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102

henk leenaers

the dispersal of metal mining wastes in the catchment of the river geul (belgium - the netherlands)

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SAMENVATTING

Inleiding en probleemstelling

De metaalmijnbouw heeft geleid tot de inbreng van zware metalen in een groot aantal riviersystemen. De daaropvolgende verspreiding van zware metalen wordt voor een belangrijk deel bepaald door de binding die de metalen aangaan met slib- en bodemdeeltjes en door de transportbanen van deze deeltjes in het het alluviale deel van riviersysteem. Nadat de slibgebonden metalen worden opgenomen in een van de hydrologische subsystemen, zoals de waterbodem en de oevergronden, blijven ze onderhevig aan processen van geomorfologische, chemische en hydrologische aard. Na sedimentatie kunnen slib en de daaraangebonden metalen worden geremobiliseerd door fysische aantasting van de rivierbodem of -oevers. Chemische processen kunnen ertoe bijdragen dat de bindingsvorm van de metalen verandert of dat ze oplossen en toetreden tot aangrenzende wateren (grond-, bodem- of oppervlaktewater) of worden opgenomen door planten. Geremobiliseerde metalen kunnen, gebonden aan slib of in opgeloste vorm, opnieuw worden getransporteerd en weer neerslaan of worden afgezet in zowel de rivierbedding als in de overstromingsvlakte. Tussen al deze processen treden complexe interacties op die bovendien van aard kunnen veranderen in de loop der tijd. Een beter begrip van de dynamische omstandigheden (het transport, de sedimentatie en remobilisatie) waaraan zware metalen in een riviersysteem worden blootgesteld, is van groot belang voor de voorspelling van het gedrag en de gevaren van zware metalen in een fluviatiele omgeving.

Het onderzoeksgebied en de doelstellingen

Het onderzoek werd uitgevoerd in het stroomgebied van de grensoverschrijdende rivier de Geul. De Geul ontspringt in het noordwesten van België en stroomt door het mergelland van Zuid Limburg naar de Maas. In de omgeving van de Belgische plaatsen Plombières en Kelmis werd vanaf de late Middeleeuwen tot het midden van deze eeuw lood- en zinkerts gewonnen en verwerkt. Door de lozing van proceswater en de opslag van mijnafval op de oevers van de Geul werden grote hoeveelheden zware metalen ingebracht in het riviersysteem. De daaropvolgende verspreiding heeft geleid tot verhoogde concentraties van zware metalen in het rivierslib en de oevergronden. De aanwezigheid van zware metalen kan een bedreiging vormen voor mens en dier in deze omgeving. Door het natuurlijk meanderende karakter van de Geul worden oude sterk verontreinigde sedimenten voortdurend opnieuw op transport gesteld en uiteindelijk afgevoerd naar de Maas. De Geul draagt daarmee bij aan de verontreiniging van deze, als bron van drinkwater functionerende, op een na grootste rivier in Nederland.
Het doel van deze studie omvatte een kwantitatief onderzoek van de verspreiding van zware metalen in het stroomgebied van de Geul. Een groot aantal van de relevant geachte processen werd bestudeerd, waarbij de nadruk lag op een samenhangende, geografische, benadering. Uiteindelijk werd een poging gedaan om met het verworven inzicht en

het verzamelde gegevensbestand een balans van sediment en zware metalen op te stellen. Binnen dit algemeen geformuleerde doel werden een aantal meer specifieke doelstellingen onderscheiden:

(1) het lokaliseren van de bronnen van zware metalen;
(2) het analyseren van de hydrologische factoren die van invloed zijn op het transport van slib en zware metalen en het kwantificeren van de vracht van deze stoffen;
(3) het in kaart brengen van overstromingsgebieden, en de verontreiniging van de oevergronden;
(4) het bepalen van de sedimentatiesnelheid van verontreinigd slib en de bergingscapaciteit van de overstromingsvlakte;
(5) het analyseren van de bindingsvormen van zware metalen in slib en bodem;
(6) het schatten van de consequenties van de aanwezigheid van zware metalen voor het milieu

Het transport van zware metalen

De relaties tussen het debiet, de concentraties van zwevend slib en de daaraan gebonden zware metalen, werden in detail onderzocht voor een hoogwaterperiode in maart 1988. Uit de onderzoeksresultaten bleek dat het debiet slechts een beperkte invloed heeft op het transport van zwevend slib en de metalen lood, zink en cadmium. Tijdens afvoerpieken is de hoeveelheid getransporteerd slib in hoge mate afhankelijk van het debiet, maar in de perioden tussen afvoerpieken wordt de kwaliteit en kwantiteit van het getransporteerde slib veeleer bepaald door de sterk variërende activiteit van de verschillende bovenstroomse bronnen van sediment. Door waarnemingen van meerdere hoogwaterperioden te combineren, was het desondanks mogelijk signifikante regressiecurves op te stellen voor de relatie tussen het debiet enerzijds en slibconcentraties en metaalgehalten anderzijds. Deze curves, met correlatiecoëfficiënten in het bereik van 0.63 tot 0.92, werden gebruikt om het jaarlijks transport van slib en zware metalen te berekenen. Uit de resultaten blijkt dat een groot deel (25-30%) van het jaarlijks transport van lood (13.9 ton), zink (70.5 ton) en cadmium (0.4 ton) plaatsvindt tijdens de enkele dagen met een debiet groter dan 10 m^3/s. In die perioden is 77-98% van de vracht van metalen gebonden aan het zwevend slib.

De kwaliteit van in de overstromingsvlakte afgezet rivierslib

Het door de Geul getransporteerde slib is een belangrijk medium voor de verspreiding van zware metalen door het riviersysteem. Middels het slib vindt uitwisseling van materiaal plaats tussen de rivierbedding, waarin het transport plaatsvindt, en de overstromingsvlakte, waar het slib tijdelijk wordt opgeslagen totdat het door oeveraantasting opnieuw op transport wordt gesteld. Direkt na een aantal hoogwaterperioden werden in de overstromingsvlakte monsters genomen van recentelijk afgezet rivierslib. Uit de analyseresultaten bleek dat er geen systematische relatie bestaat tussen het gehalte aan zware metalen in

deze monsters en hun korrelgrootteverdeling. Zowel in de fractie < 63 µm als in de fractie > 63 µm werden sterk verhoogde concentraties van lood, zink en cadmium aangetroffen. Voor lood en zink wordt in 80% van de monster de B-norm overschreden en in 25% van de gevallen de C-norm. Voor cadmium wordt de C-norm slechts in één monster overschreden, maar in bijna 40% van de monsters liggen de concentraties boven de B-norm. Met betrekking tot de chemische bindingsvorm van deze metalen kon eveneens geen verschil tussen de korrelgroottefracties worden aangetoond.
In stroomafwaartse richting neemt de totale hoeveelheid aan zware metalen in de slibmonsters af volgens een exponentieel verband met de afstand tot de bron. Over hetzelfde traject verandert de verdeling van zware metalen over de verschillende chemische bindingsvormen. Door menging met relatief schoon slib en door de interacties tussen het slib en het water neemt het aandeel van de metalen, dat in een relatief mobiele vorm (uitwisselbaar, carbonaatgebonden en gemakkelijk reduceerbaar) aanwezig is, snel toe. De mate waarin dit proces optreedt is afhankelijke van de chemische reactiviteit van de zware metalen en is het grootst voor het relatief mobiele element cadmium. Door de verandering van het chemisch voorkomen van de zware metalen in stroomafwaartse richting, wordt het positieve effect van exponentieel afnemende totaalgehalten deels tenietgedaan.

De invloed van veranderend landgebruik op de verspreiding van zware metalen

Het landgebruik heeft in Nederland sinds de jaren '50 een aantal veranderingen ondergaan. De omvang van het stedelijk gebied en het wegennet is sterk toegenomen en in de landbouw heeft een schaalvergroting en modernisatie plaatsgevonden. Deze veranderingen hebben geleid tot een afname van de capaciteit van het landschap om water te laten infiltreren en te bufferen. In het Zuidlimburgse heuvelland heeft dit geleid tot een toename van de hoeveelheid oppervlakkig afstromend water, waardoor meer wateroverlast kon optreden in stedelijke gebieden en de bodemerosie op de akkers toenam.
Uit een statistische analyse van neerslag- en afvoerreeksen bleek dat de afvoer van de Geul eveneens wordt beïnvloed door deze veranderingen in het functioneren van de hydrologische kringloop. Na een regenbui wordt in de huidige situatie voor de Geul een hogere piekafvoer geregistreerd dan in de jaren vijftig. De frequentie van hoge afvoeren is om die reden toegenomen, evenals de omvang van het gebied dat regelmatig wordt overstroomd.
Tijdens hoge afvoeren verlegt de Geul haar bedding door aantasting van de oevers. Door een reeks luchtfoto's uit de periode 1949-1985 met elkaar te vergelijken, kon worden vastgesteld dat de snelheid waarmee dit gebeurt is toegenomen en plaatselijk kan oplopen tot 5 meter per jaar. De versnelde aantasting leidt ertoe dat oude, sterk verontreinigde sedimenten - daterend uit de periode van actieve mijnbouw - opnieuw door het riviersysteem gaan circuleren. Vergelijking van de kwaliteit van recentelijk afgezet slib met die van de toplaag van de bodem in de overstromingsvlakte, toonde aan dat het recente slib in hogere mate is belast met zware metalen en daarmee een bedreiging

vormt voor de kwaliteit van de oevergronden.

Het karteren van overstromingsgebieden met behulp van een Digitaal Terrein Model

De processen die bijdragen tot de ontwikkeling van een overstromingsvlakte hebben een relatie met de hoogteligging van het terrein. De snelheid waarmee slib wordt afgezet op de oevergronden is afhankelijk van de overstromingsfrequentie, en de kwaliteit van het gedeponeerde slib is afhankelijk van de stroomsnelheid tijdens sedimentatie. Om die reden kan bij het bestuderen van deze processen naast geomorfologische kaarten en bodemkaarten, gebruik worden gemaakt van een Digitaal Terrein Model (DTM) .
Uitgaande van de informatie op de hoogtekaarten van de Topografische Dienst werden verschillende interpolatiemethoden gebruikt voor het construeren van een DTM van een deel van het Geuldal. Het fitten van mathematical splines gaf de meest betrouwbare resultaten. Door een aantal sterk vereenvoudigde verhanglijnen te construeren was het mogelijk overstromingsgebieden te begrenzen in het DTM. Verificatie van de ligging van een aantal overstromingsgebieden vond plaats met behulp van foto's die waren genomen tijdens een hoogwaterperiode in october 1986. De overstromingskaart bleek een sterk verklarend karakter te hebben met betrekking tot de concentraties van zware metalen in de bodem: 44-65 procent van de variantie in de concentraties van zware metalen in de bodem kon worden verklaard door de monsters te groeperen volgens de kaarteenheden op de overstromingskaart.

Kwantitative methoden voor het karteren van bodemverontreiniging

De hierboven besproken methode voor het karteren van overstromingsgebieden en bodemverontreiniging geeft geen informatie over de ruimtelijke variabiliteit van het gekarteerde fenomeen binnen een kaarteenheid. Er zijn een aantal interpolatiemethoden beschikbaar waarmee wel een uitspraak over de ruimtelijke variabiliteit kan worden gedaan. In de hoofdstukken 11 en 12 worden een aantal van deze methoden met elkaar vergeleken en wordt - op twee ruimtelijke schaalniveaus - hun geschiktheid voor het karteren van de bodemverontreiniging in het Geuldal geevalueerd.
In een geomorfologische eenheid werden op een regelmatig netwerk en op onderlinge afstanden van 5 meter een groot aantal bodemmonsters genomen. Drie subsets van monsters werden gebruikt om de zinkconcentraties te schatten op de lokaties in een andere subset, waar het werkelijke zinkgehalte van de bodem bekend was. Uit een statistische analyse van de interpolatiefouten bleek dat geostatistische methoden, die gebruik maken van informatie omtrent de ruimtelijke correlatiestructuur van de onderzochte variabele, beter in staat zijn een betrouwbaar ruimtelijk model van zinkconcentraties in de bodem te construeren dan andere veel gebruikte methoden. Op dit schaalniveau kon het ruimtelijk model bovendien belangrijk worden verbeterd door tijdens de interpolatie gebruik te maken van extra informatie met betrek-

king tot de hoogteligging van een niet bemonsterde lokatie. Daartoe werd gebruik gemaakt van de geostatistische interpolatiemethode die bekend staat als co-kriging.
De merites van co-kriging werden verder getest op het schaalniveau van de overstromingsvlakte. Opnieuw werden een groot aantal monsters genomen, waarvan eveneens een deel opzij werd gezet voor het valideren van de ruimtelijke modellen van zinkgehalten in de bodem. De aanvullende hoogtepunten werden gecorrigeerd voor het effect van het lengteprofiel, hetgeen de hoogte t.o.v. de rivierbedding opleverde (Relative Elevation: RE). Drie methoden werden met elkaar vergeleken: (1) lineaire regressie van RE versus het zinkgehalte, (2) kriging (zonder aanvullende hoogte-informatie) en (3) co-kriging (met aanvullende hoogte-informatie). De resultaten van dit onderzoek maakten duidelijk dat co-kriging kleinere schattingsfouten van het zinkgehalte in de bodem op niet bemonsterde lokaties oplevert dan lineaire regressie of kriging. Bovendien levert co-kriging geringere schattingsvarianties dan kriging zonder aanvullende informatie. Op deze wijze werd aangetoond dat informatie met betrekking tot het proces dat de oorzaak is van de verontreiniging, namelijk het bestand van hoogtepunten, kan worden gebruikt om het ruimtelijk patroon van de verontreiniging kwantitatief in kaart te brengen.

De depositie en berging van sediment in de overstromingsvlakte

Door de voortdurende aanvoer van slib tijdens overstromingen is de kwaliteit van de oevergronden van de Geul onderhevig aan veranderingen in de tijd. Gezien de hoge concentraties van zware metalen in het recentelijk afgezette slib is het van belang inzicht te verwerven in de snelheid waarmee dit proces plaatsvindt en in de bergingscapaciteit van de overstromingsvlakte. Cesium-137 (^{137}Cs), aanwezig in het milieu door het bovengronds testen van nucleaire wapens tussen 1954 en 1963 werd gebruikt als tracer voor de bepaling van sedimentatiesnelheden. Door het kernreacterongeval te Tsjernobyl in 1986 werd een nieuwe hoeveelheid ^{137}Cs in het milieu gebracht, waardoor het mogelijk werd dezelfde waarnemingen ook op een korte tijdschaal te doen.
Door metingen van het ^{137}Cs-gehalte van bodemmonsters genomen op verschillende diepten beneden maaiveld kon worden vastgesteld dat de sedimentatiesnelheden in het Geuldal variëren tussen 0.4 en 2.7 cm/jaar. De sedimentatiesnelheid in de periode 1986-1988 blijkt bovendien aanmerkelijk hoger te zijn dan die in de periode 1963-1986. In een studiegebied van 58.3 ha dat in detail werd bestudeerd bleek dat de bovenste 40 cm van het bodemprofiel, afgezet gedurende de afgelopen 30-45 jaar, wordt gekenmerkt door hogere concentraties van zware metalen dan het deel van het profiel op grotere diepte. Deze recente afzettingen zijn afkomstig van de erosie van verontreinigde oevers in het bovenstroomse deel van het dal.
Met behulp van de interpolatietechniek kriging werden kaarten gemaakt van de bodemverontreiniging op 10, 20, 30 en 40 cm diepte. Verontreinigingskaarten werden gebruikt voor de berekening van de totale hoeveelheid zware metalen die in het studiegebied van 58.3 ha zijn opgeslagen. De berekeningen lieten zien dat in de bovenste 100 cm van dit gebied 88.8 ton lood, 372.6 ton zink en 1 ton cadmium ligt opges-

lagen. Van deze hoeveelheid kan slechts 2-9% worden toegeschreven aan de 'natuurlijke' aanwezigheid van zware metalen.

De balans van zware metalen

Gebruikmakend van de gegevens met betrekking tot het transport, de sedimentatie, de berging en de mechanische remobilisatie van met zware metalen belast slib- en bodemmateriaal, werden voor het alluviale deel van het stroomgebied in Nederland balansen opgesteld van sediment en de metalen lood, zink en cadmium. Volgens de berekeningen bevindt zich in de overstromingsvlakte ca. $47.580 \cdot 10^6$ ton bodemmateriaal, waaraan 7461 ton lood, 19205 ton zink en 84 ton cadmium wordt gebonden. Per jaar wordt er door grensoverschrijdend transport 5325 ton sediment, 7702 kg lood, 57400 kg zink en 171 kg cadmium aangevoerd uit België, terwijl er 30565 ton sediment, 13941 kg lood, 70475 kg zink en 435 kg cadmium wordt afgevoerd naar de Maas. De herverdeling van materiaal in het stroomgebied, door met name sedimentatie en oeveraantasting, leidt tot een netto jaarlijkse afvoer van materiaal uit de overstromingsvlakte van 22925 ton sediment, 5392 kg lood, 11628 kg zink en 3.8 kg cadmium. Van de totale hoeveelheid lood, zink en cadmium die per jaar in het Nederlandse deel van de rivierbedding wordt gebracht, kan 66, 47 en 39 % respectievelijk worden verklaard door grensoverschrijdend transport, 32, 52 en 59 % respectievelijk door oeveraantasting en slechts 1-2 % door bijdragen van zijrivieren, aanvoer via hellingprocessen en aanvoer vanuit de alluviale aquifer.

Indien de vracht van zware metalen door de Geul te Meerssen wordt vergeleken met de vracht van de Maas te Eijsden, dan blijkt dat de Geul een bijdrage levert met een omvang van respectievelijk 9.7, 7.8 en 4.7 % van de vrachten van lood, zink en cadmium door de Maas. Een zelfde berekening m.b.t. de lozing van afvalwater levert de volgende percentages: de afvoer van zware metalen door de Geul naar de Maas heeft een omvang van 19.4, 16.9 en 2.3 % van de totale hoeveelheid in Nederland geregistreerde lozingen (dus niet alleen op de Maas) van respectievelijk lood, zink en cadmium via afvalwater.

De schatting van gezondheidsrisico's

De aanwezigheid van zware metalen in het slib, het water en de bodems van de Geul kan negatieve effecten hebben op de gezondheid van de mensen en dieren die in het Geuldal verblijven. Een eenvoudig model werd gebruikt om een schatting te maken van de risico's die de aanwezigheid van lood en cadmium in de bodem met zich meebrengen. De geschatte hoeveelheid ingenomen metalen werd vergeleken met grenswaarden die door de Wereld Gezondheids Organisatie worden opgegeven, de zgn. A.D.I.-waarden (Acceptabel Daily Intake).

Volgens een reëele benadering, waarbij wordt aangenomen dat beperkte hoeveelheden verontreinigd materiaal worden geconsumeerd, bleek de A.D.I. voor jonge kinderen te worden overschreden in gebieden waar de bodem loodgehalten bevat boven de B-waarde. Deze gebieden nemen ongeveer 43 % van de oevergronden in beslag en liggen vrijwel alle ten zuiden van Wijlre. De A.D.I. voor loodinname door volwassenen wordt in de reëele benadering nergens overschreden. De A.D.I. voor cadmiuminname door zowel kinderen als volwassenen wordt bij een reëele benadering evéneens nergens overschreden.

1 INTRODUCTION

1.1 Problem definition

The mining industry can be an important point source of contaminants in the environment (e.g. Adriano, 1986; Förstner & Wittman, 1983). Historic metal mining has caused the widespread dispersal of heavy metals in many fluvial systems (e.g. Lewin & Macklin, 1987; Moore et al., 1987; Rang et al., 1986; Yim, 1981; Mann & Lintern, 1983; Reece et al., 1978; Jones, 1986; Ward et al., 1977). Sediments are important carriers of heavy metals and when they become incorporated in one of the fluvial storage compartments, they have not entered a static environment. The subsequent cycling of sediments in a fluvial system is highly related to hydrological, geomorphological and chemical phenomena (e.g. Salomons & Förstner, 1984; Graf, 1985). After deposition, sediments and associated metals may be remobilized from the channel bottom or channel banks by mechanical erosion (Lewin et al., 1977; Marron, 1986). Within the sediment reservoirs chemical processes may cause the metals to migrate between the various solid storage compartments and can also lead to it being lost to enter ambient waters and biota (Chester, 1987). Remobilized metals may be transported as clastic sediments or solutes to be deposited or precipitated in a range of sedimentary environments both within the floodplain domain and the stream domain (Lewin et al., 1977). All these phenomena interact and vary in space and time. Their result is a dynamic spatial distribution of heavy metals within an alluvial area. A proper understanding of the dynamics of transportation, deposition and remobilization is essential for the prediction of the fate of sediment-bound heavy metals in a fluvial system.

1.2 Research objectives

The study area covers the catchment of the transboundary river Geul, that flows from northeastern Belgium into the Netherlands province of Limburg where it eventually flows into the Meuse (see Figure 2.1). Ever since the Middle Ages, important occurrences of metal ore have been exploited in the Belgian part of the catchment, near the towns of Plombières and Kelmis. The fluvial dispersal of mining wastes has caused enhanced concentrations of lead, zinc and cadmium in aquatic sediments and floodplain soils in both countries. These metals may affect the health of plants and animals that inhabit the riperian areas. Moreover, as the Geul continues to migrate across its floodplain, contaminated sediments are reworked and ultimately discharged into the River Meuse, which is an important source of drinking water in The Netherlands.
The objective of this study is to investigate quantitatively the dispersal of metal mining wastes in this catchment. An attempt is made to study a wide variety of relevant processes and to analyse their interactions within the complex entity of a fluvial system. Eventually, the data collected and knowledge obtained may be used to compile mass balances of sediments and heavy metals in the alluvial

area. Within this context this study aims at:

(1) identifying the sources of heavy metals;
(2) analyzing the hydrological factors that govern the mechanisms of metal transport and quantifying the transport rates of sediments and of sediment-associated and dissolved heavy metals;
(3) quantitative mapping of areas that are susceptible to flooding and of metal concentrations in floodplain soils;
(4) determining rates of sediment deposition and the mass storage of solid-bound heavy metals in the floodplains;
(5) analyzing the metal associations in aquatic sediments;
(6) environmental assessment of enhanced metal levels in the sediments, soils and surface waters of this fluvial system.

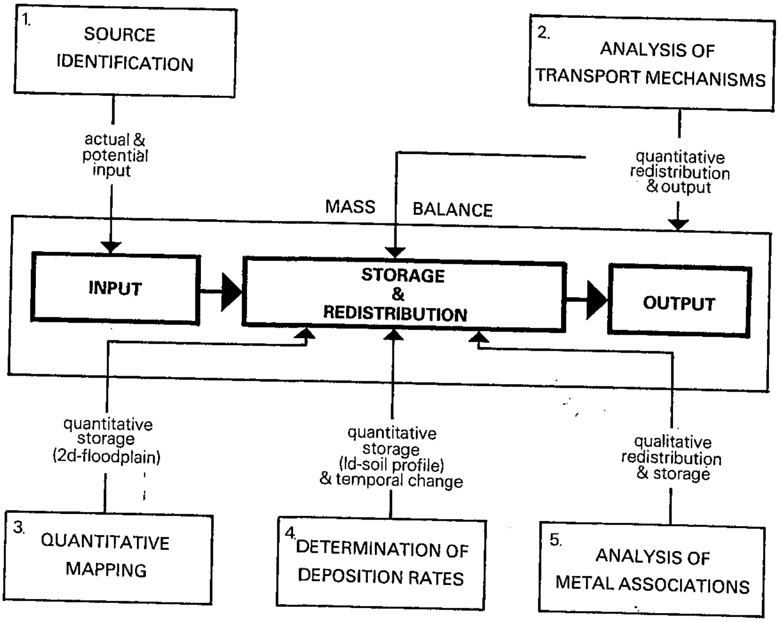


Figure 1.1 Schematic representation of the contribution of the research objectives to the compilation of an alluvial mass balance of heavy metals. (N.B.: the numbers refer to the research objectives listed in section 1.2.)

The above aims are, when achieved, all essential within the context of a mass balance study of the alluvial area (see Figure 1.1). The identification of the sources of heavy metals may provide insight into the current and potential availability of heavy metals for cycling in this fluvial system. Knowledge about the hydrological transport mechanisms may contribute to the understanding of how mass is exchanged between the metal sources and the transporting channel and how metals subsequently start cycling through the fluvial environment. The activity of the sources and the efficiency of the transport mechanism together have a quantitative control over the rate at which heavy metals enter

the alluvial domain, are redistributed thereafter and eventually leave the fluvial system. Therefore, they are thought to govern the input and output terms of the alluvial mass balance.
The (re)distribution of sediments and solid-bound heavy metals within the alluvial domain depends on the geomorphological processes that are active within the floodplain area during extreme events (i.e. floods).

Therefore, the areas that are susceptible to flooding and the pollution levels within those areas need to be mapped. Moreover, the local thickness of the contaminated soil layer will depend on the local rates of sediment deposition and erosion that may, in addition to spatial variations, exhibit considerable variations in time. Quantitative mapping techniques will be used to delineate flood zones and pollution zones in the 2-dimensional floodplain, and radio-active tracing methods will be used to relate the 1-dimensional vertical distribution of heavy metals in the soil profile to a time scale. This combined effort may provide a quantitative estimate of the total amount of heavy metals stored within the alluvial area and a qualitative estimate of the rate at which the processes of sediment deposition and remobilization take place.
In addition to estimating quantitatively the amount of heavy metals stored within the alluvial area, it is necessary to know how the metals are stored within sediments and soils, so as to be able to assess their environmental impact. The metal associations found may vary as a result of a.o. sediment-water interactions in the stream channel and diagenetic processes in the soil column. An attempt will be made to interpret the type of metal associations by taking into account the various phenomena that operate in the stream and floodplain domains.

1.3 Report structure

This thesis is a compilation of papers previously presented at scientific meetings and articles published in or submitted to international journals. References to these, in their current state slightly moderated, publications were replaced by references to chapters and paragraphs. A complete list of publications (including co-author(s) for some of them) is presented in Appendix 1. The first 6 chapters (including this introduction) were added later. Basic information on the characteristics of the study area and on the field and laboratory methods used were extracted from the original manuscripts and concentrated in seperate chapters, i.e Chapters 2 and 3 respectively. Chapters 4, 5 and 6 provide a brief (and incomplete) theoretical framework that may facilitate - to the nonspecialist - a proper understanding of the chapters following thereafter. Chapters 7-13 present the results of the investigations and they all end with a brief summary. Finally, some of the results presented in Chapters 7-13 are assembled and re-evaluated in a last synthetic chapter.
In Chapter 7 the fluvial transport of suspended sediments and dissolved and sediment-associated heavy metals is discussed. An attempt is made to identify the various sources of heavy metals and the annual mass transport is estimated. The variable quality of the sedi-

ments that are deposited on the floodplains during floods is evaluated in Chapter 8. Attention is paid to the influence of organic matter and grain size on total metal concentrations and the chemical phases of heavy metals are investigated. In addition, downstream changes of sediment quality are revealed. The effects of land use change on the discharge regime of the Geul and the dynamics of streambank erosion and sediment deposition are the subjects of Chapter 9. A quick quantitative technique for the delineation of flood zones is presented in Chapter 10, which also demonstrates the relation between floodplain geometry and soil pollution levels. Chapter 11 further explores this relation and aims at comparing various spatial prediction methods for large scale mapping of floodplain soil pollution. Chapter 12 is the logical extension of Chapters 10 and 11 in the sense that the spatial prediction techniques that perform best at a large scale are now further tested at the smaller scale of the river floodplain. In the last stage of the research, the rates of sediment deposition were estimated by measuring fallout ^{137}Cs in soil samples from various depths below soil surface. The nuclear accident at Chernobyl in 1986 provided the opportunity to study short-term sediment deposition. The results of this work are presented in Chapter 13. In the last chapter some of the results presented in Chapter 7-13 are assembled and discussed in the wider context of the geographers' perspective. A multiscale approach is used to evaluate the spatial patterns of metal pollution in this fluvial environment, mass balances of sediments and heavy metals are compiled, and an attempt is made to estimate the environmental hazards caused by enhanced levels of heavy metals in sediments, soils and surface waters.

2 THE CATCHMENT OF THE GEUL

2.1 General characteristics

The Geul river is a tributary of the Meuse river (see Figure 2.1). It rises in the municipality of Eynatten (Belgium) near the border with the Federal Republic of Germany and flows into the Meuse river near Meerssen. By then it has flowed for a distance of about 56 km, of which 36 are in the Netherlands, and has dropped 242 m. The catchment covers 350 km^2, of which 180 are in the Netherlands.

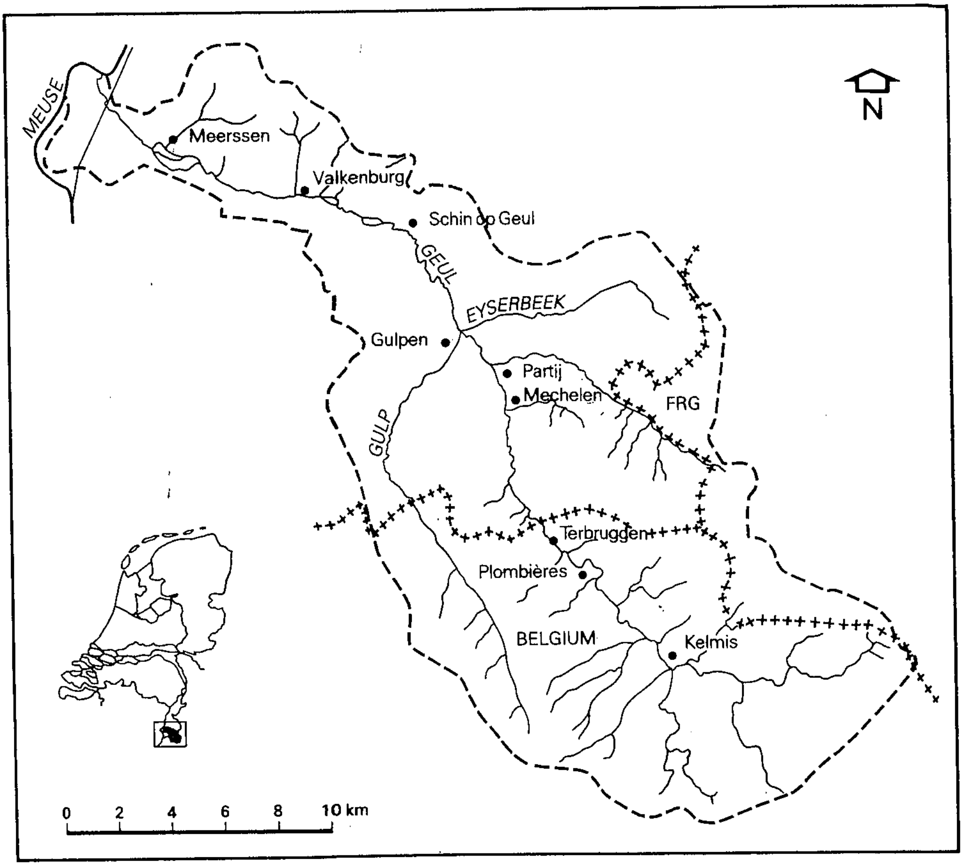


Figure 2.1 The catchment of the River Geul.

By Dutch standards the Geul is a fast flowing river. Its gradient decreases from about 20 m/km near Eynatten to about 5 m/km as it enters the Netherlands and about 1.5 m/km near the junction with the Meuse river. Because of the steep channel gradient, the Geul has incised a deep asymmetric valley in the loess-covered plateau that consists of Cretaceous limestone. The hill slopes are gentle on the western side, but steeper on the east side, where steep escarpments can be observed at the foot of the hills. The width of the valley floor varies from 200 m in Belgium to 400-800 m in the Netherlands and the alluvial deposits cover some 12 km^2 (Broek, van den & Van der Marel, 1964). The meandering river channel has a width of 3-7 meters.

2.2 Geology and geomorphology (after: Van de Westeringh, 1980)

The shape and size of the Geul valley indicate a Pleistocene origin. During the formation of the dissected plateau landscape the valley of the Geul was deepened and widened. As a result of various geological processes the cross section of the valley has become asymmetrical in many places. At the end of the Pleistocene the plateau landscape had been covered by aeolian loess.
The Geul valley was largely incised in Upper-Cretaceous lime-stones. In the floodplain of the present valley braided rivers deposited several meters of Pleistocene gravel over the Cretaceous material. Holocene sediments have been deposited on top of these gravels and give the valley its present character.
The rising temperature at the beginning of the Holocene led to the development of a forest vegetation in the South Limburg loess area. The vegetation in the wet Geul valley became a marsh forest (Havinga & van den Berg van Saparoua, 1980). The stable discharge of the Geul was determined by groundwater base flow and little or no sedimentation occurred. Locally, clay was deposited or peat was formed.
In the Roman era, the large scale clearance of the natural vegetation began. Soil erosion led to the formation of colluvium in the lower parts of the landscape. The regime of the Geul changed considerably, and from then on exhibited large differences between base flow and peak discharge. Alluvial deposits were rapidly built up and instead of peat and clay the deposits now consisted of silty loess-like material, with a differentiation of texture from the levees to the backswamps. This process intensified in the course of time, causing deposition of sediments with ever decreasing clay content. After the Middle Ages, the entire loess area was cleared and cultivated except for the steepest hills and poorest soils, where the forests remained.
In recent times, a number of factors have had an impact on the discharge regime of the Geul. As a result of an increase of the urban area and sealed roads, as well as a scale-enlargement and modernization in agricultural practice, the infiltration capacity of the physical environment has further decreased. The increasing amount of surface runoff is reflected in a flashier discharge regime of the Geul. Under the present conditions the river cuts into its former deposits, and the sand fraction predominates in the grain-size distribution of recent deposits. The Geul has cut as deep as the Pleistocene substratum of the braided river.

2.3 Soils

The characteristics of soils in the Geul valley exhibit very little variation. Only few phenomena that are the result of pedogenetic processes can be recognized: a more or less humic topsoil, gley and reduction phenomena and decalcification of the natural levee soils. Table 2.1 lists physical and chemical properties of soils in the Geul valley.

Table 2.1 Physical and chemical properties of soils in the Geul valley (n=number of samples)

	Van den Broek & Van der Marel (1964) (n=14-23)				Anonymous (1987) (n=19)	
	depth 0 - 20 cm		depth 20 - 120 cm		depth 0 - 10 cm	
property	mean	range	mean	range	mean	range
% C	-	-	-	-	5.9	3.2 - 8.5
% humus	7.1	1.7-18.5	2.4	0.2-16.1	-	-
CEC (meq/100g)	22.4	11.9-25.9	-	-	-	-
% CaCO3	< 2	-	-	-	< 0.7	-
% < 2 µm	18	9 -25	19	9 -34	17	14 -24
% < 16 µm	38	22 -54	40	18 -69	33	27 -42
% < 50 µm	87	70 -94	87	61 -99	-	-
% > 105 µm	-	-	-	-	7	3 -14
pH (KCl)	6.0	3.8- 7.0	6.2	4.4- 7.6	5.4	4.3- 6.6
pH (H_2O)	6.5	5.4- 7.2	7.0	5.4- 8.0	-	-

Van den Broek & Van der Marel (1964) suggested that textural composition (see Figure 2.2) is probably the only criterion for differentiating between the alluvial soils. Van de Westeringh (1980), who compiled a detailed soil map of the Geul valley downstream of Partij, distinguished three classes of soil texture, i.e. L, M and Z, in the alluvial deposits of the Geul. These classes record the clay content (clay %) of the loamy (loess-like) parent material and correspond with the textural classes of the Soil Taxonomy (1975):

L: 10-20 % clay ('coarse-silty');
M: 20-30 % clay ('fine-silty');
Z: > 30 % clay and
V: > 15 % organic matter ('peat or peaty material').

In general the natural levee soils have a textural class L over great depth, i.e. exceeding 120 cm and locally exceeding 220 cm. Soils situated at the transitional area between natural levees and backswamps exhibit textural class L over M, which means that within a depth of 120 cm the texture class changes from L to M. In the backswamp areas soils are found with textures of M, M over Z, Z or Z over V.

The soil map of the Geul valley (Van de Westeringh, 1980) shows that the river has formed only one meander belt along its entire course. The total width of the natural levee soil on both sides of

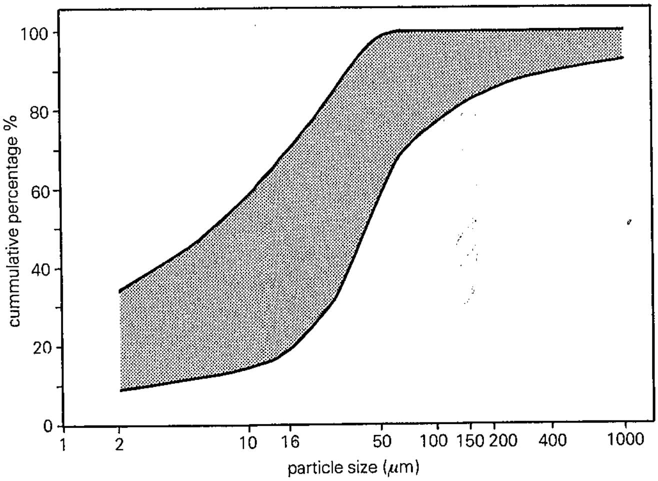


Figure 2.2 Summation curves of the granular distribution of Geul alluvia (Van den Broek & Van der Marel, 1964; redrawn).

the Geul varies from 50 to 350 m. Within the natural levee area many abandoned channel loops are found (Teunissen & van Manen, 1964). Another noticeable feature is the rarity of clayey backswamp soils, the main reason being the narrowness of the valley. Clayey and peaty soils occurring at the surface are always located opposite to the river channel in the valley cross section.

2.4 Hydrology

Annual rainfall in the catchment, based on 30 years of record, varies from 816 mm in the downstream part (gauging station Valkenburg) to 882 mm in the upstream part (gauging station Epen) (KNMI, 1982). The Geul river discharge largely depends on amounts of rainfall. At the Dutch-Belgian border its average flow is 1 m^3/s, with the maximum discharge being of the order of 30 m^3/s. These values increase to respectively 3 and 60 m^3/s as the Geul flows towards its confluence with the Meuse. Relatively low flood peaks occur within 24 hours after a period with moderate rainfall in the catchment. Prolonged rainfall may lead to overland flow because of saturation or slurrying of the topsoil. As a result, a pronounced high flow peak is rapidly produced, which may cause severe erosion of the streambanks and temporary inundation of the floodplains. The Geul river flow does not have a strictly natural character. For centuries, the discharge has been influenced by land reclamation, the construction of water mills etc.

During low flow, the suspended load of the Geul river is very small, that is of the order of 10-50 mg/l. Small amounts of these sediments are deposited on the elevated parts of its cross-section after a relatively low flood peak. At high flow stages the suspended load may increase to 4000 mg/l, causing high rates of sedimentation on the floodplains.

2.5 Mining activities

For centuries zinc and lead mining has been an important activity in the Geul basin (see Figure 2.3). Important deposits of metal ore are found near Plombières and Kelmis, both situated in the Belgian part of the basin. The exploitation of the zinc and lead ores probably began in the thirteenth century. Mining in the Moresnet area started on a commercial scale in the 15th century, when the brass industry moved to Aachen (FRG), and the heyday of mining was in the period 1820-1880.

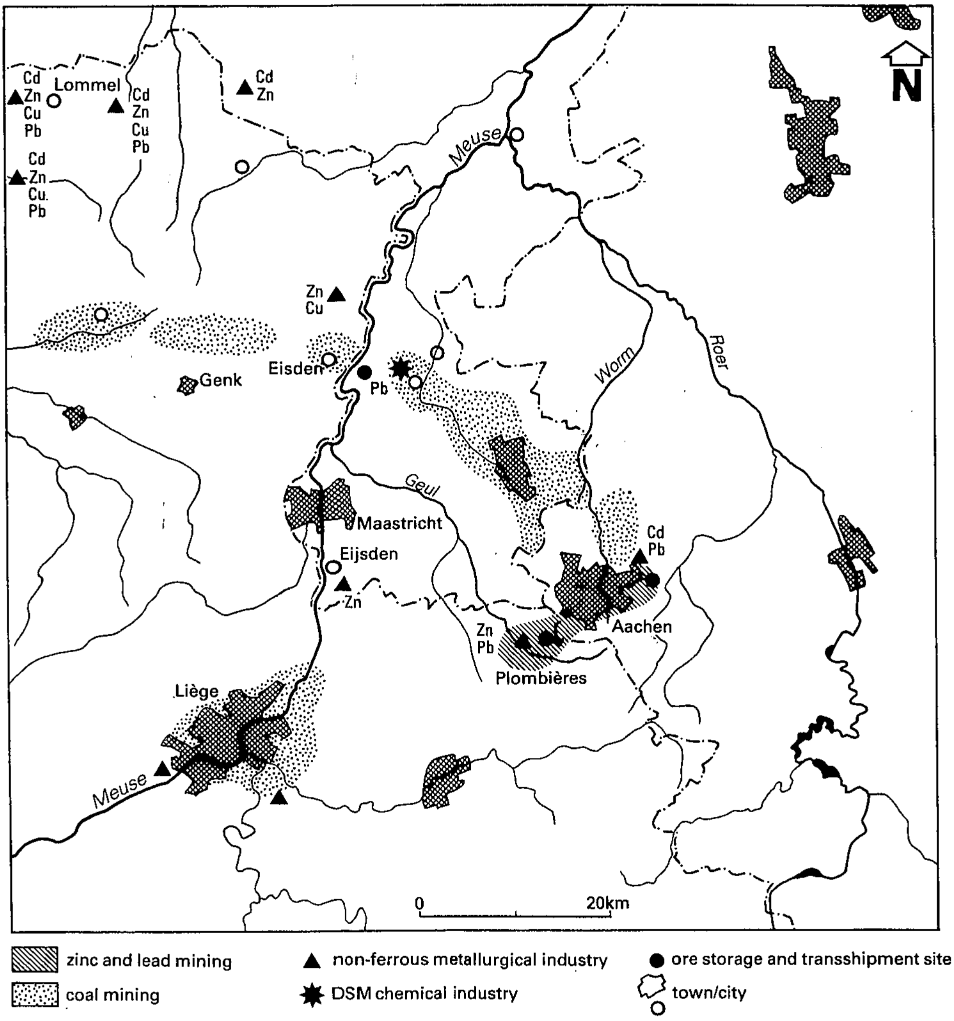


Figure 2.3 Mining activities in the study area.

During that period, maximum yearly ore production in the open-cast mines of Kelmis was about 135,000 tonnes, and 1300 men were employed in the zinc industries (Wintgens, 1981). The last mine closed in 1938, but the processing of metal ores continued until the 1950s.

The water of the Geul upstream of Gulpen was probably slightly acid, which is caused by the oxidation of sulfides (Harmsen, 1977). The sulfuric acid produced by the oxidation of pyrite, marcasite or other metal sulfides (e.g. sphalerite, ZnS) may be neutralized by calcite and dolomite, but generally the neutralization would be incomplete, and part of the sulfuric acid would remain in solution (Harmsen, 1977). The occurrence of large quantities of limonitic ferric oxides in the oxidation zone of zinc and lead ores confirms that the oxidation of iron sulfides may have been important in the acidification of surface waters in the area (Harmsen, 1977).

Weathering and erosion of ore deposits at shallow depths or outcropping in the catchment area of the Geul, have contributed to the metal contents of the Geul. Underground ore veins and beds have probably also contributed because these deposits are often associated with existing fractures and solution holes, which play a role in the underground drainage of the area (Harmsen, 1977). The major part of the Zn and Pb content of the Geul however, was due to mining activities: the exposure of sulfidic ore deposits to the influence of oxidative weathering, erosion and leaching of slag heaps and mine dumps, the discharge of waste water from ore processing (e.g. washing and flotation), and mine drainage have all contributed to the metal contents of the Geul. Table 2.2 lists metal concentrations of samples collected at the spoil heaps in Plombières (see Photo 2.1) and Kelmis.

Table 2.2 Average Pb-, Zn- and Cd concentrations (mg/kg) in spoil heaps on the river banks of the Geul

location	n	Pb	Zn	Cd
Kelmis	3	10,566	56,683	119
Plombières	6	13,907	11,728	33

Annoyance to the miners caused by excess water in the mines was common in the area and pumping installations with a capacity of 6.5 millions m^3/year were continuously in operation, but were often not sufficient to drain the mines (Engelen, 1976). A pumping capacity of 6.5 millions m^3/year would account for 10 % of the yearly discharge of the Geul near the border between Belgium and the Netherlands, so that the contribution of mine drainage to the total discharge may have been significant.

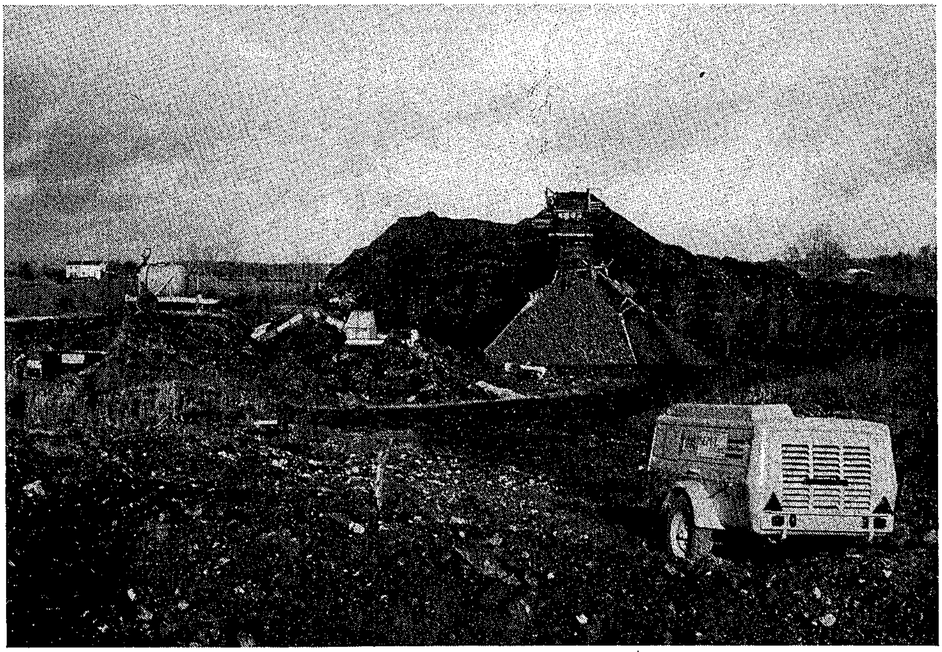


Photo 2.1 Spoil heaps on the banks of the River Geul in Plombières.

2.6 Landuse

The landuse in the Geul valley consists of farmland, mainly pasture. Villages and other buildings are mainly found on the hills along the valley, with an exception for the villages of Valkenburg and Schin op Geul, which are located on the valley floor. In the village of Valkenburg, the Geul flows through two parallel canals and here flooding occurs regularly, causing damage to houses and water works. The Geul valley is important for recreation and many camping sites are found on the valley floor and nearby the valley slopes.

3. ANALYTICAL PROCEDURES

3.1 Introduction

This chapter describes the methods used for analysing samples of water, soil and suspended sediment. Particular attention is paid to the preparation of the samples prior to analysis and to the measurent techniques used for analysing metal concentrations and ^{137}Cs activity in the samples. In addition, the importance of various sources of errors that are associated with sample treatment in the laboratory is discussed.

3.2 Sample collection and preparation

Sample sites were chosen by a method known as stratified random sampling (Gilbert, 1987). The method makes use of prior information to divide the target population into subgroups that are, to a certain extent, internally homogeneous. Each subgroup is then sampled by simple random sampling to estimate its average or total. In this study, the soil map produced by Van de Westeringh (1980) was used as the basis for the design of the sampling scheme. Within each map unit, soil samples of c. 100 grams were collected with a Dutch hand auger at randomly chosen locations and at depths of 0-10, 10-20, 20-30, 40-50 and 90-100 cm and then placed in plastic bags. For analysis of ^{137}Cs-activity, soil samples of 500-1000 g were taken in depth intervals of 0-5, 5-10, 10-15, 15-20, 20-25, 35-45 and 45-70 cm.
Water samples were collected in bottles of polypropyleen (1 or 25 liters) or brown glass (1 liter), that were cleaned with 15 % HNO_3 and demineralized water prior to sampling. Part of each 1 liter sample was centrifuged and the supernatent liquid was brought to pH 2 with HNO_3. The solids in the remainder of these samples were allowed to settle for 1-2 days, after which the clear fluid was drawn off with a siphon. The part of the sample containing the solids was then dried on a waterbath at 90-100 °C and sampled. The bulk water samples (25 liters) were passed through a continuous flow centrifuge (Hereaus, 10.000 G, capacity: 1.2 l/min) that collects the solid particles in a teflon-coated rotor chamber (Duinker et al., 1979). After centrifugation, the pH of the water samples was brought to 2 with concentrated HNO_3 and the solids were sampled.
All samples of soil and suspended sediments were dried for 24-48 hours and then crushed in a mortar and passed through a 2 mm sieve. A selected number of samples of flood deposits were separated in fractions > 63 µm and < 63 µm by sieving.

3.3 Extracting heavy metals from soil samples

3.3.1 Total extractions by nitric acid and hydrofluoric acid

For the extraction of heavy metals from samples of soil and suspended sediments, two extraction schemes were used. The method used for the routine extraction of heavy metals from solids is treatment with 25 % nitric acid (HNO_3). However, because part of the heavy metals in the Geul catchment are incorporated in crystalline minerals, they may not be completely extracted by this treatment. Therefore, it was decided to use an additional extraction method that employs hydrofluoric acid (HF).
For the routine extraction by HNO_3, one gram of the samples was put in a teflon bomb and treated with 8 ml 25 % HNO_3 (100 °C) for two hours. After cooling-off, 32 ml distilled water was added and the concentrations of lead, zinc, cadmium and copper could be measured by atomic absorption spectroscopy (see Section 3.4.1).
For the second extraction method, a 250 mg sample was put in a teflon bomb and dissolved in 10 ml HF and 10 ml of a mixture consisting of H_2O, HNO_3 and perchloric acid in the ratio 1:25:65. The bomb was put in a furnace at 100 °C for 12 hours. After cooling-off, the bombs were opened and the samples were dried at 180 °C, after which 2 ml 65 % HNO_3 and 2 ml H_2O was added and the bombs were put in the furnace again (at 100 °C) for two hours. Then, the extract was brought to 50 ml with distilled water and metal concentrations were measured.

3.3.2 The sequential extraction scheme

It is not the total amount of heavy metals but rather how it is actually stored that is important in assessing the environmental impact. The relative bonding strength of metals in different chemical phases is commonly estimated by a sequential extraction scheme (Salomons & Förstner, 1984). A number of samples was analysed in a slightly modified version of the sequential extraction scheme that was proposed by Calmano & Förstner (1983). This scheme has been applied to demonstrate the relative mobility of particle-associated trace metals in river sediments, dredged materials and sewage materials (Salomons & Förstner, 1984):

(1) exchangeable cations - 1 M ammonium acetate, pH 7, solid/solution ratio (R)=1:20, 2 hours shaking;
(2) carbonate fraction - 1 M sodium acetate, pH 5, R=1:20, 5 hours shaking at 20 °C;
(3) easily reducible phases (Mn oxide, partly amorphous Fe-oxyhydrates) - 0.1 M hydroxylamine hydrochloride + 0.01 M HNO_3, pH 2, R=1:30, 12 hours shaking;
(4) moderately reducible phases (e.g. amorphous and poorly cristallized Fe oxyhydroxides) - 0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3, R=1:100, 24 hours shaking;
(5) organic fraction, incl. sulfides - 30 % H_2O_2 + HNO_3, pH 2, 85 °C, extracted with 1 M ammonium acetate, R=1:100, 24 hours shaking
(6) residual fraction (e.g. crystalline Fe-oxides) - conc. HNO_3, 120 °C, R=1:40.

In our study only the first three leaching stages of the proposed five were used, because these are the stages that give some indication about the amount of metals that may be released when the pH and the redox potential are changed. The residual fraction (stage 6) was determined as well. The chemical analyses of the extractions were done by emission spectroscopy (see Section 3.4.1). Since stage 4 (moderately reducible fraction) and stage 5 (organic fraction) of the original scheme were not determined separately, the metals in both fractions will have been released during stage 6. When the residual fraction is referred to in this study, it means the sum of metals in stages 4, 5 and 6.

3.4 Measurement of heavy metals in solution

3.4.1 Methods

The concentrations of extracted heavy metals in solution were measured by employing their absorption- and emission spectra. The principle of absorption- and emission spectroscopy is to seperate elements into atoms at high temperature, after which optical methods are employed to measure their specific spectrums. For flame or furnace atomic absorption spectroscopy the temperature may be raised to 2500-3000 °C; for emission spectroscopy the temperature may reach as high as 7000-10,000 °C.
The Pb, Zn, Cd and Cu levels in HNO_3-extracts and Zn levels in water samples were measured by using an Instrumentation Laboratory Atomic Absorption Spectrofotometer (type IL 357) and an Atomic Absorption Spectrophotometer (AAS) model 2280 manufactured by Perkin Elmer.
For the measurement of heavy metals in HF-extracts and in extracts from the sequential extraction scheme, use was made of an emission spectrophotometer with Inductively Coupled Plasma (ICP-ES), type 34000, manufactured by the Applied Research Laboratories (ARL). This is a simultaneous, 35-channel spectrophotometer (polychromator) for multi-channel analyses. Measurements of heavy metals at the ppb (parts per billion or µg/l)-level, as found in water samples and extracts from the sequential scheme (Cd)), were done by Furnace Atomic Absorption Spectroscopy with Zeeman-effect (Zeeman/ 5000-system with HGA-400 microcomputer technology, manufactured by Perkin Elmer). In the next paragraph attention will be paid to the sensitivies, detection limits and analytical ranges of these methods.

3.4.2 Sensitivity, detection limit and analytical range of the analytical equipment

The detection limit of analytical equipment which employs absorption and emission spectra of heavy metals, is defined by the lowest measurable concentration, i.e. a signal equal to twice the background noise. The sensitivity (characteristic concentration or reciprocal sensitivity) is the concentration (in µg/ml) or the quantity (in g) of an analyte that generates a signal of 1 % net absorption. The sensitivity depends on the instrumental conditions and on

the analysed medium. The analytical range is the concentration interval in which the analytical precision has an acceptable value. The lowest concentration is generally defined by 5-10 times the sensitivity and the highest concentration is derived from the curvature of the calibration curve, which gives the relation between signal height and the amount or concentration of the element under study. This relationship is linear only up to a certain signal height, depending upon the selected resonance line, slit width, light source, rate of heating, etc. Beyond this point, the precision of the analysis decreases markedly.
The detection limits, analytical ranges and - for those employing absorption spectra - the sensitivities of the equipments used are listed in Table 3.1, 3.2 and 3.3.

Table 3.1 Analytical data of the AAS type IL 357

element	line (nm)	detection limit (μg/ml)	analytical range (μg/ml)	sensitivity 1 % absorption (μg/ml)
Cd	228.8	0.01	0.125- 3.0	0.01
Cu	324.7	0.05	0.25 - 6.0	0.03
Pb	283.3	0.1	0.5 -12	0.08
Zn	213.9	0.025	0.25 - 6.0	0.03

Tabel 3.2 Analytical data of the ICP-ES type 34000

element	line (nm)	detection limit (μg/ml)	analytical range (μg/ml)
Cd	226.5	0.002	0.002- 300
Cu	324.8	0.001	0.001- 200
Pb	220.3	0.05	0.05 -5000
Zn	213.9	0.003	0.003- 250

Table 3.3 Analytical data of the Zeeman/5000-system

element	line (nm)	detection limit (μg/l)	analytical range (μg/l)	sensitivity 1 % absorption (μg/l)
Cd	228.8	0.03	0.2- 10	0.05
Cu	324.7	0.2	1 -150	0.2
Pb	283.3	0.5	1 -150	0.5

The wide analytical range of the plasma of the ICP-ES allows the measurement of both major and trace elements in the same solution without the need for dilution. Measured concentrations with a value smaller than five times the detection limit are considered unreliable. Above this limit, the analytical error falls in the range of 2-5 % for major elements and 5-10 % for trace elements.

Because of its principle itself, flameless atomic absorption allows the analysis of elements in concentrations much lower than those determined in classical atomic absorption spectroscopy. Analysis is made for the absolute quantity of the element present in the furnace, independent of its concentration in solution, since the solvent is evaporated during the drying step. Generally, the measurable quantities are less than a nanogram. For samples of very low concentration, dispensing a larger volume into the tube leads to an increased signal, while for samples of higher concentration only very small volumes are required. A direct analysis of water of low hardness often leads to detection limits of 0.01-0.1 µg/l Cu, Zn and Pb can in most cases be determined up to a level of 50-100 µg/l. For Cd the detection limits are not always sufficient, and enrichment methods must be employed.

3.5 Errors associated with the analysis of heavy metals

A number of errors may occur during the procedure of collecting and preparing the soil samples, followed by the extraction and analysis the heavy metals. Systematic errors may occur due to (1) the use of different extraction methods and (2) the use of different measurement techniques. Random errors may result from (1) the heterogeneity of the soil sample, (2) instability of the measuring equipment and (3) the inaccuracies that are inherent to routine work in the laboratory: weighing, reading graduated scales, using pipettes, contaminations of beakers and tubes, etc.

Several experiments were carried out in order to quantify the magnitude of systematic and random errors. First, two subsamples were taken from a number of samples with a wide range of metal concentrations. One was treated with HNO_3 and one was treated with HF (see Section 3.3.1), after which the concentrations of lead, zinc, cadmium and copper in both solutions were measured by flame absorption spectometry. Linear regressions of the results of both methods yielded very large correlation coefficients (see Figure 3.1). However, for all metals investigated the line that best fits through the data intercepts the Y-axis at a value greater than zero, and for zinc and lead the slope of the best fit line differs from 1. The ratios of metals released by treatment with HNO_3 and those released by treatment with HF equal on average 0.78 for Pb, 0.85 for Zn, 0.84 for Cd and 0.81 for Cu (number of samples=14). These figures demonstrate that on average some 15-20 % of the metals in the samples is not liberated by routine extractions with HNO_3. However, given that these proportions of the heavy metals - which are probably incorporated in well-crystallized mineral structures - are not likely to be mobilized when cycling through the fluvial environment, it was decided to use the simple extraction by HNO_3 for routine measurements of heavy metals.

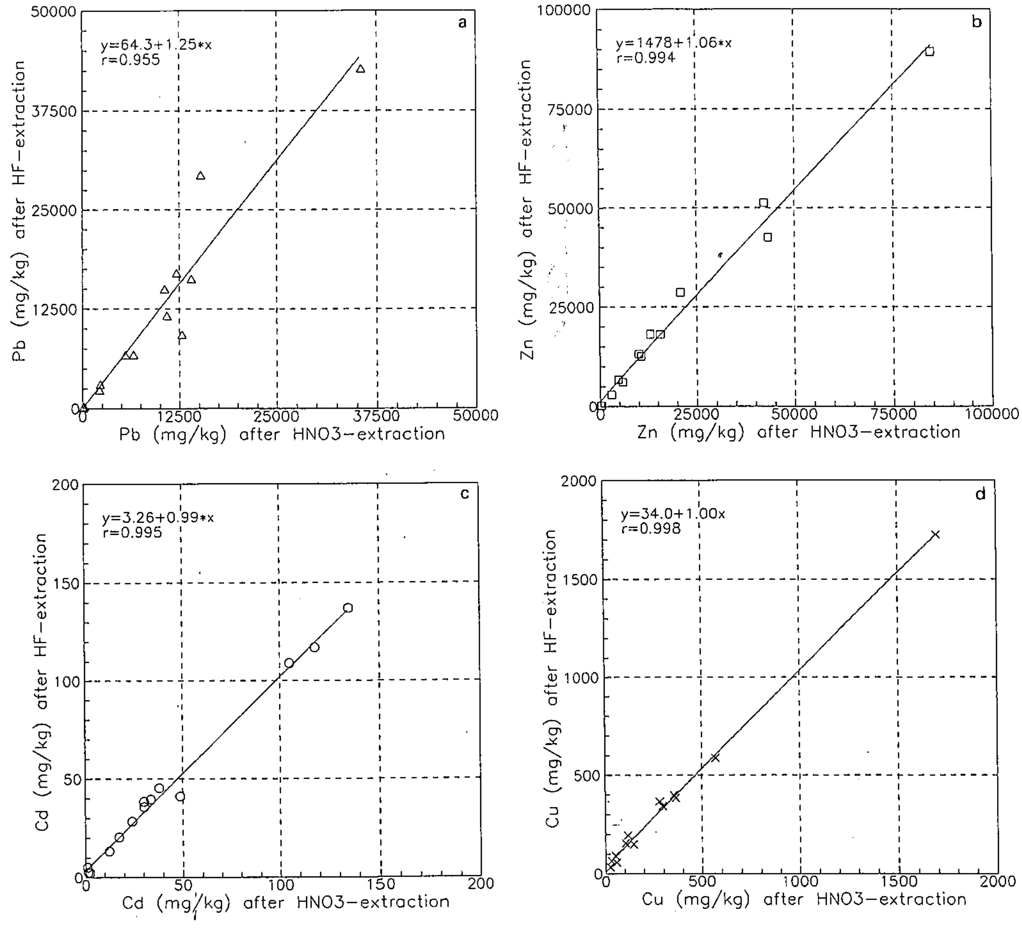


Figure 3.1 Linear regressions of metal concentrations in HF-extracts on those in HNO$_3$-extracts: a) Pb, b) Zn, c) Cd and d) Cu.

The second experiment addresses the difference between metal concentrations measured by ICP-ES and those measured by AAS. Part of the routine measurements of heavy metals in solution was done by emission spectroscopy with inductively coupled plasma, while the larger part of the measurements was done by flame atomic absorption spectroscopy (see Section 3.4.1). In order to obtain comparable metal concentrations, the extracts of a selected number of samples in each set that was measured by ICP were also measured by AAS so that correction curves could be established. Examples of such curves, covering two ranges of concentrations of lead, zinc, cadmium and copper, are presented in Figure 3.2 and 3.3. In most cases, the curves approach the line y=x quite well and so corrections were not necessary. Otherwise, mostly with respect to the measurement of lead (see Figure 3.3c), these curves were used to correct for deviations in the results obtained by measurement by ICP.

