and carbonates. The clay minerals consist of illite, kaolinite (disoriented), montmorillonite, and interlayered minerals. The sand fraction is dominated by quartz, additional constituents are feldspars, mica, glauconite, carbonates and heavy minerals. Based on its sediments, the Scheldt estuary can be divided into three zones (see Fig. 4.1):

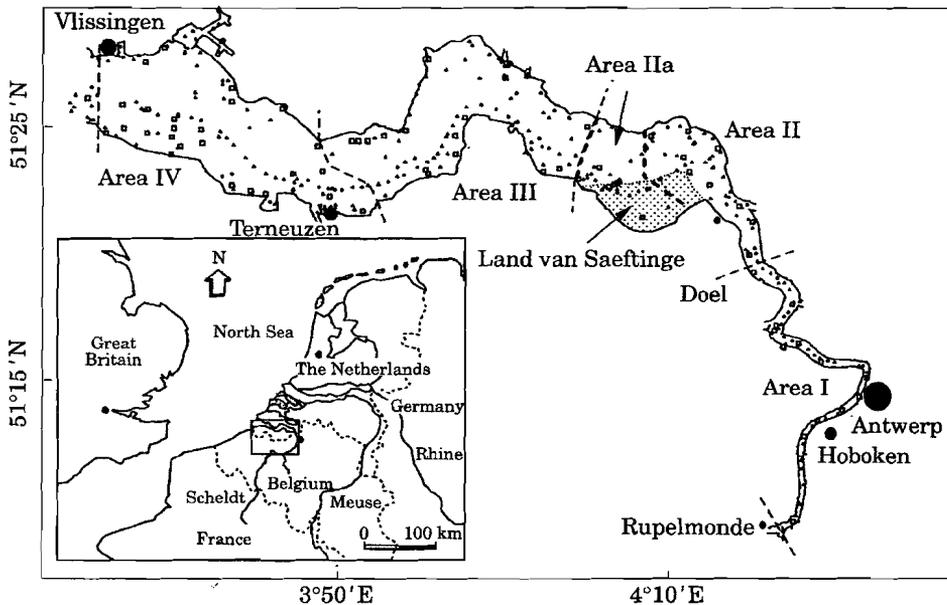


Fig. 4.1. Map of the Scheldt estuary, showing the sampling locations and the boundaries of the areas (I-IV) selected for spatial comparisons. ▲ represents bottom samplings points used; □ represents bottom sampling points discarded.

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- (1) The fresh to slightly brackish zone upstream from Antwerp. In this zone, the river channel is a narrow incision into the Boom clay substratum, giving rise to high current velocities which prevent deposition of muddy sediments. As a consequence, the bottom sediments consist of medium to coarse sands and at some places of gravels. At other places the Boom clay has no sediment cover at all and is in fact actively eroding.
- (2) The (brackish) high-turbidity zone from Antwerp to Doel. Characteristic features of this zone are intense sedimentation, the presence of a turbidity maximum and major industrial inputs. The bottom sediments consist of sands, sandy muds and muds. The clay content of the sediments typically ranges from 20-30%. In addition, fluid mud layers, 20-30 cm thick, are present at some places. The sediments are intensively dredged in order to keep the port of Antwerp accessible.
- (3) The marine zone, situated between Doel and the mouth of the estuary near Vlissingen. The morphology of the main channel changes into a complex system of sandbars and tidal gullies. The bottom sediments consist mainly of medium to coarse sands, with only exceptional mud deposits. Sedimentation of muddy sediments is very important in the salt marshes, especially in the so-called Land van Saeftinge, situated just downstream from Doel (Fig. 4.1). The clay content of the salt marshes can be as high as 50% (Oenema *et al.*, 1988). The main shipping channel is continuously dredged, the spoils being dumped within the lower estuary at several locations.

4.3. Methods

4.3.1. Data availability and evaluation

Our study started with a survey of available sediment composition and trace metal data for the Scheldt estuary. It was decided to limit the study to the organic matter content and grain-size fraction $< 16 \mu\text{m}$, as measures of bulk sediment composition, and to the As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn content. Results for certain grain-size fractions or data from sequential extractions (e.g. Saager, 1986; Baeyens *et al.*, 1988; Van Alsenoy *et al.*, 1993) were not considered. An overview of the remaining 11 trace metal datasets is given in Table 4.1. Between 1000 and 1500 analyses are available for each metal. Trace metal data are available from 1959 to 1990, allowing evaluation of temporal trends. In order to identify spatial trends, the estuary has been divided in four areas (see Fig. 4.1), comprising 6% (area I), 15% (area II), 36% (area III), and 43% (area IV) of the total surface area at half tide. With regard to the total number of samples, 8% is located in area I, 22% in area II, 24% in area III and 46% in area IV. The sampling points are, hence, more or less equally distributed over the estuary.

Tabel 4.1. Available data-sets for trace metals in sediments of the Scheldt estuary and their characteristics.

Lab. Nr.	Samples (n)	Sampling area (see Fig. 4.1)				Sampling year	Acid leach*	Analyt. method	Total number of analyses (upper value) / Number < detection limit (lower value)											Ref.
		I	II	III	IV				As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	POC	< 16 µm		
1	615	5	79	196	335	1985-90	2; 5 (Hg)	AAS	603 16	612 358	607 37	606 183	600 310	602 159	607 66	603 1	614 149	613 45	1	
2	25	3	2	7	13	1981-85	4; 1 (Hg)	AAS	7 1	25 2	11 0	18 0	7 1	10 0	11 0	14 0	22 0	22 0	1,2	
3	106	0	0	11	95	1986-89	2; 5 (Hg)	AAS	106 4	106 26	106 0	106 1	99 7	106 0	106 0	106 0	106 1	106 5	1	
4	310	42	123	29	116	1959-84	6; 1 (Cd) 7 (Hg)	AAS	260 0	254 0	302 0	302 1	261 0	282 0	253 0	302 0	308 0	308 0	3-6	
5	136	19	52	52	13	1973-85	1	AAS	82 0	134 0	136 0	135 0	2 0	136 14	134 0	136 0	131 12	129 25	7,8	
6	15	0	0	1	14	1981-85	2	AAS	8 0	15 2	13 0	15 0	6 0	13 0	13 0	15 0	13 0	13 0	1	
7	20	0	0	2	18	1982	2	AAS	20 0	20 1	20 0	20 0	20 0	20 0	20 0	20 0	20 0	20 0	1	
8	104	32	25	22	25	1978	3	AAS	- -	104 65	104 15	104 39	- -	104 52	104 51	104 0	104 0	- -	9	
9	10	0	10	0	0	1984	-	INAA	- -	10 0	- -	- -	10 0	- -	- -	10 0	10 0	10 0	10	
10	148	0	40	34	74	1985	8	ICP-AES	- -	148 0	148 0	148 0	- -	148 0	148 0	148 0	148 0	80 0	11	
11	45	20	10	7	8	1969-74	-	XRF	- -	- -	45 0	45 0	- -	- -	45 0	45 0	33 0	- -	12,13	

*1 = HNO₃, 2 = HNO₃+HCl, 3 = HNO₃+HCl+H₂O₂, 4 = HNO₃+HClO₄, 5 = H₂SO₄, 6 = H₂SO₄+HNO₃+HClO₄, 7 = KMnO₄+K₂S₂O₈, 8 = HF+HClO₄+HNO₃, Refs: 1. Data Rijkswaterstaat, Directorate Zeeland, The Netherlands; 2. Van Banning *et al.* (1984); 3. Zschuppe (1975); 4. Kerdijk (1980); 5. Salomons *et al.* (1981); 6. Kerdijk (1986); 7. Nihoul and Boelen (1976); 8. IHE (1986); 9. Gaspard (1984); 10. Marquenie *et al.* (1985); 11. Giesberts *et al.* (1986); 12. Wollast (1976); 13. Hoenig (1976).

Chapter 4

A basic problem inherent in the use of data from various laboratories over a time span of three decades is the comparability of the data. Differences in sampling and analytical procedures have to be considered before data merging can be justified (Loring and Rantala, 1988; Mudroch *et al.*, 1988). With regard to the sampling technique, most data refer to surface samples taken with a Van Veen grab. Though the depth of sampling will vary slightly between different campaigns, the variability in the dataset due to differences in the sampling technique is thought to be small. Changes in the detection limits with time play a minor role for Cd and Hg, less for Cu and Ni, and are unimportant for other metals. Differences in the analytical techniques have a greater impact, however (Table 4.1). A variety of leaching agents (from solely HNO_3 to $\text{HF-HNO}_3\text{-HClO}_4$) and detection methods (AAS, ICP-AES, XRF and INAA) have been used by the (11) laboratories involved in this study. The data obtained by the individual laboratories were compared in numerous scatterplots in order to determine the extent to which the results could be merged. It is not possible to show all the plots here, but Figs. 4.2 and 4.3 may serve as useful examples. Fig. 4.2 shows the relationship between sediment Cu and organic matter for area IV, determined by the laboratories 1-4. In general, there appears to be sufficient agreement between the results, in spite of the different leaching agents that were used (see Table 4.1). Fig. 4.3 shows the Cr content as a function of grain-size for sediments from areas III and IV for the year 1985, determined by three laboratories (1, 4 and 10). The analysed Cr content of the sediments appears to depend strongly on the digestion method employed, which is strong ($\text{HNO}_3\text{-HCl}$) for lab. 1, very strong ($\text{H}_2\text{SO}_4\text{-HNO}_3\text{-HClO}_4$) for lab. 4, and complete ($\text{HF-HClO}_4\text{-HNO}_3$) for lab. 10. This observation can be explained by the presence of a detrital (residual) metal fraction, which is not dissolved in aqua regia (lab. 1), partially dissolved in perchloric acid (lab. 4), and completely dissolved in acid mixtures containing HF (lab. 10). For metals such as Cr and Ni, the detrital fraction contains a major part of the total metal content, especially in sandy sediments which are considered here (Wollast *et al.*, 1985; Loring and Rantala, 1988). With regard to the other metals, the contribution of the detrital fraction may be relevant for (sandy) sediments of the lower estuary, but not for those of the upper estuary (areas I and II) which are far more polluted.

Based on Figs. 4.2, 4.3 and similar figures (not shown here) it was decided to merge all the data from labs. 1-9 and to reject all data from lab. 10 ($\text{HF-HClO}_4\text{-HNO}_3$ digestion) and lab. 11 (XRF). Thus, total sediment analyses were discarded, except for 10 samples from lab. 9 (INAA) because the elements analysed (Cd, Hg, Zn) have a very small residual fraction in the (polluted) sediments under consideration. Data merging was not carried out for Cr due to the dependence of the results on the leaching agent (Fig. 4.3); instead only the results from lab. 4 were used (except in Table 4.2). The trace metal contents presented in this study, obtained after strong acid leaching, can be defined as the non-detrital metal content of the sediments (total metal minus detrital metal content).

Distribution of trace metals in sediments of the Scheldt estuary

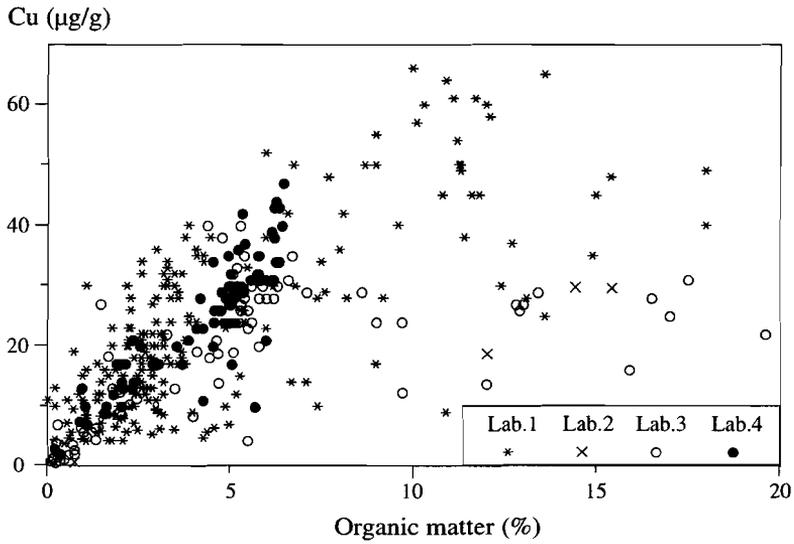


Fig. 4.2. Relation between sediment organic matter and Cu content for area IV, determined by the laboratories 1-4 (see Table 4.1).

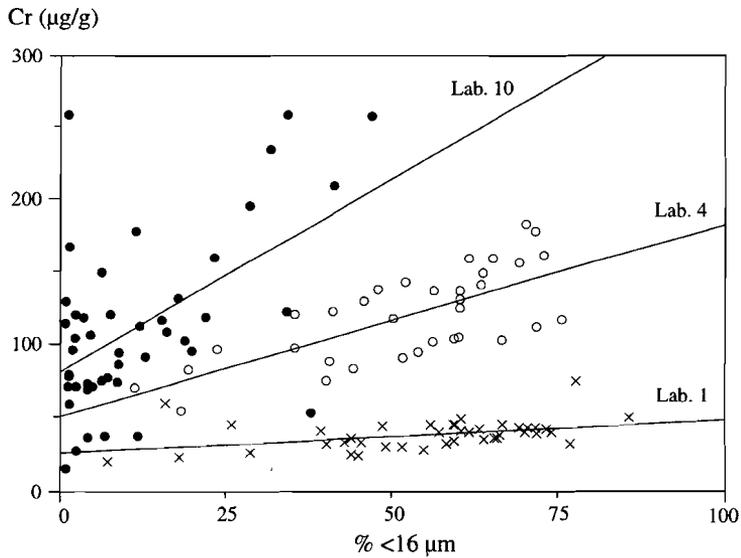


Fig. 4.3. Relation between sediment grain-size and Cr content for area III and IV, determined by the laboratories 1, 4, and 10 (see Table 4.1).

4.3.2. Statistical data-handling

After merging the data from labs. 1-9, the resulting data-set (1341 samples) was evaluated. The evaluation lead to identification of 168 atypical samples (Table 4.2), which were partially discarded (only the obvious outliers, i.e. 30 to 60 analyses of each metal, were discarded). Another 20 to 30 analyses of each metal were discarded for other reasons, e.g. no data on organic matter or grain-size available. The 1311 remaining samples (Table 4.3) were used in an analysis of variance (ANOVA) procedure, with percentage < 16 μm and organic matter content as correction variables. For Cr a similar procedure has been followed, using only the data from laboratory 4.

For the determination of spatial and temporal trends a correction method is necessary in order to eliminate the influence of differences in bulk sediment composition on the measured trace metal contents (Taylor, 1986; Klamer *et al.*, 1990). The grain-size fraction < 16 μm and organic matter content were chosen as correction variables for sediment composition, in accordance with previous studies (e.g. De Groot *et al.*, 1982; Taylor, 1986). The correction procedure, outlined in Fig. 4.4, is based on the observation (e.g. Figs. 4.2 and 4.3) that the relationship between trace metal content (y) and grain-size fraction < 16 μm or organic matter content (x) can be described by:

$$y = a \times x \quad (1)$$

with (usually) 'a' being different for each area and/or period that one wants to compare. After log transformation, equation (1) becomes:

$$\log y = \log a + \log x \quad (2)$$

In this way, lines through the origin (eqn. 1) are transformed to parallel lines with a slope equal to 1 (eqn. 2). This means that differences between areas or periods are simply given by the ordinate values (a_1 , a_2 , a_3 ; see Fig. 4.4). Moreover, it can be tested if the relationship between trace metal content and each correction variable is truly linear (i.e. if the slope equals 1). If not, equation (2) changes into a Freundlich-type equation:

$$\log y = \log a + b \log x \quad (3)$$

Regardless of the linearity of the trace metal versus correction variable relationship, the spatial and temporal distribution of trace metals in the sediments can be assessed from equation (3) by expressing, for each area and period considered, the average trace metal content at the mean percentage < 16 μm or at the mean organic matter content of all samples (\bar{x} in Fig. 4.4). The trace metal content is expressed at the mean value for a correction variable because this minimises the standard deviation, as shown in Fig. 4.4. Moreover, by expressing the trace metal content at the mean percentage < 16 μm or at the mean organic matter content of all

samples, it is assured that the normalised values are representative of the actual trace metal contents of the estuary. The correction procedure described here has been recommended by ICES (1986). All data processing was done with the statistical package SYSTAT (Wilkinson, 1988).

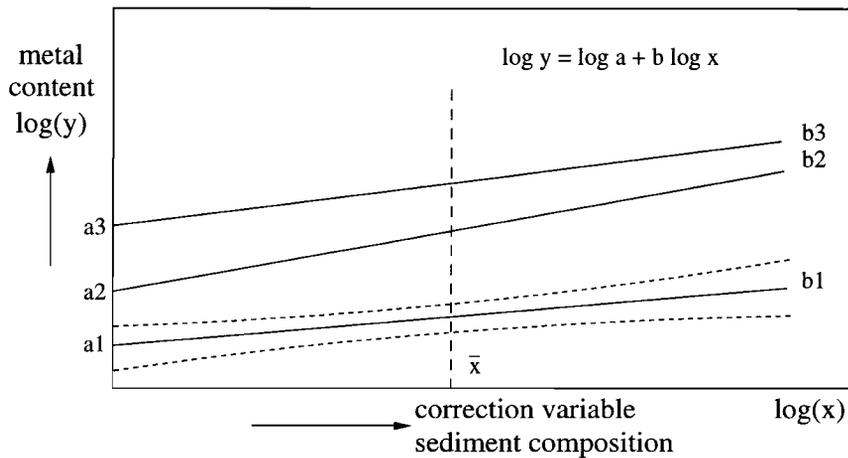


Fig. 4.4. Outline of the correction procedure followed. For each area and period, the trace metal content of the sediments is expressed at the mean percentage $< 16 \mu\text{m}$ or organic matter content of all the samples (\bar{x}). The dashed line indicates the corresponding standard deviation.

4.4. Results and discussion

4.4.1. Sample classification

As mentioned before, the sediment trace metal data from the Scheldt estuary can be divided into an atypical group (Table 4.2) and a typical group (Table 4.3). The atypical samples can be divided into three classes. The first class comprises samples with low metal and relatively high organic matter contents, taken north of the Saeftinge salt marsh (Fig. 4.1). These samples are mixtures of sands and ancient (unpolluted) peat formations, which have very low trace metal contents (Saager, 1986). The second class, fine-grained sediments with high organic matter and high trace metal contents, represents polluted harbour areas, mainly the four ferry harbours in the lower estuary and the industrial harbours of Terneuzen and Vlissingen. The third class represents individual outliers, including both low and high trace metal contents, probably related to analytical or logging errors.

Table 4.2. Composition of the atypical samples in the data set (1959-90). For each class of samples, the sediment trace metal content (median value) is listed left on top, the number of analyses right on top (between brackets), and the range in the lower line. All metal contents are in $\mu\text{g/g}$.

Sample class	As	Cd	Cr*	Cu	Hg	Ni	Pb	Zn	% OM	% < 16 μm
Peaty flats (n = 22)	7 (4) 2-12	1.6 (4) 0.2-3.8	46 (4) 18-90	21 (4) 4-45	0.54 (4) 0.05-1.1	17 (4) 5-27	35 (4) 4-79	183 (4) 43-350	4.8 (22) 2.7-13.5	9 (4) < 1-16
Polluted harbours (n = 81)	36 (34) 27-64	4.0 (29) 0.2-20	115 (19) 57-205	88 (20) 44-2600	1.2 (32) 0.02-3.3	63 (10) 44-147	165 (17) 71-410	450 (16) 250-1500	22.4 (3) 7.7-23.2	34 (2) 12-55
Miscellaneous (n = 65)	- (12) < 1-26	- (15) 0.1-3.8	- (11) 7-74	- (12) 1-766	- (22) 0.01-0.29	- (15) 3-220	- (14) 6-455	- (11) 9-345	- (19) 0.4-45.9	- (11) 1-100

* Cr data from laboratories 1-9.

Table 4.3. Composition of the typical samples in the data set (1959-90). For each sampling area, the sediment trace metal content (median value) is listed left on top, the number of analyses right on top (between brackets), and the range in the lower line. All metal contents are in $\mu\text{g/g}$.

Area	n	As	Cd	Cr*	Cu	Hg	Ni	Pb	Zn	% OM	% < 16 μm
I	98	80 (48) 9-131	8.9 (89) 0.1-45	272 (45) 48-322	88 (97) 2-207	2.33 (48) 0.01-3.95	28 (98) 2-84	118 (88) 1-338	480 (98) 23-1325	5.4 (95) 0.1-10.9	43 (66) < 1-71
II	285	18 (189) 1-94	2.2 (250) < 0.1-26	145 (114) 59-251	24 (259) 0.3-131	0.57 (182) 0.01-3.40	9 (240) 1-50	32 (237) 1-222	140 (269) 6-772	2.3 (253) 0.1-9.7	15 (247) < 1-73
III	315	6 (257) 1-28	0.5 (292) < 0.1-5.8	138 (28) 40-183	5 (302) 0.1-72	0.20 (214) 0.01-1.30	5 (299) 1-37	7 (286) 1-140	26 (300) 4-400	1.0 (311) 0.1-13.9	7 (288) < 1-81
IV	613	11 (523) 1-36	0.8 (574) < 0.1-3.5	102 (100) 31-146	17 (583) 0.2-66	0.29 (486) 0.01-1.08	13 (584) 1-56	36 (579) 1-105	113 (583) 5-355	3.0 (608) 0.1-20.1	38 (585) < 1-100

* Cr data from laboratory 4 only.

Table 4.3 represents the typical sample population. For each area, the total number of samples, the number of data for each trace metal (not all samples were always analysed for all trace metals) and the trace metal content of the sediments (median and range) is given. Based on the median values, it is clear that the trace metal content of the sediments decreases going from area I, the upper estuary with salinities less than 5, to area III and IV, the lower estuary, with salinities higher than 15. Normalisation of the results on grain-size or organic matter content leads to the same conclusion, as will be shown later. The normalisation exercise also reveals that the low trace metal levels observed in area III are partially related to the low silt and organic matter content of these sediments.

4.4.2. Extent of trace metal pollution

Anthropogenic disturbances can easily be demonstrated by comparing the actual sediment trace metal contents of the Scheldt estuary (Table 4.3) with the trace metal contents in geological formations from the Scheldt river basin and with natural background values (Table 4.4). The maximum metal contents in Table 4.3, corresponding with silty sediments from the upper estuary in 1978-1979, are enriched with respect to the estimated natural background levels by a factor of 112 (Cd), 26 (Hg), 13 (Pb, Zn), 12 (As), 7 (Cu), 5 (Cr) and 2 (Ni). In view of the high degree of industrialisation in the Scheldt watershed, this is not surprising. Based on median metal contents, the most polluted area (I) features enrichment factors of 22 (Cd), 16 (Hg), 7 (As), 5 (Pb, Zn), 4 (Cr), 3 (Cu), and 0.8 (Ni). The low enrichment factor for Ni does not represent the actual pollution status because of the incomplete digestion of the sediments (the detrital metal fraction is very important for Ni; see chapter 5). For the same reason, the actual enrichment factor for Cr is assumed to be higher.

Table 4.4. Trace metal contents in geological formations of the Scheldt river basin (aqua regia leach) and natural background values for the Rhine river (all data in µg/g).

	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
<u>Geological formations Scheldt river^a</u>								
Boom clay	-	< 1	31	17	-	25	12	51
Glauconic sands	-	< 1	48	< 1	-	12	< 1	15
Calcareous sands	-	< 1	8	5	-	3	6	14
Siliceous sands	-	< 1	14	2	-	7	4	8
<u>Natural background Rhine river</u>								
Sediments, 15 th century ^b	12	0.5	77	21	0.14	33	31	93
Medieval riverclay ^c	9	0.2	55	35	0.15	41	21	106
Estimated background Scheldt river	11	0.4	66	28	0.15	37	26	100

(a) Gaspard (1984); (b) De Groot *et al.* (1982); (c) Laane (1992).

Chapter 4

A comparison between the trace metal content of Scheldt estuary sediments and that of other European estuaries is made in Table 4.5. It should be noted that the maximum trace metal contents in the Scheldt estuary are representative of the sediments in the industrial zone (around Antwerp) in the late seventies. Today, the trace metal content of the sediments has decreased considerably. According to Table 4.5, the Scheldt estuary ranks among the estuaries strongly polluted by trace metals, especially with regard to Cd.

Table 4.5. Trace metal contents in sediments from European estuaries ($\mu\text{g/g}$), sampled over the entire salinity range. All metals were analysed by AAS after strong acid digestion, except the Humber and the Gironde samples which were analysed by XRF. Estuaries are listed in order of decreasing Zn content in the sediments (with the Scheldt on top).

Nr	Estuary	Sampling year	Cd		Cr		Cu		Ni		Pb		Zn	
			min	max	min	max	min	max	min	max	min	max	min	max
1	Scheldt	1978-1979	<0.1	44.8	31	322	<1	207	1	84	1	338	4	1325
2	Tees	1988	<0.5	8.5	10	380	10	1100	11	92	40	990	40	2900
3	Sado	1986	0.1	8.9	-	-	17	170	19	86	32	159	78	2306
4	Weser	1980-1981	<0.1	12.4	17	146	9	162	15	76	22	265	43	1432
5	Tamar	1974	<0.1	5.4	39	91	111	521	33	64	112	697	195	1150
6	Mersey	1974-1983	<0.1	5.8	<1	155	<1	219	1	364	1	741	7	994
7	Humber	1988	-	-	99	422	17	206	38	81	22	469	84	914
8	Rhine	1986	2.0	10.0	120	240	36	195	-	-	88	210	240	760
9	Elbe	1983	0.1	7.7	-	-	8	250	-	-	15	113	30	570
10	Gironde	1975-1976	0.2	7.5	-	-	7	34	3	33	3	53	7	464
11	Loire	1982-1983	<0.1	0.8	18	125	2	45	15	56	13	81	14	279
12	Krka	unknown	0.4	0.8	30	105	10	95	40	72	23	67	32	72

1. This work (see Table 4.3); 2. Davies *et al.* (1991); 3. Quevauviller *et al.* (1989) (< 63 μm fraction); 4. Calmano *et al.* (1982) (< 63 μm fraction); 5. Bryan and Uysal (1978); 6. Taylor (1986); 7. Grant and Middleton (1990); 8. Steneker *et al.* (1988); 9. Ahlf (1983) and Ahlf and Wellershaus (1984) (both < 63 μm fraction); 10. Etcheber (1979) and Donard *et al.* (1983); 11. Robbe *et al.* (1985); 12. Prohic and Kniewald (1987) (< 64 μm fraction) and Martincic *et al.* (1989) (< 75 μm fraction).

4.4.3. Spatial and temporal variations

Sediment trace metal contents were calculated for area I to IV (see Fig. 4.1) within three periods (1978-1990, 1978-1985, 1986-1990). The results apply to the average organic matter content (1.8%) and percentage < 16 μm (10%) of the entire data-set (equation 3). The normalised trace metal contents and their 95% confidence intervals are given in Fig. 4.5.

Distribution of trace metals in sediments of the Scheldt estuary

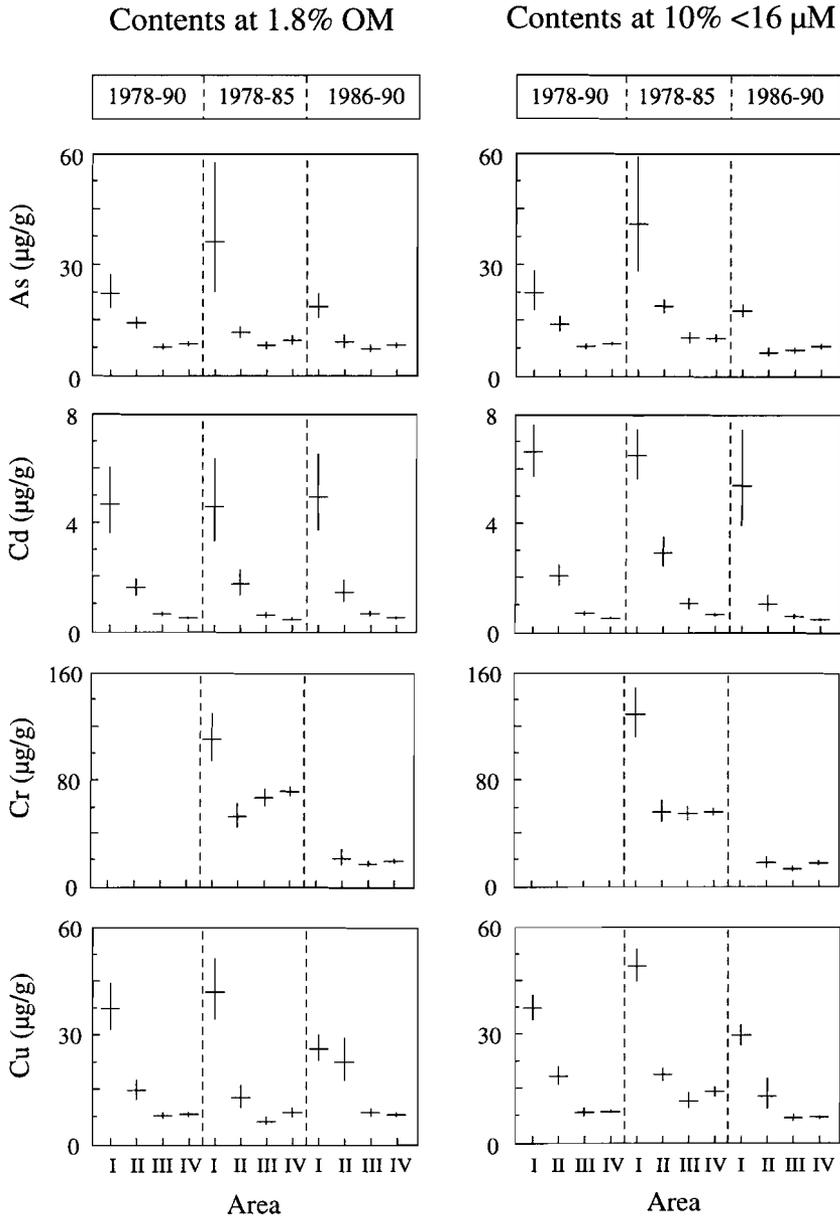


Fig. 4.5. Normalised trace metal contents for the four areas of the Scheldt estuary (see Fig. 4.1) within the period 1978-1990 (left), 1978-1985 (middle), and 1986-1990 (right). Normalisation was performed on average organic matter content (1.8%) and percentage < 16 µm (10%) of all the samples in the data-set. For each area and period considered, the mean value ± 2 SD is shown.

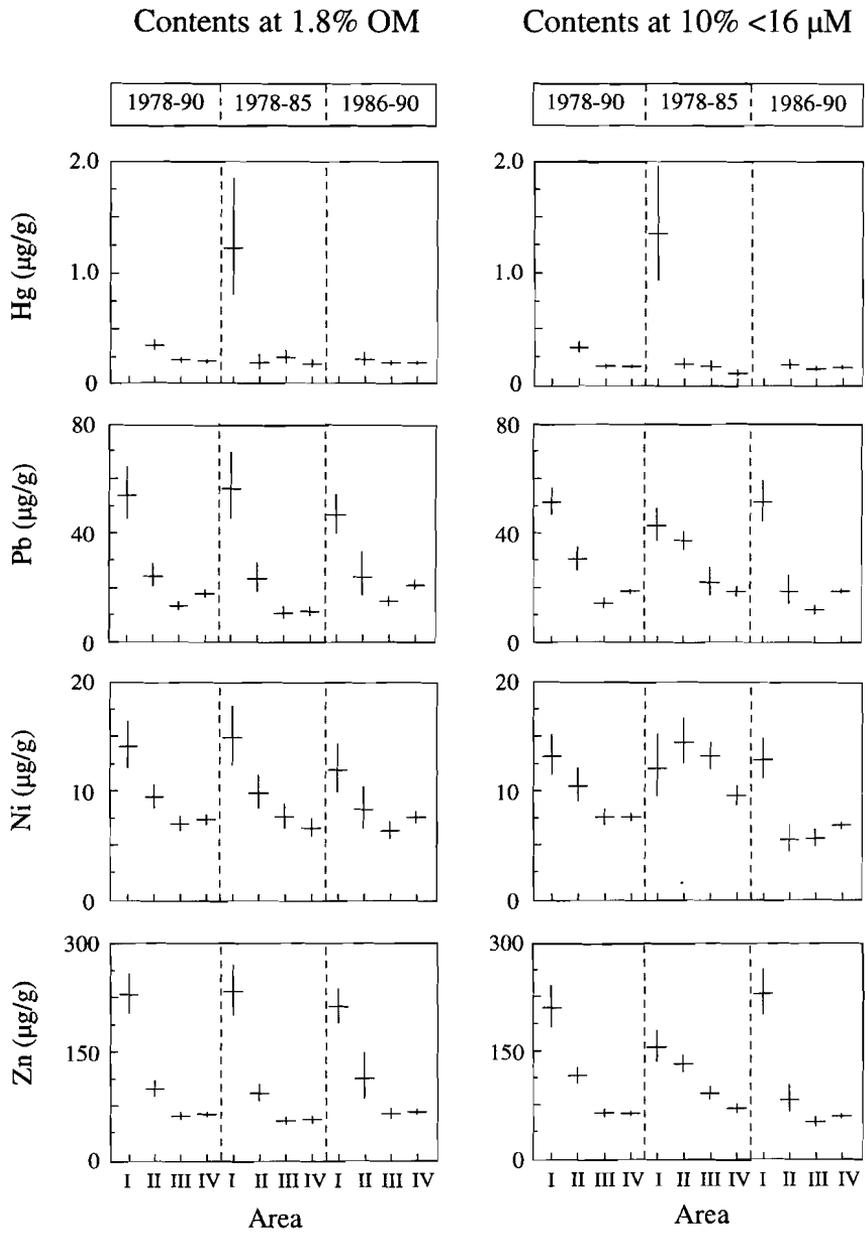


Fig. 4.5. (continued)

Distribution of trace metals in sediments of the Scheldt estuary

The main characteristics of Fig. 4.5 can be summarised as follows:

- (1) The metal contents normalised on organic matter content are, in general, comparable to the contents normalised on percentage < 16 μm . However, in a few cases the results of both normalisation procedures show major deviations (e.g. area I, period 1978-1985). One of the reasons for this is that organic matter is not a conservative variable since it is decomposed in time. In view of the long time-span considered here (12 years), normalisation based on grain-size is more straightforward than normalisation based on organic matter content.
- (2) Trace metal contents are highest in area I; the contents in area II are, in general, higher than those in area III which do not differ significantly from those in area IV. Thus, the normalised metal content of the sediments decreases when going from the upper estuary to the lower estuary, but in the lower estuary itself a constant level is reached. This distribution pattern can, to a very high extent, be explained by physical mixing of metal-rich fluvial sediments and metal-poor marine sediments (see section 4.4.6.).
- (3) The general pattern is towards constant or decreasing trace metal contents in time in the entire estuary within the period 1978-1990 (cf. 1978-1985 with 1986-1990). As an exception to this rule, the grain-size normalised Pb and Zn contents seem to have increased in area I, but this is not confirmed by the organic matter normalised contents.

