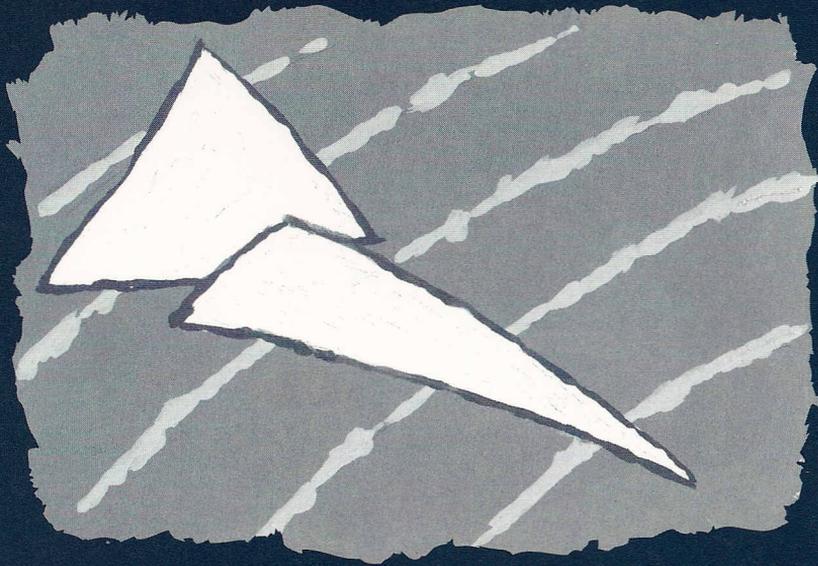


GEOLOGICA ULTRAIECTINA

Mededelingen van de
Faculteit Aardwetenschappen
Universiteit Utrecht

No. 216

Soil acidification monitoring in the Netherlands



Gerben Mol

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Soil acidification monitoring in the Netherlands

Bodemverzuringmonitoring in Nederland

(met een samenvatting in het Nederlands)

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Gerben Mol

geboren op 3 april 1971
te Koudekerke

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To my son, Camiel

“It is rare that one human activity affects just one aspect of the environment. Also, conversely, it is rare that one environmental problem is caused solely by just one kind of human activity.”

(from a paper by W. Stigliani in Environmental Monitoring and Assessment, 10, 245 - 307)

“Science is rooted in creative interpretation. Numbers suggest, constrain, and refute; they do not, by themselves, specify the content of scientific theories. Theories are built upon the interpretation of numbers, and interpreters are often trapped by their own rhetoric. They believe in their own objectivity, and fail to discern the prejudice that leads them to one interpretation among many consistent with their numbers.”

(from The Mismeasure of Man by S.J. Gould)

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VOORWOORD

“De opmerking ‘je hoeft het alleen nog maar op te schrijven’ kan uitsluitend zijn gemaakt door iemand die zich nooit langer dan vijf minuten verdiept heeft in wat dat nu eigenlijk is, schrijven.” Overtuigd van zijn intellectuele kwaliteiten ben ik niet, een liefhebber van zijn romans ben ik evenmin, maar de hier aangehaalde zin van Arnon Grunberg die hij schreef in een artikel in het NRC Handelsblad van 23 februari 2001 is een scherpe observatie. Ook voor een proefschrift, nee, zeker voor een proefschrift geldt deze constatering. Het schrijfproces dat onderdeel uitmaakt van de totstandkoming van een proefschrift is veeleer een denkproces, pas door het op te schrijven wordt de in de onderzoeksresultaten verborgen informatie ontsloten en gestructureerd. In dat schrijf-denkproces ben ik door mijn co-promotoren Simon Vriend en Pauline van Gaans ingewijd, in wat Giuseppe Frapporti in het voorwoord van zijn proefschrift “de sessies” noemt. Simon en Pauline, bedankt voor deze initiatie, ik ben er zeker van dat het me de rest van mijn leven ten voordeel zal strekken.

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De twee studenten uit Wageningen zijn bij het onderzoek betrokken geraakt door toedoen van Erwin Temminghoff, universitair docent bij de sectie Bodemkwaliteit van de Universiteit Wageningen. Ik ken Erwin al sinds mijn eerste afstudeeronderzoek in 1993. De samenwerking is altijd prettig geweest, en het verbaasde mij dan ook niet dat hij onmiddellijk bereid was om mijn onderzoek op te nemen in zijn lijst van mogelijke afstudeeronderwerpen voor Wageningse studenten. Naast de samenwerking met Esther en Gerda leverde het hernieuwde contact met Erwin vruchtbare resultaten op door de toepassing van het speciatiemodellerprogramma ECOSAT op het bodemvocht uit de zandgronden van Nederland. De combinatie van de Utrechtse en de Wageningse aanpak heeft zeker geleid tot extra inzichten. Ik wil daarom Erwin bedanken voor de ruimdenkendheid om Wageningse studenten “uit te lenen” aan Utrecht en voor de prettige en open manier van samenwerken.

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gevarieerder kunnen zijn. Met Guus Loch heb ik veel te maken gehad omdat we op een of andere manier steeds verzeild raakten in dezelfde situaties, was het niet een excursie of veldwerk, dan was het wel een congres. Altijd waren dat genoeglijke ontmoetingen, misschien wel door een gedeelde Wageningse achtergrond. Het is onmogelijk iedereen van een persoonlijk commentaar te voorzien, maar Pieter Kleingeld en Dineke van de Meent verdienen nog een aparte vermelding. Pieter toonde zich altijd bereid mee te denken over technische aspecten van het onderzoek, en hij heeft in dit onderzoek een belangrijke rol gespeeld in de ontwikkeling van de canisters die zijn gebruikt voor het uitcentrifugeren van het bodemvocht. Dineke is de laatste collega aan wie ik nog wat woorden wil wijden, maar daarmee zeker niet de minste. Zij was het van wie ik uitgebreide ondersteuning kreeg in het lab. Zij was ook degene die steeds weer die lastige vragen stelde als 'is dat wel schoon genoeg' en 'moeten die niet gekoeld bewaard worden en kan dat wel zo lang als ze niet zijn aangezuurd'. Dit dwong mij steeds weer om daar verantwoording over af te leggen en het behoevde mij voor al te laconiek gedrag.

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SAMENVATTING

Het laatste kwart van de twintigste eeuw wordt onder andere gekenmerkt door een enorme toename van het milieubewustzijn en de daarbij horende aandacht voor het ontwikkelen van een milieubeleid. Een van de instrumenten die van essentieel belang zijn voor een goed functionerend milieubeleid is de milieumonitoring, bestuurders hebben deugdelijke monitoringsystemen nodig voor het identificeren van problemen, het vaststellen van prioriteiten, en om na te gaan of de afgekondigde maatregelen het gewenste effect sorteren. Het doel van dit proefschrift is een bijdrage te leveren aan de wetenschappelijke onderbouwing van de monitoring van abiotische milieucompartimenten. Hiertoe is een onderzoek opgezet dat twee sporen volgt. Enerzijds is een analyse gemaakt van de ontwikkeling van de milieumonitoring in het licht van de ontwikkelingen in het milieubeleid in het algemeen. Anderzijds is voor een van de monitoringsystemen uit de praktijk, het bodemverzuringsmetnet, een gedetailleerde studie gedaan waarbij een uitgebreide monstercampagne de basis vormde voor een analyse van de mogelijkheden om voortschrijdende bodemverzuring te monitoren. Deel I van dit proefschrift, bestaande uit de hoofdstukken 2 en 3, beschrijft het eerste onderzoeksspoor, deel II, de hoofdstukken 4 tot en met 7, beschrijft het tweede onderzoeksspoor.

In hoofdstuk 2 worden de belangrijkste ontwikkelingen van de milieumonitoring en het milieubeleid geïnventariseerd en geanalyseerd. Deze beschrijvende en inventariserende studie is nuttig (vooral ook voor de buitenlandse lezer) omdat het merendeel van de beschreven informatie slecht toegankelijk is, het is slechts terug te vinden in beleidsnota's en andere niet gecatalogiseerde rapporten (die bovendien in het Nederlands geschreven zijn). Echter, de Nederlandse ervaring met milieumonitoring (en milieubeleid) is buitengewoon interessant vanwege de complexe situatie in een land dat een grote kleinschalig landschappelijke variatie combineert met een zeer intensief landgebruik voor functies als landbouw, industrie, en recreatie en natuur. Deze situatie vraagt om een uitgebalanceerd milieu- en ruimtelijk ordeningsbeleid waarin het monitoringsinstrument een belangrijke rol vervult. Het gaat daarbij zowel om het monitoren van de kwaliteit van abiotische milieucompartimenten en die van ecosystemen (d.w.z. met inbegrip van de biota) als om het monitoren van het milieubeleid zelf (beleidsmonitoring). In deze studie gaat de aandacht primair uit naar het monitoren van de abiotische (chemisch-fysische) kwaliteit van milieucompartimenten, een activiteit die goed ontwikkeld is gezien het feit dat voor ieder compartiment (lucht, water, grondwater, bodem) inmiddels een of meerdere meetnet(ten) zijn opgezet. Indien de ontwikkeling van deze meetnetten wordt geanalyseerd in het licht van de ontwikkeling van het milieubeleid dan worden een paar lijnen duidelijk: 1) de aandacht ontwikkelt zich van kwantiteit (grondwater- en rivierstanden) naar kwaliteit (chemische en biologische parameters), 2) er is een ontwikkeling van aandacht voor een of enkele contaminanten naar milieuprocessen als geheel (de thematische aanpak met thema's als verdroging, verzuring, en vermisting), en 3) er is een ontwikkeling van (antropocentrische) aandacht voor volksgezondheid naar integrale ecosysteem gezondheid. Nederland is een land met een hoge organisatiegraad en een hoog opleidingsniveau waarin dit soort ontwikkelingen snel plaatsvinden. Na de analyse in hoofdstuk 2 blijft echter de conclusie dat in de milieumonitoringspraktijk een stevige basis grotendeels ontbreekt omdat wisselende politieke interesse sterk doorwerkt in de praktijk van het meten. Een monitoringsysteem is naar zijn aard echter een systeem dat bedoeld is lang operationeel te zijn. Dit is slechts mogelijk als wordt uitgegaan van heldere uitgangspunten en doelstellingen die hun oorsprong vinden in wetenschappelijke kennis van het te monitoren compartiment.

Samenvatting

In hoofdstuk 3 wordt voor de monitoringsactiviteiten in het bodemcompartiment een korte analyse gemaakt van mogelijke tekortkomingen. Deze kritische analyse vormt een deel van de onderzoeksvragen die onderwerp zijn van het tweede spoor in dit proefschrift. Het bodemcompartiment werd pas als laatste voorzien van een meetnet omdat er lange tijd scepsis heerste over de mogelijkheden om trendmatige ontwikkelingen als gevolg van diffuse verontreiniging te onderscheiden van de ruimtelijke variatie die aanwezig is in de bodem. Eind jaren 80 toonde onderzoek aan dat dit met een statistisch goed ontworpen netwerk toch mogelijk zou moeten zijn. Vanaf die tijd ontwikkelen zich zowel op nationaal als op provinciaal niveau bodemmeetnetten voor drie thema's, namelijk verspreiding van contaminanten (zware metalen, pesticiden, PCB's etc.), verzuring, en vermessing. De doelstellingen van deze meetnetten zijn het vastleggen van de huidige kwaliteit en het volgen van de ontwikkelingen in die kwaliteit in de tijd. Op basis van een paar jaren monitoren van de bodemkwaliteit en de rapporten die daarover verschenen zijn wordt in hoofdstuk 3 een aantal aspecten van deze eerste pogingen kritisch beschouwd. Zaken die aan de orde komen zijn de bemonsteringstechniek, het bemonsteringsschema, het aanleggen van een monsterarchief, het concept van de homogene landschapstypen, het idee van vaste monitoringslocaties versus steeds wisselende locaties, de invloed van andere bronnen van variatie zoals seizoenfluctuaties, en de keuze van parameters binnen een meetnet.

Het tweede onderzoeksspoor richt zich zoals gezegd specifiek op de mogelijkheden voor een meetnet bodemverzuring. Het bleek noodzakelijk hiervoor een eigen bemonsteringscampagne op te zetten omdat de door de verschillende provincies verzamelde data op veel punten van elkaar verschilden. De bemonsteringscampagne bestond uit twee onderdelen. Ten eerste de hoofdcampagne waarin 92 locaties in 6 provincies eenmalig zijn bemonsterd, en ten tweede de seizoenscampagne waarin een subset van 20 locaties in de provincie Utrecht 8 keer is bemonsterd over een periode van 2 jaar (1998/1999). Alle locaties zijn naaldboomopstanden op Pleistocene zandgronden die onderdeel uitmaken van de diverse provinciale meetnetten bodemverzuring. Op iedere locatie is op twee dieptes een monster genomen volgens de procedure beschreven in Appendix A. Een uitgebreide parameterset die zowel betrekking heeft op het bodemvocht en de totale samenstelling van de vaste fase, als op de reactiviteit van de vaste fase is aan de monsters geanalyseerd. De resultaten worden besproken in hoofdstuk 4 tot en met 6. Hoofdstuk 7 vormt de synthese van het complete materiaal.

In hoofdstuk 4 worden de resultaten van de hoofdcampagne beschouwd in het licht van de processen die leiden tot bodemverzuring en de mogelijkheden die aanwezig lijken om bodemverzuring te monitoren. Begin jaren 90 is een monitoringstrategie voor bodemverzuring ontworpen die schatplichtig is aan de methoden die zijn ontwikkeld in de fundamentele onderzoekstakken, met name de zogenaamde protonbudgetten. Het resultaat hiervan is dat enkele controverses die in die tijd nog speelden in het fundamentele onderzoek doorwerken in de huidige praktijk van de bodemverzuringmonitoring en zodoende de interpretatie van de resultaten bemoeilijken. De voornaamste knelpunten hierbij zijn onderwerp van onderzoek in dit hoofdstuk, namelijk: capaciteits- versus intensiteitsparameters, de keuze van de monitoringsdoelstelling, en de natuurlijke variatie in het bodemcompartiment. Belangrijke conclusies zijn: 1) het vrijkomen van aluminium uit veldspaten en secundaire Al mineralen is de belangrijkste bron van zuurbuffering, 2) dit proces blijkt ook al onder natuurlijke omstandigheden substantieel bij te dragen, 3) de

gemiddelde uitloging van het zuurneutraliserend vermogen van de vaste fase in de bovengrond komt goed overeen met de schatting van de totale zuurbelasting sinds de laatste ijstijd; de geschatte antropogene bijdrage ligt tussen de 20% en 50%, 4) zowel in de vaste fase als in het bodemvocht is een duidelijk regionaal patroon aanwezig dat ook consequenties heeft voor parameters die algemeen gebruikt worden om de verzuringstoestand van de bodem in te schatten.

In hoofdstuk 5 staat de vaste fase van de Pleistocene zanden in Nederland centraal. Zij wordt geochemisch gekarakteriseerd aan de hand van de analyses van de 184 monsters uit de hoofdcampagne en de belangrijkste natuurlijke en antropogene bronnen van variatie worden geïdentificeerd met behulp van factoranalyse. De geochemische armoede van deze gronden blijkt uit de zeer hoge SiO_2 gehalten en de lage gehalten aan overige oxiden. Vergelijking van de totale samenstelling van de bovengrond met die van de ondergrond duidt op aanrijking van de bovengrond met S, Br, Pb, en Zn, en uitloging uit de bovengrond van Al, Na, K, en Ca. De 3 voornaamste bronnen van variatie zijn van natuurlijke aard, te weten de aluminosilicaten, het organisch materiaal (OM) met bijbehorende kationomwisselcapaciteit (CEC), en de zware mineralen. Daarnaast zijn 3 antropogene factoren geïdentificeerd. Een verdere uitwerking van de in hoofdstuk 4 gevonden geochemische regionaliteit in de Pleistocene zandgronden levert, kort gezegd, het volgende beeld op: de noordelijke provincies worden vooral gekarakteriseerd door hoge OM gehalten, de Holoceen beïnvloedde regio wordt gekarakteriseerd door mineralogische rijkdom en een afwijkende mineralogische samenstelling, en Noord Brabant heeft de armste mineralogie maar de hoogste zware mineralen en zware metalen gehalten. Ten slotte worden de normen die worden gehanteerd binnen het bodemkwaliteitsbeleid afgezet tegen de natuurlijke achtergrondgehalten in deze arme zandgronden. De conclusie is dat de normen geen voorspellende waarde hebben voor het natuurlijke achtergrondgehalte in deze gronden, een alternatieve methode wordt geïllustreerd aan de hand van de Pb en Zn gehalten.

In hoofdstuk 6 staat het bodemvocht van de Pleistocene zandgronden centraal. In de huidige bodemverzuringmeetnetten gaat de meeste aandacht uit naar het bodemvocht. Echter, de relatief hoge reactiesnelheid van dit medium maakt dat het uiterst gevoelig is voor allerlei vormen van variatie die ongewenst zijn in een meetnet omdat ze de variatie waar men op uit is kunnen overschaduwen. De bronnen van variatie die in dit hoofdstuk aan bod komen, naast een algemene chemische karakterisering, zijn chemische speciatie (verschijningsvorm), geochemische regionaliteit, en korte termijn temporele variatie. De concentraties in het bodemvocht indiceren de vergevorderde verzuringstoestand van de Pleistocene zandgronden. Het tekort aan anorganisch anionen op de ionenbalans van het bodemvocht wordt gecompenseerd door de opgeloste organische stof (DOC). Vergelijking van de concentraties aan zware metalen in het bodemvocht met die in het grondwater bevestigt de relatieve immobiliteit van zware metalen. De chemische speciatie wordt voornamelijk bepaald door de DOC concentratie, de pH en de totale kationconcentratie. Voor elementen als Al is het speciatiegedrag uitermate complex vanwege het effect dat de pH heeft op zowel de complexatie door DOC als de oplosbaarheid van mineraalfasen in de bodem. De regionale patronen in de vaste fase, met name wat betreft de reactiviteit ervan, vinden hun weerslag in de regionaliteit die aanwezig is in het bodemvocht. Ook in het bodemvocht is Noord Brabant de meest afwijkende regio, met hoge concentraties van Al en zware metalen die waarschijnlijk het gevolg zijn van de aanwezigheid van veel intensieve

veehouderij en de historie van de metaalindustrie in de regio. De kort temporele patronen van enkele belangrijke parameters zijn te relateren aan de maandelijkse temperatuur- en neerslaggegevens van 1998 en 1999. Algemene patronen die naar voren komen uit het seizoenonderzoek zijn: 1) de bovengrond is variabeler dan de ondergrond, 2) er zijn grote verschillen in temporele fluctuatiepatronen tussen locaties, 3) een milde extractie met 0.01 M CaCl_2 is in staat een gedeelte van de kort temporele variatie te dempen.

De implicaties van dit onderzoek voor de praktijk van de bodemverzuringmonitoring vormen de belangrijkste ingrediënten van hoofdstuk 7, de synthese. Aan twee essentiële voorwaarden moet worden voldaan alvorens een succesvolle monitoringsstrategie kan worden ontwikkeld. Ten eerste is een grondige kennis van de bodemverzuringprocessen nodig, en ten tweede moet de monitoringsdoelstelling duidelijk zijn geformuleerd, binnen de randvoorwaarden die het te monitoren compartiment, in dit geval de bodem, stelt. Mijns inziens is bodemverzuring een capaciteitsfenomeen; een zuurvrucht dringt de bodem binnen en wordt daar gebufferd door het oplossen van bodemmineralen. Hierbij komen kationen zoals Ca, Mg, K, Na, en Al en Fe vrij in de bodemoplossing. Het gevolg is dat de zuurneutraliserende capaciteit, de ANC, van de bodem afneemt en dat de samenstelling van de bodemoplossing verandert. In de bodem ontstaat na verloop van tijd een steady state situatie waarbij de samenstelling van het bodemvocht alleen nog drastische veranderingen vertoont als de bufferingskarakteristiek van de vaste fase verandert of wanneer de zuurvrucht sterk toe- of afneemt. Het eerste is in de Nederlandse Pleistocene zandgronden niet aan de orde omdat er nog een enorme voorraad aan alumino-silicaten in deze bodems zit, het tweede is de meest waarschijnlijk oorzaak van een veranderende bodemvochtsamenstelling. In mijn optiek zijn voor het monitoren van de verzuringstoestand van de bodem de veranderingen in de vaste fase van belang. Het is essentieel inzicht te hebben in de omvang, de snelheid, en de aard van deze veranderingen en of de veranderingen op hun beurt invloed hebben op deze karakteristieken. Pas als dit inzicht er is valt te denken aan een meetnet louter ter ondersteuning van het bodembeleid gebaseerd op een beperkte parametersselectie, tot die tijd zal de monitoring een wetenschappelijker stempel hebben met als belangrijkste doelstelling het ophelderen van bovengenoemde punten. De suggesties die hiervoor in hoofdstuk 7 worden gedaan komen in het kort hierop neer: 1) volg de ontwikkelingen in de totaalgehalten in de vaste fase m.b.v. XRF bepalingen, de voorgestelde termijn hiervoor is 10 tot 20 jaar; 2) bepaal m.b.v. een of meerdere extracties de aard en de omvang van de verschillende reactieve bufferende voorraden, de voorgestelde termijn hiervoor is 5 jaar; 3) bepaal aan een deel van de monitoringslocaties tweemaandelijks de fluctuaties in de bodemoplossing, hetzij aan uitgecentrifugeerd bodemvocht hetzij m.b.v. een milde extractie met 0.01 M CaCl_2 , dit om de vijfjaarlijkse gegevens over de reactieve voorraden juist te interpreteren, deze worden namelijk door heel extreme weergeïnduceerde schommelingen in het bodemmilieu beïnvloed. Het is hierbij van essentieel belang te benadrukken dat een zo compleet mogelijke parameterset onmisbaar is voor het verkrijgen van het benodigde inzicht, en dat voor gegevens die gebruikt worden in een monitoringssituatie goede meetresultaten een *conditio sine qua non* zijn. Speciaal de binnen-laboratorium en de tussen-jaar variatie in hetzelfde laboratorium zijn van grote importantie omdat ze gemakkelijk de trend waarnaar men in een meetnet op zoek is kunnen overschaduwen. Tot slot dient bij de interpretatie van de resultaten voldoende aandacht te zijn voor andere bronnen van variatie die verschillen tussen regio's of tussen jaren kunnen verklaren.

ABBREVIATIONS AND DEFINITIONS

Al surplus	total Al concentration of the solid phase minus the maximum amount of Al that can stoichiometrically be associated with feldspars assuming all Na, K, and Ca to be present in feldspars (unit: mol _c kg ⁻¹ dry soil)
Al/BC ratio	ratio of the Al concentration and the sum of the concentrations of the base cations (BC) Ca, Mg, Na, and K in displaced soil solution on an equivalent basis
ANC _(s)	Acid Neutralizing Capacity of the Solid phase based on total concentrations of oxides as measured with X ray fluorescence spectrometry (XRF) and defined as (unit: mol _c kg ⁻¹ dry soil): $6(\text{Al}_2\text{O}_3) + 2(\text{CaO}) + 2(\text{MgO}) + 2(\text{K}_2\text{O}) + 2(\text{Na}_2\text{O}) + 2(\text{MnO}) + 2(\text{FeO}) - 2(\text{SO}_3) - 2(\text{P}_2\text{O}_5)$
BC	base cations, viz. Ca, Mg, Na, and K
CEC	Cation Exchange Capacity, in this thesis estimated by the cation concentrations in the extractions with 0.01 M CaCl ₂ and 0.43 M HNO ₃ , and defined as (unit: mol _c kg ⁻¹ dry soil): $\text{Na}(\text{CaCl}_2) + \text{K}(\text{CaCl}_2) + \text{Mg}(\text{CaCl}_2) + \text{Mn}(\text{CaCl}_2) + \text{Fe}(\text{CaCl}_2) + \text{Al}(\text{CaCl}_2) + \text{Ca}(\text{HNO}_3)$
ΔAl	$6(\text{Al}_2\text{O}_3)_{(\text{subsoil})} - 6(\text{Al}_2\text{O}_3)_{(\text{topsoil})}$ (unit: mol _c kg ⁻¹ dry soil)
ΔANC _(s)	$\text{ANC}_{(s)(\text{subsoil})} - \text{ANC}_{(s)(\text{topsoil})}$ (unit: mol _c kg ⁻¹ dry soil)
ECOSAT	Equilibrium Calculation Of Speciation And Transport. A computer program used to make the speciation calculations in this thesis.
FBC	Feldspar related Base Cations, viz. Ca, Na, and K
mol _c	notation for mol charge equivalent common in acidification literature
NICCA	Non Ideal Consistent Competitive Adsorption. Part of the algorithm used in ECOSAT to describe adsorption of cations to DOC in a thermodynamically consistent way, considering the effects of the binding site heterogeneity of the DOC, competition between different cations and protons, both specifically and electrostatically bound, and ion specific non ideality.
PCA-V	Principle Component Analysis with Kaiser Varimax rotation. A statistical technique used to identify underlying factors that explain the correlations among a set of variables.
reactive Al	0.43 M HNO ₃ extractable quantity of Al, reactive quantities of other cations are defined similarly

1 INTRODUCTION

1.1 General introduction

The last decades of the 20th century are characterized by a vast increase in activities developed and measures taken by the authorities to accommodate the fear of environmental problems that boomed since the late 1960s. The growing environmental awareness and the subsequent incorporation of environmental values and arguments in the social discourse and practice has been multifaceted and complex. Within this diverse context, the present study took shape; a shape that reflects the socio-political aspects tied in with environmental attention in general and environmental research in specific.

Essential to this study is the increased need for the authorities to monitor the development of the quality of the environment. Policy makers need monitoring systems to identify problems, to list priorities, and to check whether measures taken have the desired effects on environmental quality. For these purposes not only monitoring systems are needed, also reference values for environmental quality are required to judge the values measured within the monitoring setting. The aim of this thesis is to contribute to the scientific foundation of environmental quality management in general and that of soil quality and soil acidification monitoring specifically.

1.2 Motivation for a focus on soil acidification monitoring

Understanding the complex soil processes and designing a strategy to monitor them is difficult in itself. Providing a meaningful and scientifically well founded critique on designs already in use, however, is even more demanding because choices were often made after ample consideration and in good conscience. As a result changes are only made when it is undeniably proved that better options are available, and even then changes are not readily made. Therefore curtailment of the subject was necessary, especially because the sampling effort took place within the framework of a 4-year Ph.D. research project. Acidification, general spread of contaminants (like heavy metals and organic micro-pollutants), and eutrophication are the three environmental themes that were eventually being monitored in the soil compartment. For several reasons soil acidification became the focus of the research campaign described in this study. First, acidification monitoring proved to constitute the major effort in provincial soil quality monitoring. Second, soil acidification is the most involved of the three themes with respect to the processes taking place in the soil as it combines many aspects of the other two themes, like for instance the availability of heavy metals and the microbial transformations of nitrogen and sulphur, with an array of phenomena unique to soil acidification. It is therefore, from a scientific perspective, the most challenging part of the soil quality monitoring networks, and, from a practical perspective, the

part most prone to flaws in design that can severely hamper the interpretation of monitoring results; a phenomenon that has (in our evaluation) indeed shown to pose problems in the practice of soil acidification monitoring.

1.3 Two lines of research

Environmental quality management is an activity that typically takes place in the field of tension between scientific insights into the intrinsic limitations of natural systems, and political aims and wishes. Environmental monitoring suffers from this phenomenon in particular. Being one of the more technical activities the limitations of the compartment monitored are felt more directly. Part I of this thesis deals with these socio-scientific issues, with a special focus on soil quality.

The initial intention for Part II was to analyze and evaluate the available data of the soil quality monitoring networks of the provinces. This proved unfeasible because of the differences in implementation among the provinces. The most important problems are that sets of parameters that have been analyzed do not match, that analyses are contracted out to different laboratories, which is an almost certain way to obtain an inhomogeneous dataset, and that the details of sampling and analysis as well as the time of year of monitoring differ per province. Moreover, the operational details sometimes contained crucial errors preventing any serious interpretation of results. A first example of such error is the sampling of fixed depths in the soil profile. This is unacceptable because it very often results in lumping together different soil horizons, thereby ignoring the fact that soil horizon differentiation is a very important feature of the soil that has to be appreciated, also within a monitoring setting. A second recurring error is the mixing of soil material for the preparation of composite samples *in the field*. This is considered an inadequate method even with sandy soils. An additional problem in the light of the soil solution displacement techniques that are generally performed within the monitoring networks, is the loss of soil moisture that results from mixing in the field.

Therefore a research dataset was created specifically for this study. The sampling and analytical procedures used (see Appendix A), although improved and extended, still resemble those of the provincial soil quality monitoring systems because an evaluation of these systems is one of the main goals of this thesis. Two obvious improvements in the sampling protocol are the sampling of soil horizons as such, independent of their exact depths in the profile, and transportation of the separate samples to the laboratory and creating composite samples in the laboratory. Furthermore, extreme attention has been paid to minimizing unwanted sources of variation such as chemical changes in the soil solution immediately after sampling and small differences in operational details of the extraction methods used in this study. Therefore the soil solution was displaced within 24 hours and critical parameters such as pH, NH₄, and the anions NO₃, SO₄, and Cl were analyzed immediately. The operational variability of the extraction methods was eliminated by preparing and analysing all samples in one batch (see for all details Appendix A). Part II thus contains a discussion of the results of the two sampling campaigns carried out for this study.

1.4 Sampling

The specific issues addressed in this study can be summarized as follows:

- what data are needed to understand and assess the soil acidity status of sandy soils?;
- is there natural spatial variation in the geochemistry of acid sandy soils, what is its nature, and what does it mean for soil acidification?;
- do the different media measured show seasonal patterns for the parameters of interest?;
- if so, how does this variation compare to the spatial variation and to the variation that is to be expected over many years?;
- what are the implications of the findings regarding the above questions for soil acidification monitoring?

This combination of research questions necessitated an extensive sampling campaign, referred to as the main campaign, and an additional seasonal campaign.

For the main campaign 92 locations in the Pleistocene areas of the Netherlands were sampled at two depths. All sampled locations, each about 10,000 m², are coniferous forest stands on sandy soils (see chapters 2 and 4 for a more detailed description of the natural setting). To increase the applicability of the results, the set of locations was selected from the monitoring sites of six of the Dutch provinces. The main campaign took place during 5 consecutive weeks in May-June 1999. The campaign was set up to address multiple aims of which the most important are identifying the parameters needed to understand soil acidification, testing the suitability of different monitoring media, and assessing the regional geochemical variability. The first two aims implied the analysis of a large set of parameters as well as the application and testing of different laboratory methods both relating to the solid phase and to the soil solution to assess their possible use as a monitoring medium. The third aim originated from the need to compare monitoring results interprovincially, which proved to be hard with the datasets gathered by the provinces. The proper way to achieve insight into this issue is to assemble a dataset that is coherent among the different provinces.

Sampling for the seasonal campaign took place during 8 sampling rounds evenly spaced over two years time (1998 and 1999). The locations that were sampled are part of the soil acidification monitoring network of the province of Utrecht (see chapter 6 for details). The sampling rounds each took about two weeks for sampling, sample treatment and the subsequent analysis of the parameters (see Appendix A for more analytical details). The focus in this campaign is on short term temporal fluctuations, a natural source of variation resulting from for instance seasonal patterns or weather induced phenomena that can interfere with monitoring results. Especially so, because displaced soil solution is the monitoring medium now favoured by many authorities. The soil solution is most likely to reflect these short term fluctuations because it is the fastest reacting phase in the soil compartment. To assess the possible influence of short term temporal variation on monitoring results and to test the sensitivity of the different media that could be adopted for monitoring, the same analytical methods as in the main campaign have been evaluated. Of course, repeated analysis of the total element content of the solid phase is not necessary because it is not prone to periodic seasonal fluctuations.

1.5 Outline

As already mentioned briefly, part I of this thesis focuses on the socio-political setting in which the environmental activities evolved. In chapter 2 the development of environmental monitoring activities is considered in the light of the developments in Dutch environmental policy in general. The geographical and political setting is clarified in short, and the concept of monitoring is delimited. The actual historical overview of developments in environmental policy and environmental monitoring consumes the major portion of this chapter. It concludes with a critical analysis of the possible obstructive nature of political influence on monitoring activities.

Part I continues with chapter 3, which forms a short prelude to the main subject of this research project discussed in part II of this thesis. This chapter gives a short analysis of the soil quality monitoring activities of the national and provincial authorities. The second half focuses on some scientific objections to the operational choices made for these monitoring networks. The findings of this short desk study formed the point of departure for the two sampling campaigns already introduced, and they will be used again in chapter 7 to guide the overall discussion.

The major results from the sampling campaigns are discussed in part II of this thesis. In chapter 4, the central chapter of this thesis, an extensive discussion is devoted to the information that can be obtained from the data with regard to soil acidification. To put the data in perspective, the chapter contains a review style introduction in which the choices made for the soil acidification monitoring networks are traced back to the historic developments in the more fundamental research arena. The aim of the discussion of the data of the main campaign that forms the major portion of chapter 4 is to clarify some of the misconceptions revealed in the introduction. Central issues in the discussion are a characterization of the major chemistry of the solid phase and the identification of the ultimate source of acid buffering, an assessment of the information that can be extracted from the different laboratory methods used, and a test of the usefulness of the historic approach to assess the acidity status of acid sandy soils in a regional setting. Further issues that are discussed in this chapter are the relative amount of the depletion of the acid neutralizing capacity due to natural and anthropogenic acid deposition, the geochemical regionality and the consequences of all aspects discussed for the practice of soil acidification monitoring.

In chapter 5 the solid phase related results from the main campaign are presented in the form of a general geochemical characterization of Pleistocene sandy soils in the Netherlands. Both the concentrations and the reactivity of the major and trace elements in the solid phase will be discussed following a four step approach. The first step involves the presentation of the concentration range of the elements in the solid phase, in combination with a comparison of these concentrations to the average upper crustal concentrations. The second step amounts to the identification of the major sources of variation in the solid phase of the sandy soils in the Netherlands. The third step further elaborates on the geochemical regionality already mentioned in chapter 4 by extending it to the trace elements and by assessing the relative importance of the sources of variation identified in step 2 in view of this regionality. The fourth and final step is concerned with defining natural background values and is therefore more directly related to environmental applications of geochemical

knowledge, as these background values can function within the policy framework of reference values.

In chapter 6 focus is on the soil solution related data and the possible sources of variation in the soil solution. The results from both the main and seasonal campaigns are dealt with in this chapter. The general chemical characteristics of the soil solution of acid sandy soils will be presented as well as the variability of its composition as result of chemical speciation, regional geochemical patterns, and short term temporal fluctuations.

In chapter 7 this thesis is concluded with a synthesis of all issues discussed in the previous chapters. Special focus is on the consequences for soil acidity monitoring, and some suggestions for future scientific research are made.

The chapters 2 to 6 are published, submitted, or intended for submission as individual, multi-authored papers. To guarantee the internal integrity of each paper, they have been used in unrevised form. Some overlap is therefore inevitable.

PART I Monitoring and Environmental Policy

Chapter 2 Environmental monitoring in the Netherlands;
past developments and future challenges

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Co-authors: S.P. Vriend and P.F.M. van Gaans

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Chapter 3 Future trends, detectable by soil monitoring networks?

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“Rather, in making management decisions about clean up programs, it is very important that the decision maker uses available knowledge to understand at least some of the contingencies, surprises, trade-offs, and risks inherent in the final plan of action. Only then will such decisions be informed, and the quality of thinking among decision makers maximized.”

(from a paper by W. Stigliani in Environmental Monitoring and Assessment, 10, 245 - 307)

2 ENVIRONMENTAL MONITORING IN THE NETHERLANDS; PAST DEVELOPMENTS AND FUTURE CHALLENGES

2.1 Introduction

Along with the growing concern for environmental problems came the interest to monitor the environment. Policy makers need methods to identify the problems, to list their priorities, and to check whether the measures taken have the desired effect on environmental quality. Time and money spent on environmental monitoring increased tremendously over the past 25 years. Illustrative of this development is the increasing number of monographs dealing with monitoring and the environment found in the catalogue of the Utrecht University and the Agralin catalogue (Fig.2.1).

Increasing attention for environmental monitoring is also indicated by the appearance of journals dedicated to this matter. Early journals are mainly focusing on medical and toxicological subjects as well as technological solutions. It was not until the 1980s before a growing number of journals emerged that are focusing on issues like impact assessment and environmental monitoring (Table 2.1).

The diversity of publications on environmental monitoring proves that it is considered an important issue in many countries and that monitoring applies to all compartments of the environment (Berger, 1997; Duijvenbooden and Lagas, 1993; Forsius et al., 1998; Gaans et al., 1995a; Hudak, 1993; Il'yin and Konarbayeva, 1996; Kas'yanova et al., 1996; Kobza, 1995; Köhl et al., 1994; Murray and Baker, 1990; Onianwa, 1988; Papritz and Webster, 1995a,b; Sanka and Paterson, 1995; Skinner and Todd, 1998; Tongway, 1995; Ukonmaanaho et al., 1998; Wraith and Das, 1998; Young et al., 1997; Zbiral, 1995).

In the Netherlands a wide variety of monitoring systems has emerged, especially during the last 25 years. The aim of this paper is to outline why and how these systems were developed, how they function, and what their potentials are for the future. We will relate their development to that of Dutch environmental policy in general. We consider this descriptive and inventory approach useful, as much of this information is virtually inaccessible for a wider public because it can only be found in uncatalogued reports and memos (written in Dutch) of the Dutch authorities and semi-governmental national institutes. Yet, because of the specific natural, demographic, and administrative aspects of the Netherlands, the Dutch experience with monitoring most certainly can be enlightening.

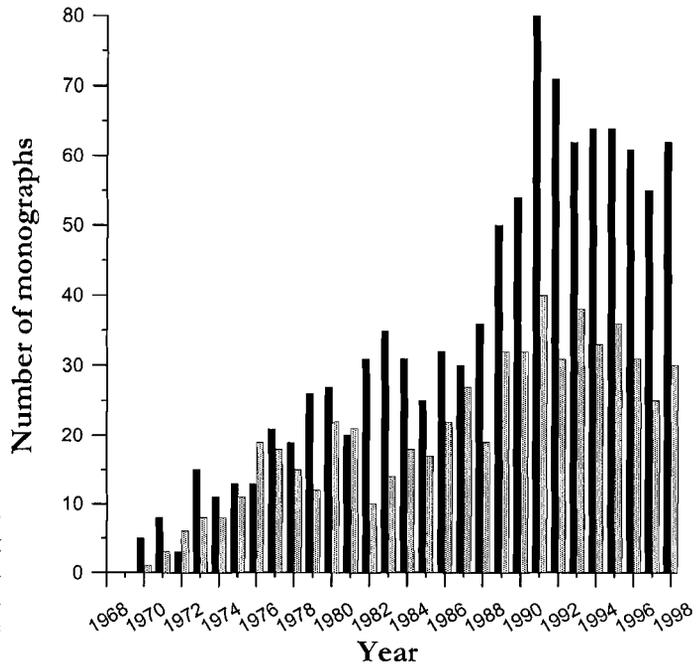


Figure 2.1
The number of monographs on environmental monitoring in two catalogues between 1970 and 1998. Agralin catalogue (black) and Catalogue Utrecht University (grey).

2.2 On the Dutch setting

2.2.1 On the Dutch environment

The Netherlands are a small country, about 37,000 km² (Bobbert, 1984), predominantly consisting of eolian, fluvial and marine sediments deposited in the Late Pleistocene and the Holocene (Staalduinen et al., 1979). Situated on the edge of the North Sea Basin, it has a flat topography. Some relief was formed during the Elsterian and Saalian ice ages (Zagwijn, 1987). Most relief was levelled by erosion and depressions were filled by sediment in the Holocene; the only features still clearly present are ice-pushed ridges (Staalduinen et al., 1979). Geomorphologic processes in the Quaternary caused a differentiation in development. This resulted in two major areas, one dominated by Pleistocene sand deposits and the other dominated by Holocene clay and peat deposits. The Pleistocene areas are generally above sea level, hydrologically dry, and poor in nutrients, whereas the Holocene landscapes, except for the coastal dunes, are mostly below sea level, hydrologically wet, and rich in nutrients (Zonneveld, 1985). A slightly more refined division can be found in figure 2.2A.

The Dutch North Sea coast has a length of about 300 km (Ven et al., 1986). Rhine, Scheldt, and Meuse are the major rivers debouching in the Dutch delta, and they determine for a large part the hydrology of the country (Breukel, 1993; Breukel et al., 1992). However, most rivers and hydrological regimes have been influenced strongly by men. In the past, marine transgressions

Table 2.1 Titles and year of appearance of some environmental journals.