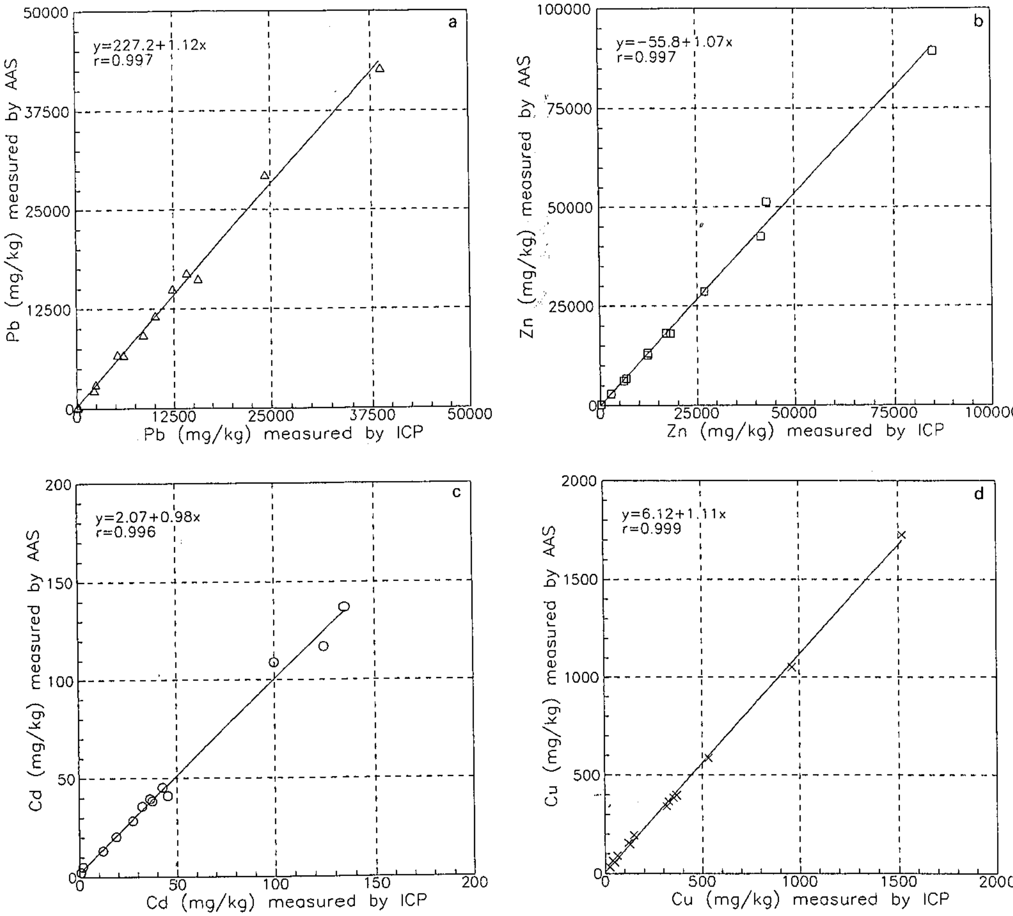


Figure 3.2 Linear regressions of metal concentrations measured by AAS on those measured by ICP: a) Pb, b) Zn, c) Cd and d) Cu (larger range of concentrations).

The sum of all possible random errors in routine sample treatment (extraction by HNO_3 and measurement by AAS) was investigated by means of treatment in duplicate of one in every 10-30 samples. Relative errors (50 % of the difference between the concentrations in the two samples as a percentage of the mean concentration in the samples) were computed and cumulative frequencies were used to characterize their distributions. Figure 3.4 shows cumulative frequencies of relative errors of metal concentrations for a set of samples that were collected in an early stage of this study, and that cover a wide range of concentrations (see Table 3.4). The random errors associated with the analyses of lead and zinc in soil samples are very similar: 85-90 % of the relative errors are smaller than 10 % and some 95 % of them are smaller than 20 %. For cadmium and copper the relative errors are

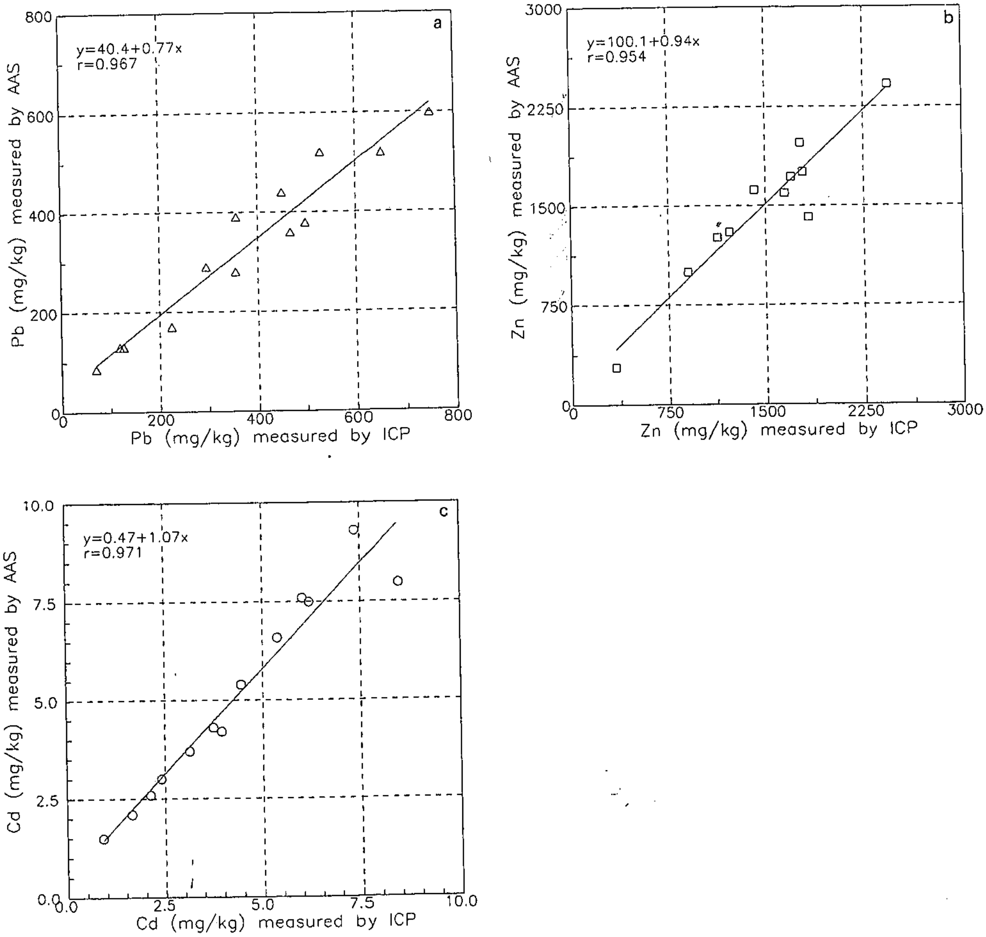


Figure 3.3 Linear regressions of metal concentrations measured by AAS on those measured by ICP: a) Pb, b) Zn and c) Cd (smaller range of concentrations).

Table 3.4 Summary statistics of metal concentrations (mg/kg) in samples that were treated in duplicate, and mean relative errors

metal	n	minimum	mean	maximum	mean error (%)
Zn	49	62	566	2050	4.7
Pb	42	27	145	533	6.0
Cd	34	0.8	3.1	8.6	12.5
Cu	40	7.9	20.3	58.3	7.1

larger and only 60 and 70 % of their errors, respectively, are smaller than 10 %. Nevertheless, the majority of the relative errors (i.e. 65-90 %) is smaller than 20 %.

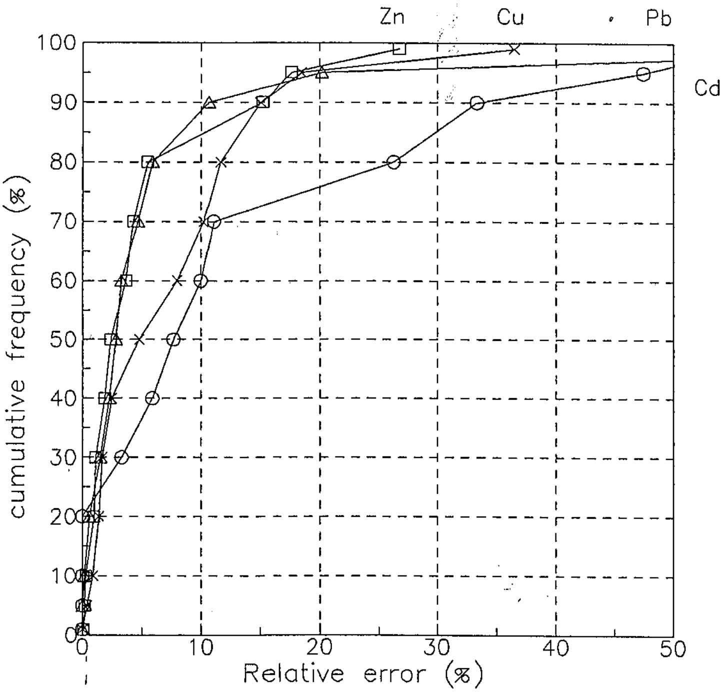


Figure 3.4 Cumulative frequency distributions of relative errors that occurred after treatment in duplicate of subsamples from the same sample.

The characteristics of the matrix, i.e. the liquid that contains the extracted heavy metals in solution, may cause the registration of a signal that does not relate to the presence of heavy metals. This phenomenon is called matrix interference and may occur when the physical and chemical characteristics of the sample and those of the standard solutions differ considerably (Pinta, 1984). Such effects may be expected when analysing strong salt solutions containing low metal concentrations, such as those produced by the sequential extraction scheme. In order to correct for this phenomenon, standard solutions of various metal concentrations were prepared in matrices of 1 M NH_4OAC, 1 M NaOAc and 0.1 M $NH_2OH.HCl$ and these were measured at least once in every series of 20 samples. Corrections for matrix interferences were carried out when the deviation between measured concentrations and known concentrations exceeded 5 %.

3.6 Measurement of ^{137}Cs activity in soil

Air dried and disaggregated soil samples of 500-1000 g were positioned around a 90 cm^3 Germanium detector inside a 5 cm lead shield. Count times were in the order of 20000 s, providing an analytical precision of better than 10 %. The ^{137}Cs- activities of the samples are deduced from the observed E_γ = 662 keV-lines. The resolution is sufficient to separate other (natural) background lines. Comparison with a ^{137}Cs-doped standard sample produced at the IRI (University Reactor Institute, Delft, The Netherlands) reactor yielded absolute activities. Results were expressed in Bq/kg and, according to the surface area of the original sample, converted to units of Bqm^{-2}.

4 HEAVY METALS IN SEDIMENTS AND SOILS

4.1 Introduction

Sediments are important carriers of trace metals in the hydrological cycle. Sediments can reflect the current quality of the system as well as the historical development of certain hydrological and chemical parameters. In addition to their significance as an indicator medium, sediments are, depending on environmental conditions, a sink or a source for trace metals in the fluvial system (see chapter 5). Metals are not necessarily fixed permanently by the sediment, but may be recycled via mechanical, biological and chemical processes, both within the sedimentary compartment and also back into the water column. Figure 4.1 gives a schematic representation of metal reservoirs and their interactions in aquatic and terrestrial systems.

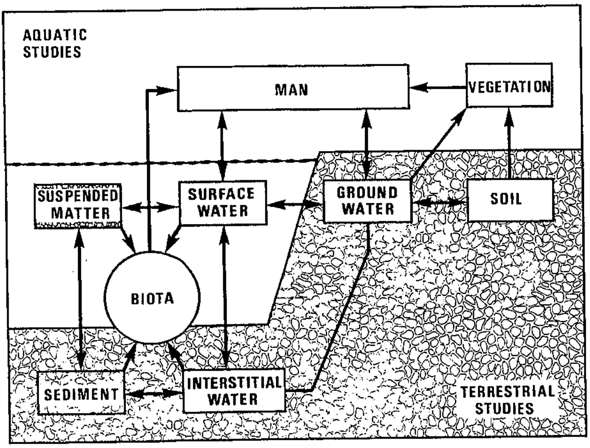


Figure 4.1 Schematic representation of metal reservoirs and their interactions in aquatic and terrestrial systems (Salomons & Förstner, 1984).

The timescale over which sediment can be stored in floodplain soils increases with the size of the river, and can be of the order of a thousand years (Leopold et al., 1964) or more. Contaminants associated with sediments stored in floodplains can affect the health of plants and animals that either naturally inhabit riperian areas, or are placed in those areas. Contaminated sediment that is stored in floodplains also may affect the water quality in alluvial aquifers.
This chapter discusses the toxicity of the heavy metals found in the soils of the study area. In addition, attention is paid to the factors affecting the geochemical mobility of heavy metals and background concentrations and quality criteria are provided.

4.2 Toxicity

No organic life can develop and survive without the participation of metal ions (Förstner & Wittmann, 1983). An element is essential when:

(1) it is consistently determined to be present in all healthy living tissues within a zoological family, whereby tissue concentrations from species to species should not vary by a wide range,
(2) deficiency symptoms are noted with depletion or removal, which disppear when the elements are returned to the tissue,
(3) the deficiency symptoms should be attributed to a distinct biogeochemical defect (on the molecular level) (Overhoff and Forth (1978) in: Förstner & Wittmann, 1983).

It is well known that the major ions such as sodium and potassium, and also magnesium and calcium, are essential to sustain biologic life. However, it is less well known that at least some further six metals, i.e. molybdenum, manganese, iron, cobalt, copper and zinc, are essential for optimal growth, development, achievement and reproduction of man and animals (Förstner & Wittmann, 1983).
Essential trace metals become toxic when the nutritional supply becomes excessive. A metal that occurs in trace amounts (smaller than 0.015 of the mass of the organism) is defined as being essential when an organism fails to grow or complete its life cycle if that metal is absent. However, the same trace metal may be toxic if concentration levels exceed those required for correct nutritional response by factors varying between 40- and 200-fold (Venugopal & Luckey, 1975). Studies pertaining to the toxicity of trace metals follow the general trend that an undersupply leads to a deficiency, sufficient supply results in optimum conditions, but an oversupply results in toxic effects and lethality in the end (Förstner & Wittmann, 1983). There is no doubt that all metals are potentially hazardous to living organisms, and not necessarily at large exposure levels. The toxicities of the heavy metals that were mined in the study area are summarized here briefly:
Zinc is one of the most abundant essential trace elements in the human body and approximately 100 times as abundant as copper (Vahrenkamp, 1973). It is a constituent of all cells, and several enzymes depend upon it as a cofactor. Zinc exhibits an intimitate connection with cadmium in the geosphere and biosphere. In soils, the ratio Cd:Zn varies from 1:300 to 1:2900 by mol (Förstner & Wittmann, 1983). Moderately increased zinc concentrations in drinking water do not induce any clinical manifestations. The results of laboratory tests on animals, however, indicate that the metabolism of humans may be affected (for example their mineral and enzyme budget), especially of children and patients already suffering from irregular metabolism. Even at relatively low levels of zinc in the soil, toxicity for plants may occur due to accumulation. Once plant leaf levels of Zn exceed 400 ppm, toxicities can be expected (Jones, 1972). When concentrations of zinc in the soil exceed 100-200 ppm, a negative impact on the yield of agricultural crops may be expected (Copius Peereboom & Reijnders, 1986).

In the industrialized world, lead enters the human body through food (655), water (205) and air (155). On average an adult person consumes 81 μg daily (with a wide range of 10-1460 μg) of which some 105 is absorbed (Copius Peereboom & Reijnders, 1986). Although lead is a nonessential element it is present in all tissues and organs of mammals. Under normal conditions more than 905 of the absorbed lead is retained in the skeleton. Since lead can remain immobilized for years, metabolic disturbances may remain undetected for years. Pb^{2+} may affect membrane permeability of kidney, liver and brain cells. This results in either reduced functioning or complete breakdown of these tissues, since lead is a cumulative poison (Förstner & Wittmann, 1983). The phytotoxicity of lead is relatively low compared with other trace elements (Adriano, 1986).

Cadmium is known as one of the most toxic metals (Förstner, 1978) and enters the human body mainly via food. Daily consumption of cadmium varies from 20-30 μg (Copius Peereboom & Reijnders, 1986), of which some 65 is absorbed. In the absence of essential trace elements such as iron and zinc, this percentage may increase to 15. Cadmium uptake due to cigarette smoking (20/day) may add 1.9 μg daily (Förstner, 1978). Cadmium accumulates with age and about 50% of the accumulated cadmium is found in the kidney and liver (Förstner, 1978). In the kidney the filtermechanism may be affected. The high toxicity of cadmium may lead to hypertension, disturbances of the metabolism of bones, damage to the central nervous system and it affects reproduction (Copius Peereboom & Reijnders, 1986).
Cadmium is known to be toxic to plants at much lower concentrations than zinc or lead (Adriano, 1986). The association of cadmium and zinc in geological deposits and the chemical similarity of the two elements carry over in the biological systems. Cadmium has no known biological functions, but zinc is an essential element. Cadmium supposedly competes with zinc in forming protein complexes, which may account in part for the toxic effects of cadmium and the ameliorative effects of zinc on cadmium toxicity (Adriano, 1986).

4.3 Metal associations in aquatic sediments

According to the classification by Goldberg (1954) natural metal enrichments in solid substances can originate from the following five sources:

(1) lithogenous formations: weathering products from the source areas or rock debris from the river bed. This material undergoes only slight change, regardless of long residence times;
(2) hydrogenous formations: particles, precipitation products, adsorbed substances, formed due to physico-chemical changes in the water;
(3) biogenous formations: biologic remains, decomposition products of organic substances as well as inorganic siliceous or calcareous shell;
(4) atmogenous formations: metal enrichment resulting from atmospheric fallout;
(5) cosmogenous formations: extra-terrestrial particles.

One could include civilizational metal enrichments among the first four processes because the by-products from the erosion of refuse dumps and mine waste are an important source of lithogenous solids as well as of soil particles, which can be carried into the aquatic system via surface runoff. Hydrogenous metal enrichments in solids may occur during the total course of a primary dissolved contaminant and the same is true for biogenous formations. Atmospheric contributions can enter water by several means, e.g. as direct input in dissolved or solid form or by way of enrichment processes in the soil and plants (Förstner & Wittman, 1983).
Despite their dissimilar origins, natural and environmentally related types of bonding have many characteristics in common. The following groups of metal associations in aquatic solid substances are of importance here:

(1) Incorporation in crystalline minerals

Heavy metals may be present as a major element in a trace material, such as Pb in anglesite ($PbSO_4$). The mobility of trace elements in these forms is dependent mainly on simple solubility and solution chemistry, or on physical processes transporting the grains (Rose, 1979). As a trace constituent in the crystal structure of a well-crystallized mineral, such as Zn in magnetite, the mobility of trace elements is dependent on the properties of the host mineral (Rose, 1979). The silicate minerals feldspar and quartz usually have very low heavy metal contents (Förstner & Wittmann, 1983)

(2) Metal precipitation

Precipitation, primarily of hydroxides, sulfides and carbonates, occurs within a water body when the solubility product of the dynamic equilibrium between solid substances and its aquatic ions is exceeded (i.e. the solution is oversaturated).

(3) Cation exchange and adsorption

A number of sediment-forming materials with a large surface area - particularly clay minerals, fresh precipitated iron hydroxides, amorphous silicic acids, as well as organic substances - are capable of adsorbing cations from solution and releasing equivalent amounts of other cations into the solution by cation exchange. The mechanism which result in cation exchange is based on the adsorptive properties of negatively charged anionic sites - $SiOH^-$, $AlOH^{2-}$, and AlOH-groups in clay minerals, FeOH-groups in iron hydroxides, carboxyl and phenolic OH-groups in organic susbstances - with respect to positively charged cations. The balancing of negative charges of the lattice is a selective process which accounts for preferential adsorption of specific cations and the release of equivalent charges associated with other species. Furthermore, all fine-grained materials with a large surface area are capable of accumulating heavy metal ions at the solid-liquid interface as a result of intermolecular forces.

(4) Sorption onto clay minerals

The clay mineral uptake capacity for ions, particularly cations, is primarily governed by: (1) broken bonds around the edges of the silicon-aluminium units, which can be balanced by adsorbing cations; (2) substitution of Si^{4+} by Al^{3+} in the tetrahedal layer and of Al^{3+} by divalent cations in the octrahedal layer of the structural units of some clay minerals (Grim, 1968). This process of substitution can leave behind unbalanced charges, which are then balanced by cations. Recent observations of natural aquatic systems have shown that adsorption of heavy metals on to clay minerals is generally unimportant (Förstner & Wittman, 1983).

(5) Adsorption and coprecipitation on hydrous Fe/Mn-oxides

The hydrous oxides of aluminium, iron and manganese, particularly the redox-sensitive Fe- and Mn-hydroxides and -oxides under oxidizing conditions, constitute significant sinks of heavy metals in aquatic systems. These hydroxides and oxides readily adsorb or coprecipitate cations and anions; even a low percentage of $Fe(OH)_3$ and MNO_2 has a controlling influence on the heavy metal distribution in an aquatic system. Under reducing conditions the adsorbed heavy metals are readily mobilized; accumulations of hydrous Fe/Mn oxides can therefore act as a major source of dissolved metals in natural waters. The latter mechanism is particularly effective in the presence of higher concentrations of dissolved organic matter.

(6) Associations with organic substances

The affinity of heavy metals for organic substances and for their decomposition products is of great importance for the behaviour of trace substances in aquatic systems. The organic matter of aquatic systems consist of the remains of biologically produced compounds (a.o. humic and fulvic acids) as well as of synthetic organic substances from industrial and agricultural applications. The attractive forces between metal ions with soluble, colloidal or particulate organic material range from weak (physical adsorption) to strong (metal chelation) (Förstner & Wittmann, 1983). Fulvic acids play an important role in the transport of heavy metals in water due to their lower molecular mass, larger number of functional groups and their much greater solubility than the humic fraction. On the other hand, the humic fraction is more important than the fulvic fraction in trace element transport and retention by stream sediments because of the greater quantity present (Jenne, 1976).

4.4 Factors affecting the geochemical mobility

Geochemically, an element introduced into the soil may end up dissolved in the soil solution or in one of the above forms. The dissolved form and exchangeable form are the mobile forms and are phytoavailable; the other forms are immobile and sometimes become mobile and phytoavailable with time. Figure 4.2 provides a schematic representation of the availability of metal forms for biological uptake. Metal activity in the soil solution is generally considered to be the result of metal equilibria among clay mineral, organic matter, hydrous oxides of Fe, Mn, and Al, and soluble chelators, with the soil pH strongly affecting these equilibria (Lindsay, 1979). Because of soil heterogeneity and inherent variability in chemical, mineralogical and physical properties of the soil, it is extremely difficult to predict the fate and behavior of heavy metals in soil without understanding the factors described below (for the larger part after Adriano (1986)).

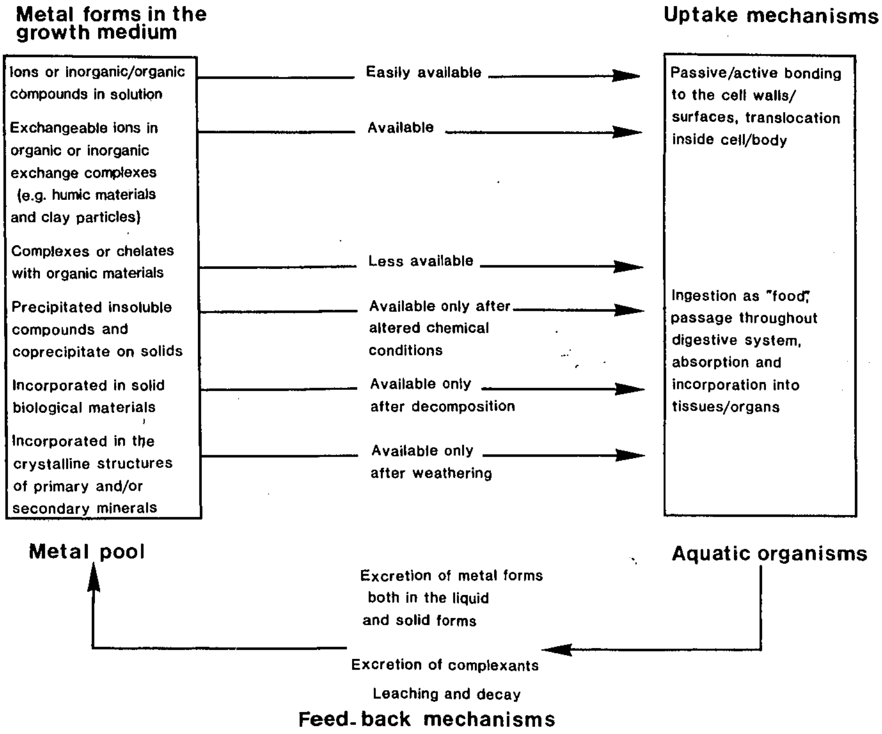


Figure 4.2 Availability of metal forms for biological uptake (Baudo, 1982; cited in Salomons & Förstner, 1984).

pH

A lowering of pH leads to the dissolution of carbonate and hydroxide minerals and - as a result of hydrogen ion competition - to an increasing desorption of metal cations (Förstner, 1978). In general, the capacity of soil for binding most trace elements increases with increasing pH. The relative mobility of some trace elements in soils as influenced by pH was summarized by Fuller (1977): in acidic soils (pH 4.2-6.6), Cd, Hg, Ni and Zn are relatively "mobile"; As, Be and Cr are "moderately mobile"; and Cu, Pb and Se are "slowly mobile". In neutral to alkaline soils (pH 6.7-7.8), As and Cr are "relatively mobile"; Be, Cd, Hg and Zn are "moderately mobile"; and Cu, Pb and Ni are "slowly mobile" (Adriano, 1986).

CEC

The sum of exchageable cations (including H^+) constitutes the cation exchange capacity (CEC), expressed in milli-equivalents (meq)/100 g material. In general, the higher the CEC of a soil, the greater the amount of metal a soil can accept without potential hazards. The CEC of soil is largely dependent on the amount and type of clay, organic matter, and oxides of iron, manganese and aluminium. With clay minerals, the exchange capacity increases markedly in the order kaolinite < chlorite < illite < montmorillonite. This increase corresponds accordingly with the reduction of particle size and the related increase of surface area. The exchange capacity of organic substances is particularly large, especially that of humic acids. A low percentage of organic matter can thus cause a marked increase in the CEC of the soil. There is much evidence to indicate that CEC can best be viewed as a general, but imperfect, indicator of the soil components that limit the solubility of metals instead of a specific factor in the availability of these metals (Adriano, 1986).

Grain size distribution

Grain size exercises a determining influence on the metal concentrations of a sediment (Förstner & Wittmann, 1983). Metals are not homogeneously distributed over the various grain size fractions and large differences in total metal concentrations can be observed in sediments sampled from a single locality. Within the grain size spectrum, the finer-grained fraction - consisting mainly of clay minerals - show relatively high metal contents. In the silt and fine sand fractions the metal concentrations generally decrease as that fraction is dominated by quartz components with low metal contents. In the coarser fractions, the presence of heavy minerals may cause the metal portion to increase once more (Salomons & Förstner, 1984). Several procedures to minimize grain-size effects on trace metal data are summarized by Förstner & Wittmann (1983). A commonly accepted correction method is based on the preferential occurrence of the heavy metals in the finest grain-size fractions. De Groot et al. (1971) found linear relationships between the amount of heavy metals and the fraction of particles smaller than 16 µm (expressed as a percentage of the $CaCO_3$-free mineral constituents in the oven-dry sediment) in samples from the river Ems (in the north of F.R.G.). The corrected metal content may be obtained by extrapolating the fraction smaller than 16 µm to 100% (De Groot et al.,1971) or to 50 percent (Salomons & De Groot, 1978).

Similar extrapolation techniques have been used for other grain size fractions (20 µm and 63 µm) by Lichtfuß and Brümmer (1977) and Smith et al. (1973) respectively. However, in order to calculate a regression line for the extrapolation procedure, a large number of samples that cover a wide range of grain size compositions is required. Therefore, Salomons and Förstner (1984) suggest to separate grain size fractions prior to chemical analysis. The fraction < 63 µm is recommended for the following reasons (Förstner & Salomons, 1980):

(1) trace metals have been found to be mainly present in clay/silt particles;
(2) this fraction is most nearly equivalent to the material carried in suspension;
(3) sieving does not alter metal concentrations - particularly when water of the same system is used;
(4) numerous metal studies have already been performed on the < 63 µm fraction, allowing better comaprison of results.

Redox potential

The water content of soils influences their capacity for trace elements through biological or chemical oxidation-reduction reactions. Sulphides of elements such as Cd, Zn, Ni, Co, Pb and Sn can form under reducing conditions. The sulphides of these elements are quite insoluble, so that their mobility and phytoavailability are considerably less than would be expected under well-oxidized soils. Exceptions are Mn and Fe in that they are more soluble under reducing than under oxidizing conditions. Oxygen deficiency leads to an initial dissolution of manganese oxides followed by that of hydrous iron oxides. Since these metals are readily soluble in their divalent states, any coprecipitates with metallic coatings become partially remobilized (Förstner, 1978).

Occurrence of synthetic complexing agents

Significant impacts on remobilization from polluted sediments may result from the growing use of synthetic complexing agents (e.g. NTA, nitrilotriacetic acid) in detergents replacing polyphosphates (Förstner, 1978). The extent of these effects depends on the concentration of the complexing agent, its pH value, the mode of occurrence of trace metals in the sediments and on the competition from other cations (Salomons & Van Pagee, 1981). The influence is two-fold: (1) the complexing agent may actively desorb heavy metals from sediments and (2) when both NTA and metals are discharged into a river system, the complexing agent may negatively influence the natural adsorption processes (Förstner, 1987).

4.5 Background levels

There are several sources of heavy metals in the environment, both natural and manmade: soil parent material, industrial processing of ores and metals, the use of metals and metal components, leaching of metals from garbage and solid waste dumps, automobile exhaust, and animal and human excretions which contain heavy metals. With the exception of the soil parent material, all are anthropogenic in nature. Soil parent material is the source of baseline or background levels. The trace element content of the soil is largely dependent on that of the rocks from which the soil parent material was derived and on the processes of weathering to which the soil-forming materials have been subjected. It is to be expected that in areas characterized by metal-bearing formations, these metals will also occur at elevated levels in the water and bottom sediments of the particular area. Obviously, mineralized zones, when economically viable, are exploited to retrieve and process the ore. This in turn leads to disposal of tailings discharge of effluents and possibly smelting operations which result in atmospheric pollution. In consequence, the general problem arises of how to distinguish between natural geologic weathering and metal enrichment attributable to human activities (Salomons & Förstner, 1984).

To determine the extent of pollution in an aquatic system by means of the heavy metal load in sediments, it is of primary importance to establish the natural level of these substances, i.e. the "precivilizational" level and then subtract it from existing values for metal concentrations in order to derive the total enrichment caused by anthropogenic influences (Salomons & Förstner, 1984). To obtain an ideal comparative basis for environmental studies, the following criteria should be fulfilled so as to achieve representative values for metal concentrations: a large number of sediment samples must be analyzed which correspond with recent deposits in their: (1) grain size distribution, (2) material composition and (3) conditions of origin. A fourth criterion is that the samples must be uncontaminated by anthropogenic influences.

Table 4.1 Local background levels of heavy metals in soils and surface waters

	soil (mg/kg)			water (µg/l)
metal	fossil deposits in Meuse basin1)	cultivated loess soils2)	reference value3)	9 tributaries of the Geul
Pb	16	30	74	4.8
Zn	44	86	109	47
Cd	0.4	0.8	0.6	0.3
Cu	19	13	30	11.6

1) Rang et al., 1986;
2) Van Driel & Smilde, 1981;
3) Anonymous, 1987a.

Table 4.1 gives a few examples of background concentrations for heavy metals in loess soils or loess-like materials in South Limburg. These background levels were established by different means. Rang et al. (1986) analyzed 22 samples of fossile eolian loess deposits in the Meuse basin, with an estimated age of 10.000 years. Van Driel and Smilde (1981) collected 40 samples from the upper 20 cm of soil profiles at 8 locations in South Limburg in cultivated loess areas. At

each location the 40 samples were mixed and then analyzed. The reference values (Anonymous, 1987b) were computed from average values of organic matter content and clay content of alluvial soils in the Geul basin (see Table 2.1). The computational procedure used is based on empirical relationships between organic matter and clay (as indicators for the CEC) and the amount of metals held onto exchange sites of organic and inorganic compounds (Anonymous, 1987b).
Local background levels for heavy metals in surface waters were computed from analytical data of water samples from 9 tributaries of the Geul in the Dutch part of the catchment (see Table 4.1).

4.6 Quality criteria

The Netherlands government has introduced a set of indicator values to determine the extent of pollution of water and soils in sanitation surveys (Anonymous, 1983). Three values, referring to total concentrations, are specified for a large number of chemical constituents: the A-value refers to an acceptable or 'natural' concentration (NB at present, government regulations require that the reference values mentioned in the previous section are used instead of the A-values); the B-value is the limit above which further investigation is deemed necessary; and if the C-value is exceeded, the feasability of removing the contaminated material needs to be investigated. The indicator values for the heavy metals in the soil are presented in Table 4.2.

Table 4.2 Indicator values for heavy metals in the soil (mg/kg) (Anonymous, 1983)

	Pollution class limits		
metal	A	B	C
Pb	50	150	600
Zn	150	500	3000
Cd	1	5	20
Cu	50	100	500

Table 4.3 Base quality standards for surface waters, and drinking water standards (μg/l)

metal	base quality standards for surface waters (Anonymous, 1987b)	drinking water standards (Anonymous, 1985b)	
		signal	maximum
Pb	≤ 50	15	50
Zn	≤ 200	-	100
Cd	≤ 2.5	1	5
Cu	≤ 50	-	100

For the assessment of surface water quality the Netherlands government has introduced a set of criteria that include values for metal concentrations (see Table 4.3). These values provide upper limits for surface waters in order to (1) cause no inconvenience (such as bad smell) to the surroundings, (2) provide adequate conditions for aquatic communities (including higher organisms such as fish) to develop and (3) allow human usage that does not require specific quality criteria (Anonymous, 1987b). For human consumption, the national legislation provides a set of drinking water standards that are also listed in Table 4.3. The signal values refer to limits above which further investigations are required.

5 THE DISPERSAL OF METAL MINING WASTES

5.1 Introduction

Mining activity and stream activity may interact in the fluvial environment (see Figure 5.1). Mobilized mining wastes may be transported as clastic sediments or solutes to be deposited or precipitated in a range of sedimentary environments, both within the floodplain domain (overbank deposits, channel cutoffs) and in the stream domain (point and channel bars and sloughs) (Lewin et al., 1977). Metal-rich sediments may be remobilized from these temporary storage compartments by mechanical or chemical means to be transported further downstream, where they may leave the fluvial system or reenter one of the storage compartments. In this chapter the processes that are responsible for the input and subsequent cycling of heavy metals in the fluvial environment are briefly discussed in general terms.

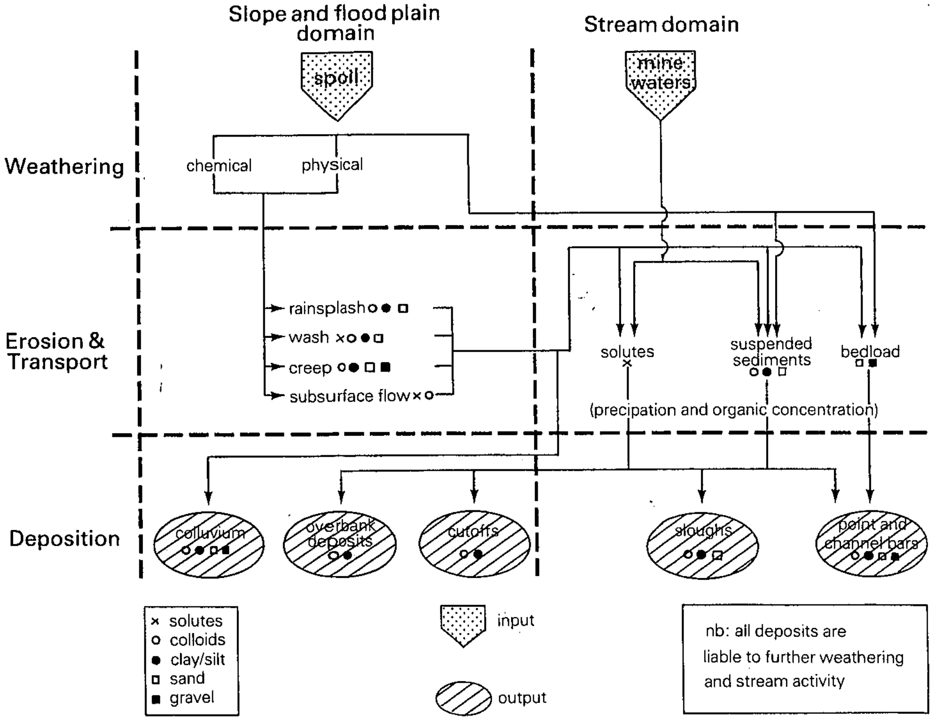


Figure 5.1 Schematic representation of the cycling of metals through a fluvial system during transport away from a point source (Lewin et al., 1977; redrawn).

5.2 Point source activity

The metal industry can be an important point source of heavy metals in the environment from (1) the mining and milling operations with problems of grinding, concentrating, transporting ores, disposal of tails along with mine and mill waste water and (2) the smelter refinery process with problems of concentrate, haulage, sintering, refining, atmospheric discharges, and blowing dust. The proportion of heavy metals released into the environment depends on the ores being processed. In the lead industry, lead, copper, zinc and cadmium can be released in substantial amounts. Similarly, in smelting zinc ores, sizeable releases of zinc, cadmium, copper and lead can occur. The impacts of atmospheric discharges from smelters can be detected within several kilometers from the point of release.

Waste dumps containing metal sulfides may continue to act as a source of heavy metals long after the mines were abandoned. Exposure of pyrite and of other metal sulfide minerals to atmospheric oxygen results in one of the most acidic of all known weathering reactions. The sulfidic components in pyrite are oxidized to sulphate, whereby acidity is generated and Fe^{2+} ions are released. Once this reaction has been initiated, a cycle is established whereby Fe^{2+} is oxidized to Fe^{3+}; the latter ion is capable of taking over the role of pyrite - thereby taking over the initial role of oxygen - to produce additional Fe^{2+} and acidity (Förstner & Wittmann, 1983). During recent years it has been emphasized that bacterial action can assist the oxidation of Fe^{2+} in the presence of dissolved oxygen (Förstner & Wittmann, 1983). In addition to chemical weathering, soil erosion processes (gullying, rainsplash, wash, creep and subsurface flow) may take place at waste dumps and transport metal-rich wastes to nearby river channels.

5.3 Dissolved and solid transport

In order to be able to understand the chemical cycles of trace metals in nature, it is necessary to know the mechanisms of their transport in rivers. This knowledge is indispensable in evaluating the fate of trace metals that man superimposes on the natural system (Gibbs, 1973). It has been suggested that the source of trace metals in aquatic systems significantly determines their distribution ratio between the aqueous and solid phases. This is especially true for river systems, where equilibrium between the solution and the dissolved phases can often not completely be achieved due to the short residence times (Salomons & Förstner, 1984). The quantitative significance of suspended sediment in heavy metal transport in fluvial systems is well established (e.g. Förstner & Salomons, 1980, Förstner & Wittmann, 1983; Bradley & Lewin, 1982; Salomons & Förstner, 1984). Data currently available suggests that the suspended load comprises more than 90 % of the particulate load in a majority of rivers (Hadley et al., 1985). The finer particles that are carried in suspension have a greater surface area and are therefore more likely to be associated with pollutants than the coarser particles transported as bedload. Computations of the dissolved transport index (DTI; Martin & Meybeck, 1979) revealed that in polluted river systems the percentage solid-bound metals of total transport varies from 30 to 98 (Salomons & Förstner, 1984).

The discharge of small streams is to a large extent governed by individual showers, whereas the discharge of large rivers is a function of seasonal phenomena (e.g. snow melt). The sediment transport shows a similar pattern, generally with a maximum flux during the rising stage of a flood. The nature and amount of the sediments depends on the yield of the catchment and on the carrying capacity of the flow. Alluvial rivers may receive sediments from upstream and from erosion in their beds, especially from concave banks in meanders. Deposition occurs on the bed and on the floodplains. The different sources contributing to the sediment load during high discharge are also reflected in the metal concentrations of the sediments (Salomons & Förstner, 1984). A general discussion of the possible relationship between metal concentrations and river discharge was presented by Hellmann (1970) from the example of zinc loads im the River Rhine (see Figure 5.2).

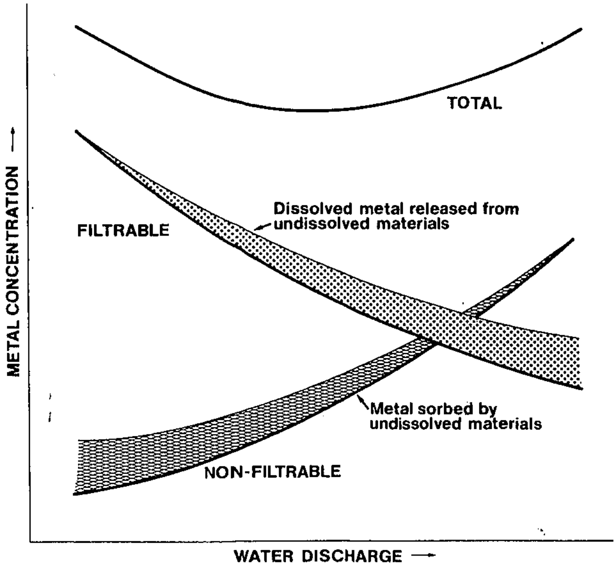


Figure 5.2 Schematic presentation of the transport modes of heavy metals (example: zinc) in rivers (Wilson, 1976).

The heavy lines represent the major developments of the solid-bound and dissolved fractions of the metal load with increasing discharge: (1) a decrease in the dissolved fraction by dilution and (2) an increase of the non-filtrable fraction as a result of re-suspension of particles from the river bed and banks. The shaded areas on the upper section of both curves indicate minor effects of sorption, as in the case of solid fractions, and remobilization from the particulates, which increase the dissolved metal load to some extent. The decrease of the amount of sorbed cations with increasing discharge can be explained 1) by the higher percentage of relatively coarse material, which usually exhibits lower exchange capacities, 2) by a lesser amount of dissolved cations due to dilution, and 3) by the shorter residence times of both solids and dissolved ions in the river channel, which in turn influence the attainment of equilibrium between both phases. On the other hand, metal cations are increasingly released from solid substances into the aqueous phase at higher water discharges owing to desorption or dissolution processes. There does not appear to be any significant variation in the total metal load with changing water discharge (Förstner & Wittmann, 1983). Contrary to what is suggested by the above general relationships, recent studies have demonstrated that when studying the transport of particulate-bound heavy metals, rating curves relating solid-bound metals to water discharge may fail to provide an adequate basis for the calculation of the mass transport of contaminants (Bradley, 1982). Dilution effects, as seen in studies concerned with soluble load, apply equally well to surface coatings of Pb, Zn and Cd while, on the falling limb of the flood hydrograph, metal concentrations may change according to the instantaneous activity of various sources (Bradley & Lewin, 1982).

5.4 Storage

Point bars, overbank deposits and abandoned channel loops are the main storage sites for sediment in the floodplains of meandering rivers. The chemically defined storage compartments of metals within these sediments were discussed in Section 4.3.1. In this section the quantitative aspects of sediment storage will be discussed.

Point bars are deposited on the insides of channel bends as the outsides of the bends are eroded during meander migration and are commonly dominated by bedload sediments. Overbank sediments are deposited by flood waters that have risen over the banks of a river during high flow stages. Overbank deposits are commonly dominated by suspended-load sediments (Allen, 1965). Channels that have been abandoned due to meander cutoffs are filled by moderate and large flows that allow water and sediment to enter the abandoned channel. Both bedload and suspended load sediments are deposited in abandoned channels.

Reported rates of overbank deposition on floodplain surfaces vary widely. Data compiled by Bridge and Leeder (1978) showed that rates of overbank deposition on floodplain surfaces with a period of record of 1000 years or less are commonly between 0.8 and 2.8 cm/yr, with rates ranging as high as 8.3 cm/yr and as low as 0.1 cm/yr. These rates may reflect increases of sediment yield of rivers resulting from land use changes. Because the introduction of pollutants into a river system is often either directly related to, or is synchronous with, the disturbance of a watershed by land use changes, these high rates of overbank deposition are relevant to the discussion of the deposition of contaminated sediments on floodplain surfaces (Marron, 1986). On floodplain surfaces, the extent of high rates of overbank deposition from the stream channel towards the valley slopes is unclear. In

his study on floodplain formation in the Beatton River Nanson (1980) reports a mean sedimentation of 6.1 cm/yr on those parts of floodplains that are less than 50 years old, a mean sedimentation rate of 0.8 cm/yr on the parts that are 50 to 250 years old, and negligable sedimentation on floodplains that are more than 250 years old. Marron (1986) provided evidence that on the floodplains of the Belle Fourche River, the thickness of metal-contaminated overbank sediments decreases with increasing distance from the stream channel.
The spatial distribution of sediment-associated metals within the floodplain area may reflect the geomorphological processes that caused the sediments to occupy their present spatial position (Leiwn et al., 1983). Wolfenden and Lewin (1977) demonstrated that in the floodplains of the polluted River Rheidol metal levels may be significantly higher in fine sediments, deposited in low energy environments such as abandoned channel loops and backwater areas, than they are in coarse bar sediments. Rang et al. (1987) demonstrated that grouping data on soil metal concentrations in accordance with map units of the German system of soil classification, that takes into account the rate of recent sedimentation, accounts for up to 70 % of the variance of metal concentrations in the Meuse floodplains.

5.5 Remobilization

Chemical remobilization

Once a metal has become incorporated into a sediment it has not entered a static environment. Diagenetic processes can cause it to migrate between the various solid storage compartments (see Section 4.3 & Section 4.4) within the reservoir itself, and can also lead to it being lost from the sediment to enter the environmental reservoirs such as ambient waters and biota. The processes involved in 'early' diagenesis, i.e. that occurring in the upper few tens of meters of the sediment column, are extremely complex and by no means fully understood. Nevertheless, the processes that most affect the characteristics of metals in sediments are associated with changes in redox potential, pH and the concentration of natural and synthetic complexing agents (see Section 4.3) (Chester, 1987). The effects of diagenetic processes can manifest themselves in various ways, including: (1) the destruction of organic matter which can give rise to post-depositional mobilization of metals, (2) the formation of new minerals and mineral coatings, (3) the ageing of minerals such as Mn and Fe oxides and oxy-hydroxides, (4) the production and dissolution of metal precipitates (e.g. oxides, sulfides) and (5) the desorption of metals from mineral surfaces following the formation of soluble organic and inorganic complexes. The fate of metals released by diagenesis depends on the physico-chemical conditions prevailing in the interstitial waters.

Mechanical remobilization

Given the often observed high deposition rates, river floodplains may be considered as efficient sinks of sediments and sediment-associated contaminants. Moreover, in a dynamic fluvial environment where the river channel rapidly migrates across its floodplain, the contaminated alluvial soils are quickly reworked so that the floodplain may also function as a diffuse, nonpoint source of contaminants (Marron, 1986; Bradley & Cox, 1986; Lewin & Macklin, 1987; Davies & Lewin, 1974; Wolfenden & Lewin, 1977). Hooke (1980) has summarized data from several studies in south-east Devon and found the bank erosion rates to vary from 0.08 to 1.18 m/yr, implying that complete floodplain reworking by the sampled rivers could occur in periods ranging from 600 to 7000 years. Leopold et al. (1974) and studies cited by Schumm (1977) indicate that the time period over which sediment is stored in many floodplains is likely to be in the order of a millenium. Contributions of streambank erosion may account for 25-60 % of the sediment load of a river, even in drainage basins which contain considerable areas of cultivated land (Grimshaw & Lewin, 1980; Robinson, 1977; Duijsings, 1985, 1986 & 1987).

A second, less efficient and short-term fluvial storage compartment is provided by the river channel. During periods of low flow, the carrying capacity (quantity of material that can be held in suspension) is low, causing a build up of in-channel deposits in depressions along the streambed or in millraces. Whenever turbulence (caused by increased flow) is sufficiently intense, the carrying capacity of the stream increases, and the increased friction along the stream bed resuspends the accumulated sediments.

Given the often fine-grained texture of these sediments, their capacity for adsorbing heavy metals may be high.

6 THE THEORY OF REGIONALIZED VARIABLES

6.1 Introduction

This chapter presents an introduction for the nonspecialist to the use of geostatistics to map and estimate contaminant concentrations and estimation errors from a set of measured contaminant concentrations. Geostatistics is a name given to a set of statistical procedures for describing the correlation of spatially distributed random variables and for performing interpolation and areal estimation for these variables (Cooper & Istok, 1988a). The fundamentals of geostatistics were developed by Krige, Sichel, and De Wijs in the 1950s to estimate ore reserves in the gold fields of South Africa (Clark, 1979; David, 1977, Henley, 1981). Matheron (1963, 1971) gave this largely empirical work its theoretical basis in the theory of regionalized variables. Recent publications (e.g. Burrough, 1986; Webster, 1985; Cooper & Istok, 1988a, b & c; Lam, 1983; Journel & Huijbregts, 1978; Burgess & Webster, 1980; McBratney & Webster, 1986) demonstrate that geostatistics are useful tools for making quantitative maps of soil properties.

6.2 Basic concepts

The theory of regionalized variables considers differences between pairs of values of a property at places separated by any distance and expresses these as variances. Differences with respect to direction can also be taken into account. Suppose we have the value z(**x**) and z(**x**+**h**) at **x** and **x**+**h**, respectively, where z(**x**) is the value of a regionalized variable at location **x**, **x** and **x**+**h** are positions with one, two or three spatial coordinates and h is a vector with both distance and direction, usually known as the lag, separating them. Then the relation between pairs of points h intervals apart can be expressed as the variance of the differences between all such pairs. The per-observation variance between pairs is half this value, thus:

$$s^2 = \tfrac{1}{2}\,[z(\mathbf{x}) - z(\mathbf{x}+\mathbf{h})]^2. \qquad [6.1]$$

In the theory of regionalized variables the quantity s^2 is called semi-variance, which is the average variance associated with differences in the value of z over a distance h. If we have, say, n pairs of observations seperated by the same lag, h, we can estimate their average:

$$\overline{s^2} = (\tfrac{1}{2}n) \sum_{i=1}^{n} [z(x_i) - z(x_i+h)]^2 \qquad [6.2]$$

To make use of this simple notion and generalize equation [6.2], certain stationarity assumptions must be made. These are as follows:

1. The expected value of z at any place x is the mean, μ:

$$E[z(x)] = \mu. \qquad [6.3]$$

(NB In the case where a 'drift' or trend is present, a suitable function, m(x), describing this 'structural' component that replaces μ in [6.3] needs to be found.)

2. For any h the difference z(xi)-z(xi+h) has a finite variance, which again is independent of x:

$$\begin{aligned} \mathrm{var}\,[z(x) - z(x+h)] &= E\{[z(x) - z(x+h)]^2\} \\ &= 2\,\gamma(h). \end{aligned} \qquad [6.4]$$

These two assumptions constitute the intrinsic hypothesis of regionalized variable theory. They assume the following model of soil variation:

$$z(x) = \mu_V + \epsilon'(x) + \epsilon''(x), \qquad [6.5]$$

where z(x) is the value of the property at position x within a region, μ_V is the mean value in that region, $\epsilon'(x)$ is a spatially random component with zero mean and variance defined by:

$$\mathrm{var}[\epsilon'(x) - \epsilon'(x+h)] = E\{[\epsilon'(x) - \epsilon'(x+h)^2\} = 2\,\gamma(h), \qquad [6.6]$$

and $\epsilon''(x)$ is a residual, spatially independent Gaussion noise term having zero mean and variance σ^2 (NB the original formulation of the theory did not include the residual error). In a large region, of course, we know that a soil property will vary from one part to another. Nevertheless, the property will commonly be locally stationary within some neighborhood V, and this condition is usually quite adequate for analyses in which h is limited to some maximum radius r within which the relationships apply. It is for this reason that the subscript V is used in equation [6.5].

Where the intrinsic hypothesis holds, we can expect the same degree of difference in the soil property at any two places h apart, whatever the actual values of the property are. In these circumstances, the sample value s^2 in equation [6.2] is an unbiased estimate of the average semi-variance, $\gamma(h)$, in the population.

6.3 The semi-variogram

6.3.1 Calculation of the experimental semi-variogram

If the conditions specified by the intrinsic hypothesis are fulfilled, the semi-variance can be estimated from sample data:

$$\gamma(h) = (\tfrac{1}{2}n(h)) \sum_{i=1}^{n(h)} [z(x_i) - z(x_i+h)]^2 \qquad [6.7]$$

where $n(h)$ is the number of pairs of sample points seperated by distance h. Difficulties arise when samples were taken at irregular intervals. This can be overcome by choosing a set of lags, h_i, at arbitrary but constant intervals d. All pairs of observations that are separated by a lag that falls in the range $h_i \pm d$ are then used to estimate the average semi-variance $\gamma(h_i)$ at average lag h_i. A plot of $\gamma(h)$ against h is known as the sample semi-variogram.

There are two sources of errors associated with the estimate of the true semi-variogram given by equation [6.7] (Journel & Huijbregts, 1978). The first source of error is from estimating the value of the true semi-variogram from the limited number of measurements that are available. This error is called the variance of estimation, and it is a function of $n(h)$, the number of sample pairs used to estimate $\gamma(h)$ for each distance or distance interval h. The second source of errors is from fluctuations of the local mean about the assumed mean. These fluctuations cause estimates of the semi-variogram to also vary from point-to-point. For small numbers of samples these errors cannot be analysed accurately. However, Journel & Huijbregts (1978) give two practical rules for estimating the true semi-variogram from a set of sample values:

1. $n(h) > 30\text{-}50$ [6.8]

2. $|h| < L/2,$ [6.9]

where $|h|$ is the magnitude of the lag h and L is the longest dimension (in the direction of h) of the area under study.

6.3.2 Theoretical semi-variogram models

In general, a few simple features contribute to the form of a semi-variogram. The semivariance at zero lag must be zero, but in practice the extrapolated semivariogram usually intercepts the ordinate at a positive value known as the 'nugget variance'. The nugget variance can arise from measurement error, discrete random variation and spatially dependent variation occurring over distances much less than the sampling interval (Oliver and Webster, 1986). In most instances it is found that $\gamma(h)$ increases from the nugget variance to a maximum level at which it levels out. Such semivariograms are said to be transitive, the maximum is known as the sill, and its value is the a priori variance of the variable (i.e. when the spatial correlation is zero). The lag at which the sill is reached is known as the range; the range is a limiting value of the lag, because beyond it there is no longer any spatial dependence. In some cases, the increase of $\gamma(h)$ appears to have no limit: the soil properties have no finite variance. Such semivariograms are said to be unbounded. Less commonly, a semivariogram has a marked reversal of slope after reaching its maximum. This indicates some degree of regular repetition in the variable: if the semivariogram fluctuates then periodicity may be inferred.

Structural analysis is the fitting of a mathematical model to the experimental semi-variogram. Any mathematical function may be used to model an experimental semi-variogram as long as it is conditional positive-definite (i.e. yields estimates with a positive estimation variance) (Olea, 1975). In practice only a few functions are used. Models are of two types depending on whether or not the experimental semi-variogram exhibits a sill. This section defines theoretical models that can be recommended for semi-variograms of soil properties. They are defined for one dimension but are safe in the sense that they are conditional positive definite in two and three dimensions.

Linear model (see Figure 6.1a)
The simplest model that can be fitted in one dimension is clearly linear. It has slope w and may have an intercept or nugget variance C_0:

$$\gamma(h) = C_0 + wh \qquad \text{for } h > 0 \qquad [6.10]$$
$$\gamma(0) = C_0.$$

In the limit w can be zero. The semi-variogram is then said to show pure nugget effect. There is no spatial dependence at the scale of investigation since all of the variance occurs within the smallest sampling interval.

Spherical model (see Figure 6.1b)
The definition of the spherical model is:

$$\gamma(h) = C_0 + C\{(3h/2a) - (h/2a)^3\} \quad \text{for } 0 < h <= a \qquad [6.11]$$
$$\gamma(h) = C_0 + C \quad \text{for } h > a$$
$$\gamma(0) = C_0,$$

where a is the range, C_0+C is the sill, and C_0 is the nugget variance as before.

Exponential model (see Figure 6.1c)
The formula of the exponential model is:

$$\gamma(h) = C_0 + C\,\{1 - \exp(-h/r)\} \qquad \text{for } h > 0 \qquad [6.12]$$
$$\gamma(0) = C_0$$

The spatially dependent variance and nugget are C and C_0 as before, and r is a distance parameter controlling the spatial extent of the function. Here $\gamma(h)$ approaches the sill asymptotically, and so there is no strict finite range. Nevertheless, it is clear that for practical purposes the semi-variance ceases to increase beyond some point, and a commonly used rule of thumb is to take this as the effective range, $a'=3r$ at which $\gamma(a')$ is then equal to $C_0+0.95C$.

Gaussian model (see Figure 6.1d)
The formula of the Gaussian model is:

$$\gamma(h) = C_0 + C\,(1 - \exp(-h^2/r^2) \qquad \text{for } h > 0 \qquad [6.13]$$
$$\gamma(0) = C_0$$

where r again is a distance parameter as in the exponential case.

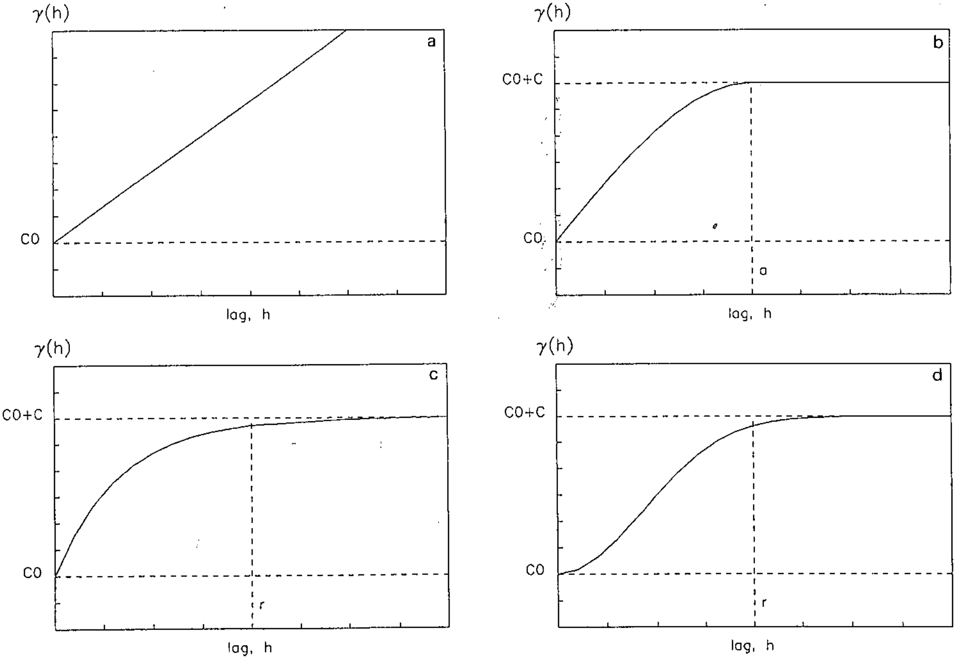


Figure 6.1 Theoretical variogram models: a) linear, b) spherical, c) exponential and d) gaussian.

If all of the semi-variograms are identical regardless of the direction of h, the spatial structure of the soil property is said to be isotropic. The spatial correlation then depends only on the distance of separation $|h|$, not on the direction. When the semi-variogram is a function of the direction of h, the spatial structure is said to be anisotropic. The isotropic structures representing the various directions of anisotropy are added together or nested to give the spatial correlation for all directions.

6.3.3 Fitting a theoretical model to the experimental semi-variogram

The procedure for fitting a theoretical model to the experimental semi-variogram consists of several steps. Preliminary estimates of model parameters (e.g. a and C_0) may be obtained by eye or by the method of weighted least squares (weighted because the number of sample pairs used to compute each point on the semi-variogram is, in general, different) (Cressie, 1985). At this stage, the fitting procedure can be guided by what is already known about the soil of a region. The investigator may wish to interpret the semi-variogram in terms of some physical processes or geologic origin, and a model that makes this possible is likely to be preferred to one that does not.

The best type of model may be determined from a set of potential models by the cross-validation procedure proposed by Delhomme (1976). This same procedure can be used to aid the identification of the best model parameters. In the cross-validation procedure, sample values are deleted from the data set one at a time and then kriging (see next section) is performed with the remaining sample values to estimate the value at the location of the deleted sample. Statistical analysis of the kriging errors (i.e., the differences between estimated values and observed values) and the standardized mean squared errors (i.e., the average of the kriging errors divided by their respective kriging variances) determine if there is a bias in the estimates and if the estimation errors are consistent with the kriging variances. To be unbiased, the average kriging error (AKE) must be close to zero:

$$\mathrm{AKE} = (1/n) \sum_{i=1}^{n} [\hat{z}(x_i) - z(x_i)] = 0 \qquad [6.14]$$

where $\hat{z}(x_i)$ is the estimated value at x_i, $z(x_i)$ is the measured value at x_i, and n is the number of samples. For the kriging errors to be consistent with the kriging variances, the standardized errors should be normally distributed with a mean close to zero and a variance close to one. The choice of model is optimized by finding the model with the minimum mean squared error (MSE):

$$\mathrm{MSE} = (1/n) \sum_{i=1}^{n} [\hat{z}(x_i) - z(x_i)]^2 = \text{minimum.} \qquad [6.15]$$

As a practical rule, the MSE also should be less then the variance of the sample values:

$$\mathrm{MSE} < \sigma^2 \qquad [6.16]$$

where σ^2 is the variance of the sample values. If MSE is less then σ^2, the kriging estimate is better than the estimate provided by the mean for all sample values. The consistency requirement is satisfied if the variance of the standardized mean squared error (SMSE):

$$\mathrm{SMSE} = (1/(n-1)) \Sigma \{[\hat{z}(x_i) - z(x_i)]^2\}/\sigma_e^2 \qquad [6.17]$$

(where σ_e^2 is the kriging variance) is in the interval $1 \pm 2\surd(2/n)$.