4.4.4. Temporal variations between 1959 and 1990

An excellent opportunity to study the trace metal pollution history of the Scheldt estuary is provided by area IIa, situated some 10 km downstream from the Dutch-Belgian border (Fig. 4.1). This area is ideal for studying temporal variations for the following reasons:

- (1) Sediment trace metal data are available for area IIa from 1959 to 1987.
- (2) The trace metal content of the suspended matter at the Dutch-Belgian border is known from 1970 on, based on water column samples collected biweekly by Rijkswaterstaat.
- (3) Trace metal profiles have been recorded in radiodated sediment cores from two salt marshes in area IIa. Although these metal profiles are disturbed by diagenetic reactions, a tentative pollution record for the estuary could be reconstructed (see chapter 5).

In Fig. 4.6, the normalised trace metal contents and 95% confidence intervals are shown for area IIa for the year (period) 1959, 1971-1979, and 1984-1987. The normalisation was based on the average organic matter content (3.5%) and percentage < 16 μm (19%) of all sediment samples from area IIa. According to Fig. 4.6, trace metal pollution was most severe in the late 1950's, decreased through the 1970's (cf. 1959 and 1971-1979) and again in the 1980's (cf. 1971-1979 and 1984-1987). The only exception to this general pattern is Ni, which shows an increasing content in the surface sediments in time.

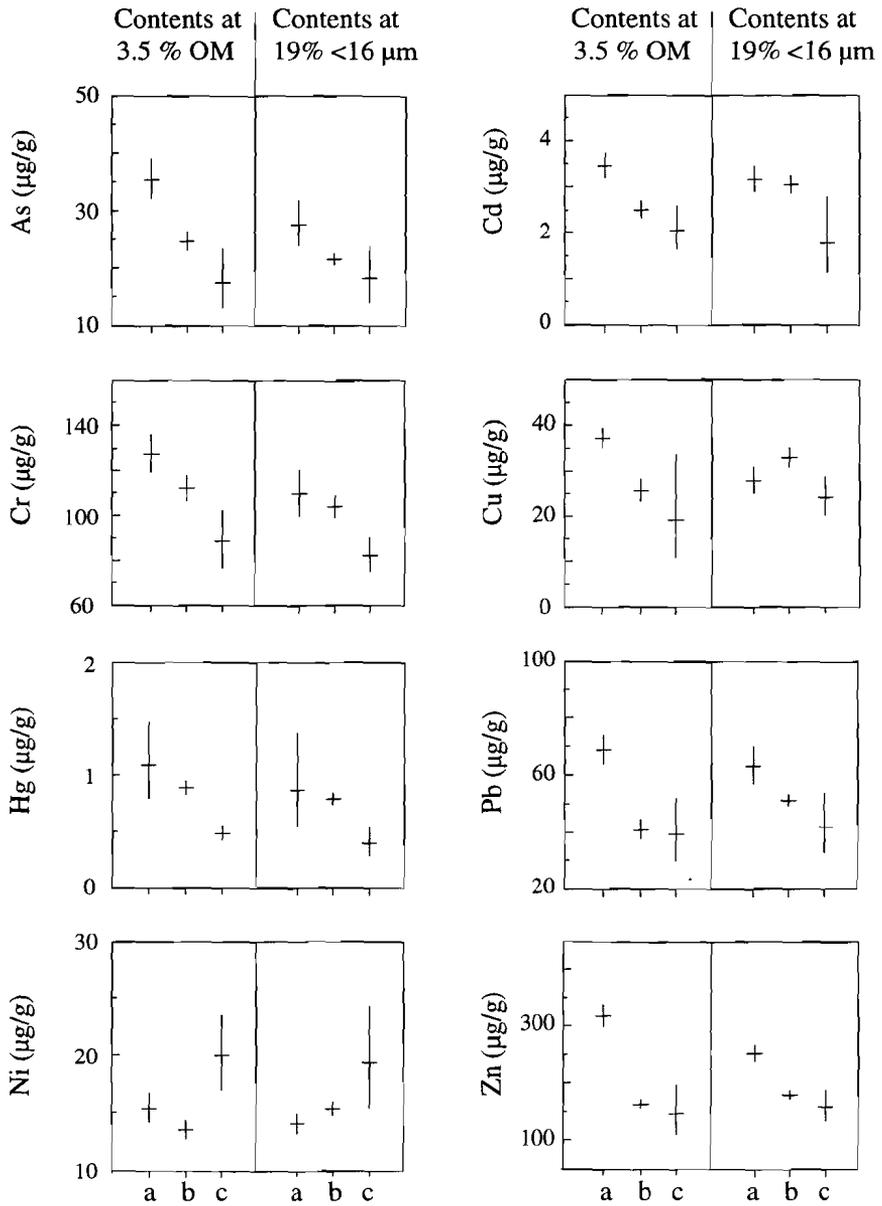


Fig. 4.6. Normalised trace metal contents for area IIa (Land van Saeftinge, see Fig. 4.1) in 1959 (a), 1971-1979 (b), and 1984-1987 (c). Normalisation was based on the average organic matter content (3.5%) and percentage < 16 µm (19%) of all the samples from area IIa. For each period, the mean value ± 2 SD is shown.

Distribution of trace metals in sediments of the Scheldt estuary

The increasing Ni content of the sediments in time is unlikely to reflect the Ni pollution history, because a similar increase is not found in the other areas. Increasing Ni emissions are, therefore, unlikely to be responsible. Instead, the increasing Ni content of the surface sediments may have a geochemical origin. It appears that Ni and Mn are closely related in the Scheldt estuary, both in the sediments (see chapter 5) and in the suspended matter (see chapter 3). Mn is mobilised in sediments under suboxic conditions (e.g. Froelich *et al.*, 1979), leading to release of adsorbed Ni. It is known that the presence of a distinct oxic top layer leads to efficient trapping of Mn and Ni (Shaw *et al.*, 1990; see also chapter 5). Hence, improved oxygenation of the surface sediments in area IIa may explain their increasing Ni content since the 1980's. The dissolved oxygen concentration observed at the Dutch-Belgian border improved suddenly after 1980 (see Fig. 1.1), which is in fair agreement with this explanation.

The trace metal composition of suspended matter at the Dutch-Belgian border, calculated from water quality monitoring data between 1972-1989, confirms that a decrease of the trace metal pollution took place after 1980, at least for As, Cd, Hg, Pb, and Zn (see Fig. 4.7). The suspended matter data also show a substantial decrease in the Cr and Hg levels in the early 1970's, whereas the Cd pollution seems to have increased between 1975 and 1980. In summary, these results suggest that the trace metal burden of the Scheldt estuary has decreased considerably over a time span of three decades (1960-1990).

4.4.5. Interelement relationships

Principal component analysis (PCA) was performed on the entire data set in order to identify the major processes that determine the sediment trace metal content. The results of the analysis are shown in Table 4.6. Three principal components have been identified, explaining 90-95% of the total variance in each area. The first component is by far the most important one, explaining 80-90% of the total variance. The two correction variables and all the trace metals contribute significantly to the first component, with loadings on the order of 0.90 in area I, II, and IV, and slightly lower in area III. These high component loadings justify the use of organic matter and grain-size as correction variables for sediment composition. The component loadings for As and (less obvious) Cd decrease from area I to area IV (i.e. with increasing salinity). This is in keeping with the significant contribution of Cd and As to the second and third component, respectively.

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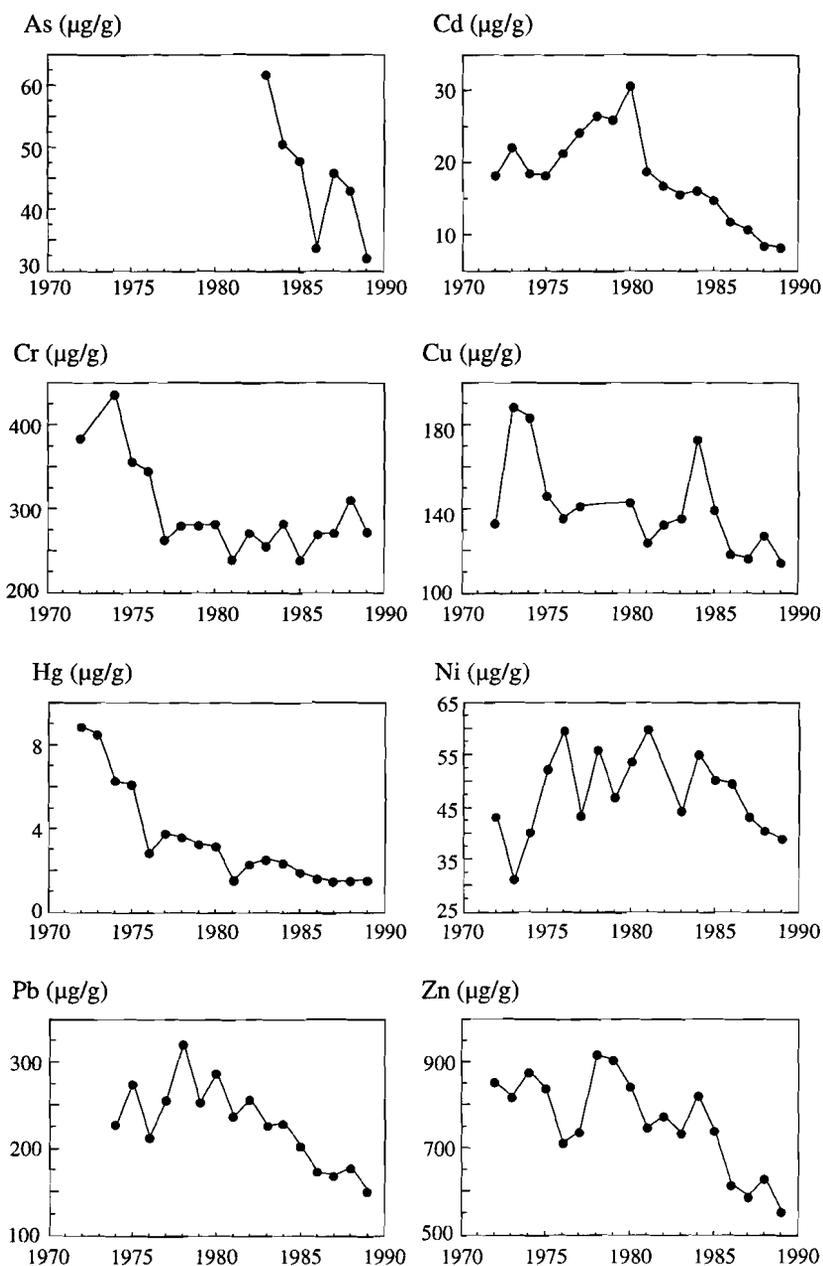


Fig. 4.7. Mean annual trace metal content of the suspended matter at the Dutch-Belgian border between 1972 and 1989.

Distribution of trace metals in sediments of the Scheldt estuary

Table 4.6. The three principal components with their component loadings for each sampling area.

Area (see Fig. 4.1)	I	II	III	IV
Variance explained (%)				
Component 1	90.3	87.0	80.9	80.9
Component 2	4.1	3.9	3.5	3.6
Component 3	-	-	5.8	6.2
Component loadings				
<i>Component 1</i>				
Organic matter	0.851	0.855	0.827	0.861
% < 16 µm	0.917	0.885	0.788	0.896
As	0.907	0.903	0.699	0.680
Cd	0.864	0.893	0.833	0.846
Cr	0.943	0.998	0.951	0.975
Cu	0.895	0.902	0.864	0.939
Hg	0.902	0.952	0.888	0.884
Ni	0.910	0.925	0.862	0.930
Pb	0.862	0.891	0.859	0.935
Zn	0.910	0.934	0.891	0.961
<i>Component 2</i>				
Organic matter	-0.291	-0.463	-0.413	-
% < 16 µm	-	-	-	0.223
Cd	0.398	0.327	0.237	-0.491
<i>Component 3</i>				
As	-	-	-0.545	-0.721

Interelement relationships in the dataset were investigated separately in area I-IV by first-order correlation analysis. The resulting correlation matrix is shown in Table 4.7. Strong interelement relationships are observed in the entire estuary, as would be expected from the PCA analysis. However, the correlation between As and either organic matter or grain-size decreases significantly from area I to area IV. Similarly, a decreasing correlation between Cd and grain-size is observed going from area I to area IV. For the other metals, the correlations with grain-size remain constant or decrease slightly in seaward direction. Thus, both the PCA and the correlation analysis indicate that the behaviour of Cd and As is different from that of the other trace metals.

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Table 4.7. Correlation matrix of organic matter, % < 16 µm and sediment trace metal contents for each sampling area.

	Area	Org. mat.	% <16 µm	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Organic matter	I	*									
	II	*									
	III	*									
	IV	*									
% < 16 µm	I	.914	*								
	II	.767	*								
	III	.630	*								
	IV	.777	*								
As	I	.872	.860	*							
	II	.860	.781	*							
	III	.582	.590	*							
	IV	.503	.469	*							
Cd	I	.677	.904	.979	*						
	II	.649	.754	.848	*						
	III	.704	.652	.560	*						
	IV	.692	.668	.534	*						
Cr	I	.959	.951	.851	.963	*					
	II	.881	.931	.951	.938	*					
	III	.948	.968	.818	.837	*					
	IV	.865	.897	.652	.843	*					
Cu	I	.785	.969	.890	.859	.969	*				
	II	.738	.864	.831	.794	.959	*				
	III	.792	.736	.644	.779	.956	*				
	IV	.796	.834	.615	.756	.918	*				
Hg	I	.863	.852	.920	.940	.910	.900	*			
	II	.832	.872	.855	.933	.969	.892	*			
	III	.814	.797	.710	.888	.778	.867	*			
	IV	.730	.778	.523	.751	.831	.779	*			
Ni	I	.804	.892	.872	.706	.977	.873	.851	*		
	II	.803	.746	.821	.842	.926	.741	.894	*		
	III	.749	.693	.601	.810	.972	.761	.853	*		
	IV	.771	.843	.636	.751	.870	.877	.799	*		
Pb	I	.821	.956	.965	.854	.973	.885	.923	.821	*	
	II	.761	.846	.811	.888	.971	.857	.907	.845	*	
	III	.766	.668	.587	.823	.937	.788	.863	.863	*	
	IV	.712	.840	.614	.763	.887	.874	.826	.862	*	
Zn	I	.871	.937	.932	.807	.953	.886	.930	.956	.887	*
	II	.848	.855	.835	.836	.965	.891	.897	.904	.855	*
	III	.856	.754	.627	.852	.859	.873	.887	.890	.863	*
	IV	.819	.839	.635	.786	.919	.897	.849	.896	.911	*

4.4.6. Particle mixing and trace metal mobilisation

The strong interelement relationships shown in Table 4.7 suggest that one common process determines the sediment composition for all trace metals. This is in good agreement with previous studies in the Scheldt estuary, which have shown that the sediment composition is governed by physical mixing of fluvial and marine sediments (Salomons and Eysink, 1981; Van Maldegem *et al.*, 1993). The contribution of fluvial particles in the bottom sediments decreases from 100% at the beginning of the salinity gradient to $\approx 10\%$ at the mouth of the estuary (Ten Brinke, 1992). The impact of particle mixing is illustrated in Fig. 4.8, which shows the average trace metal content of the sediments in area I-IV in the period 1978-1990 as a function of their marine sediment content ($\approx 0, 50, 75,$ and 90% ; Ten Brinke, 1992). Grain-size effects are eliminated by expressing all the trace metal contents at $10\% < 16 \mu\text{m}$ (i.e. 90% sand and 10% silt). The fluvial end-member composition of the sediments was chosen as the average trace metal content in area I (this is not entirely correct, because area I contains some marine sediment), and the marine end-member composition was calculated from North Sea sediment data (sand and silt, see Table 4.8). The fluvial and marine end-members are connected by a mixing line (see Fig. 4.8), which represents the composition of the sediments if particle mixing were the only process occurring in the estuary (i.e. conservative behaviour).

Table 4.8. Composition of North Sea sand and silt (Kramer *et al.*, 1989), and standardised marine end-member (MEM) composition used in Fig. 4.8 (90% sand and 10% silt).

		Sand ^a	Silt ^b	MEM
CaCO ₃	%	0.7	17.5	2.3
POC	%	0.2	9.3	1.1
Al	%	0.24	8.63	1.1
As	$\mu\text{g/g}$	1.6	22	3.6
Cd	$\mu\text{g/g}$	0.07	0.50	0.12
Cr	$\mu\text{g/g}$	18	100	26
Cu	$\mu\text{g/g}$	0.4	25	2.9
Hg	$\mu\text{g/g}$	0.02	0.10	0.03
Ni	$\mu\text{g/g}$	2.2	58	7.8
Pb	$\mu\text{g/g}$	3.8	55	8.9
Zn	$\mu\text{g/g}$	6.9	149	21

(a) Western Wadden Sea (1986), samples Zurich 4887-4889 (n = 3).

(b) Western Wadden Sea (1988), sediment core (Mokbaai), depth 28-57 cm, data extrapolated to $100\% < 16 \mu\text{m}$.

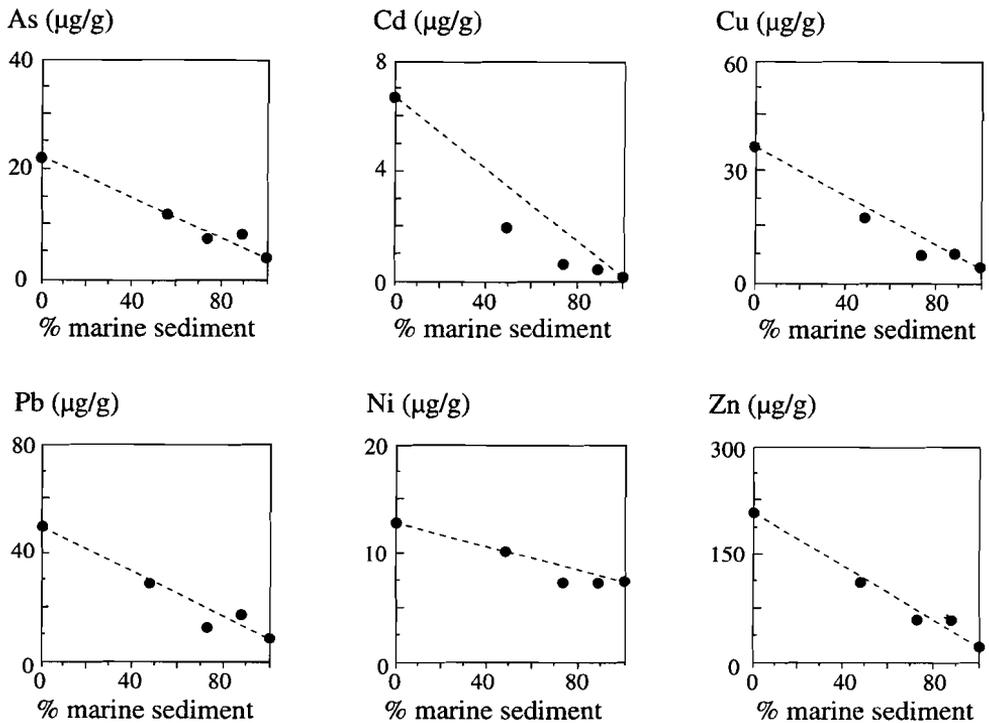


Fig. 4.8. Trace metal contents in standardised sediments of the Scheldt estuary as a function of percentage marine sediment (average contents in area I-IV within 1978-1990, normalised at $10\% < 16 \mu\text{m}$). The mixing line connecting the fluvial and marine end-members represents conservative behaviour of sediment trace metals.

According to Fig. 4.8, the As, Pb, Cu, Ni, and Zn content of the sediments is close to that predicted by the mixing line, suggesting conservative behaviour. The apparent conservative behaviour of As contrasts with the results of the PCA and correlation analysis, which would suggest mobilisation to take place. Supporting evidence for the mobilisation of As from the sediments is provided by the slope b in equation (3), which decreases from 0.6 in area I and II to 0.3 in area III and IV. Mobilisation of As is also suggested by water quality monitoring data, which frequently feature a dissolved As maximum in the lower Scheldt estuary (not shown). However, these maxima may reflect fluctuations in river discharge (Andreae and Andreae, 1989), and are thus not unequivocal evidence for mobilisation of As.

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The Cd content of the sediments lies well below the mixing line, indicating mobilisation from the sediments. Supporting evidence for mobilisation of Cd from the sediments comes from studies on pore water composition in the Scheldt estuary (see chapter 6), showing production of dissolved Cd near the sediment-water interface, associated with decomposition of organic matter and oxidation of metal sulphides (Baeyens *et al.*, 1986). Similar release of solid-phase Cd during early diagenesis has been found in sediments of Puget Sound (Emerson *et al.*, 1984) and the Laurentian Trough (Gobeil *et al.*, 1987). Dissolved metal distributions in the water column (see chapter 2) confirm that Cd mobilisation is a persistent feature of the Scheldt estuary. Mobilisation of Cu and Zn is also indicated by dissolved metal profiles, but apparently to a lower extent, in view of the conservative behaviour of Cu and Zn in the sediments.

In conclusion, the spatial distribution of trace metals in sediments of the Scheldt estuary is, to a very large extent, controlled by mixing of polluted fluvial particles and relatively clean marine particles. Superimposed on the mixing process, there are indications for mobilisation of Cd and possibly As.

Acknowledgements - Thanks are due to A. Jongejan for providing the sediment trace metal data and his assistance in completing the data-base. The statistical advice given by J. Van der Meer and the support of J. Pieters in the processing of the data is gratefully acknowledged.

Chapter 5

Historical input, mobility and retention of major elements and trace metals in salt marshes of the Scheldt estuary

J.J.G. Zwolsman, G.W. Berger and G.T.M. Van Eck

Abstract - The distribution of major elements and trace metals has been studied in two radiodated salt marsh sediment cores (core K and core E) of the Scheldt estuary, in order to determine the recent pollution history and to assess the impact of diagenetic processes. The sedimentation rates, based on ^{210}Pb and ^{137}Cs inventories, were 0.84-0.90 cm/yr in core E and 1.3-1.7 cm/yr in core K. The sediments show a vertical redox zonation with an oxic upper layer, where trace metals are mobilised, overlying a reduced layer where the metals are precipitated. Though these diagenetic processes have greatly modified the original trace metal distribution, anthropogenic maxima could be identified for Cd, Cr, Cu, Pb, and Zn during the mid sixties. A second pollution maximum was found at the end of the seventies for Cd, Cu, Pb, and Zn. The down-core distributions of Mn, Fe, total S, Ca, Sr, Co, and Ni are controlled by diagenetic processes, whereas the P profiles reflect both anthropogenic and diagenetic impacts. Rapid remobilisation of trace metals occurs after their deposition on the marshes due to the occurrence of oxic conditions in the upper sediment layer, preventing precipitation of metal sulphides from the pore waters. Though the metals are partly reprecipitated in the reduced sediment layer (e.g. as sulphides), the inventory of the cores suggests that Cr is the only metal which is completely retained by the sediments. Slight losses are observed for Fe, Co, and Pb (11-14%), moderate losses for Zn, Cu, and Ni (19-25%), and high losses for P, Mn, and Cd (40-50%). It is argued that mobilisation of trace metals is a typical feature of salt marshes where a distinct oxic sediment layer is present.

5.1. Introduction

Trace metal pollution of rivers, lakes and estuaries is a serious problem in all industrialised countries. Once released into the aquatic environment, trace metals are transferred to the sediments by adsorption onto suspended matter and sedimentation. Thus, if the sediment accumulation rate is known, depth profiles of trace metals in the sediments can be used to reconstruct the 'pollution history' of the aquatic system (Santschi *et al.*, 1984; Wong and Moy, 1984; Finney and Huh, 1989). Enrichment of trace metals in sediments does not necessarily reflect anthropogenic influence, however, but may have a diagenetic origin instead (Cornwell, 1986; Gendron *et al.*, 1986; Ridgway and Price, 1987; Finney and Huh, 1989). Diagenetic reactions are especially important near the sediment-water interface, due to the rapid transition from oxidising to reducing conditions (Santschi *et al.*, 1990; Shaw *et al.*, 1990; see also chapter 6).

The small depth of the oxic top layer in submerged coastal sediments (a few mm at most) seriously hampers the study of diagenetic processes. Salt marsh sediments provide a better opportunity to study trace metal diagenesis. The depth of the oxic layer in salt marshes can be considerable (cm to dm range), due to entry of atmospheric oxygen in the soil or in-situ oxygen release via plant roots (Lord and Church, 1983; Casey and Lasaga, 1987; Hines *et al.*, 1989). Moreover, bioturbation and physical reworking of particles are negligible in salt marshes (Stumpf, 1983). Studies on trace metal diagenesis in salt marshes are scarce, however. Trace metal profiles in salt marsh sediments were presented by McCaffrey and Thomson (1980) and Allen *et al.* (1990).

This study deals with the distribution of major elements and trace metals in two radiodated salt marsh sediment cores of the Scheldt estuary, which has a long history of trace metal pollution. Previous studies have indicated that the marshes are considerably contaminated by trace metals (Beeftink *et al.*, 1982; Oenema *et al.*, 1988). From geomorphological and sedimentological studies it is known that the marshes have continuous and rather uniform sediment accumulation rates over this century (Leemans and Verspaandonk, 1980). The objectives of this work were to reconstruct the history of trace metal pollution and to assess the influence of early diagenetic processes on the distribution of trace metals in the sediments.

5.2. Study sites and methods

5.2.1. Core sampling

The marshes under study are 'Konijnenschor' (core K) and 'Emanuëlpolder' (core E), situated near the Dutch-Belgian border in the brackish water zone of the estuary. The geomorphology of the marshes is described in detail by Beeftink *et al.* (1977) and Oenema *et al.* (1988). The salinity of the flood water ranges from 5 to 20, depending on the river discharge. The height of the sampling sites with respect to mean sea level is + 3.0 m for core

K and + 2.6 m for core E; corresponding flooding frequencies are 25 and 175 times per year, respectively. In September 1987, sediment cores were taken from the marshes using a hand-coring device. The core liners used were PVC tubes which were covered on the inside with a thin sheet of polyethylene, to minimise contamination during sampling. The length of the tubes was about 100 cm and the internal diameter was 6 cm. The cores were frozen at -20 °C until further treatment. In the laboratory, the cores were thawed and cut into sections (1-5 cm), which were freeze-dried immediately. These sections were subsampled for radiodating and chemical analysis.

5.2.2. Radiodating of the sediments

Sediment accumulation rates were determined from ^{137}Cs and ^{210}Pb profiles, which are widely used for this purpose (e.g. Silverberg *et al.*, 1986; Anderson *et al.*, 1987). Samples (1 gram dry weight) were spiked with ^{208}Po as a yield tracer, digested with concentrated mineral acids and plated on a silver disc for alpha-measurement (Flynn, 1968). Total ^{210}Pb was determined by measuring its granddaughter ^{210}Po , assuming secular equilibrium with ^{210}Pb . Excess ^{210}Pb was determined as total ^{210}Pb minus ^{226}Ra -supported ^{210}Pb , the latter being determined by measuring ^{222}Rn , generated in a closed system by ^{226}Ra . The accuracy of the ^{210}Pb measurements was within 5 %, based on counting error alone. Sedimentation rates were determined from the slope of the least-square fit for exponential decrease of excess ^{210}Pb as a function of depth in the sediments, using the constant initial concentration method (Robbins and Edgington, 1975, Goldberg *et al.*, 1977).

^{134}Cs and ^{137}Cs were measured by low-background gamma spectroscopy at 604.7 KeV and 661 KeV, respectively. The counting error in the ^{137}Cs measurements was about 25%. The counting error in the ^{134}Cs measurements was of the same order of magnitude as the measurements themselves, except for the surface sediments, for which a counting error of 35% could be obtained (due to the high ^{134}Cs content in these samples). The detection limit of the counting system used was 0.2 Bq/kg.

5.2.3. Analysis of major elements and trace metals

The methods for major element and trace metal analysis are described in detail in chapter 3. Sediment subsamples were decomposed by HF-HClO₄-HNO₃ at 90 °C in closed teflon vessels. Digestion of Si was performed after fusion with LiBO₂ at 1000 °C and dissolution in diluted HCl. Resulting solutions and reagent blanks were analysed for major elements (Al, Ca, Fe, K, Mg, Na, P, S, Si, Ti) and trace metals (Ag, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Ni, Pb, Sn, Sr, V, Zn) by ICP-AES. Organic carbon (POC) was analysed in HCl-treated samples by combustion and CO₂ analysis. The carbonate content of the samples was calculated from their Ca content, since virtually all Ca (>95%) proved to be present as calcium carbonate (as

checked for 18 samples). The salt content of the sediments was calculated from the excess Na content of the samples, assuming seawater stoichiometry. Excess Na (derived from salt) was estimated as total sediment Na (0.9-1.2%) minus the detrital Na content of suspended matter deposited on the marshes (0.5%; see Table 3.1.). Grain-size fractions of the mineral sediment fraction were determined by laser beam scattering (Malvern 3600 LBD) after treatment with H₂O₂ and HCl (to remove organic matter and carbonates). The water content of the sediments was determined gravimetrically. All contents presented in this work are expressed on dry sediment weight basis (except for water content, which is expressed on wet sediment weight basis). No correction was made for the salt content of the sediments, which was always smaller than 2.5%.

5.3. Results and discussion

5.3.1. Sedimentation rates

The profiles of excess ²¹⁰Pb, ¹³⁴Cs and ¹³⁷Cs for core K and core E are shown in Fig. 5.1. The excess ²¹⁰Pb content of the sediments shows an exponential decrease with increasing depth, indicating a constant sedimentation rate and no significant particle mixing. The absence of a mixed surface layer, which is confirmed by the ¹³⁷Cs and ¹³⁴Cs profiles, is in keeping with the fact that bioturbation and physical reworking of the sediments are limited in salt marshes (Stumpf, 1983). The sedimentation rates, determined from the slope in the excess ²¹⁰Pb profiles, are 1.32 ± 0.05 cm/yr for core K and 0.90 ± 0.06 cm/yr for core E.

The ¹³⁷Cs profiles show two maxima, located in the surface sediments and at greater depth, respectively. The surface maximum of ¹³⁷Cs (and ¹³⁴Cs) is related to the Chernobyl accident (in April 1986), whereas the ¹³⁷Cs maximum at greater depth reflects the fall-out maximum from nuclear bomb testing in the atmosphere, corresponding to the year 1963. The 1963-peak is located at 21 cm in core E and at 42.5 cm in core K, indicating mean sedimentation rates of 0.84 and 1.7 cm/yr, respectively, in the period 1963-1987. Thus, the ²¹⁰Pb- and ¹³⁷Cs-derived sedimentation rates are comparable in core E, but a slight mismatch exists in core K. This mismatch in core K was interpreted as an increase in the sedimentation rate from 1.3 cm/yr before 1963 to 1.7 cm/yr thereafter.

An independent estimate of the long-year sediment accumulation rate is provided by the geomorphology of core K. At 80 cm depth, a transition from clay to a more sandy subsoil was noted in core K, marking the beginning of salt marsh development. According to Leemans and Verspaandonk (1980), salt marsh formation started in 1933 with the introduction of *Spartina anglica*. The mean sediment accumulation rate derived from sediment morphology is 80 cm in 55 years or 1.45 cm/yr, comparing well to the radionuclide-derived sedimentation rate of 1.3 to 1.7 cm/yr in core K.

Trace metal geochemistry in salt marshes of the Scheldt estuary

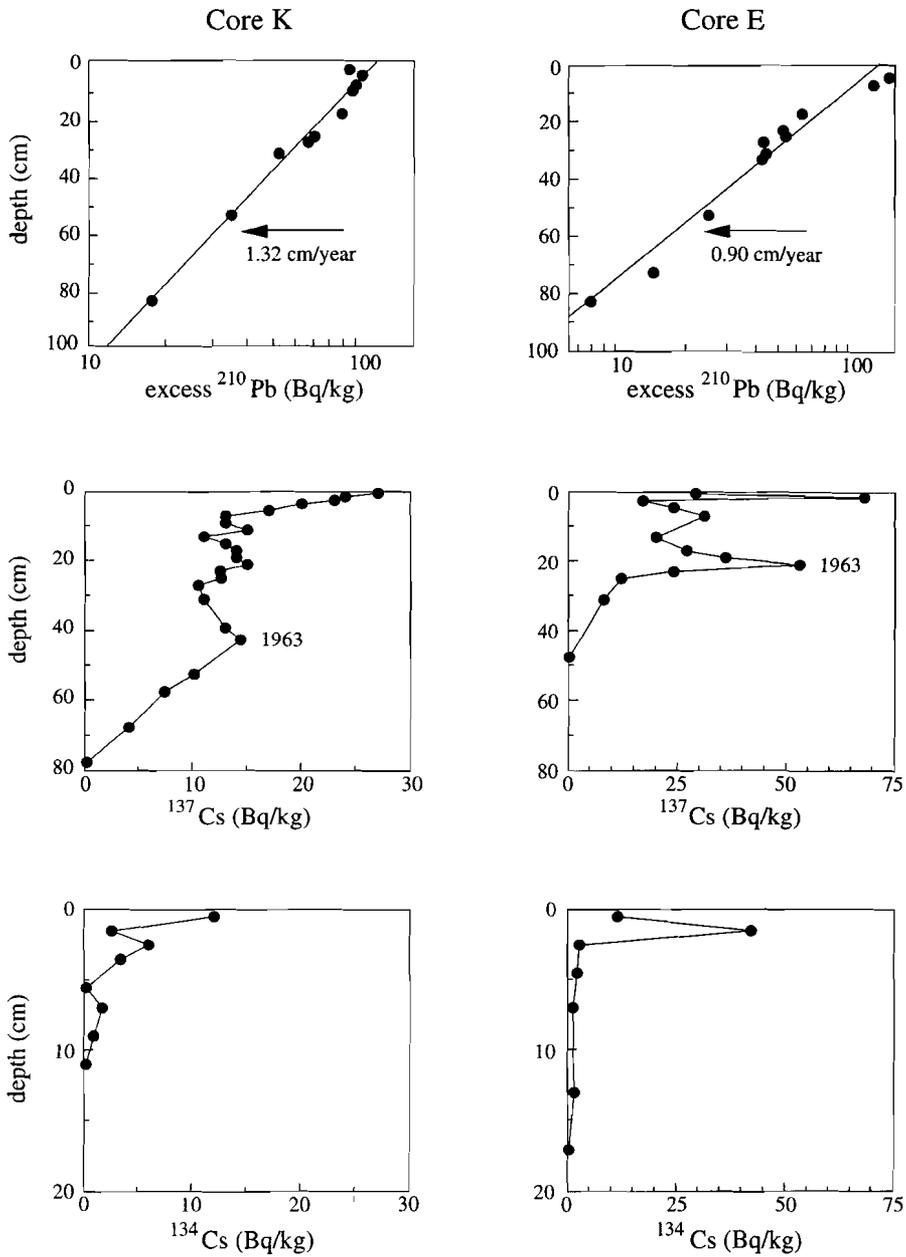


Fig. 5.1. Vertical profiles of excess ^{210}Pb , ^{134}Cs and ^{137}Cs in cores K and E. Note the different depth scale for each radionuclide. The ^{134}Cs profiles have been corrected for decay back to 1 May 1986.