JOURNAL	YEAR OF APPEARANCE
Bulletin of Environmental Contamination and Toxicology	1966
Environmental Research	1967
International Journal of Environmental Studies	1970
Environmental Pollution	1970
Journal of Environmental Quality	1972
Journal of Environmental Management	1973
Environmental Geology	1975
Environment International	1978
Environmental Impact Assessment Review	1980
Environmental Monitoring and Assessment	1981
Environmental Software	1986
Archives of complex Environmental Studies	1989

often resulted in loss of land. Since the Middle Ages the Dutch have been active in constructing dykes and reclaiming land from the sea, marshes, and other waters. Especially after World War I the increasing technical possibilities enabled the reclamation of more and more land. With high dykes and other civil technical works, the Netherlands are protected better than ever against sea and river floodings.

The Netherlands have a moderate sea climate (Cfb-climate in the Köppen system; Zonneveld, 1985). Typical values for daily average temperatures range from 2 °C in January to 17 °C in July. Mean monthly precipitation varies from around 50 mm per month in spring to about 80 mm per month in late summer (Meinardi, 1994). Net precipitation is highest in winter with a yearly excess of about 250 mm. As a result of the young sediments and the moderate climatic conditions the soils of the Netherlands are poorly developed compared to those in other parts of the world. The Dutch soil classification system distinguishes five major groups (Fig. 2.2B). From figure 2.2 it is clear that the fairly undeveloped soils can be found on the young Holocene deposits in the west. The older Pleistocene deposits in the east show more developed soils such as podsols.

The struggle between man and the sea, that has been going on for centuries, furnished the Dutch people with both the means and the attitude to zealously shape the landscape to their demands. The need for a well-considered use of the available space is enhanced by the high average population density of over 400 people per km². As a result, hardly any stretch of land and water escapes anthropogenic management.

Most people are living in the western area along the coast, in and near the big cities like Amsterdam and Rotterdam, whereas the population density in rural areas in the east, north, and south is much lower. Despite this uneven spread of population and activity, no strict spatial separation of economic functions exists within the Netherlands. Examples of this interwovenness of land use can be found in rural areas where nature generally coexists with agriculture and sometimes even with industrial activities. Within an area that is capitalized on to such an extent, the hazards of human activities to the environment are evident; environmental errors made in one field of activity immediately have repercussions on other, often more fragile, functions. A clear example of such interactions is the adverse effect that a lowering of the ground water table for agricultural purposes has on natural ecosystems, of which the majority in the Netherlands is highly dependent on water.

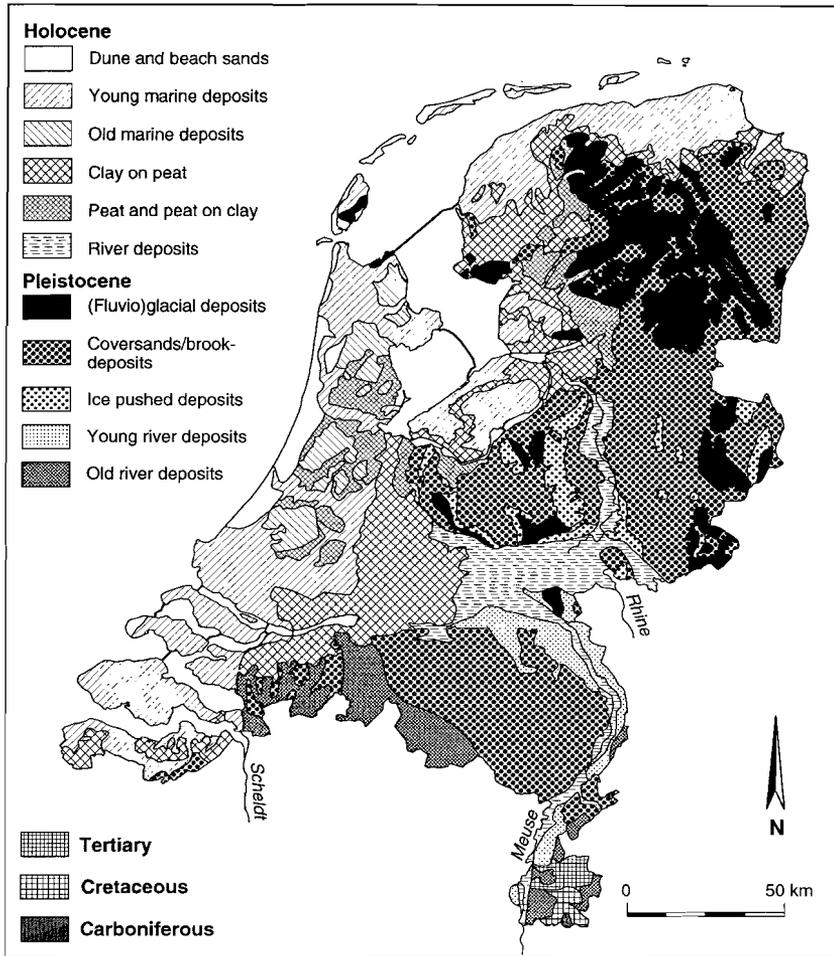
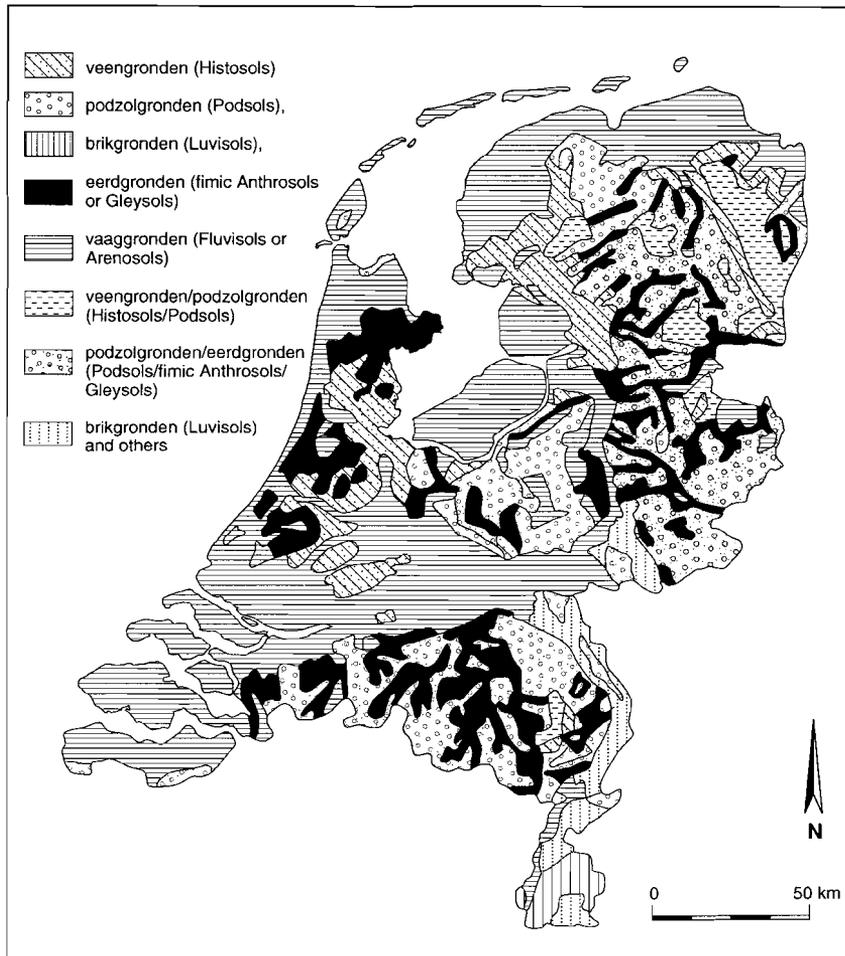


Figure 2.2 Map of The Netherlands showing a division into the major geological landscapes (A) and a division into the major soil groups (B). Map A shows the Holocene deposits subdivided into 6 groups (Dune and beach sands, Young marine deposits, Old marine deposits, Clay on peat, Peat (sometimes on clay), River deposits) that can be found in the west and in the centre (rivers) of the Netherlands. The Pleistocene deposits are subdivided into 5 groups (Glacial and fluvio-glacial deposits, Coversands and brook deposits, Ice pushed deposits, Young river deposits and Old river deposits) mainly found in the east.



(Figure 2.2 continued) In the most southern parts of the Netherlands small outcrops of Tertiary, Cretaceous and Carboniferous can be found. Map B shows the 5 major soil groups: 'veengronden' (Histosols according to FAO classification), 'podzolgronden' (Podsols), 'brikgronden' (Luvisols), 'eerdgronden' (fimic Anthrosols or Gleysols) and 'vaaggronden' (either classifying as Fluvisols or as Arenosols) (Bakker and Schelling, 1989; Driessen and Dudal, 1989). Furthermore three mixed classes have been distinguished, namely: 'veengronden' and 'podzolgronden', 'podzolgronden' and 'eerdgronden', and 'brikgronden' and others. (After: Zonneveld, 1985 and Bakker and Schelling, 1989)

The lack of unused land readily prompts a NIMBY-response, both to proposed new interferences in the environment, as to remediative actions. Responses of this kind were recently heard when decisions had to be made on large infrastructural projects, such as the high speed railroad between Paris and Amsterdam, the expansion of Schiphol airport, and the track of a railway between the Rotterdam seaport and the German hinterland. Similar reactions were heard against the construction of nuclear power plants and the storage of nuclear waste. Strong opposition was also encountered during the reclamation of the IJsselmeer-polders (between 1930 and 1968), which meant greater safety and an increase of arable land by some 150 000 ha but also the end for much commercial fishery. More recently local population complained about adverse effects of the restoration of a wetland area, which included flooded basements and the flourishing of mosquitos.

The combination of high population density, high level of industrialization, intensive forms of agriculture, a natural setting with high ground water levels and poorly buffering sandy soils - to summarize the above in Eijsackers' words (1992) - creates a complexity of the environmental landscape within the Netherlands that necessitates a balanced policy towards urban and rural management. Within this context environmental monitoring has played an important role over the last decades. The Dutch experience thereby illustrates many stages in the development of environmental and monitoring policy that may be or will be encountered in other countries as well.

2.2.2 On the Dutch administration

The administration is divided into three levels: national, provincial and municipal. Naturally, the national authorities deal with matters concerning the entire country. For environmental policy this means formulating national laws and regulations, planning of environmental targets, and establishing environmental quality threshold values. At the provincial level, the country is divided into twelve provinces (regions). The provincial authorities have to interpret and specify the national environmental guidelines into detailed regional plans. Groundwater and soil management is their direct responsibility. They also issue licences to companies and individuals that intend to develop activities in the province. They are further concerned with the approval of plans for municipal zoning and development. The municipal level, finally, is that of cities, towns, and villages, with their surrounding rural areas. As far as these rural areas are concerned, municipal authorities normally conform to provincial policy. They have the main executive tasks with respect to environmental policy, like granting permits, law enforcement, collecting of garbage and small chemical wastes (Cramer, 1991). It should be noted that with respect to soil remediation the main responsibility is with the provinces and the four largest cities (Amsterdam, Rotterdam, The Hague, and Utrecht*).

2.3 Monitoring delimited

Monitoring is a widely used term that has not been defined unambiguously. Monitoring is generally considered as the activity of following the development of the parameter(s) of concern

*Situation at the time of publication of original paper, currently more cities are responsible for the tasks mentioned.

in time and (sometimes) space (Webster's Third New International Dictionary (1965): "to keep track of, regulate, control" or "to watch, observe, check for a special purpose"). According to this general definition everything that is subject to change can be monitored, from outside temperatures to the physical condition of a person and from economical growth to the progress of environmental policy. In this paper we focus on the monitoring of abiotic (physical and chemical) parameters indicating environmental quality.

Dutch authorities have published several reports on environmental monitoring. Characterizing their view on monitoring, however, is complicated because they tend to adjust their definitions depending on political objectives. In a theoretical paper (unpublished), written by a group of people representing the national, provincial, and municipal authorities, three types of monitoring are distinguished: *environmental policy monitoring* (how is policy functioning and does it reach its goals), *target group monitoring* (do these groups in society keep the rules set by the authorities) and *environmental quality monitoring* (focussing on the actual quality of the environmental compartments).

In reality, however, this distinction is seldomly observed. When a monitoring program is set up or modified, theoretical considerations are often of no concern. As a result most programs are a blend of the three types mentioned before. The dominant view held by national and regional authorities is that monitoring is a tool for controlling the results of environmental measures. Although the aim is environmental policy monitoring, the tool actually is environmental quality monitoring; it is called *descriptive ambient monitoring* by Harvey (1981, 1982), although he recognizes the fact that it could be considered a form of *regulatory monitoring* because there is an aim to control. The specific tasks of the provinces (see section 2.2.2) make regulatory monitoring predominant on this level. The monitoring systems and parameters used here focus on small areas where industries are present and often only a few target parameters related to specific industrial activities are measured.

The second function of monitoring often encountered is the detection of changes in environmental compartments, in other words true environmental quality monitoring. The aim of this type of monitoring, called *descriptive monitoring* by Harvey (1981, 1982), is to follow the overall environmental quality of the compartment under consideration and it mainly focuses on changes in an undesired direction. Therefore the parameters selected for descriptive monitoring are more general than those for regulatory monitoring and comprise mostly the major pollutants. Descriptive monitoring also includes the spotting of calamities such as the sudden pollution of the river Rhine with chloro-nitro-benzene in 1982 and a similar case with Sandoz chemicals in 1986 (Breukel and Rodijnen, 1991). It is the predominant type of monitoring on the national level. Most national monitoring networks we will discuss in section 2.4 are of this (descriptive) nature.

To guide the discussion in this paper we would like to stress some essential aspects of monitoring and thereby delimit the term rather than give a rigid definition. These aspects are: repeated measurement over time, a clear cut choice of the object and objective, a clear cut choice of parameter(s) and a measurement protocol. All these aspects should be stated clearly in order to ensure a consistent and systematic approach.

The choice of object includes both the definition of the target environmental compartment and the selection of the actual sampling items or locations. This implies the need for a well-considered statistical (spatial or categorical) sampling design. The formulation of a measurement

protocol should not be regarded to denote rigidity in sampling and analytical procedures, as of course improved techniques and scientific developments cannot and should not be ignored. The protocol, therefore, ideally should provide procedures for a change in methodology (and matching the new with the old).

We think that stating these aspects explicitly will help to make communication about the subject easier and therefore serves to a large extent the goal of a true definition as stated by Johnson et al. (1997). In their paper on the meanings of environmental terms they say that:

"ideal scientific definitions are short, logical, preferably nontheoretical (i.e., not intimately linked to any theory or explanatory framework - unless the definition defines that theory or framework), conceptually uncomplicated, comprehensive, all inclusive, and useful (i.e. practical, applicable). Their meanings should be easily communicated and easily remembered, because long and complicated definitions are hard to remember, thus less useful."

2.4 Environmental policy and environmental monitoring

2.4.1 The early years

Environmental policy in the Netherlands has its roots in the increasing awareness that production processes, especially those on an industrial scale, have an impact on human health. Already in the Middle Ages certain measures were taken by local authorities indicating problems of nuisance (Ast and Geerlings, 1993). Only in the 19th century, however, doctors became convinced that bad hygienic circumstances causes high susceptibility to diseases. As a result some regulations and laws concerning drinking water, living and working environment, sewers and poverty were initiated at the end of the 19th century. A remnant of this period is the Nuisance Act, issued in 1896 and still operational today in cases where the authorities have to issue licenses to companies that intend to develop activities that can cause danger, damage or hindrance (see section 2.2.2). Until the 1950s this Nuisance Act was the only environmental law (Fig. 2.3).

In the beginning of the 20th century industrialism has its breakthrough in the Netherlands. The hygienic situations in both living and working environment deteriorate. This invokes (much) attention for human health issues. In this period with its flowering socialism, a conservation movement emerges with the message that nature is being endangered by the tremendous amount of resources demanded by the modern way of producing. People in this movement start the first organizations for the preservation of nature. This development did not, however, spur any monitoring activities: there was no systematic approach to gain knowledge of the environment in these years.

The Netherlands being a country rich in water, the first object of interest to the authorities obviously was water. Major concerns were to secure its availability for agricultural and domestic purposes, to regulate drainage, and to provide protection against flooding. Many of the provinces started to record ground water and surface water levels in the late nineteenth/early twentieth century. In most cases only a few observation points were surveyed on an irregular and unsystematic basis. The overall idea, however, was to gain knowledge about the characteristics of the water compartments and their possible changes. Some quality aspects also received attention. For instance, in Zeeland and Noord-Holland, two provinces close to the North Sea

coast, the chloride-concentration has been recorded since the nineteen-thirties. The interest in this quality parameter was mainly agricultural.

2.4.2 The years of growing environmental awareness

After World War II the Netherlands, like most Western countries, primarily focuses on rebuilding its society. By 1960 most of the Dutch economy has recovered and performs well. As a result materialistic and economic demands slowly make place for demands that concern clean water, clean air, silence, in short a better environmental quality. These needs felt in society were not immediately transformed into government policy. However, under the pressure of a growing environmental movement and international reports on environmental problems (e.g. Meadows et al., 1972 better known as the Club of Rome) the Dutch authorities in 1971 create a new ministry dedicated to Public Health and Environmental Hygiene. According to Tatenhove (1993) the logic behind putting together environmental hygiene and public health stems from the fact that the attention for environmental problems initially was health oriented.

Groundwater levels

Observation networks that have many characteristics of monitoring networks are slowly emerging during the 1950s. The first attempts to structure the measurements of ground water levels were done in this period by the Netherlands Organization of Applied Scientific Research (TNO). This institute developed a measurement protocol that was soon followed in most provinces (Table 2.2). Yet, the introduction of this standard procedure did not directly invoke a systematic approach to data collection. A true monitoring system, in the sense of meeting (most of) the requirements stated in section 2.3, was only installed by two provinces (Overijssel, Utrecht). Most other provinces did not reach this stage of organisation until the 1970s or even 1980s. During the 1980s provinces had to take action because due to the Groundwater Act, issued in 1981, they became the responsible authorities for groundwater.

Surface water quality

A national program for surface water started in 1950 with the monitoring of some important national waters including the North Sea and in 1953 with the monitoring of the river Rhine (Fig. 2.3; Table 2.2) (Kleijn and Leenaers, 1991; Breukel and Rodijnen, 1991). Concern for the quality of surface water rose with the onset of overall environmental awareness in the late 1960s. Surface water pollution by emissions of industries is one of the first problems being addressed, because of the obvious health aspects.

True surface water monitoring was developed only in the early 1970s when most provinces started (more or less) systematic measurement of surface water quality. As in monitoring projects for most other compartments the provinces follow the national approach, and apply it to the smaller waters that are under provincial supervision. The design of the monitoring systems differs among provinces. This depends on specific needs caused by phenomena that are typical for certain provinces. Zeeland and Noord-Holland, for example, are both coastal provinces and are therefore confronted with salt effects. Most provinces have a general quality monitoring network with some optional extras to address specific questions. The goal of these (slightly) different systems, however, is the same: following the spatial en temporal variations in surface water quality

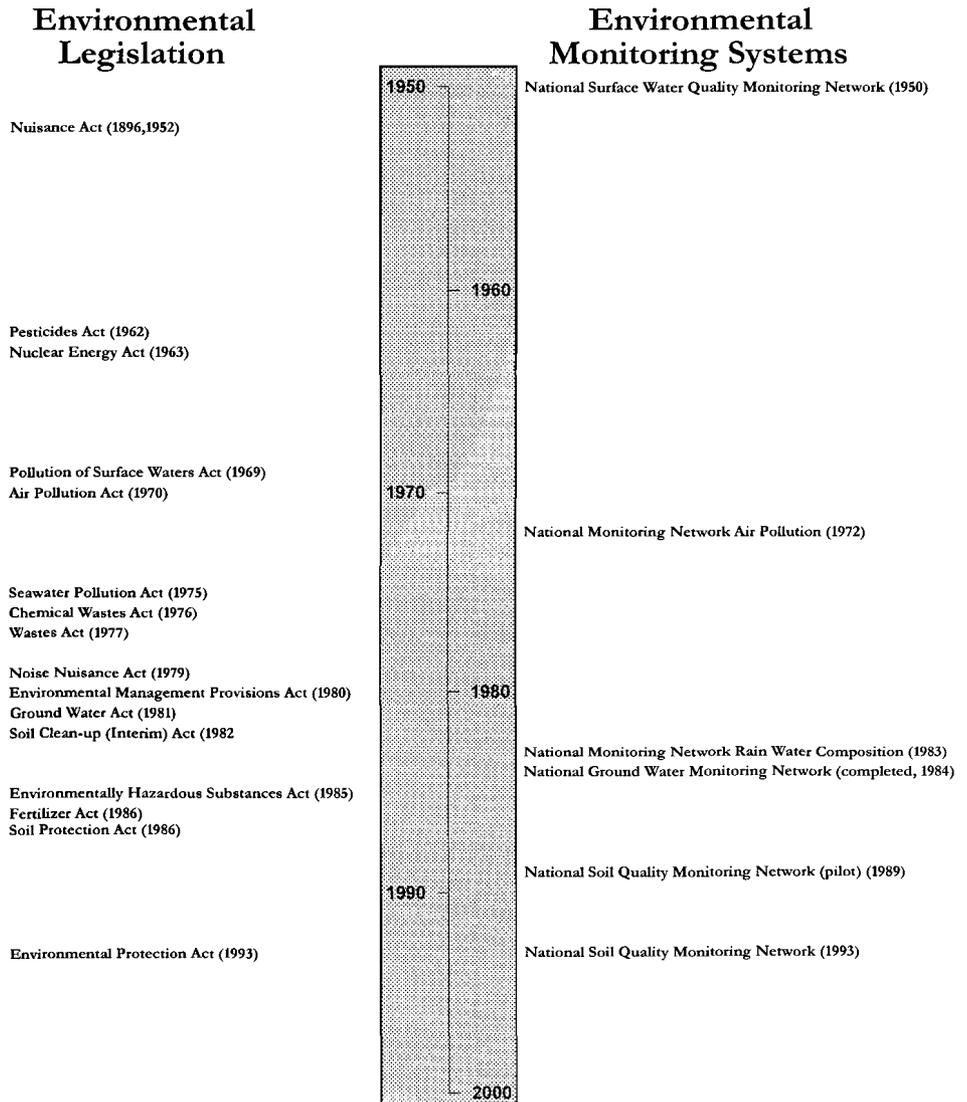


Figure 2.3
Timescale showing the chronological development of environmental legislation and subsequent national monitoring networks.

and comparing the results with the environmental standards set by the government. This is predominantly *environmental quality monitoring*.

Air quality

Another issue that drew attention was air pollution. Caused most prominently by industries emitting gasses and dust, health aspects are evident. For air pollution monitoring there is no strong relation

between national and provincial programs. Since 1972 the National Institute of Public Health and Environmental Protection (RIVM) runs a monitoring program for the general quality of the air (Fig. 2.3; Table 2.2). This national program is directed towards the major air pollutants such as SO₂, NO_x and O₃, whereas the programs initiated by the provinces often have very specific target parameters that are related to industrial activities. These activities are only allowed when the licenses mentioned before (see section 2.2.2) have been issued by the provincial authorities (Nuisance Act). To check whether the agreements on emissions stated in these licenses are kept, the provinces set up their specific monitoring programs. The provincial networks are a typical example of *regulatory monitoring* whereas the national activities are *descriptive or environmental quality monitoring*.

Rain water quality

A monitoring network for rainwater composition was developed some years later. It reached its present state of development in 1983 (Fig. 2.3; Table 2.2). The network currently contains only some 20 measuring points all over the country, i.e. 1 or 2 per province. The major goal is to determine the quality of the deposition (including nutrients, potential acidity, organic pollutants) and the resulting environmental load on water, soil, and the organisms inhabiting them. Contrary to most monitoring systems the rain water network is hardly complemented at the provincial level. Only some provinces have extended the national network to gain more insight in the spatial patterns within their province.

Sectoral policy

The development of the monitoring networks mentioned above, exemplifies that each environmental compartment is dealt with separately. This is called the sectoral (or compartmental) approach and it is mainly the result of the development of environmental policy in the Netherlands. Two aspects were crucial to this development: the administrative organization and the tenor of environmental policy (Tatenhove, 1993). The administrative organization is essentially arranged so that environmental problems and responsibilities are divided among different ministries. Ministries involved in environmental policy are of course the freshly created Ministry of Public Health and Environmental Hygiene, but also the Ministry of Transport, Public Works and Water Management (e.g. Pollution of Surface Waters Act, Seawater Pollution Act), the Ministry of Economic Affairs (e.g. Nuclear Energy Act, Mine Act), and the Ministry of Agriculture and Fisheries (e.g. Pesticides Act, Fertilizers Act). These ministries often play power games concerning the responsibilities for environmental policy. In part this causes the tenor of environmental policy in the 1970s to be compartmental and sectoral.

Table 2.2 Basic information on the major abiotic national monitoring networks. (Adriaanse, 1993; Breukel and Rodijnen, 1991; Pebesma, 1996; Frapporti, 1994; Dufour, 1998; Kleijn and Leenaers, 1991 and Duijvenbooden et al., 1993a)

National Monitoring Network	Aim	Policy aims (only when different from aim)	Parameters
Air Pollution	<ul style="list-style-type: none"> * determination of trends of important air pollutants * validation transport models 	<ul style="list-style-type: none"> * determination of type and origin of air pollutants to take adequate measures * monitoring for general health of the public 	<ul style="list-style-type: none"> * SO₂, NO_x, O₃, CO, F, aerosols, organic pollutants * measurements with indicatorplants
Ground Water Levels	<ul style="list-style-type: none"> * ground water management for agriculture and drinking water 	<ul style="list-style-type: none"> * environmental aim is to manage excessive lowering of groundwater 	<ul style="list-style-type: none"> * ground water levels
Ground Water Quality	<ul style="list-style-type: none"> * inventory the quality of the uppermost aquifer * spotting long term quality changes 	<ul style="list-style-type: none"> * information for good management and on anthropogenic influences * gathering data for operational management models 	<ul style="list-style-type: none"> * pH, EC, NO₃, Cl, SO₄, HCO₃, NH₄, Ca, Mg, Na, K, heavy metals, organic contaminants
Soil Quality	<ul style="list-style-type: none"> * relating the type of agricultural activity to the eutrofication of the soil 	<ul style="list-style-type: none"> * gaining insight into what measures will be best to reduce eutrofication and leaching of NO₃ 	<ul style="list-style-type: none"> *manure related parameters like K, NO₃, PO₄ (ortho and total), Cu, Cd, Zn * furthermore EC, pH, Cl, DOC,
Surface Water	<ul style="list-style-type: none"> * determination of actual quality and temporal and spatial trend * determination of balances for parameters combined with discharge 	<ul style="list-style-type: none"> * basic information for formulating of policy * checking of quality with threshold values 	<ul style="list-style-type: none"> * temp., pH, O₂, transparency, BOD₅, Cl, NO₃, NH₄, NO₂, ortho-P, Si * depending on survey point (10-180)
Rain Water	<ul style="list-style-type: none"> * determination rain water composition and its temporal trends to estimate wet deposition of pollutants 		<ul style="list-style-type: none"> * EC, pH, NH₄, Na, K, Mg, Ca Zn, F, Cl, NO₃, SO₄, HCO₃, PO₄ * Cd, Cu, Fe, Mn, Ni, Pb, V * sometimes As, Co, Cr, several organic pollutants

Table 2.2 (continued)

No. survey points	Comment
depending on parameter: SO ₂ 83 points NO _x 43 points O ₃ 37 points plants 33 points	<ul style="list-style-type: none"> * measurements for transport done from mobile stations * network density higher in urban and industrial areas * continuous measurement reduced to hour-averages
some 4000 points	<ul style="list-style-type: none"> * frequency of measurement: every two weeks
370 points	<ul style="list-style-type: none"> * filters at 10, 15 and 25 meters below surface level * special attention for areas used for drinking water extraction * soil type and soil use used as main criteria for positioning of survey points * frequency of measurement is once every year
* 100 farms	<ul style="list-style-type: none"> * Initial aims were determination of the actual quality and its temporal trends and gaining insight in relations between deposition and transport to groundwater validation of transportmodels, therefor try-out survey points were positioned close to points of other networks, and not limited to farmland. * Some provinces have networks that resemble the national try-out concept
* total (rivers, sea and lakes) 400 points	<ul style="list-style-type: none"> * both manual and automatic sampling * regional activities all over the country (in general with the same aim) * number of survey points varies with time * frequency of measurement varies with time and survey point (4-26 times per year) * parameters of interest change with time
20 points	<ul style="list-style-type: none"> * frequency of measurement is 2 times per month

Another cause is the first document produced by the new ministry of Public Health and Environmental Hygiene, the Priority Memorandum on the Environment (1972). This memorandum contained a thorough analysis of the background of the environmental problems and an inventory of the priorities. The list of priorities is organized per compartment and therefore it affirms the sectoral arrangement of environmental policy. Along these two lines the institutionalization of Dutch environmental policy evolves fragmentarily. During the 1970s each compartment is provided with its own laws, and responsibilities are divided over different ministries. By 1979 most compartments have specific laws (Fig. 2.3) and environmental policy reaches a certain maturity. However, initiated by the small effectiveness of the policy and by some environmental calamities like Sandoz chemicals in the river Rhine, extreme soil pollution in Lekkerkerk and Gouderak (the Netherlands), Bhopal and Chernobyl, people realize that the fragmented, sectoral approach to these problems lacks effectiveness.

2.4.3 From sectoral to integral

As a result of this realization the policy gradually focuses more on an integrative and structural approach in stead of a sectoral and ad hoc one. The most prominent document to mark this change is the Plan Integration Environmental Policy which was published in 1983. A second realization was that society is not as adjustable as was expected. As a result deregulation becomes an important issue; the authorities retreat by making less regulations and the people are increasingly arranging their own matters. These two changes have definite effects on the course of environmental policy.

Problematic with sectoral laws, developed by different ministries, is their distinctly different structure and content. To accommodate these problems the Environmental Management General Provisions Act (Wabm) was issued in 1980. This act had to bring about some tuning between the sectoral laws. During the 1980s further development of this integral approach is written down in several reports, especially in the Indicative Environmental Multi-year Programmes. Under the authority of Minister Winsemius a more consistent, managerial approach to environmental problems is established. He takes strong action and develops new ideas to disentangle the confusing multitude of environmental laws and measures. One of the new ideas is the thematic approach. This approach does not focus on certain compartments but on themes like acidification, eutrofication, spread of contaminants, removal of waste etc. To prevent that problems move to another compartment these themes are treated integrally throughout all the compartments.

As a result attention gradually shifts towards the less obvious problems. Man is gradually beginning to realize that environmental problems do not only comprise those that directly affect human health, but also those that affect ecosystems. Consequently the authorities become more interested in checking the quality of environmental compartments that are or seem to be of primary concern to nature. Especially for soil and groundwater it was realized that processes are much slower to take effect, because of a much larger buffering capacity of soil compared to air or surface water. Therefore huge amounts of contaminants can be accumulated in these compartments before negative effects occur.

Ground water quality

Ground water is the first of these “slow reacting” compartments that becomes subject to quality monitoring (Fig. 2.3), probably because it still has an obvious relation with public health as it is the major source of drinking water in the Netherlands (CBS, 1992; Dufour, 1998). While some qualitative measurements of ground water have been performed since the beginning of the century, true ground water quality monitoring started only in 1978 when the national government issued it to the National Institute of Public Health and Environmental Protection (RIVM). The national monitoring network for ground water quality was completed by 1984 (Drecht et al., 1996; Dufour, 1998; Table 2.2). The main goal (as usual) is to follow the quality of the compartment as it changes over time, and to relate these changes to either natural or anthropogenic causes. The results are directional for the management of ground water as a resource with different functions for both natural and human usage. Besides activities of the authorities and their institutions, some more theoretical, scientific efforts have been made to interpret the data collected with the network (Frapporti, 1994; Frapporti et al., 1993; Pebesma, 1996; Pebesma and Kwaadsteniet, 1997). The results of these efforts, however, have had no noticeable influence on the practical use of the collected data.

Provinces only start with ground water monitoring when, as a result of the Groundwater Act (1981), they become responsible for the ground water quality. Most provinces consider the sampling density of the National Monitoring Network insufficient for their needs and they extend the network with provincial sampling points. All these extensions were made between 1988 and 1993. The goal of these provincial monitoring systems is identical to that of the national network, but many provinces do some additional work, like the installation of a shallow filter and the measurements of additional parameters. This depends on local natural phenomena and sometimes on preferences of the people in charge resulting from differences in background and specific expertise.

Soil quality

The latest monitoring network that has been initiated is one for the soil quality in rural areas. The late appearance of this monitoring network has two main causes. First, the late awareness of the environmental importance of this compartment and its intricate and slow reactions to contaminants. Second, the scepticism concerning the possibilities of monitoring soil quality (Duijvenbooden et al., 1993; Duijvenbooden and Lagas, 1993). Natural spatial variability was considered to be of such magnitude that trends of contaminants, which resulted from diffuse pollution, could not be discerned from the natural variation. In 1984, however, the National Institute for Soil Fertility published research that suggested that with a statistically sound network design it be possible to detect relevant trends (Riem Vis et al., 1984).

In 1988/89 the National Institute for Public Health and Environmental Protection (RIVM) set up a pilot soil monitoring network on a national scale, but after evaluation in 1993 a totally different final design was chosen. The design, as it is now in use, focuses on the relation between agricultural activities (considered an important source) and soil contamination (Table 2.2). Two themes, spread of contaminants (heavy metals and organic pollutants) and eutrofication, are monitored on a small number (100) of selected farms. The reason for this rather limited choice is not entirely clear but just as with other monitoring networks the political agenda, in the early 1990s intensely focusing on sources of pollution, seems to be the deciding factor.

In 1991 the cooperating provinces commissioned a survey into the possibilities and needs for provincial soil quality networks. An environmental consultancy carried out this survey through questionnaires and interviews with many experts in the field (policy makers, consultants, and (soil) scientists). They also chose a statistical approach to the design of soil monitoring networks. The survey covered various aspects, from technical and statistical details to general issues like the status these networks could and should have within provincial policy (Kleijn et al., 1992; Kleijn and Leenaers, 1991). Following the report, some provinces set up provincial soil monitoring networks whereas others did not reach this stage yet. The provincial soil monitoring networks address three themes, viz. contaminant spread, eutrofication and acidification. They have, however, slight variations in their designs depending on problems related to specific soil and geomorphologic properties of the various provinces. Other factors influencing the details of the networks are the personal preferences of the provincial employees and the actual consultancy that was selected for the project management. Remarkably, for the soil monitoring of the themes acidification and eutrofication is that soil moisture is sampled and analyzed and not the soil material. More information on the soil monitoring networks in the Netherlands is given by a.o. Mol et al. (1998) and Busink and Postma (2000).

Planning an integral environmental policy

The idea of planning which emerged in the 1980s dominates environmental policy since 1987. From then on national, provincial and municipal authorities have to follow a twofold planning approach to environmental policy. They have to formulate an Environmental Policy Plan every four years, and based on these plans the national and provincial authorities have to produce an environmental action program every year. For the municipalities the action programmes are optional. The plans are strategic and the programs are operational (containing concrete measures and goals).

In 1988 the National Institute of Public Health and Environmental Protection (RIVM) published a report that extensively describes the environmental problems and uses the concepts of themes (acidification, eutrofication etc) and scale (local, regional, national, global etc.) to indicate their seriousness and possible approaches. The first National Environmental Policy Plan is based on this integral analysis. Integration is further emphasized - at least on paper - by the use of the concept of sustainable development in policy plans of other Ministries (e.g. the Ministries of Transport, Public Works, and Water Management and of Agriculture, Nature Management, and Fisheries).

Several advisory boards have assessed the integration. Their opinion has repeatedly been that, although looking sound in writing, its success should eventually be determined on the basis of implementation and effectuation of integral measures. On paper, however, integration reaches its pinnacle with the new Environmental Protection Act issued in 1993. But Tatenhove (1993) remarks that although the general policy seems to become increasingly integrated, the actual measures still breath compromise based on power differences between Ministries.

2.5 Summary and discussion

The (above) description of the Dutch environmental policy and monitoring situation indicates the complexity and vastness of this issue. First, we conclude that a huge effort has been made to

inventory the state of the environment and to identify the processes that lead to environmental damage. Getting equipped with the proper tools for keeping track of the development of environmental quality was another activity that developed within a few decades. This happened largely as a response to alarming publications during the late 1960s and early 1970s. The good economic situation in these years greatly improved the societal acceptance as it provided room for non-economic values. Actually, the impulse came from society through a strongly developing environmental movement that basically forced the government to take action.

Environmental issues entered the political agenda in the early 1970s and soon developed so rapidly and in so many directions that it is hardly possible to give a clear and concise account of their development. The foremost reason for this proliferation is the fast changing perception of environmental problems and their possible solutions. The second reason is the general idea, present from the beginning, that environmental problems can only be solved by governmental action. As a result authorities and politics have strongly influenced all environmental issues by their memos, reports and laws, and by the formation of national institutes for environmental research commissioned by the authorities. According to Eijsackers (1992) the advanced position of environmental policy in the Netherlands is intensified by some aspects of the Dutch administrative organization. The aspects he mentions are: a high level of organization of both the government and the non-governmental organizations, a high level of education, a well equipped research potential, and a highly developed communication system.

According to the analysis by Tatenhove (1993) the development of an environmental policy that initially had a typically sectoral arrangement mainly results from two structural circumstances. Most structural and decisive is the division of responsibilities over the different ministries. The first structural analysis of the environmental problems, however, affirms this division because it analyzes the problems and lists the priorities per compartment. Within this sectoral framework gradually all environmental compartments are provided with laws, measures and eventually monitoring networks. The first topics to be dealt with were those with obvious relations to human health; illustratively the first environmental ministry is the Ministry of Public Health and Environmental Hygiene. Not only the government's approach shows this progression, also the scientific journals concerned with the environment concentrated first on contaminants and toxicology.

During the 1980s an integral approach slowly developed because people realized that a sectoral approach is not sufficient for dealing with environmental problems that prove to be more complex than initially expected. To prevent that problems move from one compartment to another, the integral approach concentrates on themes like acidification, eutrofication, spread of contaminants, removal of waste etc. , which are treated integrally throughout all compartments. As a result attention gradually shifts towards problems that do not pose an immediate but an indirect threat to human health, or that are of major concern to certain ecosystems. The choice to concentrate on a certain theme, however, is a political decision based on other considerations than (eco)toxicological criteria alone.

The replacement of sectoral policy by integral policy looks promising. It even materializes quite well on paper, several ministries integrate environmental concepts in their plans and environmental problems are described and analyzed in an integral way throughout compartments. Success, however, should be determined on the basis of implementation of integral measures. This is still problematic. Tatenhove (1993) states that most actual measures still breath

compromise based on power differences between ministries. Janssen et al. (1988) draw a similar conclusion with respect to the contents of reports on nature and landscape policy; they notice a "lack of consistency among the different policy reports."

This is confirmed by the actual situation we found with the environmental monitoring networks. The development of these networks basically follows the development of environmental policy in general (see Fig. 2.3). Monitoring networks are essentially compartmental because measurements are made on soil, air or water etc. From the moment that the problems were assessed in a thematic way, however, the monitoring activities could have been rearranged through improved tuning of the spatial designs of the various networks. Some reports on monitoring also mention this but in most cases it never materializes.

Worse still, even within compartments the various activities throughout the country do not really match. The soil monitoring networks, for instance, are relatively modern and designed after the integral policy became operative. For this network the national authorities redesigned it completely after a trial period of 4 years, while the provinces are still using the original design and concepts (Duijvenbooden et al., 1993; Duijvenbooden and Lagas, 1993; Kleijn and Leenaers, 1991; Kleijn et al., 1992; Busink and Postma, 2000). Yet, among provinces there exist considerable differences (Mol et al., 1998). While usually provincial monitoring networks resemble those on a national scale quite closely, deviations occur for two main reasons. First because natural phenomena may be specific to a province and the network design is adapted accordingly. Second and less obvious is that provincial employees, because of differences in background and specific expertise, may arrange things differently from the initial intentions, or surreptitiously continue activities without political approval. This is enhanced by the fact that the monitoring goals are not stated with sufficient clarity, because the abstract political targets that serve as the basis for monitoring activities are very hard to translate into a concrete monitoring design. This issue is also mentioned by Janssen et al. (1988) in a report on the selection of monitoring variables for the policy on nature and landscape management. They conclude that this selection is hardly possible based on the top-down approach: going from policy targets to concrete variables. Instead, a more promising bottom-up approach, going from knowledge on the specific ecosystem to concrete variables, is suggested.