6.4 Spatial interpolation by kriging

Given a set of values $z(x_1)$, $z(x_2)$,....,$z(x_n)$, we wish to estimate the value $z(x_0)$ at a point x_0. Let our estimate be a linear sum, or weighted average:

$$\hat{z}(x_0) = \sum_{i=1}^{n} \lambda_i . z(x_i) \quad \text{with} \quad \sum_{i=1}^{n} \lambda_i = 1 \qquad [6.18]$$

where the λ_i are coefficients or weights associated with the data points. In kriging the weights are so chosen that the estimate $\hat{z}(\mathbf{x}_0)$ is unbiased and the error associated with the estimate is less than that for any other linear sum. The weights take account of the known spatial dependences expressed in the semi-variogram and the geometric relationships among the observed points. In general, near points carry more weight than distant points, points that occur in clusters carry less individual weight than lone points, and points lying between the point to be interpolated and more distant points screen the distant points so that the latter have less weight than they would otherwise have had.

The minimum variance of $\hat{z}(\mathbf{x}_0)$ is obtained when

$$\sum_{j=1}^{n} \lambda_j . \gamma(\mathbf{x}_i,\mathbf{x}_j) + \phi = \gamma(\mathbf{x}_i,\mathbf{x}_0) \text{ for all } i, \qquad [6.19]$$

and is

$$\sigma^2{}_e = \sum_{j=1}^{n} \lambda_j . \gamma(\mathbf{x}_j,\mathbf{x}_0) + \phi. \qquad [6.20]$$

The quantity $\gamma(\mathbf{x}_i,\mathbf{x}_j)$ is the semi-variance of z between the sampling points $\mathbf{x}_i$ and $\mathbf{x}_j$; $\gamma(\mathbf{x}_i,\mathbf{x}_0)$ is the semi-variance between the sampling point $\mathbf{x}_i$ and the unvisited point $\mathbf{x}_0$. Both these quantities are obtained from the model that has been fitted by the experimentally derived semi-variogram. The quantity ϕ is a Lagrange multiplier required for the minimalization.

Kriging is an exact interpolator in the sense that when the equations given above are used, the interpolated values, or best local average, will coincide with the values at the data points. In mapping, values will be interpolated for points on a regular grid that is finer than the spacing used for sampling. Similarly, the estimation error $\sigma^2{}_e$, can also be mapped to give valuable information about the reliability of the interpolated values over the area of interest.

The procedure based on equations [6.17], [6.18] and [6.19] is referred to as point kriging, because it gives estimates at points in the domain of estimation. Some features of point kriging are in some circumstances seen as shortcomings (Burgess & Webster, 1980b). Firstly, the points for which estimates are made are actually volumes of soil with the same shape and size as the volumes of soil on which the original observations were made. However, the investigator inspecting the soil by auger or in a pit usually intends that observation to represent the area surrounding it. Therefore, when interpolating he may similarly wish to interpolate an average value for an area or block many times larger than the volumes actually observed. Secondly, although a map drawn from point estimates is the most accurate isarithmic map that can be made using a set of point data, local discontinuity can seriously obscure longer range trends. Further, the positions of the discontinuities depend on the locations of particular data points. A shift in the origin or orientation of an observation grid could result in a substantially different map. This is a sampling effect that is clearly undesirable. These features of point kriging can be avoided by kriging over areas, a procedure known as block kriging, resulting in smaller estimation variances and smoother maps. In order to explain the difference between point kriging and block kriging, the equation denoting the block kriging estimation variance at block B needs to be considered:

$$\sigma^2_e(B) = E\{[z(B) - \hat{z}(B)]^2\}$$

$$= 2 \sum_{i=1}^{n} \lambda_i . \gamma(x_i, B)$$

$$- \sum_{i=1}^{n} \sum_{j=1}^{n} \lambda_i . \lambda_j . \gamma(x_i, x_j) - \gamma(B, B) \qquad [6.21]$$

(Webster, 1985). Here $\gamma(x_i, x_j)$ is the semivariance of the property between x_i and x_j, $\gamma(x_i, B)$ is the average semivariance between x_i and all points within the block, and $\gamma(B,B)$ is the average semivariance within the block. In point kriging this last term is zero - there is no variance at a point - and the quantity $\gamma(x_i, B)$ is just the semivariance between x_i and the point to be estimated. Thus, point kriging can be regarded as a special case of block kriging (Webster, 1986). By analogy with equation [6.19] the minimum block kriging variance is obtained when

$$\sum_{i=1}^{n} \lambda_i \cdot \gamma(x_i, x_j) + \emptyset = \gamma(x_j, B) \text{ for all } j \qquad [6.22]$$

6.5 Spatial interpolation by co-kriging

Co-kriging is the logical extension of kriging to situations where two or more variables are spatially interdependent and the one of immediate interest is undersampled (Alemi et al., 1988a; David, 1977; Journel & Huijbregts, 1978; McBratney & Webster, 1983; Myers, 1982 & 1984; Vauclin et al, 1983). Co-kriging may be a useful method for interpolating a property that is expensive to measure by making use of a large spatial correlation between the property of interest and an attribute that is cheaper to measure.

Just as values of a property can depend in the statistical sense on those of the same property at other places nearby, so can they be related spatially to values of other properties. Where this is so the variables are said to be co-regionalized: they are spatially dependent on one another. By analogy with the single variable, the dependence between two variables can be expressed by a cross variogram. For any pair of variables U and V, the cross semi-variance $\gamma_{UV}(h)$ at lag h is defined as:

$$2\gamma_{UV}(h) = E[\{z_U(x) - z_U(x+h)\}\{z_V(x) - z_V(x+h)\}] \qquad [6.23]$$

where z_U and z_V are the values of U and V at places $\mathbf{x}$ and $\mathbf{x}+h$. If U=V the above equation denotes the auto semi-variogram (McBratney & Webster, 1983).

The cross variogram is estimated directly from the sample data by:

$$\gamma_{uv}(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \{z_u(x_i) - z_u(x_i+h)\}\{z_v(x_i) - z_v(x_i+h)\} \qquad [6.24]$$

where N is the number of data pairs at locations x_i and x_i+h in a given distance and direction class h (David, 1977).

In the process of cross variogram fitting the Cauchy-Schwarz inequality:

$$\gamma_{uv}(h) <= \sqrt{(\gamma_u(h) * \gamma_v(h))} \quad \text{for all } h>=0 \qquad [6.25]$$

should be checked so as to guarantee a positive cokriging variance in all circumstances (Journel and Huybregts, 1978; Myers, 1982; Myers, 1984; Nienhuis, 1987).

A co-kriged estimate is a weighted average of the available data with weights chosen so that the estimate is unbiased and has minimum variance, and in practice only near observations carry enough weight to have effect (McBratney & Webster, 1983).

If there are V variables, v=1,2,....,V and each is measured at n_v places, x_{iv}, i=1,2,....,n_v, then the value of one of the variables say u at x_0 is estimated by:

$$\hat{z}_u(x_0) = \sum_{v=1}^{V} \sum_{i=1}^{n_v} \lambda_{iv}\, z(x_{iv}) \quad \text{for all } v. \qquad [6.26]$$

(McBratney & Webster, 1983). To avoid bias, i.e. to ensure that $E[z_u(x_0)-\hat{z}_u(x_0)]=0$, the weights, λ_{iv}, must sum as follows:

$$\sum_{i=1}^{n_v} \lambda_{iv}=1 \quad \text{for } v=u \quad \text{and} \quad \sum_{i=1}^{n_v} \lambda_{iv}=0 \quad \text{for all } v \neq u \qquad [6.27]$$

The first condition implies that there must be at least one observation of the variable u for co-kriging to be possible.

Subject to these conditions the weights are chosen to minimize the variance,

$$\sigma^2_u(x_0) = E[\{z_u(x_0) - \hat{z}_u(x_0)\}^2], \qquad [6.28]$$

by solving the appropriate kriging equations. There is one such equation for each combination of sampling site and property. Therefore for estimating variable 1 at site x_0 the equation for the g-th observation site of the v-th variable is:

$$\sum_{l=1}^{V} \sum_{i=1}^{n_v} \lambda_{il}\, \gamma_{il}\, (x_{il}, x_{gv}) + \varnothing_v = \gamma_{uv}(x_0, x_{gv}) \qquad [6.29]$$

(McBratney & Webster, 1983) for all $g=1$ to n_v and all $v=1$ to V, where ϕ_v is a Lagrange multiplier. Together these equations form the co-kriging system. As with simple point kriging the place to be estimated is a volume of soil with the same size and shape as those on which the original observations were made.

7 THE TRANSPORT OF HEAVY METALS

7.1 Introduction

In the fluvial environment, the transport of sediments is directly related to hydrological and geomorphological phenomena. The main processes are: erosion of the sediments from bottom or channel bank, vertical transport of particles in the water body, horizontal transport by flow, deposition on the bottom of the river and the floodplains, and compaction of the deposit. All these phenomena interact and vary in space and time. Their result is expressed in the geomorphology of an alluvial area. A proper understanding of the dynamics (erosion, transportation, sedimentation) is not only essential for most sedimentological studies but also for the prediction of the fate of sediment-bound contaminants (Salomons & Förstner, 1984; Wolfenden & Lewin, 1977; Bradley, 1984; Rang et al., 1986; Lewin & Macklin, 1987; Rang et al., 1987).

For practical reasons it is usually necessary to construct rating curves of suspended solids concentrations against discharge when attempting to calculate the solid load removed over a given time period (Finlayson, 1978; Hellman, 1987). Since discharge is often not the only important explanatory variable for suspended solids concentrations the scatter on these rating curves is often quite large. Walling (1974) attempted to overcome this problem by using seasonal curves for summer and winter and Loughran (1976) has separated "seasonal", "rising" and "falling" and "stationary" flow stages.

The quantitative significance of suspended sediment in heavy metal transport is well established (Salomons & Förstner, 1984; Bradley, 1984; Ongley, 1982). The relationship between sediment concentration and metal concentration is important in this context as it may reflect the change in total surface covering by the metals, and thus the total mass of metal transport at a given discharge (Bradley & Lewin, 1982). Bradley (1982) demonstrated the occurrence of strong negative correlations between the two properties for the River Ystwyth (Wales), but rating curves may fail to provide an adequate basis for the calculation of the mass transport of contaminants. It is often observed that at times of flood the concentrations of heavy metals carried in solution and bound to suspended particulates decrease as a result of mixing with relatively clean water and sediment. This so-called 'dilution' effect has been clearly demonstrated by many authors (e.g. Grimshaw et al., 1976; Bird, 1987; Bradley & Lewin, 1982; Salomons & Förstner, 1984; Salomons & Eysink, 1981). However, in a fluvial environment with an abundance of potentially available contaminated sediments, one may expect an increase of the solid-bound metal levels because of re-suspension of particles from the river bed and banks (Williams et al., 1973; Förstner & Wittman, 1983). Williams et al. (1966) confirmed that the turbulence present during periods of increased flow of the Ohio River at Cincinnati caused resuspension of ooze material and a corresponding rise in the metal content of suspended material.

Metal-rich sediments derived initially from historic mining and mine drainage and spoil still provide an input of metals into the River

Geul. A secondary source of metals is provided by the reworking of older, locally highly contaminated sediments along the course of the river, as the channel migrates across the floodplain. Flood conditions are required for effective removal of fines from the channel sides and for transport of appreciable quantities of sediment. In order to study the relationships between river discharge, sediment levels and associated metal concentrations under various flood stages, a flood event occurring on the River Geul in March 1988 is considered here in detail. Rating curves for suspended sediments and metal loads were established for various flood stages and the mass transport is calculated both for a single flood and on an annual basis.

7.2 Experimental procedures

The Provincial Water Authorities provide semi-continuous discharge data at 15 min intervals for gauging stations near the villages of Meerssen and Partij (see Figure 2.1). Sampling of water from the River Geul at the Meerssen gauging station was undertaken using a Manifold pump sampler set to extract samples of 1 l at hourly intervals. In common with most automatic samplers, the Manifold sampler does not provide a depth integrated sample. The samples therefore represent the finer wash load component of the river, which has a more or less stable particle size distribution throughout the flood. It is recognized that the occurrence of brief sediment 'pulses' of high sediment concentrations, cannot be registered with the Manifold sampling device. For the registration of such short term variations, continuous monitoring by turbidity meters (Truhlar, 1978) may be a useful alternative.

During conditions of low flow and at the falling stages of a number of minor floods in 1986 and 1987 bulk samples (20-60 l) were taken at three gauging stations along the Geul: Terbruggen, Partij and Meerssen, see Figure 2.1).

In order to obtain an insight into the quality of sediments which are supplied to the channel during floods, in the Dutch part of the catchment streambank deposits were sampled at various depths at those locations where marks of recent erosion could be observed. In addition, samples were taken of ooze materials from the bottom of a number of millraces and of waste materials that are still present on the river banks in the vicinity of the towns of Kelmis and Plombières (see Figure 2.1). The preparation of the samples and the extraction and analyses of heavy metals are described in chapter 3.

7.3 Flood effects

In March 1988 a flood event, with a recurrence interval of 2-3 years and a discharge peak of 37 m^3/s at the outlet, occurred in the catchment of the Geul. Figure 7.1 shows the flood hydrograph, the suspended sediment concentrations and metal levels during the course of this event. Three-hour moving averages are displayed as well. Because of malfunctioning of the sampling device, no observations could be made between 100 and 138 hrs.

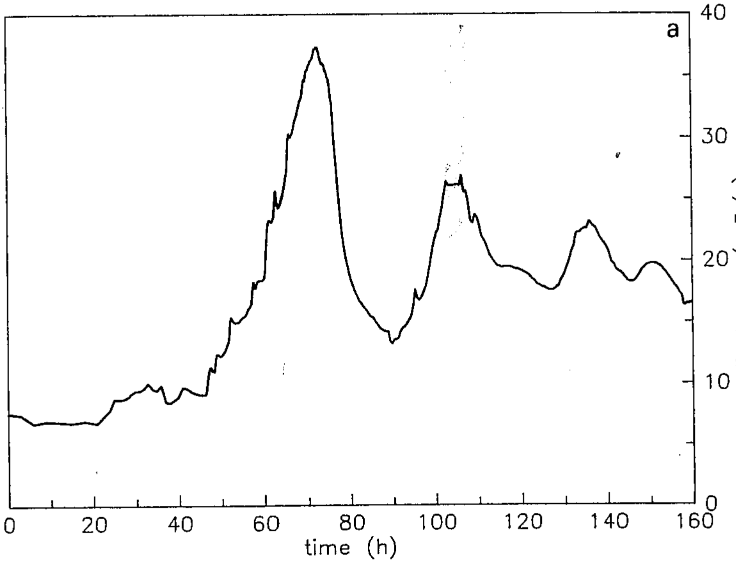


Figure 7.1a Flood hydrograph of the Geul at Meerssen (10-19 March 1988; time at beginning of flood: 10 March, 0.00 h).

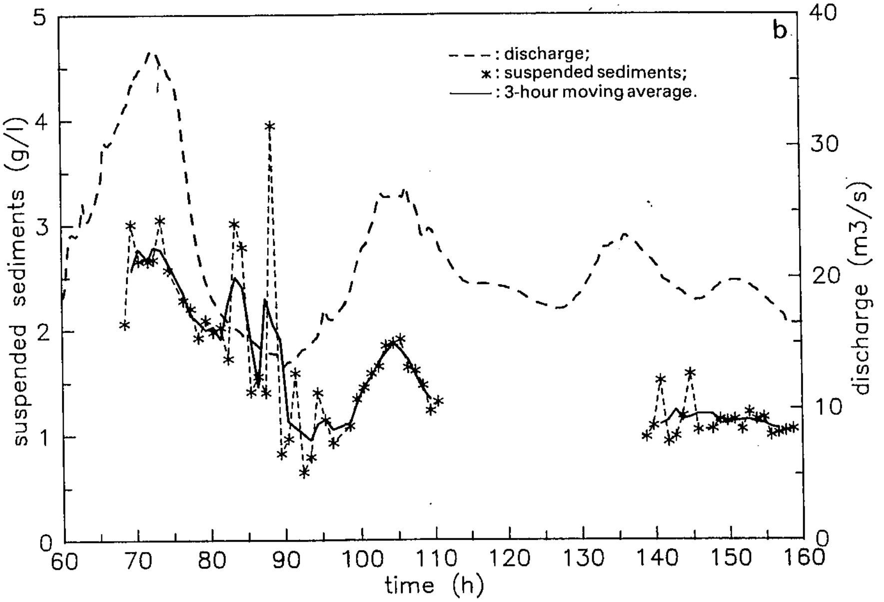


Figure 7.1b Suspended sediment concentrations at Meerssen during the March 1988 flood.

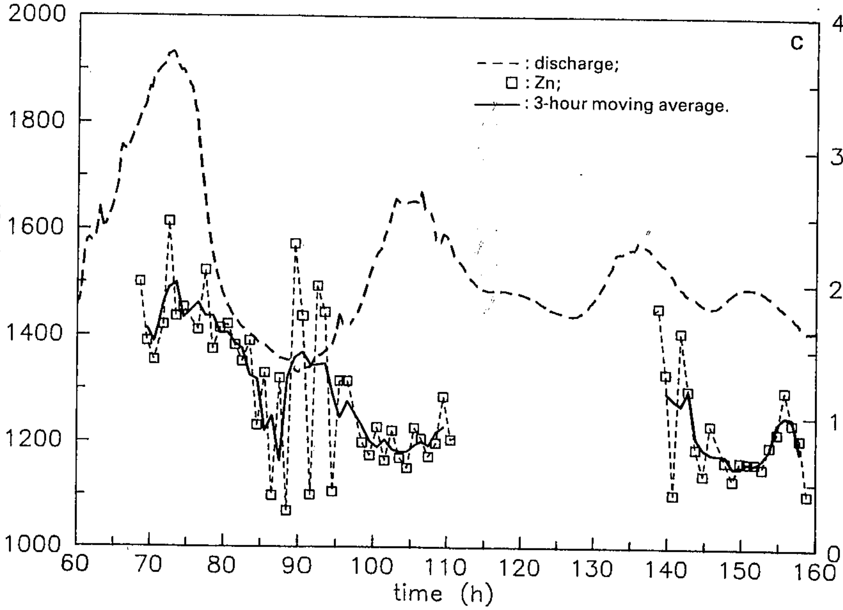


Figure 7.1c Solid-bound Zn concentrations at Meerssen during the March 1988 flood.

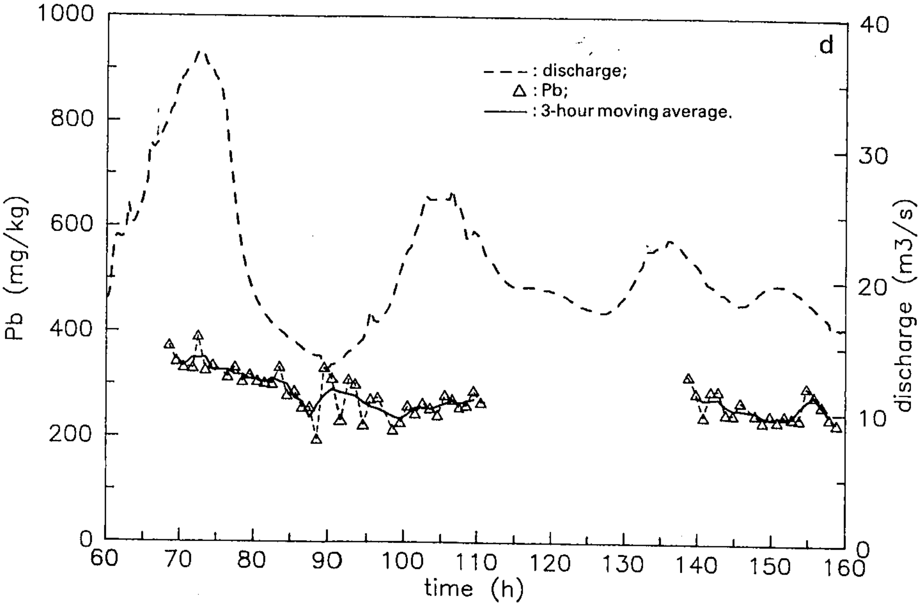


Figure 7.1d Solid-bound Pb concentrations at Meerssen during the March 1988 flood.

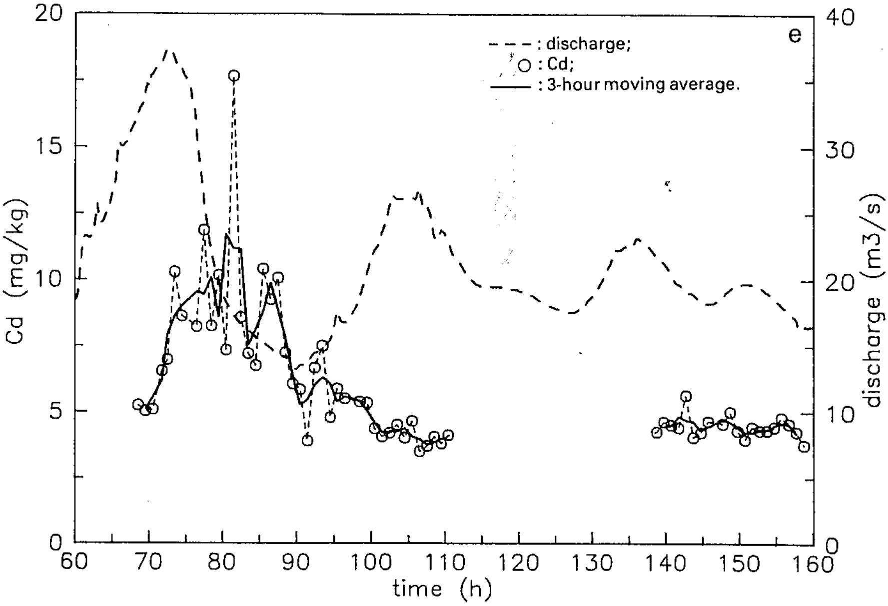


Figure 7.1e Solid-bound Cd concentrations at Meerssen during the March 1988 flood.

Unfortunately, because only few observations are available at the first rising limb of the hydrograph, the possible occurrence of a 'flushing' effect of suspended sediments, as found by Bradley & Lewin (1982) in the River Ystwyth, is obscured. It can easily be derived that the second discharge peak also coincides with a peak of suspended sediments and therefore it is assumed that at this time of the flood the amount of available sediments is still abundant. The finest sediments in the heterogeneous bed, which is not protected by coarse surface 'armour', may be suspended at relatively low shear stresses. Therefore, it seems reasonable to suppose that fine-textured bottom sediments will be carried away at an earlier flood stage than materials derived from erosion of the cohesive streambanks (which contain 20 % clay and 65 % silt).

A second observation that can be made is that the variability of sediment levels shows a certain dependence on the stage of the flood. The intermediate period between the first and the second discharge peak is characterized by highly variable sediment concentrations, whereas the pattern of sediment levels steadily follows that of discharge during the second peak. This behaviour, though less clear, is repeated in the period after the third and during the fourth discharge peak. Apparently, as the driving force for erosion and sediment transport weakens, the homogeneity of the mixture of water and sediments decreases (because of a reduced activity of sediment sources and a changed state of turbulence) and causes the occurrence of more pronounced waves of sediments.

Contrary to suspended sediment levels, none of the particulate bound metal concentrations shows a strong dependence on river discharge. Zinc levels peak at the first discharge peak, then decline during the falling stage, but fail to follow river discharge during the subsequent rising stage. Apparently, the 'dilution' effect is not a simple function of discharge and shows a time delay that may relate to a delayed activation of 'clean' sediment sources or an exhaustion of contaminated sources. The variability of zinc levels is similar to the time pattern of suspended sediments, being highest in the period between two peaks of river discharge. Figure 7.2, which highlights this period between 80 and 100 hrs, suggests that the waves of high sediment levels are characterized by relatively low Zn levels, and Zn levels peak at times of low sediment levels. Apparently, at this flood stage various sediment sources with different pollution levels and different activities supply sediments to the Geul.

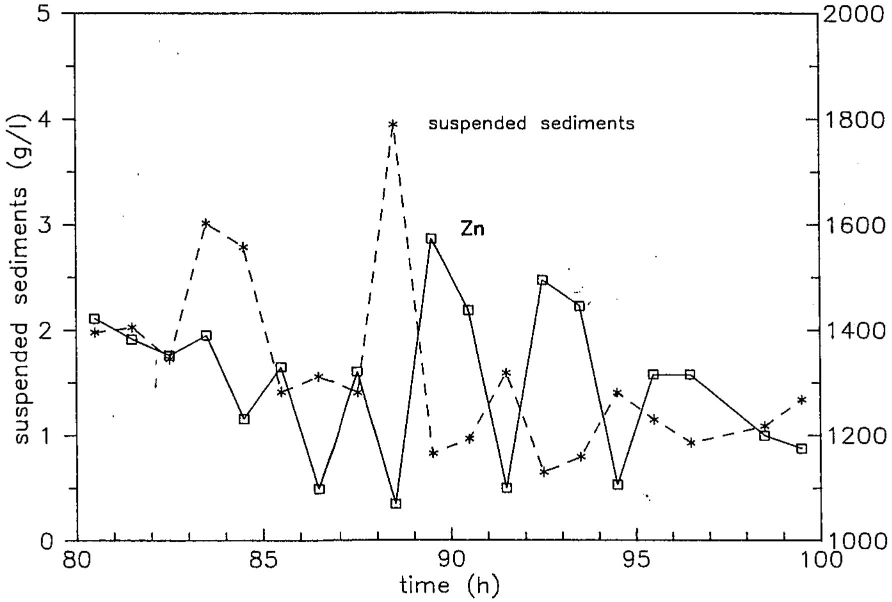


Figure 7.2 Suspended sediment concentrations and solid-bound Zn levels during the intermediate stage of the March 1988 flood.

The behaviour of particulate-bound Cd is similar to that of Zn. Cadmium concentrations rise at the first rising flood stage, peak a few hours after the discharge peak and then continue to fall, even during the rising stage of the second flood peak. The pattern of particulate-bound Pb is very stable, but shows some dependency on river discharge.

For Cd and Pb too, it can be observed that the variability is highest in the period between the first and second discharge peak, and that at this flood stage an inverse relationship exists with sediment concentration.

7.4 The transport of sediment and sediment-associated heavy metals

Rating curves relating suspended sediment levels and metal levels to river discharge were established for the entire set of sediment samples (n=72-80), for those samples collected during the March 1988 flood event (n=61) and for the samples from three stages of the latter event: "flood peaks", "intermediate stage" between peaks and "flood tail". Logarithmically transformed data, which is common practice for these type of curves, were not used because in most cases they did not result in higher values of the correlation coefficient. The correlation coefficients of linear relations between river discharge and all other properties are listed in Table 7.1.

Table 7.1 Correlation coefficients of linear relations between river discharge, and suspended sediment concentration (mg/l) and sediment-associated Pb-, Zn- and Cd-concentrations (mg/kg) (n=number of samples)

		March 1988 flood (n=61)			
	all data (n=72)	flood data	flood peaks (n=22)	intermediate stage (n=19)	flood tail (n=20)
SS*	0.74	0.53	0.84	0.01	0.12
Pb	-0.02	0.51	0.71	-0.18	0.33
Zn	-0.23	0.33	0.61	-0.13	0.35
Cd	-0.14	-0.01	0.23	0.04	0.16

* SS: suspended sediments

The amount of suspended sediments is positively correlated with river discharge. If all data are taken into account, including those derived at low flow stages, the correlation coefficient equals 0.74. In this case only, the use of $\log_{10}$-transformed data yielded a much higher correlation coefficient of 0.92. Figure 7.3 shows the corresponding sediment rating curve, where the data that were derived during the March 1988 flood event are all located within the small box in the upper right corner. When only a small part of the overall sediment rating curves is used, however, the correlation coefficient may drop drastically. During the March 1988 flood for example, the relation between water discharge and suspended sediment levels is strong during flood peaks, but very weak at the intermediate stage between peaks and at the flood tail (see Table 7.1), probably because of a reduced turbulence. The high variability of sediment levels during these stages has a negative impact on the quality of the sediment rating curve of this particular flood event (i.e. r=0.53, see Table 7.1). In view of the observations made in the previous section, it is clear that during the March 1988 flood in the River Geul both an increase of

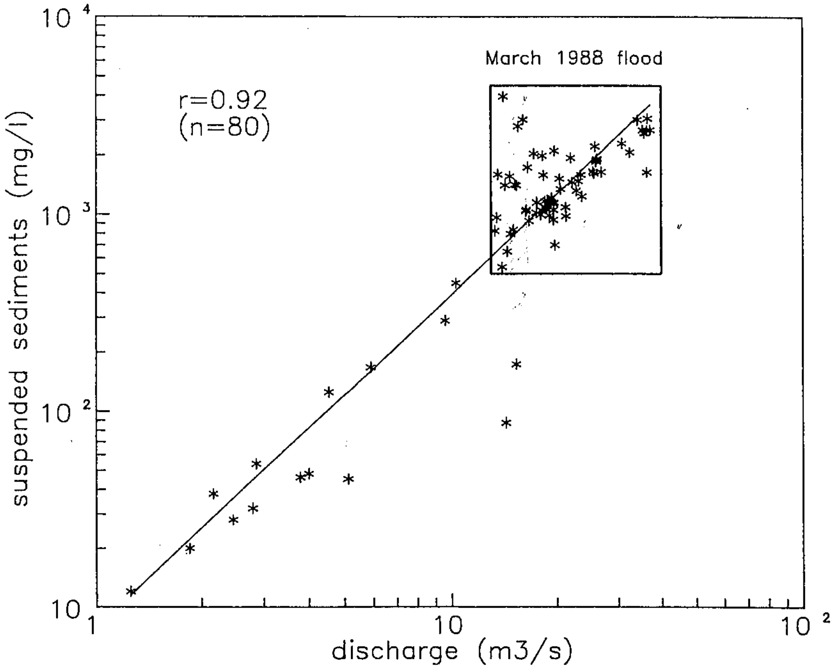


Figure 7.3 Sediment rating curve of the Geul at Meerssen.

metal levels with discharge and a 'dilution' effect occur: Zn and Cd levels peak at or immediately after the first discharge peak, but decline during the rising stage of the second discharge peak. Therefore, there is no direct relations between metal levels and river discharge (see Table 7.1). An exception can be made for Zn and Pb at flood peaks, which both show a tendency to increase with discharge, suggesting that contaminated sediment sources are activated. Another conclusion that can be drawn is that during one single flood the relations with discharge may differ considerably from the general pattern: during the March 1988 flood all metal levels tend to increase with increasing discharge, but the overall relation is one of slightly decreasing metal levels.

Figure 7.4 shows the relations between sediment concentrations and metal concentrations for the gauging station in Meerssen. The data that were collected during the March 1988 flood event are located within the rectangular box and fit quite well in the overall picture. All metal concentrations exhibit only a very weak tendency to decrease with increasing sediment concentration. Similar relations were found for data collected at the other two observation points. Although the use of logarithmic axes obscures much of the variability of the metal levels, it seems evident that the variability of metal levels cannot be accounted for in a satisfactory manner by either river discharge or suspended sediment concentration.

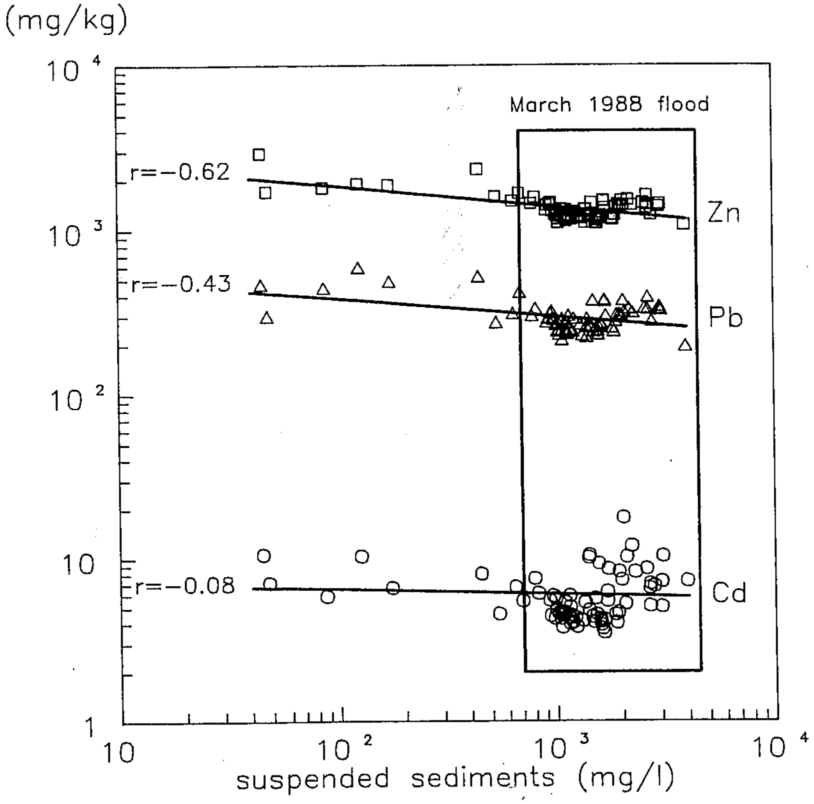


Figure 7.4 The relation between suspended sediment concentrations and solid-bound metal concentrations of the Geul at Meerssen.

From the above observations it may be concluded that the load of transported metals is governed to a limited extent by river discharge and suspended sediment concentrations. At discharge peaks, sediment levels increase and so do the concentrations of solid-bound metals. In contrast, at the intermediate stage between peaks and at the flood tail the sediment concentration is no longer a function of discharge and the occurrence of waves of relatively clean sediments, interspersed with small loads of contaminated sediments, cause quite unpredictable particulate-associated metal concentrations.

7.5 The transport of dissolved heavy metals

Table 7.2 lists the dissolved metal concentrations and the ratios of dissolved load to total load (Dissolved Transport Index (D.T.I.); Martin & Meybeck, 1979) of samples taken in Meerssen. Both properties exhibit considerable variations. The D.T.I. of the various metals indicates that the geochemical mobility probably has an impact on the concentration of dissolved metals: the D.T.I. for the relatively mobile metal Cd is much higher than those of Zn and Pb.

Table 7.2 Dissolved metal concentrations and Dissolved Transport Index (D.T.I.) in Meerssen

metal	n	concentration (µg/l) mean	concentration (µg/l) range	D.T.I. (%) mean	D.T.I. (%) range
Pb	24	10	1 - 33	5	0.3-35
Zn	70	115	50 -555	8	1.1-56
Cd	24	1.6	0.3- 6.9	23	3.6-78

For the various flood stages, correlation coefficients were computed for relationships between dissolved metals and discharge, and between dissolved metals and solid-bound metals. However, no systematic nor significant relationships were found. The fact that most samples were taken during flood conditions, when dissolved fractions usually play a minor role, may account for this and therefore further investigations are required. Nevertheless, Yeats & Bewers (1982) and Trefry & Presley (1976) also suggested that - at least in larger and less polluted systems - dissolved fractions exhibit a degree of long-term stability and are not significantly related to river discharge.

7.6 Sediment sources

During the various stages of a flood, various sediment sources with different pollution levels may be active. During periods of low flow and probably less turbulence, the carrying capacity is low, causing a build up of ooze deposits in depressions along the stream bed and in the numerous millraces of the Geul. Whenever turbulence is sufficiently intense, the carrying capacity of the stream increases, and the increased friction along the stream bed resuspends the accumulated ooze (NB the millraces are usually opened during the rising flood stage). If strong enough it will also carry away coarse and dense particulates from the river banks. It has been observed that at times of intensive rainfall the spoil heaps on the river banks of the Geul in Belgium are eroded and supply additional amounts of highly contaminated materials to the river bed.

Table 7.3 Average Pb-, Zn- and Cd concentrations (mg/kg) in waste materials on the river banks of the Geul and in ooze materials in the Geul

material	location	n	Pb	Zn	Cd
waste	Kelmis	3	10,566	56,683	119
waste	Plombières	6	13,907	11,728	33
ooze	multiple	12	306	1,476	5.5

The metal levels of ooze material in millraces of the Geul and waste materials on the river banks of the Geul are listed in Table 7.3. The set of data on metal levels of streambank deposits can be divided easily into two subsets, separated geographically by the village of Mechelen (see Figure 2.1). Upstream of Mechelen, the streambank deposits contain very high metal levels, which are more than 5 times as high as those downstream of Mechelen (see Table 7.4).

Table 7.4 Average Pb-, Zn- and Cd concentrations (mg/kg) of recently eroded streambank deposits of the Geul (n=number of samples in each depth interval)

	upstream of Mechelen (n=6-11)			Mechelen-Meerssen (n=6-24)			all data (n=15-35)		
depth (m)	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd
< 0.3	1,039	3,219	7.5	172	600	1.6	512	1638	3.8
0.3-0.6	1,191	3,865	8.3	229	680	4.4	511	1616	6.5
0.6-1.0	1,817	3,369	8.1	81	423	1.3	643	1405	5.4
> 1.0	984	2,661	17.1	68	417	1.7	315	1132	10.3
0.0-2.0*	1,266	3,261	9.7	130	518	2.3	482	1417	6.4

* all data from the above depth intervals

The average metal concentrations of suspended sediments that were collected at the three observation points along the Geul are listed in Table 7.5. It is clear that the metal levels are extremely high near Terbruggen, directly downstream of the historic mining area. As the Geul flows towards the village of Partij the metal levels rapidly reduce by more than 50 %. At this observation point the metal levels in suspended sediments nicely reflect the high metal levels in the streambank deposits upstream (see Table 7.4). Between this point and the outlet of the catchment (near Meerssen), the streambank deposits contain on average 80 % less metal (see Table 7.4) and a major - and clean in terms of metal load - tributary, the Gulp, flows into the Geul. The clean sediments that are supplied when these sources are active, cause a major downstream 'dilution' effect, resulting in relatively low metal levels at the observation point in Meerssen. Here too, a large conformity between the metal levels of suspended sediments and those of all streambank deposits and ooze deposits upstream can be observed.

Table 7.5 Metal concentrations (mg/kg) in suspended sediments of the Geul (values fro bulk water sampling in Terbruggen and Partij, and values from both bulk water sampling and pump sampling in Meerssen)

	Terbruggen (n=11)		Partij (n=14)		Meerssen (n=72)	
	mean	range	mean	range	mean	range
Pb	2,018	852- 7,048	769	615-1,016	300	196- 590
Zn	7,263	3,713-17,956	3,661	2,746-5,325	1,368	1,069-2,924
Cd	28.9	11.7- 51.7	13.8	8.6- 21.7	6.1	3.5- 17.7

It is clear that at both observation points in the Dutch part of the catchment, the average metal levels of suspended sediments exhibit a strong resemblance with those of upstream sediment sources. However, at times of flood the instantaneous quality of the suspended sediments will also depend on the sediment availability and the activity of the various sources and on the rate at which the sediments are mixed. Therefore, considerable variations of suspended sediment quality can be observed during the course of a flood.

7.7 Mass transport

Many objections have been made to using sediment rating curves for calculating mass transport (Walling, 1977; Hellman, 1987). Apart from the problems of representative sampling, analytical accuracy, the heterogeneity of the water body in the geometric cross-section and in time (diurnal variations, seasonal variations, variations from year to year), the most serious criticism concerns the changing concentrations with changing flood stages. Moreover, in the previous sections it was demonstrated that only during a limited part of a flood does the river discharge adequately account for the transport of suspended sediments and associated metals. Thus, even if it was possible to collect large numbers of samples during various seperate flood stages, it would probably not be possible to obtain an adequate set of rating curves for each stage. Given these objections to the use of rating curves, it is realized that the mass transport of a flowing water body cannot be exactly quantified, even at the cost of considerable time and effort.

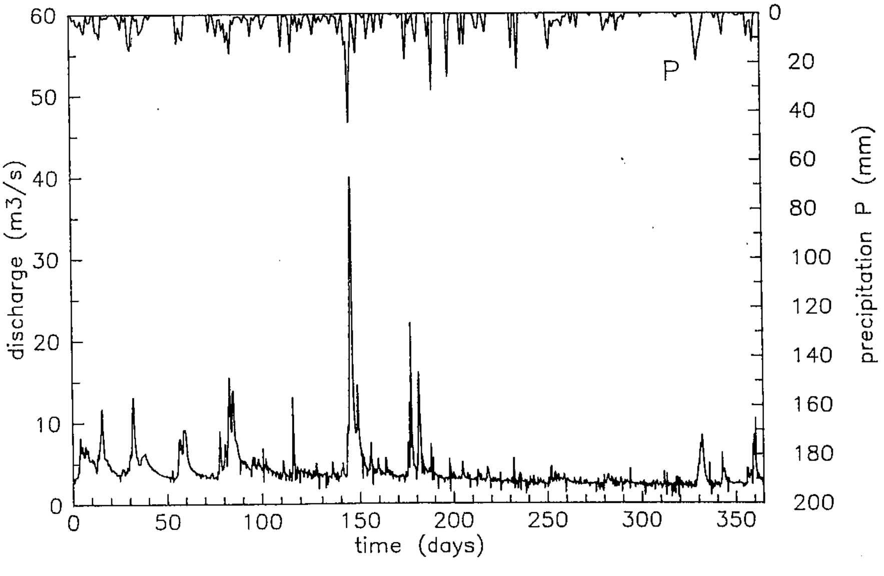


Figure 7.5 Precipitation and river discharge of the Geul (at Meerssen) in 1983.

All the same, mass transport data are absolutely necessary for mass balance calculations and the determination of trends. Therefore, given the lack of more reliable methods, probably the only acceptable method for mass transport calculations is to use transport/discharge relationships for gauging points on the river in question (Hellmann, 1987).

This section presents the results of mass transport calculations for the flood event in March 1988. Additionally, annual mass transport was calculated for 1983, a year for which a complete discharge series was available and which exhibits a flood event with the same magnitude (i.e. a peak discharge of c. 40 m^3/s and during 6 days an exceedance of 10 m^3/s) as the one in March 1988 (see Figure 7.5). The sediment rating curve (see Figure 7.3) was combined with the suspended sediments-metal levels relationships (see Figure 7.4) to yield a discharge-metal load relationship. By multiplying suspended sediment levels by solid-bound metal levels, the high variability of transported materials that occurs during the intermediate flood stage (high concentrations of "clean" sediments followed by low concentrations of contaminated sediments), is reduced. The parameters of the rating curves used are listed in Table 7.6. For the March 1988 flood event the calculated mass transport covers the period where the discharge exceeds 10 m^3/s and the rating curves were only used for those periods where no field observations were made.

table 7.6

Table 7.6 Rating curves (Y=a+bX) used for the calculation of mass transport of the Geul in Meerssen

Y	X	a	b	r
$\log_{10}$ (SS)	$\log_{10}$ (Q)	0.897	1.693	0.92
$\log_{10}$ (Pb)	$\log_{10}$ (Q)	0.687	1.439	0.79
$\log_{10}$ (Zn)	$\log_{10}$ (Q)	1.453	1.357	0.77
$\log_{10}$ (Cd)	$\log_{10}$ (Q)	-0.857	1.308	0.63

SS: suspended sediment concentration (mg/l)
Q : river discharge (m3/s)
Pb, Zn, Cd: solid-bound metal loads (µg/l)

Given the lack of a significant relationship between river discharge and dissolved metal fractions, it was decided to use average metal concentrations (see Table 7.2) for the annual mass transport calculation. However, one needs to be aware of the fact that this procedure will yield conservative figures, because the average metal levels are based on a set of samples that was for the greater part taken during high flow stages and therefore may reflect a 'dilution' effect.

The results of the calculations are listed in Table 7.7. The estimates of the large quantities of metals that pass Meerssen show that the catchment of the Geul is a major source of heavy metals to the Meuse River. Of major importance is the observation that a large part of annual transport can be accounted for by the occurrence of major floods that last only a few days. The significance of high flow stages for the transport of water, sediments and sediment-associated heavy metals is further explored in Figure 7.6, which shows cumulative percentages of annual transport as a function of flow stage.

Table 7.7 Total mass transport of suspended sediments and solid-bound and dissolved metals past Meerssen in 1983 and during the March 1988 flood event

	Annual (1983)			March 1988 flood		
	total (tonnes)	solid (%)	dissolved (%)	total (tonnes)	solid (%)	dissolved (%)
suspended sediments	30,656	100	-	14,172	100	-
Pb	13.9	89	11	3.8	97	3
Zn	70.5	76	24	19.9	98	2
Cd	0.44	50	50	0.1	77	23

Figure 7.6a shows that only 5 % of the water discharge takes place during times of a flow larger than 15 m^3/s. These larger flows occur during only c. 1 % of a one year timespan. In contrast, the occurrence of flows larger than 15 m^3/s accounts for about 50 % of the annual transport of suspended sediments. Thus, the contribution of larger flows to annual discharge is quite insignificant with respect to the transport of water, but it is very large with respect to the transport of suspended sediments. Given that suspended sediments are important carriers of heavy metals, their transport rates are also strongly influenced by the occurrence of larger floods, as is illustrated in Figures 7.6b-d. These figures show that some 30, 35 and 20 % of the annual transport of Zn, Pb and Cd in 1983 respectively, took place during the c. 1 % of the year when floods larger than 15 m^3/s occurred. The figures also demonstrate the role of metal mobility on the distribution between dissolved and solid-bound states of heavy metals during transport. Obviously, given that the water discharge is governed by the occurence of low flows, the dissolved forms of all metals are for the larger part transported during flows smaller than 15 m^3/s. However, large differences with respect to the contribution of dissolved metal transport to total metal transport can be observed. The relative immobile metal Pb is predominantly transported in a solid-bound state, i.e. about 90 %, whereas solid-bound forms of the more mobile metal Cd account for only c. 50 % of the annual transport of Cd. This difference in mobility explains why larger floods, that account for a very large part of the transport of suspended sediments, are of more importance for the total annual transport of Pb than they are for Cd.

7.8 Conclusions

During a major flood in the River Geul in March 1988, sediment concentrations and associated metal levels were highest at the first discharge peak. At a second rising stage, suspended sediments increase again but metal levels remain low, indicating the importance of a delayed 'dilution' effect.

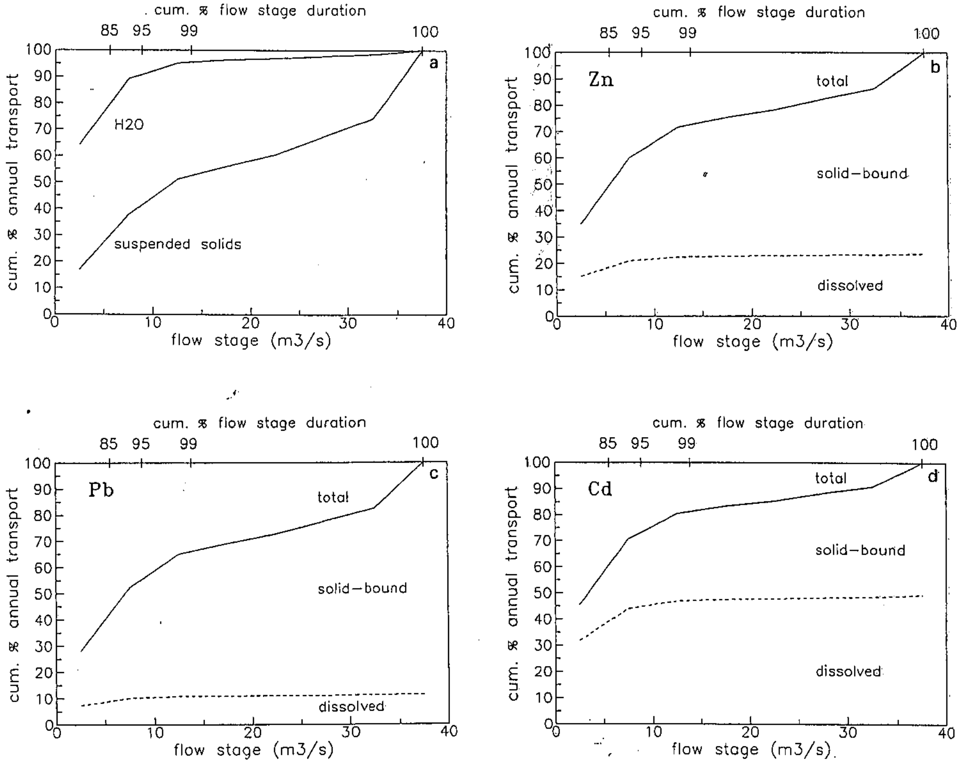


Figure 7.6 Cumulative percentages of annual transport of a) water and sediments, and dissolved and solid-bound Zn (b), Pb (c) and Cd (d) past Meerssen in 1983 as a function of flow stage.

At times of peak discharge, suspended sediment levels and solid bound metal concentrations correlate well with river discharge. However, during the intermediate stage between two discharge peaks, the role of discharge is negligable and waves of sediment reflecting various sediment sources are transported.
When the data from a number of floods in the Geul are assembled, the overall dependence upon discharge is one of rapid increase for sediment concentrations and one of slight decay for metal levels. Given the more or less constant level of solid-bound metals and a relatively small dissolved metal fraction, the mass load of heavy metals could be estimated by rating curves of discharge versus metal loads. The results indicate that a large part of annual metal transport takes place during few major flood events. Then, the dissolved fractions of Pb and Zn account for less than 5 % of the total transport, whereas 23% of Cd is transported in a dissolved state.

7.9 Summary

The relations between river discharge, sediment concentrations and associated metal levels were studied in detail for a particular flood in the polluted River Geul in March 1988. It was found that river discharge only has a limited influence on the transport of sediments and Pb, Zn and Cd. River discharge has an important effect at flood peaks, but at the intermediate stages between peaks, the quantity and quality of transported sediments depend on the variable activity of various sediment sources upstream. Nevertheless, when data from several floods were assembled, sediment and metal rating curves were obtained, which showed reasonable direct relationships (i.e., correlation coefficients of 0.63-0.92). These curves were used for mass transport calculations which demonstrate that a large part of the annual transport of sediments and heavy metals occurs during a limited number of major floods.

8 VARIABILITY OF THE HEAVY METAL CONTENT OF FLOOD DEPOSITS

8.1 Introduction

Major floods occurring at relatively infrequent intervals account for a very large part of the total mass of sediments moved by streams (see Chapter 7). During such events, erosion of the banks is enhanced and previously deposited material is liable to be picked up. If the stream should overflow its banks, the sudden loss of velocity causes bed load and suspended material to be deposited on the floodplain flanking the main stream channel. At the interface between the floodplain and the river channel suspended sediments are important carriers of heavy metals during the physical sediment exchange by erosion and sedimentation processes. Therefore, flood deposits reflect the present quality of the fluvial system and determine, to some extent, its future quality.

Much of the research concerning processes of metal transport and accumulation in aquatic environments indicates that significantly higher metal concentrations occur in finer size fractions (Salomons and Förstner, 1984). These observations have led to the development of methods to correct metal concentrations for the effects of grain size in order to accurately document lateral or vertical variations and identify trends away from a particular source (de Groot et al., 1982; De Groot et al.,1971; Salomons & De Groot, 1978; Förstner & Wittmann, 1983). A standard analysis of the less than 63 µm fraction has been suggested by Salomons and Förstner (1980). This fraction has been described as the 'geochemically active' fraction by Ongley (1982). These concepts have been developed for relatively low-energy environments where the major source of contamination is industrial effluent containing metals in solution. However, recent studies have shown that mine and smelter tailings may provide metal-rich particulate contamination so that all size fractions are important contributors to the metal concentrations in sediments (Moore et al., 1987; Brook & Moore, 1988; Bradley, 1987).

Quantitative relationships between metal concentrations and distance downstream of the source area have been established for stream sediments, in-channel deposits and floodplain deposits (Wolfenden and Lewin, 1978; Lewin and Macklin, 1987). These relations reflect the downstream decay of total metal concentrations that is the result of a complex dispersal mechanism where a number of physical and chemical processes are interactive. Once these sediments become incorporated in the floodplain soils, which act as a long-term 'sink' for heavy metal, it is not the total amount of heavy metals but rather how it is actually stored that is important in assessing the environmental impact. For the estimation of the relative bonding strength of metals in different chemical phases, extraction procedures have been developed, which are commonly combined in sequential extraction schemes (Salomons & Förstner, 1984).

The floodplain soils in the Meuse and Geul basin have high levels of pollution, brought about by mining and related industrial activities in the past (Rang et al., 1986). Given that heavy metals are derived from a variety of sources in these two fluvial systems that differ in size and in the quantity and quality of their output, different spatial distributions of pollutants and different metal associations are to be expected. This chapter examines the influence of grain size and organic matter content on total metal concentrations in flood deposits of the rivers Geul and Meuse. In addition, distance-decay models were fitted to data on total metal concentrations versus distance downstream. Heavy metals in a selected number of samples from the Geul were extracted by the sequential scheme proposed by Calmano & Förstner (1983). The downstream decay of partitioned metal concentrations is compared with the decay of total metal concentrations.

8.2 Experimental procedures

Flood deposits were sampled on a number of occasions along the course of the Meuse and Geul rivers immediately after floods had retreated. Along the Meuse river 102 samples were collected over a distance of 160 km after an exceptionally high flood in February 1984. Thirteen samples were collected in the Geul river channel at conditions of low flow in July 1986; 98 samples of flood deposits were collected after a number of floods in 1986 and 1987: these samples were obtained over a distance of 55 km.

Organic matter concentrations were determined for the Meuse samples and a subset of 25 of the Geul samples of flood deposits according to the method of Walkley and Black (1934). The same set of samples was treated with 6% H_2O_2 and 6% HCl. After wet sieving over a 50 µm sieve, the smaller grain fractions were determined by means of settling tubes. A set of sieves was used to separate the coarse fractions. Analysis of metals in all samples was done as described in chapter 3.

An additional set of 24 samples of flood deposits was collected after a major flood in the Geul in March 1987. Two samples were collected at 12 locations in the floodplain area: within an area of 100 m^2 one sample of coarse and one sample of fine-grained material (texture estimated by field techniques) was taken. Both samples were separated by sieving in fractions < 63 µm and > 63 µm. The concentrations of lead, zinc, cadmium and copper were determined by the method described in Section 3.3.1. Equal amounts of the fractions < 63 µm from the two samples at eight locations (1 upstream and 7 downstream of the source area) were then mixed and the same was done for the fractions > 63 µm. The resulting two samples therefore represent the < 63 µm and > 63 µm fractions of both coarse and fine-grained flood deposits. Organic matter concentrations were determined according to the method of Walkley and Black (1934) and equal 2.7 and 1.8% on average for the < 63 µm and the > 63 µm fractions respectively. The carbonate content averaged 2.3% for the < 63 μm and 5.0% for the > 63 μm fraction. These two sets of eight samples were analysed in a sequential extraction scheme that was proposed by Calmano & Förstner (1983) (see Section 3.3.2).

8.3 Characteristics of the Meuse basin

The Meuse river flows from its source on the Langres plateau in France west of the Ardennes through Belgium before it enters the Netherlands. From source to mouth the river is 1000 km long, of which 500 km are in France, 300 km in Belgium and 200 km in the Netherlands. The catchment area covers 33,000 km^2 (Anonymous, 1985a). The Meuse is a rainfed river: discharge fluctuates according to the amount of rain that falls in the catchment area. In Maastricht (see Figure 2.3) average discharge is 250 m^3/s. High flows occur in winter after prolonged periods of heavy rainfall in France and Belgium. An additional water supply may be provided by its tributaries during periods of snowmelt in the Ardennes. The maximum recorded discharge, registered in 1926, is 3,000 m^3/s. Large scale inundations occur when the discharge equals or exceeds 1,500 m^3/s; this happens on average once every two-and-a-half years (Anonymous, 1985).
Coal, zinc and lead mining has been carried out for centuries in the Meuse basin. The exploitation of coal mines, which probably started in Roman times, developed rapidly after the industrial revolution and reached its climax after the second world war. The availability of ore led to non-ferrous metallurgical industries being established in the Meuse basin. This branch of industry has maintained its economic importance, even though the mining of ores has virtually ceased. The presence of this metallurgical industry still exerts its influence on water quality. In contrast to the environmental releases associated with mining activities, industrial effluent only contains metals in solution (Rang et al., 1986).

8.4 Pollution levels

Meuse river

In February 1984 a period of high flow occurred, during which a maximum discharge of 2,550 m^3/s was recorded. An event like this has a recurrence interval of 50 years. Large amounts of suspended matter were transported, some of which were deposited under conditions of low flow velocity in the inundated parts of the floodplain area. Immediately after the water had receded, 102 samples of fresh flood deposits were taken along the Dutch course of the Meuse river. The average heavy metal contents of these samples are presented in Table 8.1. Frequency tables were produced displaying the quality of the flood deposits of the Meuse river in relation to the indicator values (see Section 4.5). From Figure 8.1a it can be seen that the flood deposits are appreciably contaminated with lead, zinc, cadmium and copper: for these metals the B-value was exceeded in 70, 75, 69 and 17 percent of the samples respectively. In only one case (zinc) was a C-value exceeded. Concentrations of cobalt, chromium and nickel were low and did not exceed the B-value.

Table 8.1 Average heavy metal concentrations (in mg/kg) in deposits of the Meuse and Geul rivers

river	discharge m^3/s	n	Pb	Zn	Cd	Cu	Co	Cr	Ni
Meuse	2550	102	220	83	27.6	71	20	37	38
Geul	0-10	13	428	138	24.1	-	-	-	-
	20-60	122	477	230	84.5	16	-	-	-

Geul river

Thirteen samples were collected along the course of the Geul river under conditions of low flow in July 1986. 122 samples of fresh flood deposits were collected from floodplain areas that had been inundated during floods in 1986 and 1987. The average heavy metal contents of both sets of samples are also presented in Table 8.1.

As far as lead and cadmium are concerned, there was hardly any difference in concentration between high and low flow deposits. For zinc, the concentrations found in high flow deposits were higher than those of the low flow deposits. During high flow however, contamination can be expected to be lower, because of dilution with eroded bed, bank and slope material (Förstner & Wittmann, 1983). This phenomenon does not occur, because both bed and bank material of the Geul river are locally seriously contaminated with heavy metals (Rang et al., 1986). Moreover, the spoil heaps along the Geul river probably still function as a major source of heavy metals that is activated during periods of high discharge.

The pollution levels of both lead and zinc are very high (see Figure 8.1b): the B-value was exceeded in over 80 percent of the samples and in over 25 percent of the samples the C-value was exceeded. Cadmium also occurs in enriched concentrations, but only one sample had a concentration above the C-value. For copper, the A-value was not exceeded once.

The concentrations of lead and zinc were found to be 2-3 times as high in flood deposits of the Geul as in the Meuse. This shows that the material transported by the Geul river is an important additional source of heavy metals for the Meuse river.

8.5 The effects of grain size and organic matter content

The transport of heavy metals in a polluted fluvial system mainly takes place in the solid phase, that is fixed by the suspended matter, which is a mixture of organic and inorganic material. The organic fraction is derived from natural production and both domestic and industrial waste disposal. The inorganic fraction is produced by

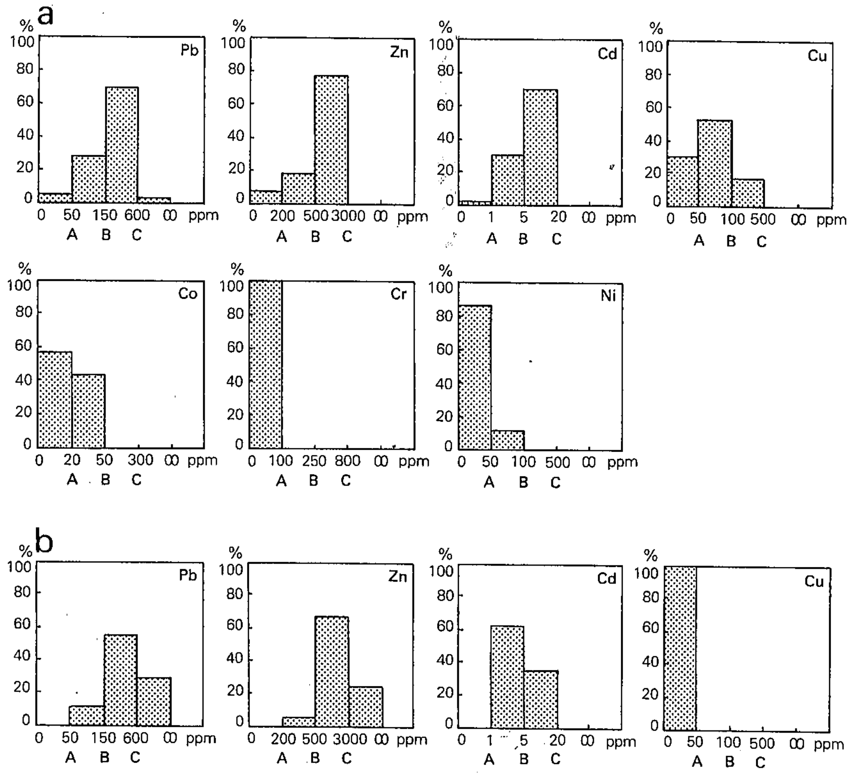


Figure 8.1 Frequency tables of metal concentrations in flood deposits in relation to the indicator values: a) Meuse river (n=102) and b) Geul river (n=122).

erosion processes in the catchment area and is partly derived from discharges of industrial and mine disposal. Heavy metals may be fixed as a result of adsorptive bonding, co-precipitation by hydrous iron and manganese oxides, complexing by organic molecules and incorporation in crystalline minerals (Förstner & Wittmann, 1983).

In general, metals are not homogeneously distributed over the various grain size fractions, and large differences in total metal concentrations are observed in sediment samples from a single locality (see Section 4.3). A commonly accepted correction method is based on the preferential occurrence of the heavy metals in the finest grain-size fractions. De Groot et al.(1971) found linear relationships between the amount of heavy metals and the fraction of particles smaller than 16 µm (expressed as a percentage of the $CaCO_3$-free mineral constituents in the oven-dry sediment) in samples from the river Ems. The normalized total metal content may be obtained by extrapolating the fraction smaller than 16 µm to 100 percent (De Groot et al.,1971) or to 50 percent (Salomons & De Groot, 1978). Similar extrapolation techniques have been used for other grain size fractions (20 µm and 63 µm) by Lichtfuß and Brümmer (1977) and Smith et al. (1973) respectively.

The flood deposits of the Geul and the Meuse rivers have different grain size distributions, and there is considerable variability within both sets of distributions. Data on grain size distributions and organic matter concentrations are presented in Table 8.2.

Table 8.2 Grain size distributions and organic matter concentrations of flood deposits. All values as % dry weight; n=no. of samples.