5.3.2. Geochemical horizons

Visual inspection of the cores led to identification of several zones with different redox and grain-size characteristics. The different sediment layers can be described as follows:

- (1) a brown top layer, 17 cm in core K and 30 cm in core E, rich in root fragments (the oxic rhizosphere);
- (2) a grey sediment layer, located between 17-30 cm in core K and 30-62 cm in core E, containing red-brown spots characteristic of the presence of Fe oxyhydroxides (suboxic);
- (3) a grey to black layer, indicative of the presence of Fe sulphides, below 30 cm in core K and 62 cm in core E (anoxic);
- (4) a mixed clay-sand structure below 70 cm in both cores due to the presence of sandy lenses.

Based on chemical composition (Al, Mn, Fe, S), three different sediment layers can be identified, namely an oxic top layer rich in clay, a reduced clayey layer, and a reduced layer with a more sandy character. The chemical composition of these layers is listed in Table 5.1. The oxic top layer of the sediments shows high concentrations of Mn and Fe but is impoverished in total S. Underneath, in the reduced sediment zone, particulate Fe and Mn concentrations decline whereas total S increases. The presence of sandy lenses below 70 cm is reflected by an increase in Si at the expense of Al in the sediments.

5.3.3. Major element and trace metal geochemistry

The distribution of major elements and trace metals in the sediments is shown in Fig. 5.2 (core K) and Fig. 5.3 (core E). The profiles have been normalised on Al to correct for differences in grain-size composition with depth (Finney and Huh, 1989). Before dealing with the distribution of trace metals, it is instructive to consider the major element geochemistry of the cores.

Al, Si, Mg, K, Ti, Li, Be and V

The profiles of Al and Si are a clear fingerprint of the morphology of the sediments, showing a clayey layer (Al-rich) on top of a sandy subsoil (Si-rich). The profiles of Mg, K, Ti, Li, Be, and V closely resemble the Al profile (not shown), reflecting their joint presence in the clay fraction of the sediments. However, Si is significantly anticorrelated to Al due to the strong association of Si with the sand fraction of the sediments.

Trace metal geochemistry in salt marshes of the Scheldt estuary

Table 5.1. Composition of the different sediment layers and mean whole core compositions.

Depth	cm	Core K				Core E			
		0-18	18-65	70-95	0-95	0-36	40-65	70-85	0-85
n		12	15	3	30	21	3	2	26
Texture		Clay	Clay	Mixed	-	Clay	Clay	Mixed	-
Redox		Oxic	Red.	Red.	-	Oxic	Red.	Red.	-
<16 µm	%	60	58	39	53	84	91	59	81
H ₂ O	%	41	39	35	38	51	52	38	49
Porosity		0.63	0.61	0.57	0.61	0.72	0.73	0.60	0.70
Salinity ^a		24	22	22	22	19	18	24	20
POM ^b	%	6.45	6.02	4.25	5.61	9.48	7.10	5.12	7.84
SiO ₂	%	58.33	58.06	66.27	60.39	46.17	50.48	57.58	49.84
CaCO ₃	%	12.52	13.84	13.80	13.56	13.89	13.90	17.91	14.68
Al ₂ O ₃	%	8.54	8.77	7.57	8.39	11.44	11.97	8.09	10.95
Fe ₂ O ₃	%	5.49	5.04	4.08	4.87	6.46	5.07	3.91	5.50
K ₂ O	%	1.93	1.99	1.88	1.95	2.21	2.42	1.87	2.21
MgO	%	1.48	1.47	1.24	1.41	1.88	1.89	1.41	1.79
Na ₂ O ^c	%	0.67	0.67	0.67	0.67	0.67	0.67	0.67	0.67
TiO ₂	%	0.56	0.55	0.45	0.53	0.61	0.64	0.54	0.61
P ₂ O ₅	%	0.56	0.33	0.15	0.32	0.51	0.22	0.14	0.34
S	%	0.26	0.88	0.89	0.76	0.21	0.44	0.75	0.40
Salt ^d	%	1.63	1.38	1.19	1.38	1.97	2.02	1.50	1.89
Mn	µg/g	1453	558	470	713	1644	311	397	959
Zn	µg/g	318	433	309	376	435	427	271	400
Ba	µg/g	284	315	297	304	319	324	274	312
Sr	µg/g	207	225	226	222	200	177	279	208
Cr	µg/g	145	178	122	156	207	147	94	165
Pb	µg/g	96	113	89	103	138	119	82	121
V	µg/g	88	87	70	82	122	120	74	112
Cu	µg/g	53	60	40	53	66	61	33	58
Li	µg/g	38	40	35	38	59	61	38	56
Ni	µg/g	43	33	25	33	52	36	24	41
Co	µg/g	13.0	11.6	10.0	11.4	15.7	12.8	9.0	13.4
Cd	µg/g	3.6	5.0	2.7	4.1	3.6	2.8	2.5	3.1
Sn	µg/g	3.3	3.0	2.1	2.8	6.0	4.6	2.7	4.9
Ag	µg/g	1.7	1.9	1.4	1.7	2.1	1.1	0.9	1.6
Be	µg/g	1.3	1.3	1.0	1.2	1.9	2.0	1.1	1.8

(a) Estimated pore water salinity, based on water content and excess-Na.

(b) Particulate organic matter (estimated as POC × 2).

(c) Based on a detrital Na content of 0.5 %.

(d) Based on excess Na (see text).

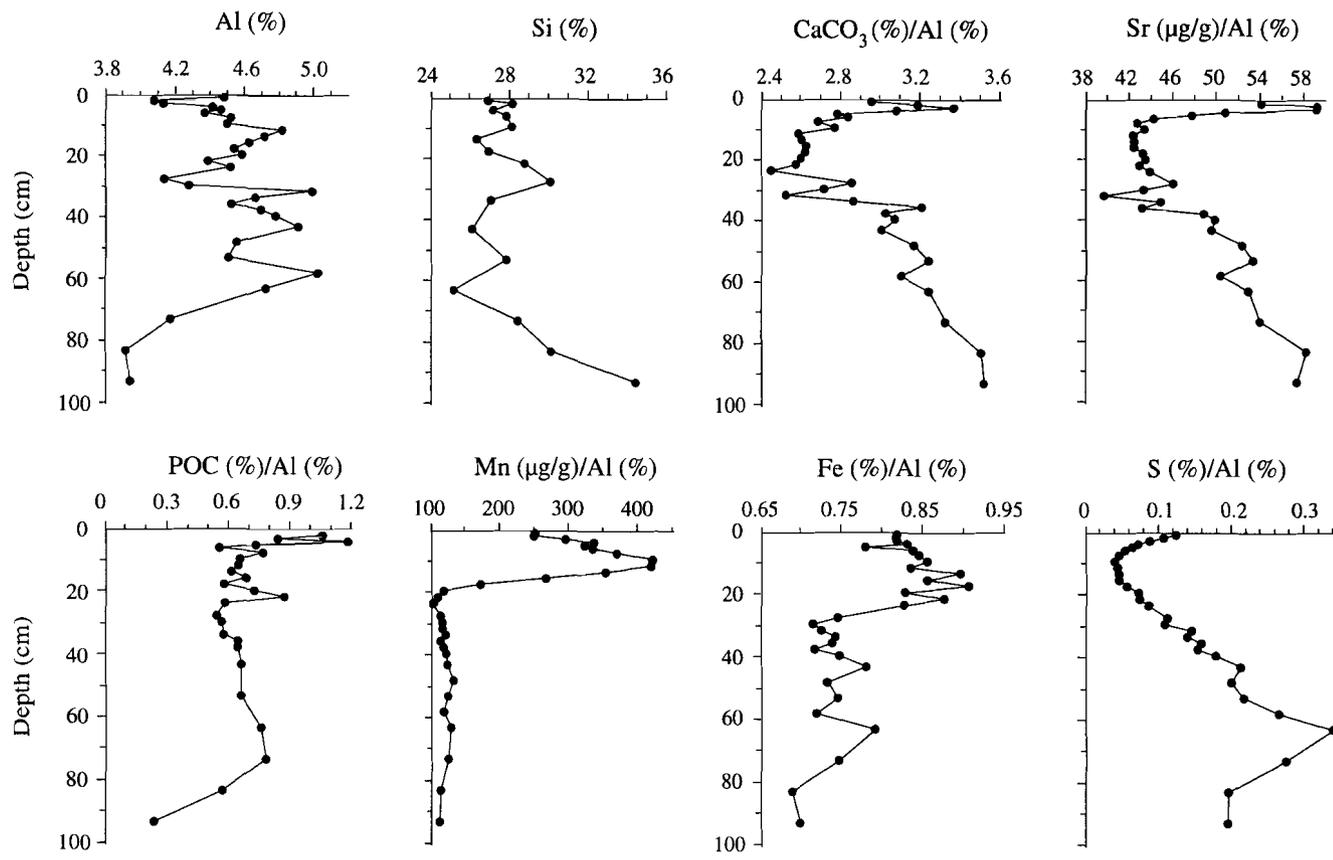


Fig. 5.2a. Distribution of major elements in core K.

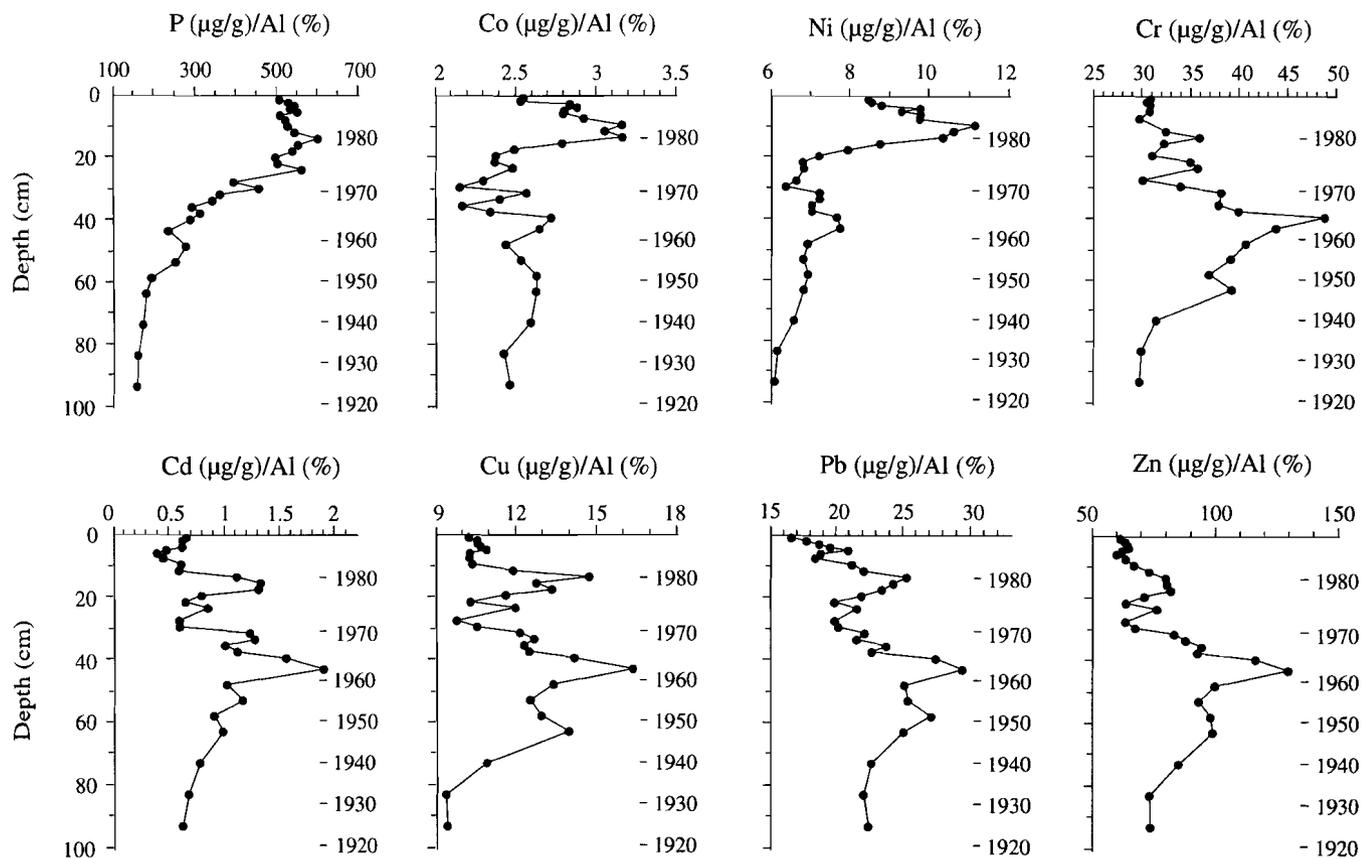


Fig. 5.2b. Distribution of phosphorus and trace metals in core K. The time scale, indicated in the profiles, is based on a sedimentation rate of 1.3 cm/yr before 1963 and 1.7 cm/yr after 1963.

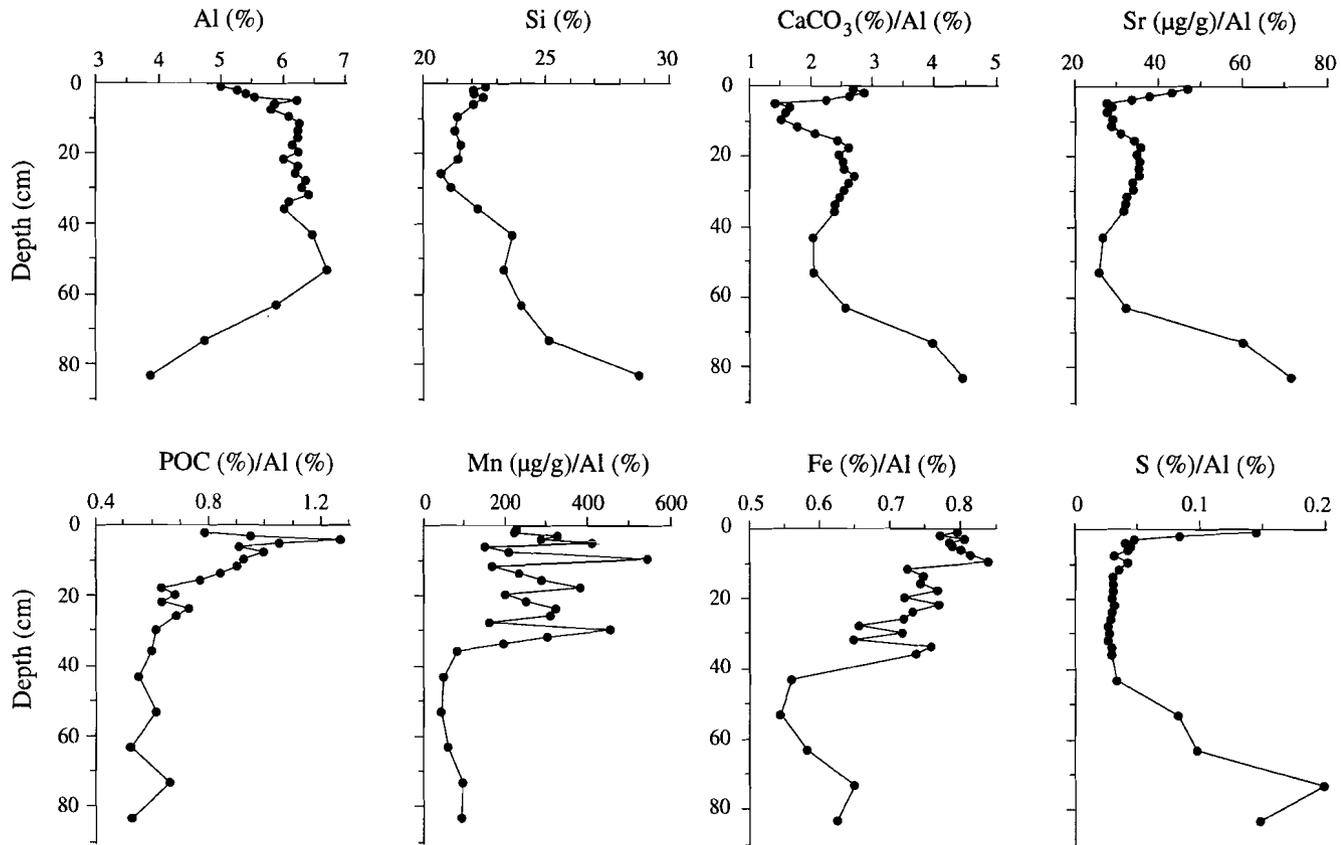


Fig. 5.3a. Distribution of major elements in core E.

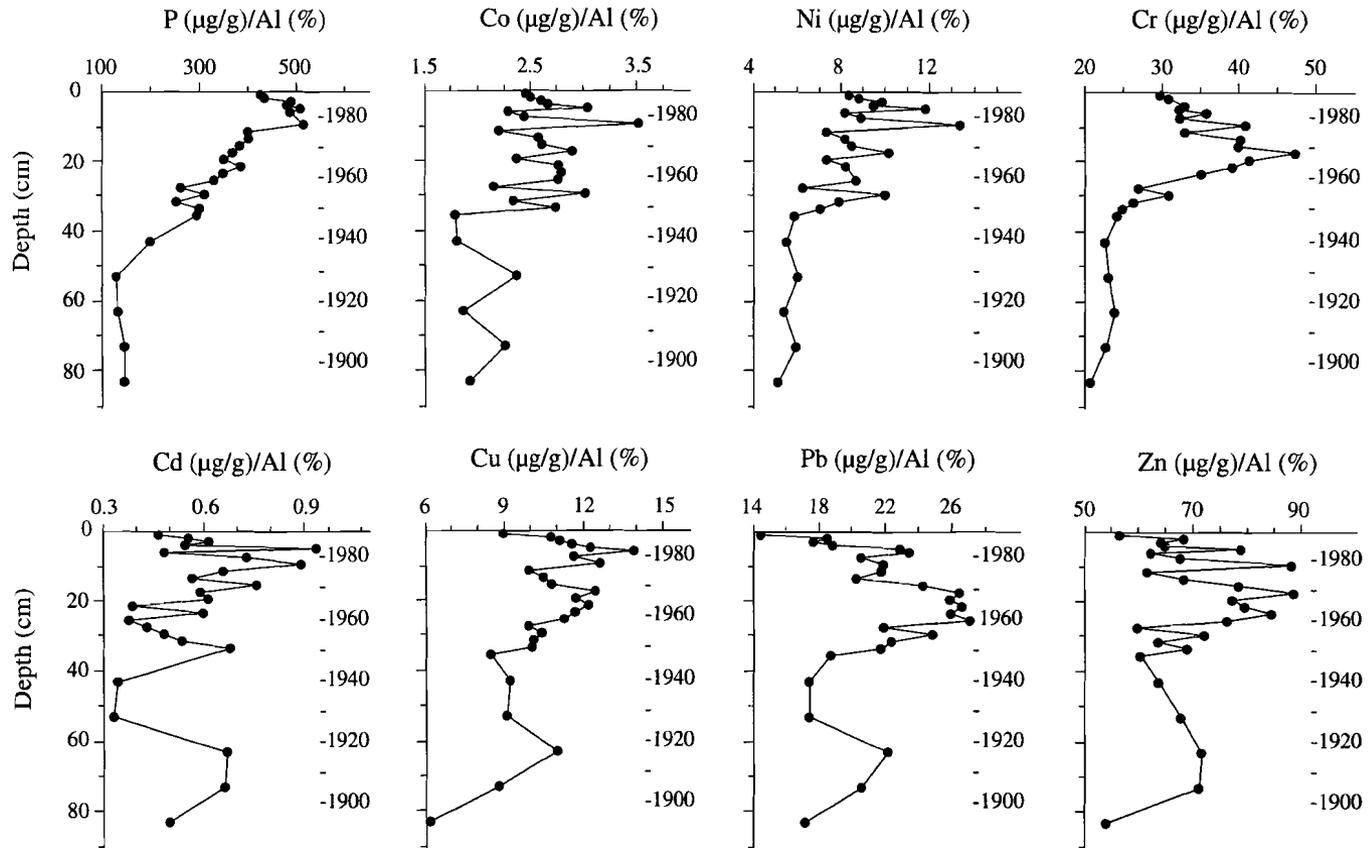


Fig. 5.3b. Distribution of phosphorus and trace metals in core E. The time scale, indicated in the profiles, is based on a sedimentation rate of 0.87 cm/yr, being the average rate determined from the ^{210}Pb and ^{137}Cs profiles.

Organic carbon

The distribution of organic carbon looks similar in both cores. High POC contents (5-7%) are found near the sediment surface due to settling of POC-rich suspended matter and subsurface production by salt marsh plants. The subsurface POC maximum observed in core E is clear evidence of the latter process. The decreasing POC content of the sediments with increasing depth indicates that decomposition dominates over production, confirming previous statements that accumulation of organic matter does not occur in Scheldt estuary salt marshes (Beefink *et al.*, 1977; Hemminga *et al.*, 1988). The predominantly mineral character of the marshes under study (see Table 5.1) is in sharp contrast with the organic-rich *Spartina* marshes of the U.S.A east coast, which have organic matter contents of 40-80% (Lord and Church, 1983; Giblin and Howarth, 1984; Scudlark and Church, 1989).

Mn, Fe, and S

The profiles of Fe and Mn will only briefly be discussed here since the diagenetic cycles of Fe and Mn are well-known (Froelich *et al.*, 1979; Shaw *et al.*, 1990; Santschi *et al.*, 1990). Particulate Mn peaks are apparent at 9-11 cm in core K and above 30 cm in core E, while Fe enrichment is obvious in the upper 20 cm of core K and the upper 35 cm of core E. These features are caused by dissolution of Fe and Mn oxyhydroxides in the partly reduced sediment layer, upward migration, and reprecipitation near the oxic-suboxic interface. Diagenetic Fe enrichment starts at greater depth than diagenetic Mn enrichment, because of the somewhat higher stability of Fe oxyhydroxides under mildly reducing conditions and the faster oxidation kinetics of Fe²⁺ compared to that of Mn²⁺.

The irregular Mn profile observed in core E is probably related to the high number of floodings of this site (175 per year), which may prevent a stable redox zonation to develop. Salt marshes which are flooded frequently have a dynamic water table, leading to short-term fluctuations of the redox boundaries (Casey and Lasaga, 1987; Hines *et al.*, 1989; Vranken *et al.*, 1990). If the position of the oxic-suboxic boundary varies continuously, formation of a sharp diagenetic Mn maximum is precluded. The pronounced Mn maximum in the top layer of core K indicates a relatively stable redox zonation (hence a stable water table), in agreement with the small number of inundations of this site (25 per year).

The distribution of total S in the cores shows the characteristic features of salt marsh sediments described extensively in the literature (Lord and Church, 1983; Giblin and Howarth, 1984; Cutter and Velinsky, 1988; Oenema, 1990). The high total S content observed at the sediment surface is caused by sedimentation of sulphide-rich suspended matter, originating from the upper estuary (see chapter 3). Oxidation of iron sulphides is responsible for the sharp decrease of the total S content in the oxic top layer of the sediments. The increase in total S below 18 cm (core K) and 40 cm (core E), and the secondary Fe maxima coinciding with the total S maxima at greater depth, reflect precipitation of iron sulphides due to sulphate reduction.

Calcium carbonate and Sr

The distribution of calcium carbonate in the sediments is related to the diagenetic processes discussed before. The carbonate content shows a rapid decline below the sediment surface in both cores, suggesting dissolution of carbonates (Oenema *et al.*, 1988). The principal reason for decalcification in the surface sediments is a transient drop in pore water pH. Subsurface pH minima are common in oxic salt marsh sediments due to acidity generating processes in the oxic sediment layer, i.e. decomposition of organic matter, nitrification and oxidation of iron sulphides (Giblin *et al.*, 1986; Luther and Church, 1988; Chambers and Odum, 1990; Vranken *et al.*, 1990). Deeper in the sediments, in the reduced sediment layer, reprecipitation of carbonates is apparent. The increase in alkalinity, generated by sulphate reduction, is responsible for this process (Oenema *et al.*, 1988; Gaillard *et al.*, 1989).

The down-core distribution of Sr resembles that of calcium carbonate, suggesting major incorporation of Sr into the carbonate fraction. The molar Sr/Ca ratio of the carbonate fraction inferred from the profiles is 0.0015, identical to the ratio observed in suspended matter of the Scheldt estuary (see chapter 3, Fig. 3.2).

Phosphorus

The distribution of P in the sediments appears to be determined both by anthropogenic influences and diagenetic processes. The sediment profiles reflect the increasing P pollution of the Scheldt estuary in the period 1920-1975, due to population growth, progressive industrial development, and the increasing use of fertilisers and synthetic detergents in the Scheldt drainage basin. However, the distribution of P is also modified by diagenetic processes, related to the redox cycling of Fe in the sediments. In the oxic surface layer of the cores, the distribution of P is related to that of Fe. Moreover, both P and Fe decrease dramatically below the oxic-suboxic interface, reflecting remobilisation of phosphate during reduction of the Fe oxyhydroxide carrier phase (Scudlark and Church, 1989; Chambers and Odum, 1990).

¹³⁴Cs and ¹³⁷Cs

The use of ¹³⁷Cs as a tool for sediment dating may not be straightforward as Cs can be mobilised in the sediments, for instance by exchange reactions with ammonium (Comans *et al.*, 1989). The extent to which Cs is mobilised in the sediments can be evaluated by comparing the observed ¹³⁷Cs penetration depth with the theoretical penetration depth, calculated from the time span between the first appearance of ¹³⁷Cs in the marine environment (1952) and the sampling date (1987), and the ²¹⁰Pb-derived sedimentation rates. The observed penetration depth in core E is at least 31 cm but less than 45 cm (see Fig. 5.1), whereas the theoretical penetration depth is 31.5 cm (using the ²¹⁰Pb-based sedimentation rate of 0.9 cm/yr). In core K, the observed penetration depth of ¹³⁷Cs is 70-75 cm, whereas the theoretical penetration depth is only 55 cm (based on a sedimentation rate of 1.3 cm/yr before

1963 and 1.7 cm/yr thereafter). Thus, diagenetic mobilisation of ^{137}Cs is apparent in core K. This does not imply, however, that the ^{137}Cs profiles cannot be used as a tool for radiodating. Diagenetic processes may smooth the original ^{137}Cs profiles, but the position (depth) of the ^{137}Cs maximum, corresponding to the year 1963, is unlikely to be affected.

The Chernobyl accident is clearly reflected by peaks of ^{134}Cs and ^{137}Cs at a depth of 1.5 cm in core E and at 0.5 cm in core K (Fig. 5.1). The initial $^{137}\text{Cs}/^{134}\text{Cs}$ ratio of the peaks (initial: ^{134}Cs corrected for decay to 1 May 1986) is 1.6 for core E and 2.2 for core K, resembling the $^{137}\text{Cs}/^{134}\text{Cs}$ ratio of atmospheric fallout in May 1986 which was about 2 (Devell *et al.*, 1986). The initial ^{134}Cs content of the sediments decreases rapidly below the surface peak, but ^{134}Cs could be detected up to 9 cm in core K and up to 13 cm in core E. The initial $^{137}\text{Cs}/^{134}\text{Cs}$ ratio of the subsurface sediments is much higher than 2, even if the high ^{134}Cs counting errors are taken into account. These findings indicate the presence of another Cs source with a high $^{137}\text{Cs}/^{134}\text{Cs}$ ratio. Due to its short half-life of 2.06 years, nuclear tests in the fifties and early sixties make an insignificant contribution to the ^{134}Cs content of the sediments. A possible source of ^{134}Cs is marine suspended matter, given the upstream transport of marine particles in the Scheldt estuary (Martin *et al.*, 1994; see chapter 3). The initial $^{137}\text{Cs}/^{134}\text{Cs}$ ratio of marine suspended matter, contaminated with Cs released by nuclear reprocessing plants in Sellafield and Cap de La Hague (Kautsky, 1986), is around 5 (Livingston *et al.*, 1982^{a,b}), which is more compatible with the isotopic ratio found in the subsurface sediments.

Co and Ni

The vertical profiles of Co and Ni in the sediments resemble each other to a large extent, reflecting the similar geochemistry of these elements noted previously by Prohic and Kniewald (1987) and Shaw *et al.* (1990). In the top layer of core K, the distributions of Co and Ni follow the Mn profile. In the top layer of core E, apparent Ni and Co enrichments coincide with local Mn peaks. The highly significant relationship between Co, Ni, and Mn in the top layer of the cores (Fig. 5.4) suggests that Co and Ni are cycled along with Mn oxides at redox boundaries. The dominant role of Mn oxides in the cycling of Ni and Co has been stressed before by Klinkhammer (1980) and Shaw *et al.* (1990). Usually, studies on trace metal diagenesis in submerged coastal sediments do not distinguish between the role of Mn and Fe oxides, due to the fact that the zones of diagenetic Fe and Mn enrichment are barely separated (Gendron *et al.*, 1986; Cornwell, 1986; Prohic and Kniewald, 1987; Finney and Huh, 1989). In the salt marsh sediments investigated here, these zones are separated by several cm, allowing distinction between the role of Mn and Fe oxides as trace metal scavenging phases. For this reason, salt marsh sediments provide a valuable tool for the study of trace metal behaviour during early diagenesis.

Trace metal geochemistry in salt marshes of the Scheldt estuary

The positive Y-axis intercept shown by the Co-Mn and Ni-Mn relationships (Fig. 5.4) indicates the presence of a second metal fraction not associated with Mn oxides. This second fraction, which is probably of detrital origin, amounts on the average 65-70% for Co and 55% for Ni in the top layer of the cores (0-24 cm in core K 0-36 cm in core E). The similarity between the profiles of Co, Ni, and Mn disappears in the reduced zone of the sediments, due to dissolution of the Mn oxide carrier phase. The small peaks of Ni and Co, observed in core K at 40-45 cm depth, can be explained by precipitation of Co and Ni with (iron-)sulphides (Morse *et al.*, 1987; Shaw *et al.*, 1990).

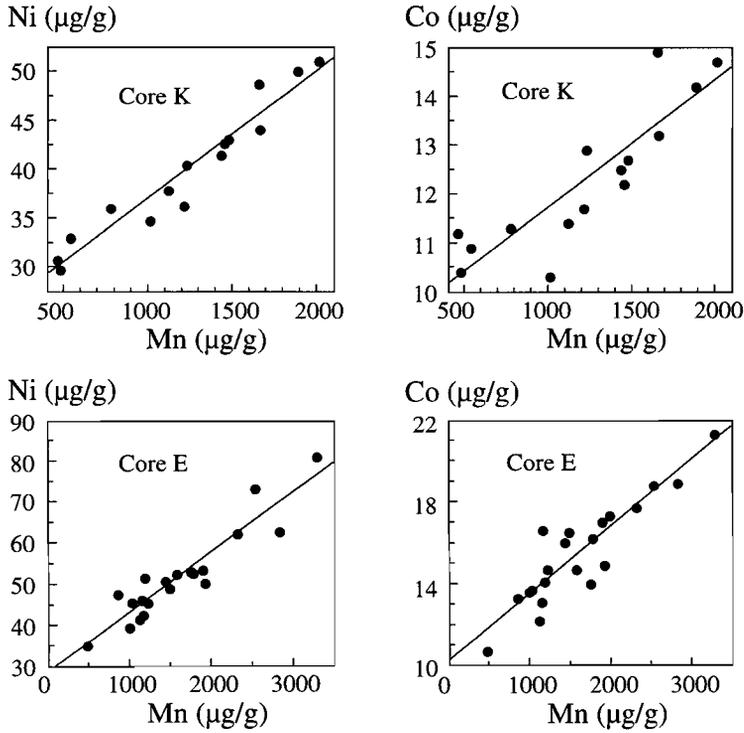


Fig. 5.4. Solid-phase Ni-Mn and Co-Mn relationships in the oxic top layer of core K (0-24 cm) and core E (0-36 cm).

Cr

The distribution of Cr in the top layer of core E is unrelated to any reactive sediment phase, such as Mn or Fe oxyhydroxides, POC or carbonates. Moreover, since the Cr peak is located in the oxic layer of the sediments, a diagenetic origin can be excluded (which is not the case for core K). Therefore, the Cr profile of core E unambiguously reflects the pollution history of this element. A continuous increase of the Cr pollution in the period 1945-1968 is apparent, reflecting economic development which started after World War II. After 1968 a major decrease of the Cr pollution has occurred, probably due to waste water purification measures.

The Cr profile of core K is in good agreement with the pollution history inferred from core E, showing a maximum in the mid-sixties, and a major decrease of the Cr pollution afterwards. However, diagenetic modifications may play a role here, since the Cr peak occurs in the reduced sediment layer. In the oxic top layer of core K, Cr will be present as Cr(VI), which is relatively mobile. After release to the pore waters, Cr(VI) may migrate downward into the reducing zone and precipitate again as Cr(OH)₃ (Gaillard *et al.*, 1986; Shaw *et al.*, 1990). This diagenetic process may cause natural Cr enrichment in the reduced layer of core K.