The very essence of monitoring is that it is meant to function over a period of time (see section 2.3). Considering the wide range of reaction times observed in nature, these periods ought to be quite extended. In other words, a solid basis is indispensable because the monitoring networks will be operational for many years to come. However, in the rapidly changing field of environmental policy and environmental management, with its different stakeholders, it is difficult to find such a solid basis. Thus, while monitoring should provide policy makers with information on how fast and in what direction environmental changes take place, a situation where a strong influence is exerted by political interests on environmental research is not a good starting point. A better strategy would be to start from well developed concepts and approaches from scientific fields like the earth and biological sciences, including their use of statistical methods. Specifically in the fields of (exploration) geochemistry, hydrogeology, soil(micro)biology, and ecology a vast amount of knowledge has been gained on how to observe and understand complex natural systems through necessarily limited sampling. This knowledge, however, seems to be somehow ignored during the development of environmental monitoring. Keeping this in mind, a deliberate change in attitude and strategy will help to develop clearer monitoring practices that are both more sophisticated and more robust.

2.6 Conclusions

Environmental monitoring of abiotic systems in the Netherlands is a well developed field of activity and encompasses all compartments in the environment (air, surface water, ground water, soil). This is a logical consequence of the natural and demographic characteristics of the country.

The sequential development of the various monitoring systems parallels that of environmental awareness and environmental policy in general throughout the Western world: from quantity towards quality, from single pollutants towards environmentally harmful processes as a whole, and from a focus on human health and safety and a sectoral approach towards integrated environmental management.

The Netherlands monitoring networks are intended to support environmental policy. Yet, most systems are designed for plain environmental quality monitoring and not for environmental policy or target group monitoring.

As a long term activity, environmental monitoring should have clear objectives based on solid scientific insights. Currently the strong political influence exerted on monitoring activities inhibits the development of sophisticated and robust monitoring designs that truly support integrated management of our complex environment.

3 FUTURE TRENDS, DETECTABLE BY SOIL MONITORING NETWORKS?

3.1 Introduction

Before any solutions for environmental problems can be suggested, a distinction should be made between natural anomalies and those resulting from human activities. Therefore, environmental compartments are increasingly subjected to quality monitoring. The diversity of publications on environmental monitoring proves that it is considered an important issue in many countries and that monitoring applies to all compartments of the environment (Duijvenbooden and Lagas, 1993; Gaans et al., 1995; Il'yin and Konarbayeva, 1996; Kas'yanova et al., 1996; Kobza, 1995; Köhl et al., 1994; Sanka and Paterson, 1995; Stein and Bouma, 1993; Webster et al., 1991; Zbiral, 1995). In the Netherlands also a wide variety of monitoring systems has emerged, especially during the last 25 years.

Recently some networks for monitoring the soil quality have enriched the Dutch world of environmental quality assessment. The comparatively late appearance of soil monitoring networks has two main causes. The first cause is the late awareness of environmental problems in compartments with great buffering capacities for and slow reactions to contaminants. The second cause is the natural spatial variability, a specific problem of the soil compartment (Duijvenbooden et al., 1993).

Natural spatial variability was considered to be of such magnitude that trends of contaminants, which resulted from diffuse pollution, could not be distinguished from the natural variation. In 1984, however, the National Institute for Soil Fertility did research that suggested that with a statistically sound network design it should be possible to detect relevant trends (Riem Vis et al., 1984). Finally, in 1988/89 the National Institute of Human Health and the Environment started with an experimental design for a national soil monitoring network. In 1993 the results of this try-out were evaluated and a final design was developed.

On the provincial (regional) level soil quality monitoring also came into focus. Regions sometimes need a differentiated approach. Because of their specific natural make-up they cannot always be subjected to national environmental quality standards.

In 1991 the cooperating provinces commissioned a survey into the possibilities and needs for provincial soil quality networks. An environmental consultancy carried out this survey through questionnaires and interviews with many experts in the field (policy makers, consultants and (soil) scientists). They also developed a statistical approach to the design of soil monitoring networks. It was a wide-ranging survey that covered various aspects, from technical and statistical details to general issues like the status these networks could and should have within provincial policy (Kleijn and Leenaers, 1991). Following the report a few provinces set up provincial soil monitoring networks whereas others did not come to this stage yet.

Sufficient experience (and data) in soil monitoring has been acquired, so that all aspects of soil monitoring can be put in perspective. In this paper we would like to make a start with this discussion and we do so by pondering upon some of these aspects.

3.2 Designs of soil monitoring networks

Although there are distinct differences, the development of national and provincial soil monitoring shows quite a few similarities. The goals of the networks, for example, are quite similar namely: to inventory the present-day quality of the soil in rural areas and to keep track of possible changes in this quality. Another similarity is the thematic approach. This approach became omnipresent in Dutch environmental policy since the notion developed that environmental issues are related through natural compartments such as soil, water and air. Three themes are considered relevant for soil quality, namely: spread of contaminants (viz. heavy metals, pesticides and PCB), eutrofication, and acidification. All soil monitoring networks have been designed along these three themes. The networks mostly consist of three parts of which the measurement of spread often forms the basis and the other two themes are extensions to the basal network. The designs will be discussed in two sections. Section 3.2.1 will deal with the development of the national soil monitoring system. In section 3.2.2 the slightly different monitoring designs used on provincial level will be discussed.

3.2.1 National level

The try-out of the national monitoring network was designed in the following way: 10 regions, more or less homogeneous in soil type and land use, were selected. They were considered to be representative of a larger part of the Netherlands consisting of comparable combinations of soil type and land use. Each of these 10 land types was sampled at 4 locations (replications). The surface area of each of these 40 locations was approximately 400 m² (20 * 20 m). At each location the soil was sampled at two depths (0-10 cm and 30-50 cm below surface level). At each depth 4 composite samples were taken, each composed of 40 subsamples. This resulted in 320 subsamples making up 8 composite samples per location. The composite samples were primarily analyzed for heavy metals, pesticides and PCB's. In addition 47 elements were determined by NAA to get a more complete view on the natural composition of the soils (Duijvenbooden and Lagas, 1993).

Results of this try-out survey indicated that taking 40 subsamples was sufficient to cover the variation within locations; concentrations measured in all 4 composite samples (of one depth) were close, so estimation of the local average was precise. Local trends can therefore probably be distinguished from the local variability with little sampling effort. The differences between locations of the same land type, however, were much larger so at least more locations (replications) per land type should be considered. Van Duijvenbooden and Lagas (1993) suggested 20 locations. It will always be harder, however, to detect regional trends than to detect local trends.

The evaluation, made in 1993, led to a new policy in which more emphasis was placed on relationships between sources of pollution and resulting changes in environmental compartments. Therefore the final design of the national soil monitoring network, as it is now

in use, focuses on the relation between agricultural activities (considered an important source) and soil contamination. The final design has 35 locations that comprise all the land of an individual farm regardless of soil type and land use. The only distinction between the farms is that they are divided in two categories of cattle intensity. Two themes are monitored, namely: spread of contaminants and eutrofication.

3.2.2 Provincial level

The provincial activities on monitoring soil quality resemble the national activities of the try-out phase in many aspects, and not the final design of the national network. The provincial soil monitoring networks also address three themes (contaminant spread, eutrofication and acidification). They have, however, a slight variation in the design. The environmental consultancy advised (Kleijn et al., 1992) that the soil monitoring network could best be designed by combining the thematic approach with an approach with regional focus, focussing on regions with high sensitivity to certain pollutants, because for these regions more detailed knowledge could prove necessary.

This regional approach means that the network consists of a basal part that covers the total area of a province and that measures the spread of contaminants. In some areas, suspected of having a higher sensitivity to eutrofication and/or acidification, extensions to the basal network are being set up for these specific themes. In the designs of some provinces, the basal network consists of both the themes contaminant spread and eutrofication. One province concentrates its efforts on the regions that are considered sensitive to eutrofication and acidification.

Also the concept of homogeneous land types is part of the provincial designs. A province is divided into a number of regions that are homogeneous in respect to soil type and land use (according to the maps used). Per region a number of locations is sampled in a way comparable to the national soil monitoring try-out. The number of locations per region can differ and is determined on the basis of statistical reasoning, prior research or a small scale pre-survey (from which the region's variability is known) and a region's total area.

3.3 Bottlenecks in monitoring soils

Closer inspection of the designs mentioned so far raised some questions that need further attention. Here we will discuss seven of these problems that will be pointed out in a general way. The aspects we would like to discuss are (a) the preparation of composite samples, (b) the sampling design, (c) the maintenance of a sample archive, (d) the concept of homogeneous land types, (e) the comparison of a network of fixed locations with a flexible network, (f) seasonal variability and (g) the choice of parameters.

(a) **Composite samples:** Guidelines on how to prepare proper composite samples are incomplete, and sometimes have a rule-of-thumb character. An example is the almost magic number of 40 subsamples, that is required for a composite sample that is representative of a land parcel. Other aspects have never been clearly stated like the size of the individual subsamples or how to homogenize the 40 subsamples into one composite sample. These properties are likely to depend on specific characteristics of the sampled material. At least with respect to the size of

the subsample it is clear that sand should be dealt with differently compared to clay or peat as they differ in texture and structure (Gy, 1979; Haar et al., 1992; Lamé, 1991). The bigger the grain size, the bigger the sample should be. Homogenizing the subsamples into a composite sample is only clearly described for clay; this is being grinded under cryogen conditions and mechanically homogenized. For sand, however, far larger amounts of sample material are involved, so homogenizing is done in the field and not in the laboratory as prescribed. There is no standardized procedure for homogenizing in the field. Some clarity in this matter, which we think adds up to a considerable amount of unwanted variability, is desirable.

(b) **Sampling design:** To make inferences about the nature of the spatial variation, a clever and sound sampling design should be used that is based on statistical theory. With such a design and its statistical background it will be possible to optimize the amount of information from a given number of samples. The aforementioned designs have a different approach: they are based on an a priori classification on the basis of soil type and land use. Because of this classification into homogeneous land types the sample locations have to be divided among these land types and therefore a restriction is imposed on their actual location within a region as a whole.

If no a priori classification was used it would be possible to use a different sampling design. This would cover the entire region and it could have, for instance, four scales at which the variability would be determined. A good example is the unbalanced sampling design described by Garrett and Goss (1980). Data obtained with these designs can easily be subjected to an Analysis of Variance and to other statistical techniques like (a posteriori) classification by cluster analysis.

(c) **Sample archive:** The maintenance of a sample archive is customary in geochemical exploration. In environmental soil monitoring in the Netherlands, however, it generally is not. The often encountered notion, especially among policy makers, is that once a sample has been analyzed it can be discarded because the concentrations are now available on paper (or some electronic equivalent). Obviously it is also very useful in environmental assessment to have a sample archive, if only to rule out a shift in analysis technique as the cause of finding a trend in concentration levels. Other advantages are that mistakes can be corrected and that additional analyses are possible.

The use of old samples can be illustrated with two examples: first an investigation by Boerma (pers. comm., 1997) from the International Soil Reference and Information Centre. In the early 1990's he analyzed some Russian soil monoliths of 1920 (the Glinka collection) and compared the results with present levels in comparable soils approximately from the same area. It was concluded that if an area became anthropogenically influenced, the levels of heavy metals changed dramatically. From the few samples that were taken and analyzed it can be seen that large differences for some heavy metals occur at sites where human activities have developed and that hardly any differences occur at sites that stayed virtually unchanged.

The second example was encountered in the Netherlands. In 1991 high Cd levels were reported in agricultural soils in the province of Zeeland (Gaans et al., 1995). A detailed follow-up survey in 1996 did not confirm these levels (de Jong, pers. comm., 1997). Fortunately the 1991 samples have been found again so a second analysis of these samples has been done. These analyses also show no higher Cd levels so probably something went wrong with the analysis in 1991.

(d) **Homogeneous land types:** Under (b) some remarks have already been made on the use of homogeneous land types. The choice of these land types on the basis of soil type and land use is quite arbitrary. Why not use other distinctive classes? Especially considering that the locations often appear to be different from what was expected from a priori classification. This leads to much unintended but unavoidable noise. This situation could be improved by using another sampling strategy. Another point of attention is whether land types that are homogeneous in soil type and land use are necessarily also geochemically homogeneous.

These problems indicate that a posteriori classification might be a better option to divide the area in intelligible parts. However, a priori defined land types may be useful as a means to stratify the population before sampling takes place.

(e) **Fixed locations vs. a flexible network:** It is generally assumed that a monitoring network should consist of fixed sampling locations. Upon closer inspection the use of fixed locations seems to present some problems. Firstly, a parcel of land is likely to get different treatment when it is publicly known to be a location in a monitoring network. Secondly, the land use of this specific location is not likely to stay the same for decades; this interferes with the a priori classification.

These problems do not occur when a network of shifting locations is used. Another advantage of such a flexible network is that eventually much more knowledge can be gathered because a growing number of locations is being measured. A disadvantage of shifting locations is that it will be more difficult to detect trends.

(f) **Seasonal variability:** Seasonal fluctuations in concentrations of some compounds - such as nitrate - in the soil moisture are generally observed. This variability often shows a kind of sinusoidal curve. Effects of this phenomenon on monitoring (and even the phenomenon itself) are not clearly understood. For instance, is it possible to choose one moment in a season and consider it representative of the average value during that year? Is it the best moment when the parameter is rather constant but at its maximum or minimum value or is it better to take a value close to the average but at a moment when change is rapid? Another point is how these moments can be determined, by the calendar or by some other measuring stick that is more related to natural cycles. We are presently conducting some research into seasonal fluctuations.

(g) **Choice of parameters:** In most cases this choice seems to be reasonable because mainly environmentally important compounds are included into the analysis. For a proper understanding of the causes of variation, however, it is essential to know the basic geochemical and mineralogical signature of the area. The parameters to which the environmentally important compounds are now related (viz. humus and lutum content) are not specific enough when natural anomalies are concerned. To get a good signature quite a different set of parameter should be analyzed. This set should at least contain more elements like the major elements and some series of elements (e.g. rare earth elements) that can indicate specific natural make-ups. It should contain parameters like CEC and base saturation. Preferably also a mineralogical analysis on some of the samples should be made because mineralogy determines a large part of the reactivity of the soil constituents.

Illustrative of this argument is research into the element levels in Dutch subsurface sediments by Huisman et al. (1997) that indicates that both our suggestions on measuring more elements and on mineralogical characterization are valid. Huisman et al. (1997) use Al and K to explain heavy metal concentrations and to distinguish between normal values and anomalies. The nature of enrichments is obtained through comparison of the higher concentration levels with those of Fe, S and K. They use these three elements as indicators for specific natural anomalies like iron oxide (Fe), pyrite (S) and glauconite (K). Glauconite occurs in samples from deep marine sediments and provides an example that mineralogical data can be indispensable in some cases. In this case high levels of heavy metals correlated with large grain sizes (sand) which seems strange. The glauconite, a clay mineral containing many trace elements, however, formed extremely large grains comparable to the (silica) sand grains usually containing hardly any trace elements.

A final point that has to be raised concerns the parameters that are used to measure eutrofication and acidification. These two themes are monitored by measuring the relevant compounds, like nitrate and phosphate etc., in the soil moisture. For a large part, this does not seem to be based on a clear and solid scientific basis. And as far as it does, it is mostly the agricultural science of soil fertility on which the parameters are based, and not environmental science. A better understanding of the truly important processes and parameters could make selective monitoring easier.

3.4 Conclusion

Soil monitoring in the Netherlands is a recent phenomenon; only the last ten years it has been the subject of interest, especially to policymakers, as a potentially adequate tool for keeping track of possible changes in the soil quality. In the Netherlands it is being introduced as such at two levels: national and provincial. Because it is such a recent development the methodology has not yet reached maturity. Therefore we have contributed to the evaluation of some of the methodological and philosophical aspects of soil monitoring through this paper. Considering the aspects we analyzed it is clear that before any truly intelligible information can be gathered with a soil quality monitoring network some very important questions have to be answered.

PART II Data on Practical and Theoretical Aspects of Monitoring Soil Acidification in Sandy Soils

- Chapter 4 Monitoring soil acidification. Conceptual considerations and practical solutions based on current practice in the Netherlands
- Submitted to Chemical Geology
- Co-authors: S.P. Vriend and P.F.M. van Gaans
-
- Chapter 5 Geochemical characterization of the Pleistocene sands in the Netherlands
- Intended for submission to The Netherlands Journal of Geosciences
- Co-authors: P.F.M. van Gaans and S.P. Vriend
-
- Chapter 6 Chemical characterization of the soil solution of acid sandy soils in the Netherlands: effects of chemical speciation, geochemical regionality, and short term temporal variability
- Intended for submission to Geoderma
- Co-authors: E.J.M. Temminghoff, P.F.M. van Gaans and S.P. Vriend

“Observations can only be made at appropriate scales.”

(from The Panda's Thumb by S.J. Gould)

““Winwood Reade is good upon the subject,’said Holmes. ‘He remarks that, while the individual man is an insoluble puzzle, in the aggregate he becomes a mathematical certainty. You can, for example, never foretell what any one man will do, but you can say with precision what an average number will be up to. Individuals vary, but percentages remain constant. So says the statistician.....”

(from The Sign of the Four by Sir Arthur Conan Doyle)

4 MONITORING SOIL ACIDIFICATION. CONCEPTUAL CONSIDERATIONS AND PRACTICAL SOLUTIONS BASED ON CURRENT PRACTICE IN THE NETHERLANDS

4.1 Introduction

4.1.1 General

Environmental monitoring, keeping track of changes in an environmental compartment with the aim to sustain or develop policy decisions, poses special demands on the type and quality of survey results and thereby on the sampling and analytical methods used. These specific requirements, however, are implicit and very often not well defined at the start of monitoring practice. Unclear choices are by nature impossible to evaluate. Difficult as it is, once a monitoring network has started authorities hesitate to make changes anyway. The research from which this paper forms part aims at a scientific evaluation of soil monitoring strategies in the Netherlands, with focus on soil acidification monitoring, to aid in the interpretation of current monitoring data and to provide recommendations for improved monitoring designs

4.1.2 Historic developments

The world of environmental monitoring in the Netherlands that developed gradually during the last three decades (Mol et al., 2001) received as its most recent addition during the late 1980s and early 1990s a soil quality monitoring network. The initial threefold aim of the network was to monitor the basic environmental soil problems acidification, eutrofication, and the spread of heavy metals and organic priority pollutants (Mol et al., 1998; Busink and Postma, 2000; Mol et al., 2001). In practice the bulk of the effort has gone into acidification.

The adequacy of available techniques for soil monitoring has been subject to some debate (see Kleijn and Leenaers, 1991). For soil acidification the choice of techniques has been strongly influenced by the more fundamental research arena, where developments were at their peak at the time. Research reports on acidification first surfaced in the 1970s (Likens et al., 1969; Likens and Bormann, 1974; Bormann et al., 1977; Cronan et al., 1978; Driscoll et al., 1980; Rosenqvist et al., 1980). Political interest was raised through alarm over dying lakes and forests, and a considerable amount of government funding was subsequently mobilized. This not only resulted in a huge research effort and a large output of papers during the 1980s (Breemen et al., 1982; Driscoll and Likens, 1982; Breemen et al., 1983; Krug and Frink, 1983; Reuss, 1983; Ulrich, 1983; Breemen et al., 1984; Galloway et al., 1984; Schnoor, 1984;

Nihlgård, 1985; Reuss and Johnson, 1985; Grinsven et al., 1986; Hallbäcken and Tamm, 1986; Reuss et al., 1986; Schnoor and Stumm, 1986; Breemen et al., 1987; Grinsven et al., 1987; Mulder et al., 1987; Reuss et al., 1987; Nilsson and Grennfelt, 1988), it also showed that the pursuit of political aims does not necessarily expedite scientific progress or aid in resolving scientific controversies. As soon as the government programmes ended (and refocused on climate) acidification research drastically declined, while several controversies that developed during the 1980s were still not resolved. This is illustrated by a paper by Krug (1991), who recapitulates some issues dating from a debate in 1984/85 (Breemen et al., 1984, 1985; Krug, 1985).

4.1.3 Scientific controversies remaining

In our opinion the main subjects of controversy still remaining to date can be summarized into three groups of discussions: a) the debate on capacity versus intensity; b) the confusion about the exact subject of acidification research: soil, ecosystem, or the surface water drainage system; and c) the discussion on the relative contribution of natural and anthropogenic sources of acidity.

The first issue can best be illustrated by the content of a set of papers by Van Breemen et al. (1983, 1984). In these papers he gives a lucid account of the processes governing acidification and alkalization in soils, illustrated with some examples. He stresses the importance of capacity factors, specifically the acid neutralizing capacity or ANC. Soil acidification is defined as the decrease in ANC. Direct determination of this change in ANC in the solid phase is considered problematic and insensitive. The absolute change in ANC is therefore calculated indirectly through so called proton budgets, using the differences between input and output concentrations of all substances involved in proton transfer processes. These concentrations of course are intensity parameters (which in Van Breemens approach are translated to capacity effects through the precipitation fluxes). Especially when dealing with the examples, Van Breemen puts considerable effort in subdividing the net fluxes into details of all back and forth processes. Obviously he is not only concerned with the absolute change in capacity and the accompanying net fluxes, but also in the current "state" of the system compared to some zero state or reference. Following a strict capacity oriented approach, this "state" of the system should be defined as the available amount of buffer or total ANC still left. In Van Breemens actualistic approach only the change in ANC can be determined, and the reference state is defined in terms of pH (an intensity parameter). The relation between pH and ANC is complex, but in an equilibrium system it should only depend on the total proton load added and the amounts of the different acid neutralizing substances. However, acidifying soils form a steady state system in which reaction kinetics are of the utmost importance. This system increasingly diverges from equilibrium with higher proton influxes (see also Gaans and Schuiling, 1997; Chadwick and Chorover, 2001).

The second issue seems obvious but is important, for if the objective of the research is ill-defined, unclear conclusions and a confusing dispute with peers are inevitable. It looks as though all possible perspectives are present in the acidification literature, from a focus on lake acidification considering the processes on catchment level (Likens and Bormann, 1974; Driscoll et al., 1980; Breemen et al., 1983; Krug and Frink, 1983; Breemen et al., 1984; Krug et

al., 1985; Grinsven 1988; Mulder, 1988; Krug and Lefohn, 1990), to a focus on forest health (Likens et al., 1969; Cronan et al., 1978; Driscoll and Likens, 1982; Krug and Isaacson, 1984; Nihlgård, 1985; Billett et al., 1990; Billett et al., 1990; Ulrich, 1995). In all approaches the soil plays a vital role because here the major acid buffering processes take place, yet few papers show an interest in the soil as such. The capacity-intensity debate is in part a corollary of the variety of perspectives. The discussion between Krug and Van Breemen (Breemen et al., 1984, 1985; Krug, 1985) is an example of what seems a different focus.

A nice example of the third issue can be found in the paper by Krug (1991). In his analysis of contemporary research on sulphur sources, he opposes the general assumption in soil acidity literature that S cannot be derived from the bedrock or primary minerals, and that hence all S should originate from atmospheric deposition. According to Krug this is unlikely because it implies that forests cannot exist without atmospheric SO₄ inputs. With sulphur being an essential macronutrient and the sulphur cycle being "notoriously leaky", non-atmospheric sulphur sources must be abundant. A systematic overestimation of the importance of anthropogenic and natural atmospheric sulphur deposition results when sulphur from natural sources like the bedrock is ignored.

It can be expected that these scientific controversies also persist in the daily practice of monitoring, as they must lead to vagueness in monitoring objectives and practices.

4.1.4 Current practice in monitoring

Despite much debate still going on in the scientific arena at the time that the soil acidity monitoring networks were initiated, a specific monitoring method as proposed by Kleijn and Leenaers (1991) was broadly accepted in the Netherlands. Organization of the monitoring networks was decentralized to the provincial level. Soil solution displaced by centrifugation was chosen as the monitoring medium by most authorities. Sampling campaigns concentrated on so-called sensitive areas considered especially susceptible to acidification (in casu coniferous forests on sandy soils). Samples were collected at two depths once every two years in spring, and only parameters of (supposedly) direct interest were analyzed. The decentralization resulted in some variation in the actual implementation, especially with regard to the choice of parameters to be monitored.

The choice of monitoring medium and depths seems instigated by the experimental methods used in determining proton budgets in soils, following the capacity approach of Van Breemen (1983, 1984). The limited number of parameters and the lack of monitoring precipitation surplus, however, cripple the interpretation of proton budgets because the measured intensity parameters can not be coupled to the capacity effect of acidification; a clear illustration of the capacity-intensity confusion.

The practical field of soil monitoring directly suffers from the margin resulting from the undefinedness of the subject of research. The choice of displaced soil solution as the monitoring medium suggests an interest in root zone conditions and forest health. The organisational positioning of the monitoring networks within provincial soil departments indicates an interest in the soil as such. The selection of coniferous forests on sandy soils as the acidification sensitive areas is ambiguous in this respect. Either the poor soils form a specific threat to the forests on top, or the scavenging potential of these forests for acid

deposition forms a specific threat to the soils underneath. This unclarity only promotes the vagueness of objectives already symptomatic to scientific activities developed by political bodies. Vague and poly-interpretable objectives do not serve as a solid base for a monitoring strategy. Consequently, the choices for operational details and the interpretation of the results become increasingly difficult, which in part is the reason for the interprovincial variation in implementation.

Interprovincial comparison of results to evaluate the respective effectiveness of environmental measures is not only hampered by these implementation differences. Regional differences in parent material that are known from classic geochemical literature (Edelman, 1933; Baren, 1934), and which will also affect monitoring results, are ignored in current monitoring practice. This is an example of a focus on anthropogenic factors only, without taking into account natural sources of variation.

In addition to these three key problems, also the temporal and small scale spatial variability of the soil solution composition and the ill-understood relation of this variability with progressive soil acidification pose problems. The variation on the time scale of interest (trends over decades) might very well be small compared to the variation on other, smaller time scales (e.g. seasonal fluctuations). Neglect of the importance of the scale at which different processes take place may lead to inefficient monitoring frequencies both in time and space.

Clearly, in practice the choice for displaced soil solution has proved problematic. Those involved find the results very hard to interpret, both within a scientific framework of forest soil acidification, as in terms of monitoring and policy objectives.

4.1.5 Objectives of this research

To address the issues raised above with regard to monitoring we launched a research project consisting of two extensive field campaigns. One focussed on small scale variation both temporal and spatial (referred to as the seasonal campaign). The other one covered a wide range of acid sandy soils in the Netherlands and focussed on the regional variation within and among provinces (referred to as the main campaign). In the main campaign also the use of total solid phase analysis by X-ray fluorescence spectrometry (XRF) was assessed. During both campaigns various methods of analysis have been used to test possible alternatives for or supplements to the analysis of displaced soil solution only. In this paper we will discuss the leading results of the main campaign covering the entire country. The specific questions we will address are:

- what is the major source of buffering in acid sandy soils?
- does a comparison between top and subsoil samples (using the subsoil as a proxy for undisturbed topsoil) offer possibilities to evaluate the acidity status of the soil, and if so what is the status of Dutch sandy soils?
- are there indications that an interprovincial evaluation of monitoring data may be hampered by regional differences in the natural setting?
- is the analysis of displaced soil solution sufficient to monitor soil acidification, and if not, what should be the alternative?

4.2 Material and methods

4.2.1 Environmental setting

The Netherlands predominantly consist of eolian, fluvial and marine sediments deposited in the Late Pleistocene and the Holocene (Staalduinen, 1979; Fig. 4.1). Situated on the edge of the North Sea Basin, the country has a flat topography, except for the southernmost part which is situated on the edge of the Ardennen Massif. The relief in the rest of the country was formed during the Elsterian and Saalian ice ages (Zagwijn, 1987). Most of this relief was levelled by erosion and depressions were filled by sediment during the Holocene; the only features still clearly present are ice-pushed ridges (Staalduinen et al., 1979). Two major geomorphologic areas are discerned, one dominated by Pleistocene sand deposits and the other by Holocene clay and peat deposits. The Pleistocene areas are generally above sea level, hydrologically dry, and poor in nutrients (Zonneveld, 1985), and therefore constitute the soils sensitive to acid deposition.

The Netherlands have a moderate sea climate (Cfb-climate in the Köppen system; Zonneveld, 1985). Typical values for daily average temperatures range from 2 °C in January to 17 °C in July. Mean monthly precipitation varies from around 50 mm per month in spring to about 80 mm per month in late summer (Meinardi, 1994). Net precipitation is highest in winter with a yearly excess of about 250 to 300 mm. As a result of the young sediments and the moderate climatic conditions the soils of the Netherlands are poorly developed compared to those in many other parts of the world.

The soils sampled for this study are situated in the Pleistocene areas (see Figs 4.1 and 4.2). On these poor soils that are of no agricultural significance one finds most of the Dutch forests. The combination of forests with their capacity to create a higher influx of potential acidity (Mulder, 1988; Heij and Erisman, 1997) and poor sandy soils with low to very low buffering capacities (Vries, 1994) creates a situation of high susceptibility to soil acidification. This is being aggravated by the extensive presence of intensive animal husbandry, which is the only profitable form of agriculture on this poor substrate. This form of agriculture emits large amounts of potential acidity in the form of NH_3 (Breemen et al., 1982; Krug, 1991; Vries, 1994).

Exact data on the yearly loads of potential acidity that are deposited on the actual locations that we sampled are not available, but general estimates can be made from the literature. The Dutch Priority Programme on Acidification (Heij and Erisman, 1995; Heij and Erisman, 1997) reports estimates of mean total acid deposition since 1980. These values range from 7215 mol_c ha⁻¹ yr⁻¹ in 1980 to 4280 mol_c ha⁻¹ yr⁻¹ in 1993. Recent data from the National Institute for Public Health and the Environment (RIVM, www.rivm.nl) show comparable figures ranging from 7330 mol_c ha⁻¹ yr⁻¹ in 1980 to 3580 mol_c ha⁻¹ yr⁻¹ in 1999. Compared to deposition rates of between 2000 and 4000 mol_c ha⁻¹ yr⁻¹ found internationally (Ulrich and Matzner, 1983; Breemen et al., 1984) this is rather high. Estimates for the actual acidification on the basis of input-output balances of soil ecosystems lead to values that vary between 2000 and 6500 mol_c ha⁻¹ yr⁻¹ in Dutch forest soils (Breemen et al., 1983, 1984).

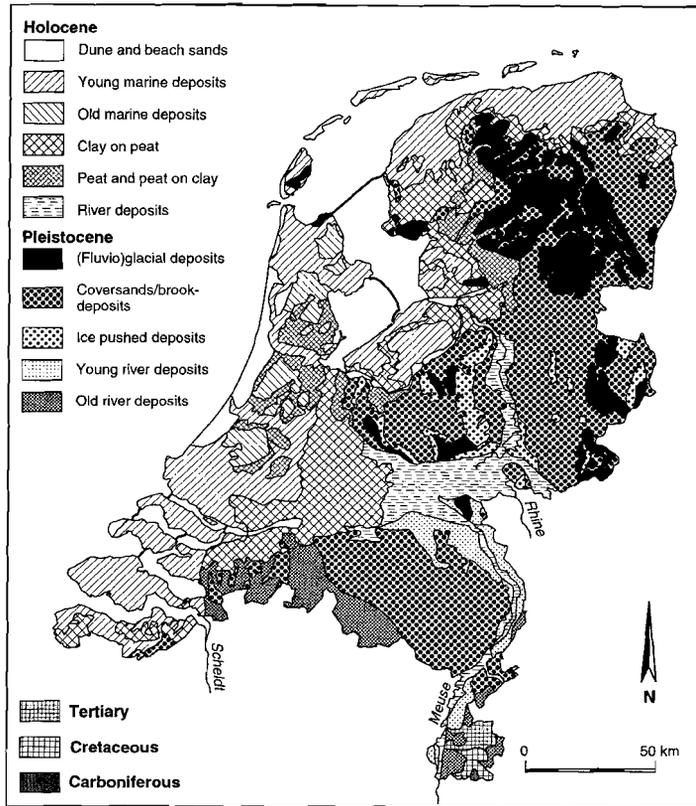


Figure 4.1

Map of the Netherlands showing a division into the major geological landscapes. (After: Zonneveld, 1985 and Bakker and Schelling, 1989)

4.2.2 Sampling and analytical procedures

Soil samples were collected at 92 locations at two depths (the first 20 cm of the mineral soil below the litter layer and a C or B/C horizon between 60 and 110 cm) resulting in 184 samples. The set of locations, each about 10,000 m², was selected from the monitoring sites of six of the Dutch provinces. All sampled locations were coniferous forest stands on sandy soils (Fig. 4.2). Sampling took place in May-June 1999 in as short a period as possible (5 weeks) to rule out seasonal effects. Each location was divided into 6 equal sections in which a randomly located sample was collected at two depths (stratified random). The 12 subsamples of 2 kg each were obtained using a so called Edelman hand auger and transported to the

Figure 4.2
Sample locations map.



laboratory in separate sampling bags as mixing of moist soil is undesirable. To keep chemical changes in the soil solution to a minimum the samples were kept at 4°C in the dark and centrifuged within 24 hours. Half of each of the 12 subsamples was centrifuged separately and a composite sample from the displaced soil solution for each depth was put together after centrifugation. The total moisture yield was recorded, the pH measured and the displaced soil solution samples were analyzed with various analytical techniques (Table 4.1). The subsample for ICP analyses were acidified to pH=1 with ultrapure HNO₃.

A composite sample of the solid phase for each depth was assembled from a second half of the subsamples by putting an equal amount of soil from each bag into a small plastic container. The soil was subsequently dried at 40°C, mixed, and sieved. The fraction < 2 mm was used for two extractions, one with 0.01 M CaCl₂ (Houba et al., 2000) and the other with 0.43 M HNO₃, both at room temperature. Both extractions were carried out by shaking a 1:10 solid-solution mixture for 2 hours, after which the supernatant was collected for further analysis. The fraction < 2 mm was also used to determine the total element content by XRF, using pressed powder tablets. Table 4.1 provides an overview of all parameters analyzed.

Table 4.1

Overview of the different chemical analyses grouped per method. The parameters discussed in this paper are in bold characters.

Method	Parameters	Analytical technique
Dry soil	dry matter content organic matter content SiO₂, Al₂O₃, K₂O, Na₂O, CaO, MgO Fe₂O₃, MnO, P₂O₅, S, Zr , As, Ba, Bi, Br, Ce, Cr, Cs, Cu, Ga, Hf, La, Nb, Nd, Nd, Pb, Rb, Sb, Sc, Sr, Th, U, V, Y, Zn	oven (105°C) loss on ignition (550°C) XRF, pressed powder tablets*
Displaced soil solution	pH Dissolved Organic Carbon NH ₄ SO₄, NO₃, Cl, PO₄ Al, K, Na, Ca, Mg, Fe, Mn , P, S Cd, Cu, Cr, Ni, Pb, Zn	TOC analyzer Spectrometry Ion chromatography ICP-AES ICP-MS
CaCl ₂ extract (0.01 mol l ⁻¹)	pH Dissolved Organic Carbon NO ₃ , NH ₄ , N _{tot} , PO ₄ , Na, K Al, Mg, Fe , Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	Organic carbon analyzer Segmented Flow Analyzer ICP-AES ICP-MS
HNO ₃ extract (0.43 mol l ⁻¹)	Al, K, Na, Ca, Mg, Fe, Mn , P, S Cd, Cu, Cr, Ni, Pb, Zn	ICP-AES ICP-MS

*The accuracy of this method for major oxides was checked and found to be excellent by re-analysis of 26 samples using glass beads.

4.3 Results and interpretation

In this paper focus is on the solid phase (major element chemistry and organic matter content; table 4.2), the related constituents in the displaced soil solution (Table 4.3), and the two extractions (Tables 4.4 and 4.5). In all cases data are available for both top and subsoil. To structure the presentation we will deal with the results in a number of subsections. The line of reasoning will go from the more basic aspects concerning the major Al bearing phases, to a discussion of the differences between top and subsoil and between regions within the country, concluding with a section on the consequences for soil monitoring practice.

4.3.1 General characterization

The XRF data corroborate the poor nature of the sandy soils with an SiO₂ content of well over 90 mass% and an Al₂O₃ content of between 1 and 4.5 mass%. The predominant Al

bearing phase in Dutch sandy soil is generally found to be feldspar (Vries and Breeuwsma, 1987; Locher and Bakker, 1990; Locher and Bakker, 1990; Salm and Vries, 2001). The classic triangular plot of the feldspar related base cations $\text{Na}_2\text{O}-\text{CaO}-\text{K}_2\text{O}$ (Blum and Stillings, 1995; Fig. 4.3) shows a mixture of sodium-rich plagioclase and K-feldspar. The few data points strongly deviating towards the CaO corner are samples containing some carbonate. The feldspar related base cations will be further referred to as the FBC, whereas the term BC (exchangeable base cations) also includes Mg.

Table 4.2

XRF results (oxides in mass%, S and Zr in mg kg^{-1} dry matter, $\text{ANC}_{(s)}$ in $\text{mol}_c \text{kg}^{-1}$ dry matter) and OM in mass% of dry matter for both top and subsoil, the last column indicates whether the topsoil is significantly different from the subsoil (+) or not (-).

	mean	st. error	median	minimum	maximum	N	top vs. subsoil
Topsoil							
SiO_2	95.96	0.152	96.1	91.9	98.8	92	+
Al_2O_3	2.23	0.079	2.15	0.71	4.30	92	+
K_2O	0.77	0.024	0.75	0.20	1.38	92	+
Na_2O	0.41	0.015	0.40	0.14	0.78	92	+
CaO^*	0.08	0.005	0.08	0.007	0.30*	90	-
MgO	0.046	0.006	0.030	0.000	0.328	92	+
Fe_2O_3	0.299	0.029	0.185	0.000	1.384	92	-
MnO	0.010	0.0004	0.009	0.006	0.031	92	-
P_2O_5	0.043	0.004	0.033	0.012	0.193	92	+
S	390	14.2	378	174	816	92	+
Zr	245	12	245	49	547	92	-
$\text{ANC}_{(s)}^*$	1.727	0.066	1.679	0.482	3.554	90	+
OM	3.82	0.21	3.86	0.38	9.62	92	+
Subsoil							
SiO_2	95.52	0.144	95.8	91.2	98.1	92	
Al_2O_3	2.51	0.074	2.37	1.13	4.73	92	
K_2O	0.85	0.022	0.83	0.41	1.45	92	
Na_2O	0.45	0.014	0.44	0.23	0.85	92	
CaO^*	0.09	0.004	0.09	0.026	0.95*	89	
MgO	0.076	0.007	0.065	0.000	0.439	92	
Fe_2O_3	0.311	0.025	0.225	0.000	1.274	92	
MnO	0.011	0.0006	0.01	0.006	0.039	92	
P_2O_5	0.023	0.002	0.018	0.011	0.095	92	
S	216	6.6	214	89	450	92	
Zr	255	14	241	54	962	92	
$\text{ANC}_{(s)}^*$	1.927	0.058	1.79	0.838	3.983	89	
OM	1.26	0.09	1.03	0.42	5.76	92	

* some outliers that clearly contained CaCO_3 were removed from the data for calculation of means and standard errors, they are however shown here as maximum values

Table 4.3

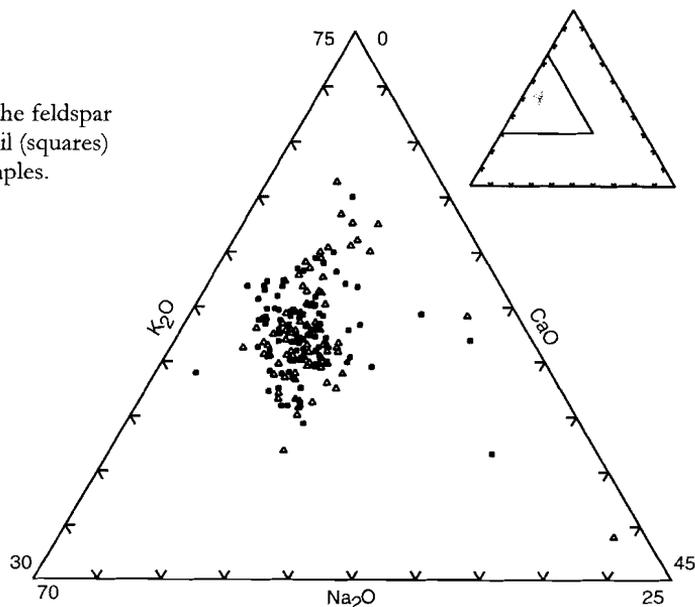
Results of the displaced soil solution for both top and subsoil. Yield in ml and the ions and DOC in mg l^{-1} , the last column indicates whether the topsoil is significantly different from the subsoil (+) or not (-).

	mean	st. error	median	minimum	maximum	N	top vs subsoil
Top soil							
Yield (ml)	53	3.6	50	5	120	90	+
pH	3.5	0.03	3.5	3.0	4.1	90	+
Al	6.0	0.26	5.53	2.11	14.62	90	+
Na	22.12	1.34	19.41	6.35	58.54	90	-
K	8.06	0.64	5.9	1.62	32.05	90	+
Ca	13.52	1.23	11.75	0.83	66.74	90	+
Mg	4.63	0.33	4.21	0.57	18.99	90	+
Fe	1.06	0.13	0.61	0.04	8.77	90	-
Mn	0.3	0.06	0.11	0.00	3.05	90	-
SO ₄	25.33	1.50	20.14	3.26	94.95	90	-
NO ₃	47.03	4.62	38.94	0.00	332	90	+
Cl	20.47	1.47	17.68	3.12	89.47	90	+
DOC	116.8	11.83	91.5	32	990	90	+
Sub soil							
Yield (ml)	66	4.3	60	5	120	89	
pH	3.78	0.03	3.8	3.3	4.6	89	
Al	7.29	0.51	5.94	1.78	23.78	89	
Na	20.67	1.25	16.22	5.36	52.86	89	
K	4.63	0.33	3.57	0.74	16.47	89	
Ca	8.37	0.85	5.02	0.76	40.04	89	
Mg	3.3	0.24	2.49	0.81	11.26	89	
Fe	0.81	0.21	0.27	0.00	16.13	89	
Mn	0.30	0.06	0.13	0.00	3.26	89	
SO ₄	27.74	2.38	21.19	2.83	130.9	89	
NO ₃	28.3	2.12	24.53	0.51	109.58	89	
Cl	24.88	1.98	19.66	5.02	140.72	89	
DOC	76.9	5.9	61	18	365	89	

A second triangular plot of $(\text{Na}_2\text{O}+\text{CaO})-\text{K}_2\text{O}-\text{Al}_2\text{O}_3$ that was proposed by Nesbitt and Young (1984, 1989) to visualize the weathering progression of rocks and minerals is shown in Fig. 4.4. With increased weathering the ratios of these elements shift towards the top of the plot (towards more Al rich secondary phases). This plot shows the same average composition in between plagioclase and K-feldspars but also the tendency to go from the base line of feldspars (midway between the base and the top of the triangle) towards products such as illite and even gibbsite. Some samples seem to be very low in weathering products but most of the samples have a secondary pool of some size.