	Geul River (flood deposits, n=25)		Meuse River (n=102)	
property	mean	s.d.*	mean	s.d.*
% org. matter	2.0	0.8	3.0	3.0
% < 2 µm	5	2	14	8
% 2-53 µm	40	15	60	20
% > 53 µm	54	16	26	24

* s.d.= standard deviation

In order to correct for the possible effects of grain size and organic matter content, linear relationships between heavy metal concentrations and a number of grain size fractions were investigated by simple regression techniques. The clay fraction and the organic matter content were used as independent variables because of their large capability to adsorb heavy metals and their relatively high cation exchange capacity. The larger fractions were also investigated in order to detect possible coarse grain size classes in which heavy metals accumulate.

Meuse river

For the metals that are present in enriched concentrations, that is lead, zinc, cadmium and, contrary to the Geul river, copper, the strongest positive correlation is found for the relation between their concentration and the fraction < 53 µm (see Table 8.3b). In this fluviatile system, the level of pollution seems to play an important role. The metals that are present in relatively low concentrations, that is cobalt, chromium and nickel, tend to correlate best with the fraction < 16 µm. However, both the differences between and the absolute values of the correlation coefficients are small, so conclusions remain tentative. None of the investigated metals correlate with the organic matter content.

Geul river

In the case of the Geul river, the conclusions for lead, zinc and cadmium are similar: as the grain size fraction becomes coarser, the positive correlation between grain size and heavy metal concentration increases, reaching a maximum for the fraction < 53 µm (see Table 8.3a). However, even for that fraction the correlation coefficient is small. Considering the results for copper, it appears that there is a larger positive correlation between concentration and the fractions

< 2 µm and < 16 µm. Apparently, the fact that the metals lead, zinc and cadmium are present in enriched concentrations determines their mode of occurrence, which is not restricted to one particular grain size fraction. Copper, on the other hand, is present in very low concentrations and behaves in a way that might be expected from the observations cited (for example De Groot et al., 1971). The different behaviour of copper is also apparent when the relations between metal concentrations and organic matter content are examined. From the high positive correlation coefficient (see Table 8.3a) it may be concluded that only copper is associated with the organic substances in Geul river flood deposits. Other researchers have also found a selective affinity between organic matter and copper. Rashid (1974) has shown that copper is preferentially sorbed (53 percent), followed by zinc (21 percent), nickel (14 percent), cobalt (8 percent) and manganese (4 percent). Leaching experiments have demonstrated that copper is more firmly associated with organic material than with other materials (Förstner and Wittmann, 1983).

Table 8.3 Correlation coefficients of linear relations between metal concentrations and soil properties

a. Geul river flood deposits (n=122)

property	Pb	Zn	Cd	Cu
% org. matter	0.20	-0.14	0.20	0.81
% < 2 µm	0.21	-0.15	0.16	0.67
% < 16 µm	0.37	0.05	0.36	0.72
% < 53 µm	0.46	0.30	0.36	0.34
% < 106 µm	0.34	0.17	0.20	0.24

b. Meuse river flood deposits (n=102)

property	Pb	Zn	Cd	Cu	Co	Cr	Ni
% org matter	0.19	0.09	0.13	0.17	0.10	0.11	0.20
% < 2 µm	0.39	0.42	0.42	0.44	0.49	0.59	0.53
% < 16 µm	0.44	0.45	0.45	0.49	0.54	0.64	0.58
% < 53 µm	0.44	0.52	0.44	0.50	0.45	0.61	0.51
% < 106 µm	0.41	0.51	0.43	0.48	0.40	0.53	0.46

For both fluvial systems, linear regressions of metal concentrations versus grain size yield the largest correlation coefficients when concentrations of background metals are studied as a function of the fraction < 16 µm. Corrections for the effects of grain size may be carried out by extrapolating the metal concentration - according to the regression lines - to some percentage of the fraction < 16 µm. However, with an exception for the case of copper in the Geul, the low correlation coefficients found suggest that this procedure is not very satisfactory. Enriched metal concentrations do not correlate very well with any of the grain size fractions. Apparently, the variety of metal sources along both rivers produces metals that are not transported in one particular grain size class. Nevertheless, a difference between the two systems can be observed. For the Meuse river, the linear relationships between clay content and the concentrations of lead, zinc and cadmium yield larger correlation coefficients than for the Geul river. Heavy metals are not discharged into the Geul in soluble form, but this does take place in the Meuse river, in addition to the discharge of solids. Thus, in the latter system metals may be sorbed from the metal-rich solution by the clay minerals, as a result of cation exchange. Adsorption processes are also facilitated by heavy metals being supplied in a mobile, soluble form. If metals are discharged into the river as solids (as happens along the Geul river) the exchange processes between the solid and liquid phases tend to be slower: the metals need to go into solution prior to fixation by fine particles. Consequently, the migration of metals from the coarse to the fine fractions occurs at a slower rate; this explains why for the Geul river smaller correlation coefficients are found for relationships between metal concentrations and fine fractions.

8.6 Downstream changes of total metal concentrations

The nature and extent to which any element is present within aqueous and solid phases will depend upon the chemistry of the metal itself, the type of source area and the range of chemical, physical and biological actions and interactions prevailing in fluvial systems (Wolfenden and Lewin, 1978). Some of the factors of the chemical environment that have an effect on the partition of heavy metals between the more mobile aqueous phase and the less mobile solid phase are: the relationship between the concentration of hydrogen ions (pH) and the oxidation potential (Eh); and the presence of organic matter, clay and hydrous oxides of iron and manganese (Rose et al., 1979). Physical factors that may produce variable rates of metal transport and deposition are: grain size, river discharge (Salomons and De Groot, 1978) and dilution resulting from mixing with material eroded from bed, banks or hillslope. The combined effect of these factors on the industrial and mining wastes present in the study areas causes heavy metals to be dispersed downstream. Figure 8.2 shows a schematic representation of some of the chemical and physical processes that determine metal exchange during transport.

Wolfenden and Lewin (1978) successfully modelled dispersal patterns of lead, zinc, cadmium and copper in active stream sediments downstream of a single source with negative exponential curves of the form:

$$\ln (Y_t) = a - b*X \qquad [8.1]$$

(where Y_t equals the total metal concentration in ppm, X is the distance downstream in km and a and b are constants). Estimates of b, obtained by regression analyses, were interpreted as single values describing overall decay factors for metals.

In the present study, both this function and a linear model of the form:

$$Y_t = a' - b'*X \qquad [8.2]$$

were fitted to the data on the deposits of the Geul and Meuse rivers.

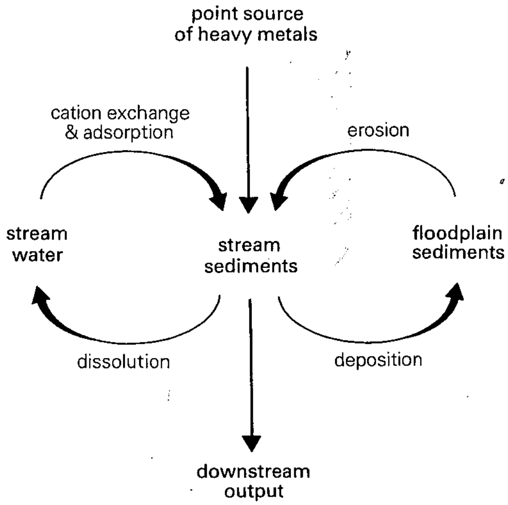


Figure 8.2 Processes of heavy metal exchange during transport of contaminated stream sediments.

For the linear model, the relative regression coefficient b'/a' may be interpreted as decay factor. The exponential model yielded larger correlation coefficients than the linear model for metal concentrations in Geul flood deposits. For the in-channel deposits the linear model yielded better results.

Meuse river

The first important finding is that for the Meuse river no relation was found between heavy metal concentrations in flood deposits and distance downstream from the possible source of that heavy metal. None of the relations was significant at the 5% level of significance. No clear decay patterns were expected for the metals cobalt, chromium and nickel, because these metals are present in background concentrations. From the lack of fit of the distance-decay models for lead, zinc, cadmium and copper, it follows that no simple decay pattern can be identified for these enriched metals either. Because the data for this study were collected along only the Dutch part of the Meuse, the occurrence of a decay pattern at the scale of the entire river course could be obscured. An alternative explanation would be that there is no sole point source of these metals in the upstream part of the catchment. The latter explanation would confirm that metal pollution of Meuse river flood deposits is mainly produced by industrial waste disposal, which is not restricted to one locality. Diffuse sources of metal may also have contributed to the somewhat random pattern of distribution.

Geul river

1. <u>Conditions of low flow</u>: The concentrations of lead, zinc and cadmium in in-channel deposits decrease downstream (Table 8.4). The linear model produces strong negative correlations. The decay rate of lead differs from that of zinc. Figure 8.3a demonstrates that zinc concentrations increase relative to lead concentrations with increasing distance to the source. At this stage, it may be useful to pay more attention to the concept of geochemical mobility. Fundamentally, the response of an element to dispersion processes is governed by its mobility, that is, the ease with which it may be dispersed relative to the matrix of other materials surrounding it (Rose et al., 1979). Perel'man (1967) obtained an empirical estimate of relative mobilities of elements by comparing coexisting mobile and immobile phases. He defined an aqueous migration coefficient K, which is equal to the content of an element in the dissolved solids of a surface water or groundwater divided by its content in the associated rock. Under oxidizing conditions (pH 5-8) he found that zinc falls in the range moderately mobile (K=1-10), in contrast to lead and copper, which are slightly mobile (K=0.1-1).

Table 8.4 Experimental fits of distance decay models to metal concentrations in Geul deposits: correlation coefficients and constants

	flood deposits (n=113) exponential model			in-channel deposits (n=13) linear model			
metal	r	a	b	r	a'	b'	a'/b'
Pb	-0.81	6.67	0.057	-0.83	905	38.6	0.043
Zn	-0.81	8.10	0.059	-0.90	2283	72.8	0.032
Cd	-0.61	1.74	0.033	-0.76	7.9	0.3	0.038
Cu	-0.17	2.91	0.021	-	-	-	-

From this observation two contrasting dispersal patterns can be derived. Because it is more mobile than lead, zinc may migrate to the liquid phase in larger quantities, producing a relatively rapid decay in the solid phase. On the other hand, high zinc concentrations in water may stimulate adsorption by fine particles. The latter process may account for a downstream increase of zinc concentrations relative to lead in flood deposits.
A complicating factor is the difference in weight between particles of galena (PbS) and sphalerite (ZnS). Galena is much heavier than sphalerite (densities 7.5 and 4.1 g/cm^3, respectively) and both are denser than the rest of the detritus. Consequently, running water might be expected to cause differential downstream movement, with the lightest material travelling furthest from the source. This process too, may produce two contrasting dispersal patterns for zinc in comparison with lead. Sphalerite particles may be transported downstream more easily, but in order to produce a relative increase of zinc in flood deposits, the particles need to be deposited. If they remain part of the suspended load a relative decrease of zinc concentrations

in flood deposits will be produced. This would indicate that zinc is being preferentially removed from the fluvial system.
The decay factors of metal concentrations at low flow stage, obtained by fitting the linear model, range from large to small in the order (see Table 8.4):

lead > cadmium > zinc

Since the sampled sediments had been deposited during the same flow stage, it can be assumed that physical factors such as discharge and dilution had the same impact on the behaviour of the different metals. The different mobilities and weights of the metals would account for the different rates of fall-off in metal concentrations. This explains why zinc concentrations in the load, which mainly consists of fine particles during these flow conditions, increase relatively during transport downstream (see Fig. 8.3a). The preferential adsorption of zinc by the fine particles and the lower density of spalerite, account for this phenomenon.

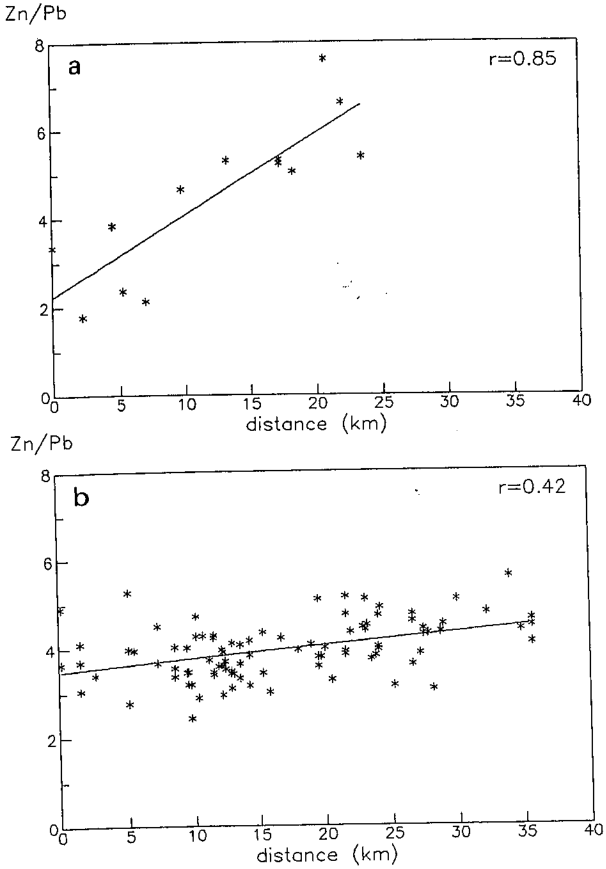


Figure 8.3 Zinc/lead ratios of Geul flood deposits in relation to the distance downstream of the point source: a) low flow conditions; b) high flow conditions.

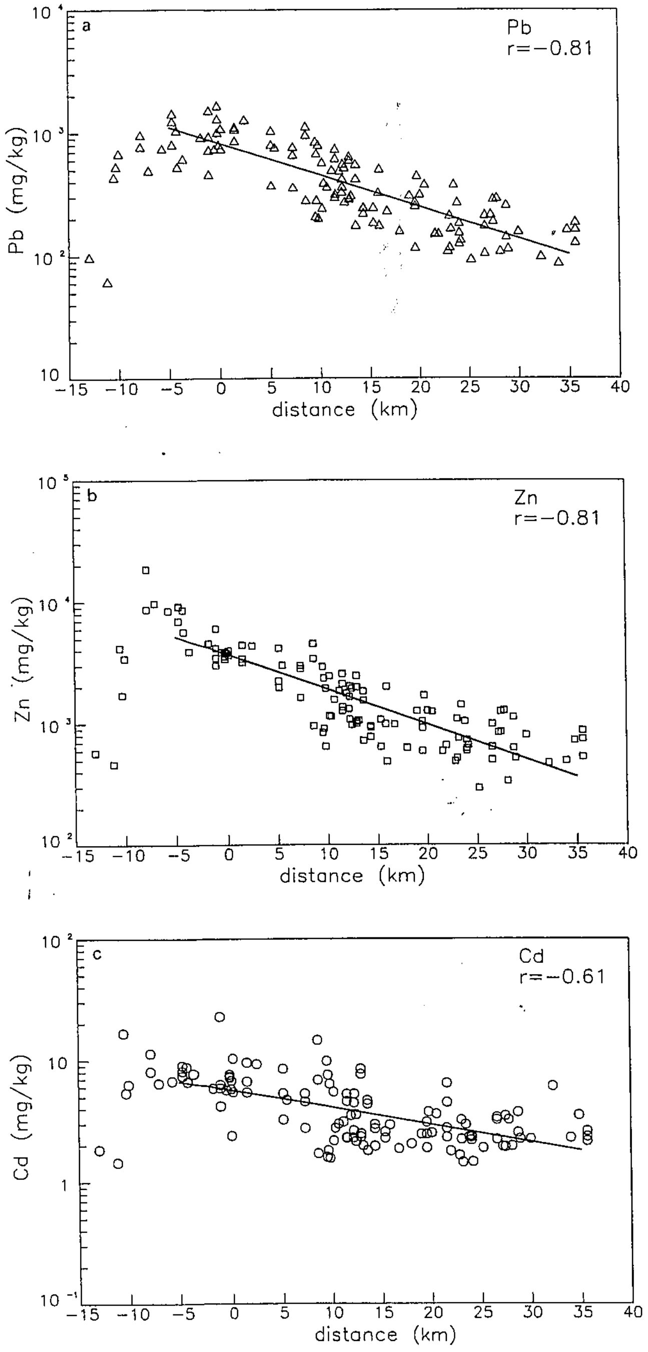


Figure 8.4 Downstream decay of total metal concentrations in Geul flood deposits at high flow conditions (N.B.: the Netherlands-Belgium border is at 0 km): a) Pb; b) Zn; c) Cd.

2. Conditions of high flow: Flowing water at high discharge has a large transport capacity. At times of flood, coarse material, including large boulders, may be moved several kilometers in a matter of hours. In addition, erosion of the river bed and the streambanks causes the supply of coarse, contaminated materials to be much larger than during low flow stages. As a result, a large load of relatively coarse material is easily transported downstream, producing high rates of metal dispersal (see Fig. 8.4a-c).

   During these conditions, lead and zinc decline at equal rates (see Table 8.4). In order to explain the different behaviour of lead and zinc during the two flow situations, we shall consider the ratio of zinc and lead concentrations along the course of the Geul river. As shown in Figure 8.3b, the Zn/Pb ratio remains fairly constant along the course of the Geul at high flow. Apparently, under these conditions the same dispersal mechanism is active for both metals. Moreover, this mechanism overrules the effect of differences in density and geochemical mobility, which play a role during conditions of low flow (see Figure 8.3a). The major factor affecting dispersal during high flows is believed to be the high energy of the fast-flowing water, causing the mixture of coarse waste materials and eroded bed and bank materials to be transported in large amounts and at high velocity. Under such conditions, all metals are transported at equal rates, causing similar dispersal patterns.

   Considering copper, it appears that concentrations in flood deposits along the course of the Geul river exhibit only a very weak relation with the distance downstream (see Table 8.4). The lack of a point source of copper in the upstream region may explain this more or less random dispersal pattern.

8.7 Chemical partitioning of heavy metals

In order to estimate the relative bonding strength of metals in different chemical phases, extraction procedures have been developed, which are commonly combined in sequential extraction schemes. An overview of these schemes, which are all based on the work of Tessier et al. (1979), is given by Salomons and Förstner (1984). A number of relatively easily separated, operationally-defined, metal-associated sediment fractions are identified, and then chemically separated in a sequential leaching scheme (Chester, 1987). Many schemes in common use include the following fractions (Salomons and Förstner, 1984): (1) exchangeable cations, (2) carbonate fraction, (3) easily reducible fraction (Mn oxide, partly amorphous Fe-oxyhydrates), (4) moderately reducible phases (e.g., amorphous and poorly cristallized Fe-oxyhydroxides), (5) organic fraction, incl. sulfides and (6) residual fraction (e.g. detrital silicates, crystalline Fe-oxides).

The rate at which metals may be released from their sediment storage hosts is strongly dependent on the diagenetic environment prevailing at the depositional site. Förstner (1985, cited in Chester (1987)) assessed metal mobility in terms of redox potential and pH. This scheme may be related to mobility within the sediment host fractions in the following general way (Chester, 1987): - redox changes have their most significant effects in releasing metals in the sequence: stage 5 (organic) > stage 3 (easily reducible) > stage 4 (moderately reducible); - pH changes have their most significant effects in releasing metals in the sequence: stage 1 (exchangeable) > stage 2 (carbonate) > stage 3 and 4 (easily and moderately reducible).

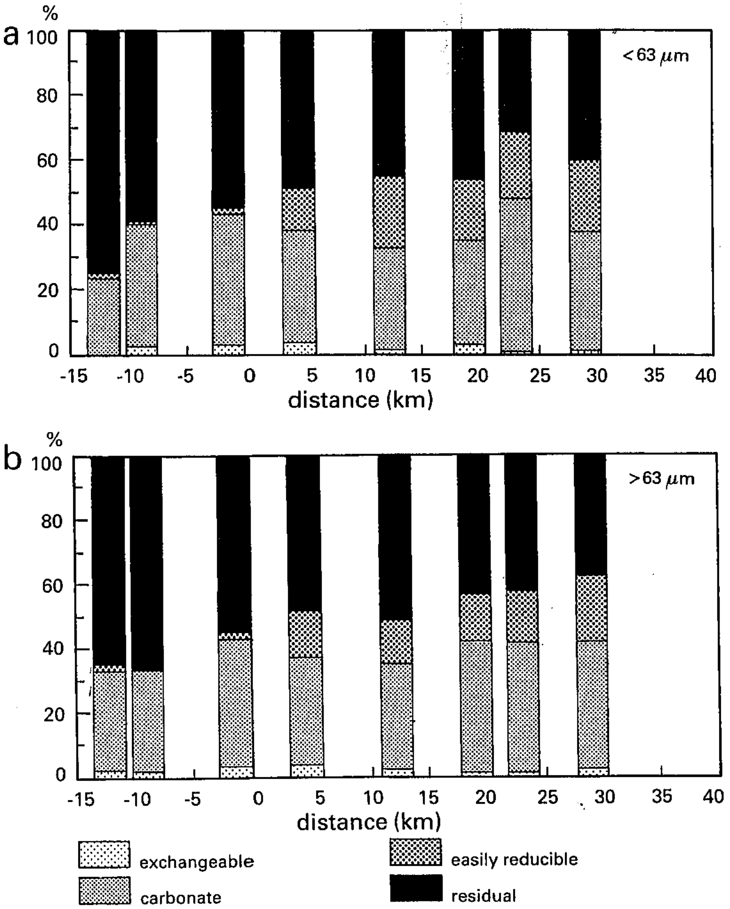


Figure 8.5 Partitioning of Pb in flood deposits of the Geul versus distance to Netherlands-Belgium border: a) in the < 63 µm fraction, b) in the > 63 µm fraction.

Figure 8.5, 8.6 and 8.7 show stacked bar graphs of the concentrations of lead, zinc and cadmium in the various chemical phases in the two grain size fractions of flood deposits of the Geul. The percentage of lead that was released during the 3 leaching stages varies from 20 to

70% in the fraction < 63 µm and from 40-60% in the fraction > 63 µm. This fraction, which may be considered potentially mobile, is a large part of the total concentrations (see Table 8.1). Lead is mainly found in the carbonate fraction (25-50%) and much less in the easily reducible (0-20%) and exchangeable (< 5%) fractions. The carbonate fraction contains metals in structural positions within calcium and magnesium carbonates and in separate carbonate phases. All these carbonates become increasingly soluble as pH declines.

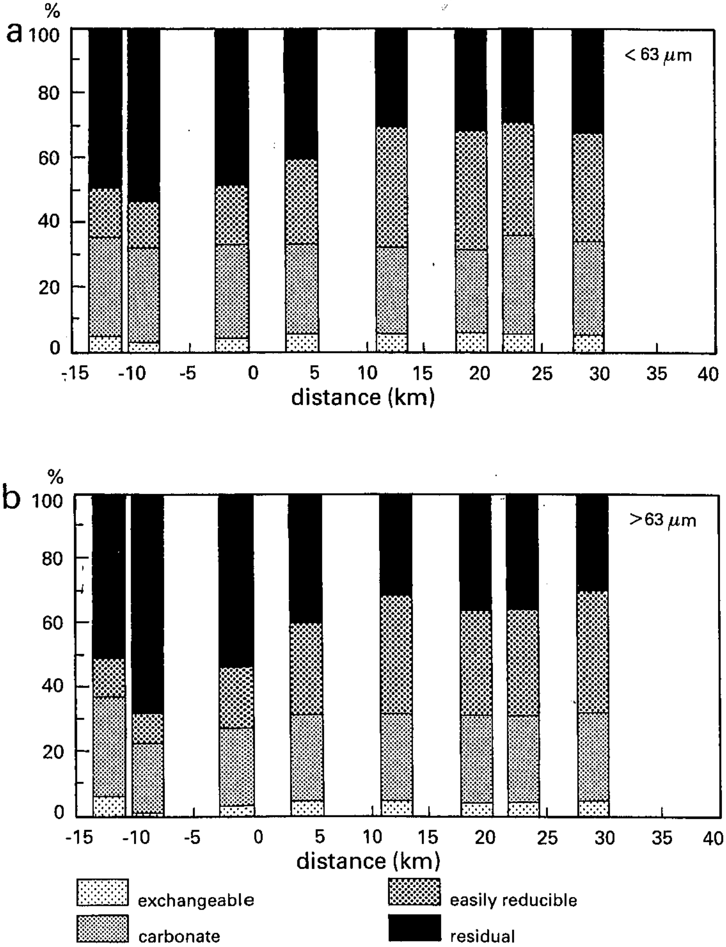


Figure 8.6 Partitioning of Zn in flood deposits of the Geul versus distance to Netherlands-Belgium border: a) in the < 63 µm fraction, b) in the > 63 µm fraction.

The results for zinc are somewhat different. The total released percentage in the first three stages is higher on average (60-70% in 10 of the 16 samples) and there is no single dominant host fraction. The carbonate fraction contains a very constant 30% zinc and the easily reducible fraction some 10-35%. Cadmium is the only one of the investigated metals that is to a considerable extent present in the exchangeable fraction (5-30%). This fraction contains metals which are in loosely-held surface associations and therefore are the most potentially mobile. The carbonate fraction contains c. 30% of cadmium in both grain size fractions and the coarser fraction (>63 µm) is relatively rich in the easily reducible fraction (10-20%).

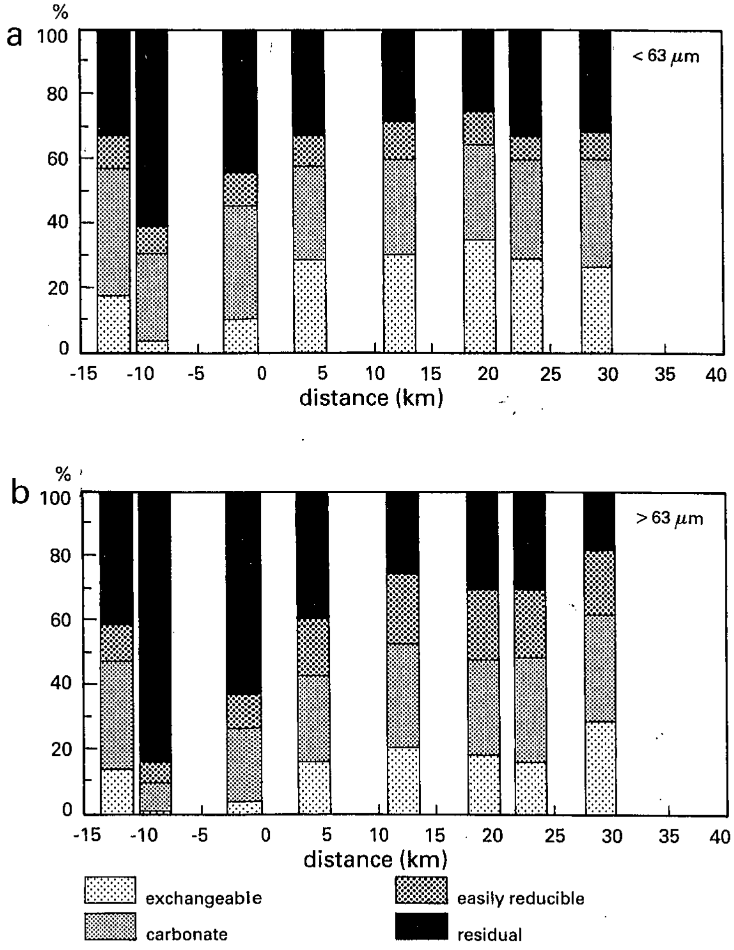


Figure 8.7 Partitioning of Cd in flood deposits of the Geul versus distance to Netherlands-Belgium border: a) in the < 63 µm fraction, b) in the > 63 µm fraction.

An important conlusion that may be drawn is that virtually no difference exists between the < 63 µm and the > 63 µm fractions both in terms of total amounts of Pb, Zn and Cd that are potentially mobile and in terms of the distribution of the metals over the host fractions. Apparently, the ore particles and tailings in the coarser size fraction are all but inert and may release their metals at rates that are of the same order of magnitude as the < 63 µm fraction.

8.8 Downstream changes of partitioned metal concentrations

In view of the fact that suspended sediments after deposition may become incorporated in floodplain soils, it is of interest to investigate not only the downstream changes of total metal concentrations but also downstream changes of the chemical phases of the metals within the sediments. Figure 8.5, 8.6 and 8.7 show that the amounts of Pb, Zn and Cd in the first three leaching stages (as a percentage of the total concentration) steadily increase with distance to the source area. For Pb and Zn, this increase is mainly due to a growing importance of the easily reducible fraction. This pattern can be observed for both the < 63 µm and the > 63 µm fractions. In contrast, Cd increases in the exchangeable fraction when the < 63 µm size fraction is studied and in the exchangeable and easily reducible fractions for the > 63 µm size fraction. The discrepancy between the chemical partitioning of metals in sediments from upstream and downstream of the source area is largest for Cd: the percentage in the three leaching stages drops from 60-70% to 20-40%, which clearly indicates the discharge of chemically different species into the fluvial system. Along the first 20-25 km from the source area the importance of the three studied host fractions (in both size fractions) increases to reach a stable partitioning that is comparable to the one upstream of the source area. This observation can be accounted for by either physical dilution with sediments that contain Cd in the latter partitioning or by the chemical release of metals from the residual fraction and the subsequent entry into other host fractions.

From Figure 8.5, 8.6 and 8.7 it becomes clear that the rate at which the residual fraction declines with increasing distance to the source area follows the sequence: cadmium > zinc > lead. The geochemical mobility of the 3 metals decreases according to the same sequence and this may indicate that the release of metals from the residual fraction, rather than dilution processes, governs the change of partitioning during transport away from the source area. Moreover, part of the relatively 'clean' sediments that would account for the dilution are older deposits whose chemical composition too would reflect the differences of geochemical mobility of the various metals.

In conclusion, the apparent positive effect of dilution processes on total metal concentrations is to a considerable extent counteracted by chemical processes that cause metals to be released from the residual host fraction (including the moderately reducible and organic fractions) and to enter potentially mobile host fractions. In other words, although total heavy metal concentrations rapidly decrease with distance from the source the chemical reactivity of those metals increases in relative terms.

8.9 Evaluating the downstream patterns

Paragraph 8.6 and 8.9 discussed the downstream changes of total and partitioned metal concentrations, respectively, of recently deposited floodplain sediments. The downstream decay patterns of potentially mobile metals were discussed in relative terms, i.e. as a percentage of observed total concentrations. By employing the exponential decay functions of total concentrations presented in Section 8.6 (see Figures 8.5-8.7), it is now possible to construct graphs of the downstream changes of potentially mobile metals in absolute terms. Potentially mobile metal fractions in the 0-2000 µm grain size fraction were computed from the partitioned metal concentrations in the grain size fractions < 63 µm and > 63 µm and their relative contributions to the total weight:

$$Y_m = F_m * Y_t \qquad [8.3]$$

$$F_m = F_{<63} * Y_{m<63} + F_{>63} * Y_{m>63} \qquad [8.4]$$

where Y_m is the concentration of potentially mobile metals (i.e. stage 1, 2 and 3 of the sequential extraction scheme) in the unseparated sample, F_m is the potentially mobile metal fraction, Y_t is the total metal concentration, $F_{<63}$ and $F_{>63}$ are the dry weight fractions of the < 63 µm and > 63 µm grain size fractions, and $Y_{m<63}$ and $Y_{m>63}$ are the mobile metal concentrations in the < 63 µm and > 63 µm grain size fractions. The exponential decay functions of total metals and the corresponding absolute concentrations of potentially mobile metals are shown in Figure 8.8.

The graphs for Pb and Zn exhibit quite similar patterns. The total concentrations increase by a factor 15 and the potentially mobile metal concentrations increase by a factor 8 due to the discharge of waste materials upstream of the Netherlands-Belgium border. In the downstream direction the total concentrations of Pb and Zn decline at equal rates due to 'dilution' and according to the fitted exponential decay functions. However, the decay of the potentially mobile fractions of Pb and Zn occurs at much slower rates, causing both lines in the graph to diverge with increasing distance to the source. This feature illustrates the efficiency of sediment-water interactions during transport away from the source to cause heavy metals to migrate between the various solid storage compartments. Nevertheless, even though the relative importance of the potentially mobile metal fractions increases, it is clear that in absolute terms their importance declines.

The downstream change of cadmium levels follows a rather different pattern. As for Pb and Zn the total Cd concentration also increase directly downstream of the point source and then exponentially declines due to 'dilution'. However, the potentially mobile Cd concentration does not exhibit a sudden increase due to the presence of the point source. This can be explained by the large chemical difference between the 'natural' Cd species present in the study area and the Cd species discharged into the Geul near Plombières and Kelmis, which is characterized by a relatively large residual fraction (see Figure 8.7). Figure 8.7 already indicated that the release of Cd from the residual fraction occurred at a higher rate than did the releases of Pb and Zn. The impact of this phenomenon on the potentially mobile Cd fraction is further illustrated in Figure 8.8c. The potentially mobile Cd concentration steadily increases along the first 15 km from 1 mg/kg near the point source to a peak of 3 mg/kg at c. 5 km downstream of the Netherlands-Belgium border. Thus, although the wastes discharged into the Geul contain Cd mainly in residual fractions, the relatively high mobility of Cd causes its potentially mobile fraction to gain importance rapidly.

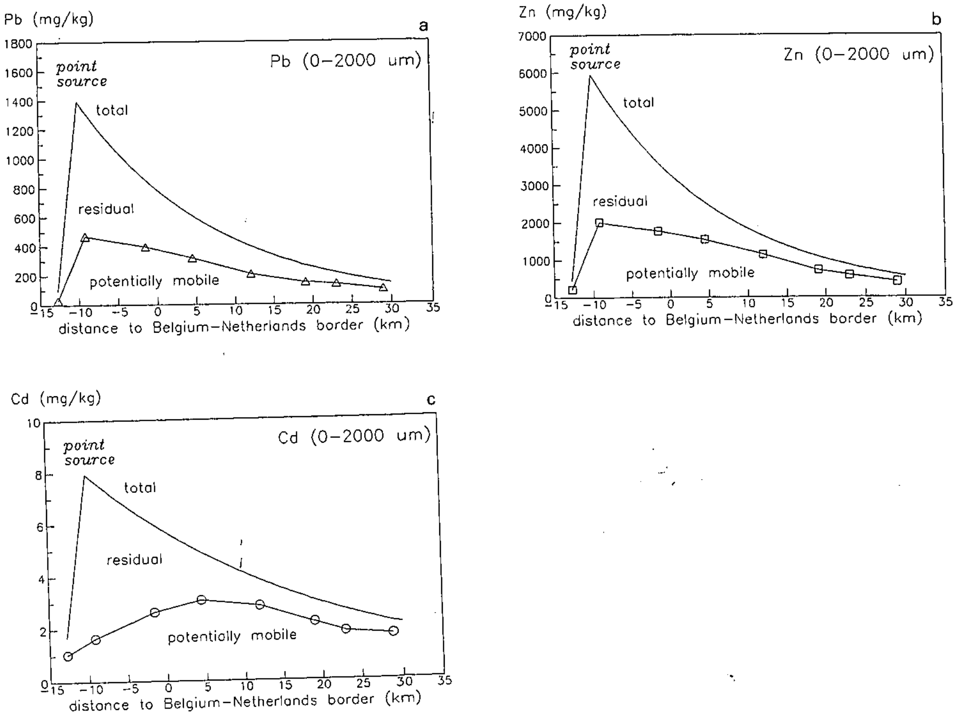


Figure 8.8 Downstream changes of total and potentially mobile concentrations of a) Pb, b) Zn and c) Cd in flood deposits of the Geul.

8.10 Conclusions

It has been shown that there are no systematic relationships between grain size or organic matter content and the concentrations of enriched metals in flood deposits of the Geul and the Meuse rivers. Correcting for grain size effects based on preferential occurrences of heavy metals in fine grain size fractions, is therefore inappropriate under these circumstances. Moreover, in the Geul river virtually no difference can be observed between the chemical partitioning of metals in the fine (< 63 µm) and the coarse (>63 µm) size fractions of flood deposits. The carbonate fraction and the easily reducible fraction are important host fractions for Pb, Zn and Cd; only Cd is present in the exchangeable fraction to a considerable extent. The total percentage of these three metals in the exchangeable, carbonate and easily reducible fractions may be as high as 60-80%.

During periods of high flow the total concentrations of Pb, Zn and Cd decrease exponentially with increasing distance to the source area as a result of mixing with 'clean' sediments. No differences can be observed between downstream fall-off rates of total concentrations of metals with different densities and geochemical mobilities. However, during the transport away from the source metals are released from the residual fraction (including here the moderately reducible and organic fractions). The subsequent entry into the potentially mobile host fractions causes a steady increase of the percentage of potentially mobile metals. As a result, even at large distances from the source area substantial amounts of potentially mobile metals are supplied to and stored in the floodplain area.

Under conditions of low flow the decay of the relatively mobile and light metal zinc in flood deposits is smaller than that of lead, indicating the importance of density differences and geochemical processes during these flow conditions.

8.11 Summary

Fresh flood deposits were sampled in the floodplains of two river systems, the Meuse and the Geul. These sediments are important carriers of contaminants during the sediment exchange between river channel and river floodplain by processes of erosion and sedimentation. As a result of industrial and mining activities, both rivers have a history of severe heavy metal pollution, especially with zinc, lead and cadmium. The recent deposits may reflect the current degree of pollution of the two fluvial systems.

There is no simple linear relationship between metal content and grain size fractions in the flood deposits of the Geul and Meuse rivers. For the Geul no differences can be observed grain size fractions > 63 µm and < 63 µm, both in terms of total concentrations and in terms of partitioned concentrations of heavy metals.

Along the Meuse, no significant decay of metal concentrations with distance downstream can be observed, because there is no single point source of heavy metals. On the contrary, along the Geul total metal concentrations decrease exponentially with increasing distance from the metal mining area in Belgium. During the transport away from the source, the heavy metals are released from the residual host fractions. Subsequently, the heavy metals enter potentially mobile host fractions (the exchangeable, carbonate and easily reducible fractions), whose relative importance increases with distance to the source area.

9 LAND USE CHANGE AND ITS IMPACT ON THE DISPERSAL MECHANISM

9.1 Introduction

The increasing magnitude and frequency of soil erosion events and claims for water damage in the hill country of the Province of Limburg (The Netherlands) during the last decades, has recently been a source of concern (Schouten et. al., 1985). Increase in urban area and the number of sealed roads, and a scale-enlargement and modernization in agricultural practice are the major causes of these changes. Such developments may have major effects on the functioning of the hydrological cycle during flood events (Hollis, 1975; Leopold, 1968). The net effects may be that a higher proportion of rainfall is translated into runoff, this runoff occurs more quickly, and floods are therefore higher and 'flashier' than before the land use changes (Hollis, 1975).

The River Geul is one of the main streams that drains the hill country of the Province of Limburg. Because the alluvial deposits are polluted with heavy metals (Rang et al., 1986), a 'flashier' discharge regime may have serious environmental implications. During high flow stages the contaminated streambank deposits are reworked, causing high metal levels in suspended sediments which may be deposited in downstream floodplains during floods (see Chapter 7). An increase of the frequency and magnitude of floods may cause an acceleration of sedimentation and an increase of the area that is regularly flooded and polluted.

9.2 Experimental procedures

Land use data of South Limburg were collected during a large scale investigation of areas that are susceptible to soil erosion and areas that suffer from water damage (Schouten et al., 1985; Van der Helm et al., 1987). Additional data on the landuse in the catchment of the Geul were derived from historical records.
Two series of continuous discharge recordings, covering the periods 1955-1958 and 1972-1986, were available for flood frequency analysis. The more recent series is based on records from a gauging station of the Provicial Water Authorities of Limburg near the village of Meerssen; the other series is based on records from a gauging station near Schin op Geul (Zeeuw, De, 1966). It has been noted that, because of the lack of major tributaries between the two gauging stations, the discharge hardly increases along this section (Heidemij, 1973). However, in order to obtain comparable discharge figures it was decided to correct for the size of the upstream catchment area: the records from Schin op Geul were multiplied by a factor 1.1. The frequencies of flood events were estimated using a Monthly Exceedance Series and the number of peaks considered was set equal to the number of record months from which the peaks were abstracted. The use of monthly data rather than the more frequently used annual series (Gregory & Madew, 1982) was chosen since our main interest was directed towards floods with short recurrence intervals. For both series it was checked that all peaks considered were independent. If the maximum discharges of

N months of record are ranked from highest (rank, m=1) to lowest (m=N), the resulting series forms N+1 rank classes. The probability of a random event of magnitude x being equal to or greater than an event ranked m is P(x) = m/(N+1), and the mean recurrence interval (in months) of this event is 1/P(x) = (N+1)/m. Discharges of specified recurrence interval are estimated by fitting an appropriate theoretical probability distribution, which normally must model the positive skew common in extreme event distributions. A Log-Pearson Type III distribution (Richards, 1982; Morel-Seytoux, 1979; Bobée, 1975) appeared to provide a good fit to the series and floods with a recurrence interval of 6, 12, 18 and 24 months were determined for the periods 1955-'58 and 1980-'86.

Since the frequency of rainstorms may have an impact on the results of a flood frequency analysis, it is necessary to compare periods that have similar rainfall characteristics. Therefore, daily rainfall figures from a gauging station in Valkenburg, covering the period 1955-'86, were used to compute for a number of periods the recurrence intervals of selected amounts of daily precipitation (based on exceedance frequencies).

During a sampling campaign in 1986 and 1987 742 samples of topsoil were collected in the Geul floodplains. The locations were chosen with the aid of a geomorphological map (Van de Westeringh, 1980), and in such a manner that all individual map units are represented in the dataset. The samples were taken at a depth of 0-10 cm and contain a volume of ca. 100 g each. The extraction and analysis of heavy metals in these samples was done as described in Section 3.3.1.

A series of aerial photographs (from 1949, 1973, 1976, 1983 and 1986) of a sequence of meander bends of the Geul was studied in order to estimate rates of channel migration. Data on metal concentrations in streambanks that exhibit marks of recent erosion were available from previous studies (see Chapter 7).

9.3 Land use changes

In the southern part of the Netherlands, the Geul valley incises a loess-covered plateau that consists of cretaceous limestone. Cultivation of the forested valley slopes began in Roman times. Ever since, soil erosion processes have supplied loess materials that are rich in the silt and fine sand fractions. As a result, the alluvial deposits have a relatively coarse texture (see Section 2.3). In this period the first soil conservation measures were taken. Within the practice of small-scale agriculture only small areas laid fallow at a time and it was common practice to lay down the steepest slopes to grass. At the dividing lines between the parcels on the valley slopes 'graften' (linchets) developed and these were kept intact by the farmers.

During the last decades the urban area and the number of infrastructural works have increased in this part of the Netherlands (see Table 9.1a). In addition, a number of changes in agricultural practice (see Table 9.1b) have had a major impact on the functioning of the hydrological cycle. Crops like maize and sugar beets are now grown instead of cereals, so that large areas lay fallow during about 6 months per year. The application of large amounts of fertilizers and insecticides

Table 9.1a Landuse (% area) in an area covering 11 municipalities in the Dutch part of the catchment of the Geul (i.e. 50 % of the total catchment area)

year	cultivated area	forest	roads & railways	urban area
1955	78	10	4	7
1985	71	11	5	12

Table 9.1b Agricultural landuse (% area) in South Limburg (van der Helm et al., 1987)

year	grass	cereals	potatoes	sugar beets	maize	other
1960	51.0	32.6	4.0	8.0	-	4.4
1976	47.2	19.6	3.8	15.4	6.0	8.1
1986	43.1	17.2	4.5	16.1	13.4	5.7

probably has a negative impact on the soil stability (Van Eijsden & Imeson, 1985), which is also affected by the use of heavy farm machinery. Other changes are the rationalisation measures that have been taken: the enlargement of parcels, the increase of the cultivated area, ploughing in a direction perpendicular to the contour lines, the removal of lynchets (old cultivation terraces) and the breaking up of pasture on the valley slopes (Schouten et al, 1985). As a result, the infiltration capacity of the soil and the area in which rainfall can infiltrate into the soil are reduced, and overland flow can take place readily on the relatively smooth impermeable surfaces. These changes have led to increasing runoff, increasing soil loss and a considerable reduction of the crop yields. Bouten et al. (1985) estimate the average soil loss on cultivated slopes in South Limburg at 15 ton/ha/yr. At these locations, the loss of yield due to erosion may be in the order of 5-10% of the total yield (Schouten et. al, 1985). However, in financial terms the water damage caused by flood events in urban areas probably is the largest burden for the communities in the study area. The estimated annual expense on maintenance and repair of infrastructural works varies from 5 to 40% of the budget for maintenance of roads of the local authorities (Schouten et. al., 1985).

9.4 Discharge regime changes

In a review of the effect of urbanization on the flood characteristics of a river, Hollis (1975), employing data from more than 15 investigations, concludes that small floods may be increased ten times by urbanization but that the effects decline in relative terms as flood recurrence intervals increase. Figure 9.1a provides flood frequency curves of a theoretical 1 mi^2 catchment in various states of urbanization, derived from the results of a large number of studies (Leopold, 1968).

The results of the storm frequency analysis are listed in Table 9.2. It is clear that both in terms of total amounts of annual rainfall and in terms of the frequency of larger storms, the periods 1955-'58 and

1980-'86 have comparable characteristics. Both periods differ considerably from the period 1972-'79, which was relatively dry. So it may be concluded that climatic change is not a long-term problem, except the period 1976-'79 was dry and therefore benign. On the basis of these results it was decided to restrict the flood frequency analysis to the former two periods.

Table 9.2 Recurrence intervals (days) of daily precipitation (mm)

precipitation (mm)	1955-'58 (906 mm)*	1972-'79 (756 mm)*	1980-'86 (943 mm)*
5	6	7	6
10	15	19	14
15	36	50	29
20	69	182	65
25	97	294	98
30	122	370	182

* mean annual precipitation

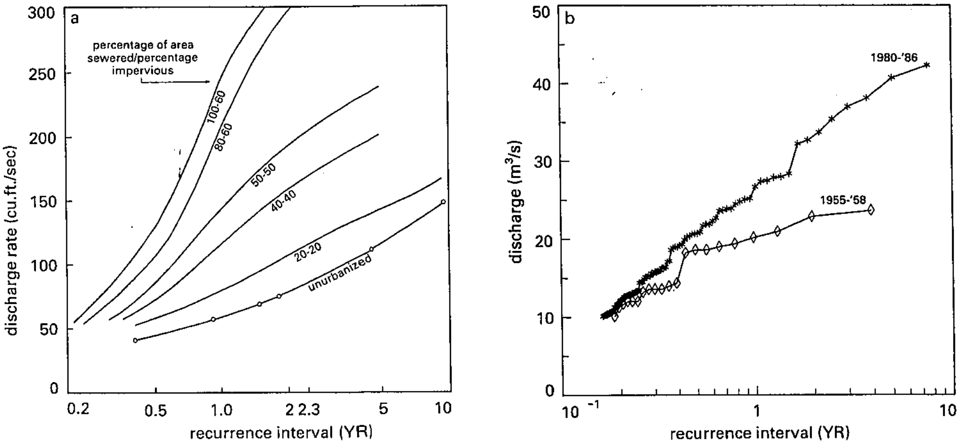


Figure 9.1 Discharge frequency curves of a) a 1 mi^2 catchment (1 mi^2=2.59 km^2) under various states of urbanization (source: Leopold, 1968; redrawn) and b) the Geul at Meerssen in the periods 1955-'58 and 1980-'86.

Figure 9.1b shows flood frequency curves of the periods 1955-'58 and 1980-'86. At very small recurrence intervals, i.e. in the order of a few months, the two curves coincide. Floods with larger recurrence intervals appear to be considerably higher in the 1980s than in the

1950s. Figures 9.1a and 9.1b exhibit similar curve shapes and both demonstrate the tendency of the curves to diverge at large recurrence intervals. This suggests that the land use changes in this study have a similar impact on flood frequency as does urbanization. Table 9.3 lists the discharges at a number of selected recurrence intervals that were derived from the fitted Log-Pearson type III frequency distributions. From these figures it follows that in the range of recurrence intervals of 0.5-2 years the flood size has increased 25-40% during the last 30 years. Because of the limited size of our data set, conclusions about floods with recurrence intervals of more than 2 years will remain tentative. Nevertheless, considering the shape of both curves, it seems reasonable to assume that for those larger floods too notable changes have occurred.

Table 9.3 Discharges Q_{RI} (m/s3) in Meerssen with different recurrence intervals RI (years)

period	$Q_{0.5}$	$Q_{1.0}$	$Q_{1.5}$	$Q_{2.0}$
1955-1958	16.4	19.7	21.7	23.0
1980-1986	20.3	26.5	30.1	32.7

The occurrence of inundation events depends on the hydrological characteristics of the individual flood as well as the prevailing surface form of the floodplain. Flooding in the Geul valley may begin locally at relatively low flow stages, i.e. at a discharge of 20-25 m^3/s (in Meerssen). Large scale inundations occur when the discharge exceeds 40 m^3/s. From the above table it becomes clear that small scale inundations occur more frequently. In the present situation local flooding can be observed at least twice a year in contrast to once every one or two years in the 1950s.

9.5 River channel migrations

A number of studies have reported changes in water and sediment yield consequent upon land use change (e.g. Cooke & Doornkamp, 1978; FAO, 1965; Glymph & Holtan, 1969; Hudson, 1979). Floods with a recurrence interval of 1.5 years (i.e., $Q_{1.5}$) can easily be increased 2.5 times downstream of urban areas (Gregory & Madew, 1982). The increase of peak discharges downstream of urban areas can give rise to enlarged channels (Knight, 1979). A substantial range of land use effects are included in recent reviews (Gregory, 1977; Gregory, 1979; Schumm, 1977).

It has been noted that during the last two decades there is a rapid increase in the local erosion of the streambanks of the Geul. In the urban areas, the channel migrations cause serious damage to sheetpilings and buildings on the river banks. Photos 9.1 and 9.2 show the effects of a major flood in February 1987 in the village of Valkenburg: the water level reached as high as the small bridge and the river banks collapsed a few hours before the flood peak (Photo 9.1),

Photo 9.1 Collapsing river banks during a flood in the village of Valkenburg.

Photo 9.2 A few hours after the flood peak at the same location as on Photo 9.1: the electricity station and the sheet-pilings are devastated.

which had a devastating effect on the sheet-pilings and the electricity station (Figure 9.2). Inspection of a sequence of aerial photographs of a small section of the river channel located in the rural area near Partij (see Figure 2.1), revealed that the local rate of channel migration may be as high as 5 meters/year (see Figure 9.2). Moreover, in a number of recent 3-4 year periods (1973-'76, 1979-'83 and 1983-'85) the channel displacement is of the same order of magnitude as in the 24 year period 1949-'73. No major storms occurred in the period 1973-'76 and no channel displacements could be seen on the photographs.

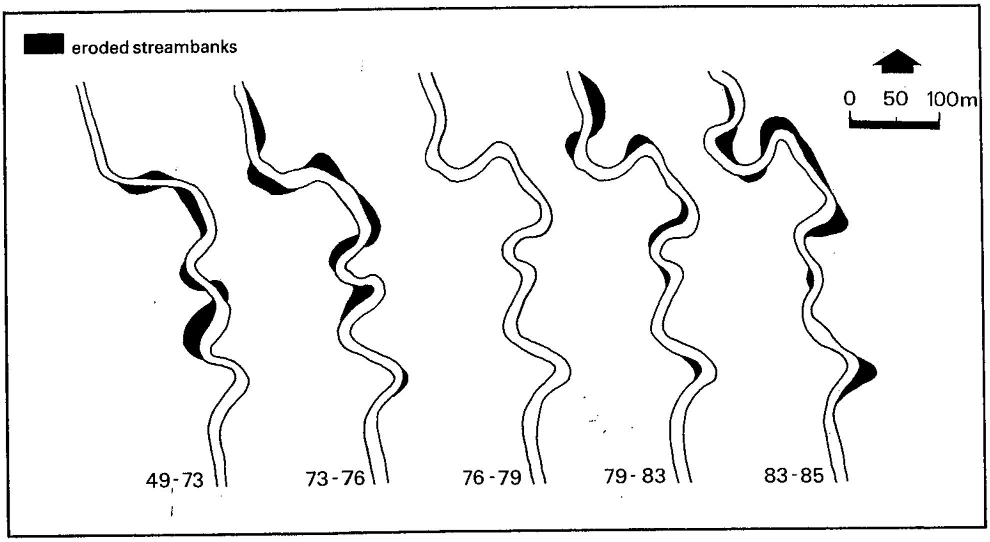


Figure 9.2 River channel changes of the Geul near Partij.

In Chapter 7 it showed that the streambanks of the Geul that exhibit marks of recent erosion may contain high concentrations of heavy metals. The C-value for Pb, Zn and Cd is exceeded in streambanks usptream of Mechelen, which contain on average 5 times as many heavy metals as those downstream of Mechelen. Through the process of streambank erosion large amounts of these historical sediments are supplied to the river channel, and these may be deposited on downstream floodplains.

9.6 The deposition of contaminated sediment during floods

Several authors have reported on the relation between floodplain soil pollution and floodplain characteristics such as inundation frequency, soil type and sedimentary environment (Wolfenden & Lewin, 1977; Rang et al., 1987; Section 5.4). Table 9.4 compares the quality of recent flood deposits with the quality of topsoils in the three major geomorphologic units that can be distinguished in the Geul valley. Remarkably, the natural levee soils are characterized by higher metal concentrations than those in the backswamp areas (see also Section 10.5).

Table 9.4 Mean metal concentrations (mg/kg) of topsoils (0-10 cm) in geomorphological units and of recent flood deposits (n: number of samples).

soil/sediment type	n	Pb	Zn	Cd	Cu
natural levee	345	373	1177	3.8	17
backswamp	118	156	509	2.8	21
colluvium	12	41	147	1.1	11
flood deposits	122	477	2308	4.5	16

However, Pb, Zn and Cd concentrations in natural levee soils are still lower than those in recent flood deposits (see Table 9.4), so that the quality of these levee soils is decreasing under influence of recent sedimentation. Moreover, the increased frequency of inundation events since the 1950s has not only reactivated the supply of contaminants by streambank erosion but may also have led to a simultaneous growth of the area where contaminated sediments are frequently deposited. Field observations at a number of floodplain locations suggested that during a single flood 20-50 cm of sediment may be deposited locally. It is concluded that in this polluted fluvial system changes of the discharge regime have a direct impact on the quality of floodplain soils.

9.7 Conclusions

Because of land use changes and changes of agricultural practice in the catchment of the Geul, the size of floods with short recurrence intervals (≤ 2 yr) has increased by 25-40% during the last 30 years. As a result, small scale inundations occur more frequently. In addition, the metal-contaminated streambank sediments are eroded at higher rates, causing high metal levels in suspended sediments which are deposited on downstream floodplains. The metal concentrations of recent flood deposits are higher than those in the (already) contaminated floodplain soils.
It is clear that the changes of the discharge regime of the Geul, induced by land use changes during the last three decades, have a major impact on the rate at which heavy metals are dispersed and on the present and future quality of floodplain soils.

9.8 Summary

In the Netherlands, as in other parts of western Europe, a slow process of land use changes began in the 1950s. Due to an increase of the urban area and the number of sealed roads, as well as a scale- enlargement and modernization in agricultural practice, the infiltration capacity of the physical environment has decreased. In the hill country of the province of Limburg this process has contributed to an increase of surface runoff, causing severe problems of water damage in urban areas and soil erosion on agricultural cropland. The discharge of the River Geul, with a catchment area of 350 km^2, depends heavily on rainfall. The increasing amount of surface runoff is reflected in a flashier discharge regime, i.e. under similar rainfall conditions a higher peak discharge is produced in the present situation, as compared to the situation in the 1950s. During floods, the contaminated streambank deposits are eroded and therefore continue to act as a source of heavy metals. This process of sediment reworking has intensified since the 1950s, as can be derived from an increase of the rate of channel migration and the frequency and magnitute of floods. As a result, the area that is regularly flooded has grown and contaminated sediments are deposited in the floodplains at higher rates.

10 FLOOD HAZARD MAPPING USING A DIGITAL ELEVATION MODEL

10.1 Introduction

Several techniques are available for providing information on the frequency and extent of flooding in river valleys. These include the use of physiography, pedology, vegetation and flood profiles and backwater curves (Wolman, 1971; Hopkins, 1968). The concept of physiographic mapping of areas subject to flood is based on the correlation of specific topographic features with flood discharges of known frequency. Once such a correlation is established where the topographic features are distinctive, large areas of a valley may be mapped with the knowledge that specific topographic levels can be associated with floods of known frequency and elevation. Mapping of flood areas by correlation of soil type or specific assemblages of plants with the known flood levels requires the same kind of established relationships. In addition, aerial photographs taken during flood events, evidence of floods from historic records, and generalization of flood heights based on records of observations at a number of locations in a given region, may provide the information to establish flood lines on a map. None of these techniques include the effects of backwater, i.e. the phenomenon that the water level gradient differs from the channel bottom gradient. Refined techniques for delineating flood lines including computations of backwater curves (e.g. Feldman, 1981; Ely & Baker, 1985), may produce flood hazard maps with a higher degree of precision but are costly since they require detailed field information (e.g. channel geometry, roughness coefficients, etc.).
Despite the uncertainties inherent in estimates of the effects of flooding, the desirability of providing timely information commensurate with the pace at which land use decisions must be made requires a quick technique for mapping flood zones that is based on available information. In this paper a mapping method will be discussed that employs readily available elevation data to construct a Digital Elevation Model (DEM). A simple model of generalized flood water levels parallel to the long profile was used to delineate flood zones in the DEM and photographs taken during a flood event were used for validation. Given the often observed relation between floodplain characteristics, such as inundation frequency, soil type and geomorphology, and the level of soil pollution (see Section 5.4), the use of the flood hazard map for mapping soil pollution is evaluated. A comparison between the applicability for this purpose of a geomorphological map and the flood hazard map is made in terms of explained variance fractions.

10.2 Experimental procedures

For a 2 km long part of the Geul floodplain (directly north of the town of Gulpen, see Figure 10.1), the approximately 1400 elevation data on the altitude map (Netherlands Topographic Survey, 1976) were digitized and used for constructing a Digital Elevation Model by spatial interpolation (see next section). The Digital Elevation Model was then related to the long profile of the river so that relative elevations could be obtained (see section on modelling flood water levels).

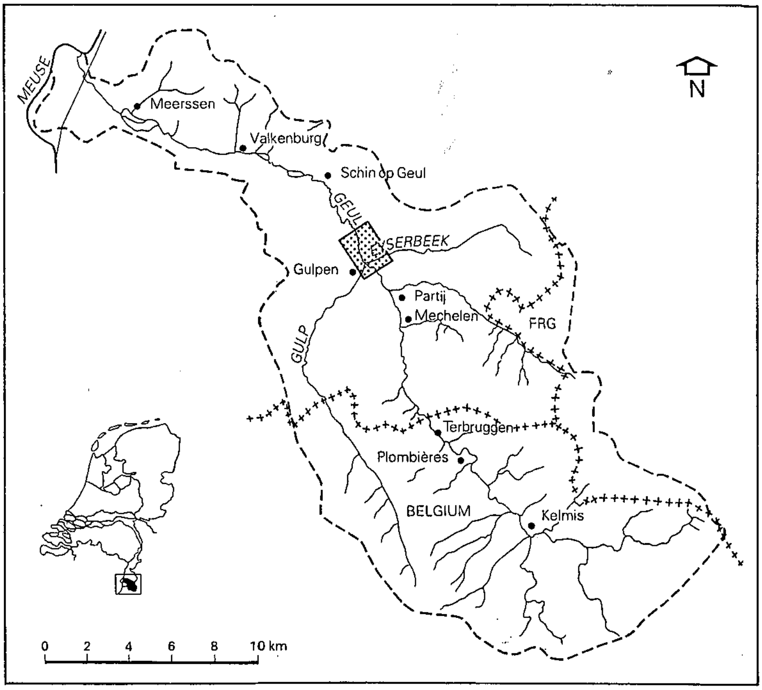


Figure 10.1 The catchment of the River Geul and the study area.

A set of data on topsoil metal concentrations was available for this part of the floodplain area of the Geul, which has a width of 300-600 m. The distances between sample locations range from 50-100 m perpendicular to the valley axis to 100-250 m parallel to the valley axis.

10.3 Interpolation and testing

Any digital representation of the continuous variation of relief over space is known as a digital elevation model (DEM). The term digital terrain model (DTM) is also commonly used. Since "terrain" is not just height but also incorporates land cover and other landscape attributes, which the DTM does not, the acronym DEM is preferred for models containing only elevation data (Burrough, 1986). The terms digital ground model (DGM) and digital relief model (DRM) have also been used by Evans (1980) and Bork and Rohdenburg (1986) respectively. In this paper the acronym DEM will be used.

A DEM may be constructed by spatial interpolation from known elevation data. Many systems of data acquisition, including unaligned or uniform random sampling, centric systematic sampling, stratified random sampling, unaligned stratified random sampling, progressive sampling and composite sampling, have been described (Cochran, 1977; Makarovic, 1973 and 1977; Ayeni, 1982; Ripley, 1981). During this study readily available data (spot heights and contour lines) derived from an altitude map (scale 1:10.000, Netherlands Topographic Survey, 1976) were used. The equidistant contour lines (0.5 m spacing) were digitized as sequences of spot heights, following a method of continuous-interval recording (Keates, 1973): the interval between coordinate positions is adjusted in accordance with the local complexity of the line that is digitized.

The interpolation methods that were used during this part of the study are simple and well known: local averaging, inverse distance weighting and fitting mathematical splines. All methods have a local character in the sense that only a limited number of data in the neighbourhood is used to compute a local estimate. During the local averaging procedure used the neighbourhood is divided into four quadrants and the nearest element in each quadrant is used for estimating $\hat{z}$:

$$\hat{z} = \left(\sum_{i=1}^{N} z_i \right) / N \qquad [10.1]$$

The inverse distance weighting method makes use of a nearest neighbour search procedure. The 8 nearest points in the neighbourhood are used for the computation of a weighted estimate:

$$\hat{z} = \left(\sum_{i=1}^{N} z_i/d_i \right) / \left(\sum_{i=1}^{N} 1/d_i \right) \qquad [10.2]$$

By this inverse distance weighting method, the influence of data declines with increasing distance from the point that is to be estimated. The mathematical spline method makes use of the same search procedure, but only four nearest neighbours were used so that the method is only slightly different from linear interpolation (that requires 3 nearest points to define a local plane). This method is named from its physical counterpart, the flexible drafting spline made from a narrow strip of plastic that can be bent to conform to an irregular shape. A drafting spline is held by lead weights called "ducks", which fix the position of the spline at their points of attachement. Between the ducks, the spline flexes into a smooth continuous form (Davis, 1986). The mathematical equivalent is thoroughly described by several authors (Davis, 1986; Lam, 1983; Dubrule, 1983). The methods described here were used to estimate the floodplain elevation at the intersections of a 40 x 40 m grid with a size of 1.4 x 2.0 km.