Cd, Cu, Pb, and Zn

The distributions of Cd, Cu, Pb, and Zn in core K resemble each other to a large extent, suggesting similarities in sources (pollution) and post-depositional behaviour. Concentration maxima are observed at depths of 13-17 cm (1978-1980) and 40-45 cm (1961-1965). It is difficult to reconstruct a straightforward pollution history from these profiles because they bear a major diagenetic impact. For instance, the subsurface maxima of Cd, Cu, Pb, and Zn are situated in the zone of diagenetic Fe and Mn enrichment, which may indicate readsorption by Mn and Fe oxyhydroxides (Tessier *et al.*, 1985; Cornwell, 1986; Finney and Huh, 1989). Thus, diagenetic processes may have modified the original trace metal distribution. Nevertheless, the profiles of Cd, Cu, Pb, and Zn in the top layer of core K seem to reflect the recent pollution history. Monitoring data of estuarine suspended matter, collected 10 km upstream from the marshes, confirm that a pollution maximum occurred at the end of the seventies, followed by a decrease of the metal load in the eighties (see chapter 4, Fig. 4.7).

Diagenetic modifications are important below the oxic-suboxic interface of core K, due to dissolution of the Mn and Fe oxyhydroxides. Trace metals released by this process will reprecipitate in the sulphate reduction layer as sulphides or (less likely) as carbonates (Gaillard *et al.*, 1986; Giblin *et al.*, 1986; Moore *et al.*, 1988; Shaw *et al.*, 1990). Thus, the increasing importance of sulphate reduction with increasing depth has probably caused trace metal enrichment in the reduced sediment layer of core K. However, since the trace metal peaks in the reduced layer (at 40-45 cm) are situated well above the total S maximum (at 60-65 cm), it may be assumed that they still reflect the pollution history, at least qualitatively.

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The trace metal profiles of core E are also altered by post-depositional processes. For instance, peaks of Cd and Zn, observed in the top layer of the sediments, coincide with local Mn enrichments, as noted before for Ni and Co (Table 5.2). Therefore, the decreasing trace metal pollution in the eighties, which is apparent in the profiles of Cu and Pb, is camouflaged in the Cd and Zn profiles of core E. The peaks of Cu, Pb, and Zn at greater depth (period 1960-1968) are beyond doubt of anthropogenic origin, because these maxima occur in the S-depleted layer. Diagenetic trace metal maxima are observed in the sulphate reduction layer of core E (below 50 cm), caused by precipitation of metal sulphides.

Table 5.2. Composition of two Mn-rich samples in the top layer of core E, compared with the average composition of the top 10 cm of the sediments (calculated without these two Mn-rich samples, n = 6).

Depth cm	Al %	Fe %	Mn µg/g	P µg/g	Cd µg/g	Co µg/g	Cr µg/g	Cu µg/g	Ni µg/g	Pb µg/g	Zn µg/g
4.5	6.21	4.89	2541	3141	5.8	18.8	200	76	73	142	488
9.0	6.08	5.09	3295	3115	5.4	21.3	248	77	81	133	535
0-10	5.47	4.34	1276	2498	3.1	13.6	178	62	49	104	349

5.3.4. Impact of atmospheric deposition

The two principal sources of trace metals to the marshes are atmospheric deposition and sedimentation of estuarine suspended matter. Atmospheric trace metal inputs were calculated from deposition data for the Southern Bight of the North Sea, assuming continuous exposure of the marshes to the atmosphere. Sedimentary trace metal inputs were calculated from measured sedimentation rates (1.7 cm/yr for core K and 0.87 cm/yr for core E), the average composition of suspended matter deposited on the marshes (known from field sampling in 1987; see chapter 3), surface sediment porosity (0.60 for core K and 0.75 for core E), and a dry sediment density of 2.5 g/cm³, according to:

$$F = r_{\text{sed}} \times (1 - \Phi) \times 2.5 \times C_{\text{spm}}$$

where F is trace metal flux (µg/cm²/yr), r_{sed} is sedimentation rate (cm/yr), Φ is sediment porosity, 2.5 is dry sediment density (g/cm³), and C_{spm} is average annual trace metal content of the suspended matter (µg/g).

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The results of the flux calculations are shown in Table 5.3. Obviously, the contribution of atmospheric trace metal inputs to the total metal load of the sediments is negligible.

Table 5.3. Sources of trace metals to the sediments.

Flux (mg/m ² /yr)	Cd	Cu	Pb	Zn
Atmospheric deposition*	0.7	5	13	30
Sedimentation (core E)	28.5	396	537	2317
Sedimentation (core K)	89.3	1238	1680	7245

* From Injuk *et al.* (1990).

5.3.5. Trace metal retention

The diagenetic processes discussed before may influence the retention of trace metals by the sediments. This section deals with the mobility of trace metals immediately after deposition. Thereafter, the long-term trace metal retention by the marshes is quantified by comparing the trace metal inventories of the sediments with the anthropogenic pollution record over the period 1925-1988.

Surface retention

The extent of post-depositional mobility in the surface sediments can be assessed by comparing their composition with the composition of sedimenting suspended matter. The composition of suspended matter in the water column near the marshes is known from field sampling, carried out between February 1987 and February 1988 (see chapter 3). In Table 5.4, the average suspended matter composition near the marshes is compared to the composition of the top 1 cm of the sediments. Grain-size differences are taken into account by expressing the sediment composition at the same Al content as that of the suspended matter.

The major element composition of the surface sediments is similar to that of the suspended matter, except for Ca, S, POC, and P. These elements appear to be lost from the surface sediments, reflecting the impact of the diagenetic processes discussed before (organic matter degradation, sulphide oxidation, and decalcification). Slight losses of Fe and major losses of Mn are apparent too, which may result from periodic shifts from oxidising to reducing conditions at the sediment surface (during inundation). The amount of P lost from the sediments is almost four times higher than that calculated from the POC decrease, assuming the Redfield stoichiometry. This may indicate preferential decomposition of organic P compounds during early diagenesis, or desorption of phosphate bound by Fe oxyhydroxides. Such a desorption process would be favoured by reducing conditions at the sediment surface, and by high pore water salinities. Average pore water salinities (Table 5.1) are about twice the salinity of mean flood water, reflecting desiccation of the sediments during atmospheric exposure (Lord and Church, 1983; Casey and Lasaga, 1987; Vranken *et al.*, 1990).

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Table 5.4. Composition of the sedimenting suspended matter and of the surface sediments (0-1 cm) of core K and core E. Major elements and trace metals are listed in order of decreasing retention (i.e. increasing mobility).

		Suspended matter	Sediment (0-1 cm)		% Retention*	
		mean \pm s.d.	K	E	K	E
Al	%	4.79 \pm 0.33	4.48	4.98	-	-
Si	%	23.09 \pm 0.90	26.87	22.50	-	-
Ti	%	0.32 \pm 0.02	0.33	0.34	111	102
Mg	%	0.93 \pm 0.05	0.93	1.02	108	105
K	%	1.74 \pm 0.03	1.60	1.67	98	92
Fe	%	4.17 \pm 0.31	3.66	3.96	94	91
Ca	%	5.94 \pm 0.38	5.29	5.36	95	87
S	%	0.74 \pm 0.03	0.55	0.72	80	94
POC	%	5.99 \pm 0.97	4.30	4.10	77	66
P	%	0.38 \pm 0.04	0.23	0.21	64	54
Li	$\mu\text{g/g}$	42 \pm 3	37	45	94	103
V	$\mu\text{g/g}$	101 \pm 6	84	98	89	93
Be	$\mu\text{g/g}$	1.6 \pm 0.1	1.3	1.6	86	96
Co	$\mu\text{g/g}$	13.8 \pm 0.6	11.4	12.2	88	85
Cr	$\mu\text{g/g}$	170 \pm 12	138	148	87	84
Ba	$\mu\text{g/g}$	315 \pm 26	270	244	92	74
Ni	$\mu\text{g/g}$	50 \pm 1	38	42	81	80
Sr	$\mu\text{g/g}$	304 \pm 10	242	233	85	74
Mn	$\mu\text{g/g}$	1438 \pm 57	1119	1122	83	75
Pb	$\mu\text{g/g}$	99 \pm 7	74	72	80	70
Zn	$\mu\text{g/g}$	426 \pm 44	274	281	69	63
Cu	$\mu\text{g/g}$	73 \pm 8	46	44	67	59
Cd	$\mu\text{g/g}$	5.2 \pm 0.7	2.9	2.3	59	42
Ag	$\mu\text{g/g}$	2.9 \pm 0.3	1.0	1.1	37	37

* Calculated as $(C_{\text{sed}} / Al_{\text{sed}}) / (C_{\text{spm}} / Al_{\text{spm}}) \times 100\%$.

Trace metals are retained by the sediments to a different extent, due to differences in particulate metal speciation. Elements associated with the detrital sediment fraction show no post-depositional mobility (Li, V, Be). Elements which are predominantly present in detrital form show low post-depositional mobility (Co, Ni, Cr). Significant mobilisation of Ag, Cd, Cu, Pb, and Zn is observed, in agreement with their predominant presence in reactive forms in Scheldt estuary suspended matter (see chapter 3). Carbonate dissolution may explain the mobilisation of Sr.

Trace metal inventories

Now that trace metal mobilisation from the surface sediments has been demonstrated, the question remains if the metals are lost to the water column or are reprecipitated during downward migration. To answer this question, the trace metal pollution record for the period 1925-1988 was estimated, and compared with the inventories of the corresponding core sections. The average trace metal content of the suspended matter deposited on the marshes was determined from monitoring data for the Dutch-Belgian border, which are available for the period 1970-1988. Since the border is located 10 km upstream from the marshes, the monitoring data have to be corrected because the trace metal content of the suspended matter decreases in downstream direction (see chapter 3). The monitoring data were corrected with an element-specific factor (0.53-0.75), deduced from field sampling in 1987-1988. Trace metal inputs in 1925 were estimated as the composition of the corresponding sediment layers of core K (90-95 cm) and core E (50-55 cm). Trace metal inputs for the period 1925-1970 were estimated by assuming a linear increase of the trace metal pollution from 1925 to 1970, similar to the pollution history of the Rhine river (Beurskens *et al.*, 1993). A summary of the trace metal and P input data is presented in Table 5.5. The inputs of Al, Ti, K, Mg, Fe, Mn, S, POC, Ca, and Co during 1925-1988 were assumed equal to those measured in 1987-1988 (these are listed in Table 5.4).

Table 5.5. Estimation of average trace metal and P content of the sedimenting suspended matter during 1925-1988 (all contents in $\mu\text{g/g}$).

Input data	Cd	Cr	Cu	Ni	Pb	Zn	P
Core E (1925) ^a	1.6	110	43	29	83	324	615
Core K (1925) ^a	2.9	142	45	29	107	351	750
SPM (1970-1988)	10.3	189	90	57	147	590	4226
Mean (1925-1988) ^b	7.4	166	73	47	129	500	2960

(a) Normalised on the Al content of the sedimenting suspended matter in 1987/88 (4.79%)

(b) Calculated using the average 1925-baseline and assuming a linear increase of trace metal pollution during 1925-1970.

In Table 5.6, the inventories of core K (0-95 cm) and core E (0-55 cm) are compared with the estimated average composition of the suspended matter deposited during 1925-1988. This comparison should be considered as tentative due to the uncertainties in the input data. The inventory of core E will not be considered in detail here, because the sulphate reduction layer of this core lies below the depth range considered here (as reflected by the low S retention).

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Table 5.6. Estimated suspended matter composition (SPM), averaged over the period 1925-1988, and of the corresponding sediment layers of core K (0-95 cm) and core E (0-55 cm).

		SPM	Sediment		% Retention	
			K	E	K	E
Al	%	4.79	4.44	6.21	-	-
S	%	0.74	0.76	0.26	111	27
Ti	%	0.32	0.32	0.37	107	90
K	%	1.74	1.62	1.91	100	85
Mg	%	0.93	0.85	1.15	99	95
Ca	%	5.94	5.43	5.50	99	71
Fe	%	4.17	3.40	4.24	88	78
POC	%	5.99	2.81	4.40	51	57
P	%	0.30	0.14	0.19	51	48
Cr	µg/g	166	156	187	101	87
Co	µg/g	13.8	11.4	14.8	89	83
Pb	µg/g	129	103	129	86	78
Zn	µg/g	500	376	430	81	66
Cu	µg/g	73	53	64	78	67
Ni	µg/g	47	33	47	75	77
Cd	µg/g	7.4	4.1	3.1	60	33
Mn	µg/g	1438	713	1185	53	64

* Calculated as $(C_{\text{sed}} / Al_{\text{sed}}) / (C_{\text{spm}} / Al_{\text{spm}}) \times 100\%$.

The inventory of core K includes the entire sulphate reduction layer, as suggested by the conservation of S in this core. The conservation of Ca in core K indicates that bicarbonate, produced in the decalcification zone, is completely reprecipitated in the sulphate reduction zone below. The high loss of POC shows that decomposition dominates over in-situ production by the marsh vegetation. Half of the P input appears to be lost from the sediments, suggesting that the marshes act as an important source of phosphate to the estuary. Phosphate exports from salt marshes have been demonstrated before by Dankers *et al.* (1984) and Whiting and Childers (1989). The P loss is two to three times higher than that calculated from the POC decrease (assuming the Redfield ratio), suggesting that desorption of Fe-bound phosphate is also involved. An important difference is observed between the retention of Fe, which is relatively high, and Mn, which is to a great extent lost from the marshes. Apparently, reoxidation processes are much more efficient in trapping Fe than Mn. Similar results have been reported for the Great Marsh, Delaware, where reoxidation reactions trap more than 96% of the Fe but only 70% of the Mn (Boulègue *et al.*, 1982).

In general, trace metal retention in core K is higher than that in core E, reflecting the importance of trace metal reprecipitation in the sulphate reduction zone (which is not included in the inventory of core E). The only exceptions are Ni and Mn, which are indeed more efficiently trapped under oxic conditions (Klinkhammer, 1980; Shaw *et al.*, 1990). Still, Cr is

the only trace metal which appears to be fully retained in core K. Slight to moderate losses (11-25%) are observed for Co, Pb, Zn, Cu, and Ni, whereas Cd appears to be lost from the sediments to a much greater extent (40%). These results suggest that the salt marshes of the Scheldt estuary may act as an important source of dissolved Cd to the water column, contributing to the observed mobilisation of dissolved Cd (and Cu) with increasing salinity (see chapter 2). Similar observations in other areas suggest that trace metal mobilisation from (salt) marsh sediments can be a general phenomenon (Simpson *et al.*, 1983; Giblin *et al.*, 1986; Allen *et al.*, 1990). Contrary to submerged sediments, salt marsh sediments usually have a well-oxidised surface sediment layer, preventing precipitation of the metals as sulphides. Instead, retention and mobility of trace metals in the surface sediments are controlled by adsorption onto Fe and Mn oxyhydroxides, oxidation of (iron-)sulphides and degradation of organic carbon. The high pore water salinities near the sediment surface, established during desiccation, will effectively reduce adsorption of trace metals (particularly Cd), due to formation of chloro-complexes (e.g. Comans and Van Dijk, 1988). Moreover, periodic shifts from oxidising to reducing conditions (during inundation) cause dissolution of the Fe and Mn carrier phases and release of associated trace metals. These mechanisms tend to keep high trace metal concentrations in solution (Boulègue *et al.*, 1982; Giblin *et al.*, 1986), which can be lost during flooding of the sediments.

5.4. Conclusions

This study has shown the great impact of diagenetic processes on the distribution of trace metals in salt marshes. After deposition on the marshes, trace metals are partially mobilised. The metals released are partly reprecipitated in the sulphate reduction layer, and partly lost from the sediments during tidal exchange. Trace metal mobilisation is favoured by a combination of factors, which are unique for salt marsh sediments. These factors include: 1) the presence of a distinct oxic top layer; 2) acidification in the top layer due to oxidation of iron sulphides and organic matter; 3) high pore water salinities during sediment desiccation; 4) periodic shifts from oxidising to reducing conditions during inundation. Since these features have been recorded in salt marshes all over the world, it follows that trace metal mobilisation from salt marsh sediments can be a general phenomenon. Future research should focus on the role of salt marshes as a source of dissolved trace metals to the water column.

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Chapter 6

Diagenetic trace metal mobilisation in sediments of the Scheldt estuary

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Abstract - Sediment cores were collected along a wide salinity gradient in the Scheldt estuary in March/April and June 1989. Cores were taken at two coastal marine stations, one brackish water station, and one station in the low-salinity, high-turbidity zone. The cores were cut into thin sections (1-2 cm), which were pressure-filtered in order to collect the pore waters (under nitrogen atmosphere). Pore waters were analysed for major elements, nutrients, Mn, Fe, sulphate, Ba, and trace metals (Cd, Cu, Zn). The trace metal profiles recorded in the pore waters are related to the position of the redox boundaries in the sediments. Oxidation of labile organic matter and sulphides leads to concentration maxima of dissolved Cd, Cu, and Zn near the sediment-water interface (SWI). The intensity of the trace metal peaks at the SWI depends on the redox condition of the surface sediments, but not on sediment trace metal content or pore water salinity. In general, high concentrations of Cd, Cu, and Zn are observed in the surficial pore waters of sandy sediments, which are mildly oxidising at the SWI. Silty sediments, in which reducing conditions are established close to the SWI, show low concentrations of Cd, Cu, and Zn in the surficial pore waters. This observation is related to trace metal scavenging by Fe oxyhydroxides near the SWI (suggested for one marine sediment core), or to precipitation of metal sulphides just below the SWI (in the low-salinity sediment cores). In the suboxic zone of the sediments, mobilisation of Cu and Zn is also observed, which is ascribed to release from Mn and Fe oxyhydroxides. Very low trace metal concentrations were found in the sulphate reduction zone of the sediments (if present), reflecting metal sulphide precipitation. The extent of post-depositional mobility of sediment-bound trace metals is also related to the position of the redox boundaries, in agreement with the pore water profiles. Thus, post-depositional mobility is minor in the sulphidic low-salinity sediments, because of efficient scavenging of trace metals released during organic matter decomposition. Diagenetic processes have a significant impact on the solid-phase distribution of trace metals in the brackish sediments, which is related to the well-resolved spacing of the redox zones in these sediments. The impact of diagenesis on the trace metal content of the marine sediments is limited, which may reflect their recent time of deposition. Due to the presence of dissolved metal peaks near the SWI, the sediments of the lower estuary may act as a source of dissolved Cd, Cu, and Zn to the water column. In the future, when oxic conditions are restored in the Scheldt river, this may also become true for the sediments of the upper estuary. Restoration of dissolved oxygen in the upper estuary is expected to cause a temporary increase in the outflow of dissolved Cd, Cu, and Zn from the sediments, because metal sulphide precipitation at the SWI would become less important than it is today.

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6.1. Introduction

A great part of the suspended matter load carried by rivers is deposited in estuaries or in the nearshore environment (e.g. Kennedy, 1984). Since most trace metals are associated to a major extent with the particulate phase, sedimentation processes may reduce the flux of trace metals to the oceans. However, significant remobilisation of trace metals may take place at the sediment-water interface (SWI), as reflected by the composition of the pore waters (Shaw *et al.*, 1990; Santschi *et al.*, 1990). While being a sink for particulate trace metals, sediments may thus act as a source of dissolved trace metals to the water column (Emerson *et al.*, 1984, Santschi *et al.*, 1990; Wallmann *et al.*, 1996). Besides their geochemical importance, pore water studies are also relevant for risk assessment. It is well-known that pore water composition is more important in determining sediment toxicity than is the solid-phase composition of the sediments (e.g. Kemp and Swartz, 1988; Di Toro *et al.*, 1992).

Previous studies on trace metal cycling in pore waters were focused mainly on (oxic) deep-sea sediments. The deep-sea pore waters are enriched in Cd and Cu, due to oxidation of biogenic material in the surficial sediments (Klinkhammer *et al.*, 1982; Sawlan and Murray, 1983; Gobeil *et al.*, 1987). The nutrient-like distributions of Cd and Cu in oxic pore waters contrast with those of Co and Ni, which are removed at the oxic-suboxic boundary due to coprecipitation with Mn oxyhydroxides (Klinkhammer, 1980; Sawlan and Murray, 1983; Heggie and Lewis, 1984; Shaw *et al.*, 1990). Compared to oceanic sediments, (subtidal) coastal and estuarine sediments are different in that the different redox zones are usually barely separated and sometimes even overlap (e.g. Elderfield *et al.*, 1981; Gaillard *et al.*, 1986). It is very hard to obtain pore water profiles of trace metals with sufficient vertical resolution (mm scale or less) in nearshore sediments, although novel gel techniques (DET and DGT) have shown promising results (Davison *et al.*, 1991, Zhang *et al.*, 1995). Similar to deep-sea pore water profiles, trace metal profiles in estuarine and near-shore pore waters show peak concentrations at the SWI, generally ascribed to decomposition of organic matter and reoxidation of metal sulphides (Elderfield *et al.*, 1981; Emerson *et al.*, 1984; Gaillard *et al.*, 1986; Giblin *et al.*, 1986; Skowronek *et al.*, 1994; Wallmann *et al.*, 1996). Reduction of Mn and Fe oxyhydroxides in the suboxic sediment layer may also contribute to trace metal mobilisation in coastal and freshwater sediments (Tessier *et al.*, 1985; Santschi *et al.*, 1990, Shaw *et al.*, 1990). At greater depth, in the sulphate reduction zone, trace metals are removed from the pore waters through precipitation as sulphides (e.g. Davies-Colley *et al.*, 1985; Gaillard *et al.*, 1986; Moore *et al.*, 1988; Wallmann *et al.*, 1996).

In this study, pore water profiles of trace metals are presented for a variety of sedimentary environments in the Scheldt estuary. The Scheldt estuary poses a highly dynamic sedimentary environment and is severely polluted by trace metals. The aims of this study were (1) to assess the distribution of trace metals in the pore waters, (2) to identify the controlling diagenetic and sedimentary processes, and (3) to investigate the effect of these processes on the solid-phase trace metal distribution in the sediments.

6.2. Sampling and analysis

6.2.1. Pore water sampling and analysis

Four sampling stations were chosen in the estuary (Fig. 1.2), covering a wide salinity gradient. Marine sediment cores were collected near the mouth of the estuary at a subtidal location (water depth 10 m) and an intertidal location (a sandflat). These locations will be referred to as Ms (marine subtidal) and Mi (marine intertidal). Brackish sediment cores were sampled at an intertidal sandflat near the Dutch-Belgian border, and low-salinity cores were collected in the (anoxic) high-turbidity zone (HTZ) near the city of Antwerp (water depth 7 m). These will be referred to as the B-cores (brackish) and the HTZ-cores, respectively. Each location was sampled twice. Sampling dates were 22 March 1989 (cores Ms1 and Mi1), 25 April 1989 (cores B1 and HTZ1), and 6-7 June 1989 (cores Ms2, Mi2, B2 and HTZ2). All sediment cores were taken by SCUBA divers and sealed under water in order to prevent oxidation of the surface sediments. Intertidal locations (Mi and B) were sampled during flood tide, when the sediments were submerged by 50-100 cm of water. The core liners used were transparent perspex tubes with a length of 50 cm and an internal diameter of 7 cm. At each location, several (visually similar) cores were collected. Immediately after collection, one of these cores was used for determination of profiles of temperature, pH, and redox potential, using specific electrodes. Afterwards, this core was discarded. The cores for pore water sampling were extruded and cut into small sections in a nitrogen-flushed glove-box within 30 minutes after collection. Section intervals were 2.1 cm for cores Ms1 and Ms2, 4.2 cm for core HTZ1, and 1.05 cm for cores Ms2, Mi2, B2, and HTZ2. Core B1 was sectioned at intervals of 2.1 cm up to 10 cm depth, and at 4.2 cm underneath. At each location (except HTZ1), two cores were cut and the corresponding sediment sections were mixed, in order to obtain sufficient pore water volume. Pore waters were extracted from the sediment sections by pressure-filtration in all-teflon Reeburgh-type squeezers in a nitrogen-flushed glove-box (system details are given in De Lange, 1992). Pore waters from muddy sediments were easily collected within one hour, but sandy sediments had to be squeezed for several hours in order to obtain a sufficiently large sample. The recovered pore waters were subsampled (8 ml) in the glove-box for analysis of chloride, sulphate, nutrients, dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC). These subsamples were stored at 4 °C in the dark and analysed within two days by standard auto-analyser techniques (Grasshoff *et al.* 1983). The remaining pore water was acidified to pH 1 with HNO₃ (p.a.), and subsampled (5 ml) for analysis of Na, K, Ca, Mg, Sr, (total) S, Fe, Mn, and Ba by ICP-AES. The Na analyses were used to calculate pore water salinities, because some Cl analyses were judged to be less reliable. The remaining acidified pore water (10-30 ml) was used for trace metal analysis (see section 6.2.2). Special care was taken to avoid contamination throughout the whole sampling and analytical procedure. All materials in contact with sediment and pore water samples (e.g. core liners, filters, squeezers, storage bottles) were acid-cleaned and flushed several times with de-ionised water prior to use. Despite the rigorous cleaning procedures, two dissolved Zn

profiles (cores Ms1 and Mi1) were discarded because of their erratic profile and very high concentration levels (up to 12 μM). These erratic Zn profiles were obtained at the start of this study and may reflect contamination which was reduced or eliminated as our work proceeded.

6.2.2. Trace metal analysis

Prior to trace metal analysis, a preconcentration step was carried out. A complexation-extraction technique (HMDC-DIPK; Dornemann and Kleist, 1979) was used to preconcentrate pore water samples of cores Ms1, Mi1 and B1. For the other cores, preconcentration was performed by coprecipitation with Co-APDC (Boyle and Edmond, 1975). Some samples were preconcentrated with both techniques. The analytical results for these samples are compared in Table 6.1, showing fair agreement for Cd, but poor for Cu (Zn was not tested). It appears that the HMDC-DIPK preconcentration technique results in lower Cu concentrations than the Co-APDC method. We suspect that in-situ formation of Fe oxyhydroxides during buffering of the pore waters to pH 4 (prior to metal complexation) interferes with the preconcentration of dissolved Cu in the HMDC-DIPK technique (formation of colloidal precipitates was sometimes observed). Adsorption of inorganic metal complexes onto Fe oxyhydroxides is unlikely at pH 4, but adsorption of organic Cu complexes is possible at low pH values (Laxen, 1985; Tessier *et al.*, 1985). It is well known that the speciation of Cu in marine pore waters is dominated by organic complexes (Elderfield, 1981; Boulègue *et al.*, 1982; Douglas *et al.*, 1986; Giblin *et al.*, 1986), contrary to the speciation of Cd. This means that formation of Fe oxyhydroxides at pH 4 may decrease the dissolved Cu concentration, but probably not that of Cd. Thus, the dissolved Cu profiles analysed after preconcentration with HMDC-DIPK should be considered with caution (cores Ms1, Mi1, and B1). Since the Co-APDC technique is based on precipitation (instead of complexation), formation of Fe oxyhydroxides at pH 4 does not interfere with the preconcentration of trace metals.

Table 6.1. Comparison of the HMDC-DIPK (1) and Co-APDC (2) preconcentration methods.

Core	Depth cm	Cd-1 nM	Cd-2 nM	Cu-1 nM	Cu-2 nM
Ms1	1.1	9.1	25.8	194	220
Ms1	3.2	19.5	21.4	17	189
Ms1	5.3	13.0	11.6	< 11	138
B1	1.1	23.0	17.8	146	151
B1	5.3	6.6	7.0	39	173
HTZ1	2.1	1.4	1.4	99	42
HTZ1	6.3	0.36	0.18	50	52
HTZ1	10.5	n.a.	0.80	27	57
HTZ1	14.7	0.44	0.27	33	44
HTZ1	23.1	0.36	0.44	11	36

n.a. = not analysed.

Zn was analysed by flame atomic absorption spectroscopy (Perkin-Elmer 430); Cd and Cu by electrothermal atomic absorption spectroscopy (Perkin-Elmer 5000) with Zeeman background correction. Detection limits were 0.18 nM for Cd, 2 nM for Cu, and 15 nM for Zn. Procedural blanks, estimated by passing distilled water through the filtration blocks, were equal to the detection limits for Cd and Zn, but 11 nM for Cu. The analytical reproducibility was within 10% for dissolved Cd (n=3) and within 5% for dissolved Cu (n=2); the reproducibility of the dissolved Zn analyses was not tested.

6.2.3. Surface water and sediment analysis

Surface water was sampled at each coring station as a reference for the pore water composition. Due to the well-mixed nature of the water column, surface water provides a fair measure of the bottom water composition. Water samples, taken from a depth of 0.5-1 m, were ship-board filtered through 0.45 μM filters in an all-teflon filtration block, placed on a clean bench. All materials in contact with trace metal samples were acid-cleaned prior to use. The filtered water samples were handled and analysed according to standard procedures, as described in chapter 2.

Prior to pore water extraction, the sediment sections were subsampled for gravimetric determination of water content. Porosity was calculated from sediment water content, assuming a dry sediment density of 2.5 kg/dm^3 . Squeezed sediment sections were stored at -20 °C and freeze-dried within three days. Sediment samples were analysed for organic carbon (POC) and inorganic carbon, using a Carlo-Erba NA1500 CN analyser. Sediment-bound trace metals were determined as described in Panatrakul and Baeyens (1991). Samples were digested completely in a mixture of HF-HCl-HNO₃; resulting solutions were analysed for Fe, Mn, and Zn by flame AAS, and Cd and Cu by electrothermal AAS. Sediment Al was determined by flame AAS after fusion with LiBO₂ and dissolution in diluted HNO₃. Detailed metal profiles were measured in cores Ms1, Mi1, B1, B2, and HTZ2; the surface layer in cores Ms2 (0-10 cm), Mi2 (0-10 cm) and HTZ1 (0-20 cm) was analysed as a whole. The results were not corrected for the salt content of the sediments, which was always less than 2.6%.

6.3. Results and discussion

6.3.1. Sediment composition and redox potential

Core Ms1 consists of coarse-grained brown sands and shell fragments. Black spots, indicative of the presence of Fe sulphides, are present below 12 cm. The redox potential in core Ms1 decreases sharply across the SWI (Fig. 6.1). Core Ms2 is composed of a coarse-grained brown sandy layer (15 cm) on top of a grey silty layer. The heterogeneous structure of this core probably reflects recent deposition of sand at the coring location, related to the

presence of mobile sand ripples in the lower estuary (Boderie *et al.*, 1993). The high redox potential found in the top layer of core Ms2 (Fig. 6.1) is compatible with its very low POC content (0.03%) and (presumed) recent time of deposition. A sudden drop of the redox potential is observed at the sand/silt interface in core Ms2 (at 15 cm depth), reflecting the difference in POC content between both sediment layers.

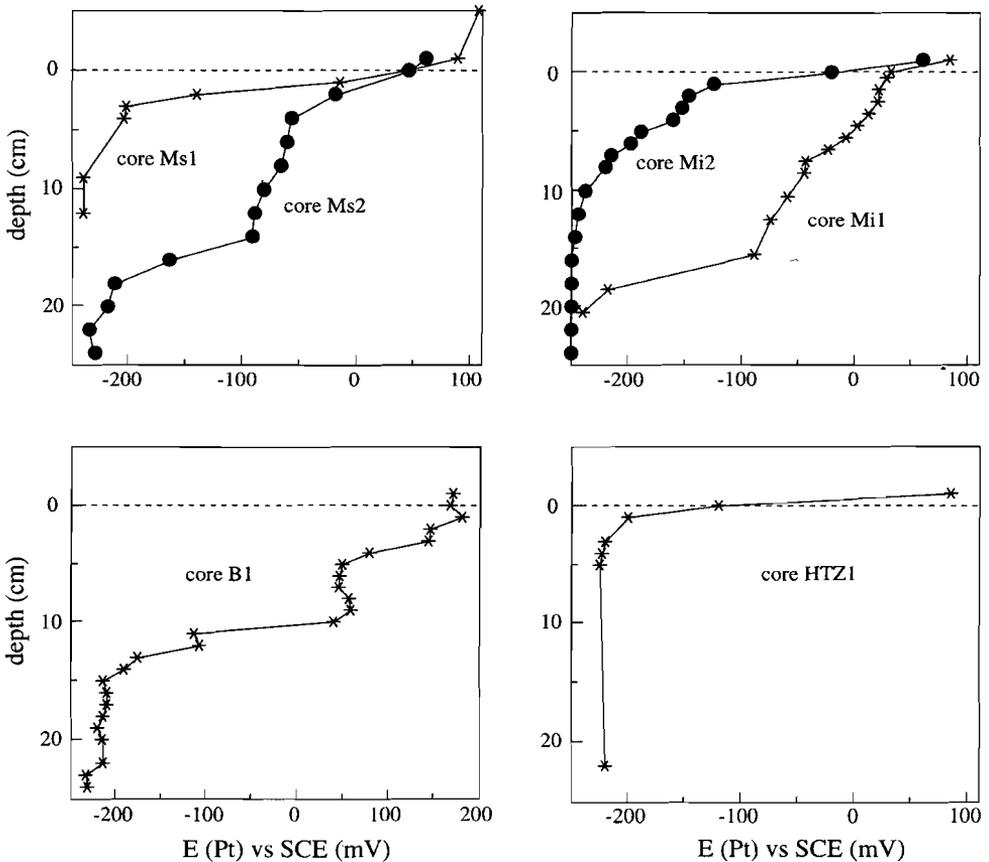


Fig. 6.1. Redox profiles for cores Ms1, Ms2, Mi1, Mi2, B1 and HTZ1, measured by a Pt electrode versus a saturated calomel electrode. No profiles were measured in cores B2 and HTZ2.

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The (intertidal) sediment cores Mi1 and Mi2 appear to be finer-grained than the (subtidal) sediment cores Ms1 and Ms2. This difference in grain-size is reflected by the chemical composition of the sediments (Table 6.2). Core Mi1 is composed of a sandy layer (0-12 cm) on top of a more silty layer (12-16 cm), as reflected by changes in Al and POC contents. The redox potential in core Mi1 (Fig. 6.1) shows a sudden drop near the sand/silt interface, reflecting the difference in POC content of the two sediment layers (similar to core Ms2). Core Mi2 is composed of silty sediments rich in POC. The profound decrease of the redox potential across the SWI (Fig. 6.1) suggests that the surface sediments are reducing, as confirmed by the dissolved Mn and Fe profiles recorded in this core (see section 6.3.3).

Table 6.2. Average composition of the marine subtidal sediments (Ms1 and Ms2) and the marine intertidal sediments (Mi1 and Mi2). The two-layer structure of core Mi1 is also shown.

Core depth (cm)	Ms1	Ms2	Mi1	Mi1	Mi2
n	8	1*	6	2	1*
porosity	0.43 ± 0.04	0.33	0.42 ± 0.05	0.56 ± 0.00	0.59
CaCO ₃ %	4.7*	1.0	13.7*	21.0 ± 1.6	22.6
POC %	0.39 ± 0.12	0.03	0.37 ± 0.14	1.37 ± 0.03	1.07
Al %	0.74 ± 0.10	0.89	1.35 ± 0.22	2.18 ± 0.06	3.10
Fe %	0.84 ± 0.07	0.47	0.70 ± 0.11	1.22 ± 0.07	1.21
Mn µg/g	140 ± 12	46	119 ± 39	227 ± 8	254
Cd µg/g	0.10 ± 0.04	0.04	0.13 ± 0.06	0.50 ± 0.02	0.52
Cu µg/g	5.1 ± 0.9	4.1	5.7 ± 1.4	12.5 ± 0.8	13.8
Zn µg/g	31 ± 6	13	29 ± 11	80 ± 0	76

* mixed sample over the indicated depth (n = 1).