To estimate the relative amount of Al in this secondary pool of weathered minerals we calculated the stoichiometric amount of Al in feldspars, assuming all Na, K and Ca to be present in feldspars. From this value we calculated the Al surplus and defined this to be present in the secondary pool. These surpluses range from about 0% to about 50% for the

Figure 4.3
Triangular plot showing the feldspar composition of the topsoil (squares) and subsoil (triangles) samples.



topsoil and from about 7% to about 50% for the deeper soil horizon (except for a few erroneous values due to CaO being present in carbonates and not in feldspars, see Table 4.6).

To gain further insight into the mineralogy and the reactive nature of the Al surpluses we compared the Al surplus in the solid phase to the Al in the HNO₃ extract, and we recalculated the Al(CaCl₂) into the Al saturation of the CEC and its total contribution to solid Al (Table 4.6) using the following formulas:

$$\text{CEC} = \{ \text{Na}(\text{CaCl}_2) + \text{K}(\text{CaCl}_2) + \text{Mg}(\text{CaCl}_2) + \text{Mn}(\text{CaCl}_2) + \text{Fe}(\text{CaCl}_2) + \text{Al}(\text{CaCl}_2) + \text{Ca}(\text{HNO}_3) \}$$

$$\text{Al}(\text{CEC}) = \text{Al}(\text{CaCl}_2)$$

and

$$\text{Al}(\text{reactive}) = \text{Al}(\text{HNO}_3)$$

with all concentrations recalculated to mmol_c kg⁻¹ dry soil. Because Na, K and Mg show similar concentration levels in both CaCl₂ and HNO₃ extracts (Tables 4.4 and 4.5), Ca(HNO₃) was used as a proxy for soil Ca in the CaCl₂ extract. The contributions of the other cations to the CEC and/or reactive phase were calculated analogously to Al. The use of CaCl₂ as the extraction medium in these acidified soils is expected to give reasonable estimates for Na(CEC), K(CEC) and Mg(CEC), but of course slightly underestimates Al(CEC). In addition to these calculations we plotted some relevant parameters against the Al surplus (Figs 4.5 - 4.11).

Table 4.4

Results of the CaCl₂ extractions of the solid phase for both top and subsoil. All results (except pH) recalculated to mg kg⁻¹ dry soil, the last column indicates whether the topsoil is significantly different from the subsoil (+) or not (-).

	mean	st. error	median	minimum	maximum	N	top vs subsoil
Top soil							
pH	3.56	0.03	3.56	3.13	4.4	90	+
Al	60.05	2.78	53.51	6.75	131.1	90	+
Na	11.42	1.5	7.3	2.5	114.9	90	+
K	12.51	1.11	10.6	2	68.5	90	+
Mg	12.62	1.34	6.6	1.56	70.97	90	+
Fe	7.11	0.58	6.14	0.62	32.67	90	+
Subsoil							
pH	4.18	0.03	4.25	3.17	4.55	89	
Al	36.87	1.84	34.79	10.8	92.06	89	
Na	7.72	0.61	5.85	0.6	31.9	89	
K	4.80	0.49	2.90	0.10	27.80	89	
Mg	5.17	0.69	2.27	0.53	32.46	89	
Fe	3.84	0.33	2.89	0.52	15.58	89	

Figure 4.4

Triangular plot showing the weathering tendency of the feldspars in topsoil (squares) and subsoil (triangles) samples.

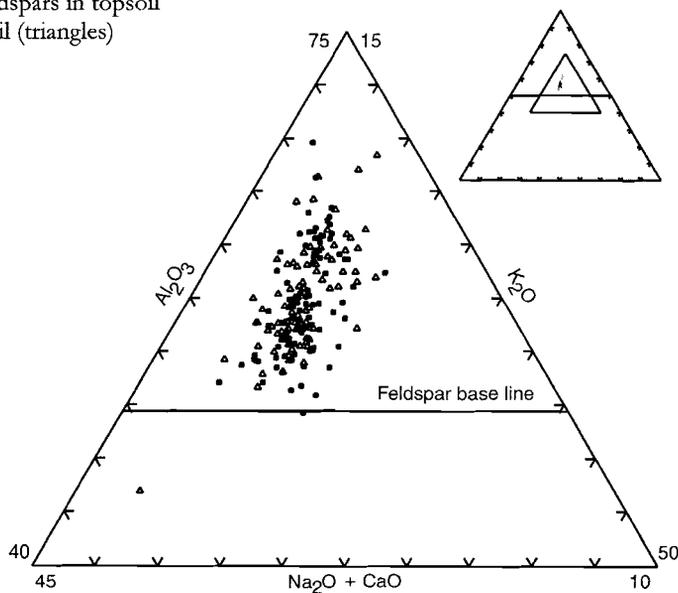


Table 4.5

Results of the HNO₃ extractions of the solid phase for both top and subsoil. All results recalculated to mg kg⁻¹ dry soil, the last column indicates whether the topsoil is significantly different from the subsoil (+) or not (-).

	mean	st. error	median	minimum	maximum	N	top vs. subsoil
Topsoil							
Al	809	44	759	147	1984	90	+
K	19.2	1.23	15.7	7.38	71.8	90	+
Na	7.3	1.15	4.94	1.65	102	90	+
Ca	55.2	8.27	29.6	2.06	563	90	+
Mg	10.2	1.28	6.17	0.89	91.5	90	+
Fe	313	39	224	42.3	3317	90	+
Mn	7.48	2.14	2.29	0.50	62.0	36*	-
Subsoil							
Al	934	41	873	228	2498	89	
K	10.6	0.52	9.2	6.21	36.6	89	
Na	4.32	0.34	3.21	1.55	18.7	89	
Ca	19.9	3.14	9.37	1.19	167	89	
Mg	3.26	0.42	1.6	0.53	20.7	89	
Fe	120	11.4	94.5	14.0	601	89	
Mn	10.4	2.62	5.34	0.51	56.8	27*	

* only the samples above the detection limit are reported, these generally coincide with the highest Fe and Al values

In sandy soils organic matter (OM) usually is the main bearer of surface charge. However, a systematic increase of CEC with the size of the secondary Al-pool is found as well (Figs 4.5 and 4.6). Reason for the double logarithmic nature of the relation of CEC with OM may be found in the heterogeneous nature of the OM and the influence of the actual pH.

The fact that Na, K, and Mg show the same levels in both the CaCl₂ en HNO₃ extracts whereas Al is about 15 times higher in HNO₃ extracts, shows that the reactive or easily dissolvable Al originates from a mineral phase that is virtually free of base cations (BC). This seems to be in agreement with the general conception that the secondary, weathering products are an important source of Al for acidity buffering. Reactive Al amounts to about 7% of total solid Al, which is about 30% of the Al surplus. Al(CEC) only forms a very small contribution to the total Al. In accordance with the preferential sorption of trivalent over divalent ions, the estimated Al/BC ratios on the CEC are higher than those measured in the displaced soil solution.

Naturally, Al in the secondary pool has as its limit the total Al content of the soil. Fig. 4.7 indeed shows a more or less linear upper limit, however, at a ratio of about 40%, with some values peaking to 50%. Thus far, we have found no explanation for not finding values closer to the theoretical limit of 100%, not even at low total Al content. The idea that the reactive or easily dissolvable Al forms part of the secondary pool is confirmed by the linear relationship between the Al(HNO₃) and the calculated Al surplus (Fig. 4.8). No relation was found between Al in displaced soil solution and the absolute or relative amounts of the Al surplus.

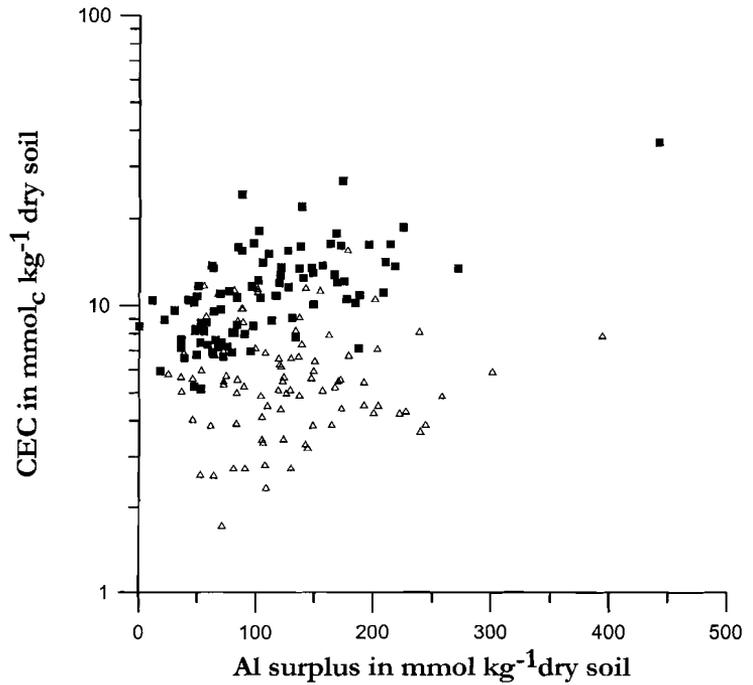


Figure 4.5
The relation between the cation exchange capacity and the Al surplus for both topsoil (squares) and subsoil (triangles).

Table 4.6

Calculated parameters: Al total, Al surplus, Al(CEC) and Al(reactive) in $\text{mmol}_c \text{kg}^{-1}$ dry soil. CEC estimate in $\text{mmol}_c \text{kg}^{-1}$ dry soil is based on all cations in CaCl_2 extract plus Ca in HNO_3 extract. Both ratios are in $\text{mmol}_c:\text{mmol}_c$, the last column indicates whether the topsoil is significantly different from the subsoil (+) or not (-).

	mean	st. error	median	minimum	maximum	N	top vs subsoil
Topsoil							
Al total	1299	45	1262	415	2529	90	+
Al surplus	329	21	289	0.78	1325	90	+
Al(CEC)	6.7	0.3	5.9	0.8	14.6	90	+
Al(reactive)	89.9	4.8	84.3	16.3	220	90	+
CEC estimate	11.6	0.5	10.8	5.2	36.6	90	+
Al/BC ratio CEC	1.36	0.11	1.1	0.03	4.13	90	+
Al/BC ratio solution	0.17	0.01	0.16	0.02	0.48	90	+
Subsoil							
Al total	1441	39	1372	66	2442	89	
Al surplus	378	20	360	75	1181	89	
Al(CEC)	4.1	0.200	3.9	1.2	10.2	89	
Al(reactive)	103.7	4.5	97.0	25.3	277.6	89	
CEC estimate	6	0.3	5.5	1.7	11.8	89	
Al/BC ratio CEC	2.1	0.17	1.84	0.08	8.71	89	
Al/BC ratio solution	0.22	0.02	0.2	0.05	0.76	89	

The soil moisture data for both pH and Al (Table 4.3) show values that are generally considered indicative of advanced stages of soil acidification, indicating acidity buffering processes involving the release of Al (Ulrich and Sumner, 1991). For instance for aluminium Mulder (1988) reports values between 3.7 and 37 mg l⁻¹ in soil solution from other sandy to loamy soils in the Netherlands, and de Vries (1994) reports values between 7 and 29 mg l⁻¹ in the soil solution from the mineral topsoil. Most authors consider the major buffering in acid sandy and loamy soils to be provided by Al release from the secondary mineral pool and from the exchange complex (Grinsven et al., 1986; Grinsven, 1988; Mulder, 1988; Mulder et al., 1989; Ulrich and Sumner, 1991; Grinsven and Riemsdijk, 1992; Dahlgren and Walker, 1993; Vries, 1994; Salm and Verstraten, 1994; Salm, 1999). They assume that once the secondary Al bearing pool has become depleted, Al-release will be severely limited as feldspar dissolution is much slower, and thus the pH will drop to values well below 3 (Mulder, 1988). However, even with extreme proton loads of well over 6000 mol_c ha⁻¹ y⁻¹ pH values below 2.5 are virtually impossible. Moreover, in our data, even in soils without a calculated secondary pool we encounter high Al levels in the displaced soil solution, demonstrating that Al release from the primary pool can also be a major, sufficiently fast, buffering process.

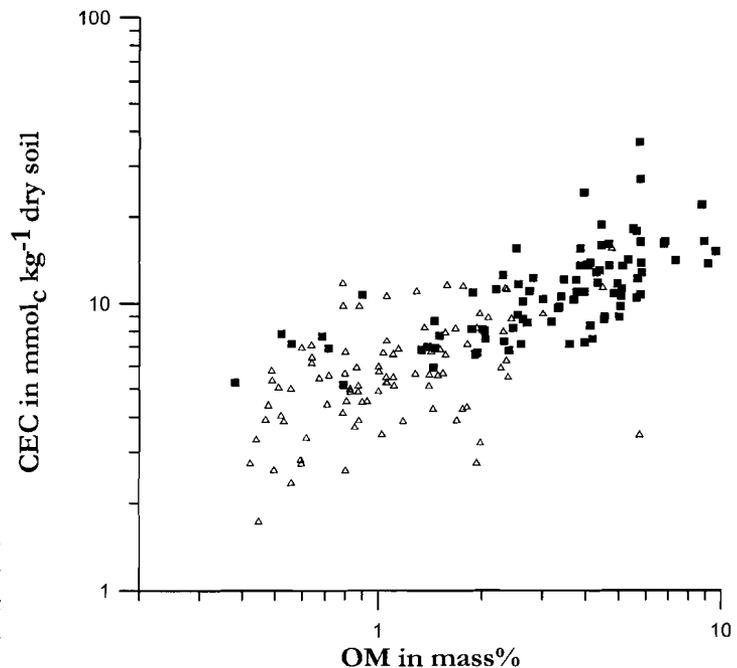


Figure 4.6

The relation between the cation exchange capacity and the OM content for both topsoil (squares) and subsoil (triangles).

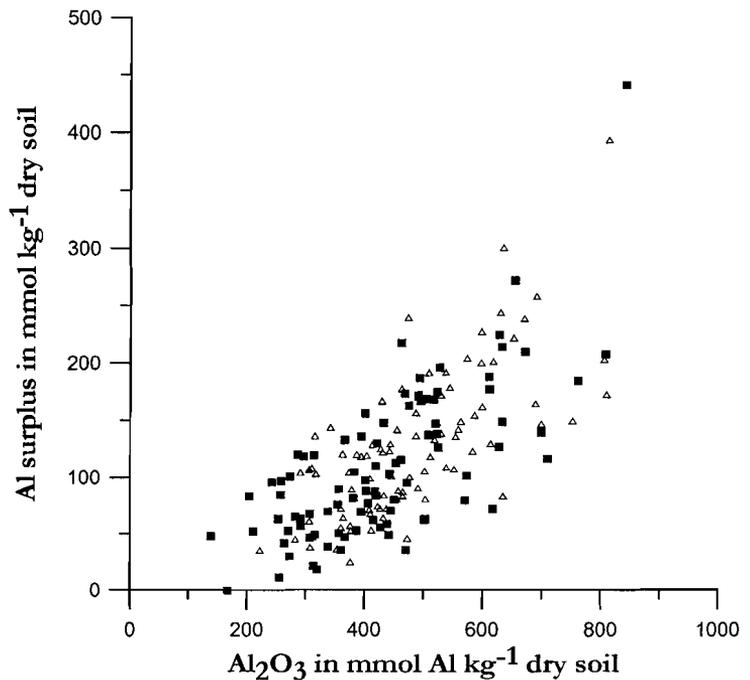


Figure 4.7

The relation between the Al surplus and the total Al₂O₃ content for both topsoil (squares) and subsoil (triangles).

For this reason the composition of the displaced soil solution has been considered in view of congruent dissolution of feldspars. The soil solution proves to be much too low in Al (or too high in FBC; Fig. 4.9), also when corrected for initial rain and seawater contributions. Thus, even at these advanced stages of acidification, in most soils the soil solution is still being provided with "surplus" of base cations either as a result of preferential leaching from the feldspar lattice, or as a result of precipitation of previously dissolved Al in secondary phases.

4.3.2 Differences between top and subsoil

The above results show some of their more interesting features when the topsoil samples are compared to the subsoil samples. With respect to the immobile, solid phase this approach is one form of what is commonly known as the historic approach, in which the current situation is compared to a pristine reference situation. Ideally this reference is a past measurement on the same location. For lack of such data, here the subsoil is used as a proxy.

The elements of major interest (Al, Ca, K, Na) in the solid phase all show a significant decrease in the topsoil compared to the subsoil, whereas OM is higher in the topsoil (Table 4.2). We used the XRF data on the total major element concentrations to calculate the acid neutralizing capacity of the solid phase (ANC_(s); Table 4.2) following Van Breemen et al. (1983, 1984):

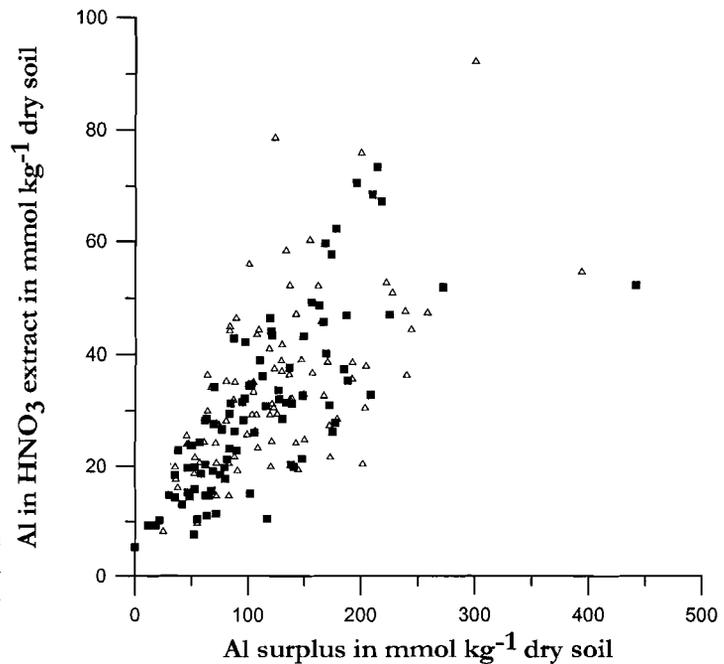


Figure 4.8

The relation between reactive Al and the Al surplus for both topsoil (squares) and subsoil (triangles).

$$\text{ANC}_{(s)} = 6(\text{Al}_2\text{O}_3) + 2(\text{CaO}) + 2(\text{MgO}) + 2(\text{K}_2\text{O}) + 2(\text{Na}_2\text{O}) + 2(\text{MnO}) + 2(\text{FeO}) - 2(\text{SO}_3) - 2(\text{P}_2\text{O}_5)$$

For a soil slice of 20 cm thickness and assuming a bulk density of 1600 kg m^{-3} this results in values ranging from about $1550 \text{ kmol}_c \text{ ha}^{-1}$ for the poorest soils to over $11000 \text{ kmol}_c \text{ ha}^{-1}$ for the few soils still containing carbonates. The average $\text{ANC}_{(s)}$ in the subsoil is $1.86 \text{ mol}_c \text{ kg}^{-1}$ dry soil and in the topsoil $1.63 \text{ mol}_c \text{ kg}^{-1}$, equivalent to about $5950 \text{ kmol}_c \text{ ha}^{-1}$ and $5200 \text{ kmol}_c \text{ ha}^{-1}$ respectively. The average $\Delta\text{ANC}_{(s)}$ of $0.23 \pm 0.08 \text{ mol}_c \text{ kg}^{-1}$ dry soil is equivalent to a proton load of $740 \pm 260 \text{ kmol}_c \text{ ha}^{-1}$.

With the few carbonate containing soils excluded from the calculations, on average 74.3% of the $\text{ANC}_{(s)}$ is contained in feldspars and 19.3% in secondary Al-phases. The remaining 6.4% is mainly associated with iron. For the *change* in $\text{ANC}_{(s)}$ relative contributions are slightly different. Congruent dissolution of feldspars on average accounts for 62.3% of $\Delta\text{ANC}_{(s)}$, and dissolution of secondary Al-phases for 24.7%. Despite of this slight over-representation of secondary Al-phases, feldspar and feldspar related Al clearly predominates. Thus, in the long term feldspar dissolution is the determinative phase in acid buffering in Dutch sandy soils, whereas depletion of the secondary Al-pool is of less importance.

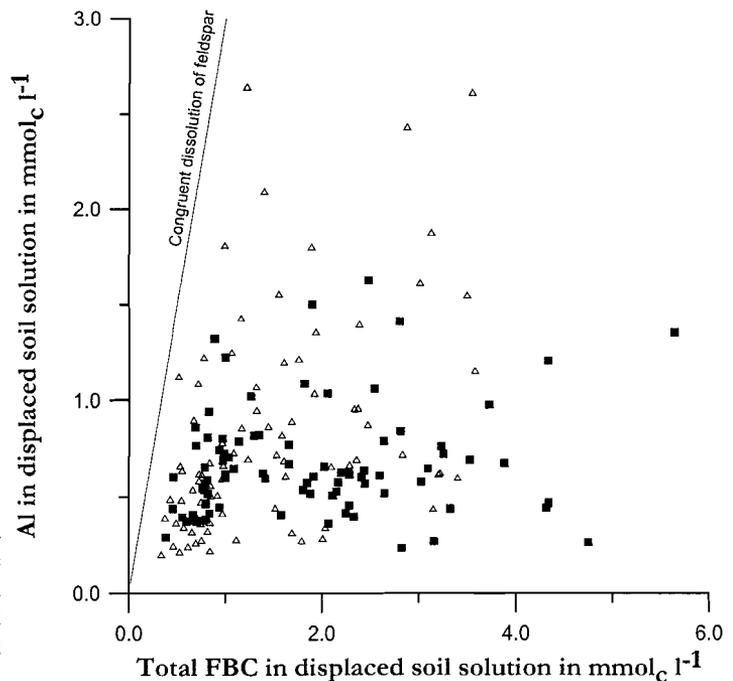
Fig. 4.10 shows the contribution of the FBC and Al to the $\Delta\text{ANC}_{(s)}$ for the individual samples. The negative values for $\Delta\text{ANC}_{(s)}$ that appear from this figure clearly show that the historic approach with the subsoil as proxy for the topsoil is not applicable to single profiles.

Locally, the subsoil may initially have been different from the topsoil. On a regional basis, however, the assumption of similar parent material for topsoil and subsoil is valid, as evidenced e.g. by the immobile element Zr (Table 4.2, Fig. 4.11). The small proportion of data points showing a relative FBC contribution that is higher than the equivalent Al contribution confirm the earlier conclusion about preferential leaching of base cations or precipitation of Al in secondary phases (Fig 4.10).

Surprisingly iron-minerals do not contribute to $\Delta\text{ANC}_{(s)}$, although the reactivity of Fe is much higher in the topsoil than in the subsoil, as evidenced by the concentrations in the HNO_3 extracts (Table 4.5). In contrast, Mg and S only marginally contribute to the total $\text{ANC}_{(s)}$ but account for about 6.5% each to the $\Delta\text{ANC}_{(s)}$. The data on the HNO_3 extracts indicate that the Mg-phase involved is not a fast reacting phase (Table 4.5). We interpret the data on Mg and Fe to indicate the presence of Mg and Fe bearing clay minerals such as biotite ($\text{K}(\text{Mg},\text{Fe})_3[\text{AlSi}_3\text{O}_{10}(\text{OH})_2]$). Upon weathering, K and possible other FBCs as well as Mg remain in solution, while Fe precipitates *in situ* as a secondary, more reactive, phase.

Figure 4.9

The relation between Al and feldspar related base cations in displaced soil solution for both topsoil (squares) and subsoil (triangles).



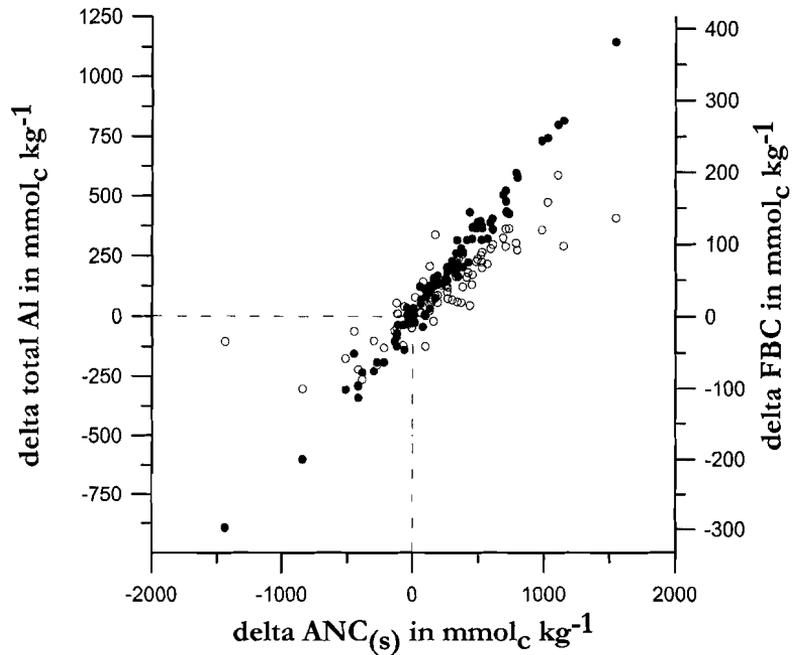


Figure 4.10

The relation between ΔAl and ΔANC (solid circles) and between ΔFBC and ΔANC (open circles).

A positive contribution of S to $\Delta\text{ANC}_{(s)}$ of course involves accumulation in the topsoil and not dissolution. In view of the oxidized nature of the soil profiles sampled, this S is most likely to be contained in organic matter, and is thereby evidence of the active role of the vegetation in acidification buffering. This phenomenon was also identified by Mayer et al. (1995, 2001) who estimated mean residence times of S in forest soils to be between several years and many decades. Novak et al. (2000) identified an S pool in forest soils in central Europe as a substantial contributor to the S fluxes in these soils. Immobilization in the soil organic matter is only part of the total vegetation uptake, so the calculated contribution of S to $\Delta\text{ANC}_{(s)}$ is a lower limit. Naturally, N is also involved in biological processes such as immobilization in organic matter. According to De Vries (1994), the actual acidification rate is less than deposition estimates suggest, due to N retention by immobilization and uptake and/or denitrification. In this view, the subject of acidification research is rigidly narrowed down. The biological soil system is set apart from the mineralogical part, where the biological role is described as reducing net inputs, and only the mineralogical reactions are considered as acidification buffering. In our approach this distinction is not made and biological and mineralogical mechanisms that counteract acid inputs in soil are treated alike.

Some straightforward calculations were made to test the plausibility of the proton load of $740 \pm 260 \text{ kmol}_c \text{ ha}^{-1}$ derived above using the historic approach. The proton load deposited over time is the result of anthropogenic influence superimposed on natural processes. For the anthropogenic part we adopted an average acid deposition of 4.0 to $6.0 \text{ kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$ over a

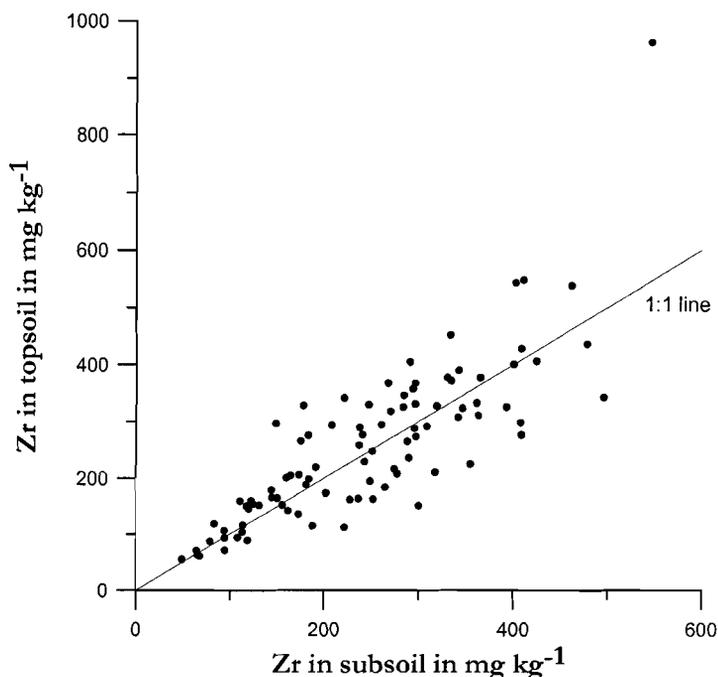


Figure 4.11
The relation between
Zr in top and subsoil.

period of 50 years, equivalent to 200-300 kmol_c/ha, in line with the reported data (Heij and Erisman, 1995; Heij and Erisman, 1997)(www.rivm.nl). This amounts to an anthropogenic contribution of between 20% and 50% to the depletion of the ANC_(s) as calculated from the XRF data. For the natural part an assumption of an average total precipitation of 800 mm y⁻¹ at pH of 5.3 and a duration of 10,000 years -the time elapsed since the last ice age- results in a natural load of 200 kmol_c ha⁻¹. CO₂-production within the soil compartment is a form of scavenging of CO₂ from the atmosphere by the vegetation. Taking this into account a net precipitation of 300 mm y⁻¹ at pH of 4.9 results in a natural load of 400 kmol_c ha⁻¹. This gives a range in the total acid load of 400-700 kmol_c ha⁻¹ since the last ice age, which matches well with the historic approach figure. With at least 20% of the depletion of the ANC_(s) due to the increased acid deposition during the last century only, compared to natural acidification taking 10,000 years to account for the remainder, the anthropogenic contribution clearly has its impact. Given that the overall contribution of Al to ΔANC_(s) is 71.4%, it must also be concluded that already under natural conditions acid buffering through Al-release contributes significantly to ΔANC_(s).

When compared to the total amount of ANC_(s) still present in the top 20 cm it can easily be calculated that with an acid deposition reduced to a critical load of about 2.0 to 2.4 kmol_c ha⁻¹ y⁻¹ (as is the policy aim in the Netherlands) the topsoil roughly has between 600 and 5500 years of ANC_(s) left. This of course assumes that the weathering rate of feldspar remains

sufficient. To get an impression of these kinetics we made some further simple calculations. Here we made the following additional assumptions: feldspar grain size in Dutch sands varies between 2 and 250 μm (Locher and Bakker, 1990), specific surface has been calculated assuming spherical particles, average surface weathering rate of feldspars under soil conditions at pH around 3.5 is between 10^{-11} and 10^{-12} mol (feldspar) $\text{m}^{-2} \text{sec}^{-1}$ (Blum, 1993; Blum and Stillings, 1995; White, 1995), bulk density of feldspars is 2650 kg m^{-3} , and the average feldspar content is 6 mass%. This results in an acid neutralizing rate of between $0.4 \text{ kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$ (250 μm , 10^{-11} feldspar $\text{m}^{-2} \text{sec}^{-1}$) and $450 \text{ kmol}_c \text{ ha}^{-1} \text{ y}^{-1}$ (2 μm , 10^{-12} feldspar $\text{m}^{-2} \text{sec}^{-1}$). Feldspar dissolution kinetics are still far from completely understood, as many mechanisms are known to exist but their quantification is still heavily debated (Blum, 1993; Blum and Stillings, 1995; Drever and Clow, 1995; White, 1995; White and Brantley, 1995) and decisive conclusions on this wide range in estimate cannot be made. However, the figures suggest that for average feldspar grain size rates will be sufficiently high. Our data also indicate that feldspar dissolution kinetics have been adequate both under natural and under aggravated acidifying conditions.

Whereas the secondary Al-pool as well as reactive Al ($\text{Al}(\text{HNO}_3)$) show an increase towards the subsoil, the CEC is about twice as high in the topsoil (Tables 4.5 and 4.6), which is primarily related to the difference in OM (Fig. 4.6). The higher CEC accounts for the higher relative contribution of CEC-bound Al to total Al, even though the Al/BC ratio is slightly higher in the deeper horizon. The latter is a reflection of the concentrations in displaced soil solution, which show a decrease of DOC, Ca, and K, and an increase of pH, Al, and the Al/BC ratio with depth (Tables 4.3 and 4.6). The observed trends in the soil solution might be indicative of biogenic degradation of DOC and uptake of nutrients.

4.3.3 Evidence for regional differences

The data in tables 4.2 - 4.6 show a wide range in many parameters indicating a large spatial variability. From a geological perspective it can be hypothesized that the spatial variability will show regional patterns and not just random variation. To improve interpretation on the interprovincial level it is essential to analyze this regionality. The solid phase has the clearest relation with geology through regionally differing parent material, whereas the soil solution has an important determinant in the parent material but will also be influenced by other phenomena such as deposition and throughfall, vegetation and groundwater.

Because these differences involve multiple elements we used a multivariate technique called fuzzy c -means cluster analysis (Bezdek, 1981; Bezdek et al., 1984; Vriend, et al., 1988). Cluster analysis is a multivariate technique developed for finding homogeneous groups in datasets. In traditional "hard" clustering the memberships of the samples are either one or zero, thus each sample belongs to only one cluster. In fuzzy clustering, samples can have memberships between one and zero, so they can belong to more than one cluster. Most samples will have a high membership in one cluster and low to very low memberships in one or two other clusters, with the memberships adding to one. The advantage of the fuzzy concept is that samples with outlying values, or samples that are otherwise hard to classify, do not mess up the cluster configuration, because their memberships are equally divided over all clusters. These samples can be considered as being unclassified.

We applied this technique to two independent subsets of the data, one including information on the major elements and the composition of the reactive phases in the solid phase, and the other including information on the soil solution and the CEC (see Tables 4.7 and 4.8 and Fig. 4.12). To meet normality demands, skewed parameters have been logtransformed prior to clustering. In both subsets a 4 cluster model worked best.

In the solid phase cluster S (for south) shows the lowest amounts of major oxides other than SiO₂ in the mineral phase, intermediate OM% and rather low concentrations in the HNO₃ extract (Table 4.7a). This cluster can be characterized as consisting of poor sands of low reactivity. It is primarily found in the topsoil of Noord Brabant (Fig. 4.12; see also Fig. 4.2). Clusters C (central) and N (north) have intermediate amounts of the non-Si oxides. Cluster C has the lowest OM% and generally the lowest concentrations in the HNO₃ extract. It can be characterized as comprising sands of intermediate mineralogical richness but low reactivity. This cluster is found in most subsoils. Cluster N has the highest OM% and the highest or second highest (Fe, Mn) concentrations in the HNO₃ extract. These samples can be characterized as sands of intermediate mineralogical richness and high reactivity. They are found mainly in the topsoils of the northern provinces and the Veluwe. Cluster E (east) has the highest amounts of non-Si oxides, rather low OM% and concentrations in the HNO₃ extracts similar to those of cluster N. This cluster, of richest mineralogical composition and high reactivity, forms a clear group (both in top and subsoil) in eastern Gelderland and the southern parts of the Utrechtse Heuvelrug and the Veluwe. In general average reactivity

Table 4.7a

Cluster centres for the solid phase related parameters. Oxides in mass% of total oxides, S in mg kg⁻¹ dry matter, OM in mass% of dry matter. Parameters in HNO₃ extract recalculated to mg kg⁻¹ dry soil. Al surplus (mmol_c kg⁻¹) was calculated from the clustercentres for Al₂O₃, Na₂O, K₂O, and CaO.

	cluster S	cluster C	cluster N	cluster E
Na ₂ O	0.31	0.42	0.42	0.62
MgO	0.01	0.05	0.04	0.12
Al ₂ O ₃	1.60	2.23	2.39	3.40
P ₂ O ₅	0.03	0.02	0.04	0.04
K ₂ O	0.58	0.78	0.81	1.12
CaO	0.04	0.08	0.09	0.14
MnO	0.01	0.01	0.01	0.02
Fe ₂ O ₃	0.07	0.20	0.24	0.59
S	355.7	203.8	414.1	270.6
OM	2.72	0.97	3.67	1.59
K(HNO ₃)	11.3	4.3	17.5	15.4
Na(HNO ₃)	5.1	2.7	6.2	4.5
Ca(HNO ₃)	26.1	7.1	41.0	35.6
Al(HNO ₃)	614.7	765.9	886.0	839.8
Fe(HNO ₃)	144.1	73.0	210.1	292.6
Mg(HNO ₃)	4.3	0.5	7.9	4.5
Mn(HNO ₃)	0.1	0.1	0.4	5.7
Al surplus	234.2	327.2	393.6	535.1

increases with increasing mineralogical richness of the clusters. On a relative basis cluster E is slightly less reactive. As was suggested earlier S content is strongly related to OM%.

The cluster analyses were performed on datasets in which both top and subsoil samples were included as individual entities, not as pairs. Thus, the cluster outcome for the solid phase does not give direct results about the acidity status of each location and its regional pattern. However, the results do indicate the relevance of distinguishing five regions (Fig. 4.12). Some regions prove to exhibit clearly differing values for $\Delta\text{ANC}_{(s)}$ (Table 4.7b). The poor sands of Noord-Brabant show the largest $\Delta\text{ANC}_{(s)}$, presumably related to the ammonia emissions from intensive animal husbandry that is especially concentrated in this area. The contribution of Al to $\Delta\text{ANC}_{(s)}$ in Noord-Brabant is near the average of 71%. The soils of the Veluwe remarkably show a negative $\Delta\text{ANC}_{(s)}$ with an Al contribution of 55%. We are inclined to ascribe this phenomenon to the extensive anthropogenic soil displacement due to the typical form of subsistence farming practiced in the Netherlands (Pape, 1970) and subsequent reforestation in the 19th century to combat drifting sands. This probably has led to vertical homogenization of the soil and a resetting of the $\Delta\text{ANC}_{(s)}$ gauge.

Table 4.7b

Regional differences in acidity status, $\Delta\text{ANC}_{(s)}$ and ΔAl are in $\text{mmol}_c \text{kg}^{-1}$ dry soil.