For validation a separate set of 53 test data was obtained by photogrammetric survey of aerial pictures (scale 1 : 10.000). The accuracy of the instrument, a Zeiss PSK, is 0.4 m vertically and 0.1 m horizontally. Measurements were made at irregular distances along transects parallel and perpendicular to the valley axis. The tests are based on absolute ($|d|$) and squared (d^2) estimation errors:

$$d^2 = (z(\text{photo})_i - z(\text{esti})_i)^2$$
$$|d| = |z(\text{photo})_i - z(\text{esti})_i| \qquad [10.3]$$

where $z(\text{photo})_i$ is the photogrammetically obtained height and $z(\text{esti})_i$ is the estimated height at location i. For visual interpretation, the errors were plotted along the transects (see Figure 10.2). In Table 10.1 the test parameters are summarized.

Table 10.1 Mean absolute and mean squared errors produced by the interpolation techniques used (n=53)

	original data	local averaging	inverse distance weighting	mathematical splines
$|d|$ (m)	-	0.79	0.83	0.57
d^2 (m^2)	-	0.97	1.07	0.59

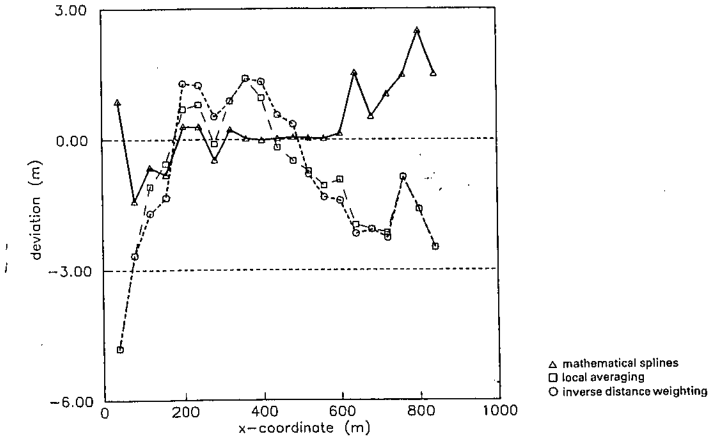


Figure 10.2 Absolute deviations of the elevation estimates from the photogrammetically obtained elevation data along a transect (the floodplain area lies between x-coordinate 150 and 600 m).

Figure 10.2 shows that on the valley slopes all methods fail to estimate the elevation accurately. However, for this study only the prediction within the floodplain area is of interest. Both Figure 10.2 and Table 10.1 show clearly that the mathematical spline algorithm performs better than the other methods and this is especially true in the floodplain area. The non-parametric Mann-Whitney-U test showed that the frequency distribution of absolute errors obtained by mathematical splines differed significantly from the distributions of the other two methods (see Table 10.2). The local averaging and inverse distance weighting methods do not differ significantly from one another in terms of absolute estimation errors. Therefore mathematical splines were used to construct a Digital Elevation Model of the study area (see Figure 10.3).

Table 10.2 Results of the Mann-Withney-U tests for differences of absolute estimation errors ($\alpha = 0.05$, sample size=53)

absolute errors by		U	one-tailed probability
method 1	method 2		
local averaging	inverse dist. weighting	1393	0.470
local averaging	mathematical splines	1052	0.013
inverse dist. weighting	mathematical splines	1026	0.009

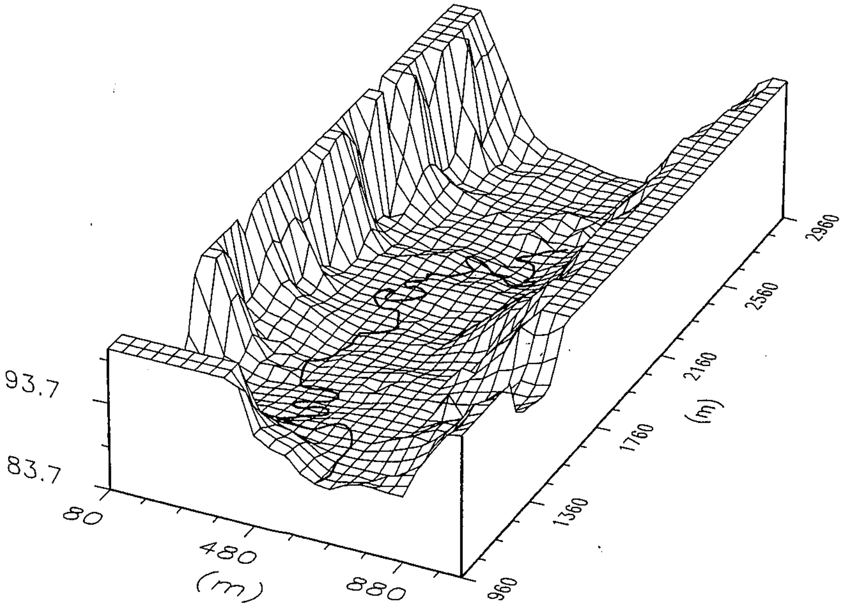


Figure 10.3 Digital Elevation Model of the study area (elevation in m).

10.4 Modelling flood water levels

In addition to the errors that may be produced when backwater effects are ignored, a number of uncertainties are associated with the practice of flood hazard mapping. The relationship between discharge magnitude and the degree of inundation is rather complex, so that a single discharge-related flood-stage is not always identifiable (Lewin & Manton, 1975). The relationship between inflow and outflow in the flooded area will vary according to the hydrological characteristics of the individual flood, such as groundwater conditions, discharge magnitude and the rate of rise and fall in the flood stage, as well as the prevailing surface form of the floodplain. The geometry of the floodplain is a complex combination of geomorphologic forms (such as natural levees, point and braid bars and cut-offs), artificial structures (such as road and rail embankments) and vegetational patterns. As a result, parts of the floodplain may be inundated in the early stages of a flooding sequence by means of for instance abandonned channel loops. A sequence of filling, transmission and drying out of the floodplain may follow, with the local pattern of inundation closely related to the local geometry of the floodplain. Greater amounts of water may be held on the floodplain during recession than at the corresponding inundation level (Hughes, 1980).

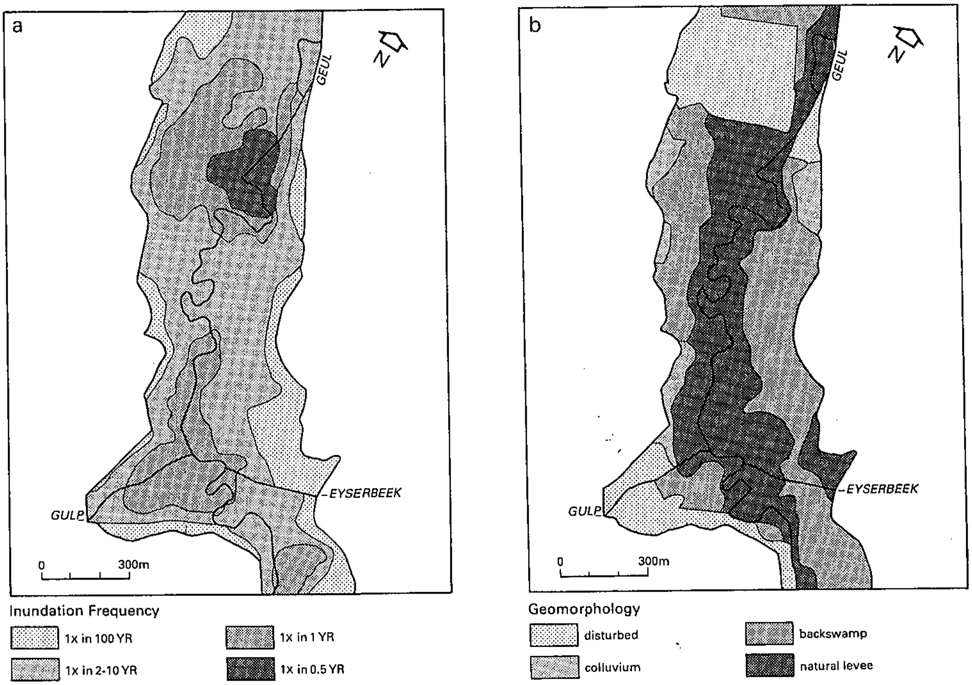


Figure 10.4 a) flood hazard map of the study area;
b) geomorphological map of the study area.

For the part of the Geul valley studied here, no flood stage observations were available. Considering this lack of data and the high costs associated with data acquisition and the computation of detailed backwater curves, it was decided to use a simple model of flood water levels parallel to the long profile of the river bed. If the flood stage at one observation point is known, the flood water level at any other location may be derived directly from the long profile by generalization of the observed water level. Because the part of the valley that is studied is only 2 km long, the application of this simple model was thought justifiable. However, it is recognized that con-

siderable errors may be expected when the model is applied to larger sections of the valley, in particular when backwater effects occur.
In practice, only a long profile of the river bed was available (Anonymous, 1939). These data were turned into a long profile of the river valley by transforming the distances along the bed to distances along the valley, i.e. along a straight line representing the general valley direction. A second order polynomial model was fitted through the elevation data and a matrix with the same dimensions as the DEM was filled with a number of identical columns containing the function values.
By subtracting this matrix from the DEM and segmenting the resulting relative elevations, a flood hazard map was constructed of the study area (see Figure 10.4a). The relative elevations were segmented using class boundaries that represent flood stages: the first boundary was set equal to the water level at bankful stage, the other boundaries are equal to increasing flood water levels with decreasing frequencies. The negative values in each class indicate the sites that are flooded during the corresponding flood stage; the positive values are the elevated parts of the floodplain that remain dry. One delineated flood zone was calibrated by means of photographs of flooded areas that were taken during a flood event in October 1986 (see for example Photo 10.1). The class boundaries were chosen at equal inter-

Photo 10.1 Flooding event in the study area in October 1986 (view to the northwest fro
the lower left corner of the flood hazard map).

vals (75 cm) and changed until the flooded areas on the photographs all belonged to one flood zone (zone 2, see Tabel 10.3a). The corresponding flooding frequency of this class was estimated by means of discharge frequency curves from the gauging station in Meerssen (see Figure 9.1b). The recurrence interval of the maximum discharge recorded at this station on the day of this event is one year. The corresponding maximum water level appeared to have no relationship with the water levels in the study area and illustrates the effect of backwater: 1.93 m above the bed in contrast to 4 m above the bed in the study area (the latter figure was derived from the difference in altitude between the long profile and the DEM). The occurrence of backwater effects in this area is not surprising if one considers that it lies in the direct vicinity of the confluence of two tributaries of the Geul, the Gulp and the Eijserbeek (see Figure 10.1).
This observation makes clear that generalizing flood water levels parallel to the long profile is a simplification that needs validation and that should only be applied to small sections of the floodplain area at a time. Nevertheless, the mere fact that it was possible to map flood zones that coincide with flooded areas on the photographs, indicates that, under the restrictions mentioned above, the model may be a useful tool when only few data on flood water levels are available. In most catchments a limited number of observations on historic and recent flood water levels (such as high water marks) is available and these may be extrapolated to areas where the occurrence of backwater effects is less evident.

10.5 The relation between floodplain characteristics and soil pollution

A number of authors have reported on the relation between floodplain soil pollution and floodplain characteristics such as inundation frequency, soil type and sedimentary environment (Wolfenden & Lewin, 1977; Rang et al., 1987; see Section 5.4). In this section the use of a geomorpholigical map and the flood hazard for mapping floodplain soil pollution will be discussed and compared.
Van de Westeringh et al. (1980) produced a soil map of the Geul floodplains that is based on vertical variations of the clay content of the silt loam soils in the Geul valley (see Section 2.3). For the purpose of this study it was possible to generalize this map (that shows five texture-based soil units) and to distinguish three major geomorphologic units: natural levee, backswamp and colluvium (see Figure 10.4b). This distinction is solely based on textural differences because hardly any difference in terms of elevation can be observed in the field. Natural levee soil profiles are characterized by coarse silt (10-20% clay) to 1.20 m; backswamps have a coarse-silty topsoil and fine silty subsoil (20-30% clay) or a clayey subsoil (>30% clay) or a subsoil of peat or peaty clay (> 15% organic matter). The mean metal content of topsoil material in each unit is shown in Table 10.3b. This table shows that there are large and significant (α=5%) differences in metal content of topsoils between the various geomorphologic units. An important observation is that, contrary to what is generally expected (see Section 4.4), coarse-textured natural levee soils have higher

levels of pollution than those in the low energy environment of backswamp areas. Because of the textural homogeneity of the flood deposits and the topsoils and the lack of pronounced levee bars, the importance of geomorphology is probably overruled by the inundation frequency. The data on lead and zinc content of the topsoil in the study area were also grouped in accordance with the 4 flood zones. The mean lead and zinc content of the samples in the zones are listed in Table 10.3a.

Table 10.3a Mean metal concentrations (mg/kg) of soils in the 4 flood zones (n=number of samples)

flood zone	inundation frequency(1/yr)	n	Zn	Pb	Cd
1	0.5	9	1452	359	3.8
2	1	18	924	237	2.7
3	2 -10	18	779	199	2.3
4	100	20	176	78	0.8

Table 10.3b Mean metal concentrations (mg/kg) in the soils of geomorphologic units (n=number of samples)

geomorphologic unit	n	Zn	Pb	Cd
natural levee	23	946	242	2.3
backswamp	19	433	110	1.1
colluvium	12	98	46	0.5

In order to meet the criteria of normally distributed observations in each class when performing an analysis of variance, the data on soil metal concentrations were transformed to ^{10}logs. For both classifications - one based on geomorphology and one based on inundation frequency - an analysis of variance was performed and fractions of explained variance (R^2) were computed. The results are listed in Table 10.4, which shows that the flood hazard map provides a better base for mapping floodplain soil pollution than the geomorphologic map. The explained variance fractions for all metals are about twice as high when the classification based on inundation frequencies is used. The explained variance fractions vary from 0.44 for cadmium to 0.65 for zinc. These figures suggest that the flood hazard map provides an adequate indication of the delineation of the flood zones and their relative flood frequencies. In addition to this, from the fact that the metal contents of the samples in flood zone 4 approach those in colluvial deposits and are significantly lower than those in the other zones, it may be concluded that the total area that is susceptible to flooding is defined properly by the boundary between zone 3 and 4.

Table 10.4 Explained fractions of the variance (R^2) of topsoil metal concentrations by inundations frequency and geomorphology

classification by	Zn	Pb	Cd
geomorphology	0.32	0.30	0.18
inundation frequency	0.65	0.57	0.44

10.6 Conclusions

Fitting of mathematical splines through readily available elevation data, proved to be an adequate method for the construction of a detailed Digital Elevation Model of the Geul floodplain area. This interpolation method provided significantly better estimates of floodplain elevation than either by local averaging or by inverse distance weighting.

By employing a simple model of flood water levels parallel to the long profile of the River Geul, it was possible to map flood zones in the Digital Elevation Model that coincide with observed flood zones on photographs taken during a flood event.

Mapping soil pollution by employing a flood hazard map yields much better results as compared to using a geomorphologic map. By means of an analysis of variance it was shown that the flood hazard map accounts reasonably well for the spatial distribution of heavy metals in the floodplain soils of the River Geul: the explained variance fractions vary from 0.44 for cadmium to 0.65 for zinc.

10.7 Summary

Geomorphological processes that are active in floodplain areas are related to terrain elevation. The rate of sedimentation, as well as the texture and the quality of the deposited sediments, depend on the frequency of flooding and the sedimentary conditions during flood events. In addition to geomorphological and soil maps, digital elevation models may provide a sound base for quantitative studies of these processes: flood hazard and, in the case that historical elevation data are available, sedimentation and erosion rates may be derived from the digital representation of relief over space.

This paper discusses the interpolation techniques and the test procedures used to compute a Digital Elevation Model of part of the floodplain area of the River Geul. It was found that fitting of mathematical splines outperforms local averaging and inverse distance weighting for estimating floodplain elevation.

A flood hazard map was constructed from a Digital Elevation Model and a long profile of the river. Photographs of a flood event were used for validation. An analysis of variance revealed that 44-65% of the variance in a set of data on flood-related topsoil metal content can be accounted for by the flood hazard map.

11 COMPARISON OF SPATIAL PREDICTION METHODS FOR MAPPING FLOODPLAIN SOIL POLLUTION

11.1 Introduction

In the Geul valley, the general pollution pattern consists of a logarithmic decay with distance to the source of contaminants (see Chapter 8), with local deviations that are caused by variations of flood frequency and sedimentary conditions during flood events (see Chapter 10). Because the pollutants constrain the land use in these areas, so detailed maps are required that delineate zones with high concentration levels. Successful attempts have been made by Wolfenden & Lewin (1977), Rang et al. (1987) and the author (see Section 10.5) to relate the pollution level of floodplain soils to floodplain characteristics such as geomorphology, inundation frequency and soil type. These studies led to the production of choropleth maps that delineated broad pollution zones, but did not provide detailed information about the continuous spatial variation of pollution levels within the zones. There are many point interpolation techniques that can provide this type of information, see for example Lam (1983) and Burrough (1986). However, to date only few attempts have been made to compare spatial prediction methods quantitatively (Bregt et al., 1987; Davis, 1976; Laslett et al., 1987; van Kuilenburg et al., 1982). Obviously, one seeks an interpolation technique that gives the best results for a given investment in observations. The aim of this study is to evaluate some of these techniques (local trend analysis, mathematical splines, inverse distance weighting, point kriging, block kriging and point co-kriging) for the purpose of mapping floodplain soil pollution. The quality of the interpolation techniques used is based on the correlation between predicted and observed values at 99 independent test locations and on the spatial distribution of prediction errors.

11.2 Experimental procedures

Field methods

In the floodplain area of the River Geul, a regular grid of 5 x 29 (grid size 5 x 5 m) was laid out near the village of Valkenburg (see Figure 2.1); 145 samples of top soil material (0-10 cm; ± 100 g) were collected. The elevation relative to mean sea level was determined for each sample location by means of a levelling-instrument and analysis of metals was done as described in chapter 3. In this paper the spatial distribution of only one metal, i.e. zinc, will be studied. Figure 11.1 shows block diagrams of both zinc levels and elevation based on data collected at the data points. It is clear that there is a strong inverse relationship between the two attributes, which can be accounted for by the fact that low-lying areas have a higher risk of inundation. Because of the supply of contaminated sediments during such flood events, the soils in low-lying regions exhibit higher metal levels. It will be shown that benefit may be drawn from the relation between zinc levels and elevation by means of a co-kriging procedure.

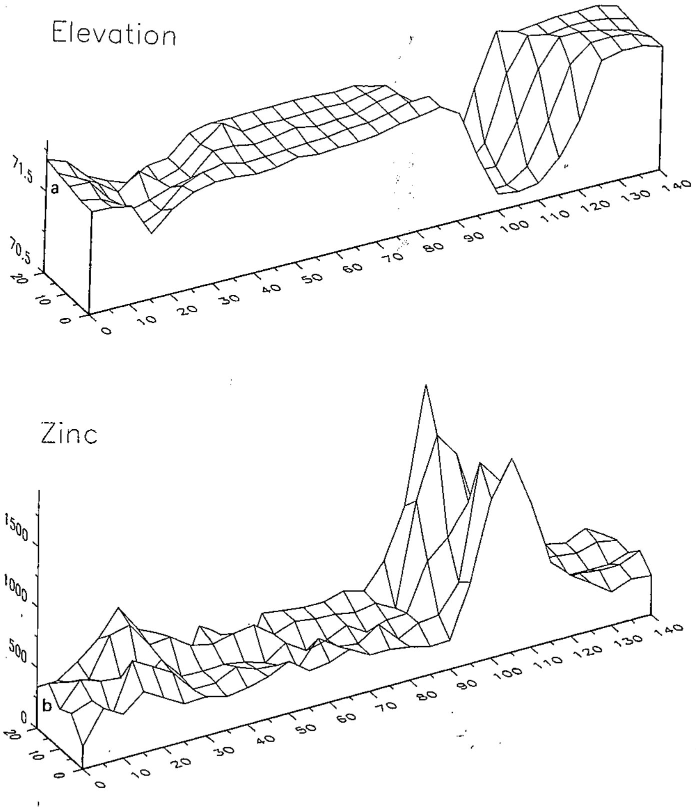


Figure 11.1 a) Digital Elevation Model of the study area (elevation in m);
b) block diagram of Zn levels (mg/kg) in the study area.

The test procedure

The set of 145 data on topsoil zinc was split into two subsets in such a manner that both sets provide a regular distribution of data points over the entire study. The larger set contains 99 data (and one missing value) and was set aside to be used for future validation. The smaller set of 44 data (and one missing value) was used for the estimation of experimental auto semi-variograms of zinc and elevation and a cross semi-variogram of both attributes. The same set was used to design three configurations of regularly distributed sample locations with different densities, containing 12, 23 and 44 data respectively (see Figure 11.2).

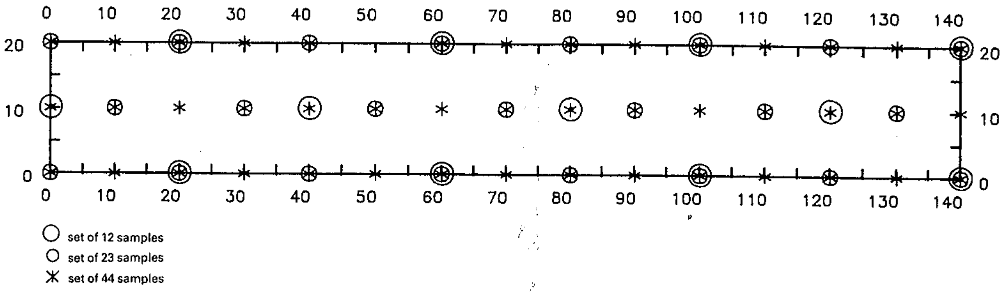


Figure 11.2 Sampling grids in the study area.

Zinc levels were estimated for each configuration - by six different interpolation methods - for points at the nodes of a grid with the same dimensions as the sampling grid. For co-kriging, the data on zinc were supplemented by all available elevation data (n=145). In order to judge the precision of the estimates and to compare the prediction methods with one another use was made of correlation coefficients of linear relations between estimated and observed zinc levels. In addition, contour maps of the absolute prediction errors were produced in order to assess their spatial distribution.

11.3 Spatial prediction methods

Fitting of local trend surfaces

The simplest way to describe gradual variations of a property is to model them by polynomial regression. The idea is to fit a polynomial surface by least squares through the datapoints, where it is assumed that the spatial coordinates X and Y are independent variables, and that Z, the property of interest, is the dependent variable. In two dimensions the polynomials are surfaces of the form:

$$Z(X,Y) = \sum_{r+s<=p} (b_{rs}.X^r.Y^s), \qquad [11.1]$$

where b_{rs} are constants and the integer p is the order of the trend surface. A thorough explanation of this technique is given by Davis (1986), Ripley (1981), Chorley & Hagett (1965) and Watson (1971). Two important disadvantages of this general trend analysis, i.e. the susceptibility to outliers and the inability to fit a low order polynomial through complex data (Burrough, 1986), can be reduced with a moving window approach: only the data that are within a specified search radius are used to estimate the property of interest by fitting a local trend surface. For our study we fitted first order local trend surfaces by using the nearest points within a search radius, that was derived from a structural analysis (see Section 11.4).

Fitting mathematical splines

Given a set of datapoints, one of the simplest mathematical expressions for a continuous surface that intersects these points is the interpolating polynomial of the lowest order that passes through all datapoints (Lam, 1983; Ripley, 1981; Dubrule, 1983; Tipper, 1979). The major deficiency of this polynomial fit is that since the polynomial is entirely unconstrained, except at the datapoints, the values attained between the points may be drastically different from those at nearby data points (Lam, 1983). This problem may be alleviated to a certain extent by employing piecewise polynomial surfaces to cover the area. For our study we used a local algorithm that exploits only the four nearest data points to estimate Z at an unvisited site.

Inverse distance weighted interpolation

The principle of distance weighting methods (Weaver, 1964; Shepard, 1968; McLain, 1976) is to assign more weight to nearby points than to distant points, which is based on the idea that observations located close together tend to be more alike than observations spaced further apart. The most common form of the weighting function is the reciprocal function $1/d^2$, where d is the distance between a nearby point and the point to be estimated:

$$Z(x_j) = \frac{\sum_{i=1}^{n} Z(x_i).d_{ij}^{-2}}{\sum_{i=1}^{n} d_{ij}^{-2}}, \qquad [11.2]$$

where the x_j are the points at which the surface is to be interpolated. For d=0 the exact value of the original sampling point has to be preserved, otherwise the function goes to infinity. By changing the value of the inverse power parameter, the distribution of weights can be varied from being highly biased in favour of the nearest data point to being nearly equal for all data points.

There are several disadvantages to inverse distance weighting methods. First, the choice of a weighting function may introduce ambiguity, especially when the characteristics of the underlying surface are not known. Second, the weighting methods are easily affected by uneven distribution of data points since unequal weight will be assigned to each of the points. Finally, because this method is by definition a smoothing technique, maxima and minima in the interpolated surface can occur only at data points. The location and magnitudes of extreme values therefore, cannot be detected when they are not included as original sample points (Lam, 1983). However, the simplicity of the principle, the speed in calculation, the ease of programming, and reasonable results for many types of data have led to a wide application of the weighting methods as well as to various improvements (Lam, 1983).

Geostatistical methods

In addition to the spatial prediction methods discussed above use was made of several geostatistical methods described in Chapter 6. These methods are: point kriging, block kriging and point co-kriging.

11.4 Estimation of the variograms for kriging and co-kriging

Most samples were located in the natural levee area where only small variations in elevation occur; 19 locations were in an abandoned channel loop of the River Geul that is incorporated in this geomorphological unit. Considering the shape of the study area, only one important direction can be recognized (parallel to the longer axis). Therefore, for this small area it was assumed that anisotropy could be ignored. Multidirectional (i.e. all directions are pooled) auto semi-variograms for zinc (see Figure 11.3a) and elevation were computed from the set of 44 data. The parameters that are required for kriging were obtained by fitting a gaussian model equation (see Section 6.3) through the estimates of experimental semivariance. The practical range was derived from this function as the lag at which 95% of the sill is reached. From Figure 11.3a it may be concluded that the nugget variance of zinc is very small, i.e. ± 4% of the sill. Considering the shape of the gaussian function for small values of the lag h, the 'true' nugget variance may be expected to be higher.

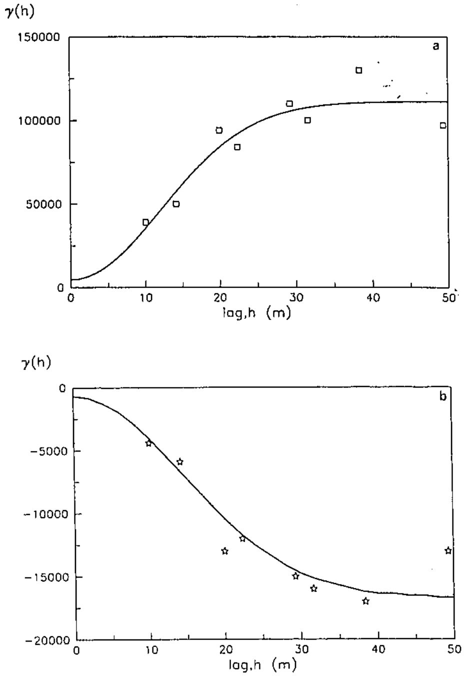


Figure 11.3 a) semi-variogram of Zn (semi-variance in $(mg/kg)^2$);
b) cross-variogram of Zn and elevation (cross-variance in $(mg/kg)^2$).

In this study, we had a good reason to choose elevation as a co-variable for estimating zinc levels by co-kriging. The strong inverse relationship between the two variables (see Figure 11.1) and the fact that the collection of elevation data is relatively cheap suggested that better maps might be produced at lower expense. The cross semi-variogram of topsoil zinc and relative elevation (see Figure 11.3b) could also be modelled adequately with a gaussian model. The cross semi-variances are negative because of the inverse relation between the properties. In the process of cross semi-variogram fitting the Cauchy-Schwarz inequality (see Section 6.5) was checked so as to guarantee a positive cokriging variance in all circumstances. The parameters of the fitted variogram models for prediction by kriging and co-kriging are listed in Table 11.1. During the block kriging procedures a block size of 20 x 20 m was used. For the other prediction methods the parameters were set in such a manner that for each estimate only data that fall within the range of the semivariogram of zinc are used: for inverse distance weighting and the local trend method the search radius was set equal to the range and for the fitting of mathematical splines the number of nearest points was set to 4.

Table 11.1 Parameters of the Gaussian variogram functions

attribute(s)	C_0	C	C_0 + C	a	a'
Zn	4588	106694	111282	17.1	29.6
elevation	417	2657	3074	23.8	40.8
Zn-elevation	- 697	- 15992	- 16689	20.7	35.8

11.5 Goodness-of-fit of the modelled zinc surfaces

Figure 11.4 shows the contours of predicted zinc levels based on interpolation from the 44 input data. For comparison, Fig. 14.4g shows the surface as derived by direct linear contouring from all 143 data points. As might be expected from its approximate nature, the fitting of first order local trend surfaces yields a rather smooth zinc surface, whose generalized nature is most striking in the vicinity of the abandoned channel where steep gradients should prevail (see Figure 11.1). Better results are obtained by fitting mathematical splines and by inverse distance weighting. The contour of 400 mg/kg zinc approximates quite well the one obtained by direct contouring of all 143 data points and the steep zinc gradients are approximated to a certain extent. All kriging methods however, are more successful in detecting the location of this anomaly. Its predicted size is smaller and its shape shows a high degree of resemblance with the pattern based on all the 143 data (see Figure 11.4g), which is especially true for the contour maps that were obtained by point kriging and point co-kriging.

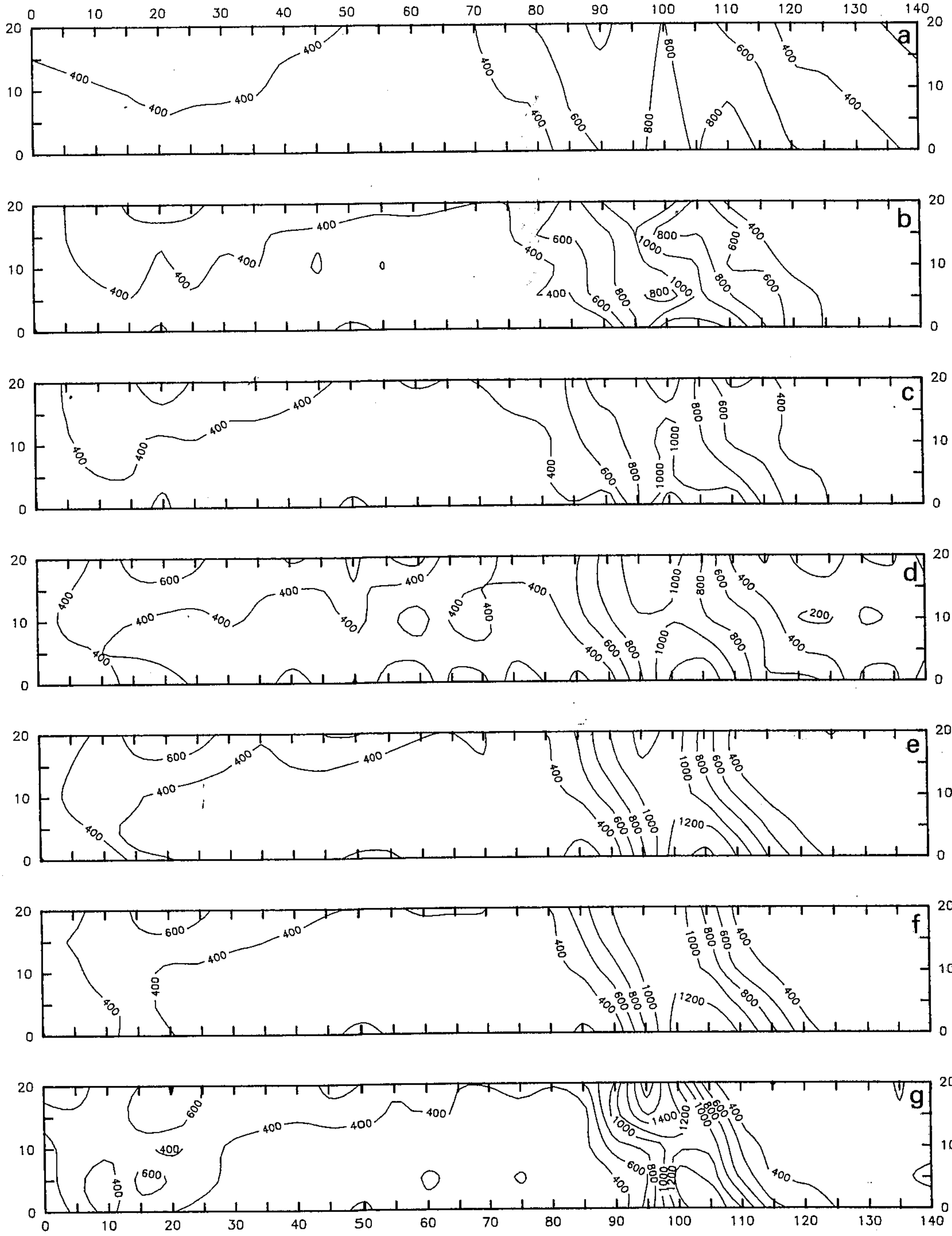


Figure 11.4 Contours of Zn levels (mg/kg) obtained from 44 data by a) first order local trend analysis, b) mathematical splines, c) inverse distance weighting, d) block kriging, e) point kriging, f) point co-kriging, and g) contours of Zn levels based on all 145 data.

In addition to the above - rather subjective - visual examination of contour patterns, correlation coefficients of the linear relations between observed and predicted zinc levels at the 99 test sites were used as a measure of goodness-of-fit (see Table 11.2). For all methods the correlation coefficients increase with an increasing number of input data. The rate at which the improvements occur however, reveals notable differences. The improvements of the local trend method occur gradually (from r=0.41/n=12 to r=0.63/n=44), whereas the performance of the splines method jumps from a very poor (r=0.10/n=12) to an acceptable level (r=0.77/n=44). This behavior illustrates the different qualities of smoothing, approximate methods and flexible, exact prediction methods.

Table 11.2 Correlation coefficients of linear relations between estimated and observed Zn levels (n=99) for 3 sets of input data

	number of input data		
spatial prediction method	n=12	n=23	n=44
first order local trend surfaces	0.41	0.57	0.63
mathematical splines	0.10	0.61	0.77
inverse distance weighting	0.77	0.75	0.83
block kriging	0.73	0.79	0.84
point kriging	0.76	0.80	0.90
point co-kriging	0.85	0.89	0.89

When only 12 data points are available, both these two methods are outperformed by the weighted local averaging methods (inverse distance weighting, kriging and co-kriging). The correlation coefficient is remarkably large for co-kriging, which illustrates the advantage of exploiting additional, spatially correlated, information when only few data on the property of interest are available. The relative benefits of co-kriging decrease as the number of data points with known zinc levels increases: for n=44 point kriging and point co-kriging perform equally well (r=0.90 and r=0.89 resp.). With this data density, the correlation coefficients of inverse distance weighting and block kriging reach to a lower level of 0.83 and 0.84 respectively. For block kriging, this can be accounted for by the fact that this method tends to smooth out extreme values over a - in this case 20 x 20 m - block. The relatively small improvements by inverse distance weighting however, are probably due to the choice of the weighting function. Since this function does not relate to the spatial correlation structure of the data, these results illustrate the undesirable dependence of this method on the input data density and/or data geometry. The fact that the correlation coefficient drops from 0.77 to 0.75 when the number of input data points is enlarged from 12 to 23 illustrates this fact.

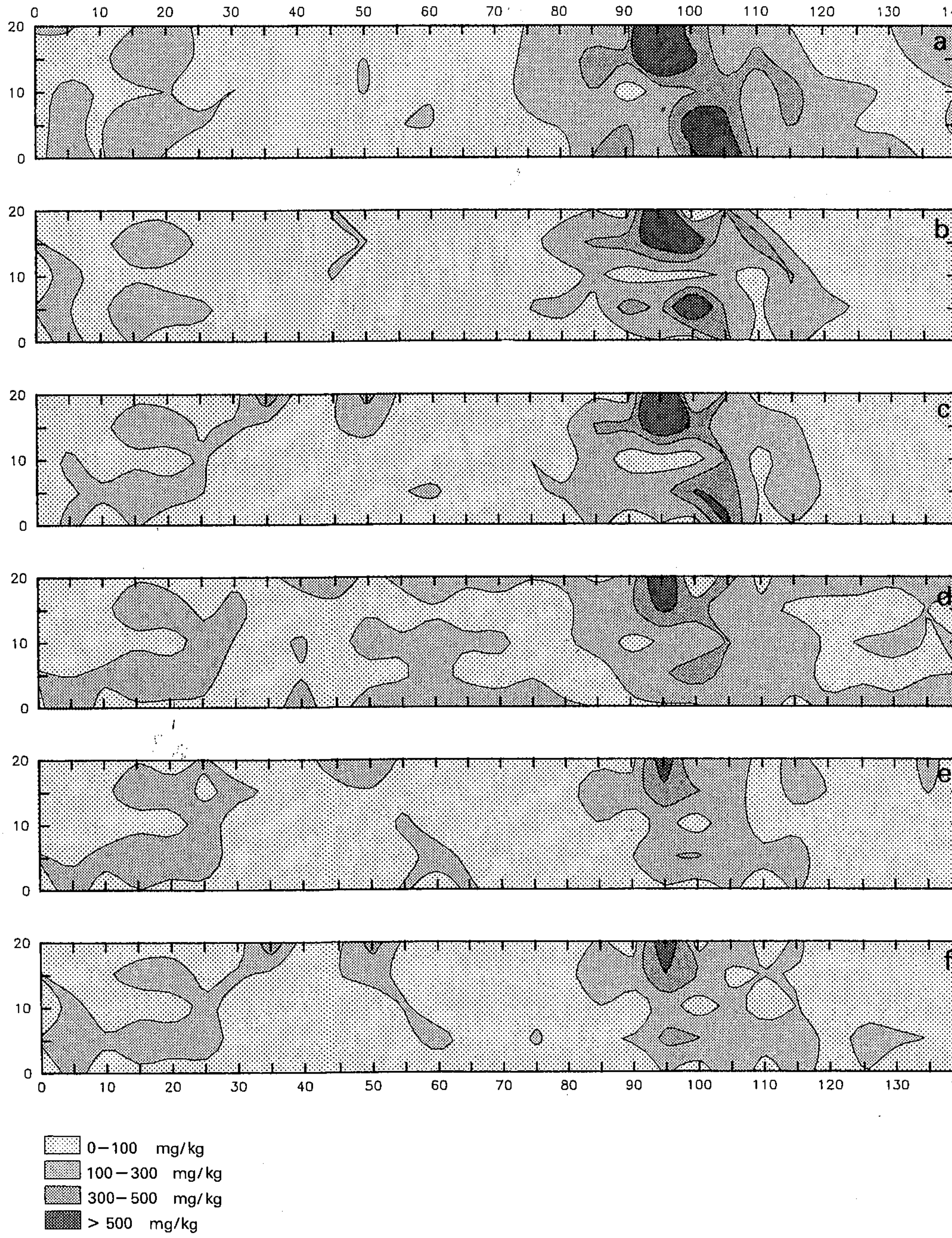


Figure 11.5 Contours of predicion errors (mg/kg Zn) by a) first order local trend analysis, b) mathematical splines, c) inverse distance weighting, d) block kriging, e) point kriging and f) point co-kriging.

11.6 The spatial distribution of estimation errors

Not only the goodness-of-fit of the spatial model but also some idea about the magnitude of the prediction errors is of importance for environmental assessment studies. Instead of using measures of central tendency and dispersion, we decided to produce contour maps of prediction errors. For each interpolation technique, the grids containing the estimates were subtracted from the grid containing the 145 data at the data points, and the absolute value of the difference at each grid intersection was computed. The resulting grids have the same dimensions as the sampling grid and contour maps of prediction errors could be produced. By this means, not only the magnitude but also the spatial distribution of prediction errors can be studied. As for the approximate methods, errors that occur at the input data locations are included in the maps. The occurrence of larger errors should preferably be restricted to small, well-defined areas. However, one should be aware of the fact that, due to their nature of generalization, approximate methods (block kriging and fitting of local trend surfaces) are likely to produce a pattern of regularly distributed errors.
Figure 11.5 shows contour maps of absolute errors (>100 mg/kg) that were obtained by interpolation from the 44 input data points. With the exception of block kriging, all methods yield large errors only in those areas where high zinc levels prevail. The errors produced by fitting local trend surfaces are, as might be expected, largest and cover a relatively large area. The error maps obtained by inverse distance weighting and fitting of mathematical splines are much alike: the area that is covered by the occurrence of errors >100 mg/kg are about equally large and in the abandoned channel a number (3-4) of extremely large errors (>500 mg/kg) occur. For block kriging the occurrence of extremely large errors is restricted to one grid cellonly, but smaller errors of 100-300 mg/kg can be observed in the entire area. Point kriging and point co-kriging combine both virtues: a relatively small area is covered by errors in the ranges 100-300 and 300-500 mg/kg and only in one grid cell is an error of > 500 mg/kg found.

11.7 Discussion

The performance of spatial prediction methods will strongly depend on the type of data that is used and on the spatial correlation structure of the data. It is therefore impossible to draw general conclusions from the results that were obtained in this case study. Nevertheless, this study illustrates some of the qualities of the methods, as will be further discussed below.
The data on zinc levels that were used as the basis for this study exhibit large short range variations (see Figure 11.1). It is clear that approximate methods, that do not aim at preserving the original data nor at exact prediction at unvisited sites, will yield a smooth zinc surface that ignores most of the extreme values. Therefore, fitting of local trend surfaces yields poor results and is not recommended for this type of data. The main purpose of using this method was to illustrate the difference with more appropriate methods.

Fitting of mathematical splines, contrary to the latter method, has the advantage that very steep gradients can easily be modelled. However, since it lacks the possibility to attach more weight to nearby points, large errors may occur when few data are available that include some data that are outside the area of short range variation. This characteristic accounts for the major improvements that can be observed when the number of data points is increased. Also, it implies that some knowledge about the occurrence and location of steep gradients is required in order to ensure that in such areas additional samples are taken.
By inverse distance weighting, the problem of attaching equal weights to all data within the search radius is to a certain extent alleviated. However, since the weights come from some convenient function and do not relate to the spatial correlation structure of the data, the results depend on the - often unknown - applicability of the chosen function. In this study the function $1/d^2$ provided excellent results with 12 data points (one has to be aware of the fact that the search radius was set equal to the range of the semi-variogram of zinc). However, compared to point kriging relatively small improvements occurred when the number of data points was enlarged, which illustrates the inability of this function to optimally exploit extra information. By choosing a few other weighting functions we found that with the set of 44 data points weighting by $1/d^4$ was slightly more appropriate: the correlation between predicted and observed values increased from 0.83 to 0.86. It is clear that in practice one will not always have the possibility to check the validity of the weighting function.
The semi-variogram model of zinc provides weights for interpolation by point kriging and block kriging. The advantage of this sample-based weighting function is best illustrated by the results of point kriging: both in terms of goodness-of-fit and the spatial distribution of prediction errors this method performs better than any of the other methods that do not use additional elevation data. The smoothing nature of block kriging is nicely illustrated by the fact that the area that is covered by small errors (100-300 mg/kg) is relatively large. Apparently, a number of pits and spikes of this size have been ignored by the spatial model. Moreover, given the shape of the study area, the block kriging procedure probably suffers from edge effects. The only method that clearly shows major advantages over all other methods is point co-kriging. Its capability to benefit from cheap additional information by making use of a strong spatial correlation between zinc levels and elevation, accounts for the fact that with 12 input data only an adequate spatial model of zinc levels could be obtained. By taking advantage of this spatial correlation when designing a sampling strategy, substantial cost reductions can be realized.

11.8 Conclusions

In the Geul floodplains, the use of mathematical splines only provides reliable estimates of zinc levels when many data are available in areas with large short range variations. Because of their ability to account for spatial dependence, local weighted averaging methods

(inverse distance weighting and kriging) require less data to provide an acceptable spatial model of zinc levels.
However, in this case study the geostatistically based sample semivariogram provides better weights for interpolating zinc levels than do inverse distance weighting functions.
Major improvements of the spatial prediction of zinc levels from sparse data points in the Geul floodplains are only given by point co-kriging with elevation as a co-variable. Because cheap elevation data not only exhibit a strong spatial correlation with zinc but also contain information on the dispersal mechanism of zinc, the results show that the co-kriging method can be greatly improved when there is a physical understanding of the contamination process. Moreover, without loss of precision a cost reduction can be realized because for co-kriging less data on zinc are required.

11.9 Summary

Several spatial prediction methods (local trend analysis, mathematical splines, inverse distance weighting, block kriging, point kriging and point co-kriging) were used to map zinc levels in a small and intensively sampled study area. Three subsets of the set of 145 data, containing 12, 23 and 44 data respectively, were used to estimate zinc levels at 99 test locations. Correlation coefficients of linear relations between observed and estimated zinc levels and contour maps of prediction errors indicate that weighted local averaging methods perform better than the other methods. In this area, point co-kriging with elevation as a co-variable outperforms all other methods when only few data on zinc are available.

12 MAPPING HEAVY METAL POLLUTION ON FLOODPLAINS BY CO-KRIGING FROM ELEVATION DATA

12.1 Introduction

Detailed planning studies in South Limburg required that the distribution of heavy metal pollution be mapped in the entire river valley both quantitatively and as accurately as possible but collecting data on the metal content of soil material is laborious and expensive. Therefore mapping the heavy metal contents directly would be expensive. In the previous chapter it was demonstrated that for large scale pollution mapping fruitful use can be made of additional elevation data that exhibit a strong spatial correlation with zinc levels. This observation suggested that elevation data, after making a correction for the river long profile, could also be used to advantage to support the small scale mapping. The data on relative elevation can be gathered cheaply and quickly either in the field or from spot heights on 1:10,000 maps (Netherlands Topographic Survey, 1976).

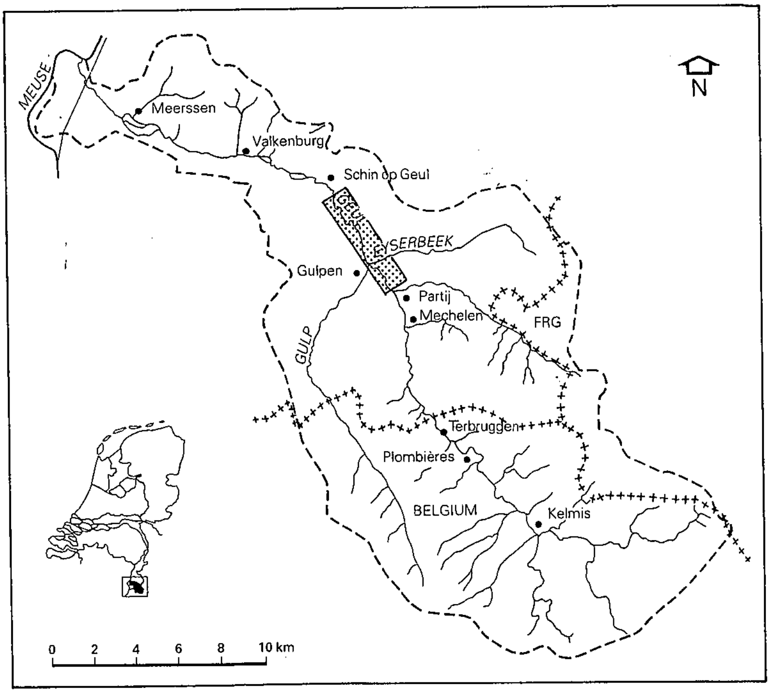


Figure 12.1 Catchment of the Geul and location of the study area.

The aim of this study was to investigate the improvements in accuracy and cost-effectiveness resulting from using co-kriging with elevation data to map heavy metal pollutants compared with simple kriging or with simple linear regression based on the correlation between metal content and relative elevation. The three techniques were used to map zinc concentrations in the floodplain soils from laboratory measurements of zinc concentrations sampled at a limited number of sites. These data were supplemented by elevation data for the co-kriging and regression mapping. The maps were tested with an independent subset of the original data (45 out of 199 sample sites).

12.2 Experimental procedures

Field methods

Samples of topsoil (0-10 cm depth; c. 100 g weight) were collected at 199 sample sites on transects in a 5 km long part of the floodplain area of the Geul near the Dutch town of Gulpen where the valley is 300-600 m wide (see Figures 12.1 & 12.2). The distances between sample

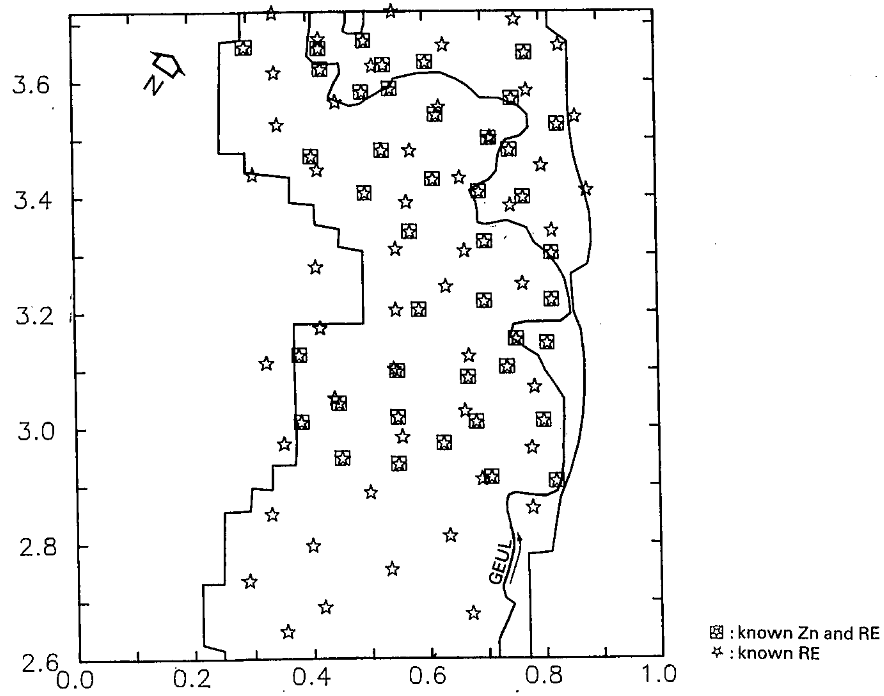


Figure 12.2 Sample locations in part of the study area.

locations range from 50-100 m perpendicular to the valley axis to 200-600 m parallel to the valley axis. Metals in the samples were extracted and measured as described in Section 3.3.1. The sample locations in part of the study area are shown in Figure 12.2. Because of the shape of the study area - its length is ten times as large as its width - it is impractical to show all data. A map of all soil samples collected in the Geul valley is provided in Appendix 3. This study presents results for the part of the study area shown in Figure 12.2.

Elevation data and sample sites

The Netherlands Topographic Survey provides altitude maps at scale 1:10,000 that show not only the contour lines but also accurately measured spot heights. Within the study area, the elevation was known directly for 309 spot heights, which did not coincide with the soil sample sites. These spot heights were supplemented by data from digitized contours to yield a total elevation data set for the study area of c. 3000 points. These data include the trend in elevation of the long profile of the river. The relative elevation (RE) of the 199 soil sample sites relative to the river bed was determined from the elevation data set by removing the trend due to the river profile and by local linear interpolation. This preparation gave a data set for the 199 sample sites where both zinc level and relative elevation were known. For co-kriging, the RE values at the 199 sample points were supplemented by the relative elevations computed by subtracting the trend from the absolute elevation at the 309 spot heights. Together with the heights at the soil sample sites they formed a set of 508 points at which the RE was known.
The set of 199 data points at which zinc levels and elevation were known was split into two. The larger set contained 154 data points that were used for computing the variograms for zinc and for the cross variogram between zinc and RE and for the point kriging of zinc. The smaller data set contained 45 data points that were to be used for validating the interpolations. For co-kriging, the 154 data points were supplemented by the 309 spot heights; the variogram of RE was also computed from these 463 RE data. The reason these extra RE data were used was to make as much use as possible of the cheap, readily available data.

Preliminary data analysis

Table 12.1 gives parameters of the frequency distributions of relative elevations (n=463) and of zinc concentrations (n=154) in the alluvial deposits. The degree of pollution of the floodplain soils can be seen from the parameters of a set of samples (n=12) taken from non-flooded colluvial loess sediments in the Geul valley, which are also in the table.
The zinc concentrations in the alluvial deposits are clearly much higher than the concentrations in sediments that are not influenced by the presence of a river. Moreover, variability of the zinc concentrations in the flood deposits is much greater than in the colluvium because of differences in the frequency of flooding and in sedimentary conditions during flood events. Regression analysis of zinc concentra

Table 12.1 Measures of central tendency and variation of relative elevations (cm) and of zinc concentrations (mg/kg) in alluvial and colluvial sediments in the Geul valley

property	n	mean	median	minimum	maximum	variance
zinc content of alluvial sediments	154	741	543	114	2270	292877
zinc content of colluvial sediments	12	147	124	68	338	5112
relative elevation	463	429	411	224	791	9032

tion versus distance downstream (as in Section 8.6) revealed that along this short distance of 5 km the decay of metal concentrations in soil material with distance parallel to the river is not significant ($\alpha=0.05$).

Table 12.2 lists the correlation coefficients of Zn and the $\log_{10}$ of Zn with RE and the $\log_{10}$ of RE. The correlations are statistically significant but lower than preliminary field studies had suggested.

Table 12.2 Correlation coefficients and parameters of linear relations (Y=a+bx) between zinc concentrations (Zn) and relative elevation (RE) (n=154)

Y	X	a	b	r
Zn	RE	1617	-206	-0.38
$\log_{10}$ (Zn)	RE	3.48	-0.17	-0.48
Zn	$\log_{10}$ (RE)	5986	-2004	-0.36
$\log_{10}$ (Zn)	$\log_{10}$ (RE)	7.19	-1.70	-0.46

12.3 Methods used for mapping

The variation of zinc concentration over the test area was investigated, using three methods:

(a) linear regression from the 45 RE data at the test locations (using the strongest relationship in Table 12.2),
(b) by point kriging from the reduced set of Zn data (n=154) and
(c) by point co-kriging from the reduced set of zinc data (n=154) and the reduced set of data on relative elevation (n=463).

Linear regression

Procedure (a) was not used to make a map; the results were evaluated by computing the absolute squared estimation errors between estimated and measured values of zinc at the 45 data points (Table 12.4).

Point kriging

Procedure (b) was used to make a map. Isotropic variograms for both zinc content and RE were computed using the standard procedures described in Section 6.3 (see Figures 12.3a & b). Each calculated

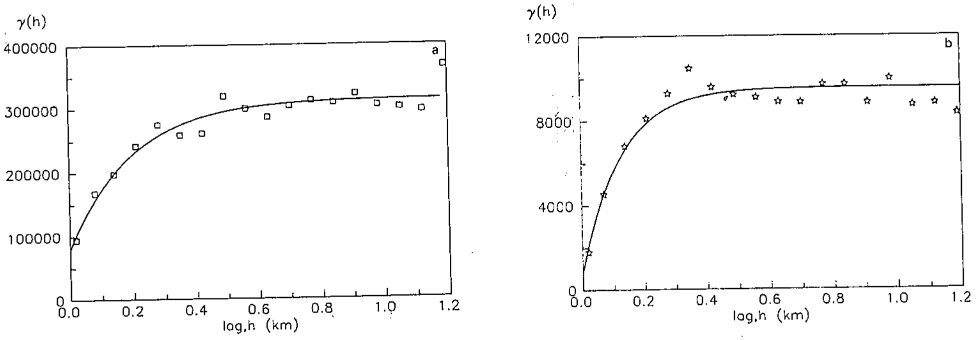


Figure 12.3 Multidirectional auto variograms of a) top soil zinc content and b) relative elevation.

semi-variance is plotted with a symbol that represents a distance class of 0.07 km. An exponential model provided a good fit to all experimental variograms. The parameters of the variogram models were fitted by a weighted least squares approximations (Cressie, 1985). By means of cross-validation it could be shown that, by using the isotropic variograms, the kriging errors are unbiased and consistent with the kriging variances. The variogram parameters are listed in Table 12.3. They show that the topsoil zinc content is highly variable and has a nugget variance that is approximately 25% of the sill.

Table 12.3 Parameters of the theoretical variogram functions

attribute(s)	nugget (CO)	sill (CO+C)	range (a')
Zn	79262	314958	0.59
RE	849	9564	0.38
Zn-RE	-4254	-20351	0.73

The relative elevation is much less variable and has a smaller nugget variance of approximately 9% of the sill. The lags at which both variograms level out to reach the sill are in the same order of magnitude, i.e. 0.4-0.6 km. Obviously, the sill variance of each property has the same order of magnitude as the total variance (see Table 12.1). The variogram model for zinc was used to interpolate the values of zinc at the nodes of a 40 x 40m grid for an area measuring 1.4 x 5.0 km (see Figure 12.4). The map was tested using the 45 test sites as above (see Table 12.4).

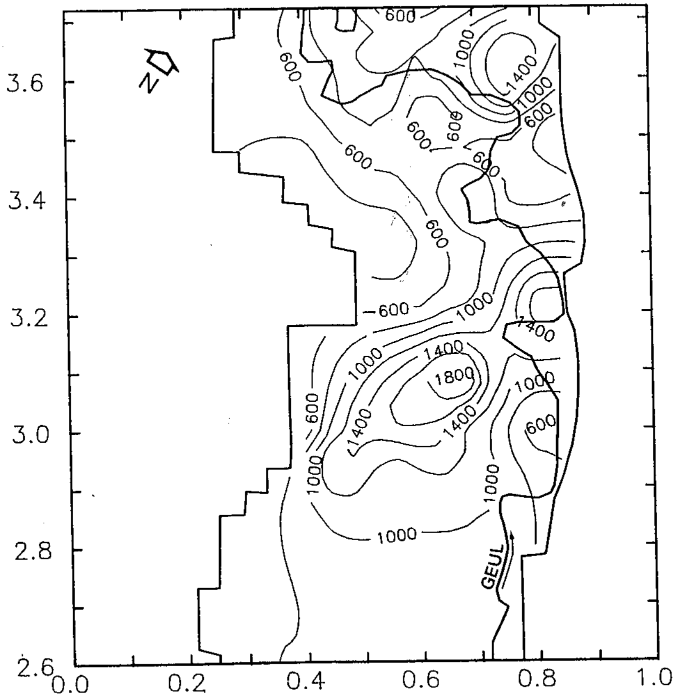


Figure 12.4 Interpolated map of top soil zinc content (mg/kg) by point kriging.

Co-kriging

Procedure (c) was also used to make a map. Figure 12.5 shows the isotropic cross variogram that was fitted by weighted least squares approximation and then cross-validated. The topsoil zinc content is negatively correlated with the relative elevation (see Table 12.2), so the cross variogram is negative. The nugget variance is approximately 21% of the sill. The zinc levels were estimated for the same grid that had been used for point kriging (Figure 12.6). The map was tested in the same way (Table 12.4).

Table 12.4 Median and interquartile range (mg/kg) of absolute and squared prediction errors (n=45)

prediction method		median	interquartile range
linear regression	(AE)	353	453
	(SE)	124,357	351,102
kriging	(AE)	311	400
	(SE)	97,014	243,853
co-kriging	(AE)	283	410
	(SE)	80,241	234,954

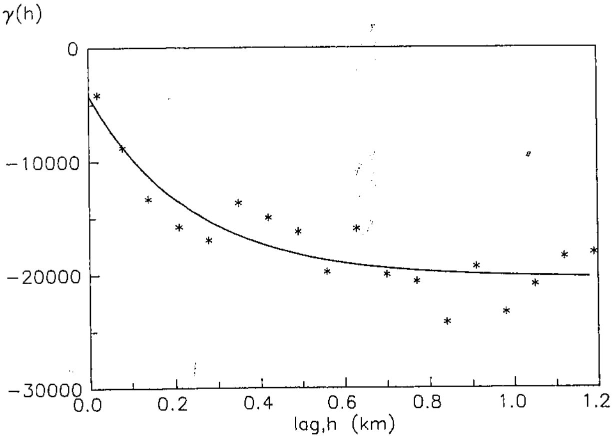


Figure 12.5 Multidirectional cross variogram of relative elevation and top soil zinc content.

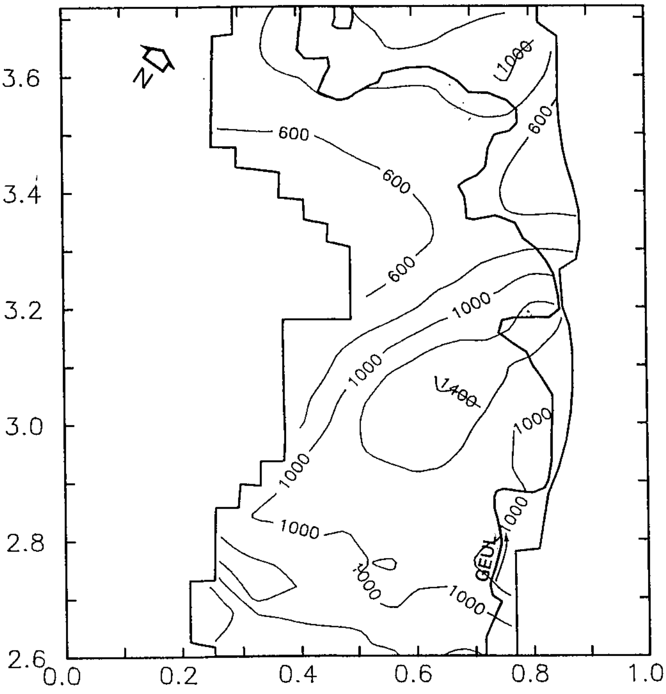


Figure 12.6 Interpolated map of top soil zinc content (mg/kg) by co-kriging.

12.4 Anisotropy effects

All the above variogram models describe isotropic variation and the results of a cross-validation procedure demonstrated that these models are valid in the sense that the kriging and co-kriging errors are unbiased and consistent with the kriging and co-kriging variances respectively. Nevertheless, in alluvial deposits with levee bars and backswamps running parallel to the general valley direction, it is clear that soil properties do not necessarily vary equally in all directions. Perpendicular to the general valley direction, short range variations are expected as a result of the presence of various types of deposits within a distance interval of only a few hundred meters: colluvial deposits along the valley slopes and alluvial deposits consisting of backswamps and levee bars along the channel margins. In the direction parallel to the river channel, the types of sediment are of a less variable nature so that a larger range of spatial variability is anticipated. It was decided to compute semi-variograms of zinc concentrations and relative elevations for these two important directions in order to gain insight in possible directional effects. Exponential models provided an adequate fit to the semi-variance estimates. Figure 12.7 shows unidirectional semi-variograms of zinc and relative elevation.