The brackish cores B1 and B2, taken from a tidal sandflat near the Dutch-Belgian border, consist of medium- to fine-grained sands. The top layer of the sediments is inhabited by a great number of macrofauna (e.g. shrimps, worms, bivalves, etc.). The trace metal content of the brackish sediments is similar to that of the silty marine intertidal sediments (Tables 6.2 and 6.3), indicating that the sediment origin is predominantly marine. The sediment colour changes gradually from brown to grey-black in the top 15 cm of the brackish cores, indicative of a gradual transition from oxidised to reduced sediments, as confirmed by the redox profile of core B1 (Fig. 6.1). The high redox potential found in the surficial sediments of core B1 may be due to microphytobenthos production (De Jong and De Jonge, 1995) or bioturbation. No redox profile was measured in core B2, but pore water profiles of Mn and Fe indicate that similar redox conditions exist in this core (see section 6.3.3).

Table 6.3. Average composition of the brackish intertidal sediments (B1 and B2) and the low-salinity sediments from the high-turbidity zone (HTZ1 and HTZ2).

Core		B1	B2	HTZ1	HTZ2
Depth (cm)		0-20	0-20	0-20	0-20
n		10	10	1*	10
porosity		0.46 ± 0.03	0.46 ± 0.04	0.70	0.77 ± 0.03
CaCO ₃	%	n.a.	6.7*	11.6	10.3*
POC	%	n.a.	0.68*	1.84	3.31*
Al	%	1.65 ± 0.20	2.10 ± 0.15	4.42	3.49 ± 0.45
Fe	%	1.53 ± 0.10	1.75 ± 0.13	4.22	3.12 ± 0.32
Mn	µg/g	281 ± 58	255 ± 100	938	497 ± 93
Cd	µg/g	0.79 ± 0.08	0.64 ± 0.18	13.6	5.5 ± 1.2
Cu	µg/g	12.4 ± 1.0	10.1 ± 1.4	79	67 ± 13
Zn	µg/g	83 ± 6	77 ± 12	336	406 ± 79

* mixed sample over the indicated depth (n = 1); n.a. = not analysed.

The bottom sediments in the high-turbidity zone consist of grey to black silty muds, exclusively inhabited by polychaetes. The chemical composition of these sediments is quite different from that of the brackish and marine sediments (Table 6.3), due to differences in grain-size and sediment origin. The predominantly fluvial origin of the sediments and their high clay content explain the high ambient trace metal levels (see chapter 4). In core HTZ1, a dramatic drop of the redox potential across the SWI is observed (Fig. 6.1). Reducing conditions are already present on top of the sediments, due to the absence of oxygen in the overlying water column. Similar redox conditions are anticipated in core HTZ2 (not measured), based on pore water profiles of sulphate and Fe (see section 6.3.3.).

6.3.2. Major ion and nutrient geochemistry

The composition of the pore waters is shown in Appendix A. Mean pore water salinities in the top 10 cm of the marine sediment cores vary from 26 to 29. The major ion chemistry of the marine pore waters is similar to that of coastal seawater. Compared to the overlying sea water, the pore waters are enriched in DIC, DOC, orthophosphate, ammonium and silicate, but depleted in nitrate, reflecting organic matter decomposition and opal dissolution (e.g. diatom skeletons). The low nutrient concentrations in core Ms2 are compatible with the low POC content of these sediments (0.03%) and their recent time of deposition. The high concentration of phosphate in the surficial pore waters of core Mi2 is probably related to release from dissolving Fe oxyhydroxides, as commonly observed in suboxic sediments (e.g. Aller, 1980; Berner, 1980). The pH is constant (7.9-8.0, n=5) in the top 10 cm of cores Ms1 and Mi1. A slightly lower pH was measured in the top 5 cm of core Ms2 (7.7-7.8, n = 2) and core Mi2 (7.55, n = 1).

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Mean pore water salinities in the top 10 cm of the brackish sediments are 11 (core B1) and 16 (core B2), comparable to the water column salinity. The high nitrate/ammonium ratio in the surficial pore waters of core B1 can be explained by the coupling of ammonification and nitrification in the surface sediments (Boderie *et al.*, 1993). The pH decreases from 8.0 (April) or 8.4 (June; primary production) in the water column to 7.2 below the SWI. With increasing depth in the sediments, the pH stabilises at a value of 7.1 in the brackish cores.

Mean pore water salinities in the top 10 cm of the low-salinity sediments are 1.9 (HTZ1) and 5.0 (HTZ2). Compared to the water column composition, the pore waters are enriched in Ca but depleted in sulphate. The increase in dissolved Ca with increasing depth, which is a typical feature of low-salinity sediments (Paalman, 1997; Van den Berg, 1998), probably reflects carbonate dissolution by CO₂, produced in the methanogenic zone of the sediments. The nutrient concentrations in the pore waters of the HTZ cores are extremely high, in keeping with the high POC content of the sediments. The pH decreases from 7.7 in the water column to 7.1 below the SWI of core HTZ1, then increases slightly with increasing depth to 7.35. In core HTZ2 the pH was not measured.

6.3.3. Redox element and trace metal geochemistry

As stated before, mobilisation of trace metals in surficial sediments is related to decomposition of organic matter, oxidation of metal sulphides, and reductive dissolution of Mn and Fe oxyhydroxides. Deeper in the sediments, trace metals can be precipitated as sulphides. The trace metal profiles shown in this section will therefore be discussed in relation to the intensity of organic matter decomposition (reflected by profiles of ammonium and DOC) and the position of the redox zones in the sediments (reflected by profiles of Mn, Fe, sulphate, and Ba). The discussion will primarily focus on the shape of the dissolved metal profiles, rather than on absolute concentration levels.

Coastal marine pore waters

The pore water profiles of the marine subtidal sediments (Ms) are shown in Fig. 6.2 and the profiles of the marine intertidal sediments (Mi) in Fig. 6.3. The atomic sulphate/sodium ratios are close to the seawater value of 0.060 and remain constant with increasing depth in all the cores, suggesting that sulphate reduction is unimportant at the depths considered here. Nitrate is rapidly exhausted in the near-surface pore waters of cores Ms1, Mi1 and Mi2 (Appendix A). In core Ms2, which is much lower in POC, nitrate is consumed to a smaller extent. Consequently, the dissolved Mn concentrations are low in core Ms2, and dissolved Fe is not detected. Reduction of Mn- and, to a lesser extent, of Fe oxyhydroxides is more important in core Ms1, which is richer in POC (0.39%) than core Ms2 (0.03%). Based on the gradients below the SWI, significant release of Mn (but not of Fe) to the overlying water column may occur in core Ms1, although reprecipitation at the SWI cannot be excluded (given

a sampling resolution of 2.1 cm). However, it is well known that reoxidation is less efficient in trapping Mn than it is for Fe, due to kinetic constraints (Froelich *et al.*, 1979; Santschi *et al.*, 1990).

Core Mi1 shows an obvious relation between POC content and the intensity of Mn and Fe reduction. Low dissolved Mn and Fe concentrations are observed in the sandy top layer of this core (0.37% POC), suddenly increasing to very high concentrations in the silty bottom layer below 12 cm (1.37% POC). The gradients across the SWI suggest that the sediments in core Mi1 may act as a source of Mn to the water column. Core Mi2 shows high concentrations of dissolved Mn and Fe at the SWI, in agreement with the high POC content of the surface sediments (1.07%). The steep gradients observed across the SWI (within a sampling resolution of 1 cm) suggests that release of dissolved Mn, and perhaps also Fe, to the water column may be important in this core. Similar outflow of dissolved Fe and Mn has been reported by Dehairs *et al.* (1989) for sediments in the Belgian coastal zone. The decrease in dissolved Mn observed below the surface maximum in core Mi2 may be due to formation of carbonates (e.g. Berner, 1980). However, solubility calculations with MINTEQA2 (USEPA, 1991) indicate that the pore waters in core Mi2 are slightly undersaturated with respect to rhodochrosite (MnCO_3). Presumably, a less crystalline Mn carbonate phase is being formed.

In general, the trace metal profiles may show two zones of metal release. Maxima of dissolved Cd and Cu are present at the SWI of the cores Ms1, Mi1, and Mi2 (also for Zn). These high peaks probably originate from oxidation of labile organic material, as suggested previously by Baeyens *et al.* (1986). Complexation with DOC, produced rapidly near the interface (see DOC profiles in Figs. 6.2 and 6.3), may stabilise these high dissolved trace metal concentrations. The role of DOC in enhancing the solubility of trace metals in pore waters is well established for Cu (see section 6.2.2.), but may also be significant for Zn (Van den Berg and Dharmvanij, 1984). Peaks of Cd and Cu are also observed in the suboxic zone of core Mi1 (below 12 cm), probably reflecting release from dissolving Mn and Fe oxyhydroxides. The gradual increase in dissolved Cu and Zn below the near-surface maximum in core Mi2 can be explained by progressive reduction of Fe oxyhydroxides deeper in the sediments.

Core Ms2 shows exceptional profiles in that concentrations of dissolved Cd and Cu increase continuously with increasing depth, although there is no Fe reduction and only little Mn reduction with increasing depth in this core. The low Cd and Cu concentrations in the surficial pore waters are compatible with the low diagenetic activity in the surface sediments of core Ms2, reflected by the low nutrient concentrations in the pore waters. Decomposition of organic matter is probably more important in the silty sediment layer of this core (below 15 cm depth). The increase in dissolved Cd and Cu with increasing depth may well be explained by production in the silty sediment layer (during decomposition of organic matter) and diffusion into the sandy top layer. The profile of dissolved Zn is clearly different from those of Cd and Cu and cannot be explained by this mechanism, however.

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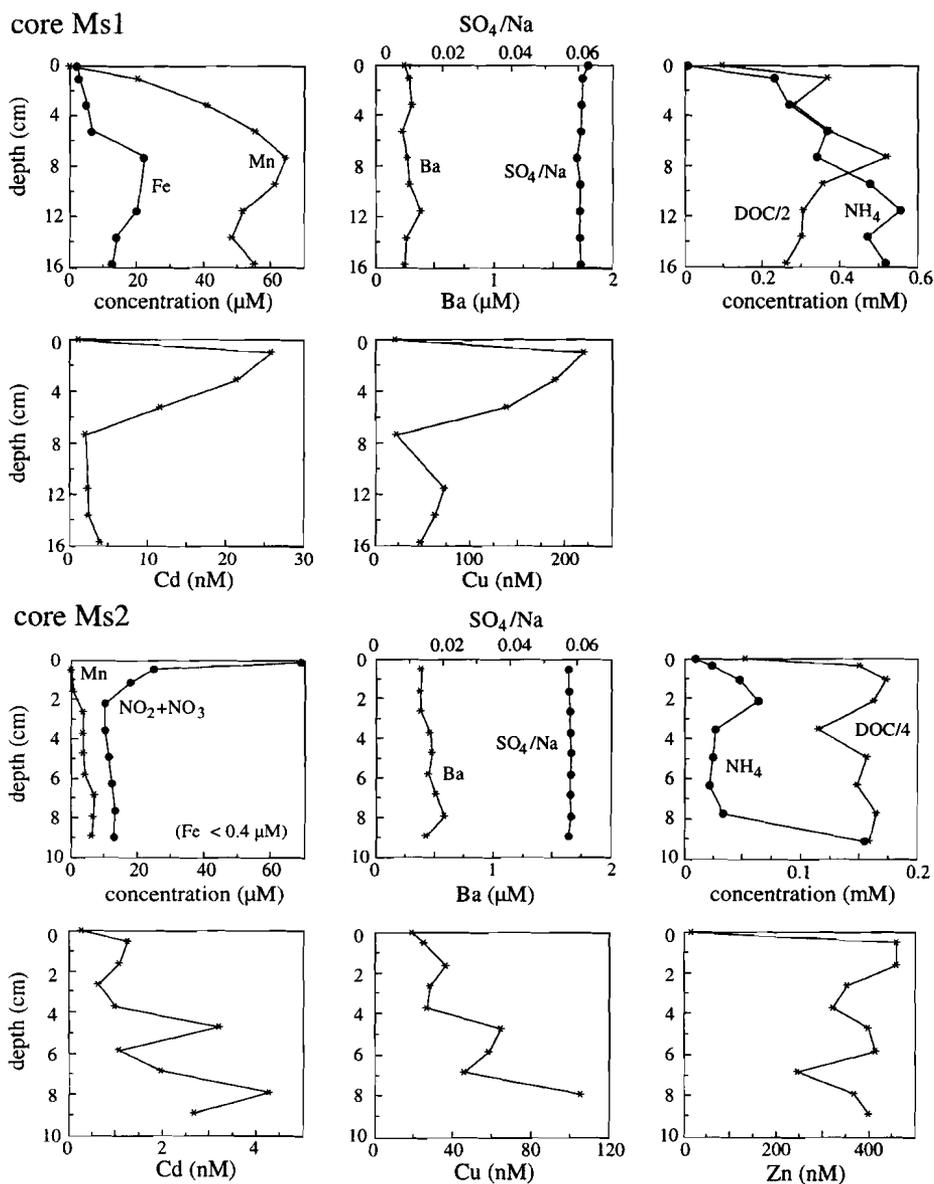


Fig. 6.2. Pore water profiles for the marine subtidal sediments (note the different depth scales). Surface water concentrations are indicated at 0 cm depth. Trace metals were preconcentrated with the Co-APDC method in core Ms2. For core Ms1, the HMDC-DIPK method was used, except the near-surface samples (1-5 cm) for which the Co-APDC data were used (see Table 6.1).

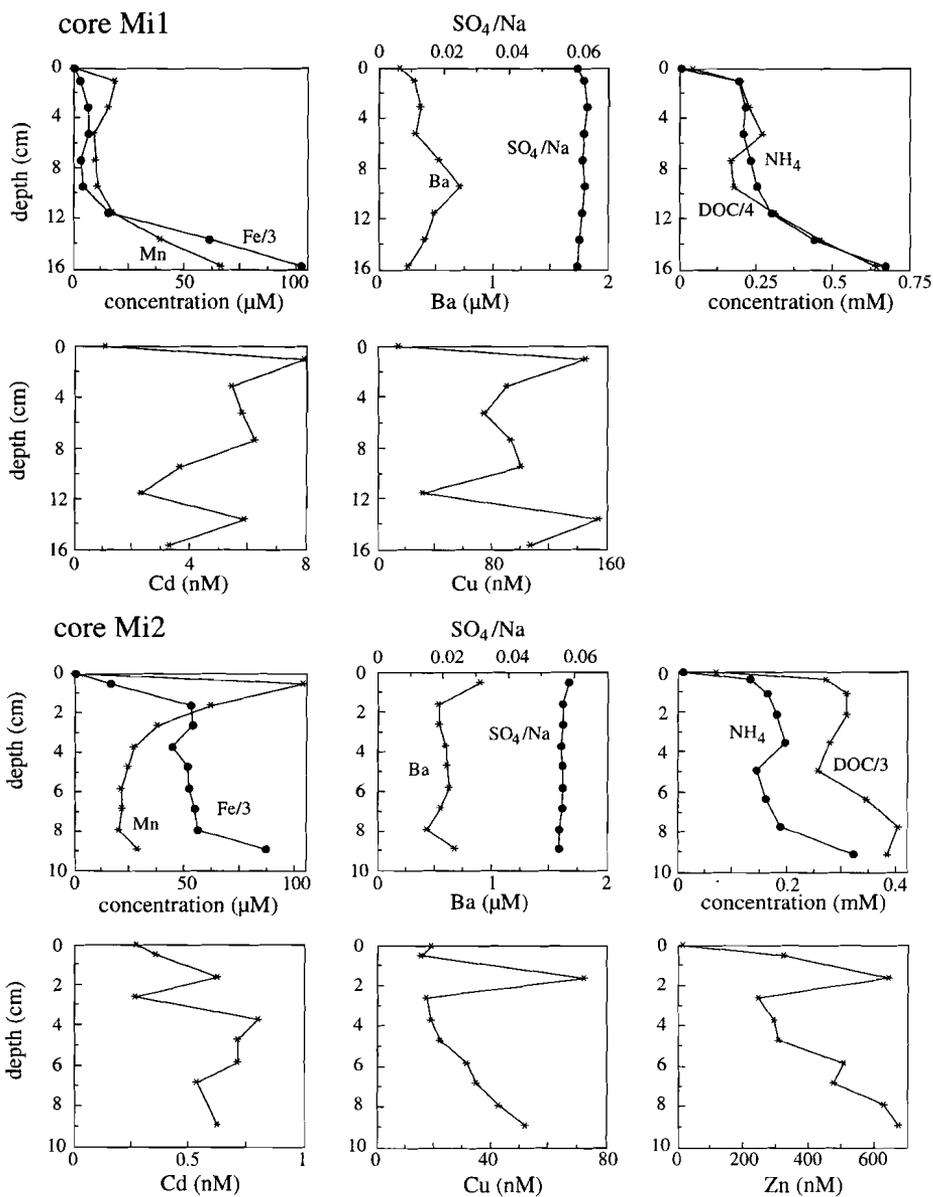


Fig. 6.3. Pore water profiles for the marine intertidal sediments (note the different depth scales). Surface water concentrations are indicated at 0 cm depth. Trace metals were preconcentrated with HMDC-DIPK in core Mi1 and Co-APDC in core Mi2.

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Brackish pore waters

The brackish pore water profiles (Fig. 6.4) reflect the well-known sequence of redox reactions discussed extensively in the literature (e.g. Froelich *et al.*, 1979; Santschi *et al.*, 1990; Shaw *et al.*, 1990). With increasing depth, sequential reduction of nitrate (only measured in core B1), Mn and Fe oxyhydroxides, and sulphate is apparent. Sulphate reduction in core B1 is reflected by the decrease in the sulphate/sodium ratio below 8 cm depth and the decline in dissolved Fe below 10 cm depth, suggesting formation of Fe sulphides. The increase in dissolved Ba with increasing depth, which is probably due to dissolution of barite, is also indicative of sulphate reduction (Brumsack and Gieskes, 1983; Van den Berg, 1998). In core B2, sulphate reduction is indicated by the sudden decrease of dissolved Fe below 8 cm depth, and the increase in dissolved Ba with increasing depth. The dissolved Mn and Fe profiles indicate that complete reprecipitation of Mn and Fe oxyhydroxides occurs below the SWI in both cores, in agreement with the oxic nature of the surficial pore waters (note the high nitrate concentrations in the top 2 cm in core B1).

The trace metal profiles show two zones of dissolved metal release. Peaks of Cd, Cu, and Zn are observed close to the SWI, related to oxidation of labile organic matter and possibly of metal sulphides, bioturbated to the surface or transported downstream from the upper estuary (see chapter 2). The high trace metal concentrations in the surficial pore waters may be stabilised by complexation with DOC and by the pH drop across the SWI (0.8-1.2 units), limiting re-adsorption onto Mn and Fe oxyhydroxides (e.g. Tessier *et al.*, 1985; 1989). Enrichment of dissolved Cu and Zn (but not of Cd) is also found in the suboxic zone of both cores (depth 3-8 cm), which is attributed to release from dissolving Mn and Fe oxyhydroxides. In the sulphate reduction zone, well-developed in core B1 only (below 8 cm depth), the dissolved Cd and Cu concentrations are much lower than in the oxic and suboxic pore waters, reflecting the impact of metal sulphide precipitation.

Low-salinity pore waters

The pore water profiles for the low-salinity sediments (the HTZ cores) are shown in Fig. 6.5. The sulphate profiles indicate the presence of a highly reducing environment, established already in the surficial pore waters. The pore waters can be regarded as sulphidic in the top 5 cm and methanogenic at greater depth. The high dissolved Mn and Fe concentrations observed in the methanogenic zone of the sediments are typical of fluvial pore waters (e.g. Paalman, 1997; Van den Berg, 1998). The dissolved Fe and Mn profiles suggest that trapping at the SWI is either incomplete or absent, which is related to the absence of oxygen in the overlying water column (Baeyens *et al.*, 1986; Sundby *et al.*, 1986). The sediments in the low-salinity zone will therefore act as a source of dissolved Fe and Mn to the water column, as suggested previously by Duinker *et al.* (1979) and Zwolsman (1994).

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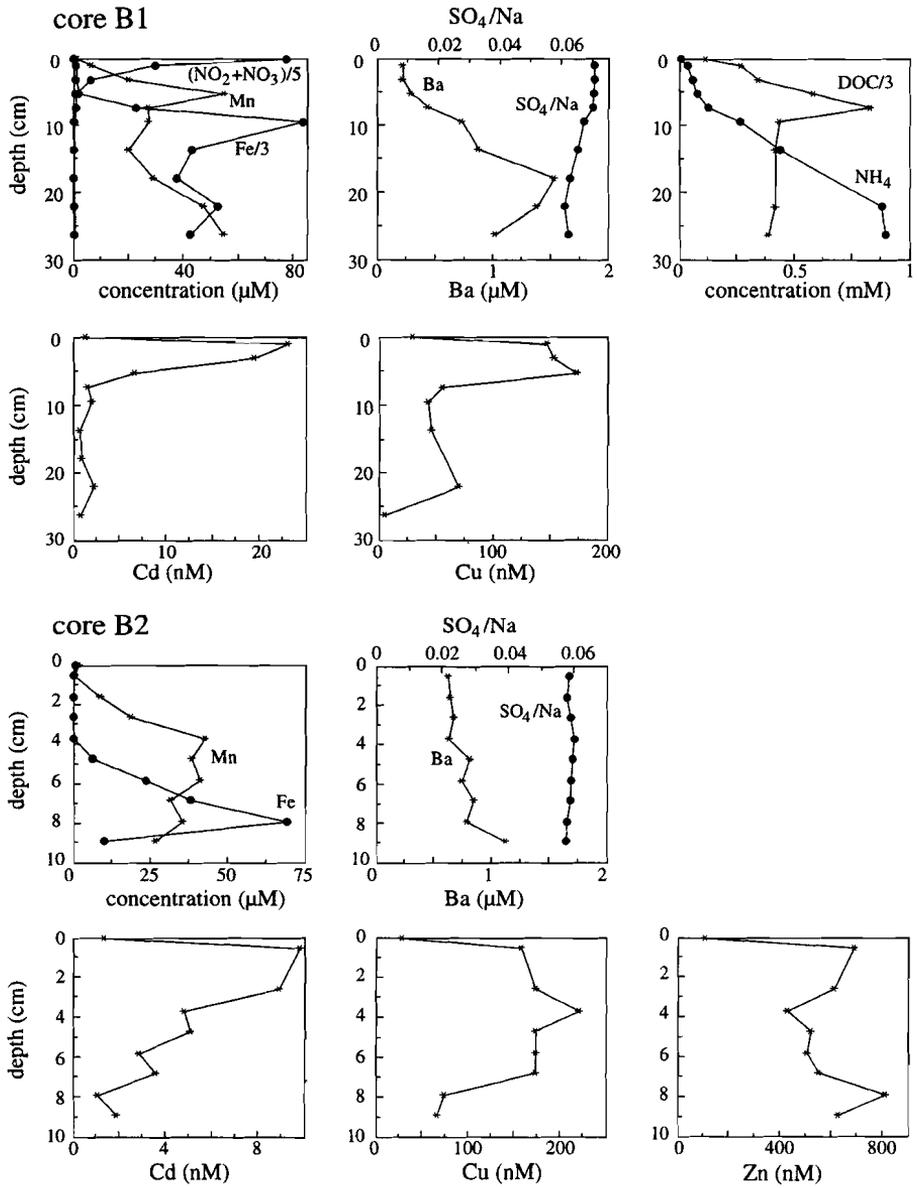


Fig. 6.4. Pore water profiles for the brackish intertidal sediments (note the different depth scales). Surface water concentrations are indicated at 0 cm depth. Trace metals were preconcentrated with HMDC-DIPK in core B1 and Co-APDC in core B2.

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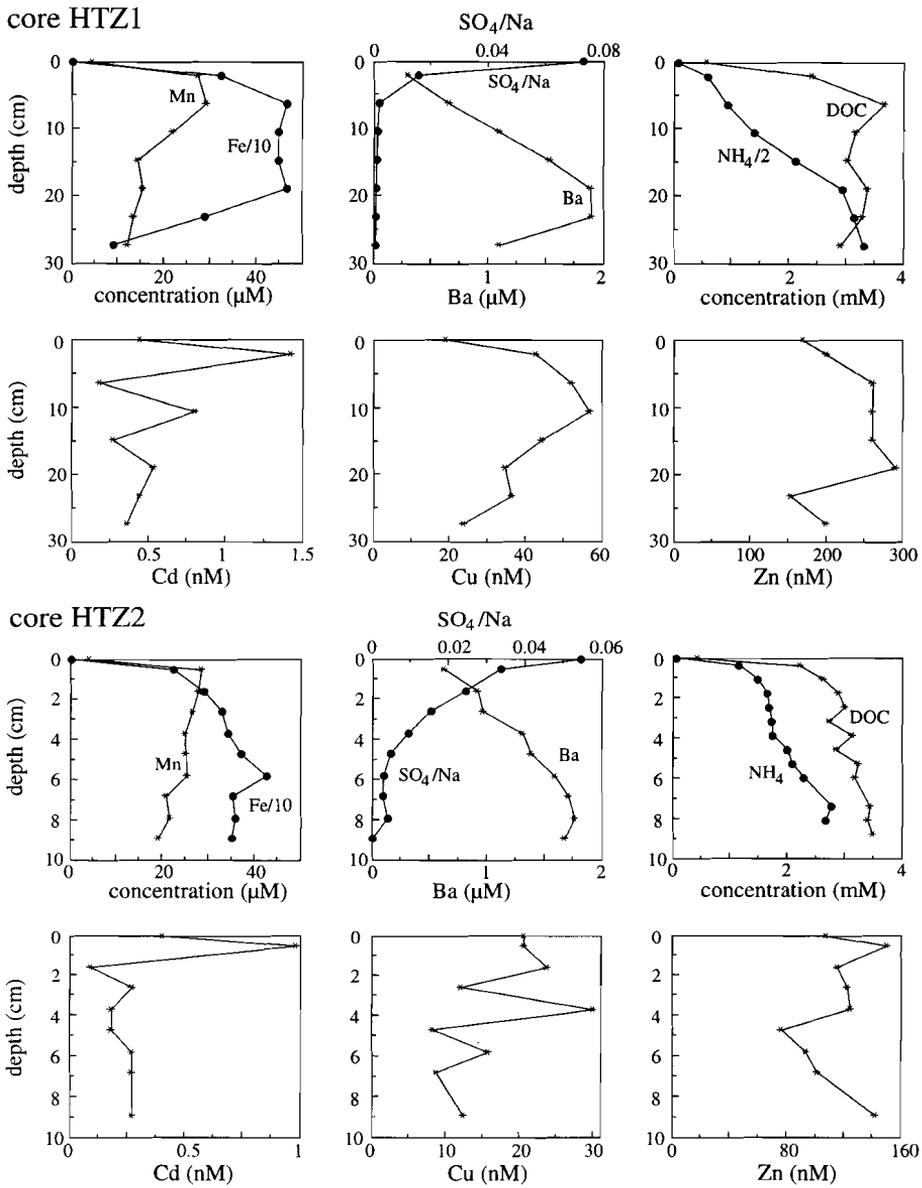


Fig. 6.5. Pore water profiles for the low-salinity sediments (note the different depth scales). Surface water concentrations are indicated at 0 cm depth. Trace metals were preconcentrated with Co-APDC in both cores.

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The pore water profiles of trace metals in the low-salinity sediments are difficult to interpret. The dissolved Cd profiles reflect production at the SWI and removal in the sulphate reduction zone. The profiles of dissolved Cu and Zn are more erratic. However, the dissolved metal concentrations encountered in the HTZ pore waters are similar to those measured in pore waters of comparable systems. In a low-salinity core of the Rhine estuary (salinity 3-5), dissolved metal concentrations in the methanogenic zone (below 3 cm depth) were found to be 35-45 nM for Cu and 130-370 nM for Zn (Paalman, 1997). In Lake Ketelmeer, a sedimentation basin of the river Rhine, the dissolved metal concentrations in the methanogenic pore waters (below 5 cm depth) ranged from 0.2 to 1.6 nM for Cd, 10 to 70 nM for Cu, and 60 to 400 nM for Zn (Paalman, 1997). Since the metal concentrations in the HTZ pore waters are of similar magnitude (Fig. 6.5), we believe that these concentrations are realistic.

Solubility calculations with MINTEQA2 were performed for core HTZ2, in order to investigate the possible formation of authigenic minerals. The results, presented as saturation index for mineral formation ($\log IAP/K_{sp}$), are shown in Fig. 6.6.

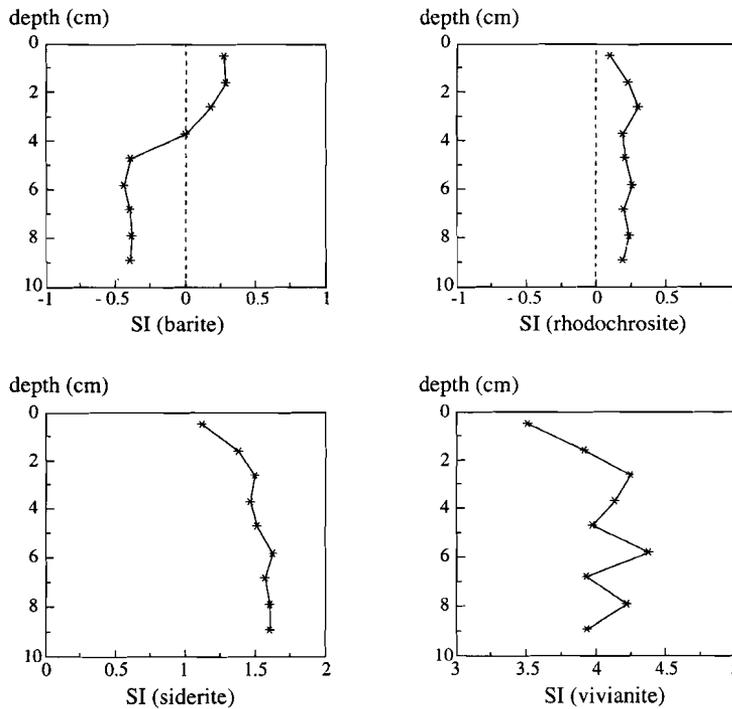


Fig. 6.6. Saturation indices ($\log IAP/K_{sp}$) for mineral formation in the pore waters of core HTZ2, calculated with MINTEQA2 (USEPA, 1991).

The saturation index for barite (BaSO_4) decreases from slightly positive values (supersaturation) in the top 3 cm of the sediments to slightly negative values underneath (undersaturation). The increase in dissolved Ba with increasing depth, observed in the HTZ cores (Fig. 6.5), is thus probably due to dissolution of barite. The dissolved Mn concentrations appear to be in equilibrium with rhodochrosite (MnCO_3) at all depths; the slightly positive saturation index may be explained by the uncertainty in the stability constant for mineral formation. The pore waters are well supersaturated with respect to siderite (FeCO_3) and highly supersaturated with respect to vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$) at all depths. This high degree of supersaturation, commonly observed in reducing pore waters, can be attributed to the slow precipitation kinetics of authigenic Fe minerals (Emerson and Widmer, 1978; Berner, 1980).

Solubility calculations for metal sulphides were performed as well. Although the dissolved sulphide concentration was not measured in the HTZ cores, its value can be estimated by assuming that dissolved Fe is in equilibrium with (amorphous) FeS. This assumption is reasonable, because of the presence of Fe sulphides in the sediments (as indicated by their grey to black colour). The solubility product for amorphous FeS was taken from Davison (1991). The average dissolved Fe concentration of the pore waters in core HTZ2 is 0.34 mM, and the pore water pH is estimated at 7.1, a value typical of sulphidic to methanogenic pore waters (measured indeed in the surficial sediments of core HTZ1). The corresponding dissolved HS^- concentration is 0.26 μM ; a reasonable value for freshwater sediments (Wallmann *et al.*, 1996). Average dissolved trace metal concentrations were used for core HTZ2, excluding the near-surface pore waters. Complexation of Cu and Zn by organic ligands was taken into account as follows. Concentrations of complexing ligands (C_L) and conditional stability constants (K_{st}) were taken from Van den Berg *et al.* (1987). Based on their five most upstream sampling stations in the Scheldt estuary (surface water), the following values were selected: $C_L = 168$ nM for Cu and 138 nM for Zn, and $\log K_{st} = 12.2$ to 13.4 for Cu and 9.6 to 10.6 for Zn. The complexing ligand concentration in the pore waters is probably higher, however, because pore water DOC in core HTZ2 is, on the average, seven times higher than the DOC concentration in the water column. Assuming a linear relationship between DOC and ligand concentrations, the concentration of complexing ligands in the pore waters was estimated at 1.2 μM for Cu and 1.0 μM for Zn. These estimated concentrations of complexing ligands are comparable to measured values of complexing capacity for Cu and Zn in estuarine and marine pore waters, which often exceed 1 μM (Van den Berg and Dharmvanij, 1984; Boussemart *et al.*, 1989). The results of the solubility calculations are presented in Table 6.4.

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Table 6.4. Saturation index ($\log IAP/K_{sp}$) for metal sulphide formation in core HTZ2, calculated with MINTEQ-A2. The HS^- concentration used was $0.26 \mu M$. Organic complexation was taken into account for Cu and Zn (see text).