	Noord-Brabant	Utrechtse Heuvelrug	Veluwe	northern provinces	Holocene influenced sites	overall average
$\Delta\text{ANC}_{(s)}$	411	237	-44	207	246	230
ΔAl	275	171	-24	148	168	164

For the soil solution related subset two clusters, T1 and T2, are clearly predominant in the topsoil whereas the other clusters, S1 and S2, contain the subsoil samples (Table 4.8; Fig. 4.12). Clusters T1 and T2 have lower pH and generally higher levels of all other parameters than S1 and S2. Cluster T1 is mainly found in the northern provinces and Utrecht whereas cluster T2 is present in the remainder of the country. Cluster T1 is characterized by the highest DOC concentrations and by high concentrations of BC in the displaced soil solution compared to cluster T2. Al concentrations in displaced soil solution in these two clusters are the same, whereas Al on the CEC in cluster T1 is lower, suggesting that the simultaneous occurrence of high DOC and BC lowers the relative amount of Al on the CEC. Cluster S1 appears in the northern provinces, eastern Gelderland and some sites in Utrecht whereas cluster S2 appears in the mineralogically poorer locations. Cluster S1 is higher in DOC, BC and Al in displaced soil solution and slightly higher in BC on the CEC than S2. Al/BC ratios in the soil solution primarily reflect regional differences, whereas Al/BC ratios on the CEC also show a clear increase from top to subsoil related to DOC.

The provenance of the respective sediments (Edelman, 1933; Baren, 1934; Tebbens et al., 1995; Huisman, 1998; Huisman and Kiden, 1998; Tebbens et al., 2000), is reflected in our findings. Noord Brabant consists of Pleistocene sediments deposited by the Meuse-Scheldt system. This system mainly supplied sediment derived from already strongly weathered Tertiary sandstone (generally diagnosed by a stable heavy mineral association) which therefore

Table 4.8

Cluster centres for the soil solution related parameters. Concentrations in displaced soil solution are in mg l^{-1} , parameters in CaCl_2 extract are recalculated to mg kg^{-1} dry soil. Al/BC ratios were calculated from the cluster centres for Al, Na, K, Mg and Ca.

	Cluster T1	Cluster T2	Cluster S1	Cluster S2
pH	3.53	3.59	3.69	3.82
DOC	117.5	82.1	80.0	51.2
K	8.10	5.38	5.24	2.85
Na	28.38	15.32	21.80	11.80
Ca	16.65	6.20	9.43	2.78
Al	6.09	5.97	6.55	4.18
Fe	0.96	0.44	0.45	0.13
Mg	5.72	2.81	3.91	1.62
Mn	0.13	0.10	0.15	0.06
SO ₄	23.2	23.3	27.6	16.2
NO ₃	28.7	30.1	28.8	18.0
Cl	22.6	17.6	22.1	13.6
pH(CaCl ₂)	3.62	3.73	3.96	4.23
Na(CaCl ₂)	9.25	7.01	6.98	5.11
K(CaCl ₂)	9.34	6.83	4.60	2.81
Al(CaCl ₂)	42.76	51.88	38.63	33.14
Mg(CaCl ₂)	10.14	4.73	3.47	0.72
Ca(HNO ₃)	45.55	24.23	20.83	7.70
Al/BC(solution)	0.25	0.49	0.39	0.54
Al/BC(CEC)	1.63	3.41	2.94	5.43

shows a low feldspar content. The Rhine system, which provided the other provinces with sediment, has a richer sediment type because of the richer parent rocks that provided the sediment load (Andel, 1950). This richer, less weathered sediment load is characterized by an unstable heavy mineral association and also contains more feldspars. In addition to the different river systems, the influence of glacial land ice should be noted. This ice mass only covered the northern half of the Netherlands, meaning that all our samples have been influenced except those in Noord Brabant. The occurrence of cluster E, highest in mineralogical richness, coincides with the edge of the Pleistocene area that is probably influenced by Holocene river deposits (Fig. 4.1.) Its relatively low reactivity is probably due to a different nature of the secondary Al pool.

Patterns in the soil solution can be linked to the richness of the parent material and to the type of vegetation. The relation with soil type is confirmed through a χ^2 test that shows that the clustering results for the solid phase and soil solution related parameters are not independent. The sites higher in DOC coincide with those higher in OM and are characterized by higher amounts of BC and Al and lower Al/BC ratios, especially on the CEC, indicating a richer (soil) ecosystem. From field observations the richer sites are known to have a higher contribution of deciduous trees in their mixed vegetation and to be located closest to agricultural activities. The vegetation on the poorer substrates is mostly less varied

consisting of one or two coniferous species and hardly any undergrowth except sometimes ferns and grasses.

4.3.4 Consequences for monitoring

A clear understanding of the phenomena involved in soil acidification is not only needed for interpreting the monitoring results, it is, in addition to a general definition of the objective, quintessential in developing a successful monitoring strategy. Only then, adequate operational choices can be made. To this end, an extensive pilot study, such as our main research campaign as discussed in this paper, is virtually indispensable. Based on the interpretation of the results we will highlight the most important consequences for soil acidity monitoring. The overall picture emerging from our data is that a thorough understanding of the processes of soil acidification can only be obtained by analyzing and interpreting a broad set of parameters providing information on both the solid phase and the soil solution. This also implies that being abreast with the acidity literature, from the many angles and scientific disciplines that are of relevance, is essential. In practice monitoring research is often much more limited, bearing the mark of a single discipline or angle (e.g. agriculture, deposition, weathering, forestry, modelling, biochemistry, soil science). This only contributes to the controversies mentioned earlier.

The methods chosen for monitoring soil acidification are crucial to the information obtained about the status of the soil. The total element analysis of the solid phase was essential in two ways, first to understand the total composition of the soil matrix that provides the ultimate buffer and second to appreciate the relative importance of the various types of reactive components in the soil. The extractive methods tested in this research project provided intelligible information on these reactive components. The results from the displaced soil solution proved harder to interpret. When concentration levels measured in this project are compared to those reported for the situation of some 15 years ago (Mulder, 1988; Vries, 1994), little change can be observed. This corroborates the idea that as long as the soil is in a certain buffering stage, a kinetic steady state, the soil solution composition will be fairly constant. It will only significantly change when the phase providing the major part of the acid neutralizing capacity during this buffering stage has been totally depleted or when a drastic increase/decrease of the proton load occurs. Only the analysis of solid phase related parameters can provide insight into the exhaustion of the $ANC_{(s)}$ in a certain buffering stage. For an insight into fluctuations in proton load, monitoring of the deposition is more straightforward.

Considering these findings, in a monitoring strategy a combination of methods giving insight into the changes in both the solid phase and the soil solution is to be preferred. In our project the data relating to the solid phase were provided by the total element analysis (XRF) and by the HNO_3 extractions. In a monitoring system the total element analysis of the solid phase should at least be determined once, to define the soil matrix in which monitoring is going to take place. An additional application of total element analysis can be found in the historic approach. The solid phase could be re-analyzed every 10 to 20 years with the earlier analysis instead of the subsoil as the reference. The HNO_3 extraction carried out on a regular basis can provide insight into the changes in the reactive Al pool. The milder extraction with

0.01 M CaCl₂ is indicative of the occupation of the CEC, and indirectly of the soil solution. When nonetheless focus is on soil solution concentrations, at least precipitation fluxes of the period preceding sampling should be considered in interpreting these intensity parameters. Some final remarks on the operational and methodological choices in a monitoring setting relate to the parameters analyzed and the practical feasibility. Sufficient parameters should be analyzed to allow comprehensive interpretation. For instance, focussing only on Al and the BC in the solid phase would conceal the significant contribution of S accumulation in acid buffering. Not taking into account DOC concentrations in displaced soil solution severely hampers the interpretation of Al/BC ratios. Solid phase extractions are far less laborious and they always give results whereas the soil solution, due to the desiccation of soils especially in summer, may fail in that respect.

A second aspect affecting the use of monitoring data is the monitoring objective. If the main interest is the progressive deterioration of the ANC then the soil solution is an inappropriate medium because of its complicated relationship with the solid phase. Given a baseline characterization of the solid phase, results from simple extracts are much more straightforward. If the main interest is to monitor the suitability of the soil for healthy forest growth then the displaced soil solution seems to be an obvious medium. Assessing forest vitality via this medium requires a thorough understanding of the effects of the soil solution chemistry on forest health. This relation, however, is still ill-understood, because of biological idiosyncrasies by which ecosystems can survive under circumstances that in the laboratory prove to be lethal (Olsthoorn, 1998). Forest vitality in Scandinavia, for example, was predicted to be much worse than it actually is. A possible explanation are the recently discovered “rock-eating” fungi that actively penetrate minerals in search for nutrients (Breemen et al., 2000a,b; Chen, et al., 2000). Therefore the practical applicability of displaced soil solution data in monitoring growing factors for forests is limited. A method more directly related to forest health may be advisable.

A third issue that affects the monitoring strategy is the regionality that exists in the parent material. Even for quite similar areas of sandy soils we have shown that both in the solid phase and in the soil solution regional differences are far from negligible. The regionality basically results from the variation in mineralogical richness of the parent material and the amount of OM that accumulated from the associated vegetation. The subsequent influence of soil type, ecosystem richness, and DOC concentration on Al/BC ratios and the equilibrium between soil solution and CEC makes clear that regional variation should be an important issue to address when interpreting soil acidity data. As soon as interprovincial comparisons are being made the regional aspect should be carefully considered, otherwise mistakes are inevitable. Even within provinces, attention should be paid to spatial differences between monitoring sites.

To sum up, only once the systematics of soil acidification are thoroughly understood will it be possible to develop a monitoring strategy based on a selection of parameters. Clear objectives should include both the subject of the monitoring effort (soil, ecosystem, drainage system) and the more specific choices on operational details. In principle the monitoring objectives can be chosen freely by the responsible authorities. However, the soil system and its specifics concerning acidification pose restraints on what is conceivable and certainly determine the effort that is needed to reach the stated goals.

4.4 Conclusions

We will summarize our major findings following the four questions stated in the introduction.

What is the major source of buffering in acid sandy soils?

- Al release is the major source of buffering, indicated by Al concentrations and pH in displaced soil solution typical of advanced stages of soil acidification;
- pH and Al concentrations in displaced soil solution in soils that are nearly depleted of secondary Al remain on the same level, indicative of the sufficiently fast dissolution of primary minerals to buffer incoming acidity;
- The predominant Al bearing phases are feldspars, making up 74.3% of the $ANC_{(s)}$, and secondary Al minerals containing no base cations, making up 19.3% of the $ANC_{(s)}$;
- Al concentrations in HNO_3 extracts, reactive Al, correlate with the secondary Al pool;
- On average, reactive Al forms 7% of total Al in the solid phase and 30% of Al in the secondary pool;
- Al/BC ratios of around 0.2 in displaced soil solution and of 2.0 on the CEC indicate a soil solution chemistry not resulting from the sole dissolution of secondary Al but with a strong contribution of dissolving BC, and the preferential adsorption of Al on the CEC;
- From the historic approach it is concluded that feldspars are the determinative phase in acid buffering in Dutch sandy soils.

Does a comparison between top and subsoil samples (using the subsoil as a proxy for undisturbed topsoil) offer possibilities to evaluate the acidity status of the soil, and if so what is the status of Dutch sandy soils?

- Application of the historic approach, using the subsoil as a proxy for the initial composition of the topsoil, proved feasible given the number of sample locations in this survey;
- On average the topsoil is depleted compared to the subsoil by $230 \text{ mmol}_c \text{ kg}^{-1}$;
- On average 62.3% is accounted for by the congruent dissolution of feldspars, and 24.7% by the dissolution of secondary Al-phases,
- The depletion calculated matches well with estimates of the proton load since the last ice age;
- The anthropogenic contribution to acidification is estimated to be between 20% and 50%;
- Al contributes 71.4% of the $\Delta ANC_{(s)}$ which indicates that Al release was already a significant process in acid buffering under natural conditions.

Are there indications that an interprovincial evaluation of monitoring data may be hampered by regional differences in the natural setting?

- Application of fuzzy c -means cluster analysis demonstrates that regionality in both the solid phase and the soil solution is evident;
- The solid phase related parameters cluster mainly on the basis of the mineralogical richness of the parent material and the OM content;
- The soil solution related parameters cluster mainly on the basis of the richness of the soil ecosystem developed, and the depth in the soil (top or subsoil);

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- The resulting regional variation in DOC and BC concentrations has a clear influence on Al/BC ratios in displaced soil solution and on the equilibrium between soil solution and CEC;
- The richer locations are mainly found in the north whereas the poorer locations are present in the south, a group of locations of notable mineralogical richness is found near the edge with the Holocene river deposits;
- Noord-Brabant shows the largest $\Delta\text{ANC}_{(s)}$ related to high ammonia emissions;
- The Veluwe area shows a negative $\Delta\text{ANC}_{(s)}$ ascribed to a resetting of the $\Delta\text{ANC}_{(s)}$ gauge due to extensive anthropogenic soil displacement.

Is the analysis of displaced soil solution sufficient to monitor soil acidification, and if not, what should be the alternative?

- Soil solution chemistry gives very limited information on the acidity status of the soil, and is also only indirectly related to ecosystem health;
- Insight into the solid phase composition and the general biogeochemical context should therefore be obtained prior to soil solution monitoring;
- A comprehensive set of parameters should be analyzed and antecedent precipitation should be considered;
- A combination of solid phase total element analysis and simple extracts such as cold 0.43 M HNO_3 and 0.01 M CaCl_2 forms a superior monitoring alternative in providing information on the overall acidity status of the soil and the contribution of the various reactive pools.

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5 GEOCHEMICAL CHARACTERIZATION OF THE PLEISTOCENE SANDS IN THE NETHERLANDS

5.1 Introduction

The increasing importance of the quality of environmental compartments in policy decisions asks for a good understanding of the natural composition and variability of these compartments. Particularly where a distinction is to be made between polluted and unpolluted situations knowledge of the normal values is indispensable. For the soil quality in the Netherlands the threshold values now in use for the environmentally important trace elements partly take into account natural variability as they incorporate dependence on the clay and organic matter content (Lexmond and Edelman, 1987). Other sources of natural variability that are not necessarily covered by this basic compositional dependence, such as regional patterns in the parent material, are not taken into account in the assessment of soil quality. Yet, several publications show that this regional variation can substantially influence the naturally occurring concentrations of various elements (Moura and Kroonenberg, 1990; Hakstege et al., 1993; Tebbens et al., 2000). Based on the major elements in the solid phase, Mol et al. (subm.) established that even for a rather homogeneous group of Pleistocene sandy soils a distinct regional pattern exists. This pattern is of consequence to soil acidification and it is likely to be of importance to other environmental processes as well. The new geochemical baseline for Dutch soil quality, a policy aim for 2005, should therefore incorporate natural patterns of trace element variability. In addition to establishing the extent and regional distribution of the natural variation, knowledge should also be acquired on the processes and agents causing variation between and also within geochemical regions. Understanding these controls of natural variability can substantially improve the quality of decisions in environmental management (Stigliani, 1988; Darnley, 1997).

Soil development in the Netherlands must be considered within the geological context of young unconsolidated sediments of marine, fluvial, glacial, or eolian origin. Classic research on the natural variation of the Dutch sediments dates from the first half of the 20th century (Edelman, 1933; Baren, 1934; Andel, 1950). The main focus was on regional patterns in mineralogy, inspired primarily by a general geoscientific interest. At the time, analytical techniques for the routine quantitative analysis of the chemical composition of the solid phase were not yet available. Recent research on sediment characterization tends to include the complete analysis of the sediment chemistry. Provenance and sedimentary history are still of concern, but also the establishment of a geochemical baseline is aim of research (Moura and Kroonenberg, 1990; Hakstege et al., 1993; Darnley, 1997; Plant et al., 1997; Tebbens et al., 2000). In general, the provenance related research still makes extensive use of mineralogical

characteristics of the sediment (Tebbens et al., 1995). The mineralogical framework forms one of the factors controlling the concentrations of the various (trace) elements.

Environmental interest has inspired a broad range of research that specifically addresses the geochemical variability of sediments in the Netherlands. Huisman's research, for instance, is mainly concerned with the overall chemistry of the deeper sediments; he investigates the formations deposited between the Miocene and the Holocene (Huisman et al., 1997; Huisman, 1998; Huisman and Kiden, 1998; Huisman et al., 2000^{a,b,c}). One of Huisman's conclusions is that for the realization of geochemical maps or geochemical baseline databases total element analysis by X-ray fluorescence spectrometry is particularly useful because it is cheap, quick, and provides multi-element data. To answer specific questions about speciation, small-scale distribution, or reactivity, additional analyses can then be chosen with care. On the basis of the factors controlling the geochemical variability in the deeper Dutch sediments, Huisman proposes a method to predict natural background concentrations of (environmentally) important (trace) elements. He evaluates this approach as performing better than the correction for clay and organic matter now in use in the environmental management of soil quality. He stresses, however, that this method is based on Early Pleistocene subsurface sediments and that research on the best predictors in recent sediments is needed. Moura and Kroonenberg (1990) focus on the Quaternary sediments of the Meuse and the Rhine in the southeast of the Netherlands. They conclude that specific element associations can be attributed to specific minerals, and that much variation is due to minerals and rock fragments not normally studied in routine sediment petrology. Sediment petrological studies can therefore give misleading estimates on the overall mineralogical richness of the sediment. The major factors they identify as controls of the geochemical variability are the grain size effect (spherical sand particles behave different from platy phyllosilicates) and the provenance of the sediment. The combined effect of these controls led to a regional pattern in the Meuse terraces in the southeastern Netherlands. In a similar study Hakstege et al. (1993) focus on the Holocene clays of the Rhine and Meuse rivers in central-eastern Netherlands and found that 70% of the geochemical variability is determined by geological processes. Old and recent floodplains can be distinguished on the basis of their bulk geochemistry. The study of Tebbens et al. (2000) concentrates on Meuse sediments from recent glacial and interglacial periods. They conclude that there is considerable compositional variation between those periods due to both depositional processes, such as sorting, and post-depositional processes, such as the formation of siderite and vivianite.

While the above studies have contributed significantly to the awareness of the distinct natural variability of sediments, both in time and space, this kind of research is still relatively undervalued. Especially because only specific deposits have been studied, knowledge on the subject is still incomplete. A pilot study concerning the monitoring of soil acidification has yielded an extensive dataset from the Pleistocene sands for large parts of the Netherlands. As regionality was one of the issues of interest a comprehensive set of parameters including many environmentally and otherwise interesting trace elements was analyzed. Although the sampling scheme was not designed to cover all geochemical variation in these sands, we felt that the resulting dataset could serve as a valuable source for the general geochemical characterization of the Pleistocene sands in the Netherlands, discussed in this paper.

First, the geochemical composition of these sands is compared to the average composition of the upper crust. This way we can trace the idiosyncrasies of the Pleistocene sands in the Netherlands, expressing them in terms of relative enrichment or depletion. A second step entails the identification of the major geochemical and environmental agents and processes that control the variability in these soils. To that end, we choose factor analysis, a multivariate statistical technique based on correlation patterns between parameters. Next in the analysis is a further characterization of the regional geochemical patterns, found in a prior classification based on the major elements (Mol et al., *subm.*), by providing the essential statistics on the trace elements for the regions distinguished. Also the relative importance of the factors controlling the natural variability within each of the distinguished regions will be assessed. Finally the possibilities to estimate natural background values for these soils are discussed. The line of reasoning suggested by Huisman (1998) and Tebbens (2000) combined with the concept of using subsoil concentrations as a proxy for the natural levels in the topsoil is used to predict natural concentrations of trace elements. This approach is tested for these poor sandy soils and compared to the current approach in environmental soil quality assessment.

5.2 Materials & methods

5.2.1 Environmental setting

The Netherlands, situated on the edge of the North Sea Basin, predominantly consist of eolian, fluvial and marine sediments deposited in the Late Pleistocene and the Holocene (Staalduinen et al., 1979). The country has a flat topography with the exception of the southernmost part, which is situated on the edge of the Ardennes Massif. This hilly area also features sediments dating from the Carboniferous and the Cretaceous near or at the surface. Some moderate relief in the remainder of the country was formed during the Elsterian and Saalian ice ages (Zagwijn, 1987). Most of this relief was levelled by erosion and depressions were filled by sediment during the Holocene; the only features still clearly present are ice-pushed ridges (Staalduinen et al., 1979). Geomorphologic processes in the Quaternary caused a differentiation in development. This resulted in two major areas, one dominated by Pleistocene sand deposits and the other by Holocene clay and peat deposits. The Pleistocene areas are generally above sea level, hydrologically dry, and poor in nutrients, whereas the Holocene landscapes, except for the coastal dunes, are mostly below sea level, hydrologically wet, and rich in nutrients (Zonneveld, 1985). A more refined division can be found in figure 5.1. As a result of the young sediments and the moderate climatic conditions the soils of the Netherlands are poorly developed compared to those in many other parts of the world. The least developed soils can be found on the young Holocene deposits in the west. The older Pleistocene deposits in the east generally show more developed soils such as podsoles.

The soils sampled for this study are situated in the Pleistocene areas (see Fig. 5.2). Based on the 1: 250.000 soil map, they are all classified as sandy soils, which was confirmed in the field. The sub-classification used in this map employs morphometric pedogenic features, such as the presence, thickness, and color of E and B horizons. The origin of the parent material is not taken into account systematically, and anthropogenic activities that lead to a separate soil class are limited to physical disturbances. This morphometric soil classification is based on vertical

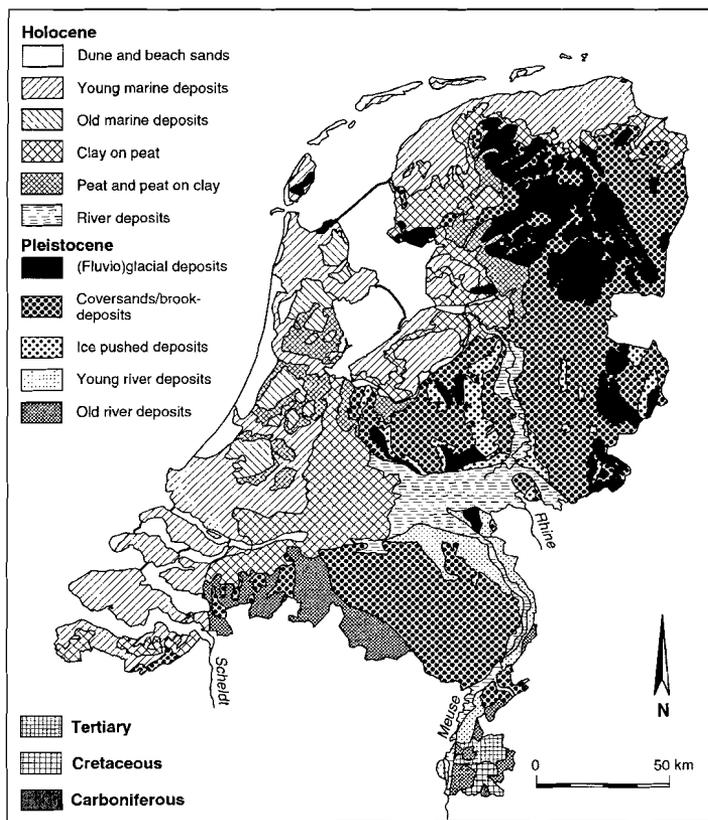


Figure 5.1

Map of the Netherlands showing a division into the major geological landscapes. (After: Zonneveld, 1985 and Bakker and Schelling, 1989)

differentiation features that can be distinguished in the field, and was deemed not directly suitable as a base for the present geochemical research. The poor sandy soils are of no agricultural significance and have low reactivity and generally low capacities for retaining pollutants. Land use is an environmentally unfortunate combination of coniferous forests with a high scavenging potential for air pollutants and intensive, substrate independent, animal husbandry that emits large amounts of ammonia (Breemen, et al., 1982; Krug, 1991; Vries, 1994). In addition to soil acidification this bears the environmental threat of leaching of heavy metals to the groundwater. This is especially salient since the Pleistocene deposits hold the major fresh water aquifers in the Netherlands (Frapporti et al., 1996).

Figure 5.2

Map of the Netherlands showing the sample locations and the regions discussed in section 5.3.4.



5.2.2 Sampling and analytical procedures

Soil samples were collected at 92 locations at two depths (the first 20 cm of the mineral soil below the litter layer and a C or B/C horizon between 60 and 110 cm) resulting in 184 samples. The set of locations, each with a surface area of about 10,000 m², was selected from the monitoring sites of six of the Dutch provinces. All sampled locations were coniferous forest stands on sandy soils (Fig. 5.2). Sampling took place in May-June 1999. Each location was divided into 6 equal sections in which a randomly located sample was collected at two depths (stratified random). A composite sample of the solid phase for each depth was prepared in the laboratory. The soil was subsequently dried at 40°C, mixed, and sieved.

The fraction < 2 mm was used to determine the total element content by X-ray fluorescence spectrometry (XRF) using pressed powder tablets. This fraction was also used for an extraction with 0.43 M HNO₃ at room temperature. The extraction was carried out by shaking a 1:10 solid-solution mixture for 2 hours, after which the supernatant liquid was collected for further analysis. Our aim was to gain insight into both the total element concentrations of the solid phase as well as the amount of readily reactive constituents present in these soils. We therefore did not choose extractions with aqua regia as is customary in Dutch environmental soil assessments, but we opted for Huismans suggestion and chose a combination of XRF analysis

and a rather mild extraction with HNO_3 . This combination provides us on the one hand with total element data of higher accuracy and precision than those obtained with aqua regia. On the other hand the HNO_3 extractions are much milder than those with aqua regia and they therefore give a better indication of the reactivity of the soils components. For a comprehensive account of the details of all analyses see Appendix A.

5.3 Results and interpretation

5.3.1 General geochemical characterization

The range of concentrations of both the total element content of the solid phase and the reactive part of the most important elements in the Pleistocene sandy soils in the Netherlands is presented in table 5.1. The mineralogical pooriness of these soils is evident from this table. Quartz is the dominant mineral resulting in SiO_2 levels well over 90 mass%. The second most abundant oxide is Al_2O_3 with levels up to 4.5 mass%. All other oxides are typically below 1% with some values just over 1% for K_2O and Fe_2O_3 . Modest accumulation of organic matter (OM) has occurred in these soils, especially in the topsoil, resulting in mean OM contents of a few mass%.

The geochemical idiosyncrasy of the Pleistocene sands can be illustrated by comparing the concentrations of major and trace elements with the average concentrations in the earth's upper crust. We therefore calculated the ratios between the concentrations in our dataset and the average upper crust concentrations and plotted the resulting distributions as boxplots (Fig. 5.3). It is evident that most elements, except Si, Zr, Hf, Cr, and Pb, have been depleted compared to the upper crust. The major elements Ca, Mg, and Fe, related to limestone, dolomite and ultramafics, show the strongest depletion. This is in accordance with the high susceptibility of these rocks to chemical weathering. Other major elements are less depleted with clear peaks for K and Ti. Potassium in these soils is mainly present in K-feldspar, the feldspar least prone to weathering, and Ti is largely related to the heavy mineral fraction, in general a weathering resistant type of mineral. The high ratios of Cr, Hf, and Zr corroborate the resistance of heavy minerals, in this case chromite and zircon, to chemical weathering. The patterns of the other trace elements are less explicit although many can be related to chemical similarities between major and trace elements, such as for instance Ba and Rb show levels similar to K, Sr resembles Ca, Ni shows its ferromagnesian affinity, and V displays levels similar to Al and Ti. The major patterns of depletion and enrichment are in agreement with the general idea on the weathering progression of the various rockforming minerals, often depicted as the Bowen series (see for instance Levinson, 1974).

A second feature that is evident from table 5.1 and figure 5.3 is the difference between the topsoil and the subsoil for many elements. Mol et al. (subm.) interpreted this difference for the major elements in relation to acid leaching of the top soil. For trace elements the differences constitute both depletions of the topsoil compared to the subsoil as well as enrichments. P_2O_5 , Pb, and S for instance show clear enrichments that may be related to anthropogenic activities. Br also shows higher values in the topsoil than in the subsoil, which suggests that Br is being enriched via the atmosphere. There is, however, no regional pattern that indicates a source, like for instance sea spray. A third phenomenon (Table 5.1 and Fig. 5.4) is the difference in

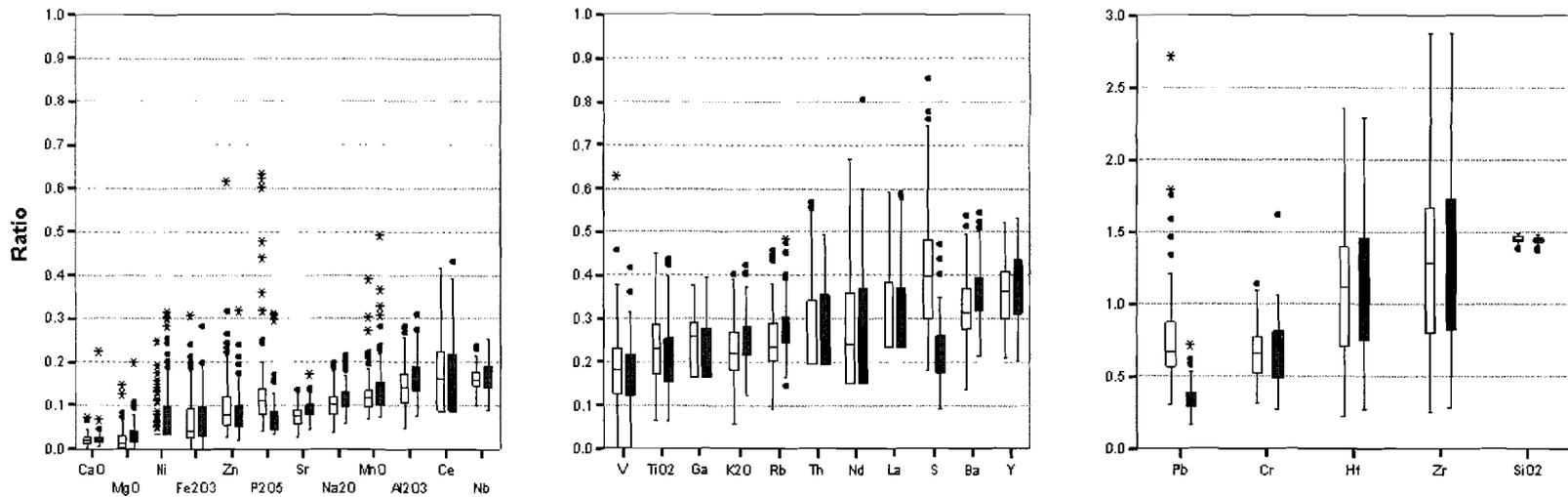


Figure 5.3

Boxplots of the ratios of the concentrations in the Pleistocene sandy soils and the average upper crust concentrations as catalogued by the Geochemical Earth Reference Model, values based on Taylor and McLennan (1995), Wedepohl (1995), and Gao et al. (1997) for both topsoil (light) and subsoil (dark).

Table 5.1

Overview of the total element concentrations of the solid phase (XRF, oxides in mass% of total oxides, traces elements in mg kg⁻¹ dry matter), OM content (in mass% of dry matter) and HNO₃ extractions (results recalculated to mg kg⁻¹ dry soil). The last two columns show the detection limit where appropriate, and whether the topsoil differs significantly from the subsoil (+ top is higher, - topsoil is lower) or not (*). The < symbol indicates values below the detection limit.

	minimum		25 percentile		median		75 percentile		maximum		def. lim.	top vs. sub
	top	sub	top	sub	top	sub	top	sub	top	sub		
Al ₂ O ₃	0.71	1.13	1.63	2.05	2.15	2.37	2.60	2.89	4.30	4.73		-
CaO	0.01	0.03	0.05	0.06	0.08	0.09	0.11	0.12	0.30	0.95		*
Fe ₂ O ₃	0.00	0.00	0.12	0.14	0.19	0.23	0.41	0.43	1.38	1.27		*
K ₂ O	0.20	0.41	0.63	0.74	0.75	0.83	0.91	0.96	1.37	1.45		-
MgO	0.00	0.00	0.01	0.03	0.03	0.07	0.06	0.09	0.33	0.44		-
MnO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.03	0.04		*
Na ₂ O	0.14	0.23	0.31	0.38	0.40	0.44	0.47	0.51	0.78	0.85		-
P ₂ O ₅	0.01	0.01	0.02	0.01	0.03	0.02	0.04	0.03	0.19	0.10		+
SiO ₂	91.87	91.18	95.25	94.82	96.10	95.82	97.04	96.39	98.76	98.07		+
TiO ₂	0.04	0.04	0.11	0.10	0.15	0.14	0.19	0.16	0.29	0.29		*
OM	0.38	0.42	2.32	0.72	3.86	1.04	5.07	1.57	9.62	5.76		+
Ba	75.4	117.7	153.1	175.1	172.8	194.3	203.2	216.0	297.5	301.0		-
Br	<	<	<	<	7.0	<	10.0	<	43.0	17.0	6.0	*
Ce	<	<	<	<	10.4	9.8	14.4	13.9	26.5	27.8	8.0	*
Cr	11.2	9.6	18.6	17.3	23.0	22.9	27.1	28.5	40.2	57.2		*
Ga	<	<	<	<	4.4	2.8	4.9	4.7	6.4	6.7	4.0	*
Hf	1.3	1.6	4.2	4.4	6.5	6.2	8.1	8.5	13.7	22.7		*
La	<	<	<	<	<	<	11.4	11.1	17.8	17.8	10.0	*
Nb	2.6	2.3	3.5	3.1	4.2	4.3	4.5	4.8	6.2	6.6		*
Nd	<	<	<	<	6.3	7.3	9.3	9.5	17.4	21.0	5.6	*
Ni	<	<	<	<	<	<	<	1.8	5.0	6.3	1.0	*

Pb	6.2	3.4	11.5	6.0	13.5	6.9	17.5	7.9	54.5	14.5		+
Rb	10.3	16.4	22.7	27.3	26.3	30.2	32.3	33.9	51.4	54.3		-
S	174.0	89.0	287.8	167.8	377.5	214.0	458.3	248.3	816.0	450.0		+
Sb	<	<	<	<	<	<	<	<	4.8	5.4	3.8	*
Sc	<	<	<	<	<	<	<	<	3.6	2.8	1.7	*
Sn	<	<	<	<	<	<	<	<	5.7	5.2	3.9	*
Sr	9.7	16.0	20.8	27.4	26.5	30.9	31.5	35.6	48.6	60.9		-
Th	<	<	<	<	<	<	3.6	3.8	6.1	5.3	3.0	*
V	<	<	7.7	7.4	10.9	10.1	13.9	13.0	37.8	25.1		*
Y	4.6	4.5	6.6	6.9	8.0	7.8	9.0	9.5	11.5	11.7		*
Zn	1.8	1.3	4.0	3.6	5.7	4.9	8.6	7.1	43.7	22.5		+
Zr	48.8	54.5	154.3	158.1	245.0	241.5	318.2	328.9	546.9	962.3		*
Al(HNO ₃)	146.7	227.9	499.4	659.5	759.1	872.0	1027.6	1140.5	1984.4	2498.4		-
Ca(HNO ₃)	2.1	0.0	20.4	5.6	29.9	9.6	52.7	16.6	1288.2	957.9		+
Fe(HNO ₃)	42.3	14.0	149.8	56.2	227.7	97.7	385.5	151.5	3316.8	601.1		+
K(HNO ₃)	7.4	1.0	12.1	1.0	15.9	7.7	21.6	10.7	111.3	63.0		+
Mg(HNO ₃)	0.9	0.4	4.2	0.4	6.2	1.1	11.8	2.6	91.5	116.1		+
Mn(HNO ₃)	<	<	<	<	<	<	1.9	1.1	69.1	56.8	0.5	*
Na(HNO ₃)	0.7	0.7	3.6	2.4	4.9	3.2	7.0	4.5	102.1	18.7		+
P(HNO ₃)	<	<	<	<	9.9	12.2	25.6	27.6	326.1	213.7	2.0	*
S(HNO ₃)	1.4	1.4	10.5	10.6	13.5	13.1	17.3	20.8	45.6	48.7		*
Cd(HNO ₃)	0.002	0.000	0.022	0.002	0.050	0.005	0.090	0.013	0.392	0.153		+
Cr(HNO ₃)	0.02	0.08	0.20	0.27	0.30	0.36	0.49	0.46	4.12	0.92		*
Cu(HNO ₃)	0.16	0.01	0.40	0.13	0.55	0.18	0.86	0.26	8.55	1.29		+
Ni(HNO ₃)	0.04	0.02	0.18	0.05	0.23	0.08	0.29	0.11	1.13	0.74		+
Pb(HNO ₃)	1.35	0.40	5.50	0.77	7.23	1.07	9.86	1.48	38.81	7.17		+
Zn(HNO ₃)	0.70	0.42	1.35	0.69	1.95	0.88	2.74	1.14	20.59	3.86		0

reactivity displayed by the various parameters. These differences are manifested in HNO_3 extraction efficiencies ranging from less than 1% for Na and K to more than 50% for Pb in the topsoil. Differences in reactivity and differences between top and subsoil are interrelated as reactivity does not only differ between elements but for some elements also between top and subsoil. Ca, Fe, Ni, Pb and Zn are clearly more reactive in the topsoil, whereas P and S are more reactive in the subsoil.

5.3.2 Factor Analysis

Multivariate statistical techniques are well suited for disclosing the causes of variability in large datasets as they consider the total correlation structure of the complete dataset at once. To this end, factor analysis has been used successfully in the earth sciences (Spencer et al., 1968; Dekkers et al., 1986; Dekkers et al., 1989; Frapporti et al., 1996; Reymont and Jöreskog, 1996). To identify the phenomena underlying the variation present in our dataset we studied the correlation patterns through Principal Component Analysis with Kaiser Varimax rotation (PCA-V). To meet normality demands skewed parameters were logtransformed prior to PCA-V, practically this means that only the concentrations in the HNO_3 extracts were logtransformed. Most parameters shown in table 5.1 were used in the PCA-V, except for Br, Ce, Ga, La, Nd, Sb, Sc, Sn and Th, which had more than 25% of values below the detection limit. Although Ni also had 33% below the detection limit it was included because of its environmental importance; the results of the analysis were found not to be affected by the detection limit problem of only this one parameter. Inclusion of SiO_2 did not lead to singularity problems. The correlation patterns were of course interpreted with consideration of the potential influence of closure effects. The chosen number of components was based on a combination of the Gutmann criterion (extracting only components with eigenvalues higher than 1), scree plots (plot of eigenvalues against component number), and the geochemical interpretability.

Including both total element concentrations of the solid phase as well as concentrations in the HNO_3 extracts resulted in 6 factors (Table 5.2), providing insight into the mineralogy and reactivity of the soil constituents. Three natural and three anthropogenic factors were identified.

Factor 1: Alumino-silicates

The first factor has high positive loadings of Na_2O , K_2O , Al_2O_3 , MgO , CaO , Fe_2O_3 , Rb, Sr, and Ba, and a negative loading of SiO_2 , indicating that alumino-silicates explain a large amount of the chemical variation in Pleistocene sandy soils. The opposite loading of SiO_2 confirms the quartz enrichment which is also manifested in figure 5.3. The dominant minerals are quartz and feldspars. Exploratory XRD analysis of a subset of samples in four grainsize classes revealed only trace amounts of clay minerals, especially in the soils highest in Al_2O_3 .

Factor 2: Organic Matter and CEC related parameters

The second factor, with high loadings of OM, P_2O_5 , S, Pb, $\text{K}(\text{HNO}_3)$, $\text{Na}(\text{HNO}_3)$, $\text{Ca}(\text{HNO}_3)$, $\text{Mg}(\text{HNO}_3)$, $\text{Cd}(\text{HNO}_3)$, $\text{Ni}(\text{HNO}_3)$, $\text{Pb}(\text{HNO}_3)$, $\text{Cu}(\text{HNO}_3)$, and $\text{Zn}(\text{HNO}_3)$, relates to the influence of organic matter in these soils. In sandy soils OM is the main bearer of surface charge and the concentrations in the HNO_3 -extract are indicative of the amount of base cations

Table 5.2

Factor model for the results of the total element analysis (XRF), the OM content, and the weak HNO₃ extraction. Factor loadings between -0.3 and 0.3 have been omitted to enhance the clarity of presentation.