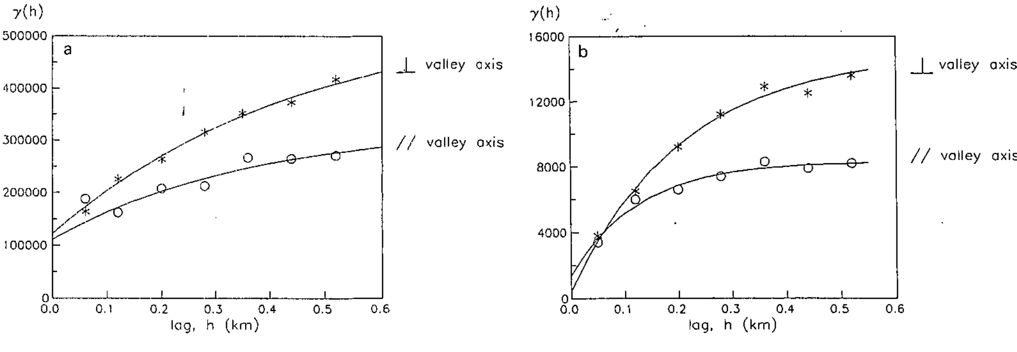


Figure 12.7 Directional semi-variograms of a) topsoil zinc content and b) relative elevation.

The results confirm that indeed larger short-range variations occur in the direction perpendicular to the valley axis: the slopes of the variograms of zinc and relative elevation in this direction are steeper than they are in the direction parallel to the valley axis. Moreover, the sill values of both properties in this direction are considerably higher than those parallel to the valley axis. This phenomenon is called <u>zonal</u> anisotropy (Journel & Huybregts, 1978). The nugget

effects of all unidirectional variograms are in the same order of magnitude as those of the multidirectional variograms.
McBratney & Webster (1986) note that no one has reported this type of variation in soil in the horizontal plane before and to our knowledge no software is available for spatial prediction by kriging or co-kriging that takes into account zonal anisotropy. However, given that the isotropic variogram models are valid in terms of the criteria discussed in Section 6.3.3, it was decided not to take directional effects of variation into account.

12.5 Comparing the three methods

Table 12.4 gives the results of comparing the estimates obtained by the three methods with the known zinc concentrations at the 45 test sites. The table reveals notable differences between the performance of the three methods. Both kriging methods outperform linear regression. Furthermore, despite the weak correlation between topsoil zinc and relative elevation, the co-kriging procedure has managed to take advantage of that relation giving smaller estimation errors than simple kriging.

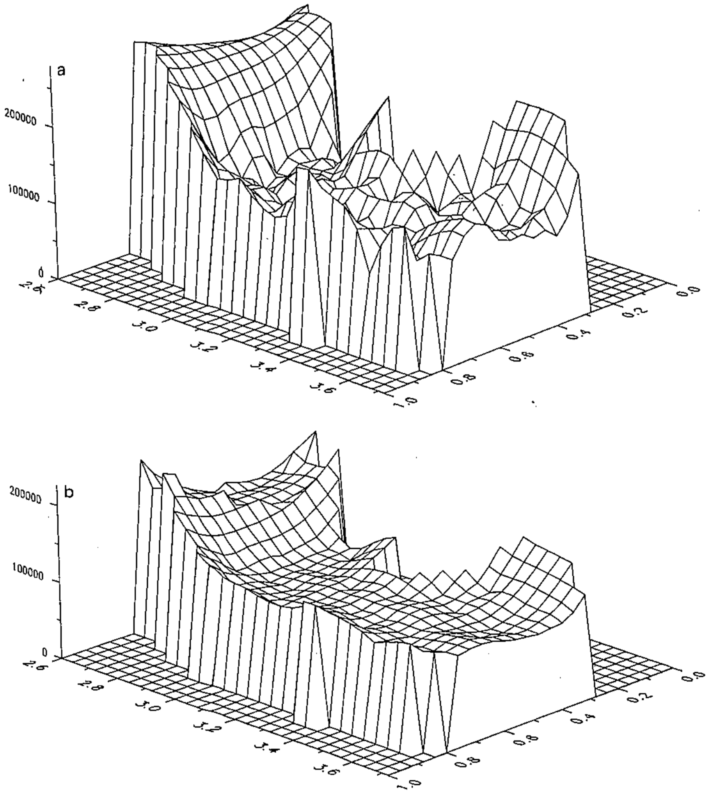


Figure 12.8 Estimation variance of Zn ($(\mathrm{mg/kg})^2$): a) point kriging; b) point co-kriging (view from the north).

The maps of the study area, as interpolated by kriging and co-kriging (Figures 12.4 and 12.6), have a similar pattern of contour lines, but the map produced by simple kriging accentuates the extreme values (e.g. in the vicinity of (0.8,3.6) and (0.7,3.1)) in terms of both the absolute value of the peak and the size of the area that it covers. It is difficult to judge this discrepancy. The detection of extreme values certainly is a virtue, but the overestimation of the size of its area (probably due to the lack of data on RE) is less desirable.

The value of co-kriging over simple kriging is evident in the southern part of the area where few data on zinc content were available. Because of the scarcity of data in the immediate neighbourhood, the kriging estimates of zinc form a smooth surface that tilts towards the mean zinc content of the data set (e.g. 741 mg/kg; see Table 12.1). In contrast the co-kriged map shows more detail and the estimates are larger than the mean. These estimates have been improved as a result of the presence of more data on the co-variable, the relative elevation. However, because the contour interval and the number of lines that is displayed are chosen arbitrarily, the maps need to be interpreted with caution.

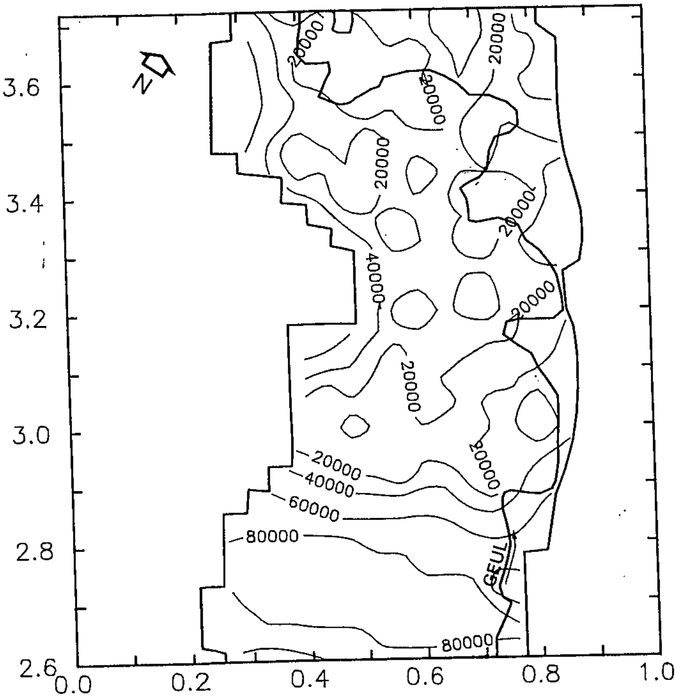


Figure 12.9 Contour map of the difference of estimation variance between kriging (Figure 12.8a) and co-kriging (Figure 12.8b).

The differences between the results obtained by simple kriging and by co-kriging can be seen in Figures 12.8 and 12.9, which show respectively block diagrams of the estimation variances of both methods and contour lines of the difference between the two block diagrams. The figures show the reduction of the estimation variance achieved by the co-kriging procedure. In the northern part of the area the estimation variance is quite stable and is about 10-20% less than the variance of the kriged estimates. For both methods it can be observed that in the southern part of the area the estimation variance is considerably larger. There, the discrepancy between the methods is even more pronounced: the estimation variance obtained by co-kriging being only 70% of that obtained by kriging.

12.6 Conclusions

Elevation data can be used to advantage in a co-kriging procedure for mapping alluvial topsoils polluted with zinc in the floodplain of the Geul. Because elevation data are readily available on the altitude map of the Netherlands Topographic Survey the improvements cost very little additional expense. Despite the weak correlation (r=-0.38) between topsoil zinc and relative elevation it was possible to obtain more accurate estimates of zinc content by point co-kriging than by point kriging or by simple linear regression. Moreover, the variances of the estimates of point co-kriging are substantially less than those obtained by point kriging.

12.7 Summary

The floodplain soils of the river Geul are heavily polluted with zinc brought from spoil heaps further upstream. Because the frequency of flooding depends on landform, pollution levels in floodplain soils are negatively correlated with the variations in elevation of the floodplain surface relative to the river bed.
The co-regionalization between relative elevation and zinc concentrations in soils was used to map the zinc concentrations from 154 observations by co-kriging. The relative merits of point co-kriging and point kriging for mapping zinc pollution levels are compared in terms of kriging variance. For testing, 45 samples were withdrawn from the prediction procedure so that the accuracy of the methods could be expressed and compared in terms of squared and absolute estimation errors.
Point co-kriging yields more precise estimates of zinc concentrations in terms of estimation variances, than those obtained either from univariate point kriging or from a linear regression with relative elevation.

13 DEPOSITION AND STORAGE OF HEAVY METALS IN RIVER FLOODPLAINS

13.1 Introduction

Floodplains may act as sinks of sediment-bound contaminants during periods of inundation, providing long term storage (Bradley, 1987; Marron, 198?; Lewin & Macklin, 1987). However, relatively little information exists regarding the magnitude of depositional losses that may occur (Walling et al., 1986). A number of authors have shown that fallout ^{137}Cs may be a useful tracer for the determination of erosion and deposition rates in a variety of environments, such as reservoirs (Ritchie et al., 1973; Robbins et al., 1977), agricultural fields and watersheds (McHenry & Ritchie, 1977a & b; Bachhuber et al., 1987; Ritchie et al., 1974; McCallan et al., 1980; Loughran et al., 1982; Martz & De Jong, 1987; Vandenberge & Gulinck, 1987; Walling et al., 1986) and river floodplains (Ritchie et al., 1975; Walling et al., 1986; Walling & Bradley, 1988).

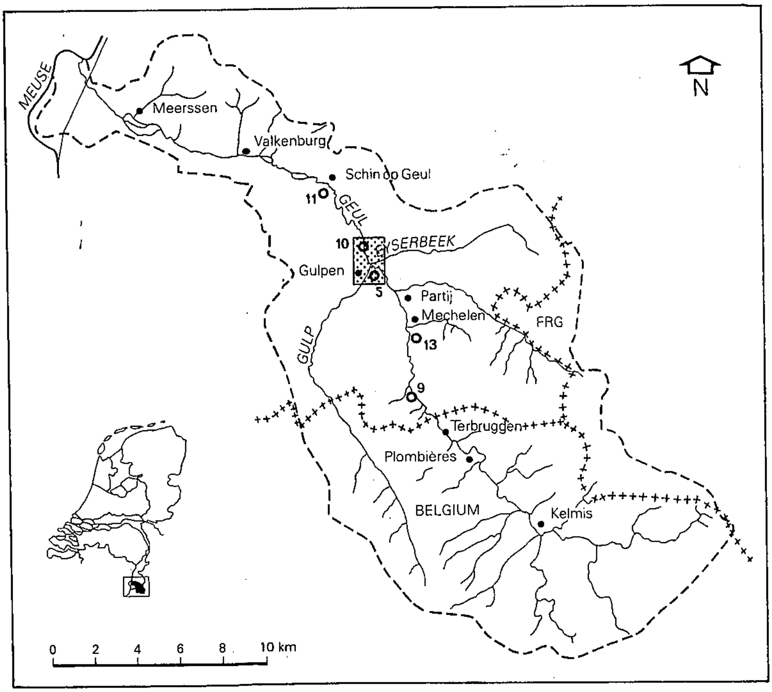


Figure 13.1 Catchment of the Geul, location of the study area and locations of sampli for ^{137}Cs analysis.

Because of the continuous supply of fresh sediments within a floodplain, the quality of the alluvial topsoils in a contaminated river system may exhibit large variations in time. Given the fact that the contaminants may restrict the landuse in these areas, quantitative mapping techniques are required that delineate up-to-date pollution zones. When studying floodplain soil pollution, these techniques can also be used to reconstruct past pollution patterns once the local deposition rates are known, and the bulk storage of contaminants may be estimated.

Because of the high concentrations of heavy metals in recent flood deposits (see Section 8.4) and the often observed large amounts of sediments that are deposited during individual floods, investigations were carried out to provide insight in the rate of sediment deposition and the implications for the quality of topsoils in the Geul floodplains. ^{137}Cs was used to estimate deposition rates at a number of locations and contour maps of soil metal concentrations at various depths below surface were constructed from 65 data by kriging for a 2-km long part of the Geul floodplain. In addition, these data were used to estimate the bulk storage of heavy metals in floodplain soils.

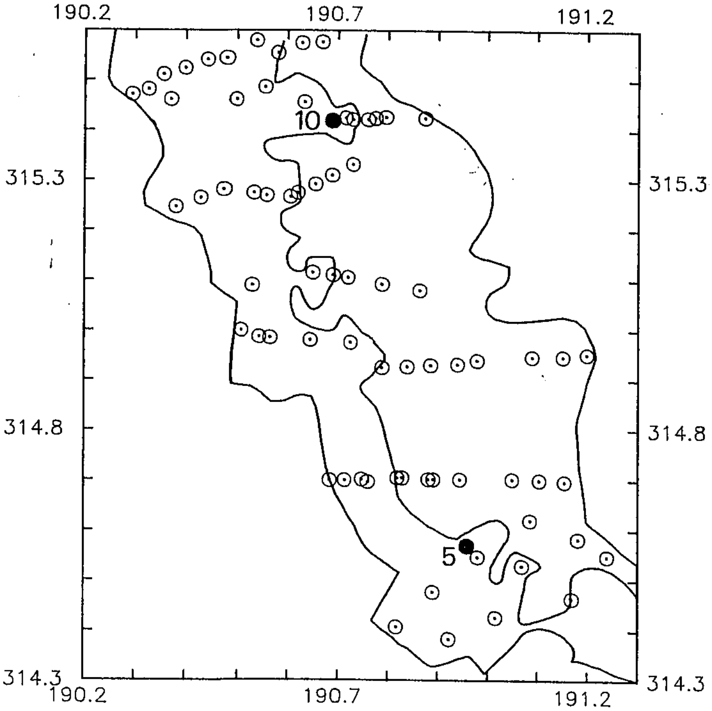


Figure 13.2 Locations of detailed sampling for heavy metal analysis.

13.2 Experimental procedures

At 65 sites in a 2 km long part of the Geul floodplain (see Figure 13.1 & 13.2), soil samples (c. 100 g weight) were taken at depths of 0-10, 10-20, 20-30, 30-40, 40-50 and 90-100 cm in the summer of 1986. A subset of samples at depths of 50-60, 60-70, 70-80 and 80-90 cm was collected at eleven of these locations. Most sample locations were chosen along transects (see Figure 13.2) and so that each unit of the available soil map (Van de Westeringh et al., 1980) was represented in the data set. These data were supplemented by 28 data of topsoil (0-10 cm) metal levels in the vicinity of the study area, that were collected during a previous sampling campaign. These additional data were used during the spatial interpolation procedure in order to minimize edge effects. At five locations in the Geul valley (see Figure 13.1), two of which were in the area of detailed sampling (see Figure 13.2), depth-integrated soil samples of 500-1000 g were taken at depth intervals of 0-5, 5-10, 10-15, 15-20, 20-25, 35-45 and 45-70 cm in June 1988. Extractions and measurements of heavy metals in the 65 samples and the analyses of ^{137}Cs activity in the 35 larger samples were done by the methods described in Chapter 3.

13.3 Estimating sediment deposition rates by using Cs-137

Sources and pathways of ^{137} Cs

Caesium-137 (^{137}Cs) is present in the environment as a product of the atmospheric testing of nuclear devices during the late 1950s and early 1960s and fallout of this radioactive isotope was first documented in 1954. Rates of fallout reached a maximum in 1963 and declined rapidly after the nuclear test ban treaty (Ritchie et al., 1975). Reports state a total amount of 4700 Bqm^{-2} having arrived in the Netherlands over this period (Anonymous, 1986). Caesium-137 has a half-life of 30.1 years and some 47-59 percent of the total input of this radioisotope between 1954 and 1963 could still remain within the system. A second source of ^{137}Cs in Europe is the fallout from the Chernobyl nuclear reactor accident on April 26th 1986. In the period following this accident, the amount of fallout ^{137}Cs was very much determined by the precipitation at a particular location and in South Limburg it may vary from 1500 to 3000 Bqm^{-2} (Anonymous, 1986). Existing evidence indicates that on reaching the soil surface as fallout ^{137}Cs is rapidly and strongly adsorbed in the upper horizons of the soil and that further downward translocation by physical-chemical processes is limited (Tamura, 1964). Subsequent movement of ^{137}Cs is therefore associated with the erosion, transport and deposition of sediment particles (e.g. Rogowski & Tamura, 1970a & b; Campbell et al., 1982). Depositional sinks within a fluvial system may be characterized by a concentration effect of ^{137}Cs. Walling & Bradley (1988) demonstrated that ^{137}Cs levels of suspended sediments may have increased by up to two orders of magnitude after the Chernobyl accident. The increased ^{137}Cs concentrations in suspended sediments can be accounted for by the adsorption of Chernobyl ^{137}Cs fallout by the soil and other surface particulates and the subsequent mobilisation and transport of such particles to the streams and through the river system. If deposition occurs, the concentrations of ^{137}Cs in the associated deposits are likely to be considerably in excess of those in the in situ soil from which the sediment is derived, because of the predominance of fine-grained particles to which ^{137}Cs is preferentially adsorbed. Moreover, significant amounts of ^{137}Cs could accumulate in the depositional sinks provided by river floodplains so that the total content of ^{137}Cs in these deposits could be greater than those in undisturbed soils.

Estimation of deposition rates

Measurements of the distribution of ^{137}Cs within the soils and sediments of a floodplain system provide a means of documenting both the magnitude and the spatial patterns of deposition over the past 35 years. If the baseline input of ^{137}Cs from atmospheric fallout to the floodplain surface can be established, comparison of the ^{137}Cs content of the soil profile with the baseline affords a means of detecting areas of deposition. Enhanced levels of ^{137}Cs activity will be associated with deposition of suspended sediment eroded from elsewhere in the drainage basin. Reduced levels will similarly be associated with areas of scour, where sediment has been eroded from the floodplain surface. The additional ^{137}Cs that was deposited after the Chernobyl accident may provide the opportunity to study short term erosion and deposition patterns.

The amount of fallout ^{137}Cs deposited in this part of the Netherlands before the Chernobyl accident was 4700 Bqm^{-2} (Anonymous, 1986), of which some 2050-2750 Bqm^{-2} will remain at present. The sum of estimated dry deposition and measured wet deposition of ^{137}Cs after April 1986 in the study area equals approximately 2200 Bq/m^2 (Anonymous, 1986), of which 2130 will remain. This amount is equal to c. 44-51% of the total amount of 4200-4900 Bq/m^2 actually present in the soil. In the Geul floodplains this percentage may be considerably higher, as a result of the deposition of suspended sediments.

The vertical distributions and total activities of ^{137}Cs in the soil profiles are shown in Figure 13.3. All ^{137}Cs profiles exhibit two distinct peaks. The lower peaks are found between 12.5 and 40 cm depth, and the upper peaks occur at or a few centimeters below soil surface. Assuming that the lower peak of ^{137}Cs in each profile corresponds with the peak ^{137}Cs-fallout in 1963, and that the upper peak corresponds with the Chernobyl accident in April 1986, the deposition rates between 1963 and 1986 for valley-sediment profiles can be estimated. For the five floodplain soil profiles considered here, the deposition rates vary from 0.43 to 1.43 cm/y in the 23 year period 1963-1986 (see Table 13.1). These figures imply that since 1963 some 10-35 cm of fresh sediment has been deposited in this area, providing a new root zone for the vegetation.

All ^{137}Cs profiles exhibit very distinct peaks of Chernobyl-^{137}Cs. The ^{137}Cs-concentration in the upper 5 and 10 cm of the profiles in Figure 13.3a-e correspond to inputs ranging between of 3829 Bq/m^2 and 7261 Bq/m^2. These values are considerably in excess of that reported for this area in the literature (Anonymous, 1986), i.e. values within a range of 1500-3000 Bq/m^2. The excess ^{137}Cs found in the alluvial soils

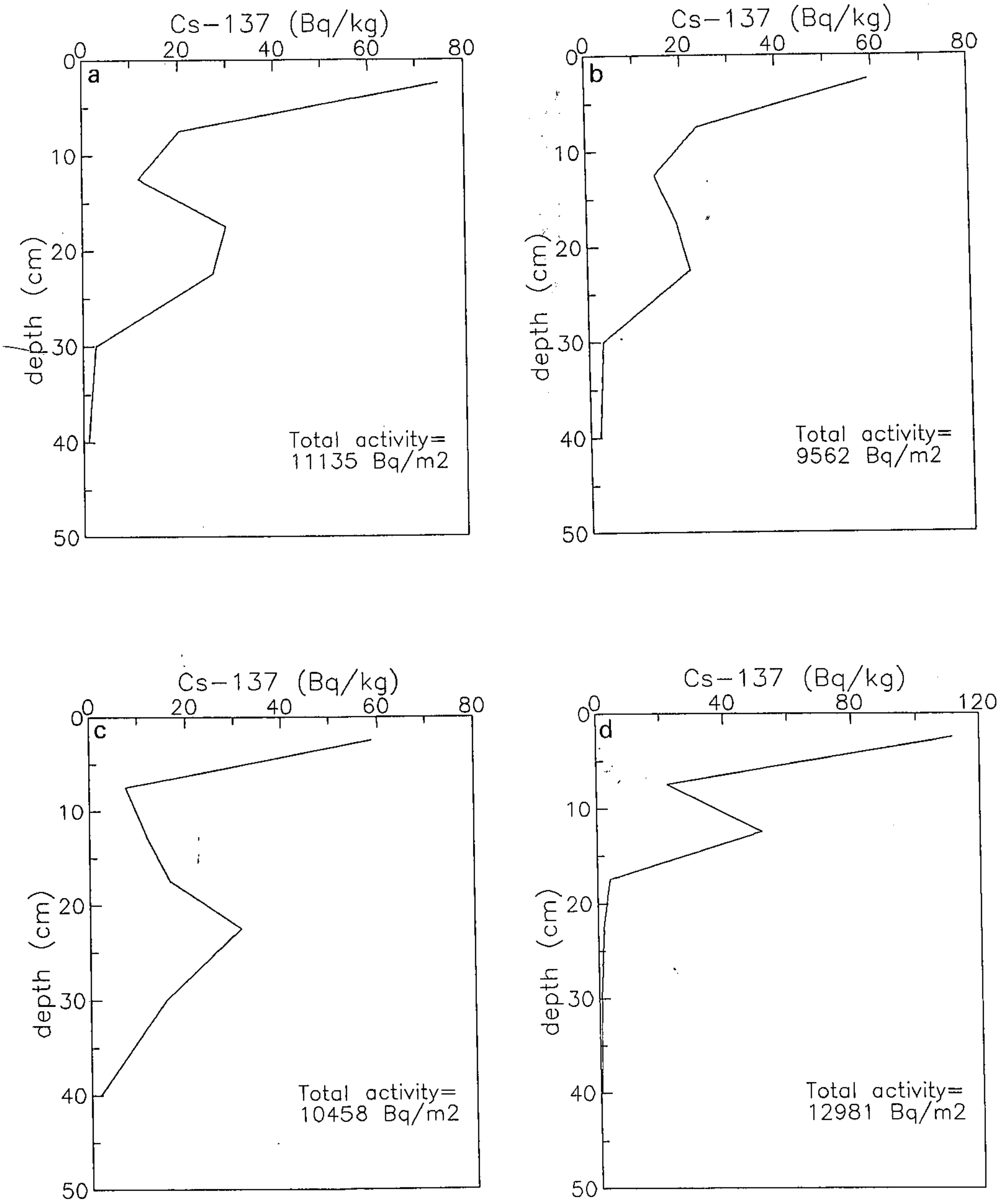
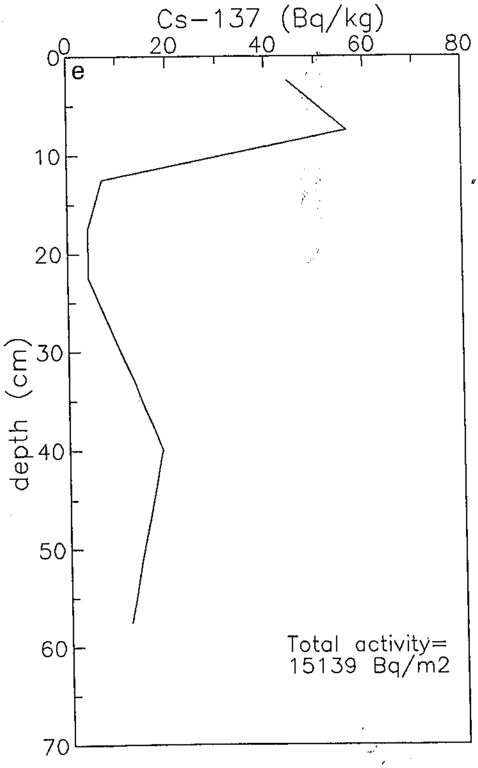


Figure 13.3 ^{137}Cs profiles of five floodplain soils.



in the Geul floodplains is therefore likely to be the result of deposition of ^{137}Cs-rich suspended sediments after April 1986. Following the arguments of Walling et al. (1986), it is assumed that the ^{137}Cs content of suspended sediments is directly proportional to the ^{137}Cs activity of surface soils within the basin. This assumption implies that not the concentration of ^{137}Cs in the soil but rather the total ^{137}Cs activity is affected by deposition of suspended sediments (however, recent investigations by Walling and Bradley (1988) have shown that the ^{137}Cs-concentrations of suspended sediments may be in excess of those of floodplain soils). Therefore, the data on excess ^{137}Cs activity can be used to estimate deposition rates in the period April 1986-June 1988. The average ^{137}Cs-concentration in the upper 5 cm of the presented soil profiles is 67.6 Bq/kg. By employing this value, the excess ^{137}Cs would account for the deposition of 19-58 mm of suspended sediment with this ^{137}Cs concentration. The corresponding annual deposition rates are listed in Table 13.1.

Table 13.1 Estimated sediment deposition rates (cm/yr) in the periods 1963-1986 and April 1986-June 1988

profile nr.	1963-1986	April '86-June '88
5 *	1.41	2.33
9	0.65	1.43
10 *	0.87	0.89
11	0.87	0.90
13	0.43	2.70

* located in the area of detailed sampling

This table shows that deposition rates in the Geul valley are high and exhibit large spatial variability. Moreover, all values in the more recent period are larger than those in the period 1963-1986, suggesting that over a short time span the deposition rates may be considerably in excess of the long term mean. A more detailed sampling program is planned in order to analyse the variation of deposition rates across the floodplain from the channel margin to the outer boundary.

13.4 Variations of heavy metal concentrations in the soil profile

Given the observed deposition rates and the fact that large quantities of heavy metals are associated with the suspended sediments in this fluvial system (see Chapter 7 & 8), it was decided to study the vertical distribution of heavy metals in the soil profile in order to be able to elucidate quality variations in time,
Figure 13.4a, b & c show the vertical variations of average soil heavy metal concentrations and their standard deviations. Between 50 and 90 cm only 11 observations were available in each 10 cm depth interval, the remainder of the data come from 65 observations in each 10 cm depth interval. It can easily be seen that metal concentrations are highest and most variable at the soil surface and then steadily decrease with depth. Between 50 and 90 cm metal levels approach background levels and exhibit very little variation. Here, they may be underestimated because of the limited number of data. Locally, for instance in abandoned channel loops, metal levels at this depth may even be higher than those at the soil surface, as they may reflect the past deposition of coarse, highly contaminated mining sediments (Rang et al., 1986). Nevertheless, the general picture of decreasing pollution with depth is clear and is also supported by the fact that at 100 cm depth metal levels are lower than those at 50 cm depth. From this observation it may be concluded that even now, some 100 years after the heyday of mining, the quality of topsoils in this area continues to decrease. More specifically, the upper 40 cm of the soil profile contain the highest metal levels and represent sediments that were only deposited during the past 30-45 years.
This may seem to be extreme, but can be explained when the location of the study area is examined. In Section 7.6 it has been demonstrated that the streambank deposits upstream of Mechelen exhibit metal levels that are some 500% higher than those downstream of Mechelen, which suggests that the dispersal of major contamination from Belgium has only reached as far as that point. As these streambank deposits con-

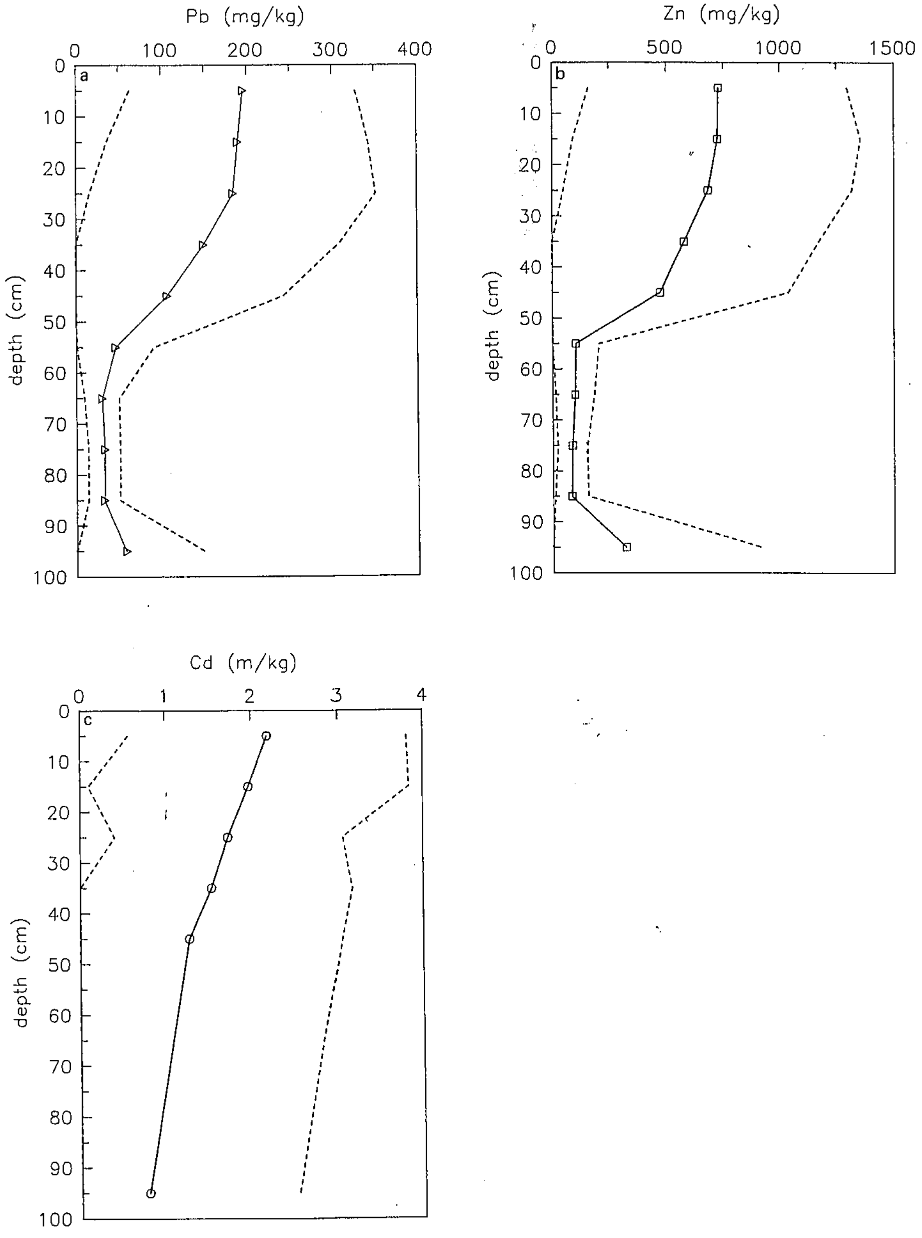


Figure 13.4 Average concentrations (solid line) and standard deviations (dashed lines) of a) Pb, b) Zn and c) Cd (mg/kg) in soils in the study area (depth intervals 0-50 cm and 90-100 cm: n=65 per 10 cm interval; 50-90 cm: n=11 per 10 cm interval).

tinue to be reworked during high flow stages, considerable amounts of highly contaminated sediments are supplied to the channel and transported further downstream. During the transport away from the source, dilution effects will cause a decrease of metal levels (see Chapter 8) but in the study area, which is located only a few km downstream of Mechelen and which is liable to frequent inundations due to backwater effects, they may still be higher than in the actual topsoil on which the suspended sediments are deposited. In other words: upstream streambank deposits containing high metal levels determine the actual and future quality of downstream floodplain soils. The continuous exchange of sediments between the floodplains that provide temporary storage and the river channel through which downstream transport takes place, causes a wave of contaminants to slowly progress through the catchment, thereby depositing sediments with relatively high metal levels on top of already contaminated alluvial soils.

13.5 Spatial patterns of soil metal concentrations

Topsoil metal concentrations

Experimental variograms were calculated for concentrations of Pb, Zn and Cd at a depth of 0-10 cm. Theoretical variogram functions were fitted through the semi-variance estimates by weighted least squares approximation and the validity of the models was checked by cross-validation. The parameters of the fitted variogram functions and the results of cross-validation are given in Table 13.2.

Table 13.2 Parameters of the exponential variogram functions and results of cross-validation of semi-variograms of metal concentrations in the upper 10 cm of the soil profile (n=92)

metal	depth	C_0	C	a	AKE	SMSE	MSE	σ^2
Pb	0-10	7903	22782	282	-2.0	0.78	12115	23503
Cd	0-10	0.8	2.9	298	0.04	1.01	1.77	4.1
Zn	0-10	63015	346561	120	-10.9	0.77	195214	362085

The variograms of concentrations of Pb, Zn and Cd at 0-10 cm are shown in Figure 13.5. These variogram functions were used to krige topsoil metal concentrations. The resulting contour maps are shown in Figure 13.6a, b & c. All metals exhibit a similar pattern of decreasing concentrations with increasing distance to the river channel and peak concentrations in the southern part of the area where, as mentioned before, backwater effects are likely to occur. Given the facts that pronounced levee bars are a rare phenomenon in the Geul floodplains, that metal concentrations of flood deposits are higher than those in the topsoil and that heavy metals are evenly distributed over all grain size fractions (see Section 8.4 & Section 8.5), it is suggested that factors such as the frequency of flooding and the rate of sediment deposition govern the actual quality of topsoils. Therefore, topsoil metal levels are relatively high near the river channel and in

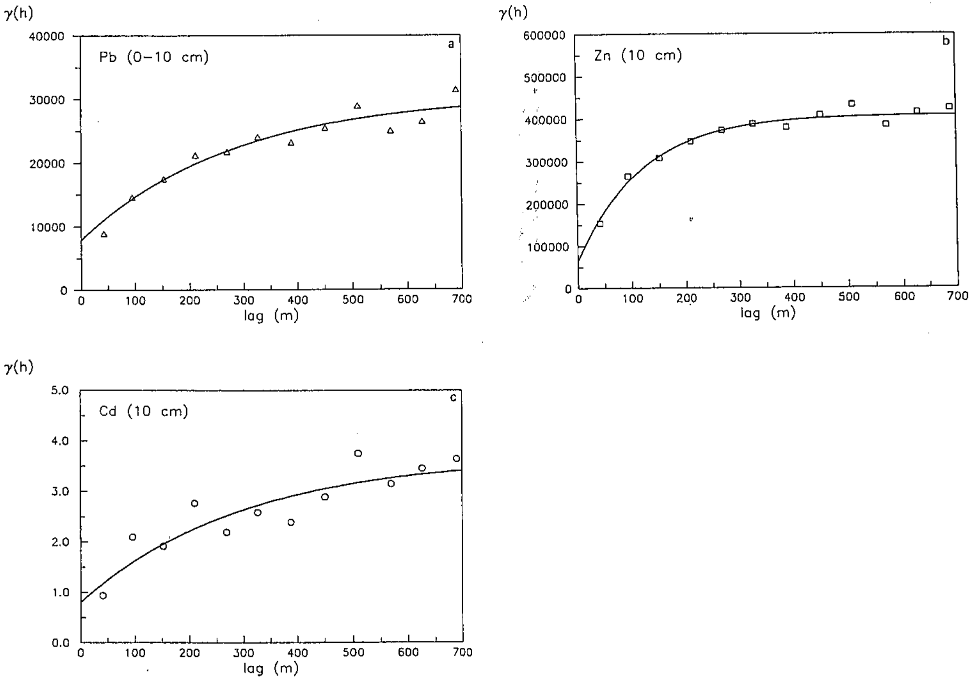


Figure 13.5 Semi-variograms of concentrations of a) Pb, b) Zn and c) Cd in the soil at a depth of 0–10 cm.

backwater areas, which are characterized by high inundation frequencies and high rates of sediment deposition.

Subsoil metal concentrations

Given the fact that both inundation frequency and deposition rate vary in space and time, it will be virtually impossible accurately to reconstruct past pollution patterns by producing maps of metal concentrations in the subsoil. The larger the actual distance to the river channel, the smaller actual deposition rates will be and therefore at different locations the pollution level, even at small depths, will represent different time periods. Because, as a result of channel migrations and variable hydrological and climatological conditions, actual deposition rates and flood frequencies may differ considerably from those in the past, the picture becomes all the more complicated. However, notwithstanding these sources of variation, the construction of pollution maps for the subsoil may provide some idea about the extent to which sediments that have been deposited in the past are contaminated, both in terms of pollution levels and in terms of the size of the contaminated area.

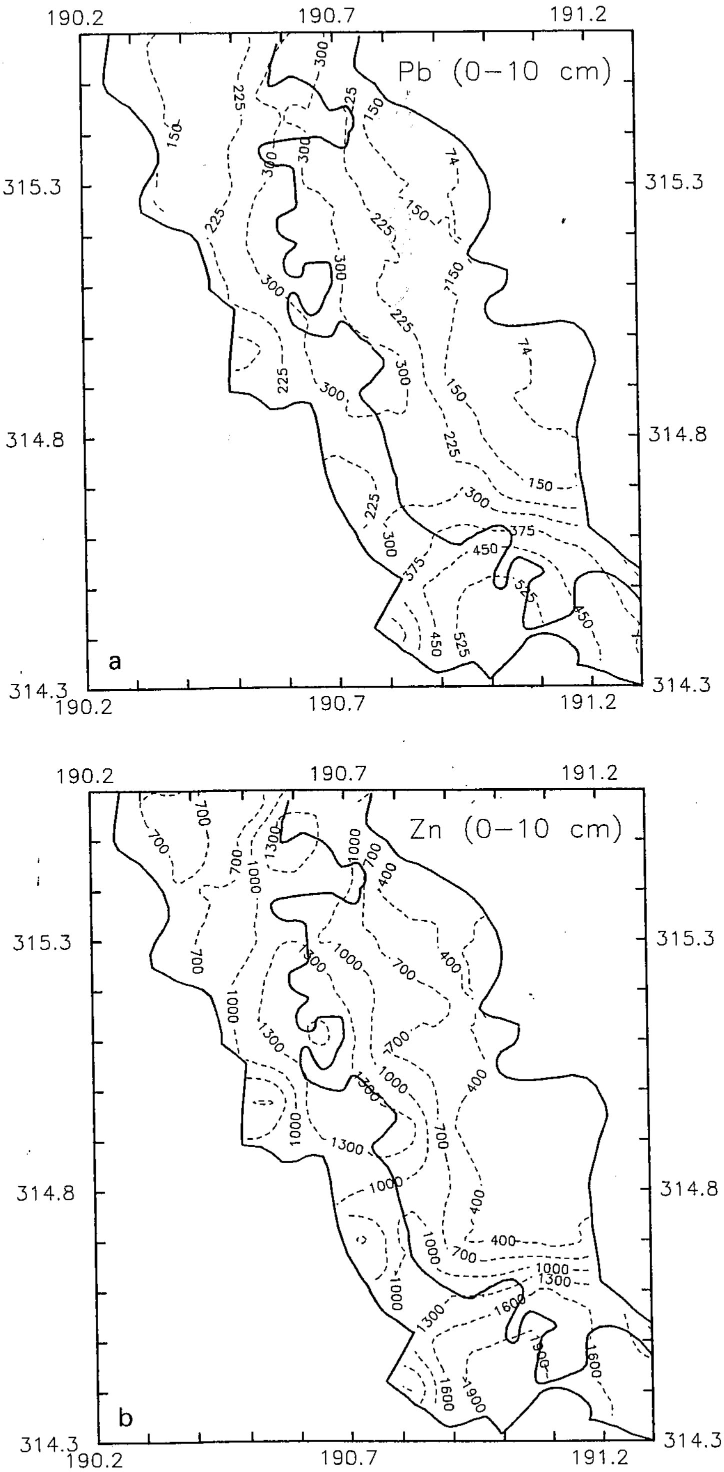


Figure 13.6 Contour maps of concentrations of a) Pb and b) Zn (mg/kg) in the soil at a depth of 0-10 cm.

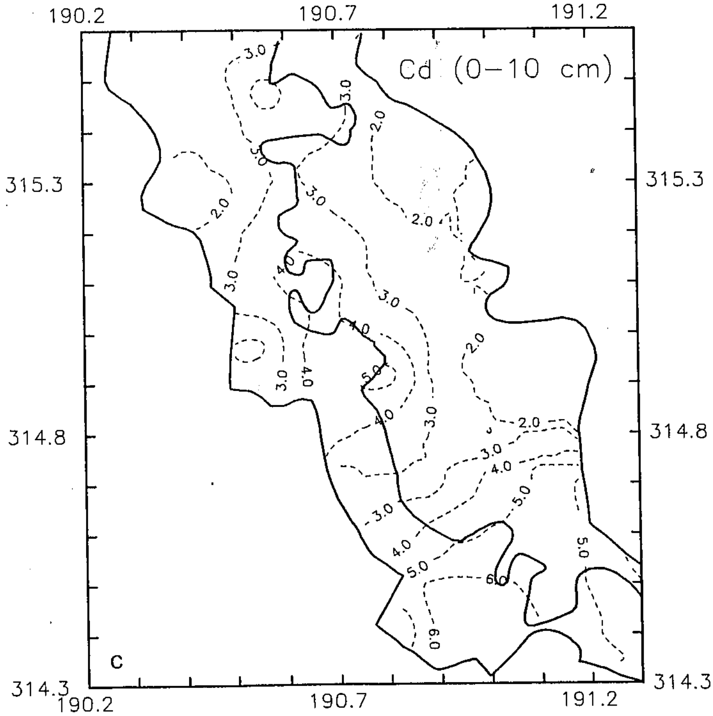


Figure 13.6 Contour maps of concentrations of c) Cd (mg/kg) in the soil at a depth of 0-10 cm.

Table 13.3 Parameters of the exponential variogram functions and results of cross-validation of semi-variograms of Zn concentrations at various depths in the soil profile (n=65)

metal	depth	CO	C	a	AKE	SMSE	MSE	σ^2
Zn	10-20	170930	278241	98	-31.0	0.72	240389	407995
Zn	20-30	150000	297824	87	-5.5	0.69	230764	408258
Zn	30-40	212300	186641	57	-34.1	0.68	240071	362786

Table 13.3 lists the parameters of the exponential variogram functions that were fitted through semi-variance estimates of Zn at various depths and the results of the cross-validation of the models. Figure 13.5b demonstrated that the exponential variogram of Zn at 0-10 cm provided an excellent fit. Figure 13.7a, b, c & d indicate that with increasing depth the spatial correlation structure of Zn becomes less clear, i.e. the nugget effect is larger and the spatial correlation is restricted to shorter ranges, where only few observations are available. At a depth of 40-50 cm, the data from our sampling scheme no

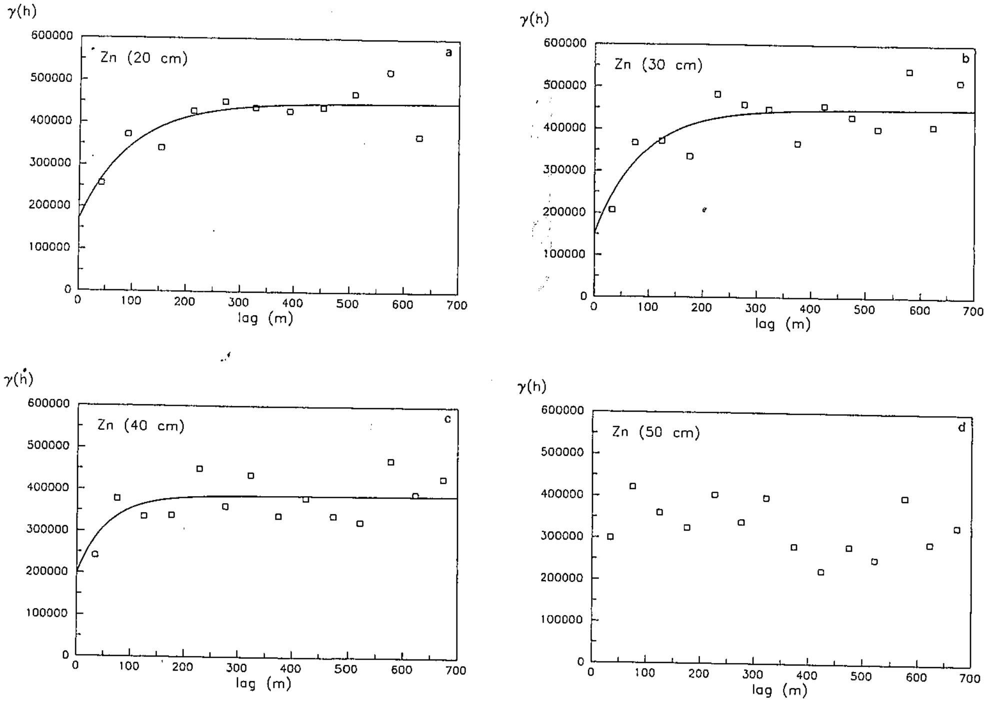


Figure 13.7 Semi-variograms of Zn concentrations in the soil at depths of respectively a) 10-20 cm, b) 20-30 cm, c) 30-40 cm and d) 40-50 cm.

longer provide short range semi-variance estimates that are significantly lower than those at larger ranges and therefore the variogram represents 'pure nugget'. The size of the inundated area during a flood or sequence of floods will strongly determine the scale at which spatial correlation of metal levels in the deposited sediments will occur. If each depth interval would represent a time slice, it could have been presumed that an increasing magnitude of flood events would account for the fact that at the soil surface the spatial correlation exhibits the largest range. However, since the time scale and the spatial scale interfere, the complexity of the correlation structure increases with depth yielding a far more complex situation. At the soil surface, this complexity is smallest and therefore variogram models representing actual or very recent spatial correlation structures can be fitted with an adequate accuracy.
The semi-variogram of Zn at 30-40 cm was used to produce a contour map of Zn concentrations by ordinary kriging (Figure 13.8). The contour pattern exhibits a high degree of resemblance with the one of Zn levels at 0-10 cm (see Figure 13.6b), indicating the importance of similar dispersal processes. However, the absolute Zn concentrations at 30-40 cm are some 300 mg/kg lower on average: the contours of 1000

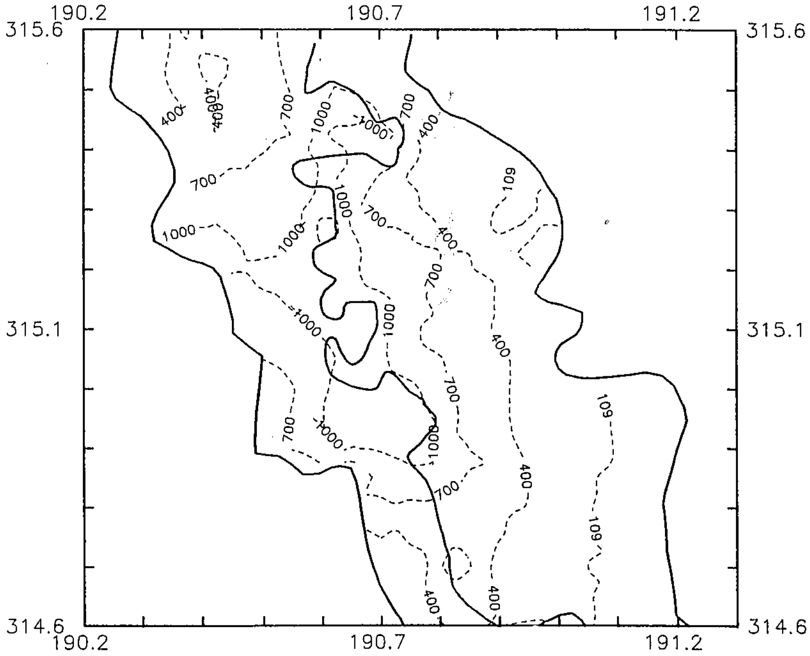


Figure 13.8 Contour map of Zn concentrations (mg/kg) in the soil at a depth of 30-40 cm.

and 700 mg/kg Zn at 30-40 cm depth replace the contours of respectively 1300 and 1000 mg/kg Zn at 0-10 cm depth. These results confirm that on average the pollution level decreases with increasing depth (see Figure 13.4) and demonstrate that at this depth too the occurrence of peak concentrations is restricted to small areas that are in the direct vicinity of the river channel.

Figure 13.9a & b show block diagrams of the kriging variance of the estimates of Zn concentrations at 0-10 and 30-40 cm respectively. These diagrams clearly illustrate the fact that, as mentioned above, the quality of the spatial model of Zn decreases with increasing depth. At 30-40 cm the nugget variance is three times as large as it is at 0-10 cm, causing high base levels of estimation variance in the entire area. Moreover, as at 30-40 cm the range of the variogram is considerable smaller, the variance minima that result from the presence of data locations become less prominent. The overall tendency is one of larger and more stable variances with increasing depth. Ultimately, at depths below 40 cm, the block diagram of estimation variance consists of a flat surface representing 'pure nugget'. There, the spatial component of the variability of pollution levels is too complex to be revealed by our sample geometry because various time stages that are characterized by different pollution levels and different flood sizes are represented within one single depth interval, causing large short range variations.

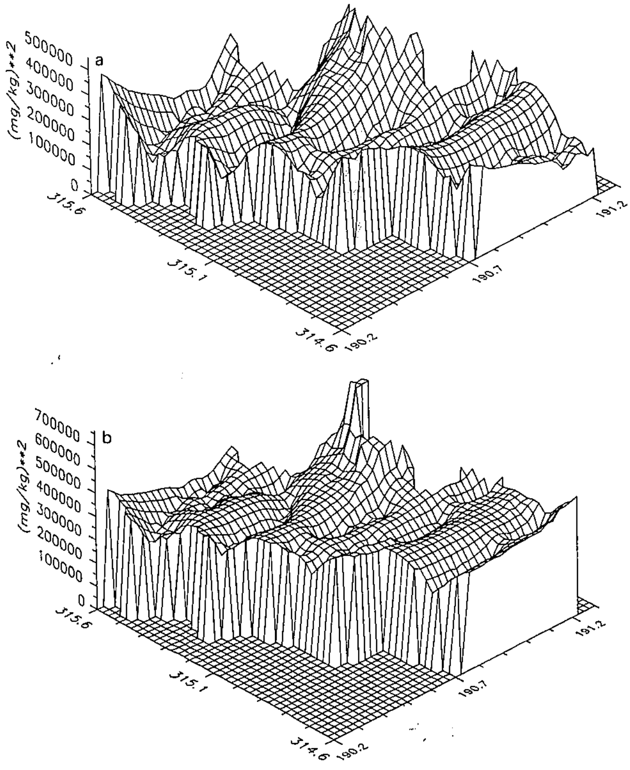


Figure 13.9 Block diagram of the estimation variance of Zn at depths of a) 0-10 cm and b) 30-40 cm.

13.6 Mass storage calculations

Metal storage calculations of contaminated floodplain deposits are important for two reasons. First, they provide a measure of efficiency of storing contaminated sediments. Second, they provide an illustration of the ability of mine wastes to become long-lived, non-point sources of contaminants. Given the high dynamics of erosion, transportation and deposition of contaminated sediments in the Geul valley, highly contaminated sediments that are stored in the upstream part of the catchment will migrate in a downstream direction. As seen now in the study area, this process will result in the build-up of soils with increasingly higher metal levels. In the long term, as the channel continues to migrate across the floodplain, all the heavy metals that are actually stored within its area will be reworked and eventually discharged into the Meuse river.

Maps of metal levels at various depths may be used in an integration procedure to compute the storage of heavy metals in the study area. However, in the previous section it was shown that the spatial correlation structure of soil metal levels at depths exceeding 40 cm below surface cannot adequately be modelled with the current data. Therefore the best spatial prediction of a metal concentration at a given location and at a depth greater than 40 cm would be the mean of all samples at that depth. An alternative method is to compute depth-averaged metal concentrations at each location and then compute semi-variance estimates for these average values. The latter procedure was followed and spherical variogram functions could be fitted through the semi-variance estimates (see Table 13.4).

Table 13.4 Parameters of the spherical variogram functions and results of cross-validation of semi-variograms of average metal concentrations in the upper 100 cm of the soil profile (n=65)

metal	depth	C_0	C	a	AKE	SMSE	MSE	σ^2
Pb	0-100	500	9962	94	-3.6	0.77	5522	9561
Cd	0-100	0.1	1.6	76	-0.07	1.17	1.37	1.53
Zn	0-100	80000	223633	67	-38.3	0.64	165787	281180

These variogram functions were used to krige average Pb, Zn and Cd concentrations in the upper 100 cm of the soil profile. The amount of stored metals was computed from the grid by summing the products of the soil volume in each gridcell, the bulk density of 1300 kg/m^3 and the average metal concentration. The calculations were split into two: metals in those gridcells that had average metal levels below reference values were summed seperately from those that are higher. The results of the storage calculations are listed in Table 13.5. It is clear that in this relatively small area large amounts of heavy metals are stored in the floodplains. The contribution of background metal concentrations is very small (less than 10%) so that it may be concluded that most of the stored metals have reached this temporary sink after dispersal away from the historic mining area in Belgium. The values in Table 13.5 also illustrate the efficient manner in which floodplains are capable of storing contaminants: the total amount of metals stored in the upper 100 cm of this area, which covers only 8% of the total alluvial area that has an average thickness of 300 cm, is 2.5-8 times as large as the total annual output of metals from the catchment (see Table 7.7). In Chapter 14 estimates of the total amounts of heavy metals stored in the alluvial area of the Geul will be presented.

Table 13.5 Total amounts of heavy metal stored in the upper 100 cm of soils in the study area (58.3 ha) and annual catchment output

metal	storage (tonnes)	background (%)	contamination (%)	annual output (tonnes)
Pb	88.8	9	91	11.1
Zn	372.6	2	98	62.1
Cd	1.03	4	96	0.4

13.7 Conclusions

A limited number of measurements of ^{137}Cs has demonstrated that sediment deposition rates in the Geul floodplains are high and may range from 0.4-2.7 cm/yr. In an area of detailed sampling, the upper 40 cm of the soil profile that represent sediments deposited during the past 30-45 years, contain much higher metal concentrations than those at greater depths. These recent deposits are derived from erosion of upstream, severely contaminated, streambank deposits.

Actual and past pollution patterns were mapped by kriging of metal concentrations at various depths. The contour maps show that the pollution levels are highest near the river channel and in backwater areas, and illustrate the predominant role of inundation frequency and sediment deposition rate on the dispersal of heavy metals in floodplains. At depths larger than 40 cm, the spatial correlation structure of metal concentrations becomes less clear as a result of the spatial variability of deposition rates, causing sediments with different ages to be represented within the same depth interval. Therefore, at 30-40 cm depth the estimation variance of metal concentrations predicted by kriging is much higher than at the soil surface.

Calculations of the mass storage of heavy metals demonstrate the capability of floodplains to provide extremely efficient sinks of contaminants. The amount of heavy metals stored in the study area, that covers only some 8% of the total floodplain area, is 2.5-8 times as large as the annual catchment output of heavy metals.

The results of this investigation demonstrate that the large amount of contaminated sediment that is stored in the floodplains of the Geul is efficiently reworked. The rapid dispersal of solid-bound heavy metals may have serious implications for the future quality of downstream floodplain soils.

13.8 Summary

The continuous supply of fresh sediments during floods causes the floodplain soils in the Geul valley to exhibit large quality variations in time. By measurements of ^{137}Cs sediment deposition rates in part of the floodplain area were determined at 0.4-2.7 cm/yr. Analyses of soil metal concentrations at various depths in an area of detailed sampling revealed that the upper 40 cm of the soil profile, which was deposited during the past 30-45 years, exhibit the highest metal levels. The geostatistical interpolation technique point kriging was used to map actual and past pollution patterns. It was shown that, as a result of variable deposition rates, the spatial correlation structure of soil metal concentrations becomes less clear with increasing depth/age. Kriged maps of average metal concentrations in the upper 100 cm of the soil profile provided the basis for the calculation of the mass storage of heavy metals.

14 SYNTHESIS

14.1 Introduction

In the previous chapters the phenomena controlling the dispersal of metal mining wastes in the Geul valley were discussed. Given the structure of this thesis, which comprises a number of seperate papers and publications that discuss only one topic at a time, it was decided - from considerations of clarity - to add this last, conclusory chapter. In the following sections some related results with respect to spatial modelling of metal pollution (Section 14.2) and mass flows of sediments and heavy metals (Section 14.3) are assembled and discussed in a wider context. In addition, a brief summary is provided of a research project commissioned by the Limburg Department of Works, that aimed at mapping soil pollution in the entire valley and to assess possible health risks. During this project the methods and data described in this thesis were used.

14.2 Multiscale spatial models of metal pollution

Several methods for modelling the spatial patterns of metal concentrations in sediments were discussed. The observed spatial variations are caused by a number of spatial processes operating with various intensities over a range of scales. These models are summarized in Table 14.1 and are now discussed in a broader context.

Table 14.1 Spatial models of metal pollution at various scales and their relation with physical factors and sample geometry

				variogram parameters	
Scale	Dominant factor	Sample distance	Spatial model	C_0	C_0+C
river valley	dilution during transport away from the source	irregular, 1D ± 300 m	log-linear regression	742,669	742,669
floodplain	inundation frequency & geomorphology	irregular, 2D ± 100 m	analysis of variance/ (co-)kriging	79,262	314,958
Geomorphologic unit:					
1. including abandoned channel loop	elevation (dm)	regular grid, 2D mesh size 5 m	co-kriging	18,350	147,082
2. excluding abandoned channel loop	elevation (cm)	regular grid, 2D mesh size 5 m	(co-)kriging	2,907	7,500

Scale level 1: the river valley

Table 14.1 demonstrates that the spatial pattern that can be observed shows a dependence on the scale of observation, on the processes that operate at that scale and on the geometry of the sample design. At the scale of the entire river valley, in first instance 25 samples of fresh flood deposits were taken along a line (the river channel) at irregular intervals of 1-2 km. Regression of exponential distance-decay models provided high correlation coefficients that could only be improved slightly by taking 97 additional samples (see Section 8.6). These additional samples, providing a set of 122 data with an average intersample distance of c. 300 m, were taken in order to analyse the spatial correlation structure of metal concentrations in the soil. For that purpose, the exponential trends were removed from the data and variograms were computed for the residuals. This structural analysis yielded variogram that represented 'pure nugget' of 743,000 (see Figure 14.1a). Two reasons may be put forward to account for this lack of spatial correlation. Firstly, the process of dilution with increasing distance to the source may produce a spatial pattern that can adequately be modelled by a 1-dimensional log-linear trend and the residuals from the trend consists of random noise that does not incorporate a spatial component. Secondly, as described below, spatial correlation only occurs at distances shorter than 300 m, so that the sample design used is not able to show these short range variations.

Scale level 2: the river floodplain

At the scale of the river floodplain, where the downstream trend is no longer significant, samples were taken at shorter distances (i.e. c. 100 m) and in a two dimensional space. In this area processes of filling, transmission and drying out take place during floods and the local pattern of inundation and flow velocity strongly depend on the local geometry of the floodplain. As a result, the sedimentary conditions exhibit large spatial variations, causing highly variable soil metal concentrations. The multidirectional exponential variogram of Zn at this scale level has a range of 600 m, indicating that beyond this distance zinc concentrations in the soil are no longer spatially dependent (see Figure 14.1b). The sill at which the variogram levels out is c. 50% lower than the nugget effect of the variogram at the scale of the river valley. The influence of the geometry of the floodplain on the spatial model of zinc concentrations shows itself in three ways: (1) the classification of zinc data in accordance with map units on the flood hazard map provided high fractions of explained variance (see Section 10.5), (2) the floodplain geometry exhibits strong directional features (such as small natural levee bars running parallel to the river channel) that are reflected in the two directional variograms of zinc: parallel to the valley axis the spatial variation has a smaller gradient and a lower sill value than the one perpendicular to the valley axis (see Figure 12.7); (3) the strong coregionalization between zinc concentrations and the elevation relative to the river bed (which may be regarded as a measure of inundation frequency) could be used to improve the spatial model of zinc concentrations in the soil (see Chapter 12).