	C (nM)	$\log K_{st}$	C_L (μM)	mineral	saturation index
Cd	0.22	-	-	greenockite	3.34
Cu	16	12.2 - 13.4	1.2	covellite	8.37 to 9.57
Zn	110	9.6 - 10.6	1.0	sphalerite	0.39 to 1.38
Zn	110	9.6 - 10.6	1.0	amorphous ZnS	-1.27 to -2.26

K_{st} = stability constant for organic complexation; C_L = complexing ligand concentration

According to Table 6.4, the pore waters in core HTZ2 are supersaturated with respect to pure metal sulphides, except for amorphous ZnS. Supersaturation is most extreme for CuS, as frequently observed in reducing pore waters (Boulègue *et al.*, 1982; Giblin *et al.*, 1986; Paalman, 1997). This apparent supersaturation may be related to underestimation of the degree of organic complexation, as both the stability constant (K_{st}) and the concentration of Cu-complexing ligands (C_L) had to be estimated. It is possible that pore water ligands form even more stable complexes with Cu than surface water ligands, due to the presence of organo-sulphur compounds (e.g. thiols) with a very high affinity for trace metal binding (Boulègue *et al.*, 1982; Shea and MacCrehan, 1988). Moreover, in Fe-dominated systems (as is the case for the HTZ cores), it has been proposed that trace metals are adsorbed, rather than precipitated, onto Fe sulphides (Cooper and Morse, 1998). Finally, the degree of crystallinity of sulphide minerals being formed is questionable, and so are the solubility products (as shown for ZnS in Table 6.4). Thus, the apparent supersaturation with respect to pure metal sulphides does not rule out the possibility that metal sulphides are being formed. In fact, it is reasonable to assume that formation of metal sulphides does occur, given the high contents of acid-volatile sulphide in the sediments from the HTZ ($20 \pm 1 \mu mol/g$), exceeding the simultaneously extracted metal fraction by a factor of two to three (Kerdijk *et al.*, 1993). According to Di Toro *et al.* (1992), this would imply that Cd, Cu, and Zn (and other trace metals) will be precipitated as sulphides.

6.3.4. Dissolved trace metal maxima at the sediment-water interface

The concentrations of dissolved Cd, Cu, and Zn in the near-surface pore waters (0-2 cm depth) of the eight cores studied are shown in Fig. 6.7. The dissolved metal concentrations in the surficial pore waters range from 0.5-26 nM for Cd, 22-220 nM for Cu, and 130-690 nM for Zn. From Fig. 6.7 and Tables 6.2-3, it is obvious that there is no relation between sediment trace metal content and the metal concentration in the pore waters. For example, the lowest concentrations of dissolved Cd, Cu, and Zn are present in the pore waters of the HTZ cores, which have the highest solid-phase metal contents (see Table 6.3). Also, the pore water concentrations are not related to salinity, contrary to the dissolved metal concentrations in the

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water column (see chapter 2). The highest concentrations of Cd and Cu are found in the surficial pore waters of cores Ms1, B1 and B2, i.e. in mildly oxidising surface sediments (absence of Fe reduction). The lowest dissolved metal concentrations are observed if the surficial pore waters are reducing (cores Mi2, HTZ1, and HTZ2). These observations indicate that the redox status of the surficial sediments controls the pore water trace metal concentrations. The only exception to this general rule is core Ms2, which shows no Fe or Mn reduction near the SWI but has very low trace metal concentrations in the surficial pore waters. This can be explained by the extraordinary low organic matter content of these sediments (0.03 % POC) and their recent time of deposition.

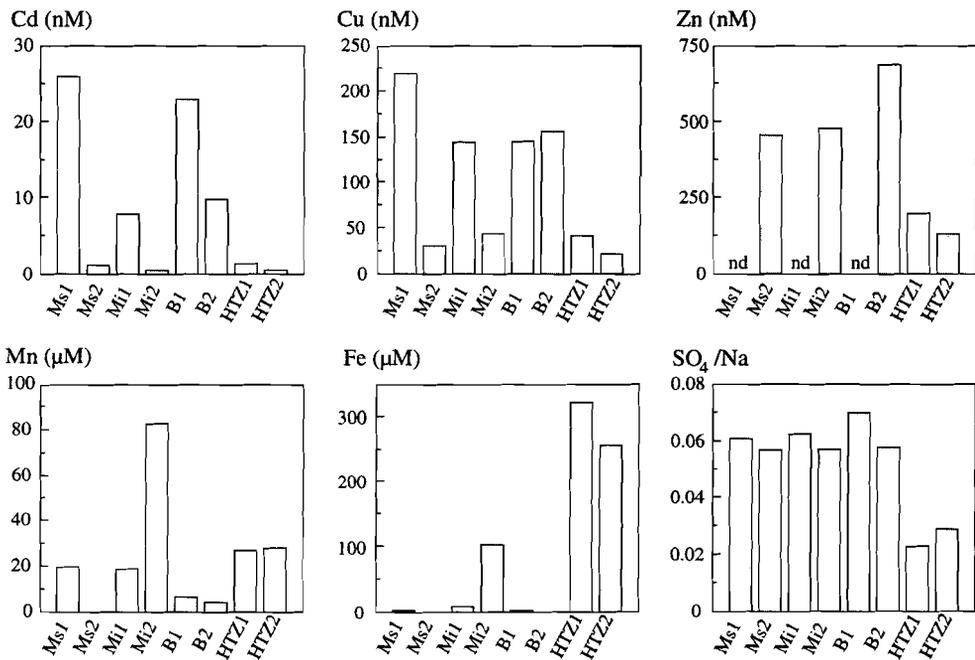


Fig. 6.7. Pore water composition of the surficial sediments of the marine, brackish, and low-salinity cores (depth 0-2 cm, except core HTZ1: 0-4 cm). nd = no data available.

The low trace metal concentrations in the near-surface pore waters of the HTZ cores can be explained by the occurrence of sulphate reduction near the SWI. Using a simple steady-state advection-diffusion model, with (sub)oxic respiration in the surface sediments and sulphate reduction underneath, Paalman (1997) has demonstrated that the intensity of the dissolved Cd peak near the SWI depends on the thickness of the (sub)oxic sediment layer. The more production of dissolved Cd (through organic matter decomposition) and removal (through sulphide precipitation) are separated in depth, the higher the dissolved Cd peak at the SWI will be. The reason for this is that the loss of Cd to the sulphate reduction zone depends on the rate of diffusion, hence on the distance between the Cd production and removal zones. Similar reasoning applies to the Cu and Zn maxima at the SWI. The low dissolved trace metal concentrations at the SWI of core Mi2 must have another reason, since sulphate reduction does not occur in these pore waters. Scavenging of Cd, Cu, and Zn, liberated during organic matter decomposition, by in situ produced Fe oxyhydroxides may be responsible for this (e.g. Tessier *et al.*, 1985; Santschi *et al.*, 1990). The dissolved Fe profile of core Mi2 shows a decline of the dissolved Fe concentration in the top 2 cm of the sediments, due to precipitation of Fe oxyhydroxides, diffusion to the water column, or both (see Fig. 6.3). Unfortunately, no vertical profile of solid-phase Fe is available to confirm the possible precipitation of Fe oxyhydroxides at the SWI in this core.

6.3.5. Post-depositional mobility of Cd, Cu, and Zn

It is well known that diagenetic processes can change the distribution of trace metals in sediments, both in freshwater and in marine environments (e.g. Gobeil *et al.*, 1987; McKee *et al.*, 1989; Shaw *et al.*, 1990; Wallmann *et al.*, 1996). Regressions between trace metal composition and Al can be used in order to quantify the impact of diagenetic modifications on the initial metal distribution in the sediments (Skowronek *et al.*, 1994). In three of the five cores which have been analysed in detail, a fair linear relationship between sediment Al and trace metal content is apparent (Ms1, Mi1, and HTZ2; see Fig. 6.8), reflecting the joint presence of trace metals and Al in the clay fraction of the sediments (e.g. Windom *et al.*, 1989^b). This means that variations in the solid-phase trace metal composition with depth are primarily related to grain-size, hence diagenetic modifications are relatively small. For the marine sediments, this can be explained by their recent time of deposition. The absence of major diagenetic impacts on the trace metal distribution in core HTZ2 is related to the occurrence of sulphate reduction near the SWI, leading to scavenging of trace metals, mobilised by organic matter decomposition, as sulphides. In this way, the original trace metal distribution is preserved in the HTZ sediments.

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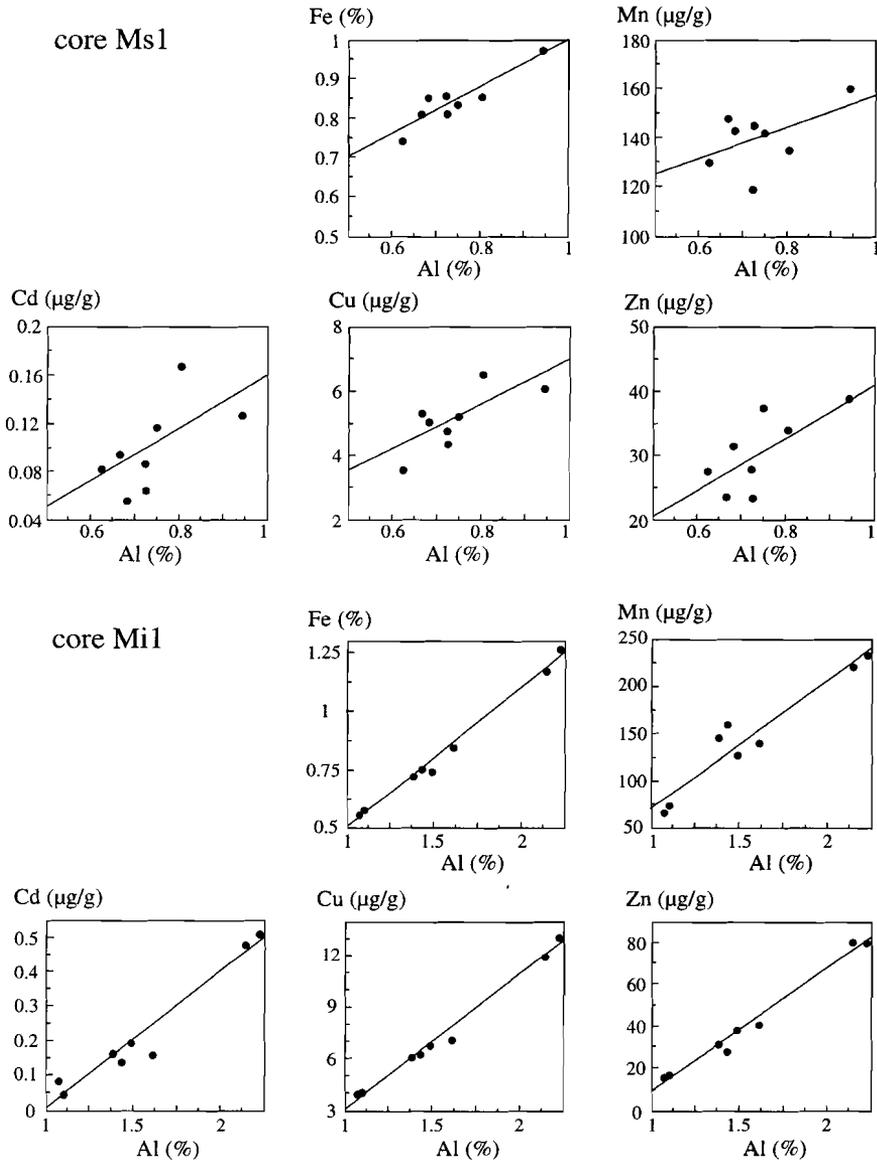


Fig. 6.8a. Solid-phase metal-Al relationships in core Ms1 and Mi1 (depth 0-16 cm).

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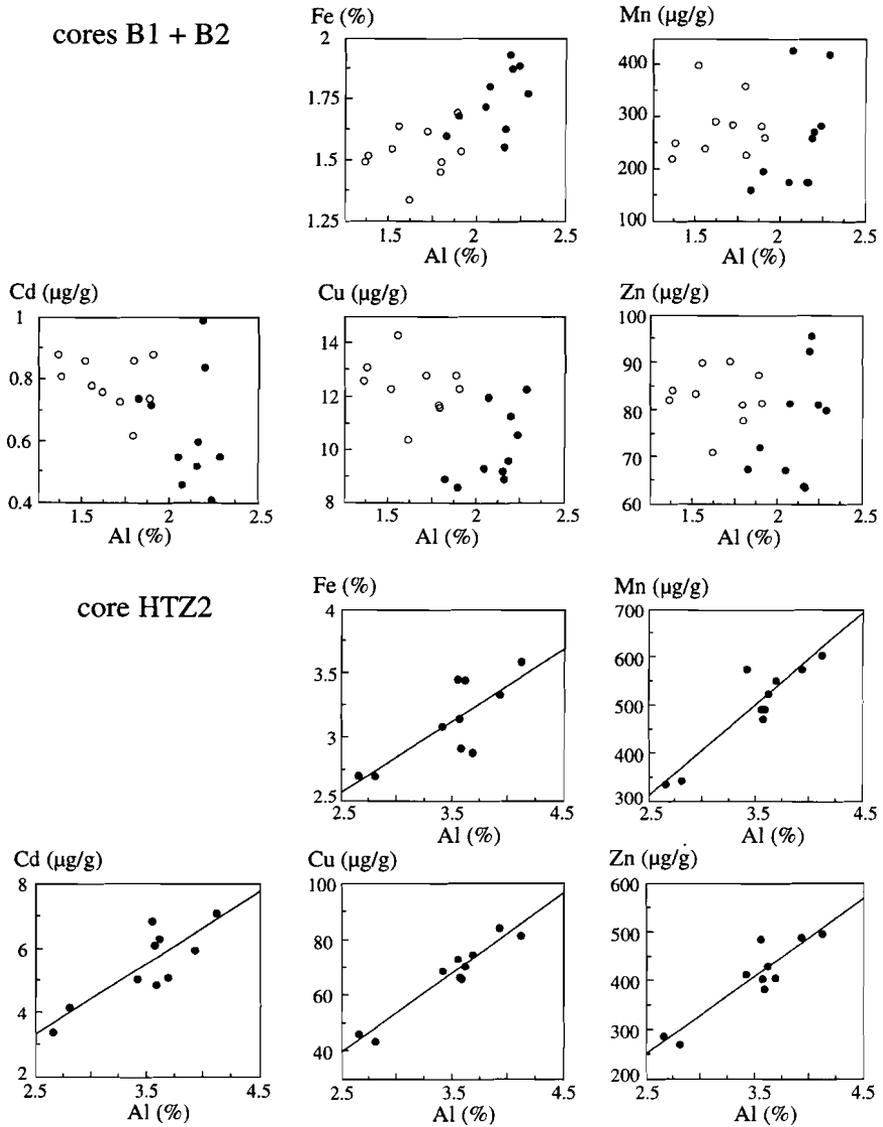
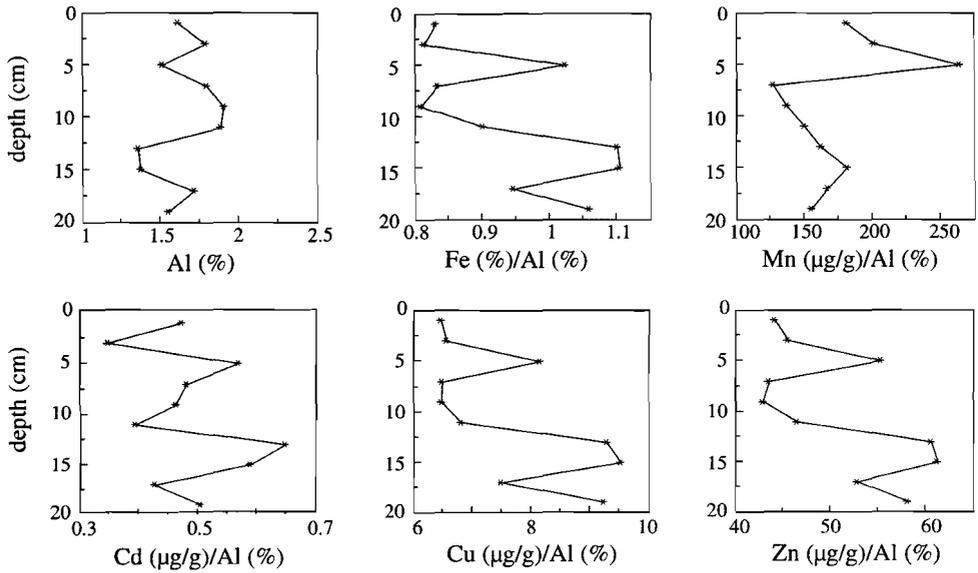


Fig. 6.8b. Solid-phase metal-Al relationships in core B1 (o), B2 (•), and HTZ2 (depth 0-20 cm).

In the brackish sediment cores (B1 and B2), no relationship exists between solid-phase Al and trace metal contents (Fig. 6.8), indicating major impact of diagenetic processes. The solid-phase metal profiles, normalised on Al, are shown in Fig. 6.9. Normalisation on Al is essential in order to correct for grain-size effects. The near-surface maxima of solid-phase Mn and Fe in core B1 (at 5 cm depth) and core B2 (at 3 cm depth) are obvious diagenetic fingerprints. These peaks are due to oxidative precipitation of dissolved Mn and Fe, produced in the Mn and Fe reduction zones underneath. The minima in solid-phase Fe and Mn, occurring at a depth of 9 cm (Fe) or 7-9 cm (Mn), reflect reductive dissolution of Mn and Fe oxyhydroxides. Indeed, the pore water profiles indicate a source of dissolved Fe at 8-9 cm depth (Fig. 6.4). The dissolved and solid-phase Mn profiles are compatible for core B2 (Figs. 6.4 and 6.9), with particulate Mn peaking 1 cm above the dissolved Mn maximum, suggesting reoxidation of dissolved Mn. In core B1, however, the dissolved and particulate Mn maxima coincide (at 5 cm depth), which may be explained by insufficient sampling resolution (2-cm intervals), or by a recent shift of the redox boundaries in the sediments (Gobeil *et al.*, 1987; Shaw *et al.*, 1990). Diagenetic enrichment of solid-phase Fe and, to a lesser extent, Mn is also observed in the sulphate reduction zone of the sediments (below 10 cm), which can be attributed to precipitation of Fe sulphides and (Ca)-Mn carbonates (Berner, 1980; Elderfield *et al.*, 1981; Gaillard *et al.*, 1989).

The solid-phase profiles of Cu and Zn peak in the zone of diagenetic Fe and Mn enrichment. These results suggest that Cu and Zn, mobilised at the SWI, are (partly) readsorbed by Fe and Mn oxyhydroxides. At greater depth, where these host phases are destroyed, Cu and Zn are released to the pore waters, as suggested by the minima in solid-phase Cu and Zn at 7-9 cm depth (B1) or 9-11 cm depth (B2). The sudden increase in solid-phase Cu and Zn below 11 cm depth is probably caused by metal sulphide precipitation. The pore water profiles of dissolved Cu and Zn are consistent with this explanation (Fig. 6.4). The solid-phase Cd profiles show a minimum in the surface sediments, suggesting that readsorption of Cd by Mn and Fe oxyhydroxides cannot keep up with its production at the SWI. A similar coupling between solid-phase and dissolved Cd was reported previously by Gobeil *et al.* (1987) for sediments of the Laurentian Trough. Formation of chlorocomplexes after release to the pore waters may well explain the limited extent of Cd readsorption (e.g. Comans and Van Dijk, 1988). Precipitation of Cd in the sulphate reduction zone, as suggested by the dissolved Cd profiles (Fig. 6.4), is confirmed by the maximum in solid-phase Cd below 10 cm depth (Fig. 6.9). In conclusion, there is evidence that the distribution of solid-phase Fe, Mn, Cd, Cu, and Zn in the brackish sediments has been changed by diagenetic processes. The extent of post-depositional mobility appears to be related to the vertical spacing of the redox boundaries, as proposed before by Shaw *et al.* (1990). In salt marsh sediments of the Scheldt estuary, where the redox zones are much better resolved (e.g. an oxic top layer of 20-30 cm), the impact of diagenetic processes on the solid-phase trace metal profiles was found to be even more important (see chapter 5).

core B1



core B2

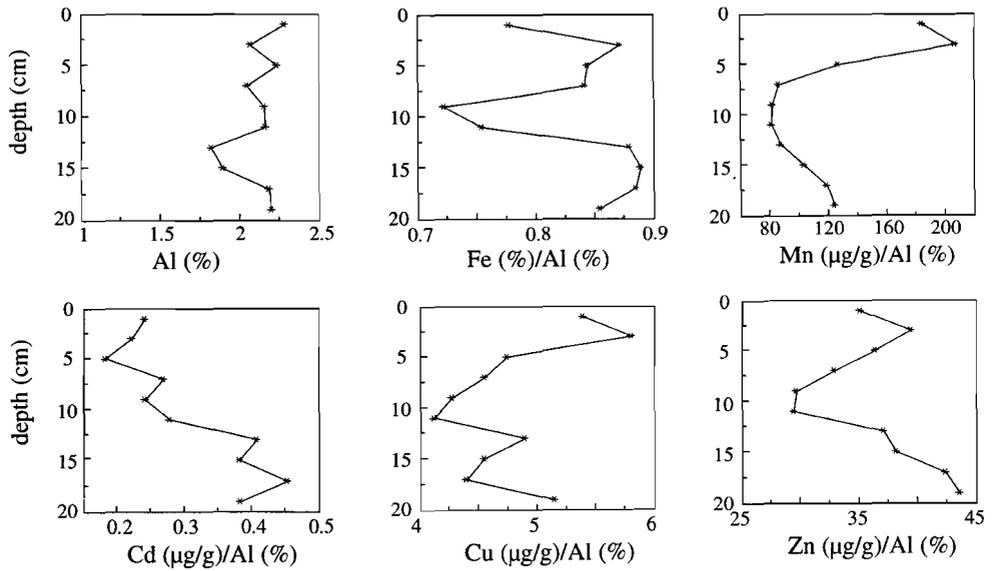


Fig. 6.9. Solid-phase profiles of Al, Fe, Mn, Cd, Cu, and Zn in cores B1 and B2.

6.4. Conclusions and environmental implications

Due to the presence of a near-surface concentration maximum in the pore waters (Figs. 6.2-4), the brackish and marine sediments may act as a source of dissolved Cd, Cu, and Zn to the water column. Diagenetic mobilisation in the upper estuary seems less significant due to the occurrence of sulphate reduction close to the SWI. However, restoration of the oxygen saturation in the upper Scheldt estuary, a major goal of its present-day management, will probably increase the dissolved Cd, Cu, and Zn concentration near the SWI (see section 6.3.4.), and hence increase the outflow of these metals from the sediments in the upper estuary. It is well known that reoxidation of anoxic sediments may lead to increased fluxes of dissolved Cd, Cu, and Zn to the water column (Westerlund *et al.*, 1986; Kerner and Wallmann, 1992; Riedel *et al.*, 1997). The effect of dissolved oxygen restoration in the upper estuary may therefore be an increasing flux of dissolved Cd, Cu, and Zn to the coastal zone, as suggested before in chapter 2.

The results of this study may also be of ecotoxicological significance. It was found that there is no relationship between the trace metal content of the sediments and the dissolved metal concentrations in the pore waters (Fig. 6.7). Thus, estimating the dissolved metal concentrations in these pore waters according to equilibrium partitioning theory (Van der Kooij *et al.*, 1991) would yield erroneous results. The absence of a relation between solid-phase metal and pore water composition is in agreement with general observations that there is no a priori relationship between contamination of sediments by metals and biological effects (Luoma, 1989). Secondly, it was found that dissolved trace metal concentrations are usually higher in (oxidising) sandy sediments than in (reducing) silty sediments (Fig. 6.7). The high concentrations of dissolved trace metals in the surficial pore waters of sandy sediments (even so when they are hardly contaminated) may influence their toxicity to sediment-dwelling organisms. The general implication is that the biological availability of trace metals in oxic sandy sediments is higher than that in reducing silty sediments (although the contamination of the sediments will usually be the opposite). This conclusion is supported by field and laboratory studies of Cu availability to the sediment-dwelling bivalve *Macoma balthica* (Absil, 1993). The highest bioaccumulation and the strongest effects were observed in sediments with the lowest silt and clay fractions.

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Appendix A(1): Major element composition of the pore waters

core	depth cm	Sal. -	H ₂ O %	Por. -	T °C	pH -	Cl mM	SO ₄ mM	tot-S mM	Na mM	K mM	Mg mM	Ca mM	Sr μM
Ms1	0	27.3			7.4	7.8	434		22.9	365	7.7	39.5	9.0	71
Ms1	1.1	26.2	23.6	0.44	7.4	8.0	452	23.5	21.4	351	8.0	37.4	8.8	76
Ms1	3.2	27.1	23.7	0.44		8.0	394	19.9	22.1	363	8.0	38.6	8.8	77
Ms1	5.3	26.5	22.5	0.42	7.4	8.0	373	19.6	21.5	354	7.8	37.8	8.6	76
Ms1	7.4	28.3	22.1	0.42		8.0	360	18.3	22.4	378	8.5	39.1	9.0	79
Ms1	9.5	27.2	19.8	0.38	7.4	8.0	402	20.6	22.0	364	8.0	38.5	8.8	78
Ms1	11.6	27.8	20.5	0.39			438	21.4	22.4	372	8.1	39.5	9.0	79
Ms1	13.7	26.8	29.7	0.51	7.6		425	21.8	21.7	359	7.8	38.3	8.8	76
Ms1	15.8	26.2	24.7	0.45	7.5		414	21.0	21.2	351	7.6	37.7	8.7	76
Ms2	0	28.1			14.9	8.7	438	22.5						
Ms2	0.5	29.0					468	23.1	22.2	388	8.6	42.0	7.4	56
Ms2	1.6	29.3	15.6	0.32			470	23.1	22.4	391	8.7	42.3	7.4	56
Ms2	2.6	29.6					474	23.0	22.8	397	8.9	42.8	7.6	57
Ms2	3.7	29.0				7.8	468	23.0	22.4	388	8.7	42.2	7.5	56
Ms2	4.7	29.4	16.4	0.33			471	23.0	22.8	393	8.8	42.9	7.8	58
Ms2	5.8	29.6	17.1	0.34		7.7			22.9	396	8.9	42.9	7.7	58
Ms2	6.8	29.1					465	22.9	22.5	389	8.7	42.4	7.5	57
Ms2	7.9	29.1					468	22.9	22.6	390	8.7	42.6	7.8	58
Ms2	8.9	29.3					465	22.4	22.4	392	8.8	42.4	7.5	57
Mi1	0	30.0			7.4	7.8	459		24.3	401	8.6	42.0	9.3	76
Mi1	1.1	26.2				8.0	364	20.1	21.9	350	8.0	37.4	8.8	73
Mi1	3.2	24.9	25.0	0.45		8.0	349	19.3	21.2	333	7.6	36.1	8.5	70
Mi1	5.3	24.8	23.4	0.43		8.0	398	21.7	20.8	332	7.7	35.3	8.1	69
Mi1	7.4	25.3	19.6	0.38		8.0	397	21.3	21.0	338	7.8	36.0	8.3	70
Mi1	9.5	30.3	19.3	0.37		8.0	399	21.4	25.5	406	9.4	43.5	10.0	85
Mi1	11.6	27.1	27.4	0.49			400	21.3	22.5	362	8.5	38.0	8.8	75
Mi1	13.7	26.4	33.2	0.55			400	21.1	21.7	354	8.3	37.0	8.8	73
Mi1	15.8	25.5	33.7	0.56			399	21.2	20.7	342	7.9	36.2	8.3	70
Mi2	0	28.1			15.0	8.7	438	22.5						
Mi2	0.5	28.2					456	22.9	22.0	378	8.9	41.8	8.2	59
Mi2	1.6	29.1					458	23.0	21.9	389	9.1	42.2	7.9	59
Mi2	2.6	28.2	47.6	0.69			453	22.7	21.3	377	8.7	41.0	7.4	56
Mi2	3.7	28.6				7.6	455	22.7	21.4	382	8.8	40.8	7.3	55
Mi2	4.7	27.9	42.5	0.65			456	22.6	21.0	373	8.7	39.9	7.2	54
Mi2	5.8	28.0	40.9	0.63					21.1	375	8.7	40.0	7.3	54
Mi2	6.8	28.6	33.4	0.56			454	22.5	21.6	383	8.9	41.0	7.6	56
Mi2	7.9	28.1	27.9	0.49			446	22.1	20.8	376	8.9	39.5	7.0	54
Mi2	8.9	27.8	29.5	0.51			451	22.2	20.6	372	8.8	39.7	7.3	55

Diagenetic trace mobilisation in sediments of the Scheldt estuary

Appendix A(1): (continued)

core	depth cm	Sal. -	H ₂ O %	Por. -	T °C	pH -	Cl mM	SO ₄ mM	tot-S mM	Na mM	K mM	Mg mM	Ca mM	Sr µM
B1	0	12.9			8.9	8.0	200	10.9						
B1	1.1	11.7	28.1	0.49		7.2	169	10.6	11.0	157	4.1	17.7	5.4	34
B1	3.2	11.1	25.4	0.46	9.0		173	10.4	10.4	148	3.9	16.7	5.1	33
B1	5.3	11.1	24.2	0.44		7.3	171	10.3	10.4	149	3.9	16.7	5.2	34
B1	7.4	11.1	22.3	0.42	8.9		175	10.4	10.4	148	3.9	16.4	5.1	34
B1	9.5	11.4	24.1	0.44		7.3	178	10.1	10.2	153	4.1	16.7	5.2	35
B1	12.6	12.2	27.0	0.48	8.8	7.2	192	10.6	10.6	163	4.3	17.3	5.2	37
B1	16.8	14.6	22.8	0.42	8.9	7.2			12.2	195	4.9	20.8	6.2	45
B1	21.0	15.3	27.0	0.48	8.9	7.1	243	12.3	12.4	205	4.9	22.0	6.4	47
B1	25.2	15.6	26.8	0.48	8.8	7.1	259	13.1	12.9	209	5.1	22.8	6.7	48
B2	0	16.3			14.0	8.4	255	13.6						
B2	0.5	16.5							12.9	221	4.8	23.6	5.3	25
B2	1.6	15.9	30.8	0.53		7.2			12.3	213	4.7	22.6	5.1	22
B2	2.6	15.7	28.4	0.50			248	10.0	12.3	210	4.6	21.5	4.9	21
B2	3.7	15.5	27.0	0.48		7.2			12.5	208	4.5	21.3	4.9	21
B2	4.7	16.0	22.8	0.42					12.7	214	4.7	22.7	5.1	23
B2	5.8	16.2	22.3	0.42		7.2			12.8	217	4.7	22.8	5.3	23
B2	6.8	16.2	21.8	0.41			242	8.7	12.7	216	4.7	23.0	5.3	24
B2	7.9	16.5	22.9	0.43		7.2			12.8	221	4.8	23.5	5.4	24
B2	8.9	17.4	25.6	0.46		7.1			13.4	233	5.1	25.1	5.7	27
HTZ1	0	2.9			11.0	7.7	41	2.9						
HTZ1	2.1	1.6	54.2	0.75	11.0	7.1	24	<1.0	0.5	22	0.7	3.7	4.7	14
HTZ1	6.3	1.9	46.2	0.68	10.9		32	<1.0	0.1	25	0.8	4.4	6.4	23
HTZ1	10.5	2.3	53.6	0.74	10.9		39	<1.0	0.1	31	1.0	5.0	7.1	31
HTZ1	14.7	2.9	45.3	0.67			49	<1.0	0.1	39	1.3	6.0	7.8	41
HTZ1	18.9	3.6	42.1	0.65	10.8	7.2	56	<1.0	0.1	48	1.5	7.0	8.0	43
HTZ1	23.1	4.3	42.4	0.65	10.7		62	<1.0	0.1	58	1.8	8.0	7.8	45
HTZ1	27.3	4.7	48.0	0.70	10.6		68	<1.0	<0.1	63	1.8	8.3	7.4	42
HTZ2	0	5.1			17.6	7.8	80	4.2						
HTZ2	0.5	5.8	64.5	0.82			78	1.7	2.6	77	1.6	9.1	4.8	9
HTZ2	1.6	5.5	65.3	0.82			74	<1.0	1.8	74	1.5	9.0	5.3	12
HTZ2	2.6	5.3	59.3	0.78			68	<1.0	1.1	71	1.5	8.8	5.5	14
HTZ2	3.7	5.0	54.2	0.75			67	<1.0	0.6	67	1.5	8.7	6.3	18
HTZ2	4.7	4.9	55.5	0.76			63	<1.0	0.3	66	1.5	8.7	6.6	20
HTZ2	5.8	4.9	56.5	0.76			61	<1.0	0.2	66	1.5	8.8	7.1	23
HTZ2	6.8	4.5	51.9	0.73					0.2	60	1.4	8.2	7.4	24
HTZ2	7.9	4.6	58.1	0.78			59	<1.04	0.2	61	1.5	8.4	7.3	23
HTZ2	8.9	4.2	57.9	0.77			55	<1.04	<0.1	57	1.4	7.9	7.4	24