	Alumino-silicates	Organic matter/CEC	Heavy minerals	Reactive Fe	Reactive Al	P and Mn	Commun.
explained variance	28.7	20.9	13.2	6.6	5.4	6.5	
Al ₂ O ₃	0.92						0.97
CaO	0.81						0.84
Fe ₂ O ₃	0.74			0.49			0.88
K ₂ O	0.97						0.96
MgO	0.82						0.84
MnO	0.68					0.49	0.78
Na ₂ O	0.86						0.79
P ₂ O ₅		0.50				0.64	0.81
SiO ₂	-0.93						0.99
TiO ₂			0.87				0.94
OM		0.83					0.81
Ba	0.95						0.93
Cr	0.36		0.75	0.33			0.84
Hf			0.93				0.88
Nb	0.33		0.82				0.82
Ni	0.73			0.33			0.71
Pb		0.60		0.51			0.65
Rb	0.95						0.96
S		0.85					0.85
Sr	0.93						0.91
V	0.51		0.52	0.33			0.77
Y	0.56		0.57				0.72
Zn	0.54	0.31		0.45		0.38	0.84
Zr			0.93				0.88
Al(HNO ₃)			0.37		0.80		0.81
Ca(HNO ₃)		0.81					0.80
Fe(HNO ₃)		0.43		0.68			0.72
K(HNO ₃)		0.75					0.70
Mg(HNO ₃)		0.92					0.91
Mn(HNO ₃)	0.55					0.63	0.79
Na(HNO ₃)		0.72					0.60
P(HNO ₃)						0.82	0.81
S(HNO ₃)					0.79		0.65
Cd(HNO ₃)	-0.45	0.71		0.30			0.82
Cr(HNO ₃)	0.36				0.60		0.58
Cu(HNO ₃)		0.64		0.37		0.37	0.70
Ni(HNO ₃)		0.85					0.81
Pb(HNO ₃)		0.79		0.48			0.87
Zn(HNO ₃)		0.78					0.79

(BC) and heavy metals on the CEC (see also Mol et al., *subm.*). The specific behaviour of the heavy metals is being determined by more than one factor and will be further discussed in section 5.3.3. P and S are common elements in OM and they therefore show good correlations with this factor. P_2O_5 also has a high loading on factor 6. S follows the pattern of OM exceptionally well both in terms of regionality (see section 5.3.4) and in terms of the difference between top and subsoil (Fig. 5.5). Mol et al. (*subm.*) argue that high atmospheric S inputs are being accumulated in the OM of the topsoil which thus provides part of the acid neutralizing capacity. This is a common phenomenon in many acid soils (Mayer et al., 1995; Novák et al., 2000; Mayer et al., 2001).

Factor 3: Heavy Minerals

The third factor is characterized by high loadings of TiO_2 , Cr, Y, Zr, Nb, and Hf, which indicates the presence of heavy minerals such as garnet, rutile, titanite, zircon, ilmenite and chromite. A heavy mineral factor is usually found to explain part of the geochemical variability (Moura and Kroonenberg, 1990; Huisman, 1998; Tebbens et al., 2000). These minerals are susceptible to concentration or depletion during transport and sedimentation as a result of their density and their restriction to the finer sand fraction (Moura and Kroonenberg, 1990), which finds an expression in the geochemical variability of the sediments as well. Some of the associated elements, most notably V, Ti and Y, can also occur in phyllosilicates (Moura and Kroonenberg, 1990). This is reflected in the loadings of, in this case, V and Y on the aluminosilicate factor.

Factor 4: Reactive Fe

The fourth factor has high loadings for Fe_2O_3 , Zn, Pb, $Fe(HNO_3)$, and $Pb(HNO_3)$. Figures 5.3 and 5.4 and table 5.1 show that the variation in the elements that dominate this factor, lead and iron, largely result from distinct differences between top and subsoil. The difference in iron between top and subsoil is not manifested in the total Fe content but solely in the amount of $Fe(HNO_3)$. Reactive Fe is much larger in the topsoil, indicating the presence of different Fe-phases. We consider this to be the result of extensive acidification of these poorly buffered soils. The main part of the proton load is buffered by the dissolution of feldspars, but also Fe bearing silicate minerals are affected by the incoming acid. The pH of these soils however is not sufficiently low to support Fe in dissolved form, so transport through the soil profile does not or hardly happen. Instead, Fe forms secondary phases, probably in the form of coatings on sand grains. In the field brown to reddish brown sand grains were frequently encountered. Of course this process mainly occurred in the topsoil because acidity enters the profile from above. Field observations confirm that coated sand grains primarily occur in the topsoil. Both the formation of secondary Fe phases and the enrichment of the soil with Pb via atmospheric deposition typically occur in the topsoil. Fresh secondary Fe phases are known to form an excellent association with Pb, either through adsorption or co-precipitation (Schindler and Stumm, 1987; Cornell and Schwertmann, 1996; Zachara et al., 2001).

Factor 5: Reactive Al

The fifth factor shows high loadings of $Al(HNO_3)$, $S(HNO_3)$, and $Cr(HNO_3)$. We interpret the two dominant elements in this factor, $Al(HNO_3)$ and $S(HNO_3)$, as related to soil acidity. Like

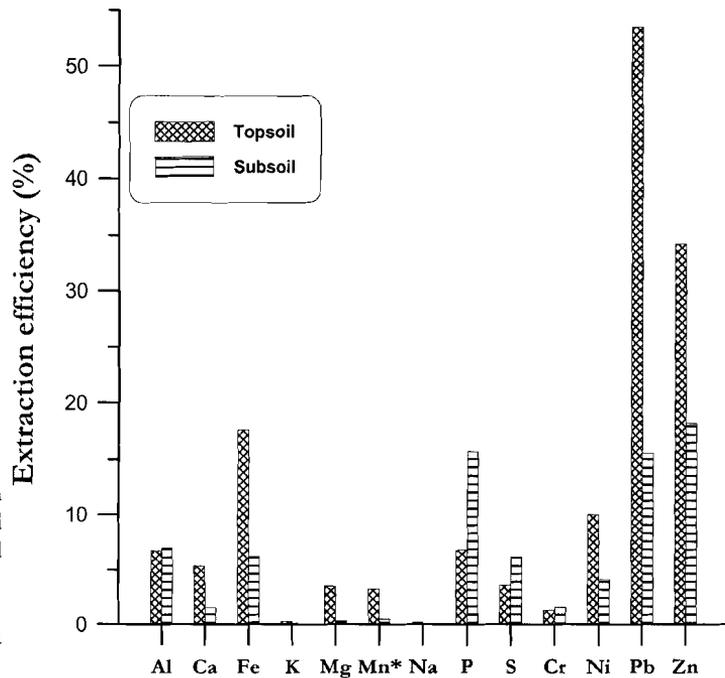


Figure 5.4

HNO₃ (0.43 M) extraction efficiency of selected elements for top and subsoil.

* Mn is affected by a high number of detection limits.

iron in factor 4, Al is released from the solid phase by incoming acidity; Al-phases, notably feldspar, are the most important in acid buffering. Unlike the case for iron, the pH of the soils is sufficiently low to keep Al mobile in solution. This results in a depletion of the topsoil compared to the subsoil (see Al in Table 5.1). The entire profile presents enough micro-environments where secondary Al phases can precipitate and reactive Al occurs both in top and subsoil, with a slight preference for the subsoil. Deposition of SO_x is one of the major contributions to the incoming acidity. Part of this S is immobilized in the topsoil associated with OM (see factor 2). Based on concentrations found in soil solution and thermodynamic reasoning, jurbanite (AlSO₄OH) is frequently mentioned as a possible secondary mineral in acid soils (Prenzel and Schulte-Bisping, 1995; Larssen et al., 1999). Whereas this S containing secondary Al phase has never been actually determined, the loadings on this factor also suggest a common behaviour of (temporarily) mobile S and Al. Reactive Cr is most likely present in trivalent form and as such mimics reactive Al.

Factor 6: P and Mn

The sixth factor has high loadings of P₂O₅, MnO, Mn(HNO₃), P(HNO₃), and Cu(HNO₃). The combination of Mn, P and Cu suggests the influence of local anthropogenic phenomena. Application of manure and pesticides on neighbouring parcels in agricultural use could very well affect forest locations through the air by drift, explaining P₂O₅, P(HNO₃), and also Cu(HNO₃). Cu is used as a food additive to increase food conversion in fattening pigs. The

occurrence of MnO and $Mn(HNO_3)$ points to redox processes whereby, similarly to Fe and Al, Mn is transformed into a reactive form. Both hypotheses are supported by field observations. In most cases the sites scoring high on factor six either were in close proximity of agricultural activities or clearly exhibited redox related stains in the lower part of the profile, sometimes in combination with a drainage impairing loamy layer.

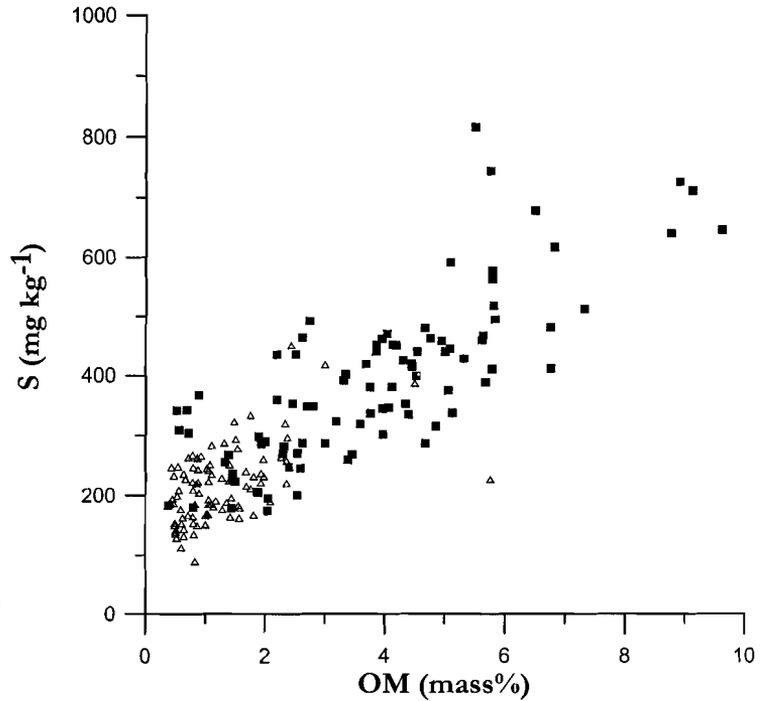


Figure 5.5
The relation between total S concentration in the solid phase and the OM content for both topsoil (squares) and subsoil (triangles).

5.3.3 Heavy metals, reactivity and enrichment

The PCA-V results (Table 5.2) clearly show that the potentially polluting heavy metals have the highest scores on the OM factor. However, all heavy metals also have scores on other factors, most notably on the three anthropogenic factors. Hence, the general picture that the heavy metals are bound by the OM related CEC can be refined by analysing the differences in their behaviour. We shall discuss both the factors that contribute to their variability and the differences between total concentrations and reactivity.

Cr and Ni are the heavy metals with a predominantly 'natural behaviour'. For both total and reactive Cr no differences between top and subsoil are observed. This indicates that neither enrichment nor leaching have taken place, which is in line with the hypothesis based on the factor model that most Cr is associated with the heavy mineral fraction. This idea is supported

by the much lower extraction efficiency for Cr compared to that for the other heavy metals (Fig. 5.4), and by the behaviour of reactive Cr in the factor model. Reactive Cr is the only heavy metal that is primarily related to the reactive Al factor, indicating dissolution of aluminosilicates rather than the CEC as its source. Median total levels of Ni are below the detection limit while maximum concentrations are similar for both top and subsoil. However, Ni is more reactive in the topsoil, resembling the behaviour of Fe. This suggests the presence of Ni in the aluminosilicate fraction in these soils. Magnesium and Fe rich aluminosilicates usually also contain a certain amount of Ni which of course is also released upon acid buffering. Whereas Mg is mobilized, Ni, like Fe, is in situ turned into a more reactive form. Based on the PCA-V result we conclude that this reactive Ni is bound largely to OM.

The enrichment of the topsoil with the major polluting heavy metals Pb and Zn is evident. It mainly shows in the increased reactive concentrations but, especially for Pb, also in the total element concentrations of the solid phase. Atmospheric deposition is a well established source of both elements, and given their moderate to low mobility, this explains the enrichment of the topsoils. Anthropogenic Pb mainly stems from exhaust fumes, anthropogenic Zn is usually attributed to emissions from metal industries such as zinc smelters. Like for most heavy metals the enrichment is in a reactive form, correlated with OM and with secondary Fe minerals. For Pb this leads to an increase of the total concentration by a factor of two, and an extraction efficiency of over 50% in the topsoil (Fig. 5.4). For Zn the relative contribution of the anthropogenic source is less.

For Cd and Cu no total element concentrations could be determined because only a few samples had values above the limit of detection. However, the concentrations of Cd and Cu in the HNO₃ extracts show differences between top and subsoil indicating that these heavy metals are also enriched in the topsoil. The PCA-V shows the general heavy metal association with OM and secondary Fe for both Cd and Cu, with Cu also loading on the P-Mn factor. Also for these two elements atmospheric deposition is a well established pathway, with the metal industry as the major source of Cd and agricultural activities such as manure application and the use of soil disinfectants and other pesticides as the source of Cu, which is confirmed by the association with the P-Mn factor.

5.3.4 Geochemical regionality

In an earlier paper Mol et al. (subm.) focussed on the acidification characteristics of the soils sampled. To assess the regional geochemical patterns a multivariate statistical technique for finding homogeneous groups in datasets called fuzzy *c*-means clustering was used (Bezdek, 1981; Bezdek et al., 1984; Vriend et al., 1988). The cluster analysis was performed on the macro chemical elements related to the solid phase. The five regions that were identified after clustering could mainly be distinguished on the basis of their mineralogical richness and their organic matter content. They are, from north to south, 1) the northern provinces (Friesland, Groningen, Drenthe), 2) the Veluwe, 3) the Utrechtse Heuvelrug, 4) a region with Holocene river influence which is positioned along the river Rhine, and 5) the eastern part of Noord Brabant (see Fig. 5.2). In this section we will discuss the trace elements in the light of this regionality and we will assess the importance of the PCA-V factors identified for each of the 5 regions.

In table 5.3 the general characterization of the five regions is presented. Figures 5.6 and 5.7 show boxplots of the factorscores for each factor per region, for top and subsoil separately. The phenomena underlying the regionality are of course in part reflected in the 6 factors that explain the overall variability. The alumino-silicate factor evidently is a 'regional' factor, showing widely differing median scores *between* the regions. Similarly, the OM-factor is a typical 'top/subsoil' factor, with scores of opposite sign for topsoil and subsoil. However, the alumino-silicate factor could also be termed a typically 'Holocene' factor, because of the much larger variability *within* this region, especially in the subsoil.

Factor 1: Alumino-silicates

The 'regional' alumino-silicate factor primarily reflects the variation in mineralogical richness between the five regions, which is similar for top and subsoil (Figs 5.6 and 5.7). Noord Brabant contains the poorest sandy soils whereas the Holocene influenced sites possess the richest mineralogy. This pattern also emerges from table 5.3. The region of Holocene influence, which follows the river Rhine and crosses the Pleistocene area in the central part of the Netherlands from east to west (Fig. 5.2), has the highest amounts of major oxides other than SiO₂ and of all trace elements, except Zr and Hf. The larger variance in the subsoil for the Holocene influenced region and the positive skewness, as displayed in the distribution of the factor scores (Fig. 5.7), may reflect the variation in degree of Holocene influence. In Noord Brabant trace element levels are higher than should be expected from the major oxide contents. This is in part related to a high level of heavy minerals (Fig. 5.8, see factor 3), and in part to a high anthropogenic input from zinc smelters as well as intensive animal husbandry (see factors 2 and 4). The northern provinces, the Utrechtse Heuvelrug, and the Veluwe show trace element levels in accordance with their intermediate mineralogical richness.

Factor 2: Organic Matter and CEC related parameters

Apart from the obvious difference between top and subsoil for all regions, the OM factor clearly separates the northern provinces from the other regions. The top/subsoil dichotomy is shown for all OM-related trace elements in table 5.3. The northern provinces derive their separate position from the highest OM and S content they exhibit, particularly in the topsoil; the subsoil shows a marked difference in that it has a much larger range in factor scores than the other regions. Except for Zn and Cd, the high levels of OM in the northern provinces are not accompanied by high levels of (reactive) trace elements in the topsoil. The pattern for Zn and Cd is therefore interpreted as an OM-independent regional (local) aspect.

Factor 3: Heavy Minerals

The heavy mineral factor is a typical 'regional' factor, with identical patterns for top and subsoil indicating the high resistance of these minerals to weathering. Noord Brabant clearly shows higher heavy mineral concentrations than the average Pleistocene sandy soil, whereas the Utrechtse Heuvelrug and the Veluwe show lower than average concentrations (Figs 5.6 and 5.7). The importance of the heavy mineral fraction in the poor sands of Noord Brabant is evidenced by the high values of Zr and Hf, and to a lesser extent TiO₂ and Cr. Although Cr displays similar levels in the Holocene influenced region, the relation with Al₂O₃ (Fig. 5.8) visualizes the difference in mineralogy. We hypothesize that Cr in the Holocene influenced

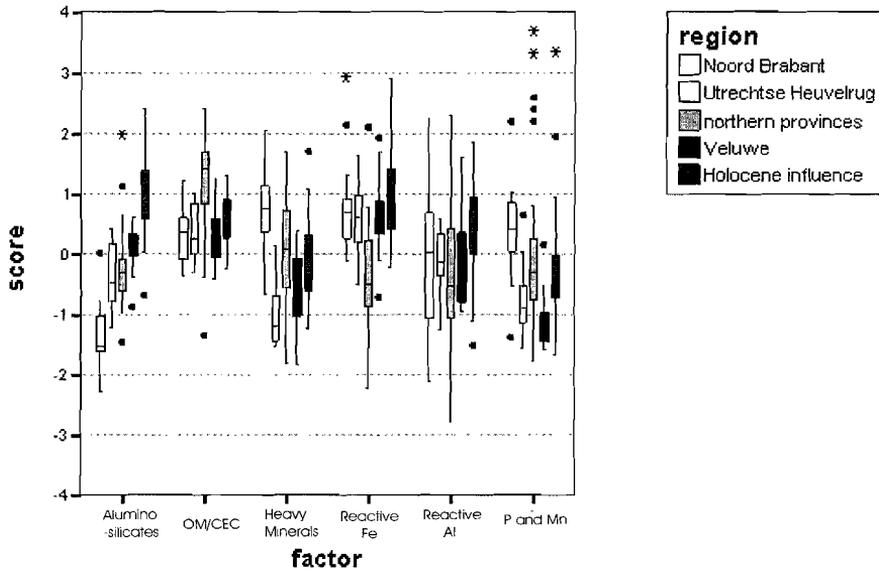


Figure 5.6
Boxplots of the factor scores per region for each factor in the topsoil. The regions are arranged in the order of ascending median factor scores on the Alumino-silicate factor.

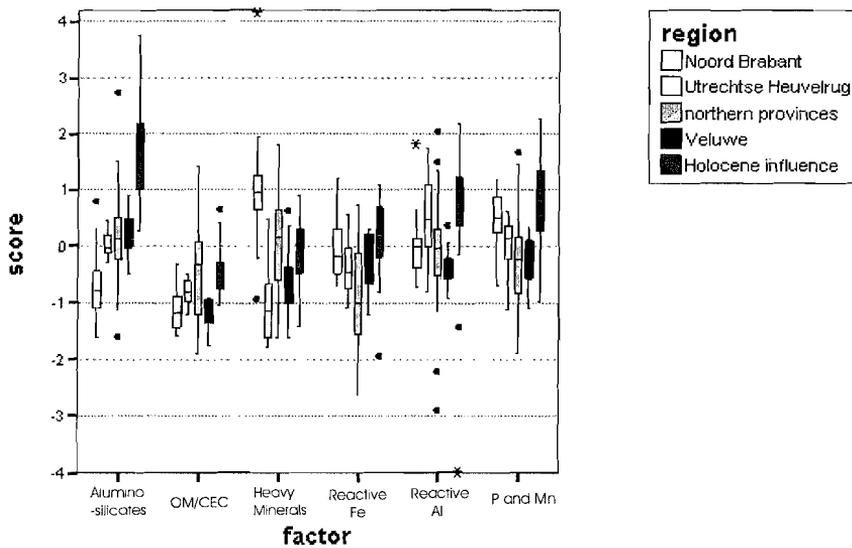


Figure 5.7
Boxplots of the factor scores per region for each factor in the subsoil. The regions are arranged in the order of ascending median factor scores on the Alumino-silicate factor.

Table 5.3

Median values for both top and subsoil per region of the total element concentrations of the solid phase (XRF, oxides in mass% of total oxides, trace elements in mg kg⁻¹ dry matter), OM content (in mass%

TOPSOILS					
	Noord Brabant	Utrechtse Heuvelrug	Veluwe	northern provinces	Holocene influenced sites
Al ₂ O ₃	1.48	1.99	2.31	2.07	3.18
CaO	0.03	0.05	0.10	0.08	0.13
Fe ₂ O ₃	0.15	0.14	0.29	0.17	0.56
K ₂ O	0.47	0.76	0.84	0.74	1.02
MgO	0.006	0.029	0.031	0.028	0.085
MnO	0.008	0.007	0.010	0.009	0.013
Na ₂ O	0.26	0.37	0.52	0.40	0.60
P ₂ O ₅	0.034	0.024	0.026	0.038	0.039
SiO ₂	97.43	96.45	95.50	96.17	94.07
TiO ₂	0.175	0.085	0.120	0.152	0.154
OM	3.86	3.43	2.43	4.52	3.49
Ba	122.0	179.4	191.9	172.4	223.2
Br	7.0	5.6	<	8.0	<
Ce	10.7	<	9.1	9.2	15.0
Cr	27.5	16.1	22.3	21.5	27.1
Ga	<	<	4.6	4.4	5.2
Hf	8.2	3.4	6.0	6.7	4.7
La	<	9.1	<	<	11.8
Nb	4.4	3.5	4.0	4.2	4.4
Nd	6.9	<	<	6.2	8.0
Ni	<	<	<	<	1.3
Pb	13.1	12.4	13.2	13.0	20.0
Rb	18.8	27.6	29.3	25.7	38.3
S	392.0	264.5	309.0	463.0	303.0
Sr	15.7	25.5	31.7	26.3	34.6
Th	<	<	<	<	<
V	10.7	7.9	10.3	10.6	14.1
Y	8.2	6.5	7.4	7.7	8.7
Zn	6.1	3.9	5.0	5.2	9.6
Zr	334.8	115.5	243.1	250.9	175.6
Al(HNO ₃)	854.8	696.4	527.2	706.6	795.6
Ca(HNO ₃)	23.8	20.4	22.9	67.8	34.0
Fe(HNO ₃)	171.3	166.5	218.8	208.5	456.3
K(HNO ₃)	12.0	12.7	14.6	22.8	17.3
Mg(HNO ₃)	4.0	5.1	5.4	14.7	7.2
Mn(HNO ₃)	<	<	<	0.6	2.7
Na(HNO ₃)	3.5	4.8	3.8	7.5	5.0
P(HNO ₃)	12.6	<	<	10.8	18.0
S(HNO ₃)	12.2	10.9	12.1	14.5	17.7
Cd(HNO ₃)	0.13	0.03	0.02	0.06	0.01
Cr(HNO ₃)	0.38	0.29	0.30	0.21	0.53
Cu(HNO ₃)	0.70	0.45	0.47	0.45	0.73
Ni(HNO ₃)	0.23	0.24	0.15	0.27	0.23
Pb(HNO ₃)	8.52	6.12	6.50	6.32	10.57
Zn(HNO ₃)	2.61	1.17	1.20	2.37	1.77

Table 5.3 (continued)

of dry matter) and weak HNO₃ extractions (results recalculated to mg kg⁻¹ dry soil).

	SUBSOILS				
	Noord Brabant	Utrechtse Heuvelrug	Veluwe	northern provinces	Holocene influenced sites
Al ₂ O ₃	1.97	2.21	2.35	2.33	3.29
CaO	0.05	0.07	0.10	0.10	0.13
Fe ₂ O ₃	0.23	0.16	0.25	0.18	0.60
K ₂ O	0.65	0.83	0.85	0.83	1.07
MgO	0.065	0.048	0.057	0.046	0.135
MnO	0.008	0.008	0.009	0.010	0.017
Na ₂ O	0.33	0.47	0.51	0.44	0.63
P ₂ O ₅	0.019	0.017	0.014	0.015	0.034
SiO ₂	96.35	96.06	95.76	95.91	94.00
TiO ₂	0.161	0.081	0.092	0.143	0.148
OM	0.87	1.17	0.55	1.06	1.23
Ba	165.8	193.5	195.2	193.2	229.8
Br	<	<	<	<	<
Ce	9.4	<	9.7	8.2	14.3
Cr	29.7	17.1	17.4	20.2	26.5
Ga	<	<	3.7	4.3	4.9
Hf	8.9	4.1	4.2	6.3	5.4
La	<	<	<	<	<
Nb	4.9	3.3	3.4	4.6	4.7
Nd	6.5	8.1	7.3	6.6	8.6
Ni	<	1.2	<	<	3.5
Pb	5.8	7.0	6.3	6.8	8.9
Rb	24.6	31.6	31.3	29.3	40.9
S	236.0	172.0	153.0	241.0	204.0
Sr	23.3	29.5	32.8	31.8	38.9
Th	<	<	<	<	3.7
V	10.4	7.7	8.0	9.9	13.4
Y	8.5	6.6	7.3	7.7	9.6
Zn	5.4	3.8	4.7	4.4	10.1
Zr	367.7	133.4	165.4	247.5	205.4
Al(HNO ₃)	829.5	835.6	620.9	893.6	1185.9
Ca(HNO ₃)	5.7	7.6	6.3	13.2	16.0
Fe(HNO ₃)	98.2	51.9	82.2	82.8	218.0
K(HNO ₃)	7.1	3.6	6.5	10.0	9.2
Mg(HNO ₃)	0.4	0.7	0.5	2.5	2.0
Mn(HNO ₃)	<	<	<	<	9.7
Na(HNO ₃)	2.4	3.6	2.9	3.4	3.7
P(HNO ₃)	13.6	12.0	4.5	8.9	42.2
S(HNO ₃)	12.2	15.1	11.0	12.9	28.5
Cd(HNO ₃)	0.01	0.01	0.00	0.01	0.00
Cr(HNO ₃)	0.36	0.39	0.28	0.32	0.47
Cu(HNO ₃)	0.18	0.16	0.15	0.15	0.34
Ni(HNO ₃)	0.07	0.10	0.04	0.09	0.10
Pb(HNO ₃)	0.95	1.08	0.70	1.09	1.65
Zn(HNO ₃)	0.90	0.66	0.59	0.93	1.04

region is to a much larger extent found in aluminosilicates whereas Cr in Noord Brabant is predominantly present in the form of chromite or some other Cr containing heavy mineral. The low heavy mineral content of the Utrechtse Heuvelrug and the Veluwe may be attributed to the influence of eolian processes (drifting sands) that resulted from a too intensive form of subsistence farming practiced in these regions during the Middle Ages.

Factor 4: Reactive Fe

The reactive Fe factor incorporates 'top/subsoil' features as well as a notably lower median level and high variability in the northern provinces (Figs 5.6 and 5.7). The low scores in the northern provinces are related to the high amount of extractable Ca in this region compared to other regions, especially in the topsoil. The Holocene influenced region is highest in reactive Fe both in top and subsoil, which is accompanied by high concentrations for total Fe_2O_3 , Cr, Ni, Pb, V, and Zn, and reactive Cr, Cu, and Pb. Extraction efficiencies for most elements are average or low. The high score of the Holocene influenced region on this factor is therefore related to the primary mineralogical richness and not to a high degree of transformation of Fe into secondary phases.

Factor 5: Reactive Al

The reactive Al factor manifests itself as a 'topsoil' factor, in that it shows much wider ranges in top than in subsoil for all regions. Apparently, the micro-variability in pH conditions in the topsoil that regulate Al-precipitation is also much larger. No clear regional picture emerges from figures 5.6 and 5.7, the Utrechtse Heuvelrug and the Holocene influenced region are somewhat higher in the subsoil. The position of the Holocene influenced region is again not the result of a high degree of Al transformation but of the overall mineralogical richness of this region.

Factor 6: P and Mn

The P and Mn factor again shows a 'regional' character. The different patterns in top and subsoil confirm the in part anthropogenic character of this factor. In the topsoil Noord Brabant shows the highest factorscores, and the Veluwe and the Utrechtse Heuvelrug show the lowest factorscores. These latter two regions also show small topsoil variability. Cu, as related trace element, is also high in the topsoils of Noord Brabant. This pattern can be explained by the close proximity of agriculture in many of the small forest sites in Noord Brabant, whereas the Veluwe and the Utrechtse Heuvelrug hold the largest continuous forested areas in the Netherlands. The most striking feature in the subsoil is the high position of the Holocene influenced region. This phenomenon is also reflected in table 5.3, from which it is clear that not only P and Mn but also S and many trace elements are high and highly extractable in this region.

5.4 Discussion: natural concentrations vs. reference values

As mentioned before, the more recent geochemical surveys often serve the purpose of establishing a geochemical baseline of natural values that can be helpful in assessing the chemical soil quality and establishing threshold values for this quality. In this section we

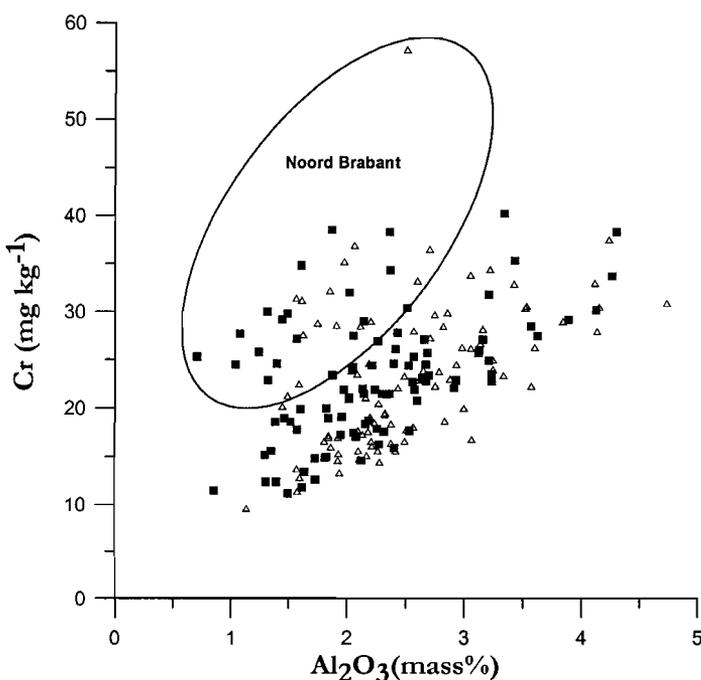


Figure 5.8

The relation between the total Cr concentration (XRF) in the solid phase and the Al₂O₃ content (XRF) for both topsoil (squares) and subsoil (triangles). The ellipse indicates the samples from Noord Brabant which are anomalously high in Cr.

contribute to this aim using the line of reasoning followed in the studies of Huisman (1998) and Tebbens (2000), which amounts to predicting trace element concentrations through (multiple) linear regression on the concentrations of some of the major oxides. Huisman's suggestion to follow a stepwise introduction of predictors beginning with Al₂O₃ proved useful in the Pleistocene sandy soils. We use this regression approach in conjunction with the concept of using the subsoil as a proxy for the topsoil. This concept used to be a regularly mentioned approach in various branches of soil science, from assessing the soil acidity status of soils (Breemen et al., 1983) to establishing the natural background values for environmentally important elements (Lexmond and Edelman, 1987), but because of a generally negative perception of the possibilities of this approach it has largely been abandoned. The two main objections against the approach are 1) the vulnerability to inhomogeneity of the profile because the parent material of the topsoil differs from that of the subsoil, and 2) downward transport of pollutants. Both phenomena cause the subsoil to be a questionable proxy for the topsoil, in the first case because it is intrinsically dissimilar to the topsoil and in the second case because it is just like the topsoil affected by anthropogenic enrichments.

In a study in the province of Zeeland, however, the enrichment of the topsoil with respect to heavy metals could be deduced from the very high correlations that existed between the heavy metals and the Al content in the subsoil (Gaans et al., 1995). Assuming this relation to be also valid in the topsoil, the amount of heavy metals in excess was considered to be of anthropogenic origin. The suitability of this approach in Zeeland probably resulted to a large

Figure 5.9

The relation between the total Pb concentration (XRF) in the solid phase and the Al_2O_3 content (XRF) for both topsoil (squares) and subsoil (triangles). The lower line represents a linear regression on the subsoil data ($R^2=0.40$), the upper line represents the reference value currently used in environmental soil management.

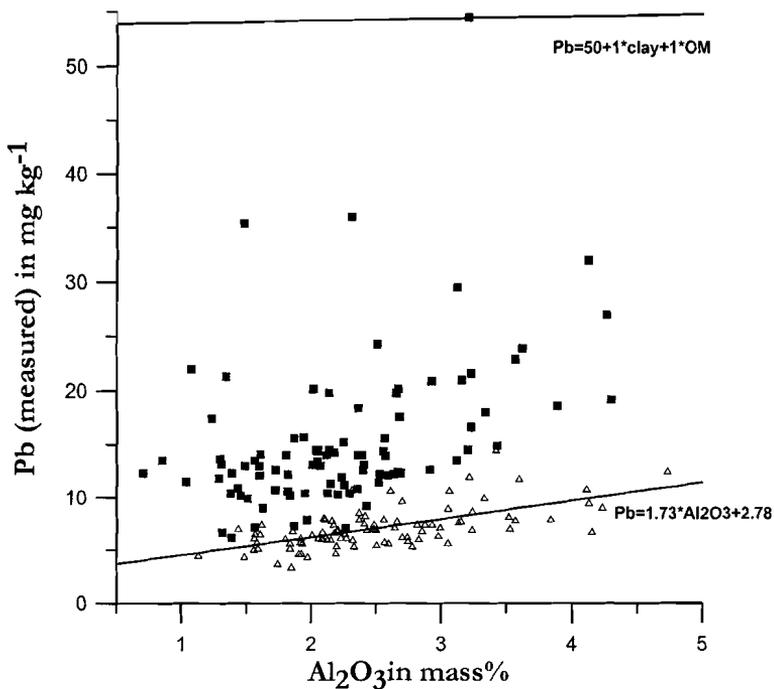
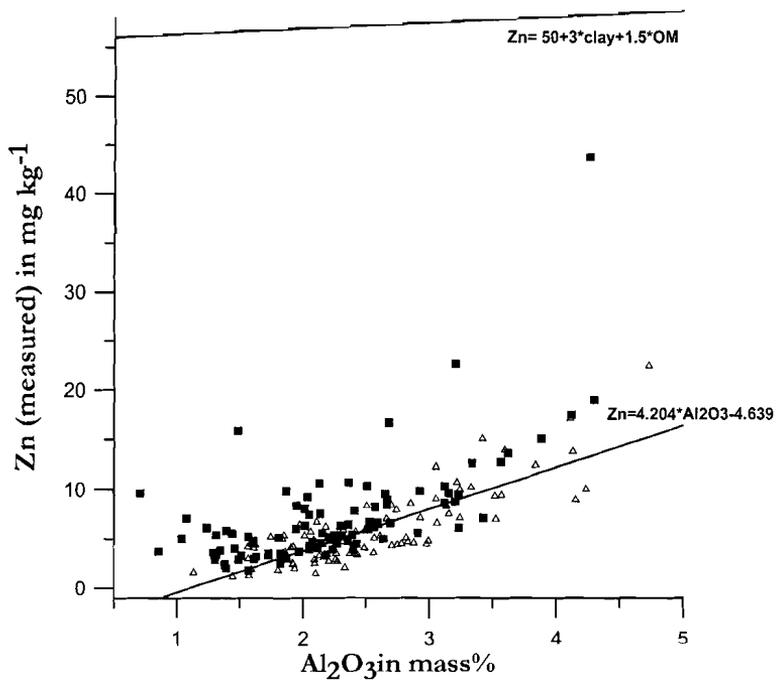


Figure 5.10

The relation between the total Zn concentration (XRF) in the solid phase and the Al_2O_3 content (XRF) for both topsoil (squares) and subsoil (triangles). The lower line represents a linear regression on the subsoil data ($R^2=0.68$), the upper line represents the reference value currently used in environmental soil management.



extent from the fact that Zeeland consists largely of clayey soils that on the one hand cause the composition of the profile to be homogeneous, and on the other hand prohibits to a large extent the mobility of cations. To assess the range of applicability of this concept we tested it for the heavy metals Pb and Zn in the virtually clayless Pleistocene sandy soils in this study. In addition to the lack of adsorptive constituents, these soils contain soil solutions with high levels of DOC which facilitates transport of cations that easily form organo-complexes.

From scattersplots versus Al_2O_3 it was clear that in the subsoil Al has a good correlation with both Zn and Pb. A linear regression model based on this relation in the subsoil was used to predict the natural levels of Zn and Pb in the topsoil, as graphically depicted in figures 5.9 and 5.10. For both heavy metals the concentrations in the topsoil are evidently higher than those in the subsoil. A linear regression model with only Al as predictor describes the natural levels of both elements well. Especially the explicit enrichment of Pb in the topsoil can be quantified with this method. The enrichment for Zn is less pronounced because the Zn load that is deposited is lower and probably also because Zn is a more mobile element that is transported downward through the profile to some extent.

Despite the drawbacks mentioned, we judge this method as a potentially promising approach even for these extremely poor sands. Even in the very low concentration range of Pb and Zn the relation with Al proved to have distinguishing power to identify samples that are enriched compared to the natural background concentrations. In this respect it does more justice to nature than does the correction for clay and organic matter content that is now in use in the environmental management of soil quality. To illustrate this, the background values predicted by this approach have been added to figures 5.9 and 5.10. It is evident that for the Pleistocene sandy soils, which cover a considerable part of the Netherlands, these values are of no use to distinguish between natural and enriched levels. In defence of the authors of these threshold values it can be mentioned that they established them principally to pinpoint situations that were undoubtedly anthropogenically enriched and they therefore aimed for an upper threshold that necessarily ignored the subtle variabilities and enrichments due to diffuse pollution. The general conception of these threshold values, however, is that they represent natural background values, and this is, at least for these poor sandy soils, clearly not the case.

An often used argument to play down methods that are a better approximation of the natural situation is that they are too sophisticated and too involved to use routinely in environmental research. In this case, however, determining the total element concentrations by XRF is a cheap, easy and quick way of characterizing soil samples, much more practical than determining the clay content for instance. Even more important, the XRF measurements have a much higher accuracy and precision than the determination of the clay content. So both the practical applicability and the sensitivity of the approach described call for a careful re-assessment of what is the best way to estimate natural background concentrations of soils.

5.5 Conclusions

The major conclusions will be presented following the four steps of the analysis.

- Pleistocene sandy soils are geochemically poor soils with SiO₂ concentrations well over 90 mass%, Al₂O₃ concentrations generally below 4 mass% and other major oxides generally below 1 mass%.
- Compared to the average concentration in the earth's upper crust all major oxides except SiO₂ have been depleted. The strongest depletion is shown by the elements associated with the most weatherable rocks and minerals such as Ca, Mg, and Fe.
- Differences between top and subsoil suggest enrichment in the topsoil for some elements, like S, Br, Pb and Zn, and depletion for other elements, like Al, Na, K, Ca.
- A relatively mild extraction at room temperature with 0.43 M HNO₃ indicates differences in reactivity at the basis of which lie differences in mineralogy.
- Through multivariate analysis of the dataset by PCA-V three natural and three anthropogenic factors were identified. The natural factors explain about 60% of the total variation and the three anthropogenic factors explain about 6% each, adding up to about 80% explained variance.
- The three natural factors are the alumino-silicates, the OM with related CEC, and the heavy minerals. The anthropogenic factors are reactive Fe, reactive Al, and a P-Mn factor.
- Cr and Ni are the most naturally behaving heavy metals. Cr is mostly related to heavy minerals and is therefore not very reactive and does not show differences between top and subsoil. Ni is released upon the weathering of Mg and Fe bearing silicates and subsequently turned into a more reactive form mainly related to OM, especially in the topsoil.
- The reactive parts of Pb, Zn, Cd, and Cu are higher in the topsoil. These metals enter the topsoil via the atmosphere, Pb stems from exhaust fumes, Zn and Cd from the metal industry, and Cu is mainly related to agricultural activities.
- Within the Pleistocene sands a clear geochemical regionality is present based on the mineralogical richness and on the richness of the (soil) ecosystems. The northern provinces are characterized by high OM concentrations, the Holocene influenced region is characterized by its mineralogical richness and its different mineralogical composition, and Noord Brabant shows the poorest mineralogy but with high heavy mineral and heavy metal concentrations. The latter are both natural and anthropogenic in origin.
- Good estimations of natural background concentrations of heavy metals can be obtained from their relation with Al in the subsoil. Enrichment of the topsoil can subsequently be estimated with this relation. This approach is more in line with nature's variability than the approach now in use in the practice of environmental management.

6. CHEMICAL CHARACTERIZATION OF THE SOIL SOLUTION OF ACID SANDY SOILS IN THE NETHERLANDS: EFFECTS OF CHEMICAL SPECIATION, GEOCHEMICAL REGIONALITY, AND SHORT TERM TEMPORAL VARIABILITY.