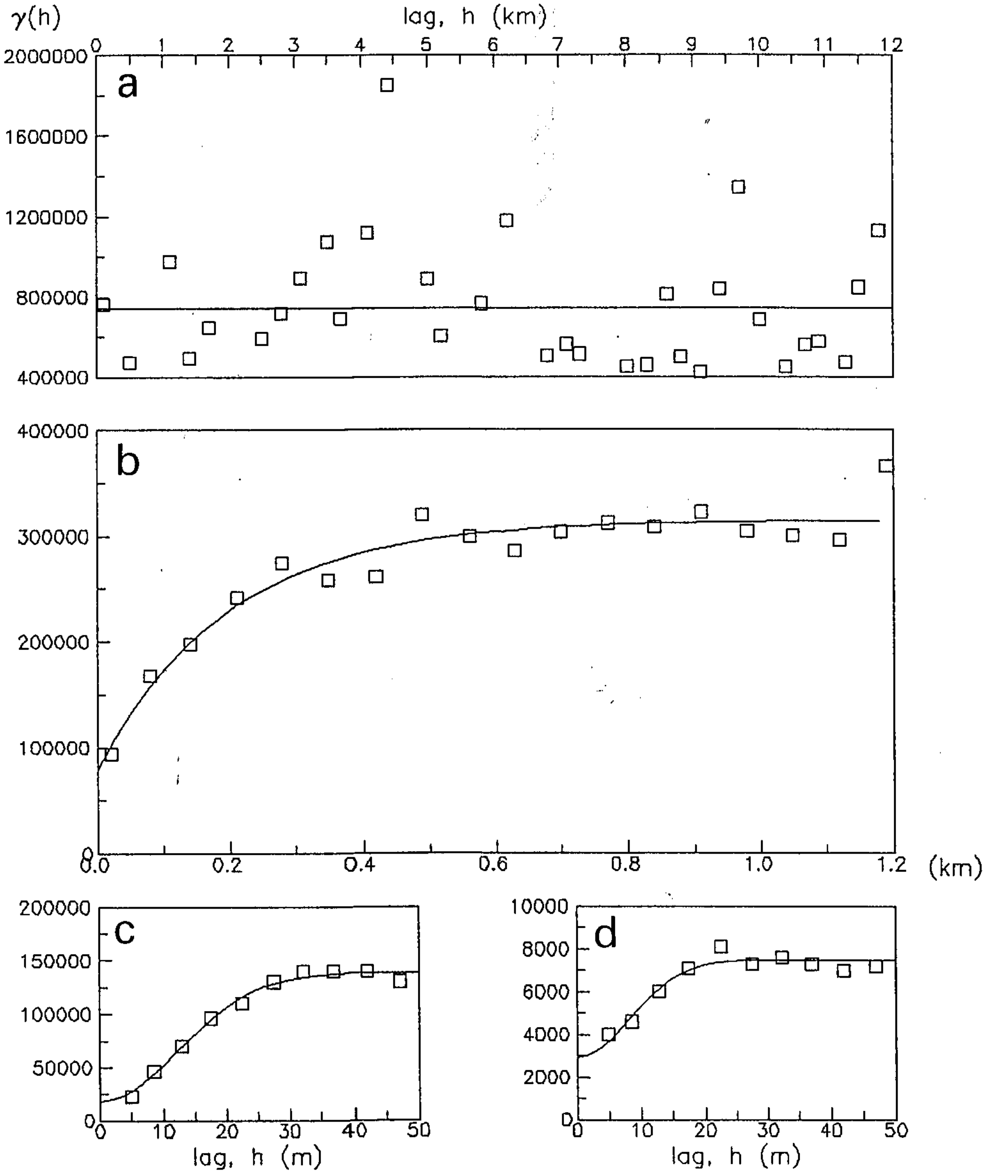


Figure 14.1 Semi-variograms of zinc concentrations in sediments at various scale levels: a) river valley (de-trended data), b) river floodplain, c) geomorphological unit including abandoned channel and d) geomorphological unit excluding abandoned channel.

Another interesting feature at this scale is demonstrated by Figure 13.7, which shows that the spatial correlation structure of metal concentrations in the soil becomes less clear with increasing depth below the soil surface. Apparently, given the large spatial variability of sediment deposition rates, the sediments at larger depths are not related to one another in terms of their age and consequently the spatial dependence, which is believed to be the result of processes occurring within a limited time span, is affected.

Scale level 3: a geomorphological unit

At a larger map scale, i.e. within one geomorphological unit, the influence of differences of elevation can be shown in two different ways. As described in Chapter 11, in a natural levee area that incorporates an abandoned channel 145 samples were taken at 5 m intervals on a regular grid. The variogram of zinc was computed from a subset of 45 of these data (see Figure 11.3a). Figure 14.1c shows the 'true' gaussian variogram of zinc computed from all 145 data. The sill of the variogram in Figure 14.1c levels out at a value that has the same order of magnitude as the nugget effect of Figure 14.1b. Thus, at very short lags the zinc concentrations in the soil exhibit a strong spatial correlation, that cannot be detected when sample distances of 100 m are used. At this scale too, fruitful use could be made of elevation data in a co-kriging procedure of mapping zinc concentrations (see Chapter 11). However, the presence of the low-lying abandoned channel (see Figure 11.1a), where very high zinc concentrations prevail, may strongly affect the shape of the variogram: clearly, the intrinsic hyphothesis (stationary mean and variance) is locally invalid. Moreover, one may argue that the abandoned channel is part of another geomorphological unit than the natural levee itself. Therefore, the data collected in the abandoned channel were removed from the data set and again a variogram was computed (Figure 14.1d). The fitted gaussian variogram function demonstrates that indeed the underlying spatial correlation structure significantly differs from that shown in Figure 14.1c. Although the shape of the two variograms is quite similar, both the nugget effect and the sill value are much lower when the data from the abandoned channel are disregarded.

The above observations at three scale levels demonstrate that every time an area is resampled at a larger scale, new spatial structures are discovered that were previously regarded as spatially unstructured and uncorrelated noise (the nugget effect). By increasing the scale of observation (i.e. by zooming into smaller areas), the influence of the relevant processes at the smaller scale are eliminated and replaced by the influence of some other process that dominates at the larger scale. Simultaneously the observed a priori variance (C_0+C) of the variable is substantially reduced.

The average nugget effect at the scale of the river valley exceeds the sill value at the scale of the river floodplain by a factor two. However, it may be anticipated that the local nugget at the scale of the valley may differ considerably from the mean. Figure 14.2 shows the residual Zn concentrations in flood deposits after making a correction for the downstream trend. It can be seen that the variability is largest in the south and from there exponentially decreases with increasing distance to the source of contamination, yielding a cone-shaped pattern of points in the graph. This graph strongly suggest that the local nugget depends on the distance downstream.

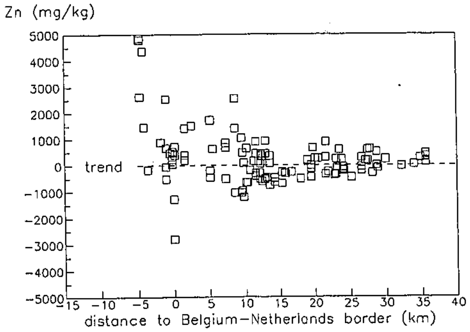


Figure 14.2 Residual Zn concentrations (mg/kg) in flood deposits after making a correction for the exponential downstream decay.

Despite the 'pure nugget' observed at the scale of the river valley, a strong spatial correlation was discovered at the scale of the floodplain (where the distance to the source of contamination is irrelevant) when the sampling distance was adjusted to the scale at which the dominant processes operate (i.e. flooding and sediment deposition). A more detailed study at the scale of a geomorphologic unit revealed that here the sill value has the same order of magnitude as the nugget effect at the previous scale and that the nugget effect could be further reduced. Ultimately, the influence of elevation differences was for the larger part eliminated by disregarding data that were collected in the abandoned channel loop. Again the nugget effect is further reduced and now approaches the order of magnitude of the expected relative measurement errors. The latter are c. 5% on average (see Section 3.5), which would indicate that in this area, where zinc concentrations vary between 200 and 800 mg/kg, a nugget effect of 10^2-40^2 or 100-1600 may be expected, which is close to the observed nugget effect of 2907.

14.3 The compilation of budgets of sediment and heavy metals

14.3.1 The sediment budget

Geomorphologists have traditionally studied erosion of landscapes by analysis of individual erosion processes, measurement of sediment yield at one or more points along a river and stratigraphical analysis of deposits. These approaches however, have rarely been used collectively to provide a framework for understanding soil and sediment movement through drainage basins. Many current problems in basic and applied geomorphology and ecology can better be addressed when placed in a broad, conceptual framework by analysis of a sediment budget (Swanson et al., 1982).

In this section an attempt will be made to construct a tentative sediment budget for the alluvial area of the Geul in the Netherlands from the data presented in the previous chapters. This budget will provide the basis for the construction of budgets of lead, zinc and cadmium, whose cycling in the fluvial environment is to a large extent associated with the routing of sediments. The following budget terms are taken into account:

- fluvial input (across the border between Belgium and the Netherlands)
- fluvial output (past the gauging station in Meerssen)
- tributary and hillslope contributions
- sediment deposition in the floodplains
- streambank erosion
- short-term storage in the stream domain
- long-term storage in the floodplain domain

The fluvial output term was quantified in Section 7.7 by using discharge data for the year 1983 and a rating curve of suspended sediment concentrations versus discharge. It is realized that, because no data are available on the magnitude of bedload transport, the calculated transport rate provides an underestimation of the true transport rate. Nevertheless, the contributions from streambank erosion and tributaries and hillslopes yield loess-like sediments only, and field observations suggested that the sediments that are deposited in the floodplains do not contain particles coarser than fine sand. Therefore, the coarser bedload (sand and pebbles), which is mainly derived from channel incision, probably does not play an important role in the dispersal of sediment associated heavy metals.

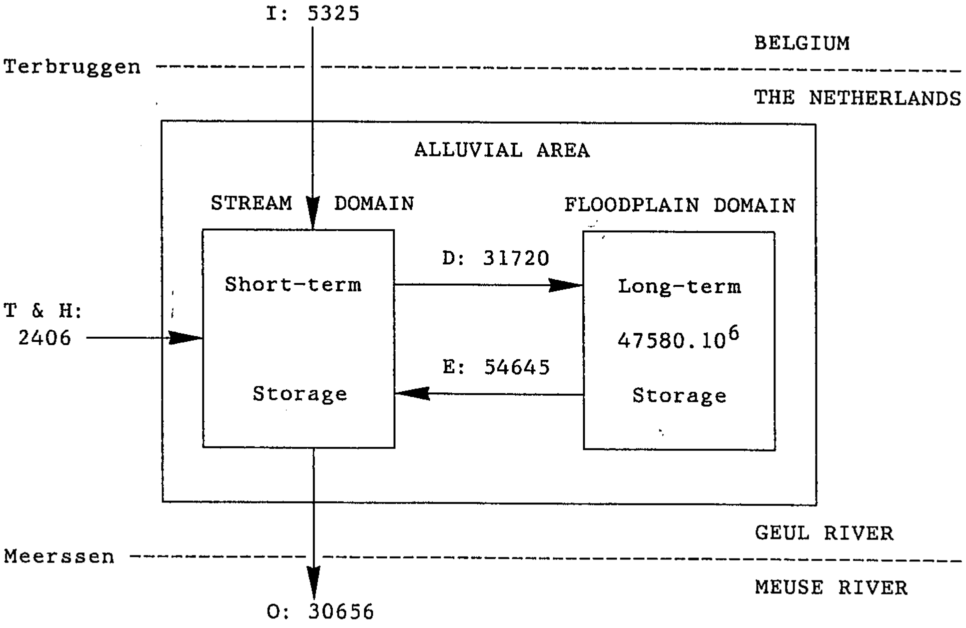
The fluvial input term was estimated analogous to the method described in Section 7.7. Because no discharge data are available for the point where the Geul crosses the border between Belgium and the Netherlands, discharge data from a nearby gauging station (Partij) were used after making a correction for the size of the upstream catchment area: the discharge data were multiplied by 0.8 before calculating the sediment transport. Given the abundance of sediments available for transport, it was assumed that the relationship between river discharge and suspended sediment concentration in Terbruggen would not differ significantly from that in Meerssen. Therefore it was decided to employ Figure 7.3 for the computation of fluvial sediment input. The estimated fluvial sediment input is listed in Table 14.2.

Table 14.2 Total mass transport of suspended sediments and solid-bound and dissolved metals past Terbruggen and Meerssen in 1983

	Terbruggen			Meerssen		
	total (tonnes)	solid (%)	dissolved (%)	total (tonnes)	solid (%)	dissolved (%)
suspended sediments	5,325	100	-	30,656	100	-
Pb	7.7	88	12	13.9	90	10
Zn	57.4	50	50	70.5	74	26
Cd	0.17	58	42	0.44	53	47

Once the input and output of sediment through the river channel were estimated, the sediment yield from the Dutch part of the catchment could be derived from their difference. Now the magnitude of the other budget terms needed to be estimated and these would have to account for this annual sediment production. However, the available data do not allow precise and independent estimates of the various terms. As for the sediment deposition in the floodplains, 5 profiles of ^{137}Cs were available (see Section 13.3) that provide an indication of maximum possible deposition rates because the profiles are all located near the channel margins. These data, therefore, cannot be interpreted as overall deposition rates. With regard to streambank erosion, a detailed field survey was carried out in the summer of 1988 during which the streambanks along the entire channel reach were carefully inspected and sampled, and the amount of recently eroded material was estimated at c. 100 locations. The metal concentrations of the samples were presented in Section 7.6. However, it was not possible to relate the amount of eroded sediment to a period of time better defined than 1-3 years. Thus, in addition to the unknown magnitude of tributary and hillslope contributions, both the floodplain deposition term and the streambank erosion term cannot be estimated with a high degree of precision. Nevertheless, given the fact that the metal concentrations of all studied sediments are known, it is possible - once an estimate is made on one of the unknown terms, say the deposition rate - to derive the others from the fact that only one possible mixture of the other types of sediment can account for the fluvial output of both suspended sediment and an associated heavy metal. It is realized that by employing this rough estimation procedure the objective path of estimating the individual budget terms independently is abandoned, so that one will always yield a correct budget for the sediments and at least one of the investigated heavy metals, in this case zinc. Nothwithstanding these and other drawbacks, it is stressed that for practical purposes at least some indication about the relative importance of the various budget terms is required. Because the available data do not allow a more accurate approach, the presented budgets of sediments and heavy metals should be regarded as tentative.

Figure 14.3 presents a tentative budget of sediments for the alluvial area of the Geul in the Netherlands. The floodplain storage was derived from the volume of the alluvial soils. The storage of fine-grained sediments in the stream channel could not be quantified but numerous field observations suggested that - with an exception for millraces, where the flow velocity of the water is very low - this is very small and it was decided to neglect this term. The deposition term is based on an estimated average sediment deposition rate of 2 mm/yr, which is clearly much lower than the range of 4-27 mm/yr presented in Section 13.3. Consequently, the streambank erosion term would account for 96% of the amount of eroded material estimated in the field, which implies that all observed marks of recent erosion were caused within the time span of 1 year. The contribution of streambank erosion to the total load of suspended sediments is very large: the net effect of sediment exchange between the river channel and the floodplain accounts for 75% of the sediment yield of the catchment. Given the estimated long-term storage, it follows that complete reworking of the floodplain would take about 2000 years, which is in agreement with the periods mentioned for other catchments in the literature (see Section 5.6). The implications of this sediment budget for the cycling of heavy metals in the river system are discussed in the next section.



I : fluvial Input
T&H: Tributary and Hillslope contributions
D : floodplain Deposition
O : fluvial Output
E : streambank Erosion output

Figure 14.3 Tentative sediment budget of the alluvial area of the Geul in the Netherlands (values in tonnes).

14.3.2 The budgets of heavy metals

The sediment budget and the budget of sediment associated zinc were computed simultaneously in the manner described in the previous section. The estimated fluvial input and output terms are listed in Table 14.2. Given the known lead and cadmium concentrations of flood deposits and streambank deposits, and assuming that sediments supplied by tributaries and derived from hillslopes contain reference metal concentrations (see Table 4.1), the budgets of sediment associated lead and cadmium could be computed. In addition to these terms, the magnitude of the following flows of other than sediment-associated heavy metals were estimated:

- leaching of heavy metals from the alluvial soils (that enter the stream via the alluvial aquifer);
- athmospheric fallout;
- agricultural additives.

The amount of leached heavy metals was estimated from the effective precipitation surplus (238 mm/yr) and the average concentrations of dissolved heavy metals in the Dutch reach of the Geul (see Table 14.3). The latter figures are assumed to have the same order of magnitude as the metal concentrations in the alluvial aquifer. The contribution of atmospheric fallout was derived from data provided by KNMI/RIVM (1982); the contribution of additives such as fertilizers, manure and sewage sludge is based on values presented by Oh (1987). Given that the landuse in the alluvial area of the Geul is mainly pasture, the uptake of heavy metals from the soil by plants was not taken into account because these ultimately return into the soil via excrements and organic matter.

Table 14.3 Average metal concentrations (µg/l) in stream water in the catchment of the Geul

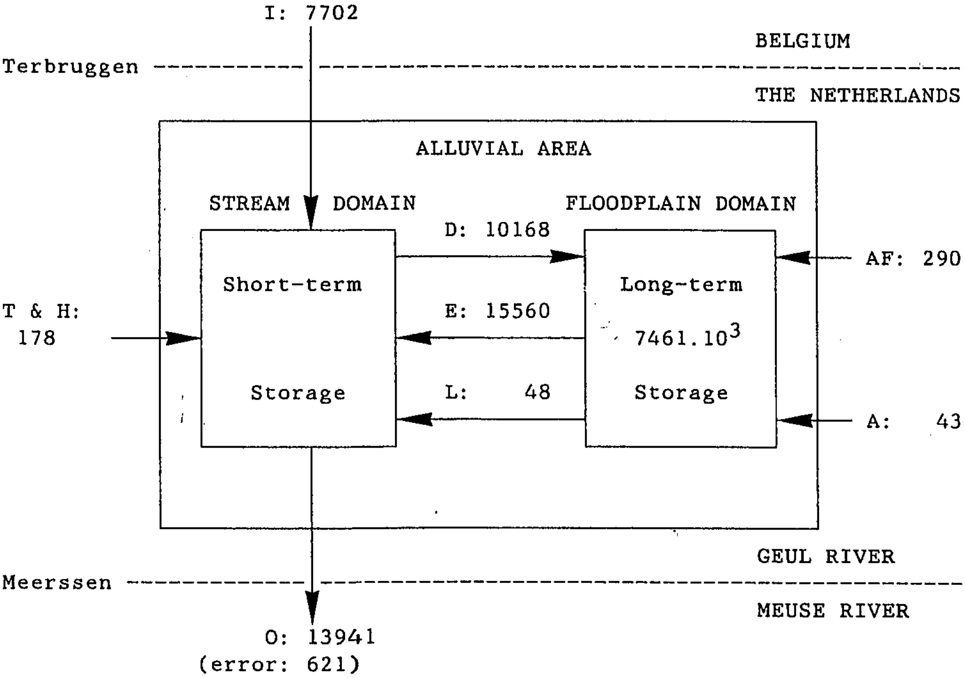
	Netherlands (n=9)	Belgium (n=16)
Pb	16.7	45.3
Zn	411	521
Cd	0.9	1.2
Cu	22.7	18.8

The storage of heavy metals in the floodplains was estimated by employing the data on metal concentrations of streambank deposits. It was assumed that at the boundary between colluvial and alluvial deposits, the thickness of the contaminated soil layer is zero and linearly increases from there to the observed thickness along the channel margin. The remainder of the soil volume was assumed to contain reference metal concentrations (see Table 4.1). This procedure yielded the values presented in Table 14.4, which shows that some 50-75% of the storage of heavy metals can be accounted for by the presence of contaminated sediments that occupy only 15% of the total volume of soil.

Table 14.4 Total amounts of heavy metal stored in alluvial soils (0-300 cm) in the study area (12.2 km^2)

	storage (tonnes)	background (%)	contamination (%)
Pb	7461	47	53
Zn	19205	27	73
Cd	84	34	66

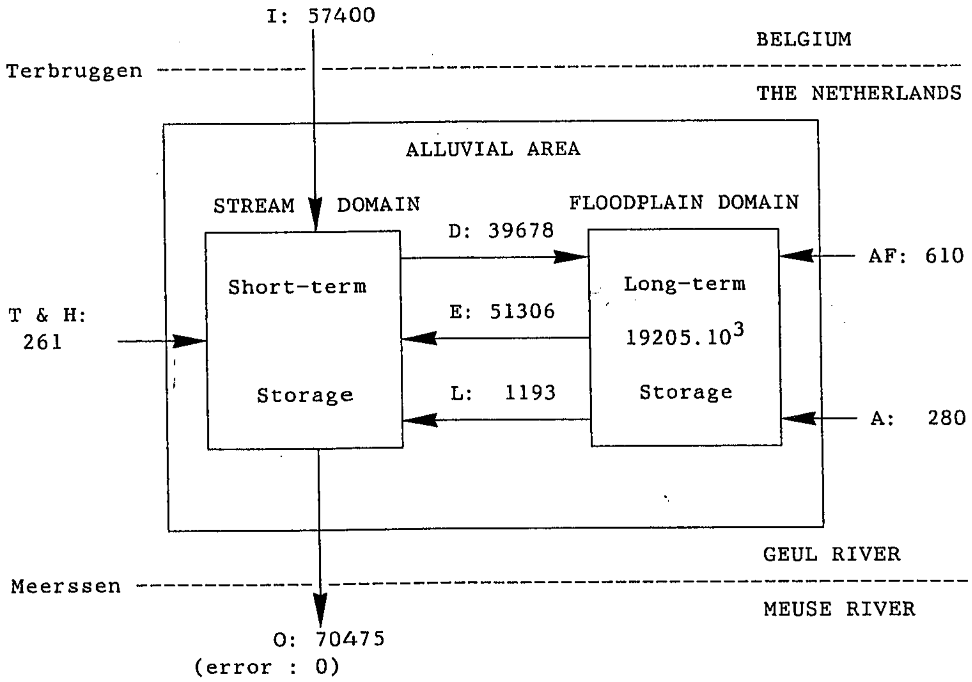
The tentative budgets of lead zinc and cadmium are presented in Figure 14.4, 14.5 & 14.6. As a consequence of the procedure followed, the catchment output of zinc can be explained completely by the flows of zinc in the diagram. Once the sediment budget and the zinc budget were established, the lead and cadmium budgets could be computed by



I : fluvial Input
T&H: Tributary and Hillslope contributions
D : floodplain Deposition
E : streambank Erosion
L : Leaching
AF : Atmospheric Fallout
A : Additives
O : fluvial Output
error: unexplained output

Figure 14.4 Tentative lead budget of the alluvial area of the Geul in the Netherlands (values in kg).

scribing the known concentrations of these metals to the corresponding flows of sediment. This procedure yielded very good results for the lead budget, where the unexplained catchment output is less than 5% of the total output. For cadmium however, 59% of the catchment output remains unexplained by the estimated flows of cadmium. A possible explanation for this discrepancy would be that, as shown in Section 7.7, due to its high mobility flows of dissolved cadmium are of much greater importance than those of lead and zinc. The dissolved catchment output of cadmium for example, accounts for 47% of the total catchment output, whereas the corresponding percentages of lead and zinc are only 10 and 26 respectively (see Table 14.2). Because the estimated internal flows of heavy metals in the alluvial area heavily depend on the estimated flows of sediment and sediment-associated metals, an underestimation of dissolved flows may have occurred, and consequently the largest errors are found for the more mobile metal cadmium.



I : fluvial Input
T&H: Tributary and Hillslope contributions
D : floodplain Deposition
E : streambank Erosion
L : Leaching

AF : Atmospheric Fallout
A : Additives
O : fluvial Output
error: unexplained output

Figure 14.5 Tentative zinc budget of the alluvial area of the Geul in the Netherlands (values in kg).

The metal budgets (see Figure 14.4, 14.5 & 14.6) clearly illustrate the importance of sediment exchange between the river channel and the floodplains. The supply of heavy metals to the floodplains due to sediment deposition is several orders of magnitude larger than the contributions of atmospheric fallout and the supply of additives. Moreover, it is clear that the streambanks are now functioning as a major, non-point source of heavy metals that accounts for a very large part of the cycling of metals in this fluvial system: 66, 47 and 39% of the amounts of lead, zinc and cadmium respectively, that enter the river channel to be redistributed by processes of transport and deposition, are supplied to the channel by undermining of the streambanks. The transboundary input of heavy metals accounts for another 32, 52 and 59% of the amounts of lead, zinc and cadmium respectively discharged in the channel, leaving only 1-2% for the contributions of tributaries, hillslopes and the alluvial aquifer.

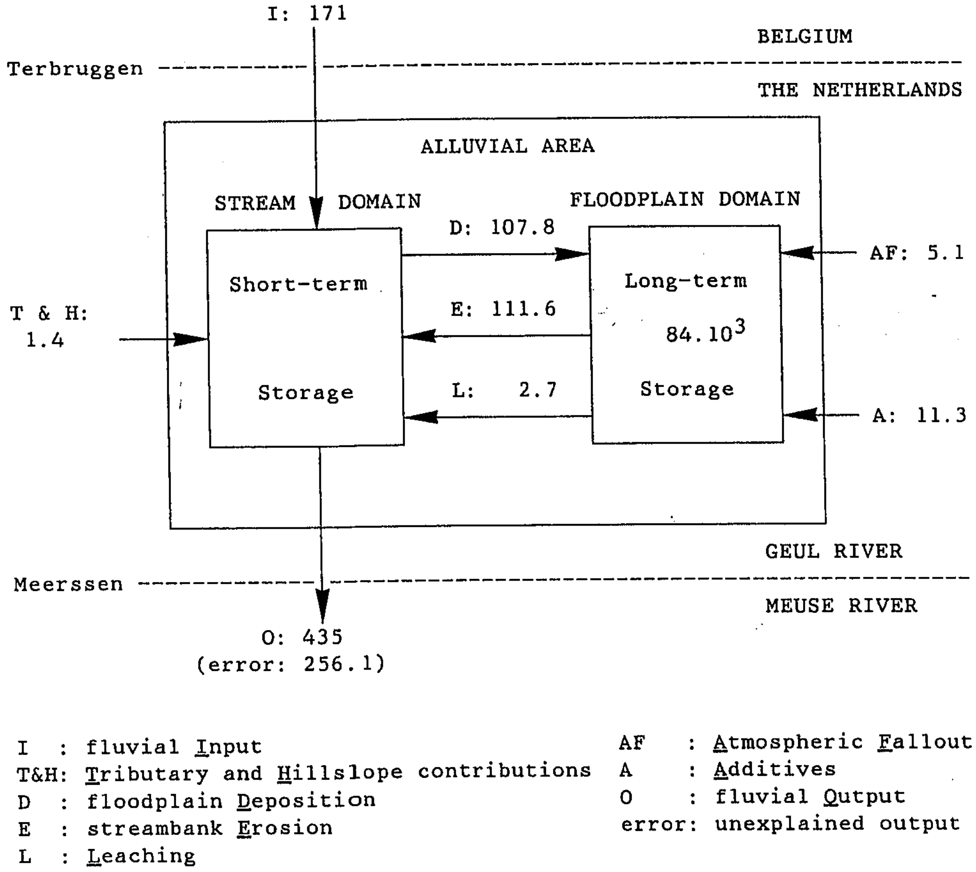


Figure 14.6 Tentative cadmium budget of the alluvial area of the Geul in the Netherlands (values in kg).

14.3.3 The significance of the Geul as a source of heavy metals

The significance of the Geul as a source of heavy metals to the environment can now be assessed. Table 14.5 compares the transport rates of water, sediment and heavy metals by the rivers Rhine and Meuse with those of the Geul. It is clear that - in terms of the transport of sediment and water - the catchment output of the Geul is negligable as compared to the combined import via the rivers Rhine and Meuse. Both the mass of sediment and the volume of water discharged annually into the Meuse by the Geul are less than one percent of the import into the Netherlands by the these two large inetrnational rivers. However, unless its insignificance in terms of sediment and water transport, the Geul carries loads of lead, zinc and cadmium that are of the order of 5-10% of the amounts of these metals transported across the border annually by the Meuse. When compared to the annual transport of lead, zinc and cadmium by the Rhine at Lobith, the load of the Geul has the order of 3-6% These values suggest that the contributions of small rivers, of which the Geul is only one in a large collection of contaminated transboundary rivers in the Netherlands, may play a significant role in terms of emissions of heavy metals into the environment at a national scale. Moreover, if the contributions of the Geul are considered in relation to discharges of heavy metal-contaminants through industrial effluent, it becomes clear that they are of major importance. Table 14.5 also lists estimated annual discharges of heavy metals through industrial effluents and sewage. In this context, the

Table 14.5 Water discharge, sediment transport and some tentative data for heavy metal transport by the rivers Rhine, Meuse and Geul, and heavy metals in industrial effluent

	annual flows				
	water (10^9 m^3)	sediment (10^6 tonnes)	Zn (tonnes)	Pb (tonnes)	Cd (tonnes)
Rhine (1987) 1)	69.4 4)	2.8	2360	278	6.9
Meuse (1986) 2)	10.3 4)	0.5	906	144	9.3
industrial 3) effluent (1985)	?	?	417	72	18.7
total	> 79.7	> 3.3	3683	494	34.9
Geul (1983) 5)	0.13	0.03	70.5	13.9	0.4
as % of Rhine	0.18	1.1	3.0	5.0	6.3
as % of Meuse	1.2	6.2	7.8	9.7	4.7
as % industrial effluent	?	?	16.9	19.4	2.3
as % total	> 0.16	> 0.9	1.9	2.8	1.2

1) River Rhine at Lobith, source: RIWA (1989)
2) River Meuse at Eijsden, source: RIWA (1988)
3) source: CBS (1988)
4) long term mean
5) River Geul at Meerssen (see Table 7.7)

catchment output of the Geul would account for a large part (up to 19.4%) of the total industrial discharge of heavy metals into surface waters in the Netherlands. As a result of government regulations the discharge of contaminated industrial effluent is now rapidly decreasing. Simultaneously, the relative importance of the contributions of small contaminated rivers, such as the Geul, increases. Given the diffuse nature of part of the source - the streambank deposits along the river channel - and the fact that some 55, 81 and 39% of the catchment output of lead, zinc and cadmium respectively can be accounted for by transboundary fluvial transport (see Section 14.3.2), it is clear that it is impossible to control the activity of the sources by national legislation. Reducing the contributions of streambank erosion would require gross measures such as sanitation of the Geul valley, canalization of the river channel or enforced land use changes. Reducing the transboundary transport would require similar measures to be taken in Belgium and - to start with - the sanitation of the waste dumps near the towns of Plombières and Kelmis.

14.4 Health risk assessment

The data collected during this study were used during a joint research project carried out by the University of Utrecht and C.S.O. Consultants for Environmental Management and Survey and commissioned by the Provincial Department of Works of Limburg. The aim of this study was to map soil metal concentrations in the entire Geul valley and, given the landuse, to assess the health risk in a number of pollution zones, defined by the indicator values in Table 4.2. The co-kriging procedure described in chapter 12 was used to map zones of zinc, lead and cadmium concentrations in the soil from all available sample data. A model for health risk assessment with respect to the the effects of lead and cadmium was applied for each pollution zone. The following sections provide a brief summary of the results of this investigation. For more detailed information, refer to Leenaers et al. (1989).

14.4.1 Pollution maps for planning

The Department of Works of Limburg required two types of maps of metal concentrations in floodplain soils. For long term planning at the scale of the Province, maps are needed that show broad pollution zones with known metal concentrations and known associated constraints to the land use in terms of health risk for men and animals. For short term planning, detailed maps are required that provide information on the pollution level in a single field or vegetable garden, so that measures can be taken at a local scale. In order to satisfy both criteria it was decided to produce detailed maps of concentrations of zinc, lead and cadmium by co-kriging and then to generalize these maps to yield maps that show broad pollution zones.
745 Data on soil metal concentrations and c. 10,000 data on relative elevations were available for the entire Geul floodplain. The sample

locations are shown in Appendix 2. The detailed maps of zinc, lead and cadmium concentrations were produced by co-kriging from data on relative elevations (see Chapter 12). In the southern part of the valley near the border with Belgium the concentrations of all metals exhibit large short range variations and - locally - extremely high values. As a result, given the sample density, it was not possible to model the spatial correlation structure of metal concentrations in this relatively small area and no contour maps could be produced. Moreover, the use of $\log_{10}$-transformed data did not provide improvements with respect to the modelling of the spatial correlation structure. The generalization in the remainder of the valley was established by drawing contours that correspond with the reference values for each metal (see Table 4.1) and the indicator values (see Table 4.2), yielding 4 pollution zones for each metal (see Appendix 3, 4 and 5). The mean and 90-percentile of metal concentrations in the soils of the zones are listed in Table 14.6.

Table 14.6 Soil metal concentrations (mean and 90-percentile in mg/kg) in pollution zones of lead, zinc and cadmium (n=number of samples)

pollution zone	Pb			Zn			Cd		
	n	mean	90%	n	mean	90%	n	mean	90%
< REF*	187	52	70	22	88	105	37	0.3	0.4
REF-B	239	104	136	358	292	443	597	2.2	3.7
B-C	246	289	460	328	1138	2200	104	7.7	10.7
>C	73	1071	1477	37	3650	4597	7	26.4	39.8

* REF (=reference value): see Table 4.1;
B and C-value: see Table 4.2

The spatial distributions of the pollution zones of lead and zinc exhibit a high degree of similarity. Concentrations exceeding the C-value are found mainly to the south of Mechelen and are restricted to small areas near the channel margins. Concentrations exceeding the B-value are found in large areas along the channel margin as far downstream as the village of Wijlre. Between Wijlre and the village of Meerssen, the areas covered by pollution zones B-C decrease in size and here concentrations between the reference value and the B-value dominate. In the entire valley, the concentrations tend to decrease with increasing distance to the channel margin. Concentrations below the reference value are only found along the edge of the valley, where the influence of fluvial processes is small.

The pollution map of cadmium is characterized by an almost complete lack of spatial differentiation and a predominance of concentrations between the reference value and the B-value. Soils with concentrations exceeding the C-value or below the reference value do not cover a significant area and concentrations between the B- and C-values are restricted to soils in a few small areas south of Mechelen and one near Gulpen.

14.4.2 Health aspects

The health aspects of enhanced concentrations of lead and cadmium in the soil were investigated because of their relatively high toxicity (see Section 4.2). The followed method is based on estimates of amounts of diet constituents that are consumed and the corresponding concentrations of lead and cadmium in these diet constituents. The total intake is then compared with standards set by the W.H.O. (1972 & 1973) for heavy-metal contaminants, the so-called acceptable daily intake (A.D.I.). Given that lead and cadmium both affect the kidney and the liver, units of A.D.I. (Intake/A.D.I.) of the two metals may be added to assess their combined effect. A distinction is made between the health risks for children (1-5 years old, c. 14 kg body weight) and those for adults (body weight c. 60 kg), and between a realistic and worst case approach. In the latter approach larger amounts of the diet constituents containing higher metal concentrations (i.e. the 90-percentile of concentrations in that zone instead of the mean, see Table 14.6) are supposed to be consumed. The first step of the procedure is the computation of the base level intake, that is the intake of lead and cadmium in a situation where no enhanced metal concentrations are found in the soil. Then, the additional intake due to soil pollution is computed for each pollution zone and for a specific type of land use, and the sum of the base level intake and the additional intake are compared to the acceptable daily intake. In the next section, the estimated total intake by people staying in a recreation area will be discussed.
Finally, the concentrations of lead, zinc and cadmium in the soil are compared with indicator values that refer to the maximum concentrations thay may occur in the soil without causing damage to the yield of the growing crops or to the health of grazing animals

Base level intake of heavy metals

The base level intake of lead and cadmium by humans is caused by the presence of these metals in standard food, drinking water, air and cigar and cigarette smoke. In addition, children may - when playing - consume small amounts of soil and dust that contain low concentrations of heavy metals, even though the dust is not polluted. Moreover, when not carefully cleaned, small amounts of soil may remain attached to vegetables that are consumed. In the realistic approach the intake of soil by children in the Geul valley is estimated at 0.2 g/day and in the worst case approach it may be as high as 1.1 g/day. For adults these values are estimated at 0.02 and 0.3 g/day respectively. Based on the amounts of standard food, water, air, smoke and soil and dust that are consumed and the concentrations of lead and cadmium in these constituents, the base level intake by children and adults was computed. The results, expressed in units of A.D.I., are listed in Table 14.7.
The values in this table illustrate that the base level intake by children exceeds the A.D.I. of lead and cadmium in the worst case approach and that, after addition of lead and cadmium, also in the realistic approach the A.D.I. is exceeded. Thus, even when no soil pollution is at hand, the combined daily intake of lead and cadmium is

larger than the acceptable standard. It is clear that in this situation every additional intake of one of these metals must be assessed critically.

Table 14.7 Base level intake of lead and cadmium, expressed in units of A.D.I. (=Intake/A.D.I.)

	child (1-5 yr)		adult	
metal	realistic	worst case	realistic	worst case
Pb	0.66	1.85	0.27	0.61
Cd	0.72	1.34	0.43	0.82
	+	+	+	+
Pb + Cd	1.38	3.19	0.70	1.43

Additional intake due to soil pollution in recreation areas

Additional intakes of heavy metals in recreation areas may occur through consumption of two diet constituents: (1) contaminated soil (by children playing) and (2) contaminated surface water (during swimming). People consuming vegetables grown in their own garden may incur additional risks. However, the study of the migration of heavy metals from soils to plants is beyond the scope of this research. Calculations taking into account enhanced metal concentrations in vegetables, derived from studies in other areas, are provided by Leenaers et al. (1989). Estimated amounts of daily consumption of contaminated diet constituents in recreation areas are listed in Table 14.8.

Table 14.8 Estimated daily consumption of contaminated diet constituents in recreation areas

	child (1-5 yr)		adult		
	realistic	worst case	realistic	worst case	units
soil	0.20	1.10	0.02	0.30	g
water	0.05	0.15	0.02	0.07	l

The amounts of diet constituents listed in Table 14.8 and their known concentrations of lead and cadmium, were used to estimate the total daily intakes of lead and cadmium in each pollution zone. The results are listed in Table 14.9.

Following the realistic approach, the daily intake of lead by children exceeds the A.D.I. in those recreation areas where lead concentrations in the soil exceed the B-value. In this situation, 43- 76% of the total intake (including base level intake) can be accounted for by the intake of contaminated soil and water. The combined intake of lead and cadmium by children causes an exceedance of the A.D.I. in all pollution zones, whereas for adults no exceedance in any of the zones occurs.

Table 14.9 Total intake of lead and cadmium in the pollution zones, when used as recreation area (values expressed in units A.D.I.=Intake/A.D.I.)

metal	concentration in soil	child (1-5 yr)		adult	
		realistic	worst case	realistic	worst case
Pb	REF-B*	0.78	3.09	0.27	0.67
Cd	REF-B	0.75	1.62	0.43	0.83
Pb + Cd	REF-B	1.53	4.71	0.70	1.50
Pb	B-C*)	1.15	6.33	0.28	0.75
Cd	B-C	0.81	2.03	0.43	0.84
Pb + Cd	B-C	1.96	8.36	0.71	1.59
Pb	> C	2.71	17.50	0.32	0.98
Cd	> C**	-	-	-	-

* REF (reference value), B and C: see Table 4.1 and 4.2;

** these concentrations are only found in an insignificantly small part of the Geul valley (see Table 14.5).

Following the <u>worst case approach</u>, the intake of lead and cadmium by children will cause an exceedance of the A.D.I. in the entire valley, even if only one of these metals would be present in soil and water. The additonal intakes due to the presence of contamination accounts for 40-89 % of the total lead intake and for 17-34% of the total cadmium intake. The combined intake of lead and cadmium by children will lead to an exceedance of the A.D.I. by a factor 4.7 to 20.7 (17.5 due to lead intake plus 3.2 due to base level intake); for adults these values vary between 1.5 and 1.8, which is only slightly higher than the base level intake of 1.43 A.D.I.-units.
It may be concluded that in existing or planned recreation areas in the Geul valley, the presence of heavy metal-contaminants will mainly affect young children as a result of the facts that (1) they are more susceptible to contaminants (i.e. a lower A.D.I.) and (2) they tend to consume more of the contaminated diet constituents. Exceedance of the A.D.I. for lead, following the realistic approach, may occur in areas where the concentrations in the soil exceed the B-value. Given the fact that the sample locations are more or less regularly distributed over the valley floor, it may be derived from Table 14.6 that these areas occupy ca. 43% of the alluvial area. The larger part of this area lies in the vicinity of the Belgium-Netherlands border. The combined intake of lead and cadmium will cause exceedance of the A.D.I. in the entire river valley. Preliminary evidence suggests that, when the consumption of contaminated vegetables is additionally taken into account, locally exceedance of the A.D.I. may be expected for adults as well (Leenaers et al., 1989). Further investigations are planned in order to estimate this contribution more precisely.

Consequences for agricultural landuse

The enhanced levels of heavy metals in the soil may affect the health of grazing animals and the magnitude and the quality of the crop yield. The Dutch Ministry of Agriculture provides a set of signal values for heavy metals in the soil, which may be interpreted as concentrations that, when exceeded, may cause a reduction of crop yield or may affect human health when contaminated agricultural products are consumed. The signal values are listed in Table 14.10.

Table 14.10 Signal values for metal concentrations in the soil (mg/kg) for various types of agricultural landuse/products.

landuse	Pb	Zn	Cd	Cu
consumer crops	200	350	1.0	200
pasture	200	350	3.0	-
grazing sheep	-	-	-	30
grazing cattle	-	-	-	80

The exceedance percentages in Table 14.11 suggest that the enhanced concentrations of lead, zinc and cadmium in the soil mean that it is unwise to grow crops for human consumption in large parts of the Geul valley or to utilize the land as pasture.

Table 14.11 Exceedance of the signal values in Table 14.9 for soils in the Geul valley (number of samples=746)

landuse	Pb	Zn	Cd	Cu
consumer crops	34%	66%	88%	0%
pasture	34%	66%	33%	-
grazing sheep	-	-	-	7%
grazing cattle	-	-	-	0%

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APPENDIX 1

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1988 Variability of the metal content of flood deposits. Environmental Geology and Water Science, 11, 1, 95-106. Co-authors: M.C. Rang & C.J. Schouten.

1988 Soil pollution and flood hazard mapping by using a Digital Elevation Model (poster presentation). EUROCARTO VII, Enschede, The Netherlands, September 1988.

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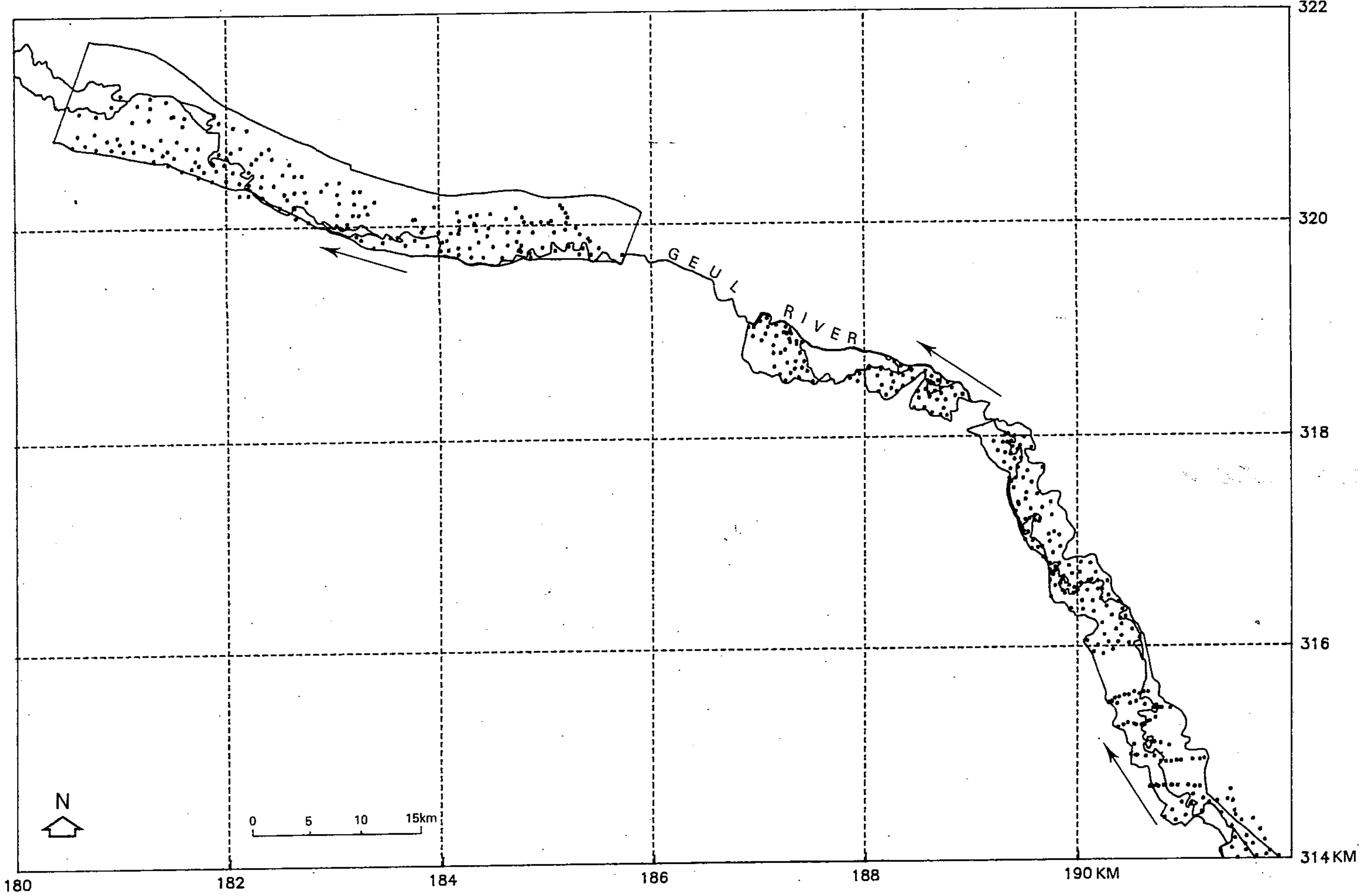

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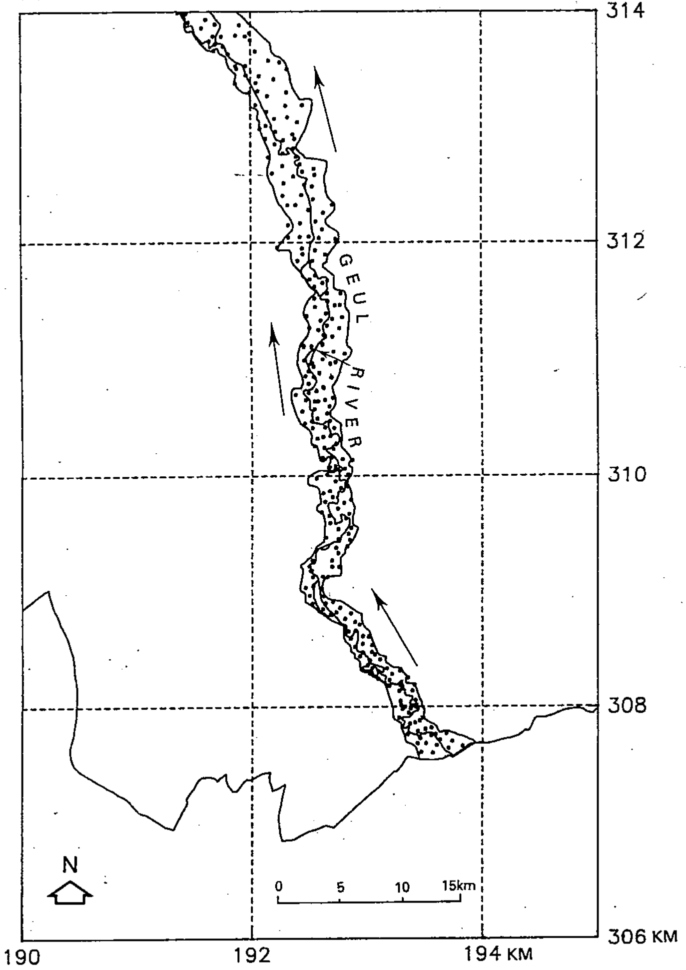

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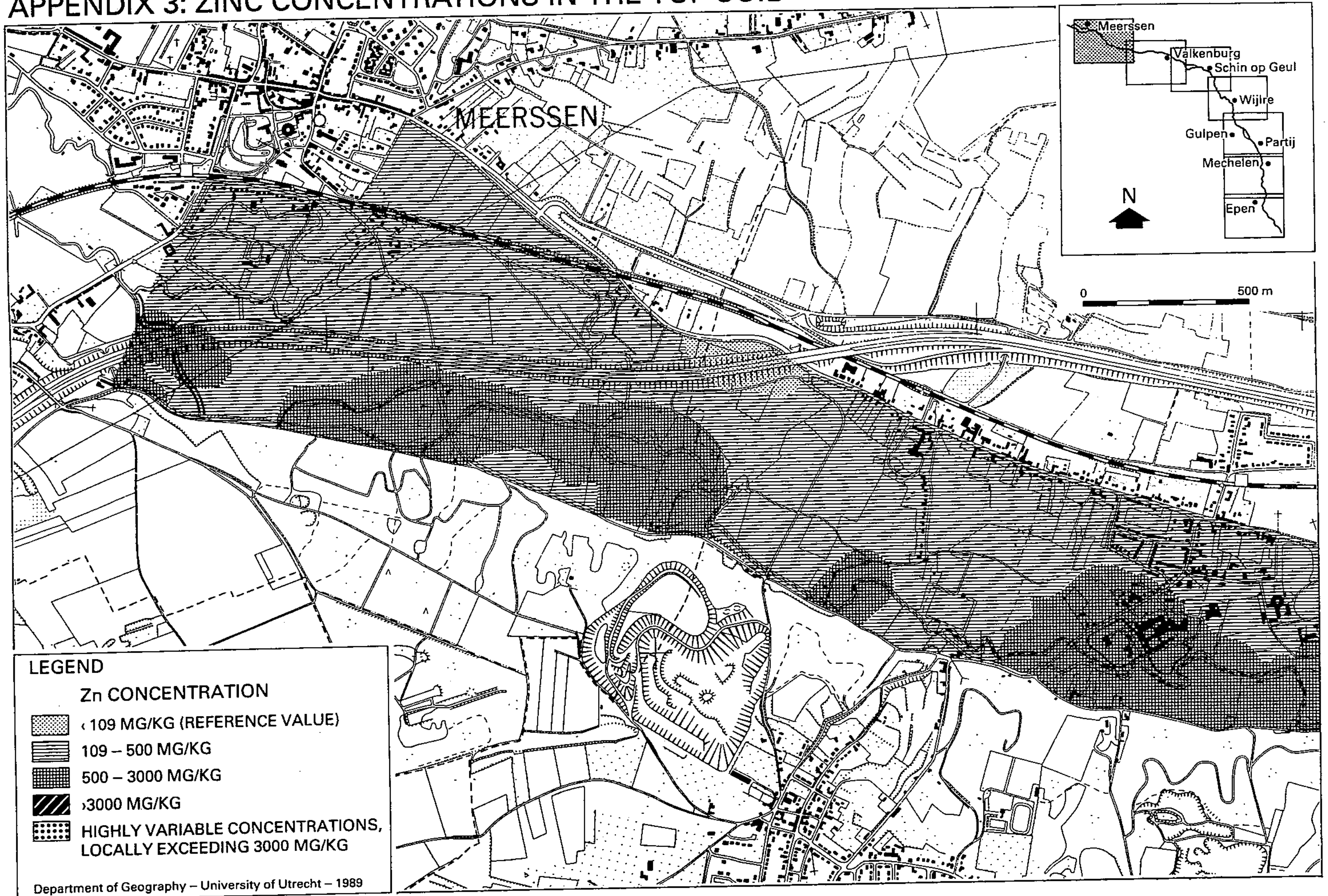

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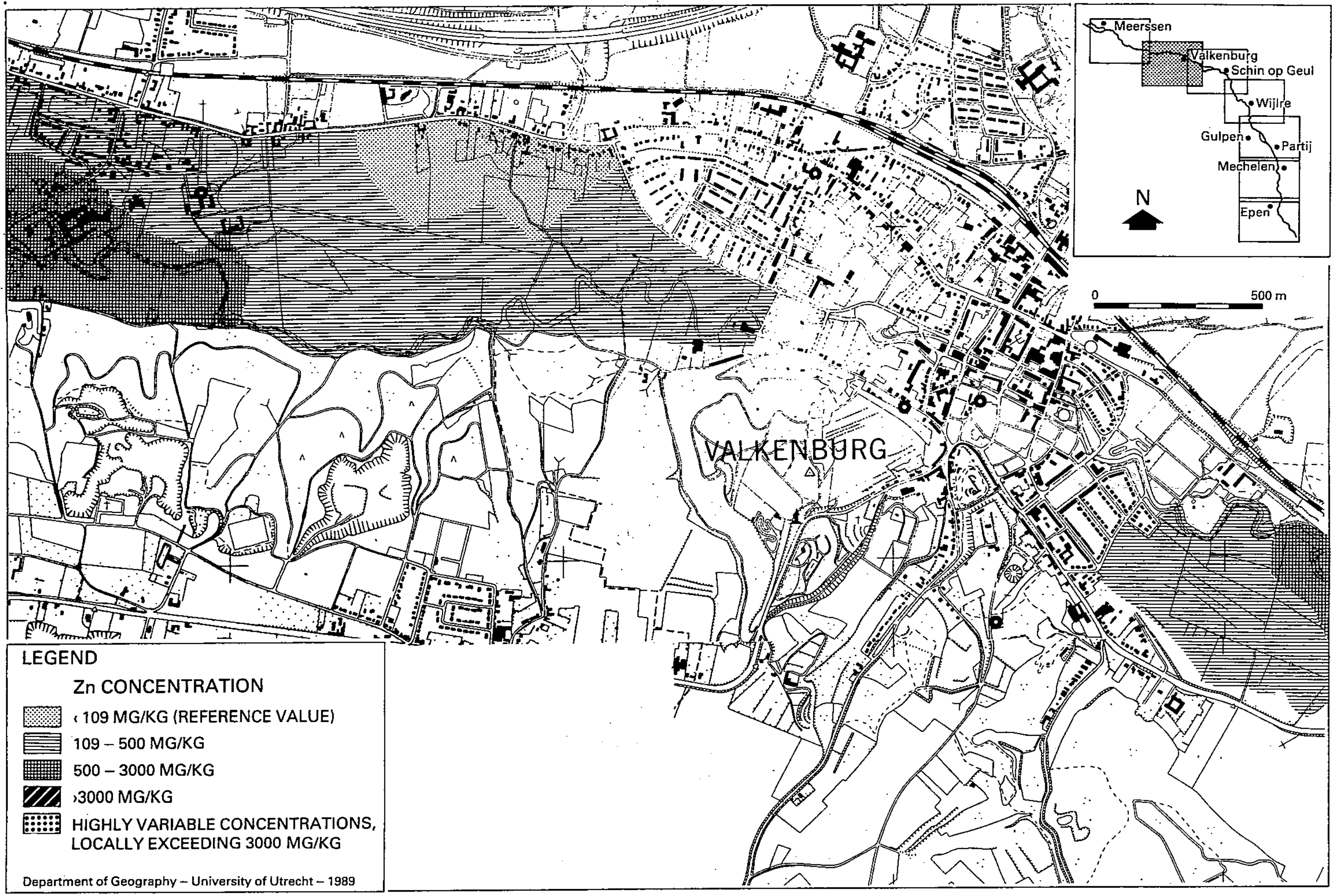

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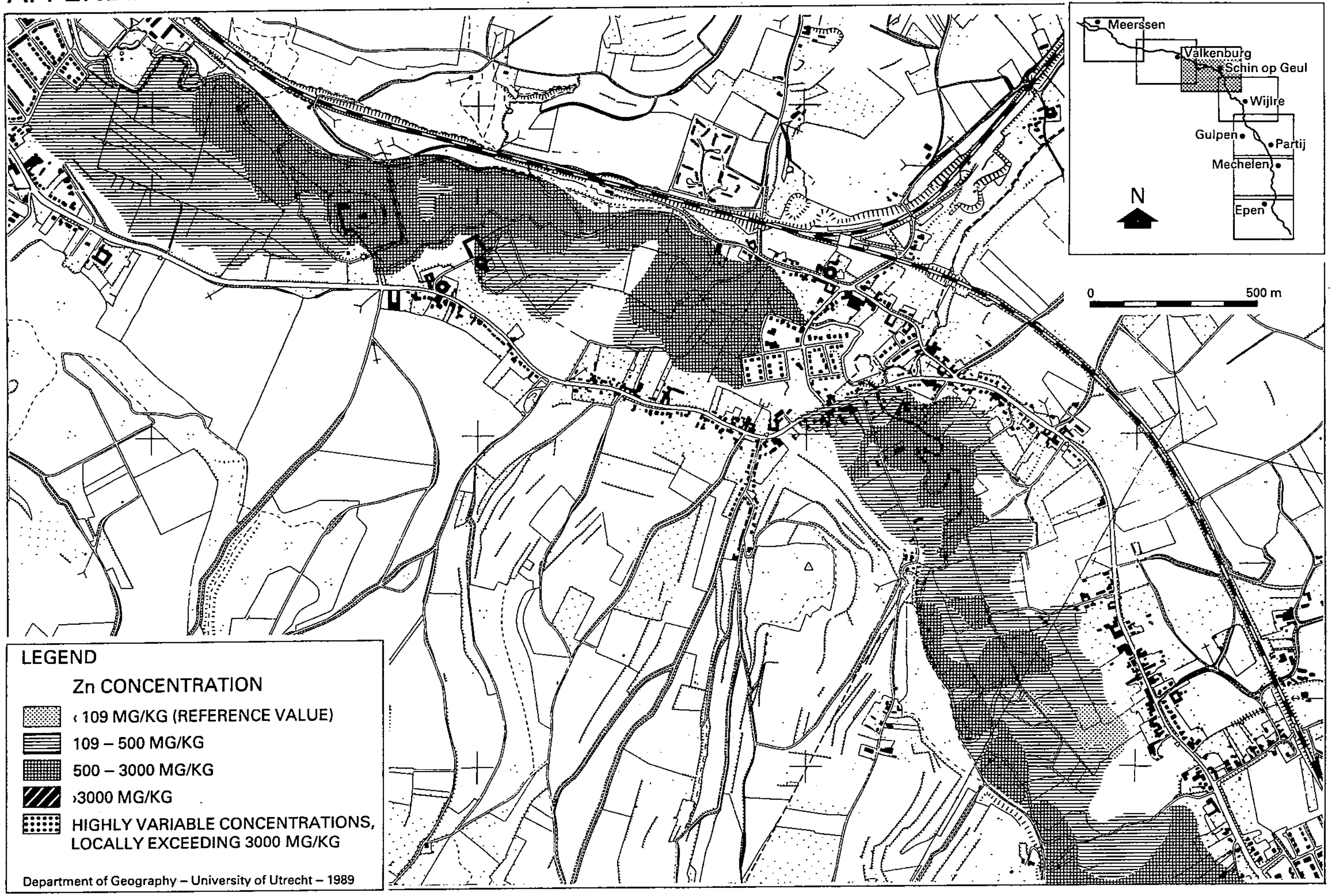

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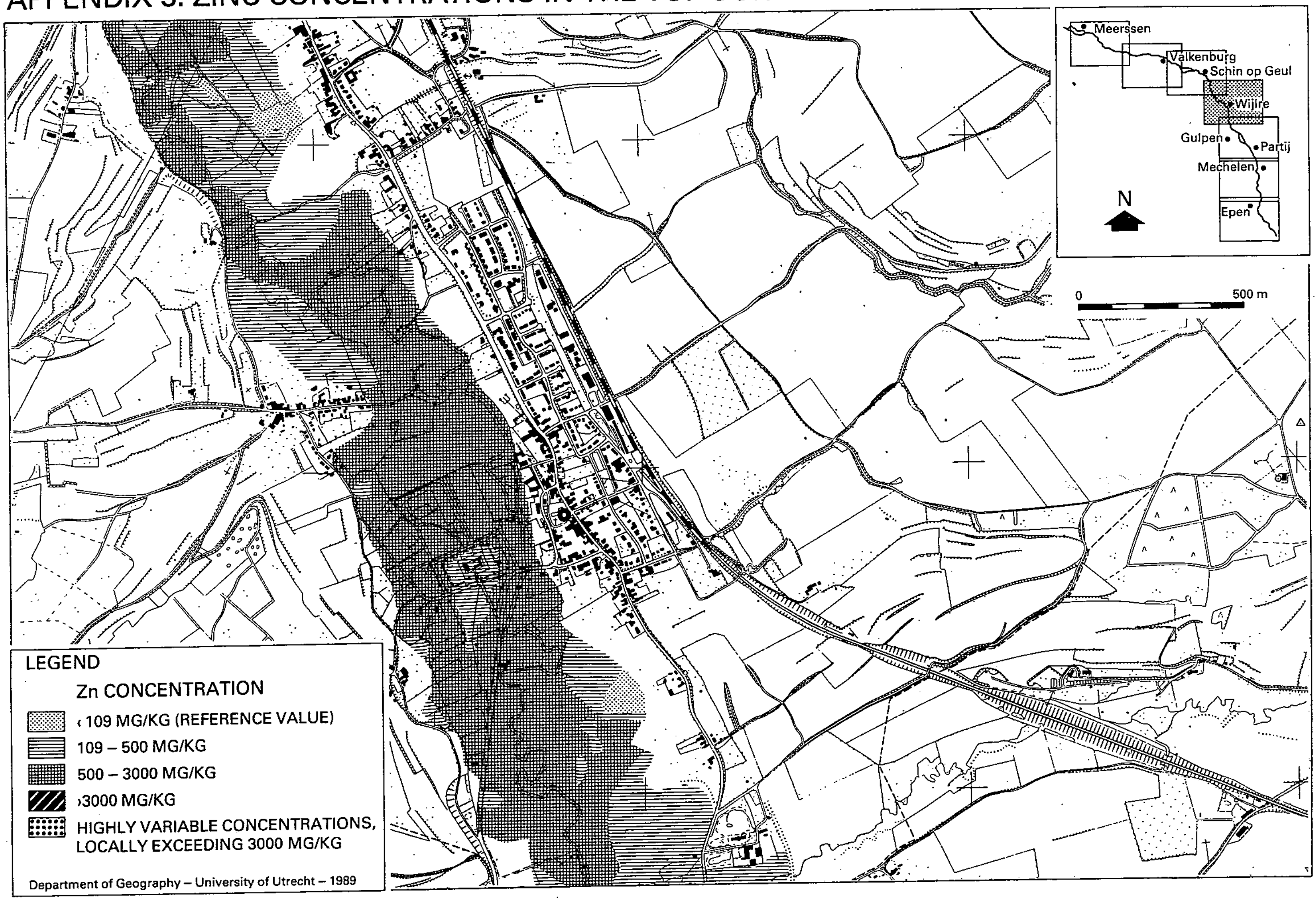