Chapter 6

Appendix A(2): Nutrient and trace metal composition of the pore waters

core	depth cm	DIC mM	DOC mM	NH ₄ μM	NO ₂ μM	NO ₃ μM	PO ₄ μM	tot-P μM	tot-S μM	Mn μM	Fe μM	Ba μM	Cd nM	Cu nM	Zn nM
Ms1	0	2.40	0.19	6	2.7	128	3.8	12.3	51	<0.1	2.2		1.2	20	
Ms1	1.1	3.50	0.73	229	0.3	2	6.5	<8.7	123	20.3	2.7	0.28	25.8	220	
Ms1	3.2	4.16	0.56	268	0.2	2	5.6	9.1	143	40.9	4.9	0.30	21.4	189	
Ms1	5.3	4.16	0.74	365	0.1	9	7.4	9.1	176	55.3	6.5	0.22	11.6	138	
Ms1	7.4	4.41	1.04	339	0.1	5	8.5	22.4	188	64.4	22.1	0.27	2.0	22	
Ms1	9.5	4.16	0.71	476	0.1	5	7.3	<8.7	183	61.3	9.0	0.28			
Ms1	11.6	4.00	0.61	555	<0.1	1	8.0	15.3	173	51.6	19.9	0.38	2.4	72	
Ms1	13.7	4.33	0.60	469	0.1	3	10.3	16.4	190	48.2	13.8	0.26	2.4	63	
Ms1	15.8	4.58	0.52	515	<0.1	3	10.2	16.1	197	55.0	12.5	0.24	3.9	47	
Ms2	0	2.16	0.21	9	2.1	69	2.6		14	<0.1	<0.4		0.3	19	15
Ms2	0.5	2.50	0.60	23	4.9	20	4.0	<8.7	35	<0.1	<0.4	0.38	1.2	25	459
Ms2	1.6	2.66	0.69	47	4.6	13	4.1	<8.7	46	0.7	<0.4	0.38	1.1	36	459
Ms2	2.6	2.83	0.65	63	3.5	6	5.5	13.5	67	3.6	<0.4	0.38	0.6	28	352
Ms2	3.7	2.58	0.46	26	2.4	8	5.5	<8.7	59	3.6	<0.4	0.46	1.0	27	321
Ms2	4.7	2.58	0.62	24	3.0	8	5.7	<8.7	58	3.7	<0.4	0.48	3.2	65	398
Ms2	5.8							9.6		4.1	<0.4	0.45	1.1	58	413
Ms2	6.8	2.50	0.59	21	3.8	8	5.3	<8.7	56	7.0	<0.4	0.51	2.0	46	245
Ms2	7.9	3.08	0.66	33	4.1	9	5.5	14.4	51	6.6	<0.4	0.58	4.3	105	367
Ms2	8.9	4.58	0.63	154	3.7	9	7.7	<8.7	82	6.2	<0.4	0.43	2.7		398
Mi1	0	2.30	0.17	5	1.5	96	3	<9	40	<0.1	1		1.1	14	
Mi1	1.1	3.50	0.77	191	1.0	6	8	14	101	18.7	9	0.31	7.9	145	
Mi1	3.2	3.08	0.90	213	0.1	5	12	17	93	15.8	19	0.36	5.4	90	
Mi1	5.3	2.33	1.07	205	0.1	3	16	21	97	9.0	20	0.32	5.8	74	
Mi1	7.4	2.91	0.67	230	<0.1	5	11	10	91	10.0	10	0.52	6.2	93	
Mi1	9.5	2.91	0.70	251	<0.1	5	12	14	94	10.8	12	0.71	3.6	100	
Mi1	11.6	3.58	1.23	298	<0.1	2	21	24	135	17.6	47	0.48	2.3	31	
Mi1	13.7	4.41	1.83	437	0.1	4	49	62	146	39.2	183	0.40	5.9	154	
Mi1	15.8	5.41	2.56	671	<0.1	6	75	87	156	66.4	307	0.26	3.3	107	
Mi2	0	2.16	0.21	9	2.1	69	3		14	<0.1	<1		0.27	19	15
Mi2	0.5	2.83	0.81	131	2.4	7	10	51	138	103.5	49	0.89	0.36	15	321
Mi2	1.6	3.00	0.92	163	1.6	4	26	103	207	61.9	158	0.53	0.62	72	642
Mi2	2.6	3.16	0.92	180	1.9	8	66	127	334	37.7	160	0.54	0.27	17	245
Mi2	3.7	2.91	0.83	195	2.0	6	89	122	349	26.9	133	0.59	0.80	19	291
Mi2	4.7	2.83	0.77	143	1.4	5	80	119	291	24.4	154	0.60	0.71	22	306
Mi2	5.8							116		21.2	156	0.62	0.71	31	505
Mi2	6.8	2.83	1.03	160	1.9	4	67	113	228	21.7	164	0.55	0.53	35	474
Mi2	7.9	3.00	1.21	187	3.0	10	86	110	234	20.2	167	0.43	1.51	42	627
Mi2	8.9	3.91	1.15	321	1.1	4	103	136	281	28.7	260	0.68	0.62	52	673

Diagenetic trace mobilisation in sediments of the Scheldt estuary

Appendix A(2): (continued)

core	depth cm	DIC mM	DOC mM	NH ₄ μM	NO ₂ μM	NO ₃ μM	PO ₄ μM	tot-P μM	tot-S μM	Mn μM	Fe μM	Ba μM	Cd nM	Cu nM	Zn nM
B1	0	2.90	0.34	4	6.1	357	8		121	1.5	0.5		1.3	29	
B1	1.1		0.80	34	19.8	129	16	20	105	6.6	2.7	0.22	23.0	146	
B1	3.2		1.02	56	3.5	28	19	25	162	20.0	2.3	0.22	19.4	153	
B1	5.3		1.75	76	0.7	3	24	30	250	54.6	5.7	0.29	6.6	173	
B1	7.4		2.48	124	0.3	5	49	68	277	27.3	68	0.44	1.5	55	
B1	9.5		1.30	263	0.4	1	121	158	420	27.3	251	0.73	2.0	42	
B1	12.6		1.25	436	0.4	<1	134	152	463	20.0	129	0.87	0.7	46	
B1	16.8							194		29.1	113	1.53	0.9		
B1	21.0		1.25	878	0.3	2	180	245	726	47.3	158	1.38	2.2	69	
B1	25.2		1.16	892	0.4	1	183	220	719	54.6	127	1.02	0.8	5	
B2	0	2.78	0.31	3	6.5	256	9		38	1.5	0.5		1.7	35	84
B2	0.5							50		0.2	<0.4	0.62	9.8	157	688
B2	1.6							37		8.6	<0.4	0.64			
B2	2.6	5.91	1.21	280	1.6	2	113	51	406	18.5	<0.4	0.67	8.9	173	612
B2	3.7							54		42.5	<0.4	0.63	4.8	220	428
B2	4.7							73		38.2	6.1	0.81	5.1	173	520
B2	5.8							87		40.9	23.4	0.74	2.8	173	505
B2	6.8	7.41	1.68	517	0.5	<1	75	103	463	31.4	37.9	0.84	3.6	173	551
B2	7.9							102		35.2	69.1	0.78	1.1	74	811
B2	8.9							110		26.6	9.9	1.12	1.9	66	627
HTZ1	0	3.9	0.56	106	14.3	421	9		192	4.7	1		0.44	19	168
HTZ1	2.1	15.9	2.39	1135	0.2	<1	26	132	312	27.3	322	0.29	1.42	42	199
HTZ1	6.3	18.4	3.66	1835	0.2	<1	33	136	287	29.1	466	0.65	0.18	52	260
HTZ1	10.5	20.0	3.16	2763	0.4	1	11	129	277	21.8	448	1.09	0.80	57	260
HTZ1	14.7	24.5	3.01	4191	0.2	1	14	142	348	14.2	448	1.53	0.27	44	260
HTZ1	18.9	29.8	3.36	5833	0.6	2	17	158	363	15.3	466	1.89	0.53	35	291
HTZ1	23.1	35.5	3.27	6240	0.2	2	227	313	498	13.3	286	1.89	0.44	36	153
HTZ1	27.3	34.4	2.89	6597	0.1	1	339	420	534	12.0	90	1.09	0.36	24	199
HTZ2	0	3.5	0.42	64	20.3	317	12		130	4.1	1		0.40	20	107
HTZ2	0.5	20.5	2.20	1149	1.0	12	94	153	342	28.4	224	0.62	0.98	20	150
HTZ2	1.6	28.6	2.88	1642	0.3	<1	139	166	388	27.8	289	0.92	<0.18	24	115
HTZ2	2.6	27.9	2.99	1671	0.6	<1	132	164	392	26.5	328	0.96	0.27	12	122
HTZ2	3.7	28.0	3.12	1735	0.5	1	149	160	399	24.9	342	1.31	0.18	30	124
HTZ2	4.7	31.6	2.83	1992	0.4	1	210	160	417	25.0	371	1.38	0.18	8	76
HTZ2	5.8	32.3	3.16	2277	0.4	1	91	156	431	25.3	426	1.58	0.27	16	93
HTZ2	6.8	33.8	0.00	2763	0.4	2	93	118	449	20.8	352	1.70	0.27	9	101
HTZ2	7.9	36.5	3.39	2663	0.3	2	95	163	456	21.5	357	1.76	1.25	28	245
HTZ2	8.9	36.1	3.48		0.4	1	98	116	470	19.1	350	1.67	0.27	12	142

Chapter 7

Modelling the geochemistry of trace metals in the Scheldt estuary

7.1. SAWES - The water quality model for the Scheldt estuary

7.1.1. General model description

The knowledge obtained on trace metal behaviour in the Scheldt estuary has been implemented in a mathematical water quality model, described in detail in Van Gils et al. (1993) and Ouboter et al. (1998). The SAWES model is an important tool to support policy development and management of the estuary. The model, a one-dimensional, deterministic, dynamic box-model, simulates the major physical, chemical, and biological processes within the estuary. The basis of the model is the water quality model DELWAQ (Delft Hydraulics, 1995). A one-dimensional approach is chosen because the Scheldt is a well-mixed estuary; hence the longitudinal gradients are much greater than the lateral or vertical gradients. The main characteristics of the SAWES model are: (1) conservation of mass for all modelled substances; (2) transport of dissolved substances, calculated by the advection-dispersion equation; (3) transport of particulate substances (such as adsorbed metal species), based on suspended matter transport equations; (4) chemical equilibrium for rapid chemical reactions, e.g. partitioning and speciation of trace metals; (5) kinetic process formulations for slower reactions, e.g. nitrification and sulphide oxidation. The freshwater and sediment balance and the inputs of chemical substances into the estuary serve as input to the SAWES model.

The physical schematisation of the estuary in the model is as follows. The estuary is divided into 14 homogeneous boxes (Fig. 7.1). Exchange between adjacent boxes is based on freshwater inflows. The water depth used in the model is the average depth for each box. The hydrodynamic coefficients used in the advection-dispersion equation are based on tidal-averaged flows. The tidal-averaged transport of water and dissolved substances is based on the measured chloride concentrations and the chloride balance for each box.

Suspended matter transport is based on a one-dimensional cohesive sediment balance, constructed by Van Maldegem et al. (1993). The balance is based on suspended matter inputs, sedimentation rates, dredging figures, and other data. The input of riverine suspended matter into the estuary in 1987 was estimated at 400 kton/yr, and the input of marine suspended matter at 200 kton/yr. Most of the suspended matter is deposited in the high-turbidity zone between Antwerp and the Dutch-Belgian border, and in the Saeftinge marsh near the border. Special attention has been given to the exchange of suspended matter with the subtidal sediments. Sediment dynamics appear to affect not only the fate of contaminants, but also the

adaptation time of the system to changes in external contaminant loads (as discussed later). Exchange between the sediments and the overlying water column is largely determined by the presence of mobile sand ripples (Boderie et al., 1993). These ripples cause an exchange rate between the silt in a sediment layer of 0.5 m with the overlying water of twice a year. Due to the great amount of silt in the sediments, the equilibration time of the model is about 15 years.

The redox chemistry is modelled by the following processes: exchange of oxygen and carbon dioxide with the atmosphere, mineralisation of organic matter, nitrification and denitrification. The process formulations used are generally accepted (Stumm and Morgan, 1981; Di Toro et al., 1987). Decay reactions are based on first-order kinetics including an exponential temperature function, as well as a dependency on oxygen concentration. The pH in the water column is calculated as a function of alkalinity and CO₂ concentration by the thermodynamic equilibrium model CHARON (Smits et al., 1985). Since primary production affects both the oxygen balance and the cycling of nutrients and trace metals (see chapter 2), a phytoplankton module was constructed, discriminating between diatoms and non-diatoms.

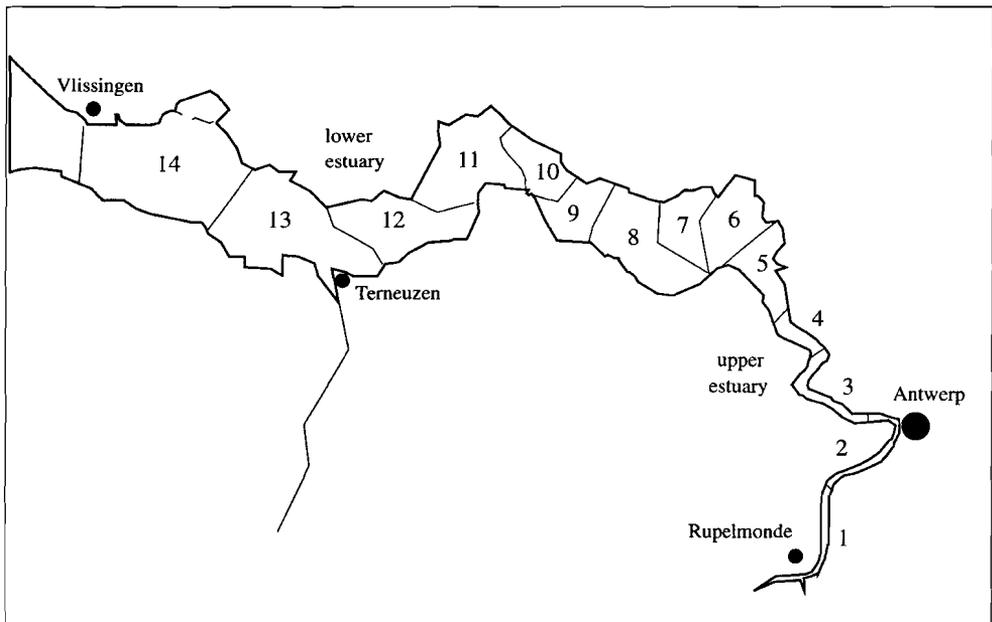


Fig. 7.1. Physical schematisation of the Scheldt estuary in the SAWES model.

7.1.2. Trace metal modelling approach

The trace metal modelling approach is based on the results described in chapters 2-3. The basic assumption is that the suspended matter contains two different metal fractions, called the equilibrium and non-equilibrium metal fraction, respectively. The equilibrium metal fraction is in adsorptive equilibrium with the dissolved metal concentration, whereas the non-equilibrium metal fraction, representing trace metals bound by sulphides, does not directly contribute to adsorption-desorption reactions. The metal sulphides in the suspended matter are slowly oxidised, depending on oxygen concentration and temperature. The metals, liberated during sulphide oxidation, are added to the equilibrium metal fraction, becoming available for exchange reactions. The dissolved metal speciation and the corresponding trace metal content of the suspended matter in equilibrium with the dissolved metal concentration are subsequently calculated by the chemical equilibrium model CHARON. An outline of the trace metal modelling approach is presented in Fig. 7.2.

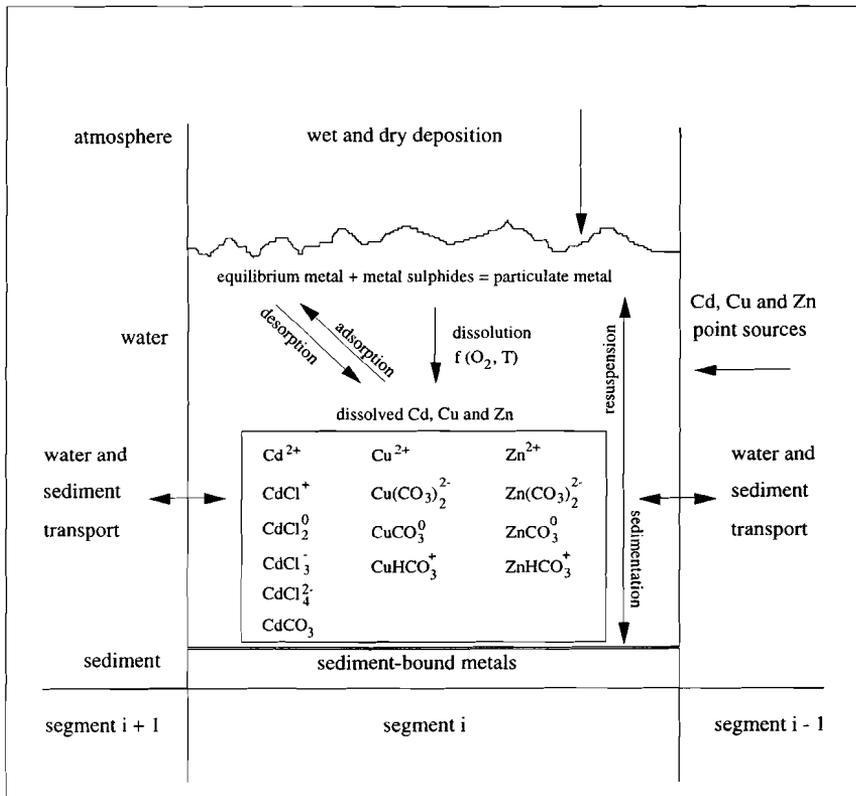


Fig. 7.2. Schematic outline of the trace metal modelling approach.

The model was calibrated with the data of eight field surveys, carried out between February 1987 and February 1988 (see chapters 2-3). Firstly, the dispersion coefficient was estimated by fitting simulated (tidal-averaged) chloride profiles to the measured chloride profiles (after correction for tidal stage). Then, the calculated profiles of dissolved oxygen, nitrogen species (ammonium and nitrate), and the algae module were calibrated to the field results (by adjusting process parameters, such as rate constants). Finally, the dissolved metal profiles were calibrated. To this end, the water and suspended matter samples were divided in classes with or without sulphides, based on the magnitude of the partition coefficient K_d . Samples without metal sulphides (low K_d 's) were used in the chemical equilibrium model CHARON to calibrate the adsorption characteristics of the suspended matter. For this purpose, an auto-calibration procedure was used (Ouboter and De Rooij, 1990). Samples with metal sulphides were used to calibrate the kinetics of metal sulphide oxidation, as a function of temperature and dissolved oxygen concentration.

7.2. Model results for the years 1978 and 1987

The results of the calibration of the SAWES model are given in Fig. 7.3, showing the measured and simulated results for the May 1987 survey. The measured and simulated general water quality variables are consistent. The observed oxygen depletion in the upper estuary is primarily caused by high nitrification rates (reflected by the profiles of ammonium and nitrate) and, to a smaller extent, by decomposition of the organic load. Almost all of the organic nitrogen is mineralised and ammonium is completely nitrified in the estuary. The major features of phytoplankton dynamics, i.e. mortality of freshwater algae in the upper estuary and primary production in the lower estuary, are reproduced by the model. The pH profile is reproduced as well.

The trace metal simulations are somewhat less accurate, although the major features of the behaviour of trace metals in the estuary are reproduced. The simulated trace metal composition of the suspended matter reflects the mixing of metal-rich fluvial particles with metal-poor marine material. The modelled profiles of dissolved Cd, Cu, and Zn reflect their mobilisation in the brackish water zone, induced by oxidation of trace metal sulphides and formation of metal complexes. In addition, adsorption of dissolved Cd and Zn is simulated in the lower estuary, related to the increase in ambient pH levels (direct biological uptake was not considered by the model). However, a major difference is apparent between the measured and simulated dissolved metal concentrations. The principal reason for this difference is the high sensitivity of the metal sulphide oxidation rate on the dissolved oxygen concentration. Slight deviations in the simulated dissolved oxygen profile result in significant changes of the simulated dissolved metal concentrations.

Modelling the geochemistry of trace metals in the Scheldt estuary

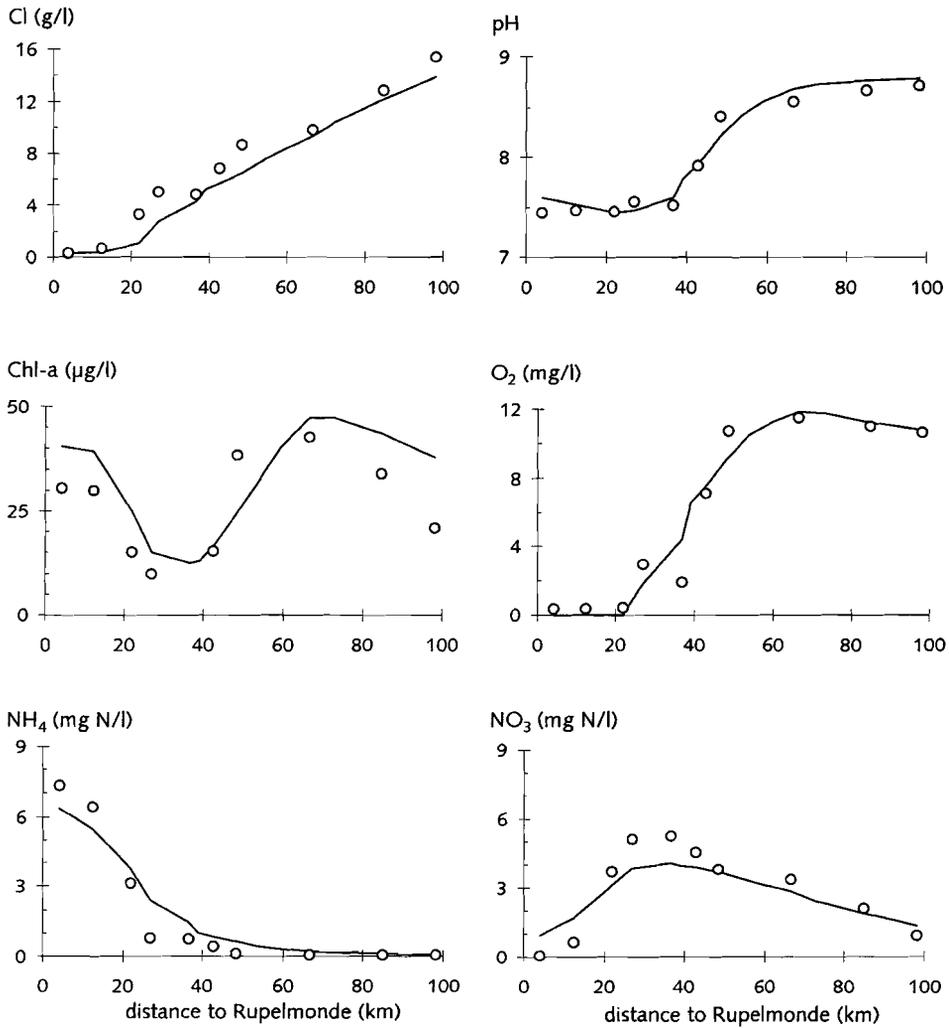


Fig. 7.3a. Simulated and measured profiles of chloride, pH, dissolved oxygen, chlorophyll-a, ammonium, and nitrate in the Scheldt estuary in May 1987 (calibration results).

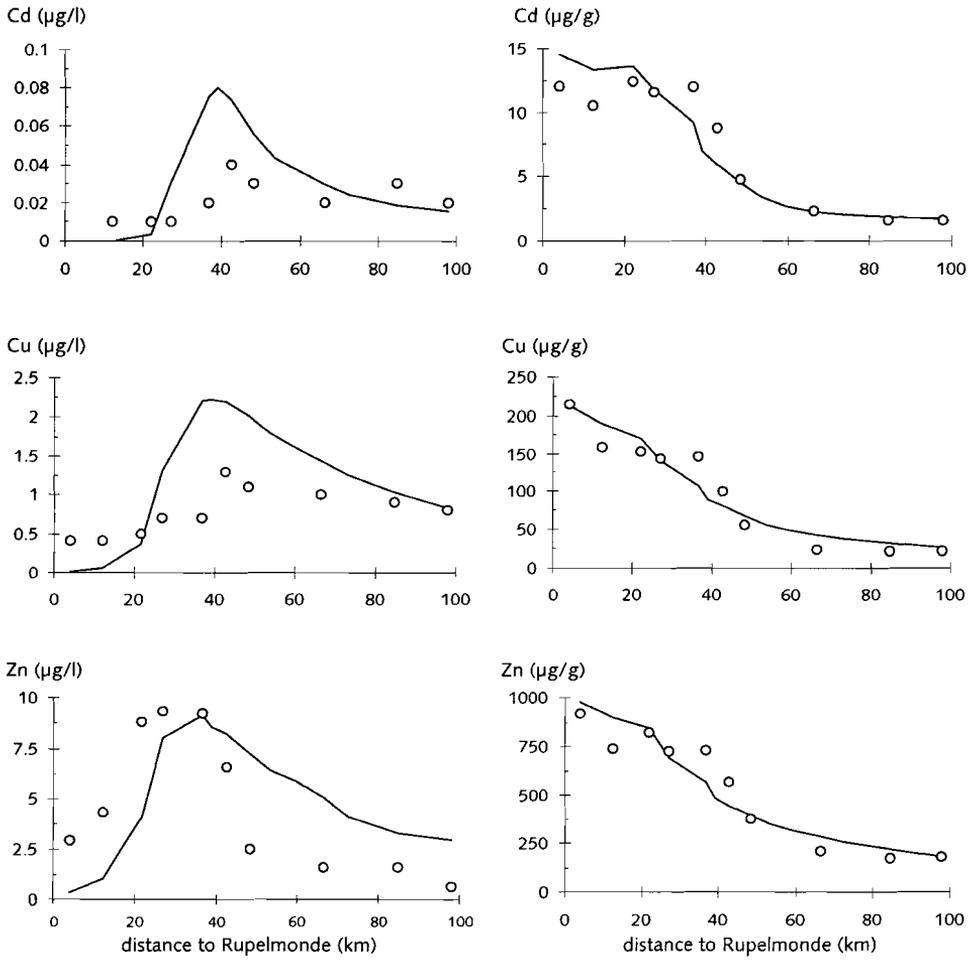


Fig. 7.3b. Simulated and measured profiles of dissolved and particulate Cd, Cu, and Zn in the Scheldt estuary in May 1987 (calibration results).

After the calibration of the model for the year 1987, an attempt was made to reproduce the data of Duinker et al. (1982^a) for an October 1978 survey. This was done by estimating, in an iterative way, the discharges of trace metals, organic matter and nutrients, as well as the contents of trace metals in the sediments, in the late seventies. The simulations were run with the sediment and water balance for the year 1987. The dissolved Cd and Zn concentrations, simulated by the model, are shown in Fig. 7.4. The SAWES model, calibrated for the year 1987, reproduces the dissolved Zn profile very well. The general features of the dissolved Cd profile are reproduced too, but the model seems to underestimate the actual Cd concentration levels. The deviation at low salinities may be explained by analytical problems or underestimation of the Cd load imposed on the model. Another difference between model and field results concerns the height of the dissolved Cd peak around salinity 20. This can be explained by underestimation of the Cd load to the estuary, but may also be related to the uncertainty in the process parameters describing the oxidation rate of Cd sulphide (as mentioned before).

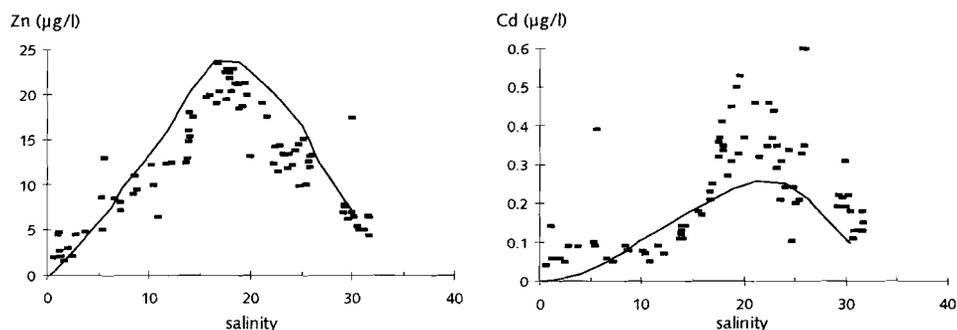


Fig. 7.4. Simulated and measured profiles of dissolved Cd and Zn in October 1978 (data from Duinker et al., 1982^a).

It should be noticed that the SAWES model accurately predicts the position (salinity) of the dissolved Cd and Zn maxima in October 1978. This result is encouraging because the redox status of the estuary has improved over the years. In October 1987, the anoxic zone was limited to low salinities (0-4), whilst the entire upper estuary was anoxic in October 1978 (salinity 0-13). This means that the mobilisation of trace metals (through oxidation of metal sulphides) occurred more downstream in October 1978, resulting in dissolved metal peaks at relatively high salinities (see Table 2.5). This dependency of the dissolved metal profiles on the redox status of the estuary is correctly reproduced by the SAWES model. These results indicate that the geochemical mechanisms of trace metal mobilisation in the Scheldt estuary in October 1978 are similar to those existing in 1987. Hence, the SAWES model, calibrated on the year 1987, may be used to reconstruct the historic behaviour of (dissolved) trace metals in the Scheldt estuary, characterised by more reducing conditions and higher trace metal inputs.

7.3. Trace metal retention in the Scheldt estuary

Using the SAWES model, it is possible to quantify the retention of trace metals in the estuary (through sedimentation). However, the meaning of this information is very limited. The model runs (not shown here) clearly show that the calculated retention is strongly determined by the choice of the initial trace metal contents in the sediments. Starting with uncontaminated sediments, high retentions are calculated because a large part of the total metal input will be adsorbed by the sediments. Starting with high contents in the sediments (relative to the suspended matter composition), part of the sediment-bound trace metals is liberated, resulting in low apparent retentions. The equilibrium retentions of Cd, Cu, and Zn, calculated by the model for the year 1987, are 43%, 45%, and 48%, respectively. These figures refer to the situation in which equilibrium is reached between the metal discharges into the estuary and the sediment trace metal contents. This is obviously not the case in 1987, because in the eighties the metal inputs into the estuary were drastically reduced (see chapters 3-5), whereas the metal contents in the sediments (partly) reflect the historic metal inputs. This means that the actual trace metal retention in the estuary in the year 1987 was lower than that calculated by the model.

Acknowledgements - Thanks are due to R. Nolting for providing the data published in Duinker et al. (1982^a), and to N. De Rooij for his assistance during the development of the model and the execution of the model calculations.

Chapter 8

Present-day trace metal geochemistry in the Scheldt estuary

8.1. Introduction

This thesis is based on a data set which goes back one decade ago (1987/88). In the nineties, several developments relevant to the water quality of the Scheldt estuary have taken place. These are the ongoing reduction of trace metal inputs, a gradual improvement in the redox condition of the upper estuary, and the removal of vast amounts of polluted sediments in the upper estuary (Salden, 1998). For these reasons, the water quality of the Scheldt estuary has changed. This may also affect the cycling of trace metals. In this chapter, recent data are presented on the general water quality and trace metal concentrations in the estuary, collected in 1995/96. The results for this campaign are summarised and compared to the results obtained in 1987-88.

In general, the analytical methods used in 1995/96 are similar to those used in 1987/88. Dissolved Cd, Cu, and Zn were preconcentrated and analysed by flame AAS (Zn) or GF-AAS with Zeeman background correction (Cd and Cu). Suspended matter was sampled by flow-through centrifugation, digested with HF-HNO₃-HClO₄, and analysed by ICP-AES or GF-AAS (Cd). The analytical quality, assessed by analysing certified reference materials, was acceptable for all the elements presented here, except for particulate Cd which may have been overestimated somewhat in 1995/96. Therefore, direct comparison of the results in 1987/88 and 1995/96 is, generally, justified.

8.2. River water composition: 1995/96 versus 1987/88

Ten sampling cruises were carried out between May 1995 and June 1996. Based on water temperature and chlorophyll-a profiles, these can be divided into three winter cruises (nrs. 6-8), three spring cruises (nrs. 1, 9 and 10), and four summer cruises (nrs. 2-5). Sampling dates, river discharge, and composition of the incoming river water are shown in Table 8.1. During the warmer period, the river water is anoxic to suboxic, similar to the situation in 1987 (cf. Tables 2.1 and 8.1). During winter (cruises 6-8), the river water is not completely devoid of oxygen, but the concentrations are very low (10-25% saturation). The dissolved Cu and Zn concentrations in the river water show a seasonal pattern, similar to that observed in 1987/88. In general, the dissolved Cu and Zn concentrations are high during the winter, but low during spring and summer (except for Cu in cruise 2).

Table 8.1. General water quality and dissolved metal concentrations in the Scheldt river at the beginning of the salinity gradient in 1995/96.

nr	Date yymmdd	Q m ³ /s	Sal.	T °C	SPM mg/l	Chl-a µg/l	pH	O ₂ µM	NO ₃ µM	Cd nM	Cu nM	Zn nM
1	950531	108	0.30	18.4	97	41	7.40	0	161	0.02	7.6	38
2	950707	67	0.41	22.1	67	116	7.52	23	189	0.09	16.4	40
3	950816	37	0.92	23.6	42	183	7.54	26	254	0.05	4.7	32
4	950914	51	1.02	18.5	163	173	7.64	9	228	0.11	5.2	69
5	951026	48	1.39	15.0	134	82	7.46	14	157	n.a.	n.a.	n.a.
6	951208	52	0.65	5.1	164	31	7.51	43	171	0.25	9.6	139
7	960111	76	0.56	4.0	298	35	7.73	31	176	0.11	14.8	147
8	960229	128	0.51	4.9	100	31	7.66	77	319	0.04	21.7	216
9	960424	51	1.13	13.8	109	32	7.59	8	103	<0.02	5.8	93
10	960606	51	0.81	19.4	230	18	7.63	15	81	0.03	2.7	15

n.a. = not analysed.

In Table 8.2, the average composition of the incoming river water in 1995/96 is compared to that in 1987/88. For a meaningful comparison, it is necessary to discriminate between winter conditions (defined by low water temperatures) and spring-summer conditions. The following observations on water quality development can be made. In the first place, it should be noticed that the river discharge was low in 1995/96, viz. less than half of that in 1987/88. This would have led to a decreasing redox potential in the river water and the upper estuary (Somville and De Pauw, 1982), provided that the organic load of the river water would have remained constant. During winter, however, the redox potential of the river water in 1995/96, characterised by the relative concentrations of dissolved oxygen, nitrate, and ammonium (Billen, 1975; Somville and De Pauw, 1982), is only slightly lower than that in 1987/88 (see Table 8.2). During spring and summer, the redox potential of the river water in 1995/96 is higher than that in 1987, as shown by the shift from ammonium to nitrate in the river water (Table 8.2). It can, therefore, be concluded that the input of degradable organic matter into the river water has decreased significantly between 1987 and 1996.

Another interesting point is the increase in phytoplankton biomass, as reflected by the high chlorophyll-a concentration in the river water in 1995/96, especially during the summer (see Tables 8.1-2). This may be related to the improved oxygenation of the river water in 1995/96. The dissolved Si concentration in the river water is inversely related to chlorophyll-a in 1995/96 (not shown), suggesting that part of the phytoplankton biomass consists of (freshwater) diatoms. This increase in phytoplankton biomass may pose a threat to the permanent restoration of dissolved oxygen in the river water and the upper estuary, a primary goal of today's estuarine management.

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Table 8.2. Average composition of the incoming river water during typical winter (December-March) and spring-summer (April-October) conditions in 1987/88 and 1995/96.

		Winter 1987/88	winter 1995/96	spring/summer 1987	spring/summer 1995/96
Q	m ³ /s	187 ± 55	85 ± 39	126 ± 42	59 ± 23
T	°C	5.4 ± 2.0	4.7 ± 0.6	17.1 ± 4.2	18.7 ± 3.5
Sal.		0.5 ± 0.1	0.6 ± 0.1	0.7 ± 0.3	0.9 ± 0.4
SPM	mg/l	90 ± 23	187 ± 101	109 ± 80	120 ± 63
Chl-a	µg/l	5 ± 7	32 ± 3	25 ± 21	92 ± 67
pH		7.2 ± 0.1	7.6 ± 0.1	7.6 ± 0.1	7.5 ± 0.1
DIC	mM	4.2 ± 0.5	3.8 (n=1)	4.3 ± 0.4	3.5 ± 0.4
DOC	µM	560 ± 50	468 ± 33	524 ± 35	433 ± 49
O ₂	µM	78 ± 54	50 ± 24	5 ± 2	13 ± 9
NO ₃	µM	296 ± 85	222 ± 84	34 ± 38	168 ± 63
NO ₂	µM	22 ± 11	6 ± 3	13 ± 14	26 ± 14
NH ₄	µM	266 ± 83	419 ± 20	387 ± 97	229 ± 132
PO ₄	µM	9 ± 3	12 ± 4	21 ± 4	13 ± 2
Si	µM	236 ± 32	246 ± 26	230 ± 14	144 ± 67
Cd	nM	0.18 ± 0.07	0.13 ± 0.11	0.10 ± 0.11	0.05 ± 0.04
Cu	nM	29 ± 5	15 ± 6	10 ± 6	7 ± 5
Zn	nM	291 ± 40	167 ± 42	45 ± 26	48 ± 28

The dissolved Cd concentrations in the river water have remained constant between 1987/88 and 1995/96, given the uncertainty in the average values. This is also the case for the dissolved Cu and Zn concentrations during spring and summer. However, during the winter, the dissolved Cu and Zn concentrations are almost half as low in 1995/96, compared to those in 1987/88. This difference cannot be ascribed to a change in redox potential of the river water, which is similar for these winter periods. The decrease in dissolved Cu and Zn is, therefore, likely to reflect a decrease in metal inputs into the Scheldt river. This explanation is supported by changes in the fluvial suspended matter composition between 1987 and 1996.