6.1 Introduction

The current protocol for monitoring soil acidification in the Netherlands developed in a period of sophisticated acidification research during which highly detailed ion balances for the most important cations and anions were the main focus (see Mol et al. *subm.*). Many operational details in the protocol have been inspired by this process-oriented research. The predominant characteristic of the chosen methodology is the analysis of displaced soil solution. Since the early nineties, soil acidification is being monitored by collecting samples every two years at two depths, displacing the soil solution in a centrifuge and analyzing it for a limited set of parameters. Mol et al. (1998; *subm.*) already discussed some theoretical and practical drawbacks of the soil monitoring protocol, one of the most disturbing being the vulnerability of the chosen monitoring medium to different kinds of variation that are not directly the result of ongoing soil acidification. In this paper we will further discuss the characteristics of the soil solution in acid sandy soils in the Pleistocene areas in the Netherlands, the majority of which accommodates coniferous forest. The analysis includes the effects of chemical speciation, geochemical regionality, and short term temporal variability.

The chemical behaviour of poor acid sandy soils such as the Pleistocene sandy soils in the Netherlands is known to be heavily dependent on the amount of organic matter (OM) in the solid phase and the amount of dissolved organic carbon (DOC) in the soil solution (Krám et al., 1997; Wessel, 1997; Qualls, 2000; Stigliani, 1988; Gustafsson et al., 2000; Chadwick and Chorover, 2001). Mol et al. (*subm.*) found the DOC concentrations of these soils to be both high and highly variable. From the literature it is well known that high concentrations of DOC strongly influence the chemical speciation of many elements, including Al and the heavy metals (Gerke, 1994; Dong et al., 1995; Wesselink and Mulder, 1995; Wilson and Bell, 1996; Clark et al., 1998; Temminghoff, 1998; Strobel et al., 2001; Temminghoff et al., 1997; Temminghoff et al., 1998). In these acid soils, the speciation of Al is especially interesting because of the combination of high and highly variable DOC concentrations and a pH that is in the range where Al concentrations are high and Al speciation is highly pH dependent (Weng et al., *accepted*; Weng et al., *accepted*). The speciation of Al influences the total amount of Al in solution and its mobility in the profile and as a result also the weathering of

Al bearing minerals (Blum and Stillings, 1995; White and Brantley, 1995; Lundström et al., 2000; Stefánsson et al., 2001). Binding of Al to DOC also influences the complexation behaviour of heavy metals through competition for binding sites and through coagulation of the DOC which affects the solubility and mobility of DOC bound components like heavy metals (Weng et al., accepted). Heavy metal mobility as affected by chemical speciation is of special concern in acid sandy soils that combine a low binding capacity of the solid phase with high DOC levels, particularly where these soils are covering aquifers used for the extraction of drinking water (Wilkens, 1995).

Geochemical regionalism has been shown to exist in both the solid phase and the soil solution of the Pleistocene sandy soils of the Netherlands (Mol et al. *subm.*). The regional differences in the soil solution, which proved to be related to those in the solid phase, are primarily governed by the concentrations of DOC and base cations, which subsequently influence the behaviour of Al both in solution and on the CEC of the solid phase. As a result, regionalism is a meaningful phenomenon in the interpretation of the acidity status of these soils. In combination with the chemical speciation of the soil solution, which is also strongly governed by DOC, these regional patterns are of the utmost importance in assessing the chemical patterns emerging from the soil acidification monitoring results.

Short term temporal variation, which includes for instance weather influenced variability and seasonal patterns, has been studied with respect to different substances and environmental compartments, and with respect to various temporal and spatial scales (Poulson et al., 1995; Angulo-Jaramillo et al., 1997; Iqbal et al., 1997; Jackson and Pardue, 1997; Kolpin et al., 1997; Ratha and Venkataraman, 1997; Zwolsman et al., 1997; Laverman, 2000; Dinelli and Lombini, 1996; Kubilay et al., 1997; Kohn et al., 1998; Mohanty et al., 1998; Wardle, 1998; McLean and Huhta, 2000; Wallander et al., 1997; Bardgett et al., 1997; Görres et al., 1998; Ponizovskiy and Polubesova, 1990; Papritz and Webster, 1995; Papritz and Webster, 1995). Of special interest in this research is the literature on temporal fluctuations in the soil and soil solution chemistry of acid sandy soils. Although widely varying results are reported, most authors agree on the existence of seasonal patterns for various important parameters of the soil. Particularly the elements that are obviously involved in the biological cycle, such as N and P, are reported to show distinct seasonal patterns (Magid and Nielsen, 1992; Henrich and Haselwandter, 1997; Yin and Foster, 1993). However, also elements that have a less obvious relation to biology, such as the base cations and SO_4 and even Fe, Cl, pH, DOC and Al, have been shown to fluctuate seasonally (Castelle and Galloway, 1990; Grieve, 1990; Yin and Foster, 1993; Wesselink et al., 1994).

The consequences of these sources of variation for soil acidification monitoring, especially when displaced soil solution is the only medium used in monitoring, are evident. Speciation for example causes part of the Al to be organically complexed, this increases the total amount of Al in solution because precipitation of or adsorption to the solid phase is related to free Al^{3+} and not to the organically complexed Al species (Gerke, 1994; Dong et al., 1995; Wesselink and Mulder, 1995; Clark et al., 1998). Regionalism affects the composition of the soil solution mostly indirectly, first as a result of the regionalism in the parent material (Grieve, 1999; Frei et al., 2000), and second as a result of the (soil) ecosystem that develops on this substrate. These two factors influence the amount of cations released into the soil solution (mostly related to the weathering characteristics of the parent material) and also the DOC

concentration in the soil solution (which is the result of a complex interaction between the type of OM produced by the ecosystem, the concentrations of the macro-elements such as Al and Ca in solution, and the pH). As a result, also the chemical speciation may be prone to regionality. Short term temporal variability is particularly manifest in the soil solution and it can therefore be a disturbing factor in the interpretation of current monitoring results; it interferes with the long term temporal variation (a multi-year trend) which of course is the main objective of any environmental monitoring system. The question is whether the short term variation overshadows the long term variation.

The issues raised above formed part of a study concerning the monitoring of soil acidification. The study consisted of two field campaigns. One covered a wide range of acid sandy soils in the Netherlands and focussed on the regional variation within and among provinces and is referred to as the main campaign (see also chapter 1). The other focussed on short term temporal variation and is referred to as the seasonal campaign. During both campaigns various methods of analysis have been used to test possible alternatives for or supplements to the analysis of displaced soil solution only. In this paper we discuss the results of both campaigns with respect to the soil solution. We characterize its chemical composition and explore the chemical speciation of some important elements. The next step in the analysis is a further characterization of the regional geochemical patterns that were found in a prior classification based on the major elements in the solid phase and the soil solution (Mol et al., *subm.*). Finally the short term temporal variability is evaluated by comparing the temporal and spatial variance components. The robustness of the soil displacement method and of the alternative methods towards short term temporal variability are tested.

6.2 Materials and methods

For the main campaign soil samples were collected at 92 locations at two depths (the first 20 cm of the mineral soil below the litter layer and a C or B/C horizon between 60 and 110 cm) resulting in 184 samples. The set of locations, each about 10,000 m², was selected from the monitoring sites of six of the Dutch provinces. All sampled locations were coniferous forest stands on sandy soils (Fig. 6.1). Sampling took place in May-June 1999. For the seasonal campaign a subset of 20 locations was sampled 8 times during a two year period (1998 and 1999). For logistic reasons the subset was located in close proximity of the laboratory, namely on the Utrechtse Heuvelrug. In this campaign soil samples were collected (and treated) identical to the main campaign resulting in 40 samples per sampling round, and a total of 320 samples. Sampling took place in April, August, September/October, and November/December of both 1998 and 1999.

Each location was divided into 6 equal sections in which a randomly located sample was collected at two depths (stratified random). The 12 subsamples of 2 kg each were obtained using a so called Edelman hand auger and transported to the laboratory in separate sampling bags as mixing in the field of moist soil is undesirable. To minimize chemical changes in the soil solution the samples were kept at 4°C in the dark and centrifuged within 24 hours. The 12 subsamples were centrifuged separately and a composite sample from the displaced soil solution for each depth was put together after centrifugation. The total moisture yield was

Figure 6.1

Map of the Netherlands showing the sample locations and the regions discussed in section 6.3.3.



recorded, the pH measured and the displaced soil solution samples were analyzed with various analytical techniques (see Table 6.1). The subsamples for ICP analyses were acidified to pH=1 with ultrapure HNO₃.

A composite sample of the solid phase for each depth was prepared from a second part of the subsamples by putting an equal amount of soil from each bag into a small plastic container. The soil was subsequently dried at 40°C, mixed, and sieved. The fraction < 2 mm was used for two extractions, one with 0.01 M CaCl₂ (Houba et al., 2000) and the other with 0.43 M HNO₃ (Otte et al. 2000), both at room temperature. Both extractions were carried out by shaking a 1:10 solid-solution mixture for 2 hours, after which the supernatant was collected for further analysis. Extraction methods are notoriously sensitive to variability in the operational details, such as the sieving and/or grinding efficiency, exact composition of the extractant, temperature, shaking time and intensity, and separation method of extract and solid. To minimize these effects, all extractions were prepared and analyzed within one batch. For logistic reasons, however, the samples of the seasonal campaign were prepared and analyzed at a different laboratory (and hence in a separate batch) from that of the main campaign. For the samples of the main campaign only, the fraction < 2 mm was also used to determine the total element content by X-ray fluorescence spectroscopy, using pressed powder tablets. Table 6.1 gives an overview of the analytical methods used; for a

comprehensive account of the details of all analyses see appendix A and a detailed description of the environmental setting see chapters 2 and 4. The total element analysis of the solid phase (XRF) and the HNO₃ extraction were aimed at characterizing the solid phase and its reactivity. The CaCl₂ extraction and the displaced soil solution are used as models for the chemical composition of the soil solution.

Table 6.1

Overview of the different chemical analyses grouped per method.

Method	Parameters	Analytical technique
Dry soil	dry matter content organic matter content SiO ₂ , Al ₂ O ₃ , K ₂ O, Na ₂ O, CaO, MgO Fe ₂ O ₃ , MnO, P ₂ O ₅ , S, Zr, As, Ba, Bi, Br, Ce, Cr, Cs, Cu, Ga, Hf, La, Nb, Nd, Nd, Pb, Rb, Sb, Sc, Sr, Th, U, V, Y, Zn	oven (105°C) loss on ignition (550°C) XRF, pressed powder tablets*
Displaced soil solution	pH Dissolved Organic Carbon NH ₄ SO ₄ , NO ₃ , Cl, PO ₄ Al, K, Na, Ca, Mg, Fe, Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	TOC analyzer Spectrometry Ion chromatography ICP-AES ICP-MS
CaCl ₂ extract (0.01 mol l ⁻¹)	pH Dissolved Organic Carbon NO ₃ , NH ₄ , N _{tot} , PO ₄ , Na, K Al, Mg, Fe, Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	Organic carbon analyzer Segmented Flow Analyzer ICP-AES ICP-MS
HNO ₃ extract (0.43 mol l ⁻¹)	Al, K, Na, Ca, Mg, Fe, Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	ICP-AES ICP-MS

*The accuracy of this method for major oxides was checked and found to be excellent by re-analysis of 26 samples using glass beads.

6.3 Results and discussion

6.3.1 General chemical characteristics

The range of concentrations of the most important components in the displaced soil solution and the CaCl₂ extracts of the Pleistocene sandy soils in the Netherlands is presented in table 6.2. The acidified nature of these soils is evident from this table; especially pH and Al values in the displaced soil solution are in the range generally reported for acid soils in the Netherlands (Mulder, 1988; Ulrich and Sumner, 1991; Vries, 1994; Mol et al., submitted). The

Table 6.2

Overview of the concentrations in the displaced soil solution (yield in ml, all major elements and parameters in mg l^{-1} , trace elements in $\mu\text{g l}^{-1}$) and the 0.01 M CaCl_2 extract (all major elements and parameters are recalculated to mg kg^{-1} dry soil, trace elements to $\mu\text{g kg}^{-1}$). The last column shows the detection limit where appropriate. The < symbol indicates values below the detection limit.

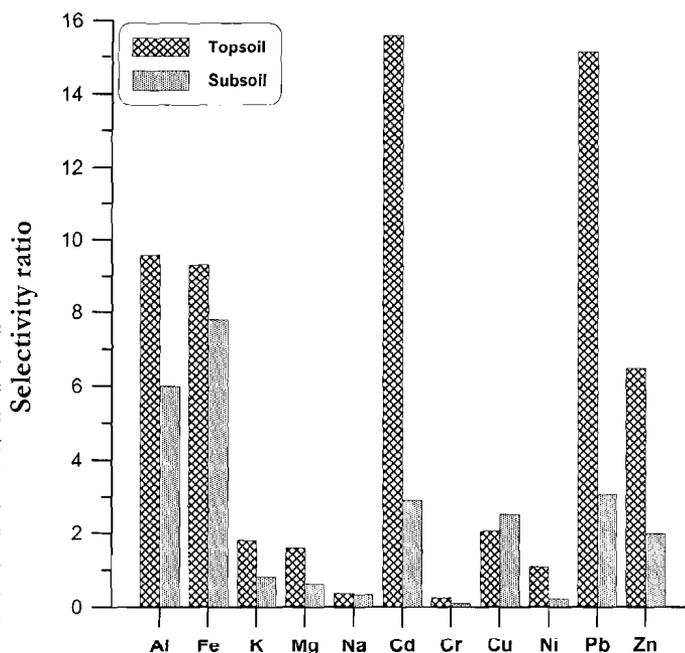
	minimum		25 percentile		median		75 percentile		maximum		det. lim.
	top	sub	top	sub	top	sub	top	sub	top	sub	
Yield	5	5	30	24	50	60	80	100	120	120	
pH	3.0	3.3	3.4	3.6	3.5	3.8	3.7	3.9	4.5	5.3	
DOC	32.0	18.0	71.0	43.0	91.5	61.5	126.3	90.3	990.0	365.0	
Al	1.60	1.78	4.01	3.27	5.53	5.74	6.87	8.61	14.6	23.8	
Ca	0.83	0.76	3.85	2.26	12.51	5.50	18.87	13.53	66.7	54.2	
Fe	0.04	0.01	0.33	0.12	0.62	0.26	1.32	0.60	8.8	16.1	
K	1.62	0.74	3.99	2.54	5.90	3.59	9.32	5.32	32.0	16.5	
Mg	0.57	0.81	2.13	1.52	4.24	2.57	6.22	4.50	19.0	11.3	
Mn	0.00	0.00	0.04	0.03	0.11	0.12	0.33	0.26	3.0	3.3	
Na	6.35	5.36	11.52	10.48	19.99	16.59	29.64	27.23	58.5	52.9	
Cl	3.1	5.0	10.7	13.7	17.7	19.8	23.5	30.6	89.5	140.7	
NO ₃	0.5	0.5	20.8	16.1	38.7	25.1	60.9	37.6	332.1	109.6	
NH ₄	0.0	0.0	0.3	0.2	1.2	0.5	1.7	0.8	16.9	4.9	
SO ₄	3.3	2.8	17.0	13.1	20.1	21.3	30.6	35.5	95.0	130.9	
S	2.4	1.8	5.7	4.1	7.6	7.8	10.5	12.2	34.5	43.3	
P	0.07	0.03	0.11	0.06	0.17	0.08	0.29	0.12	2.84	0.62	
Cd	<	<	1.0	0.6	1.8	1.4	2.9	3.3	10.4	30.6	0.1
Cr	3.2	1.9	5.4	5.2	7.9	8.0	10.2	13.0	26.2	52.2	
Cu	4.5	3.1	9.2	7.2	13.4	9.7	18.3	15.0	40.5	130	
Ni	25.8	17.7	34.7	41.5	59.7	62.8	89.6	96.7	339	648	
Pb	3.7	1.9	9.4	3.9	18.7	6.2	31.1	10.7	107	35.1	
Zn	83.7	79.8	139	163	197	247	308	358	987	2864	

pH(CaCl ₂)	3.1	3.2	3.4	4.1	3.6	4.3	3.7	4.3	4.7	5.5	
DOC(CaCl ₂)	45.7	10.7	92.5	35.7	120	49.0	154	69.5	255	199	
Al(CaCl ₂)	6.56	5.84	41.1	26.5	52.9	34.4	78.1	45.5	131	92.1	
Fe(CaCl ₂)	<	<	2.14	<	5.77	2.00	9.39	3.39	32.7	15.6	0.5
K(CaCl ₂)	2.00	<	6.28	2.30	10.6	2.90	15.9	5.65	68.5	27.8	0.1
Mg(CaCl ₂)	1.56	<	4.19	<	6.74	1.59	22.2	3.42	71.0	70.0	0.7
Na(CaCl ₂)	2.50	<	4.90	3.95	7.30	5.50	11.6	9.30	115	31.90	0.5
NO ₃ (CaCl ₂)	<	<	<	<	1.4	<	1.8	1.35	25.4	6.80	0.07
NH ₄ (CaCl ₂)	1.70	<	3.80	0.70	5.25	0.90	8.00	1.33	18.9	7.40	0.01
PO ₄ (CaCl ₂)	<	<	<	<	0.08	0.07	0.11	0.10	1.49	0.27	0.04
					0	0	0	0	0	0	
Cd(CaCl ₂)	2.0	<	15.0	0.7	28.0	4.0	53.3	8.3	236	55	0.7
Cr(CaCl ₂)	<	<	<	<	2.0	<	6.3	3.3	31	39	0.7
Cu(CaCl ₂)	1.0	<	13.8	14.8	27.5	24.5	44.0	37.3	403	217	0.7
Ni(CaCl ₂)	<	<	20.8	0.7	65.0	13.5	93.3	43.5	340	219	0.7
Pb(CaCl ₂)	8.0	<	180	10.8	283	19.0	444	29.5	3061	139	0.7
Zn(CaCl ₂)	422.0	53.0	863	303	1271	486	1841	718	7462	15840	

literature on acidification in Dutch sandy soils also shows concentrations of base cations that are in the range found in this study. Considered in view of the congruent dissolution of feldspars, the dominant reactive minerals in these soils, Mol et al. (subm.) show that the concentrations of the base cations in the displaced soil solution are too high, also when corrected for initial rain and seawater contributions. This indicates that the soil solution is still being provided with more base cations than it is with Al. Mol et al. (subm.) argue this to be the result of preferential leaching from the feldspar lattice, or of precipitation of previously dissolved Al in secondary phases. In general, concentrations of Fe and Mn in displaced soil solution are low, with the exception of a few locations.

The results of the CaCl_2 extraction show that the proportions on the CEC differ from those in the solution (see also Fig. 6.2). Al and Fe clearly show a stronger affinity for the CEC than the base cations (see also Mol et al., subm.). Remarkably the pH values in the CaCl_2 extracts do not differ from those in the displaced soil solution of the topsoil and are actually higher in the subsoil samples, whereas they are generally found to be lower. In the extraction 30 ml of liquid was used per 3 g soil (liquid solid ratio 10:1), whereas after centrifugation the average yield from 3 kg soil was about 60 ml (liquid solid ratio 0.02:1), and the dry matter content indicates an average liquid solid ratio of about 0.1:1. For the extraction this results in an enormous volume in which the pH has to be lowered by proton release. In these poor sandy soils the amount of exchangeable H^+ is not sufficiently large to produce this generally observed decrease. In addition it should be noted that to lower the pH from 3.5 to 3.0 much more protons need to be released than to produce a pH decrease from e.g. 6.0 to 5.5.

Figure 6.2
Relative affinity for the CEC expressed as a selectivity ratio of the concentration in the 0.01 M CaCl_2 extract (recalculated to mg kg^{-1} dry soil) and the concentration in the displaced soil solution (in mg l^{-1}) for a selection of elements in both top and subsoil.



Anion concentrations in the displaced soil solution, especially NO_3 and SO_4 , are relatively high, as can be expected in soils that are acidified to a large extent by the deposition of compounds like SO_x , NO_x and NH_x (Heij and Erisman, 1997). They do, however, not balance the cation concentrations, an anion deficit exists, a phenomenon also found in other research (Gower et al., 1995). As is evidenced by figure 6.3, this deficit is counterbalanced largely by the high DOC concentrations present in these solutions, which complexes part of the cations. The rather large spread in the relation shown in figure 6.3 probably results from the heterogeneity of the DOC which causes it to bind different amounts of cations depending on its exact chemical composition, and of course depending on the pH, because in this pH range proton binding dominates the DOC binding capacity (see section 3.2). NH_4 concentrations are generally low to very low, probably due to fast nitrification in the topsoil. The simultaneous presence of NO_3 and NH_4 indicates that these soil solutions are still far from equilibrium.

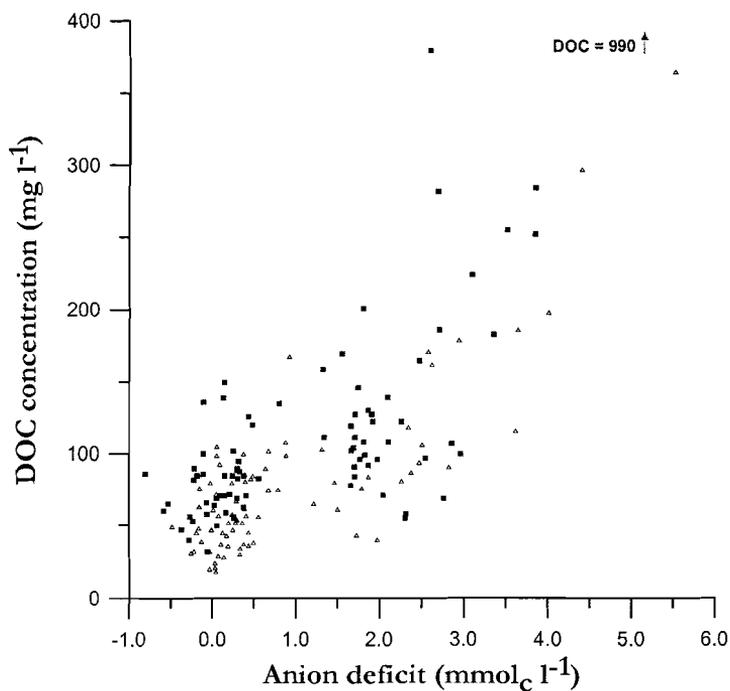


Figure 6.3

The relation between the DOC concentration (mg l^{-1}) and the anion deficit ($\text{mmol}_c \text{l}^{-1}$) for both topsoil (squares) and subsoil (triangles).

The heavy metal concentrations are very low with values generally below 1 mg l^{-1} for the displaced soil solution and below 1 mg kg^{-1} dry soil for the CaCl_2 extracts. As no reference values for heavy metal concentrations in the soil solution exist, we compared them to the ranges found in the ground water of the Netherlands as interpreted by Frapporti et al. (1996). They distinguished 7 ground water types for the Netherlands of which two are of interest to this study, namely the *precipitation* groundwater type and especially the *polluted* groundwater

type, which are both found in the sandy infiltration areas (Table 6.3). Cadmium and Cu concentrations in the soil solution displaced from the Pleistocene sandy soil show slightly higher values than those of the polluted groundwater type as identified by Frapporti et al. (1996). Also Zn concentration levels in both top and subsoil are in the high range of what was found in the polluted water type, whereas Pb is clearly much higher. Nickel and Cr appear to be about thrice as high. The relatively high levels of heavy metals in the displaced soil solution can in part be explained by pH, which is much lower than in the groundwater types, and by the much higher levels of DOC (Table 6.3). The comparison underlines the relative immobility of soil heavy metals towards the groundwater, as evidenced especially by Pb.

The differences between top and subsoil that exist in the solid phase (chapter 5) are reflected in the heavy metal concentrations of the CaCl_2 extracts and not in the displaced soil solution, with the exception of Pb which is also higher in the soil solution of the topsoil (Table 6.2). From figure 6.2 it can be concluded that metals like Cd, Pb, and Zn behave differently from metals like Cr and Cu. Chromium and Cu have a low affinity for the CEC whereas Cd, Pb, and Zn have a much higher affinity. This results in clear enrichments of the topsoil with respect to Cd, Pb, and Zn in the CaCl_2 extracts and no enrichments of the topsoil for Cr and Cu. The important role that complexation to dissolved organic matter plays in these differences will be addressed in the next section.

Table 6.3

The data for the heavy metals ($\mu\text{g l}^{-1}$), pH and DOC (mg l^{-1}) reported by Frapporti et al. (1996) for two of the 7 groundwater types they distinguished and for the top and subsoil solution of this study. Ranges given are the 15 to 85 percentile interval.

	Polluted groundwater	Precipitation groundwater	Topsoil solution	Subsoil solution
Cd	0.2 - 2.9	<0.15	0.6 - 5.0	0.4 - 4.9
Cr	<0.5 - 3	0.6 - 4.5	4 - 13	4 - 17
Cu	<0.9 - 13	<0.9	8 - 22	6 - 18
Ni	4 - 56	0.6 - 7.5	29 - 120	33 - 147
Pb	<3	<3	8 - 41	3 - 12
Zn	10 - 325	<10	116 - 364	140 - 439
pH	4.25 - 5.25	5.25 - 6.3	3.2 - 3.8	3.5 - 4.0
DOC	1.5 - 5.8	1.5 - 13	64 - 153	33 - 105

6.3.2 Chemical speciation

In the introduction it was made clear that chemical speciation can have a profound impact on the soil solution characteristics, especially when DOC concentrations are high. To elucidate the chemical speciation behaviour of the soil solution of the Pleistocene sandy soils in the Netherlands we used the chemical speciation program ECOSAT (Keizer and Riemsdijk, 1994) focussing on Al, Cd, and Cu in the displaced soil solution. ECOSAT applies the usual thermodynamic relations to calculate the distribution of inorganic species, the interaction with dissolved organic matter is described with the so called Non Ideal Consistent Competitive Adsorption Donnan model. The NICCA-Donnan model describes, in a thermodynamically

consistent way, the interaction between cations (including protons) and DOC considering the effects of the binding site heterogeneity of the DOC, competition between different cations and protons, both specifically and electrostatically bound, and ion specific non ideality (for detailed discussions on the theoretical considerations see Kinniburgh et al., 1996 and Kinniburgh et al., 1999). Aluminum, Cd, and Cu were chosen because Al and heavy metals are of major interest in acid soils and because for these cations thoroughly validated generic model parameters are available (Milne et al., 2001; Weng et al., accepted; Weng et al., accepted). As model input we used the major chemistry of the displaced soil solution as measured (Na, K, Ca, Mg, Al, Cd, Cu, Cl, SO₄, DOC and an ionic strength calculated on the basis of the major ions).

The results of the calculations are presented in table 6.4 in the form of the percentages by which the most important species contribute to the total concentration. It is clear that DOC is indeed an important constituent of the soil solution because for all three elements complexation by DOC can lead to percentages of complexed species of up to almost 100%. The importance of complexation by DOC, however, is different for each parameter. Copper shows the strongest binding to DOC with median values of 98% in both top and subsoil. Cd shows the weakest binding to DOC with median values of about 25% for both top and subsoil. Al holds an intermediate position with median percentages of about 44% for the topsoil and 35% for the subsoil.

Table 6.4

Minimum, median, and maximum contributions (in %) of the relevant species of Al, Cd, and Cu as calculated with ECOSAT for both top and subsoil.

	TOPSOIL			SUBSOIL		
	minimum	median	maximum	minimum	median	maximum
Al ³⁺	1.6	46.0	73.4	0.3	52.8	72.9
Al(OH) ₂ ⁺	0.0	0.2	1.5	0.1	0.4	8.3
AlOH ²⁺	0.1	1.0	3.1	0.3	1.8	6.2
AlSO ₄ ⁺	0.1	6.4	19.9	0.1	6.7	28.3
Al-DOC	7.5	43.6	97.4	4.5	34.8	95.1
Cd ²⁺	3.0	70.1	88.6	2.7	71.7	87.3
CdCl ⁺	0.0	2.4	9.0	0.1	2.7	15.5
CdSO ₄ ⁰	0.1	2.1	7.2	0.0	2.1	9.6
Cd-DOC	3.3	25.7	97.3	3.6	23.3	97.5
Cu ²⁺	0.0	1.7	25.7	0.0	1.7	15.9
CuSO ₄ ⁰	0.0	0.0	1.3	0.0	0.0	1.1
Cu-DOC	73.1	98.3	100	83.7	98.3	100

Differences in speciation between top and subsoil solution are to be expected on the basis of the differences in almost all compounds that are important for speciation (see Table 6.2). The results in table 6.4, however, show that for Cd and Cu no significant differences in speciation between top and subsoil exist. This phenomenon is probably the result of the increase in pH that accompanies and in part compensates the decrease in DOC concentration

Figure 6.4

The relation between the percentage free Al^{3+} and pH in the displaced soil solution as calculated with ECOSAT. The three symbols used indicate a division of the samples based on their DOC concentrations. The four lines represent theoretical relations calculated with a fixed amount of DOC (indicated in the figure) and the median values of the dataset from the main campaign for Na, K, Ca, Mg, Al, Cd, Cu, Cl, SO_4 , and ionic strength.

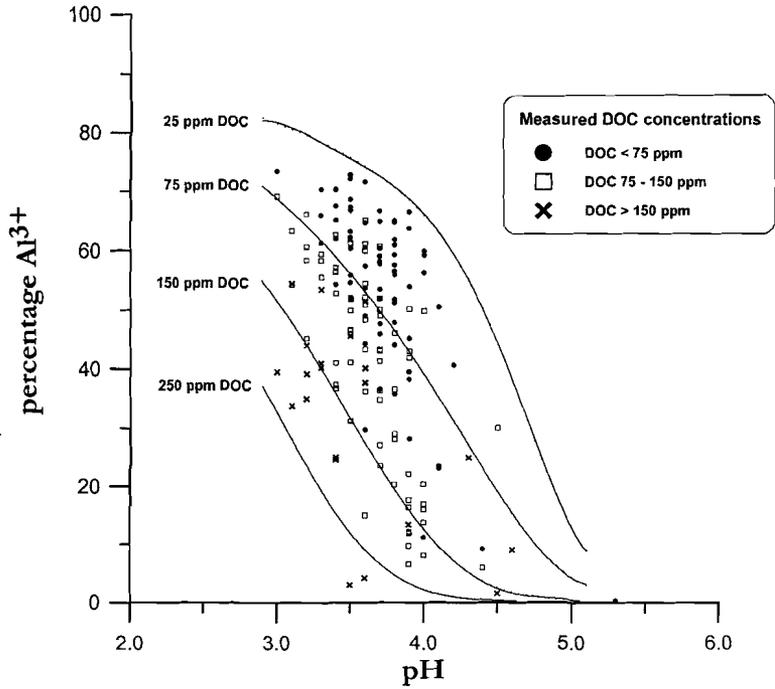
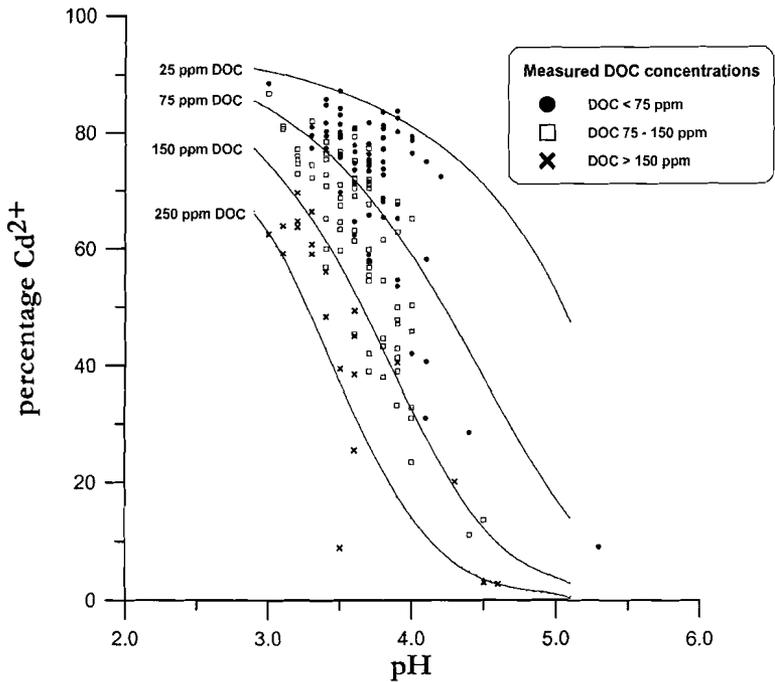


Figure 6.5

The relation between the percentage free Cd^{2+} and pH in the displaced soil solution as calculated with ECOSAT. See for further explanation the caption of Fig.6.4.



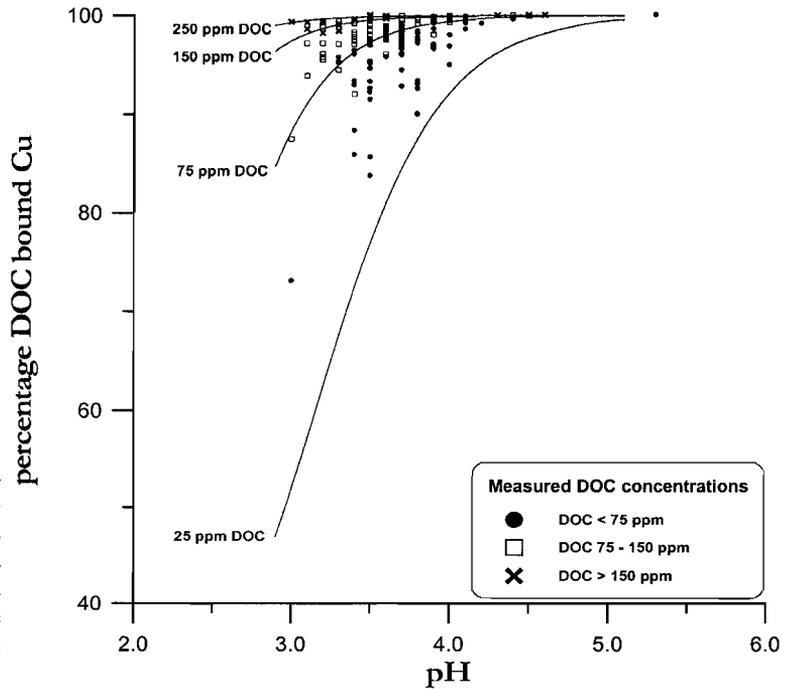


Figure 6.6
 The relation between the percentage DOC bound Cu and pH in the displaced soil solution as calculated with ECOSAT. See for further explanation the caption of Fig.6.4.

from top to subsoil (see Figs 6.4 and 6.5). Protons are dominating the binding capacity of DOC with a median relative occupation of 94.4% for the topsoil and 92.2% for the subsoil. Aluminum in solution is affected by the pH in two important ways. Not only does the complexation of Al by DOC increase with increasing pH due to the diminishing competition of protons, also the total Al concentration decreases due to the reduced solubility of mineral phases (Weng et al., accepted). However, a higher median percentage of free Al^{3+} and a lower median percentage of DOC bound Al are found in the subsoil. Apparently for Al, the decrease in DOC with depth cannot be fully compensated by the combined pH effects. Moreover, neither total nor free Al concentrations decrease with depth as expected from pH, which must be ascribed to slow kinetics. Increase in total concentration also favours a higher percentage of the free ionic form (see below).

The free ionic forms of Al, Cd, and Cu are considered the environmentally most important because of the generally high availability for uptake by plants and high toxicity (Fergusson, 1990). As already evident from the discussion above, the two parameters of major importance in controlling the amount of the elements occurring in free ionic form are the pH and the DOC concentration. The effect of these two master variables has been depicted graphically in figures 6.4 to 6.6. The occurrence of deviations from the general picture demonstrate a higher degree of complexity of the speciation behaviour. In most cases these deviations could be explained by a high or low total amount of the metal in solution, the occurrence of other

Table 6.5

Median values for both top and subsoil per region of the concentrations in the displaced soil solution (yield in ml, all major elements and parameters in mg l⁻¹, trace elements in µg l⁻¹) and the 0.01 M CaCl₂

TOPSOIL					
	Noord Brabant	Utrechtse Heuvelrug	Veluwe	northern provinces	Holocene influenced sites
Yield	30	80	50	70	30
pH	3.4	3.5	3.6	3.4	3.6
DOC	93	111	71	96	83
Al	7.31	5.40	5.27	5.17	5.12
Ca	6.68	9.98	3.09	18.47	8.74
Fe	0.52	0.55	0.62	1.20	0.59
K	4.81	5.44	3.97	7.62	6.12
Mg	2.99	3.96	2.09	5.77	3.54
Mn	0.13	0.05	0.07	0.09	0.47
Na	13.12	22.22	12.16	28.57	13.14
Cl	16.9	12.1	7.1	24.3	14.2
NO ₃	45.5	29.3	28.5	31.1	54.0
NH ₄	2.8	1.4	1.0	1.0	1.3
SO ₄	26.1	19.9	15.7	18.2	23.8
S _{tot}	10.1	7.6	5.3	7.9	7.6
P _{tot}	0.2	0.2	0.1	0.3	0.2
Cd	5.8	1.8	1.5	1.0	2.0
Cr	8.3	6.5	7.4	9.4	7.2
Cu	17.8	14.2	14.6	10.6	14.2
Ni	77.7	35.9	47.5	70.9	58.4
Pb	15.8	27.1	21.4	19.6	20.9
Zn	393	165	174	161	234
pH(CaCl ₂)	3.5	3.6	3.6	3.5	3.7
DOC(CaCl ₂)	131	120	95	117	136
Al(CaCl ₂)	65.0	62.8	48.4	42.8	59.4
Fe(CaCl ₂)	4.6	4.4	6.0	3.4	10.0
K(CaCl ₂)	7.0	9.4	7.3	13.4	11.7
Mg(CaCl ₂)	3.7	4.8	3.6	13.2	6.6
Na(CaCl ₂)	5.9	5.3	6.3	11.1	6.0
NO ₃ (CaCl ₂)	1.5	1.6	1.4	0.5	1.5
NH ₄ (CaCl ₂)	4.7	4.4	4.4	8.0	4.5
PO ₄ (CaCl ₂)	1.0	2.0	1.0	0.4	1.1
Cd(CaCl ₂)	77	26	10	28	14
Cr(CaCl ₂)	2	<	<	5	3
Cu(CaCl ₂)	28	21	48	15	40
Ni(CaCl ₂)	40	31	<	89	73
Pb(CaCl ₂)	359	239	438	230	523
Zn(CaCl ₂)	1820	820	717	1517	1132

Table 6.5 (continued)

extract (all major elements and parameters are recalculated to mg kg⁻¹ dry soil, trace elements to µg kg⁻¹).

	SUBSOIL				
	Noord Brabant	Utrechtse Heuvelrug	Veluwe	northern provinces	Holocene influenced sites
Yield	90	65	120	90	20
pH	3.7	3.8	4.0	3.7	3.9
DOC	45	63	28	76	65
Al	8.35	6.33	4.56	5.64	3.99
Ca	3.97	2.64	2.18	9.11	7.73
Fe	0.27	0.21	0.07	0.48	0.20
K	3.05	3.29	3.57	3.83	3.95
Mg	1.81	2.33	1.48	4.46	2.99
Mn	0.14	0.05	0.14	0.05	0.69
Na	11.66	17.79	10.46	26.08	15.53
Cl	14.5	26.2	8.5	24.9	16.3
NO ₃	25.5	26.7	23.0	18.7	34.0
NH ₄	0.5	0.7	0.4	0.5	0.8
SO ₄	25.8	22.2	12.5	14.1	27.8
S_tot	9.9	6.8	3.7	7.2	9.4
P_tot	0.1	0.1	0.0	0.1	0.1
Cd	5.2	1.2	1.8	0.6	2.1
Cr	7.7	6.7	3.5	12.2	6.2
Cu	10.5	9.4	9.4	9.5	13.0
Ni	88.9	52.6	33.2	67.1	60.2
Pb	6.2	7.5	4.3	4.9	8.8
Zn	445	294	211	175	243
pH(CaCl ₂)	4.3	4.2	4.3	4.1	4.3
DOC(CaCl ₂)	43	56	36	63	44
Al(CaCl ₂)	33.4	46.8	20.9	38.4	29.2
Fe(CaCl ₂)	1.3	3.0	<	2.8	<
K(CaCl ₂)	2.9	2.6	2.9	2.3	2.9
Mg(CaCl ₂)	<	1.5	<	3.7	0.8
Na(CaCl ₂)	7.3	6.4	5.3	6.5	4.2
NO ₃ (CaCl ₂)	1.2	0.6	<	<	0.9
NH ₄ (CaCl ₂)	0.8	1.0	0.9	1.0	1.0
PO ₄ (CaCl ₂)	1.0	1.4	1.1	<	1.1
Cd(CaCl ₂)	6	7	<	1	4
Cr(CaCl ₂)	<	<	<	4	1
Cu(CaCl ₂)	38	21	36	15	25
Ni(CaCl ₂)	<	<	<	49	<
Pb(CaCl ₂)	16	19	<	23	19
Zn(CaCl ₂)	326	538	238	635	387

complexing anions was never of influence. For Cd the decrease in the percentage of the free metal under influence of pH and DOC is less pronounced as it is for Al. Figure 6.6 shows that for Cu to occur in its free ionic form both DOC concentrations and pH have to drop to really low values. The variation in affinity for complexation to dissolved organic matter among the metals clearly affects their affinity for the solid phase CEC. Copper has a low affinity to the CEC, whereas Cd, which is much less complexed by DOC, shows a higher affinity for binding to the CEC (see Fig. 6.2).