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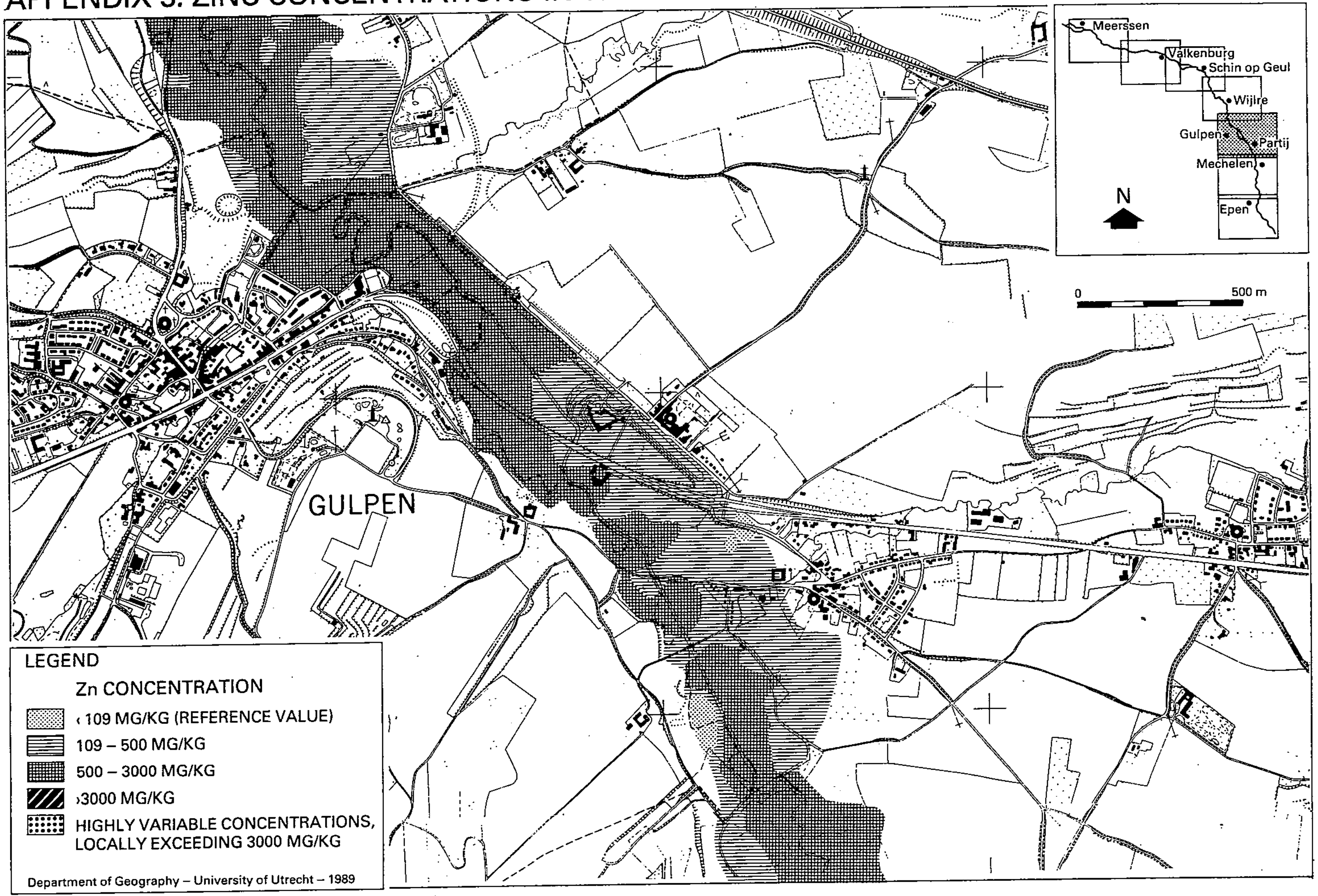

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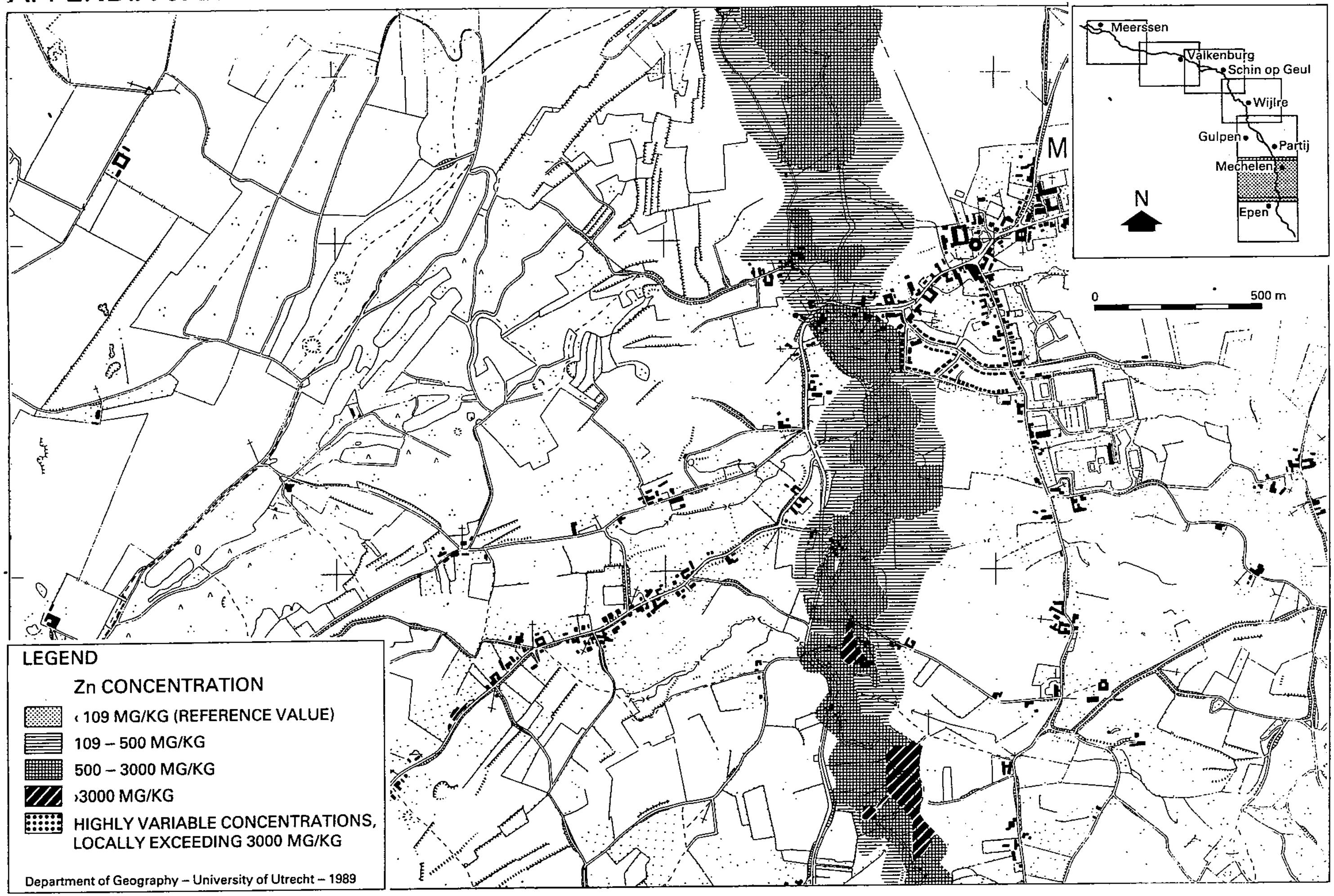

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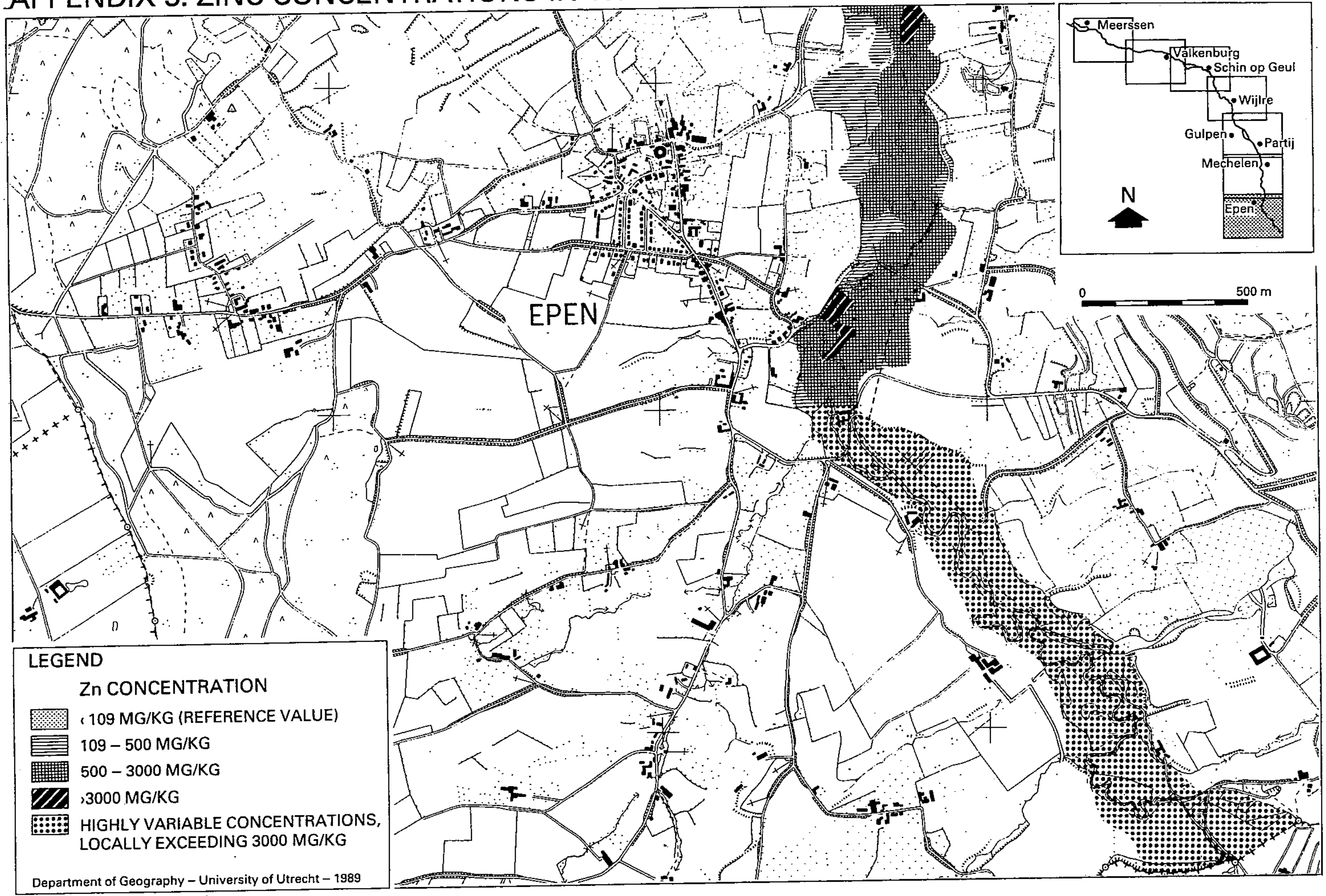

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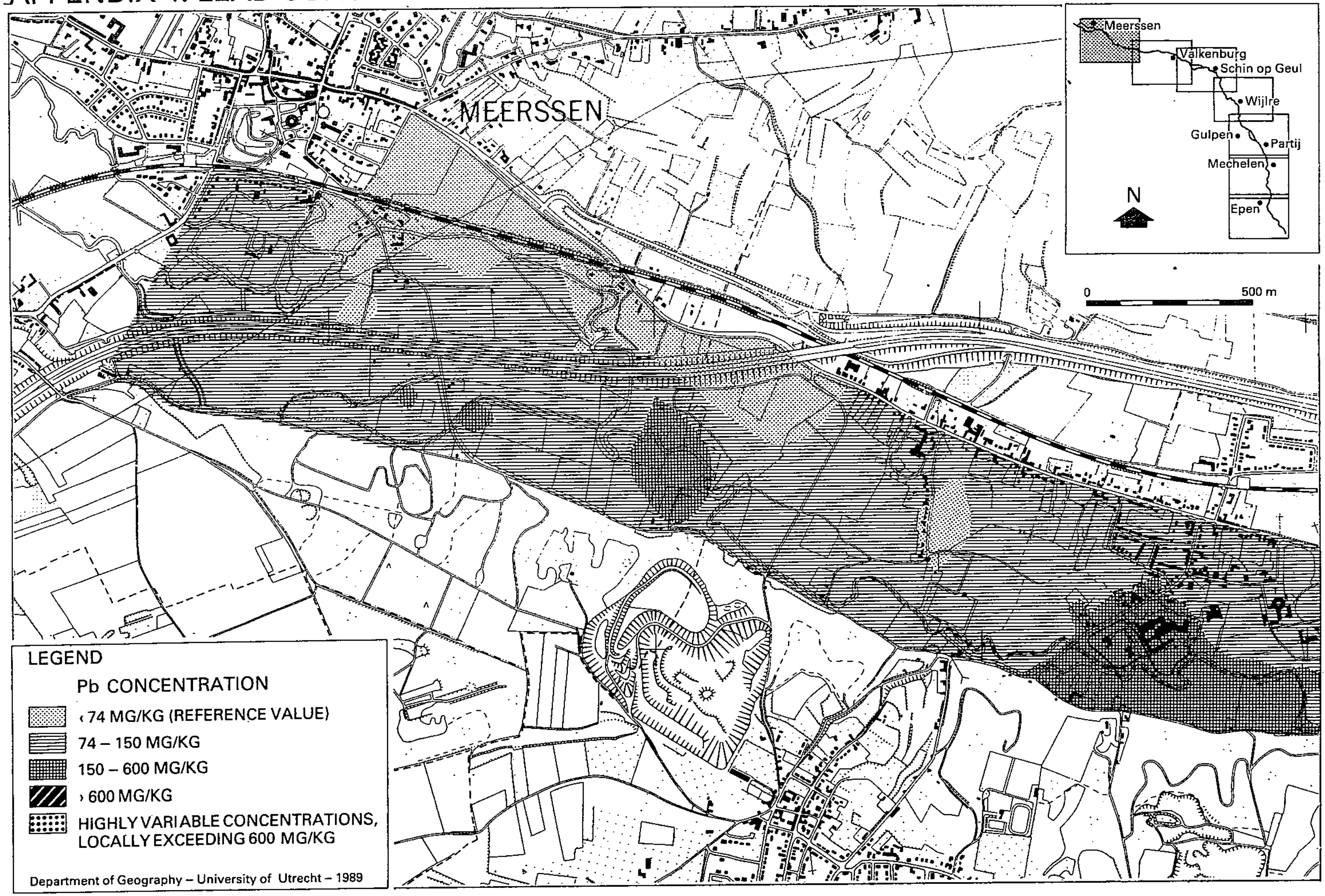

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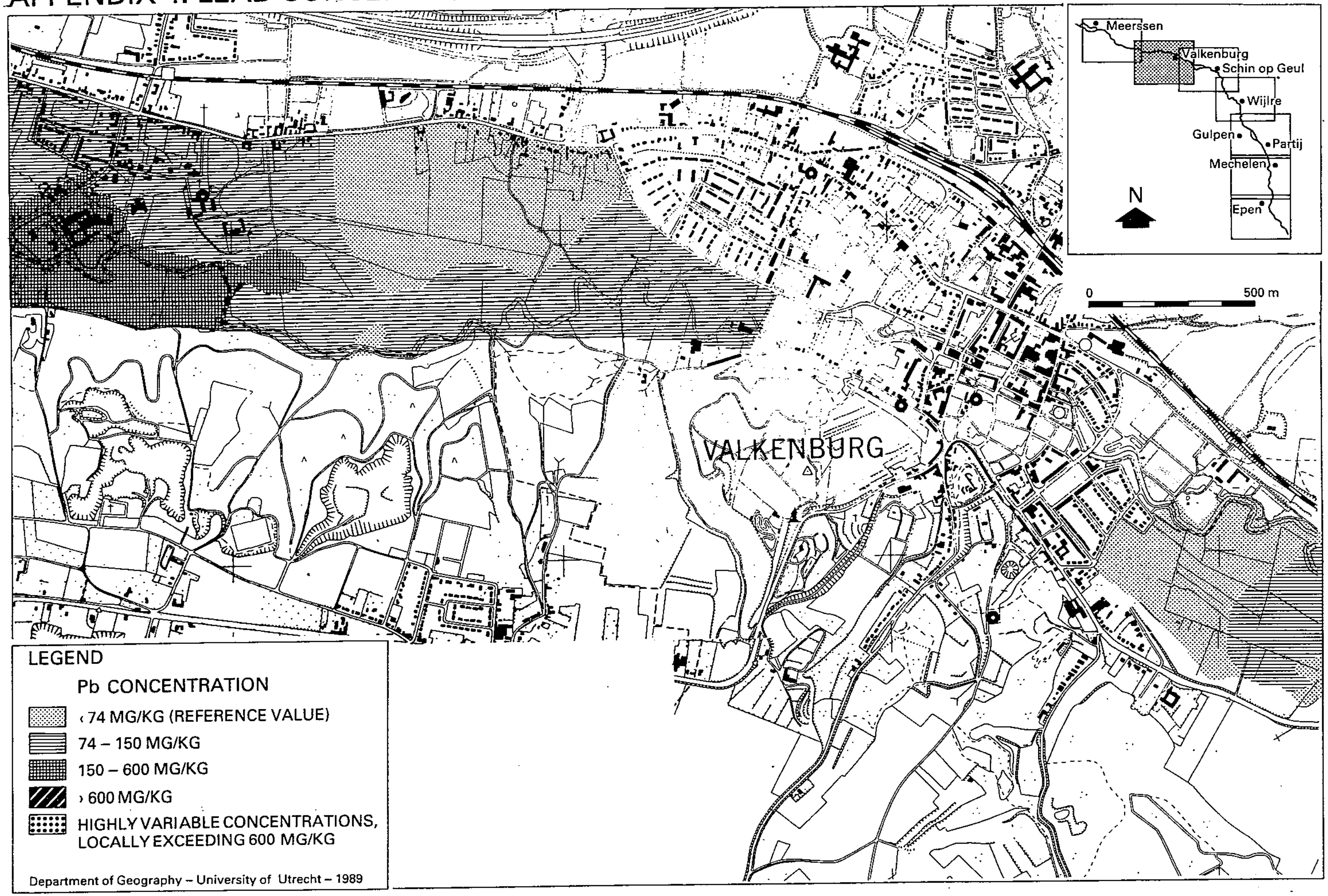

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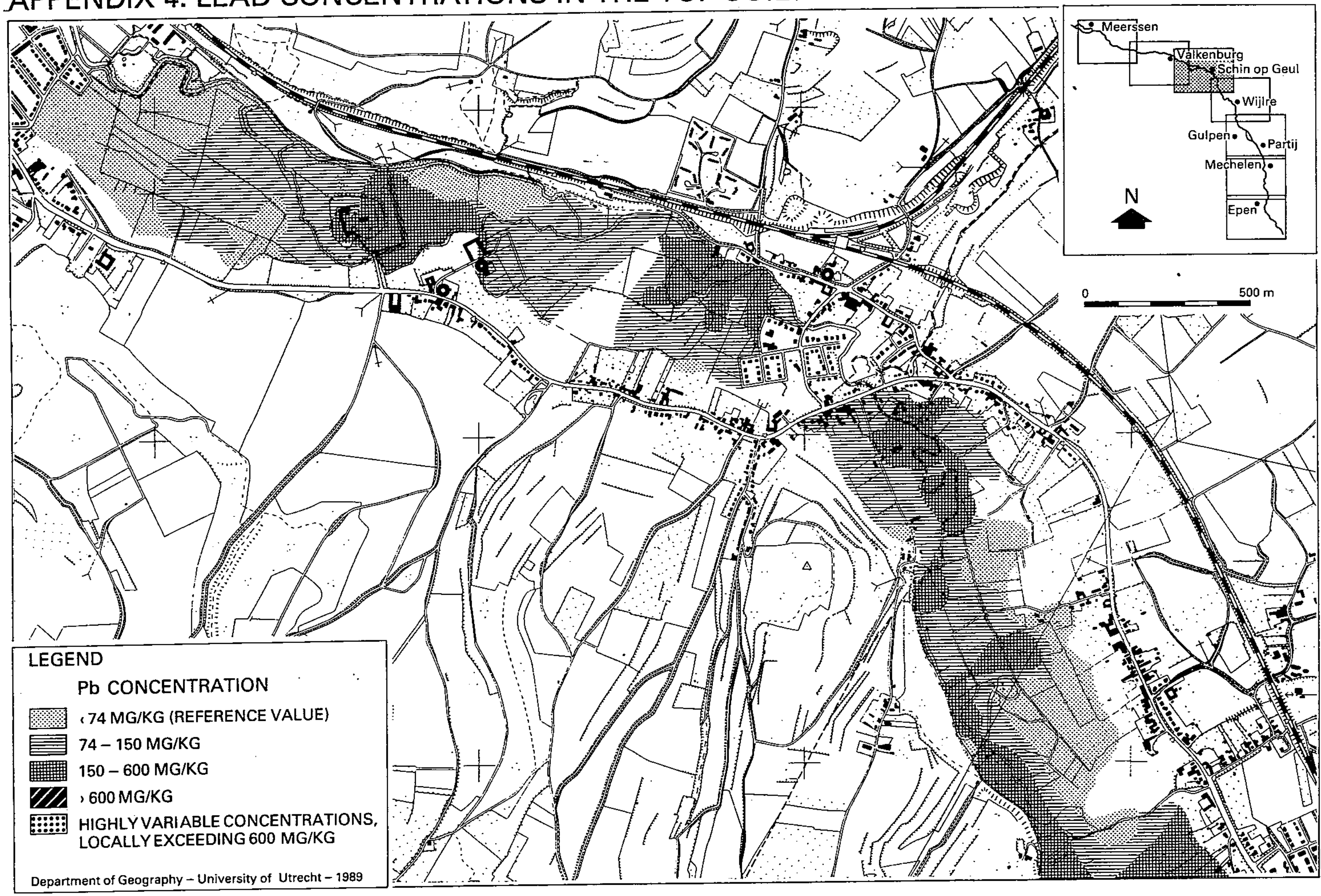

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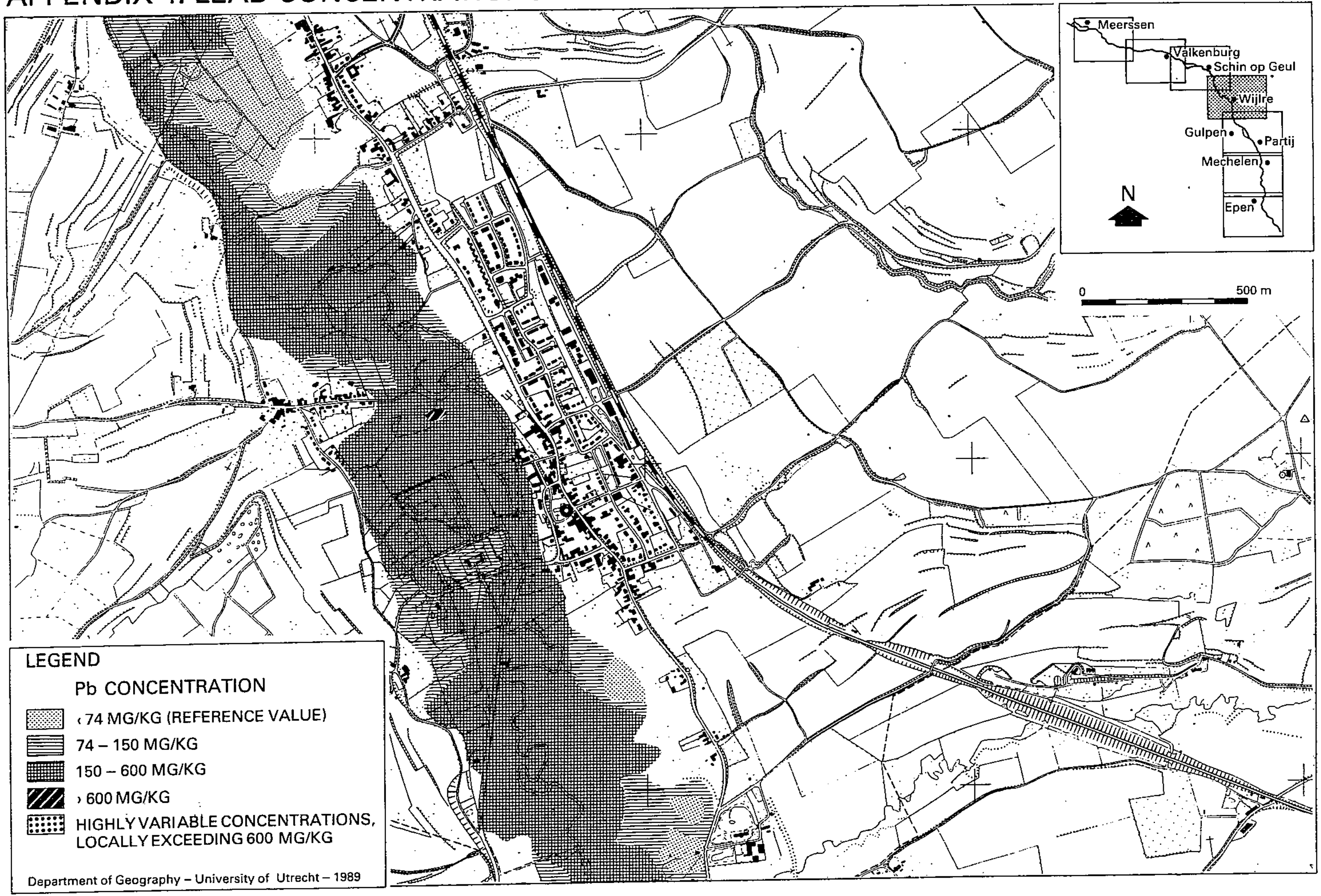

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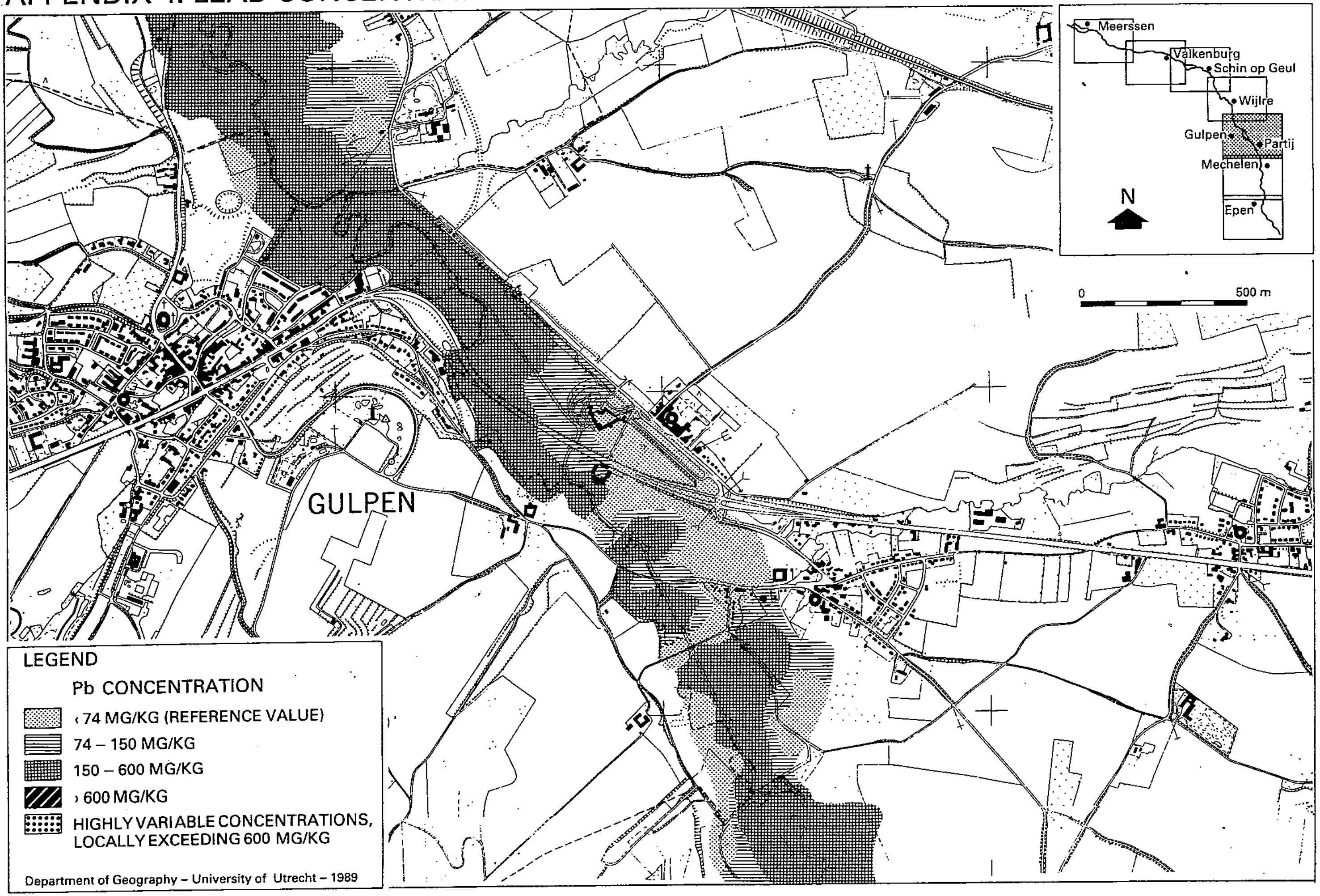

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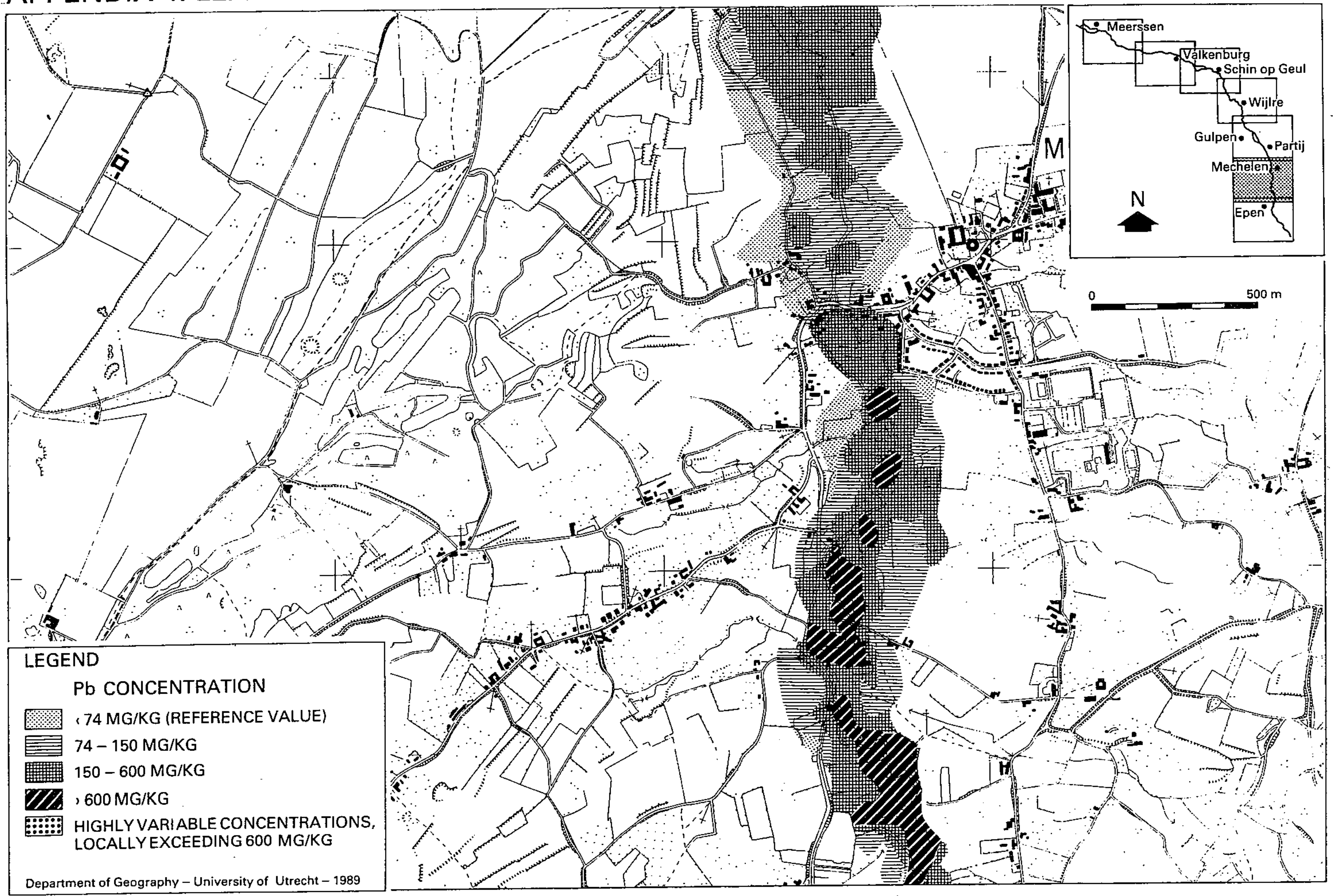

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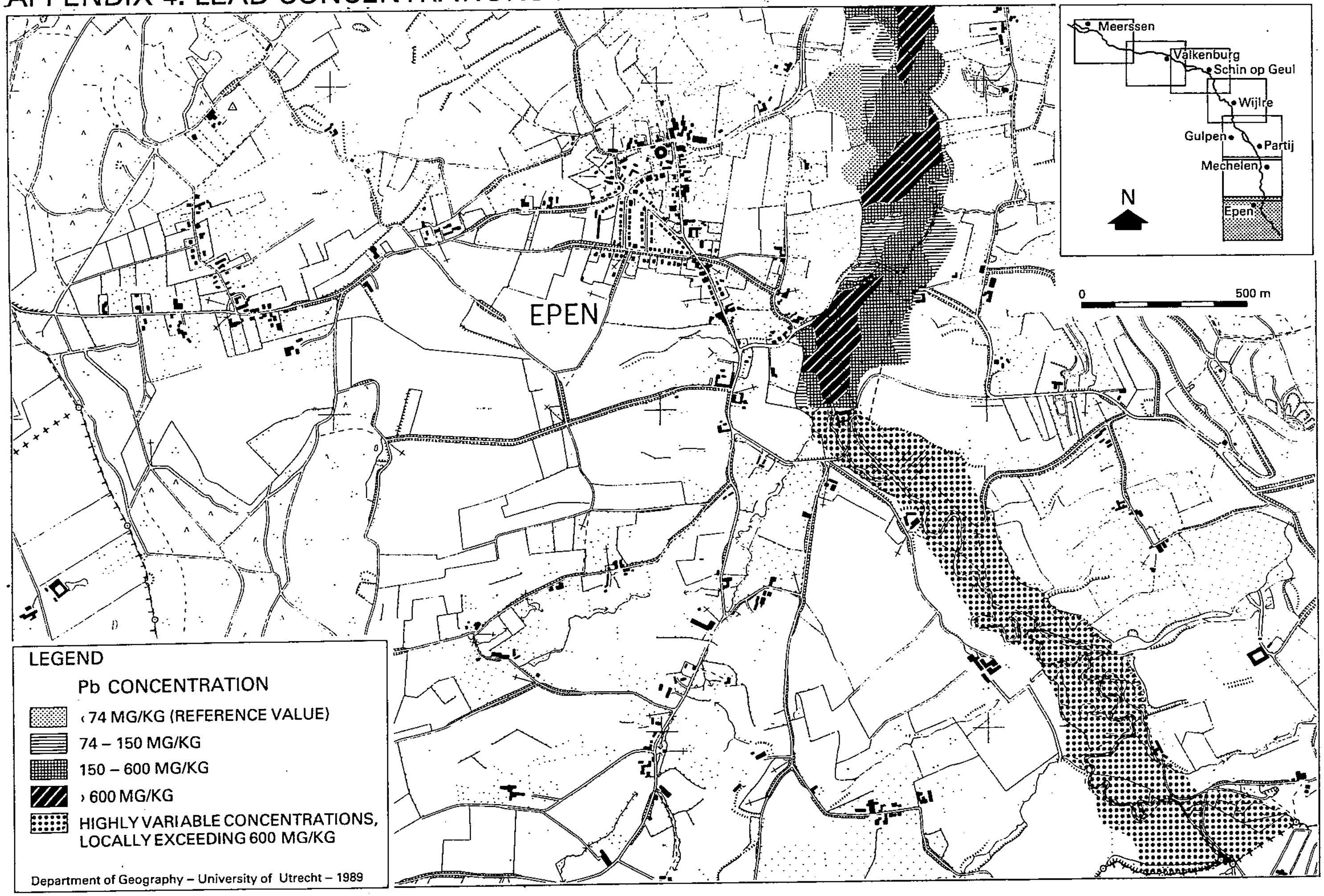

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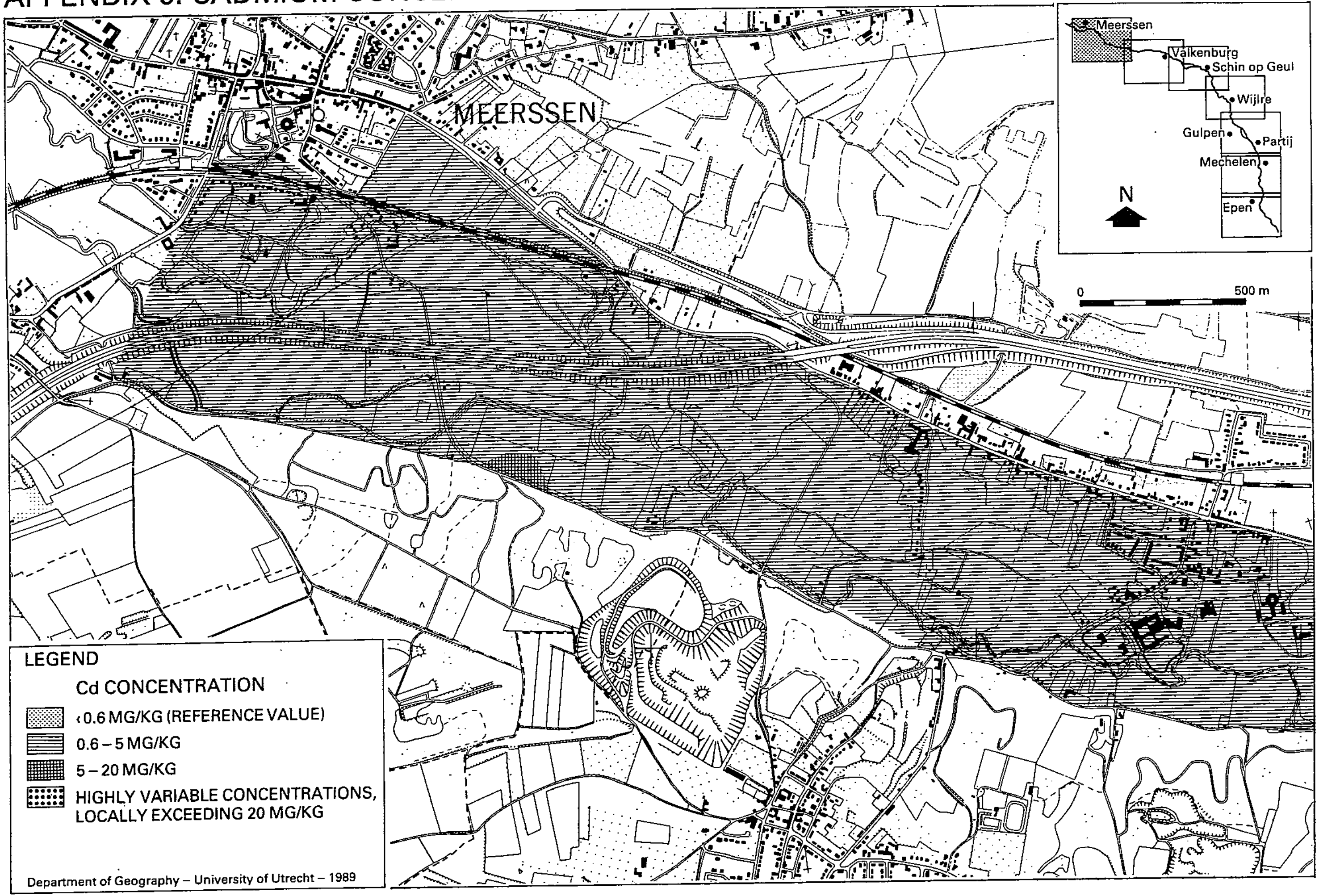

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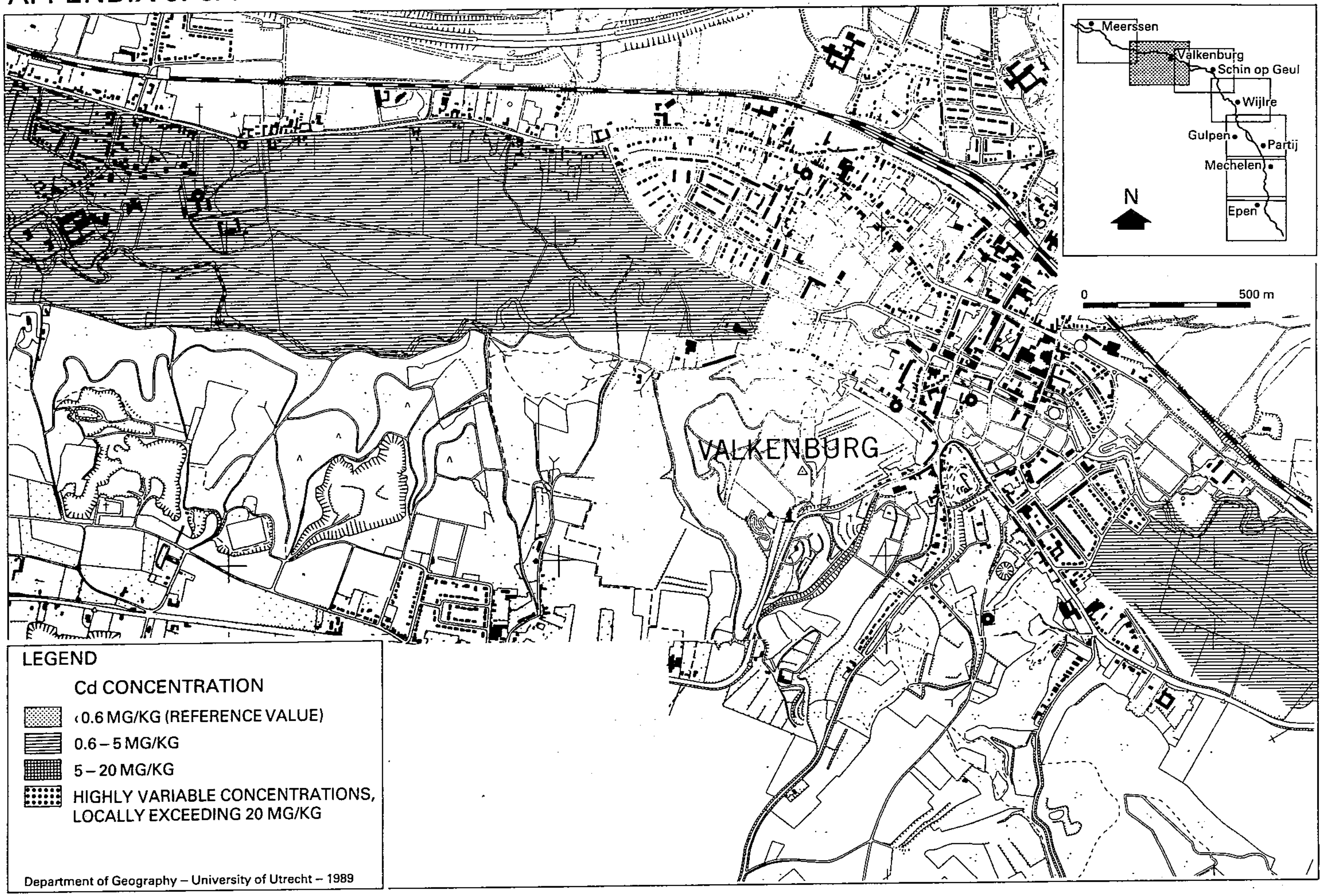

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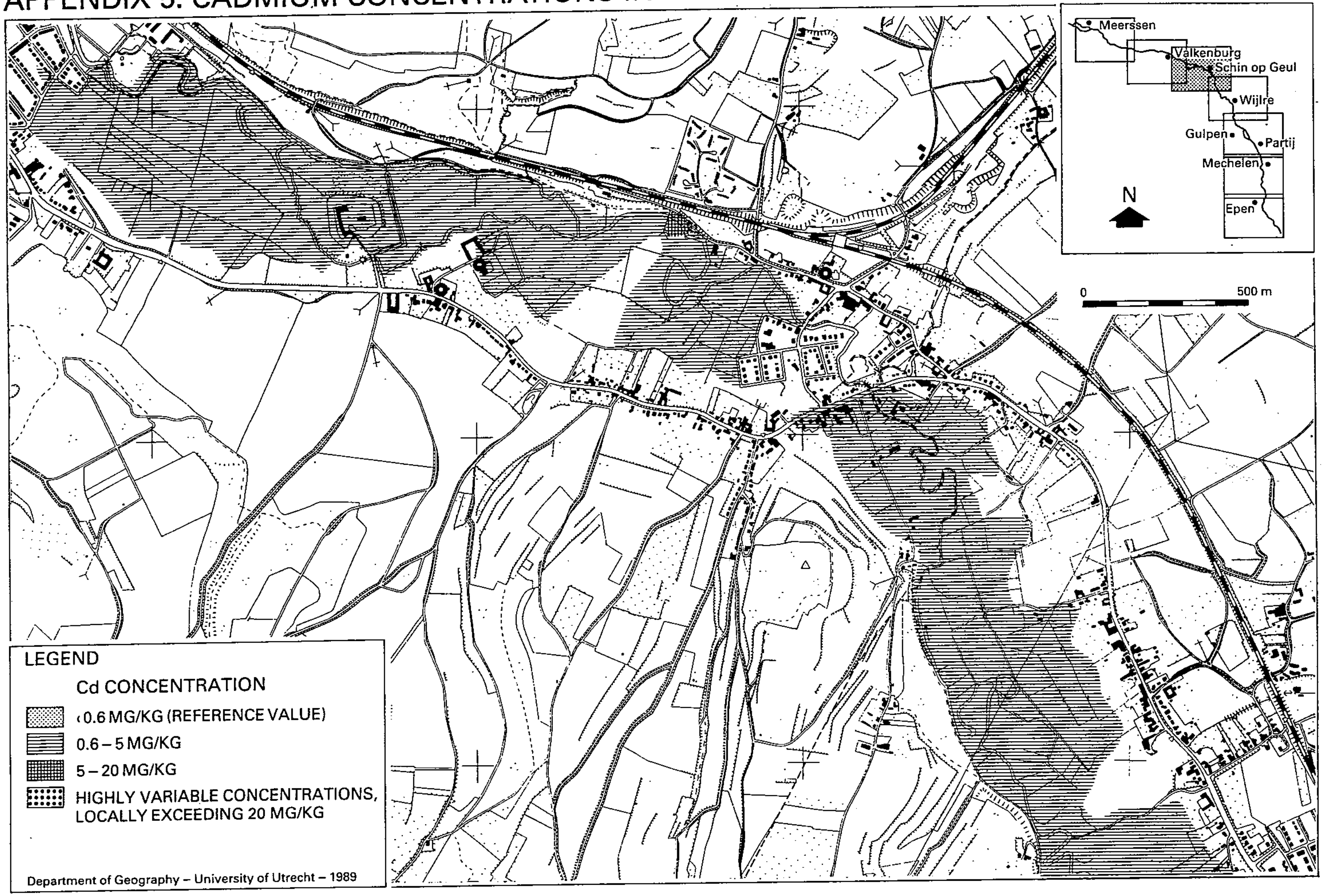

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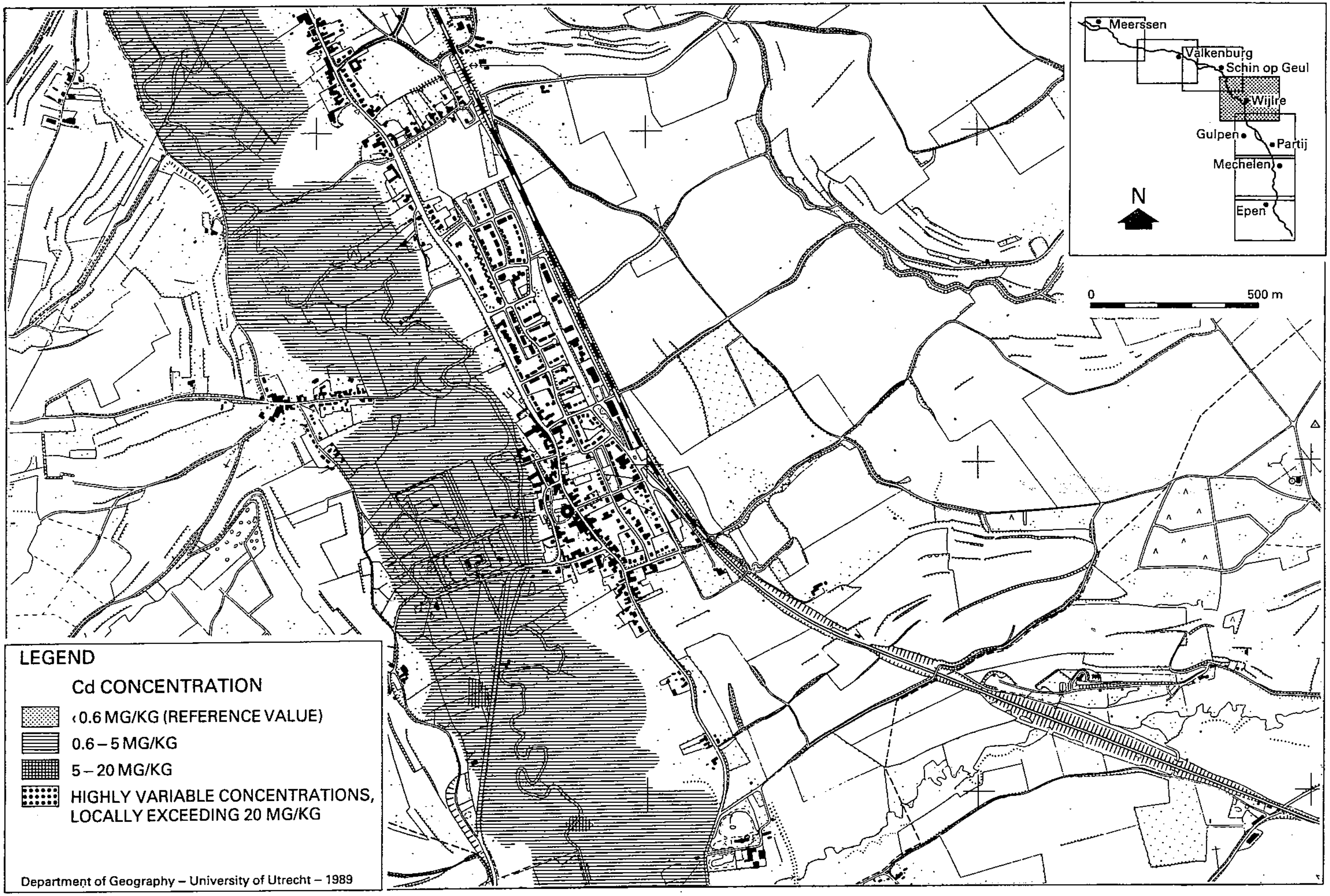

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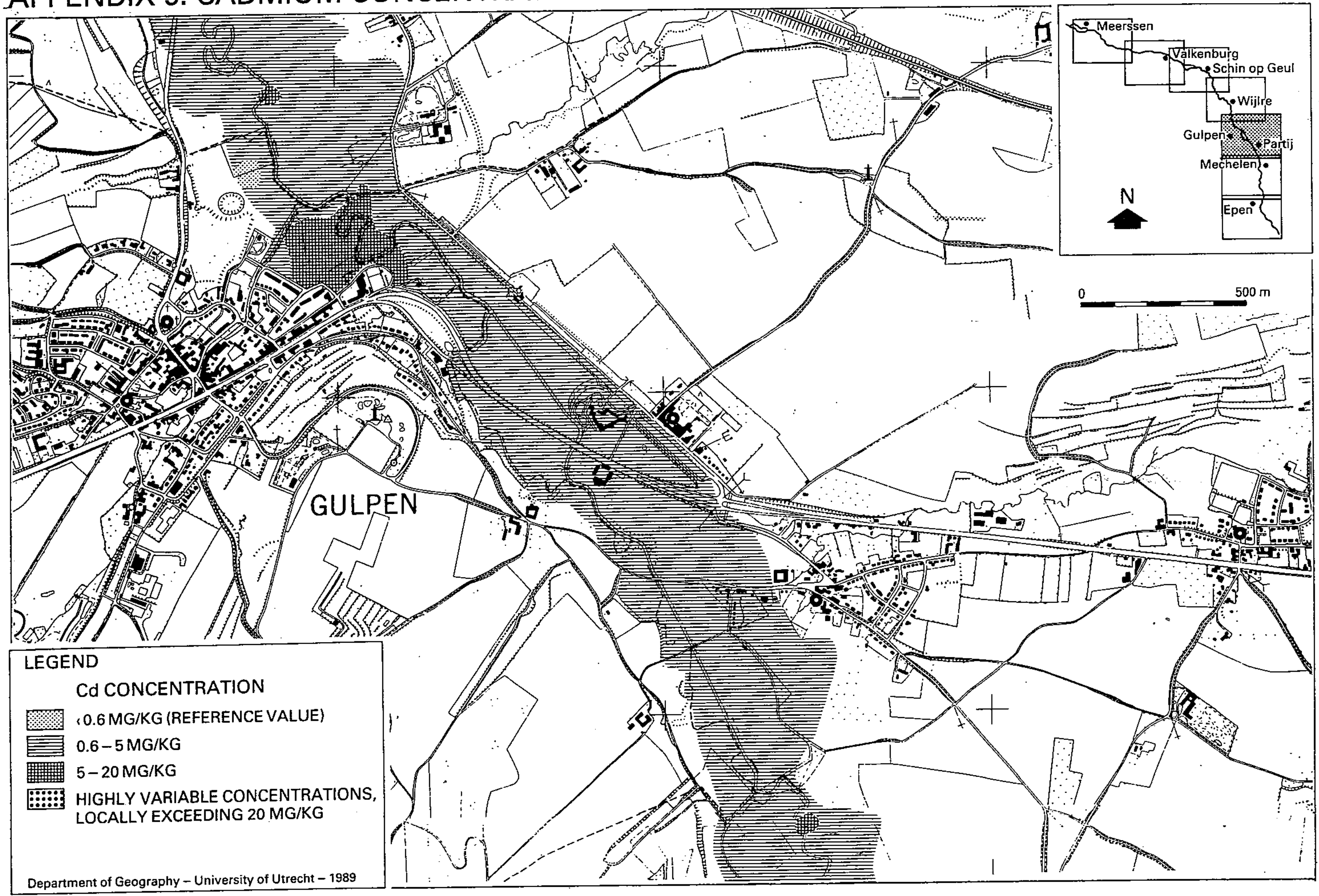

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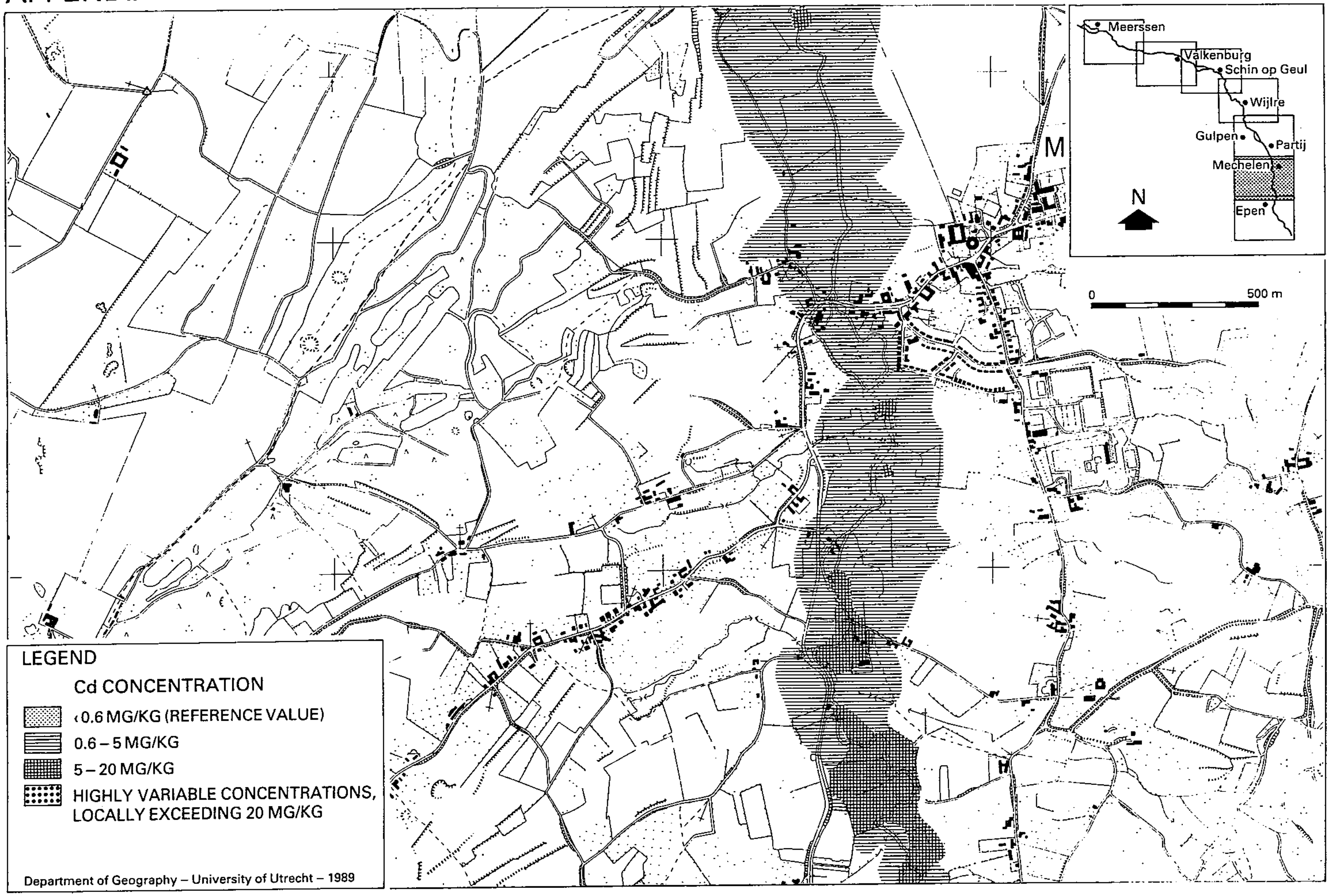

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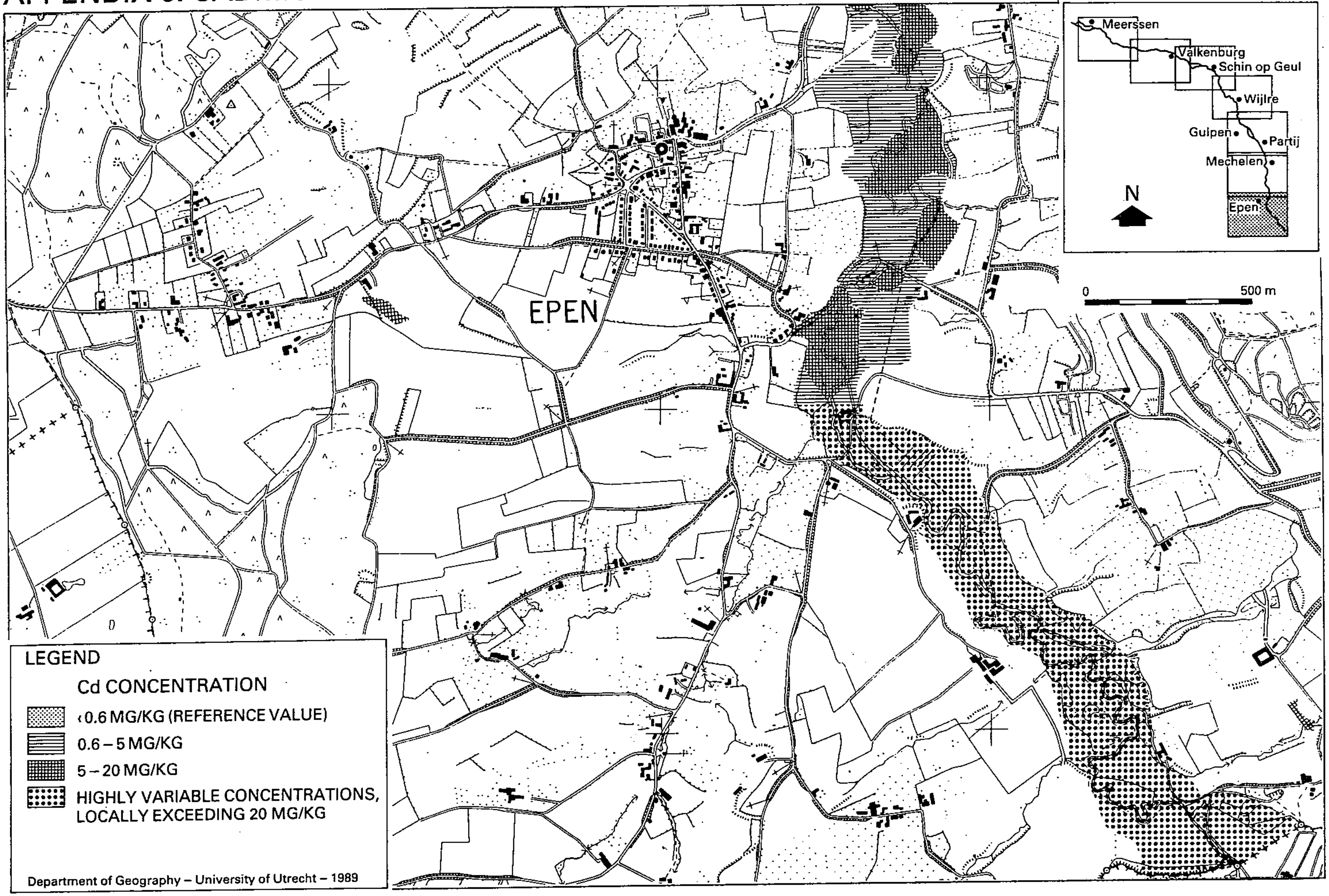

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