8.3. Suspended matter composition: 1995/96 versus 1987/88

A convenient way to compare the suspended matter composition of the estuary in 1995/96 to that in 1987/88 is to consider the composition of the fluvial and marine end-members. For, the composition of estuarine suspended matter is usually intermediate between that of the end-members, except for Mn, Fe, and S (see chapter 3). The average composition of the end-members in 1987/88 and 1995/96 is compared in Table 8.3. Seasonal differences in suspended matter composition, which are relatively small for the fluvial end-member but may be important for the marine end-member (see chapter 3), are ignored here.

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Table 8.3. Average composition of the fluvial and marine suspended matter of the Scheldt estuary in 1987/88 (n = 8) and 1995/96 (n = 10).

		fluvial SPM 1987/88	fluvial SPM 1995/96	marine SPM 1987/88	marine SPM 1995/96
CaCO ₃ *	%	11.0 ± 5.4	12.5 ± 3.0	27.6 ± 3.5	27.2 ± 2.9
POC	%	7.1 ± 1.7	6.2 ± 1.7	5.0 ± 3.4	3.2 ± 1.2
Al	%	4.5 ± 0.2	4.4 ± 0.7	4.5 ± 0.9	4.0 ± 0.7
Ca	%	4.1 ± 0.5	4.8 ± 0.8	9.9 ± 1.5	9.2 ± 0.6
Fe	%	4.6 ± 0.3	4.3 ± 0.5	2.9 ± 0.6	2.6 ± 0.5
K	%	1.56 ± 0.10	1.53 ± 0.23	1.64 ± 0.12	1.48 ± 0.22
Mg	%	0.66 ± 0.05	0.71 ± 0.12	0.98 ± 0.15	1.02 ± 0.11
N	%	0.48 ± 0.11	0.76 ± 0.29	0.51 ± 0.41	0.50 ± 0.24
Na	%	0.40 ± 0.04	0.37 ± 0.06	0.59 ± 0.08	0.62 ± 0.32
P	%	0.74 ± 0.09	0.52 ± 0.05	0.21 ± 0.09	0.14 ± 0.04
Ti	%	0.34 ± 0.02	0.25 ± 0.03	0.30 ± 0.05	0.23 ± 0.04
Ag	µg/g	5.5 ± 1.2	5.1 ± 1.2	2.3 ± 0.7	<0.2
Ba	µg/g	461 ± 29	339 ± 24	235 ± 34	203 ± 23
Be	µg/g	1.5 ± 0.1	1.7 ± 0.4	1.4 ± 0.3	1.5 ± 0.3
Cd	µg/g	12.2 ± 1.2	6.5 ± 1.2	1.2 ± 0.5	1.0 ± 0.2
Co	µg/g	16.1 ± 1.3	13.5 ± 1.8	9.5 ± 2.1	7.4 ± 2.2
Cr	µg/g	285 ± 24	155 ± 21	110 ± 22	78 ± 19
Cu	µg/g	213 ± 42	112 ± 18	29 ± 10	22 ± 7
Mn	µg/g	866 ± 146	1073 ± 296	1047 ± 182	799 ± 177
Ni	µg/g	62 ± 3	42 ± 5	35 ± 6	26 ± 7
Pb	µg/g	207 ± 40	157 ± 22	63 ± 13	51 ± 20
Sr	µg/g	226 ± 28	241 ± 36	411 ± 19	380 ± 29
V	µg/g	89 ± 4	91 ± 16	95 ± 20	85 ± 19
Zn	µg/g	1039 ± 128	644 ± 69	196 ± 35	157 ± 34

* Calculated from inorganic carbon.

Considering the fluvial suspended matter composition, the following changes are apparent between 1987/88 and 1995/96. In 1995/96, the fluvial suspended matter is enriched in Ca, Mn, and N. This can be explained by the change in river water chemistry which has taken place between 1987 and 1996 (see section 8.2). The increase in particulate N is probably related to the increase in phytoplankton abundance (see Fig. 3.6); the increase in particulate Mn is related to the improving redox potential of the river water. The increasing Ca content of the fluvial suspended matter may be explained by the increase in pH, observed during winter (see Table 8.2). The lowest Ca contents in the fluvial suspended matter were observed during the winter cruises in 1987/88 ($3.8 \pm 0.4\%$, versus $4.8 \pm 0.3\%$ for the winter cruises in 1995/96). The low pH of the river at that time (7.1 to 7.3) may have caused dissolution of carbonates in the fluvial suspended matter. The trace metal content of the fluvial suspended matter shows a major decrease between 1987/88 and 1995/96, amounting to 16% for Co, 24% for Pb, 32% for Ni, 38% for Zn, and 45-47% for Cd, Cr, and Cu. These data reflect a decrease in the metal inputs into the Scheldt river between 1987 and 1996. Decreasing contents are also observed for Ti (25%), Ba (26%), and P (30%).

The major ion composition of the marine suspended matter in 1995/96 is similar to that in 1987/88. This is not surprising, as the composition of North Sea suspended matter is unlikely to change significantly within one decade. There is a difference in the trace metal composition of the marine end-member, however, with generally lower contents in 1995/96. The reason for this is that the 'marine end-member', defined here as suspended matter collected at the mouth of the Scheldt estuary (city of Vlissingen), still contains 10-20% of fluvial suspended matter (Verlaan et al., 1998). Due to the higher discharge in 1987/88, the salinity at the mouth of the Scheldt estuary was lower in 1987/88 than in 1995/96 (26.4 ± 2.6 vs 28.8 ± 1.4 , respectively). As a result, the percentage of fluvial suspended matter at the mouth may have been higher in 1987/88, leading to higher trace metal contents in the suspended matter.

8.4. Seasonal water quality profiles: 1995/96 versus 1987

8.4.1. Developments in general estuarine chemistry

For a meaningful comparison of the estuarine chemistry in 1987/88 and 1995/96, it is necessary to discriminate between different seasons. In Fig. 8.1, profiles of the general water quality variables are shown for typical winter, spring, and summer conditions in 1987 and 1995/96 (February, May, and August, respectively). Compared to the situation in 1987, the following features are observed in the profiles of 1995/96:

- (1) A decrease in the suspended matter concentration in the upper estuary, reflecting enhanced sedimentation in this area due to removal of sediments;
- (2) An increase in the chlorophyll-a concentration in the river water, as mentioned before (see Table 8.1);
- (3) An increase in pH levels, all over the estuary, during winter, and a less pronounced pH minimum in the upper estuary during spring and summer. The latter feature is related to the fact that most of the nitrification has already taken place in the river water in 1995/96;
- (4) A general increase in the redox potential of the upper estuary, all over the year. This is indicated by the quicker restoration of dissolved oxygen in the upper estuary (note that the anoxic zone has disappeared), the shift of the nitrate maximum to lower salinities, and by the lower concentrations of ammonium in the upper estuary during spring and summer. The spring and summer profiles of nitrate and ammonium indicate that nitrification was confined to the upper estuary in 1987, but shifted to the river and the low-salinity zone in 1995 (note the difference in nitrate concentrations in the incoming river water). This is in keeping with the conclusion of Billen (1975) that the nitrifying population in the Scheldt estuary is mostly made up of freshwater bacteria.

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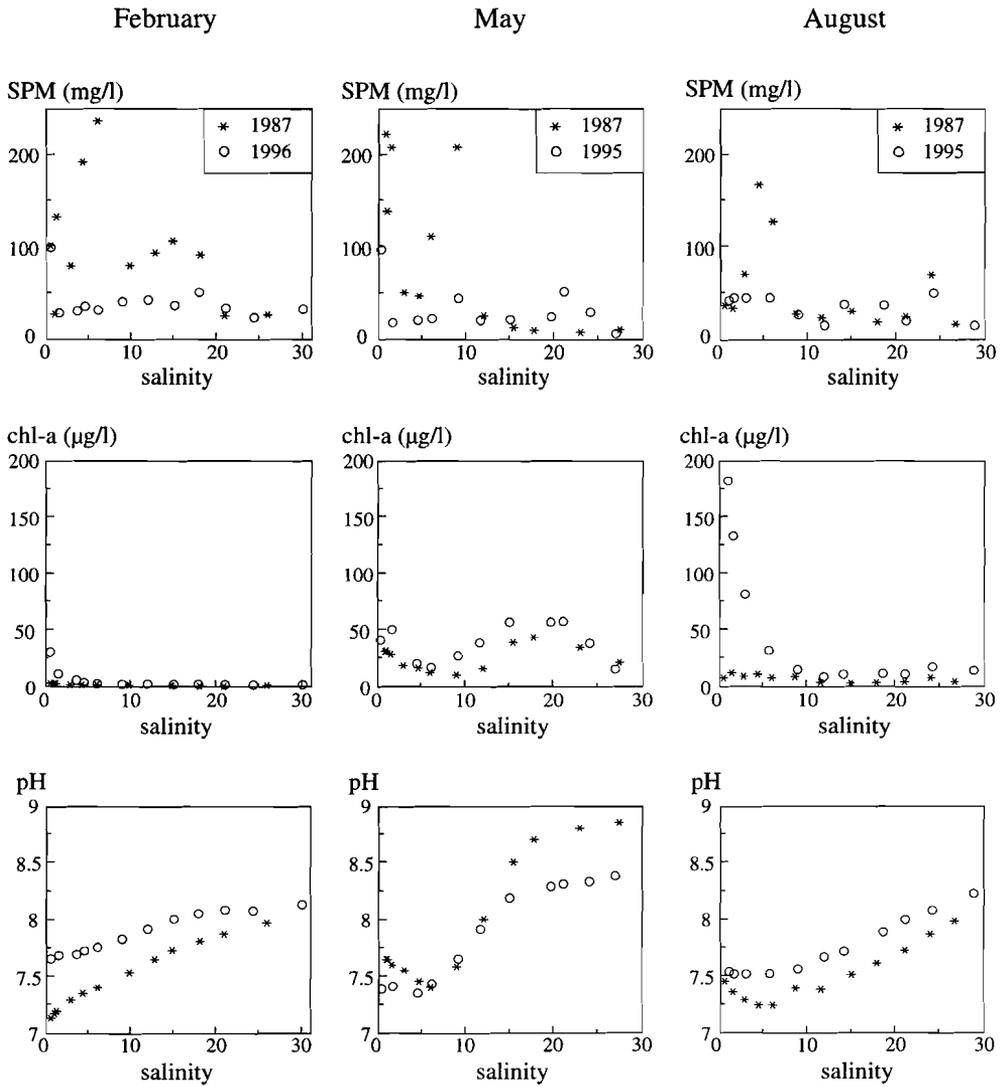


Fig. 8.1. Seasonal profiles of general water quality variables in the Scheldt estuary in 1987 and 1995/96.

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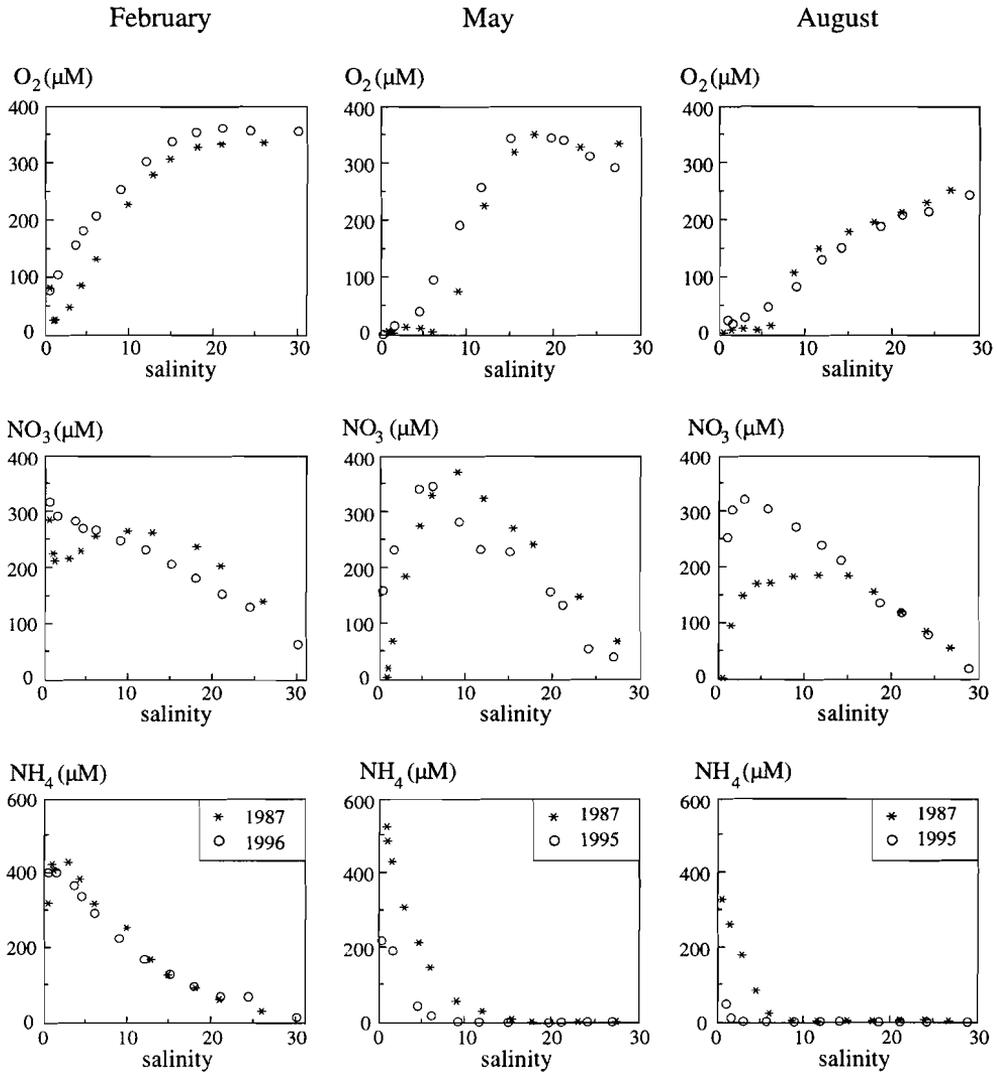


Fig. 8.1. (continued)

8.4.2. Developments in trace metal geochemistry

Seasonal profiles of dissolved and particulate Cd, Cu, and Zn in 1987 and 1995/96 are given in Fig. 8.2. The geochemical processes inferred from these profiles are discussed in chapters 2 and 3. Here, the emphasis will be on the differences between the profiles in 1987 and 1995/96. The winter profiles of dissolved Cd show a reduction of the Cd peak in 1995, which can be explained by a reduction of the Cd load of the estuary (as confirmed by the particulate Cd profiles). During spring, the Cd profiles of 1987 and 1995 are similar, Cd mobilisation being counteracted by primary production (see the chlorophyll-a profiles in Fig. 8.1). An important difference is observed in the summer profiles of dissolved Cd, with rapid mobilisation in 1995, whilst mobilisation starts later (i.e. at higher salinity) in 1987. This observation is related to the improved redox potential of the upper estuary during the summer of 1995, leading to faster oxidation of metal sulphides (e.g. derived from resuspension of reduced sediments) in the upper estuary. For Cu, enhanced mobilisation in the upper estuary is observed in 1995/96 for every season studied. The dissolved Zn profiles in 1995/96 are similar to those in 1987. Considering the fact that the Zn content of the suspended matter has decreased substantially, it may be concluded that the mobilisation of Zn has increased between 1987 and 1995.

Considering the trace metal composition of the suspended matter, the upper estuary features lower contents of particulate Cd, Cu, and Zn in 1995/96. This can easily be explained by a reduction of trace metal inputs into the estuary which has taken place between 1987 and 1996. In the lower estuary, however, the particulate trace metal contents in 1995/96 are equal to, or even higher than, those in 1987. This observation is related to the removal of polluted sediments in the upper estuary (Salden, 1998). Between 1992 and 1996, some 2.5 Mton of silty sediment has been dredged from the entrance channels to the sluices of Antwerp harbour, twice as high as the external supply of mud to this area from the Scheldt river and the North Sea. The difference is explained by an internal source, namely erosion of ancient sediments in the upper estuary. Part of these sediments, which are highly contaminated, remain in suspension and are transported to the lower estuary. Mixing of this ancient material with recent suspended matter may explain the relatively high trace metal contents in the lower estuary in 1995/96.

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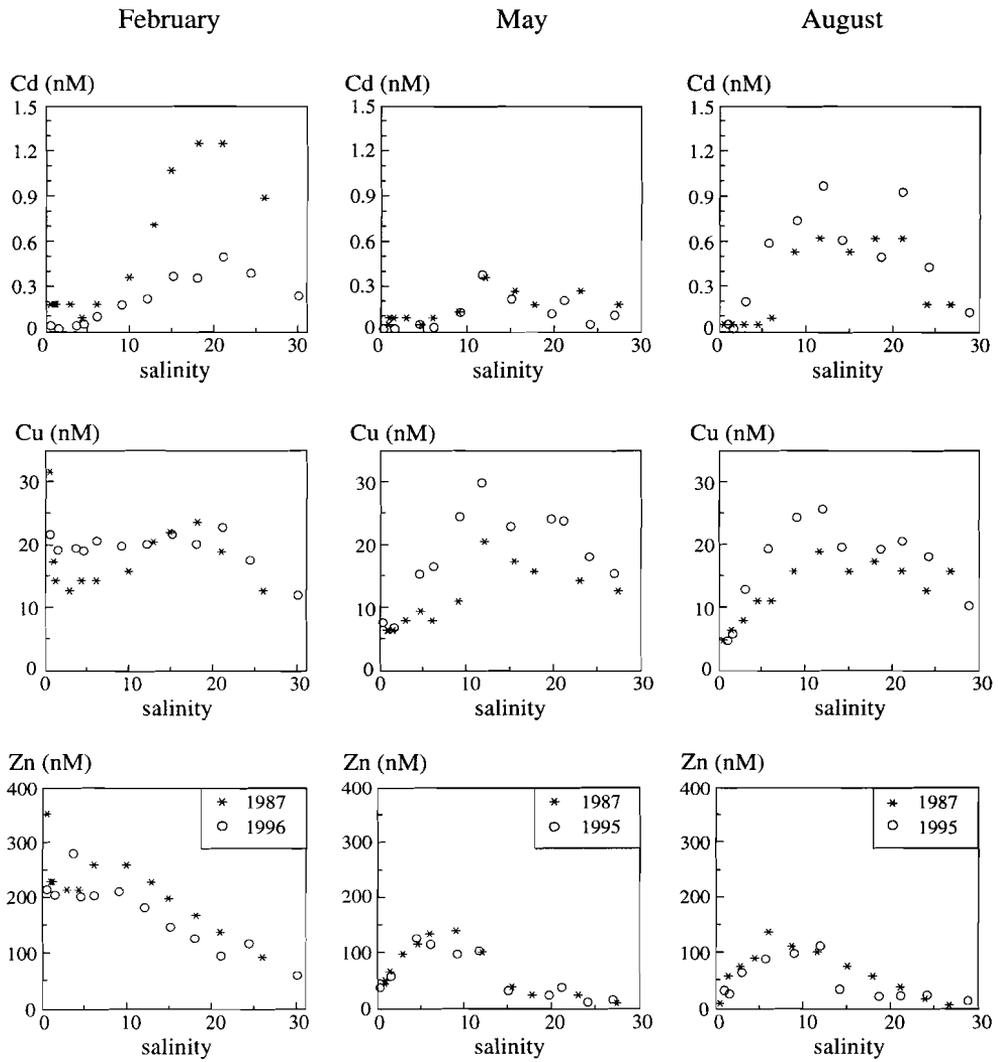


Fig. 8.2a. Seasonal profiles of dissolved Cd, Cu, and Zn in the Scheldt estuary in 1987 and 1995/96.

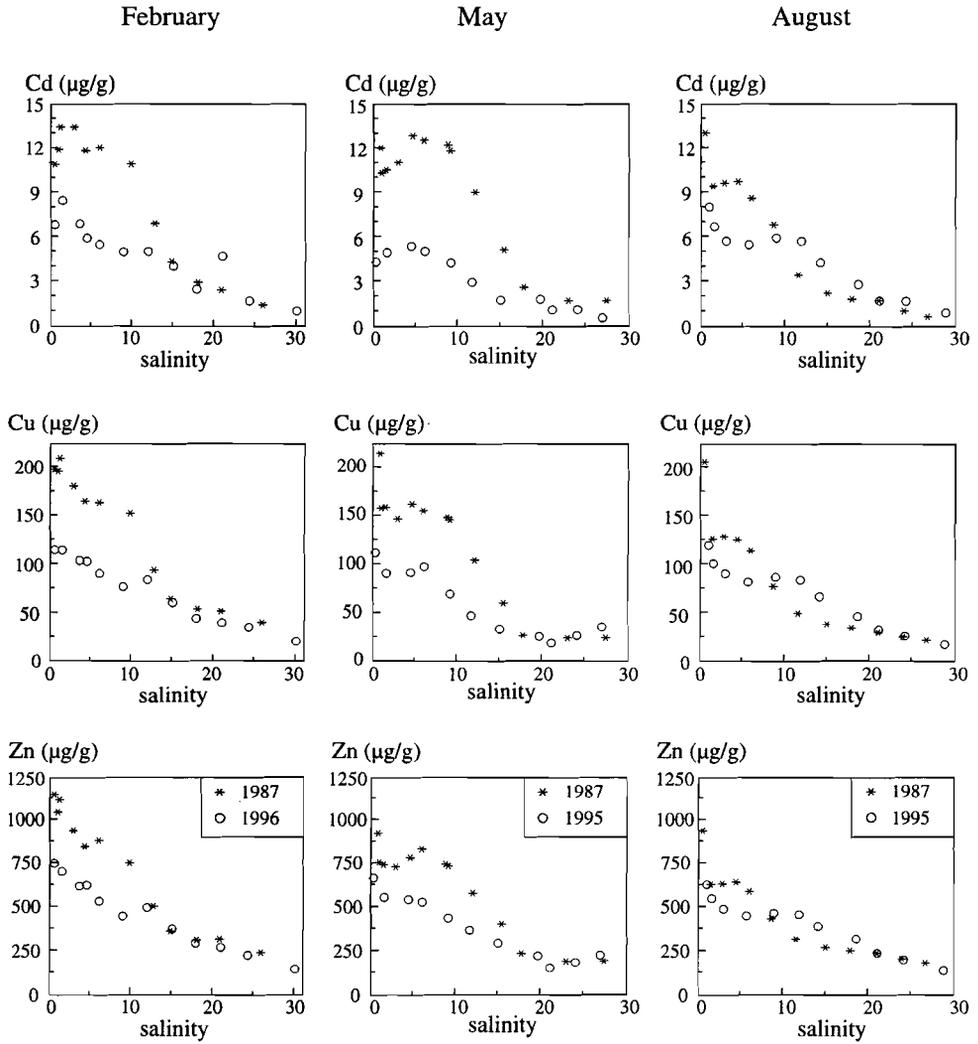


Fig. 8.2b. Seasonal profiles of particulate Cd, Cu, and Zn in the Scheldt estuary in 1987 and 1995/96.

8.5. Future perspectives

In the previous section, it has been demonstrated that the redox chemistry of the Scheldt river has improved between 1987 and 1996. However, it is also clear that full restoration of dissolved oxygen in the river water is still far beyond reach. The reduction in organic load of the river water has mainly resulted in increased nitrification in the river water itself. Only after conversion of ammonium to nitrate, the dissolved oxygen concentration is expected to increase further in the river water and the upper estuary.

It should also be stressed here that, under unfavourable conditions (low river flows and high temperatures), severe anoxia may still occur in the upper estuary. Extensive anoxic zones were observed in April and June 1996 (up to salinity 9!), following a long period of low river discharges. As an example, the estuarine profiles for the June 1996 cruise are compared to those of the May 1995 cruise in Fig. 8.3. This comparison readily shows the impact of the redox chemistry on the distribution of ammonium, nitrate, the pH, and dissolved Cd, Cu, and Zn within the estuary. Typical features of the June 1996 cruise are the high concentration of ammonium and the low concentration of nitrate in the incoming river water, the pH minimum in the upper estuary, and the slow mobilisation of Cd, Cu, and Zn in the estuary (note the shift of the dissolved metal peaks to higher salinities in June 1996). These features are all related to the presence of an anoxic zone in the river water and the upper estuary, as discussed before.

In conclusion, this comparative study has confirmed our general view that trace metal mobilisation in the Scheldt estuary is related to the evolution of the redox potential in the water column. The increase in redox potential of the river water, brought about between 1987 and 1996, has resulted in increased mobilisation of Cd, Cu, and Zn in the upper estuary. Therefore, the decrease in trace metal inputs to the Scheldt river, which is reflected by the fluvial suspended matter composition, is not reflected by the dissolved metal concentrations. Over the time span considered, the dissolved metal concentrations in the upper estuary have remained the same (Zn) or have even increased during the summer (Cd) or over the year (Cu). These findings indicate that complete restoration of the dissolved oxygen concentration, a major goal of estuarine management, will further increase the dissolved trace metal concentrations in the (upper) Scheldt estuary. This unintended effect of water quality improvement can be lifted by removal of the polluted sediments in the upper estuary and by a further reduction of the trace metal inputs into the Scheldt river and its tributaries.

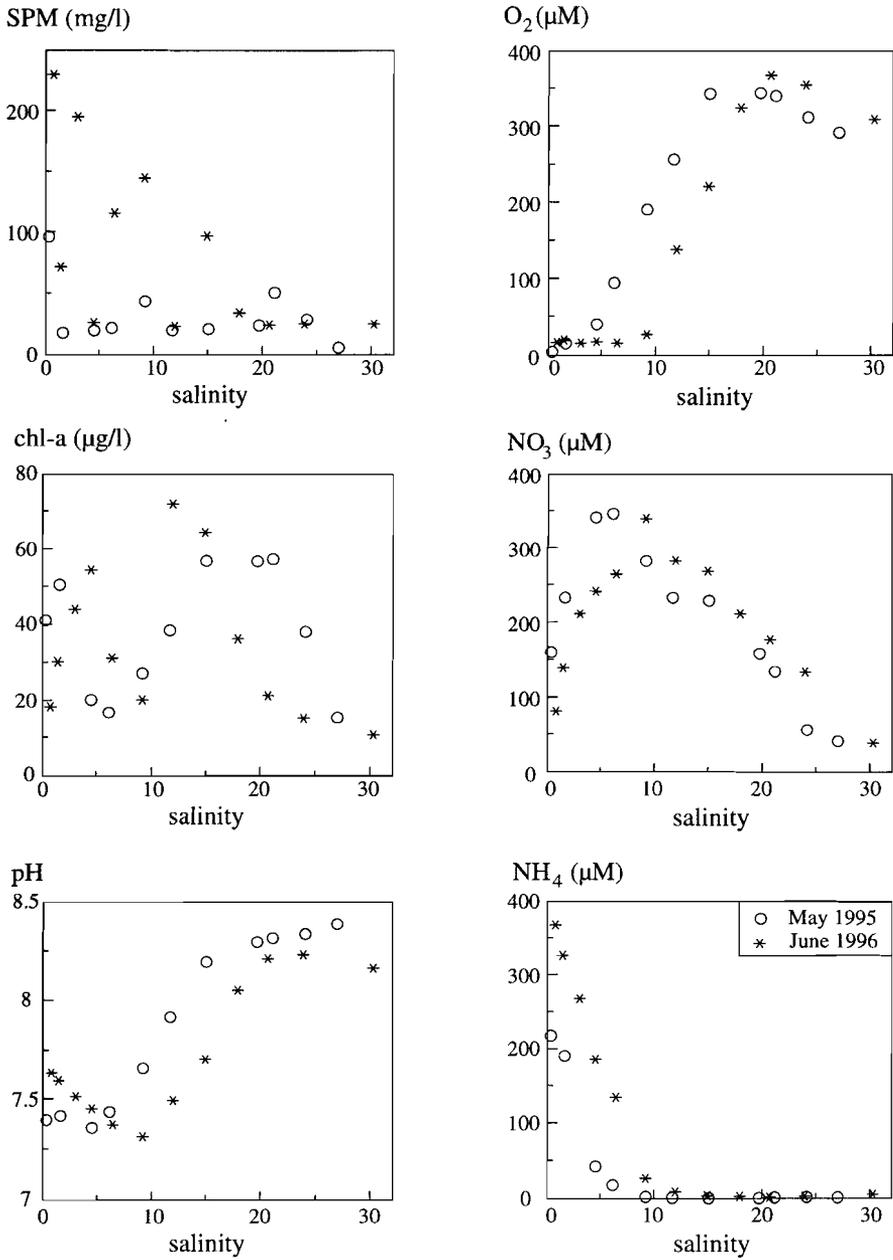


Fig. 8.3a. Profiles of general water quality variables in the Scheldt estuary in May 1995 and June 1996.

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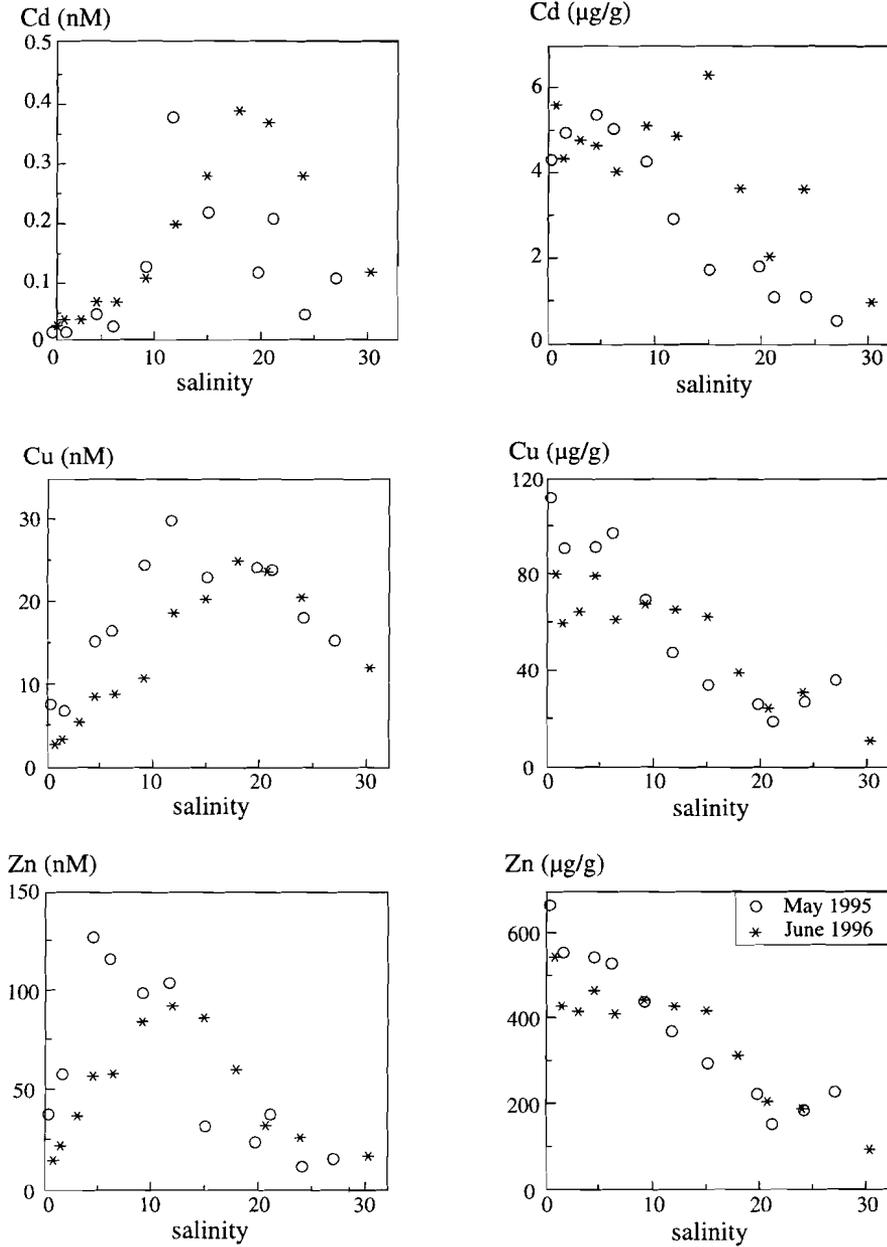


Fig. 8.3b. Profiles of dissolved and particulate Cd, Cu, and Zn in the Scheldt estuary in May 1995 and June 1996.

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Curriculum Vitae

Gertjan Zwolsman werd geboren op 2 maart 1961 in Ermelo. Hij behaalde zijn VWO-diploma in 1979 aan College Nassau-Veluwe te Harderwijk. In datzelfde jaar begon hij aan de studie Scheikunde aan de Universiteit Utrecht. Het kandidaatsexamen werd afgelegd in 1983 en het doctoraalexamen in 1987 (cum laude). Het doctoraalexamen omvatte de disciplines anorganische chemie en geochemie. Hierna werd begonnen met het promotieonderzoek bij de toenmalige Dienst Getijdewateren (thans RIKZ). Het veldwerk vond plaats in de periode 1987-1989. In 1989 en 1990 was hij als toegevoegd onderzoeker werkzaam op het Instituut voor Aardwetenschappen (Universiteit Utrecht). Gedurende deze periode werd de basis gelegd voor dit proefschrift. Van 1991 tot 1994 was hij werkzaam als projectleider waterkwaliteit op het Waterloopkundig Laboratorium. Sinds september 1994 is hij als senior medewerker en staflid verbonden aan het Rijksinstituut voor Integraal Zoetwaterbeheer en Afvalwaterbehandeling (RIZA), afdeling Watersystemen-Transport (WST), te Dordrecht.