6.3.3 Regional variability

Mol et al. (subm.) addressed the regional variability that exists in the Pleistocene sandy soils in the Netherlands, both with respect to the acidity status of the soils as well as with respect to the geochemical variability of the solid phase. To identify these regional geochemical patterns a multivariate statistical technique for finding homogeneous groups in datasets called fuzzy c -means clustering was used (for an explanation see Bezdek, 1981; Bezdek et al., 1984; Vriend et al., 1988). The cluster analysis was performed on the macro chemical elements of both the solid phase and the soil solution (see chapters 4 and 5 for detailed results). The five regions that were identified after clustering could mainly be distinguished on the basis of their mineralogical richness and their organic matter content. They are, from north to south, 1) the northern provinces (Friesland, Groningen, Drenthe), 2) the Veluwe, 3) the Utrechtse Heuvelrug, 4) a region with Holocene river influence which is positioned along the river Rhine, and 5) the eastern part of Noord Brabant (see Fig. 6.1). This pattern is in part reflected in the soil solution by a differentiation in base cation and DOC concentrations, which subsequently determines the relative occupation of the CEC (Mol et al., subm.). In this section we will further discuss the soil solution chemistry in view of this regionality.

The general characterization of the soil solution and the CaCl_2 extracts in the five regions is presented in table 6.5. Some notable patterns are addressed in this section. The pH of the various regions does not differ significantly, owing to the logarithmic scale and the already very low pH values of around 3.5. The pattern in DOC concentrations in displaced soil solution does not reflect the regional pattern of OM in the solid phase (Mol et al., subm.). DOC concentrations are remarkably high in the Utrechtse Heuvelrug, which just has average OM content, and they are about average in the northern provinces, where OM content is highest. Apparently, the specific composition of the OM and the overall chemical composition of the soil solution rather than simply the amount of OM determine how much DOC is formed. The patterns displayed by the base cations and also Cr and Ni reflect the relatively high reactivity of the solid phase in the northern provinces (Mol et al., subm.), as well as the influence of sea spray in this region (see also the Cl concentration). The low reactivity of the solid phase in the Veluwe is also evident in the base cations, which have the lowest concentrations in displaced soil solution. The regional variation of Al in combination with that of the base cations results in highly variable Al/Ca ratios, which thus probably reflects more than just differences in acidification status.

Patterns in the heavy metal concentrations follow that of Al and primarily show the separate position of Noord Brabant. Both in the displaced soil solution and in the CaCl_2 extract the concentrations of Cd, Cr, Cu, Ni, and Zn are relatively high, a notable

phenomenon considering the mineralogical poorness of Noord Brabant in comparison to the other 4 regions (Mol et al., *subm.*). For Cd and Zn this regionality can be explained by the history of industrial zinc smelting in Noord Brabant and just across the border in Belgium. Copper is probably related to the abundant presence of intensive livestock farming in this region, as Cu is used to increase food conversion in fattening pigs. Lead is the only heavy metal not notably higher in Noord Brabant; especially in the CaCl₂ extract Pb patterns reflect the traffic intensity in the different regions. Also the accumulation in the topsoil is clearest in the CaCl₂ extract.

Despite the regionality in many of the parameters involved in speciation, including the master variable DOC, the chemical speciation of Cu, Cd, and Al hardly differs among regions. This is probably due to the large range of most parameters together with the largely independent variability of their concentrations. Speciation regionality is restricted to Noord Brabant with respect to Al and Cd. Here the high total concentrations of Al and Cd in solution result in systematically high percentages of these metals to be present in the free ionic form.

6.3.4 Short term temporal variability

Fluctuations in time are known to exist for almost all parameters in the soil solution (Magid and Nielsen, 1992; Henrich and Haselwandter, 1997; Yin and Foster, 1993; Castelle and Galloway, 1990; Grieve, 1990; Yin and Foster, 1993; Wesselink et al., 1994). The results reported in the literature indicate that systematic patterns are very hard to identify, both concentration levels and fluctuation patterns differ from year to year. In the seasonal campaign of this study an attempt was made to provide insight into the consequences of these fluctuations for the practice of soil acidification monitoring. An overview of the weather conditions previous to and during the sampling campaign is presented in figure 6.7. Figure 6.8 shows the average yield of soil solution displaced by centrifugation. Figures 6.9 and 6.10 give the average patterns of some important elements in both the displaced soil solution and the CaCl₂ extract, and figure 6.11 specifies the fluctuation patterns of two Al species in comparison to the fluctuations of total concentrations. Tables 6.6 and 6.7 present a summary of the extent to which the most important parameters fluctuate per location for both top and subsoil. Tables 6.8 and 6.9 show the results of an analysis of variance, a statistically more rigorous way to compare the amount of variation caused by temporal and spatial effects for both displaced soil solution and CaCl₂ extracts.

The year 1998 turned out to be the wettest and one of the warmest years of the 20th century, whereas 1999 was the hottest year since the start of weather monitoring in 1706. Especially July 1999 was very hot and also extremely dry. This caused the majority of sample locations not to yield displaced soil solution in August and September/October 1999 (Fig. 6.8). Year-to-year as well as seasonal and short-term weather induced fluctuations are reflected in the concentration variability in displaced soil solution over time (Fig. 6.9). In both top and subsoil solutions, Si and Al show steadily decreasing concentrations in 1998 in response to the high precipitation and resulting dilution, and steadily increasing concentrations in 1999 in reaction to the drier conditions. All anions, including Cl, show a

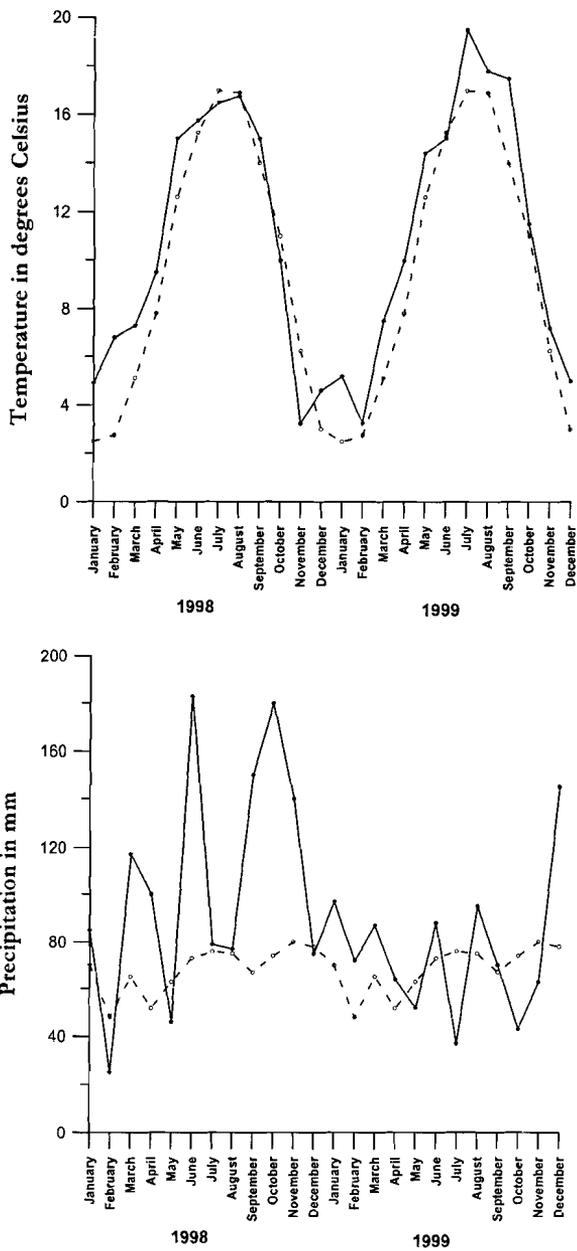


Figure 6.7

Mean monthly temperature and precipitation for the years 1998 and 1999. The solid lines indicate the temperature and precipitation in these years, the dotted lines are the long term averages. (Source: the Dutch weather and seismology institute, KNMI)

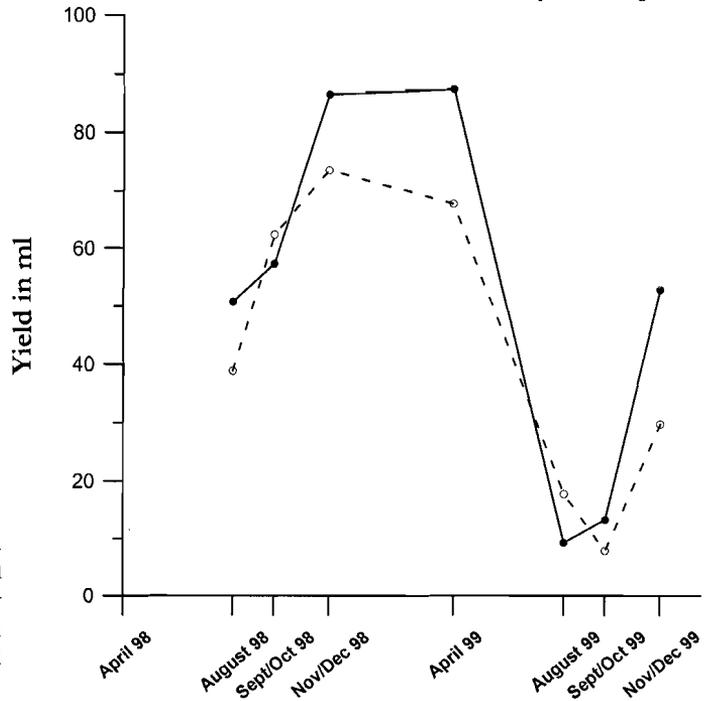


Figure 6.8

Temporal fluctuation in yield (ml) of soil solution displaced by centrifugation for both topsoil (solid line) and subsoil (dashed line).

similar trend. Effects are more pronounced in the topsoil than in the subsoil, resulting in the “crossover” of the curves for Si and Al in Fig. 6.9. At first sight the pH pattern seems inconsistent with the pattern for Si, Al, and the anions. The wet year 1998 shows an increase in the proton concentration instead of dilution. This is interpreted as resulting from a more or less constant pH of the incoming rain water in combination with a less effective acid buffering due to the higher percolation rate. This in turn may explain in part the decrease in concentrations of Al and Si. The pH difference between top and subsoil is remarkably constant. August 1999 forms an exception, the low pH in the topsoil in this month probably reflects a short term evaporation effect, which is also discernable in the Al and Si patterns. The base cations (illustrated by Mg and Ca) exhibit typically seasonal patterns, related to temperature and growing season. They have increasing concentrations in spring and decreasing concentrations in autumn in the topsoil, with peak values in summer and low values in winter. Also the evaporation peak in August 1999 is clearly visible. Whereas the year-to-year patterns are expressed in both top and subsoil solution, the seasonal and short term weather induced patterns are mainly represented in the topsoil concentration fluctuations.

Comparison of figures 6.9 and 6.10 demonstrates that CaCl_2 extractions are much less variable, in time as well as among the locations, than displaced soil solution for important elements like the base cations (illustrated by Mg), Al and the pH. Simply for this reason the CaCl_2 extract would be the more preferable medium for monitoring. The much more straightforward relations between pH and the other parameters, a lower pH is accompanied by higher Al and base cation concentrations, are also evidence of the more stable and robust nature of a weak extraction as compared to displaced soil solution

Table 6.6

The fluctuation index defined as (maximum - minimum)/median for some relevant parameters in the displaced soil solution and the CaCl₂ extracts of the topsoil for each location.

	Locations																			median	
	90	91	92	93	94	95	96	121	122	124	125	128	129	130	134	135	136	137	138		139
Yield	1.50	2.00	1.58	1.45	1.33	3.17	2.40	1.71	1.58	1.71	1.04	4.22	3.80	1.60	2.11	0.90	2.22	1.74	1.88	1.54	1.71
pH	0.33	0.21	0.15	0.67	0.22	0.09	0.15	0.16	0.13	0.33	0.31	0.12	0.23	0.16	0.18	0.24	0.30	0.12	0.12	0.17	0.17
DOC	0.78	0.76	1.66	2.10	0.59	0.09	0.98	0.37	0.42	1.06	1.21	1.49	1.16	1.29	0.42	1.27	0.08	0.52	0.98	0.51	0.88
Al	1.46	1.14	0.91	1.01	1.24	1.09	0.75	1.98	0.91	1.60	0.53	0.94	0.93	0.44	0.90	1.37	0.79	0.51	1.13	2.17	0.97
Ca	1.36	3.93	3.90	2.64	1.82	1.14	2.89	0.85	4.50	0.93	4.96	1.69	1.95	6.29	1.71	1.88	2.95	1.19	2.44	3.51	2.19
K	0.51	1.02	3.98	0.55	0.99	1.18	1.22	0.86	0.70	0.76	2.74	0.92	0.68	1.13	0.47	0.94	1.02	0.34	1.65	2.51	0.96
Mg	0.71	1.95	1.96	0.85	1.83	1.25	1.15	1.44	1.73	1.39	1.57	1.10	0.41	2.20	0.94	1.46	1.10	1.25	1.15	3.10	1.32
Na	1.39	2.45	0.56	0.93	0.98	0.73	1.93	1.50	1.73	1.38	1.30	1.01	0.60	2.30	1.06	1.25	1.01	1.03	0.76	0.74	1.05
Si	0.90	2.26	1.47	0.93	0.93	0.65	1.35	1.17	1.60	1.04	0.97	1.03	2.02	1.11	0.47	0.71	1.57	0.72	1.61	1.07	1.06
Cl	0.78	0.74	0.58	0.51	0.22	0.72	1.10	0.51	0.55	0.42	0.58	1.28	0.76	0.65	0.70	0.74	1.34	0.13	1.63	0.41	0.67
NO ₃	1.67	1.20	0.35	0.70	0.26	1.05	1.54	0.21	1.25	0.63	3.60	0.87	0.60	0.71	1.16	1.05	2.48	0.57	0.66	1.07	0.96
NH ₄	2.27	3.06	2.74	1.49	3.17	0.46	2.15	2.52	2.01	1.34	6.08	1.33	1.50	0.83	1.74	1.65	0.59	1.75	1.04	1.21	1.70
SO ₄	0.62	0.58	0.98	0.47	0.22	0.47	0.73	0.90	0.60	1.04	0.66	0.90	0.77	0.98	0.52	0.92	2.17	0.42	1.04	0.46	0.69
S_tot	0.77	0.44	0.75	0.99	0.36	1.32	0.80	0.80	0.58	1.22	1.21	0.95	0.57	1.37	0.47	0.98	0.39	0.71	1.11	0.75	0.78
pH(CaCl ₂)	0.19	0.38	0.15	0.12	0.15	0.08	0.06	0.05	0.15	0.16	0.16	0.08	0.11	0.09	0.10	0.06	0.09	0.07	0.07	0.08	0.10
Al(CaCl ₂)	0.40	1.47	0.25	0.39	0.26	0.73	0.30	0.37	0.29	0.29	0.26	1.18	0.32	0.67	0.43	0.29	0.42	0.48	1.04	0.62	0.39
K(CaCl ₂)	0.72	1.22	0.49	1.04	0.58	0.37	0.45	0.49	0.93	0.61	0.77	0.44	0.25	0.38	0.25	0.88	0.38	0.42	2.00	0.73	0.54
Mg(CaCl ₂)	1.16	0.95	0.73	1.28	1.41	1.12	1.18	0.90	0.97	1.11	1.53	1.08	1.63	0.88	1.16	0.72	1.04	0.88	1.02	1.06	1.07
Na(CaCl ₂)	1.86	1.58	1.19	2.41	1.18	1.20	1.00	1.39	1.48	1.05	1.04	1.04	1.27	2.62	2.19	1.51	5.90	1.13	1.33	2.37	1.36
NO ₃ (CaCl ₂)	2.47	0.59	1.41	3.64	1.88	1.43	3.11	1.21	0.93	1.34	0.95	0.88	1.21	1.70	0.96	2.48	2.83	0.76	3.88	6.73	1.42
NH ₄ (CaCl ₂)	2.71	3.81	0.61	2.04	0.75	0.94	3.09	0.48	0.94	0.64	0.72	1.11	0.80	0.58	1.25	2.67	0.50	1.39	0.79	0.78	0.87
median	0.90	1.20	0.91	0.99	0.93	0.94	1.15	0.86	0.93	1.04	1.04	1.03	0.77	0.98	0.90	0.98	1.02	0.71	1.11	1.06	

Table 6.7

The fluctuation index defined as (maximum - minimum)/median for some relevant parameters in the displaced soil solution and the CaCl₂ extracts of the subsoil for each location.

	Locations																			median	
	90	91	92	93	94	95	96	121	122	124	125	128	129	130	134	135	136	137	138		139
Yield	2.67	2.73	2.62	2.71	4.00	2.40	1.13	1.88	2.27	1.48	2.38	2.86	1.41	1.65	3.20	0.61	1.89	2.00	1.62	2.29	2.28
pH	0.26	0.26	0.18	0.28	0.21	0.12	0.17	0.13	0.17	0.25	0.24	0.07	0.25	0.24	0.14	0.16	0.24	0.15	0.15	0.22	0.19
DOC	0.50	0.69	1.25	1.02	1.30	1.44	1.37	0.78	2.53	1.91	1.37	1.11	1.43	1.51	0.62	0.63	0.48	0.56	0.66	6.42	1.18
Al	1.76	1.07	2.00	0.67	0.40	1.84	2.71	0.82	1.17	2.11	0.50	0.53	0.79	2.17	0.71	2.43	0.75	2.16	0.79	0.75	0.94
Ca	1.35	0.73	2.23	1.04	0.44	0.61	1.12	0.41	7.25	1.01	1.83	2.17	1.55	1.53	2.52	2.23	4.49	0.96	1.42	2.73	1.48
K	1.54	1.03	0.65	0.59	2.97	0.32	0.68	0.34	0.72	1.50	0.72	1.44	1.01	0.98	1.41	1.05	0.66	0.71	0.84	3.06	0.91
Mg	1.84	0.72	1.78	0.85	0.50	0.60	2.46	0.23	2.75	1.23	1.40	0.62	0.80	0.67	0.80	0.65	1.51	0.45	0.92	2.57	0.83
Na	1.96	0.87	1.24	1.29	0.61	1.88	1.18	1.02	1.74	2.34	1.10	0.55	0.67	0.62	1.29	3.68	0.80	1.43	0.68	0.69	1.14
Si	0.69	0.82	0.91	0.99	0.42	0.62	1.30	0.78	1.11	0.82	0.74	1.04	1.44	0.60	0.78	0.55	0.62	0.74	0.65	0.78	0.78
Cl	0.80	0.24	0.69	0.30	0.28	0.56	0.46	0.55	0.40	1.51	0.63	0.61	0.69	0.52	0.80	1.77	0.60	0.60	0.94	0.32	0.60
NO ₃	0.90	0.74	0.94	1.13	0.60	0.90	0.93	0.56	0.92	0.99	1.17	0.94	0.42	1.15	0.84	2.03	3.11	0.71	1.31	0.53	0.92
NH ₄	1.02	0.80	1.02	3.48	1.22	0.67	0.64	0.26	2.98	0.77	7.63	0.61	2.05	2.47	0.76	1.58	1.00	0.91	1.26	1.14	1.02
SO ₄	0.92	0.90	1.07	0.59	0.22	0.43	1.02	0.83	0.77	0.78	1.83	0.59	0.71	0.89	0.97	2.59	1.14	0.79	1.48	0.78	0.86
S _{tot}	1.40	0.42	0.90	0.93	0.58	1.45	4.00	0.81	0.63	1.18	1.07	0.50	0.72	0.99	0.36	4.82	1.19	1.59	1.66	1.21	1.03
pH(CaCl ₂)	0.06	0.08	0.08	0.04	0.04	0.09	0.06	0.04	0.08	0.04	0.07	0.14	0.04	0.12	0.17	0.02	0.10	0.12	0.05	0.04	0.06
Al(CaCl ₂)	0.59	0.79	0.91	0.36	0.56	1.37	0.64	0.55	1.27	0.46	0.56	0.92	0.52	1.52	2.00	0.41	1.31	0.71	1.13	0.51	0.68
K(CaCl ₂)	*	*	*	*	*	1.00	*	*	*	*	*	*	*	1.00	*	*	*	*	1.00	*	1.00
Mg(CaCl ₂)	1.65	1.47	1.66	1.18	1.92	2.64	1.64	2.78	2.08	2.07	1.31	1.49	2.63	1.43	2.92	2.06	2.17	2.20	2.71	2.17	2.07
Na(CaCl ₂)	*	*	1.21	2.35	1.34	1.13	1.00	1.26	*	1.09	1.00	1.36	*	1.73	1.67	1.00	1.00	1.41	1.08	*	1.21
NO ₃ (CaCl ₂)	1.38	0.72	1.95	0.84	2.83	1.92	1.28	1.74	0.88	0.97	1.35	2.47	1.00	1.97	1.96	0.95	0.78	0.74	0.93	0.49	1.14
NH ₄ (CaCl ₂)	2.12	7.22	1.41	1.28	1.50	1.20	3.11	2.64	1.20	1.02	1.05	2.42	1.15	1.38	1.05	2.77	1.26	1.33	1.51	0.70	1.35
median	1.35	0.79	1.14	0.96	0.59	1.00	1.12	0.78	1.17	1.05	1.08	0.93	0.80	1.15	0.91	1.32	1.00	0.77	1.00	0.78	

The soil solution of acid sandy soils

Chapter 6

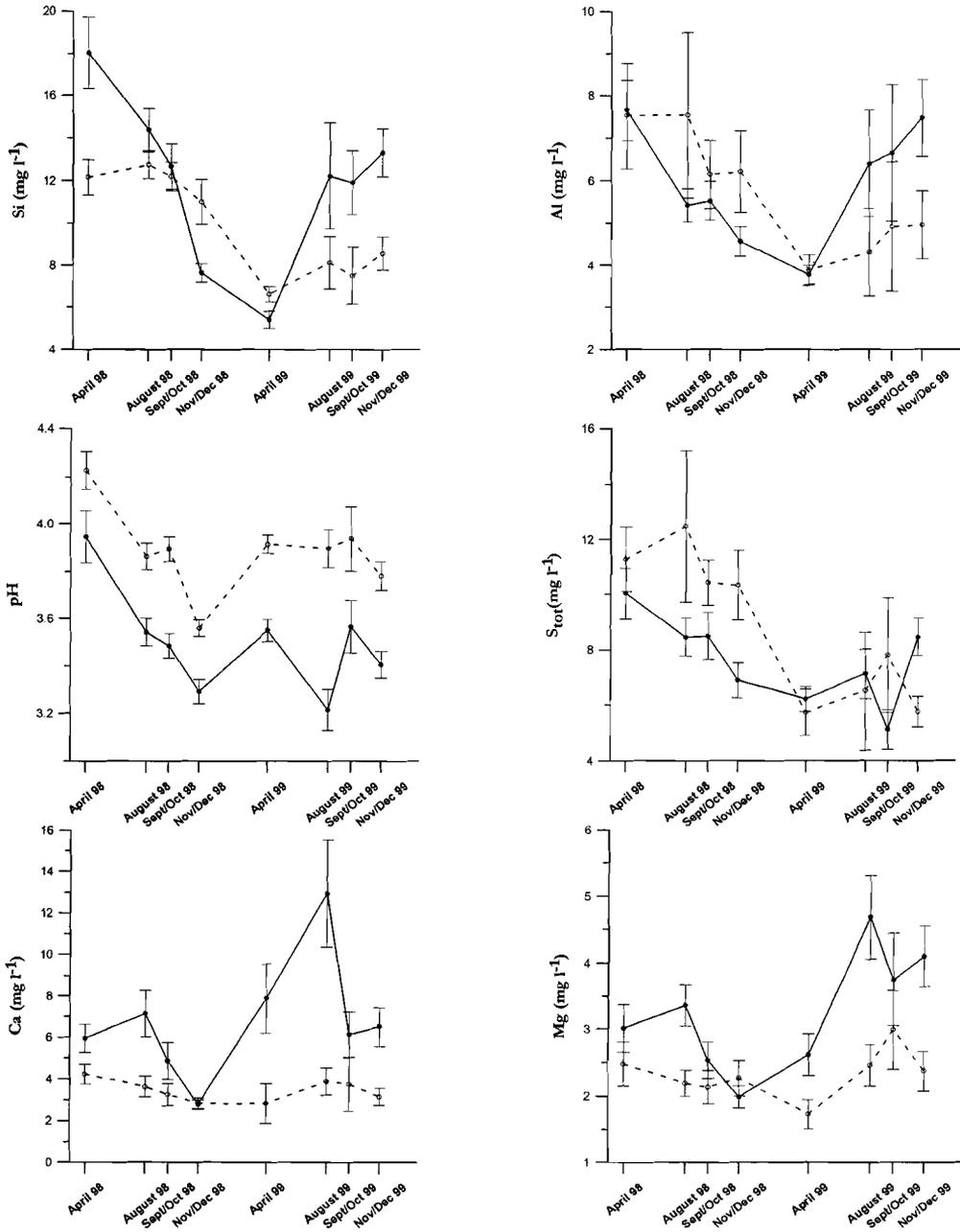


Figure 6.9

The temporal patterns of some parameters in the displaced soil solution for both topsoil (solid line) and subsoil (dashed line). Deviation bars indicate the standard error of the mean.

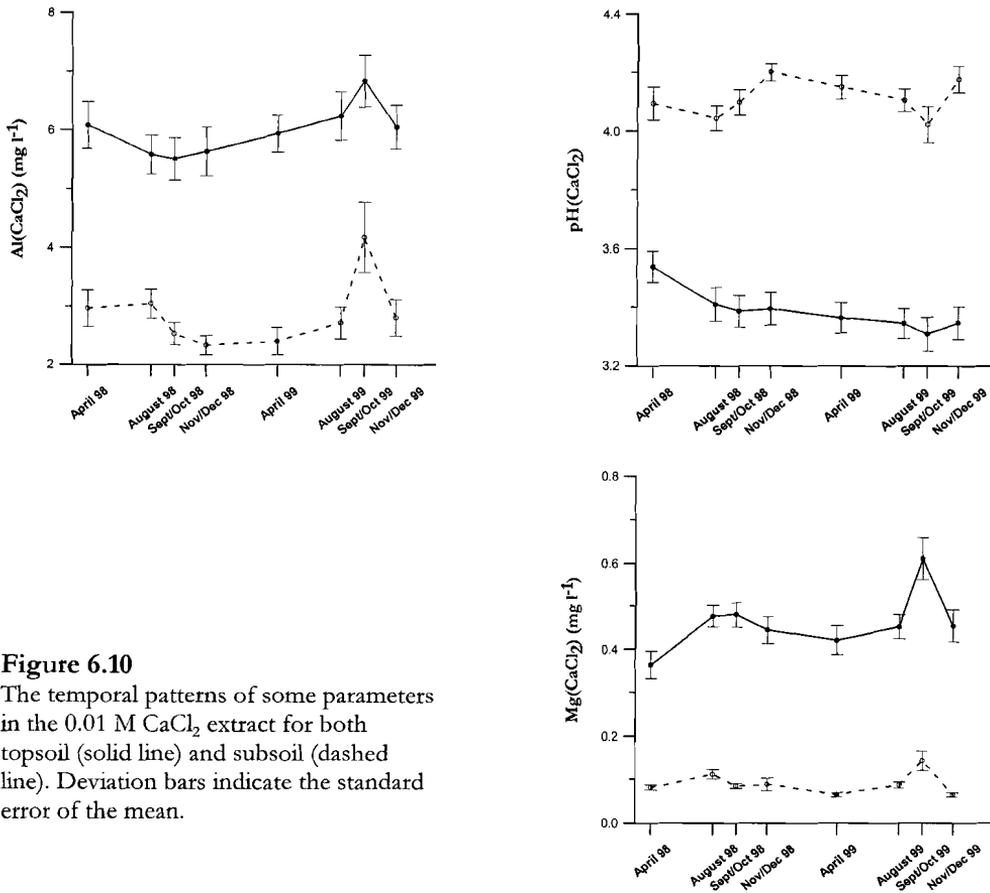


Figure 6.10
 The temporal patterns of some parameters in the 0.01 M CaCl₂ extract for both topsoil (solid line) and subsoil (dashed line). Deviation bars indicate the standard error of the mean.

The patterns in figures 6.9 and 6.10 are based on the median values of 20 locations per sampling round. The deviation bars already indicate that individual locations may depart from the average pattern. To straightforwardly compare locations, sampling depth, parameters, and methods, the relative amplitude of the individual fluctuations was calculated (Tables 6.6 and 6.7). From these tables a few phenomena are evident. The various locations indeed show large differences in temporal variability, sometimes with fluctuations of similar magnitude in both top and subsoil (e.g. location 121 is low and location 96 is high in top and subsoil), and sometimes with large differences between both depths (e.g. location 139 is high in topsoil and low in subsoil, and location 90 is low in topsoil and high in subsoil). The temporal variability in the topsoil is slightly to clearly higher than in the subsoil for most parameters; notable exceptions are DOC, Na, SO₄, and S_{tot} in displaced soil solution, and Al, Mg, and NH₄ in the CaCl₂ extract. Differences in temporal variability between the various parameters are also evident, some show small to very small temporal fluctuations (pH, pH(CaCl₂) and Cl) and some show large fluctuations (Ca and NH₄). Finally a comparison of the two methods leads

to the conclusion that, especially for the more variable topsoil, the CaCl_2 is successful in damping the short term temporal variability to some extent.

The results of the analysis of variance (Tables 6.8 and 6.9) confirm that the weak extraction with CaCl_2 results in much smaller random and systematic temporal variability as compared to displaced soil solution. They also confirm that this variability is higher in the topsoil than in the subsoil. Calcium, pH, and Al in the topsoil, parameters of prime interest in monitoring, are among the parameters that have the highest percentages of error and sampling round variance in displaced soil solution. The error variance in tables 6.8 and 6.9 also includes possible systematic interaction effects between sampling round and sampling location, i.e. the systematic but not 'average' reaction of a location to temporal factors. The laborious nature of the sampling procedure involving displacement of soil solution, however, precluded the incorporation of duplicate sampling, which would have allowed quantification of this interaction effect vis-à-vis the true error. The relatively high temporal variances for K in the CaCl_2 extract must be ascribed to the high analytical variance in the concentration range near the detection limit.

Table 6.8

Analysis of variance results for some parameters in the displaced soil solution quantifying the amount of variance (in %) explained by sampling round (short term temporal variation) and by sampling location (spatial variation). The * symbol indicates a non-significant result.

	Sampling round	Sampling location	Error	Number of rounds	Number of locations
Topsoil					
pH	33.7	35.1	31.2	8	20
DOC	4.1*	44.8	51.0	7	20
Al	21.5	43.1	35.4	8	20
Ca	19.1	24.4	56.5	8	20
K	4.4*	39.2	56.4	8	20
Na	13.0	24.4	62.8	8	20
Mg	20.0	33.3	46.7	8	20
Si	44.1	30.2	25.6	8	20
SO_4	19.9	42.2	37.3	5	20
NO_3	11.2	51.8	37.1	5	20
Cl	30.8	30.4	38.7	5	20
Subsoil					
pH	43.8	31.7	24.6	6	20
DOC	13.0	31.3	55.7	6	20
Al	4.6*	59.0	36.4	6	20
Ca	4.5*	25.9	69.6	6	20
K	7.8	41.3	50.9	6	20
Na	16.2	30.0	53.8	6	20
Mg	2.8*	49.0	48.2	6	20
Si	25.8	46.1	28.1	6	20
SO_4	21.1	44.8	34.2	5	20
NO_3	7.1	67.3	25.6	5	20
Cl	16.6	47.0	36.4	5	20

Table 6.9

Analysis of variance results for some parameters in the 0.01 M CaCl₂ extract quantifying the amount of variance (in %) explained by sampling round (short term temporal variation) and by sampling location (spatial variation).

	Sampling round	Sampling location	Error	Number of rounds	Number of locations
Topsoil					
pH	7.1	75.4	17.4	8	20
Al	3.8	69.7	25.7	8	20
K	22.5	24.5	53.0	8	20
Mg	16.9	31.9	51.2	8	20
NO ₃	13.5	23.2	63.3	8	20
Subsoil					
pH	6.4	73.1	20.5	8	20
Al	11.8	59.4	28.8	8	20
K	-	-	-	-	-
Mg	19.9	25.4	54.7	8	20
NO ₃	10.7	35.2	54.1	8	20

The usefulness of calculating the chemical speciation of the soil solution in view of the short term temporal variability has been assessed as well. It was hypothesized that fluctuations in the parameters controlling speciation might have counteracting effects and result in more constant patterns for the free cations. ECOSAT calculations of the speciation Al, however, disproved this hypothesis. Free Al³⁺ and DOC bound Al, the two most important Al species, follow the respective patterns of total Al and DOC in solution (see Fig. 6.11).

6.4 Conclusions

The major conclusions per subject are summarized in a staccato way.

- Concentrations in displaced soil solution, especially pH and Al, indicate that the Pleistocene sandy soils in the Netherlands are in an advanced state of acidification.
- Aluminum, Fe, Cd, Pb, and Zn show a higher affinity to the CEC than the base cations.
- The exchangeable amount of acidity in these acid sandy soils is not sufficiently large to produce the generally observed decrease in pH in the CaCl₂ extract, in part caused by the large volume of extractant and in part as a result of the already very low pH of between 3.0 and 4.0.
- The anion deficit in the displaced soil solution is balanced by DOC.
- Comparison of the heavy metal concentrations in displaced soil solution with those in the groundwater confirms their immobility.
- DOC concentration, pH and total cation concentration are the master variables controlling the chemical speciation of the soil solution in acid sandy soils. For elements like Al, speciation behaviour under acid circumstances is especially intricate because of the

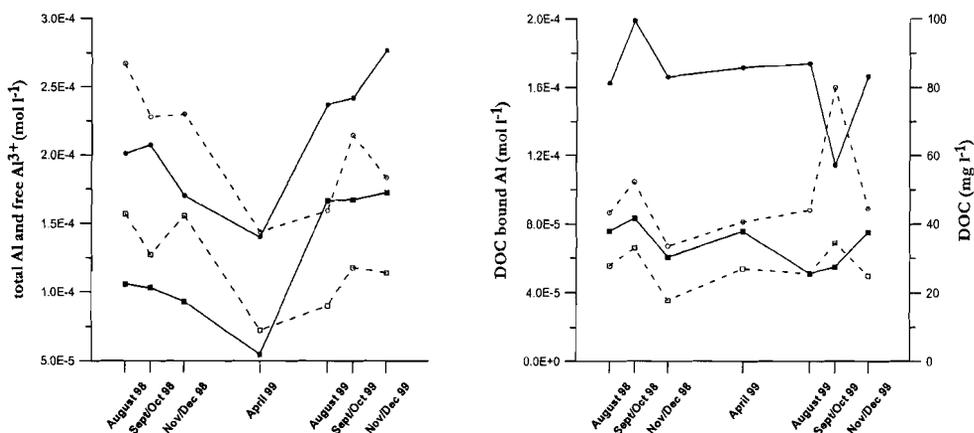


Figure 6.11

The temporal patterns of total Al and DOC concentrations (circles) compared to those of free Al³⁺ and DOC bound Al (squares) as calculated with ECOSAT for both topsoil (solid line) and subsoil (dashed line).

combined pH effects on both the complexation by DOC and the solubility of the mineral phases.

- Speciation behaviour affects the affinity for the CEC, the highly complexed element Cu has a low affinity whereas the much less complexed element Cd has a high affinity.
- Regional patterns in the solid phase are in part reflected in the soil solution. Especially the reactivity of the solid phase can be identified in the regional patterns of the soil solution. Formation of DOC is not simply linked to the OM content of the solid phase.
- Noord Brabant is the region most clearly set apart with high concentrations of both Al and heavy metals in both displaced soil solution and CaCl₂ extract despite the mineralogical poorness of the solid phase. This is primarily due to the presence of intensive livestock farming and a history of industrial zinc smelting.
- Pb patterns in the soil solution largely reflect traffic intensity.
- Speciation regionality also sets Noord Brabant apart with a higher amount of free Al³⁺ and free Cd²⁺ as a result of the high total concentrations of Al and Cd. The remaining regions show such a large and independent variation of the speciation master variables that no further regionality in speciation is present.
- Specific short term temporal fluctuations for some important parameters in displaced soil solution could be related to the seasonal and monthly temperature and precipitation data.
- General patterns emerging from the temporal study are that: 1) the topsoil is more variable than the subsoil, especially with respect to typical seasonal fluctuations; 2) large differences in temporal fluctuation behaviour exists between locations; and 3) a weak extraction with

CaCl₂ partly eliminates the short term temporal variability present in the displaced soil solution.

- The hypothesis that free cation concentrations would be more constant in time as a result of the counteracting effect of the different speciation master variables was disproved.

7 SYNTHESIS

The general aim of this thesis is to contribute to the scientific foundation of environmental quality management. Stressing the importance of a solid scientific foundation to support environmental policy is far from obsolete considering the most recent government report on acidification (Min. VROM, 2001). Two problematic aspects in the relation between policy and science that are again evident from this report are the strong inward tendency evidenced by a disproportionate focus on research instigated by governmental bodies and a limited attention for the developments in a broader scientific context, and the style of policy memoranda and reports that stands out in general, imprecise, and fuzzy wording resulting in easily misinterpreted statements. Furthermore, the strong orientation towards modelling far into the future, which often leads to oversimplification especially when questionable criteria such as the Al/BC ratio are used, is equivocal. In addition, the obfuscative effect of the constantly changing delineation of the environmental themes (acidification in this report includes air pollution related phenomena such as ozone, fine dust particles, and even heavy metals and persistent organic pollutants), leads to an environmental policy that lacks connection to the processes in nature.

The specific focus of this thesis is to contribute to the scientific foundation of soil acidification monitoring, which forms part of the multitude of environmental policy supporting systems. As described in chapter 1, the research project was therefore arranged in such a way that the results would both satisfy the needs and questions of those involved in soil acidification monitoring as well as the often more rigorous criteria deemed necessary from a scientific perspective. The connection with the practical field was secured through regular contacts with employees managing the monitoring networks, and by keeping the sampling procedure closely related to that used in practice while staying within the boundaries necessary from a scientific perspective. To procure the aim of this thesis, in section 7.1 the possibilities for soil acidification monitoring are discussed in view of the knowledge gained through this study. Suggestions of a purely scientific nature or specifically addressing the scientific community are made in section 7.2.

7.1 Implications for the practice of soil acidification monitoring

Before a successful monitoring strategy can be developed two conditions must be met. First, a thorough understanding of the processes involved in soil acidification is needed. On the one hand, this asks for pilot studies in which a wide range of parameters is determined to unravel and quantify acidification processes in general as well as the idiosyncrasies of the soils to be monitored. On the other hand it is absolutely necessary to be abreast with the multifarious acidity literature to correctly interpret the results of such pilot studies. Second, the exact monitoring goal has to be clarified. Laying down the monitoring objective comes second because it has to be done within the limitations inherent in the soil compartment. Considering this thesis as a pilot study on which to base a monitoring strategy, some ideas on how to monitor soil acidification will be sketched.

Ongoing soil acidification really is a capacity phenomenon; incoming acidity is being buffered by the dissolution of minerals in the soil, a process that consumes protons and releases cations such as Ca, Mg, K, Na, Al, and Fe. As a result the total acid neutralizing capacity of the solid phase ($ANC_{(s)}$) decreases, which is the generally accepted definition of soil acidification. The results from this study confirm that the Pleistocene sandy soils are in a stage of soil acidification that is generally considered advanced. This judgement is primarily based on intensity parameters such as pH and Al and BC concentrations in the soil solution, which are essentially reflecting the alumino-silicate buffering stage of these soils. Changes in the $ANC_{(s)}$ are likely to be reflected in the soil solution only when the buffering characteristic of the solid phase changes abruptly (e.g. no carbonates left, which necessitates buffering by silicates) or when the proton load drastically increases or decreases. The buffering characteristic of the soils under consideration is unlikely to change abruptly in the near future because a large pool of alumino-silicates is still present (see chapter 4). Changes in the proton load, for instance as a result of successful environmental measures, are the most likely cause for changes in the composition of the soil solution. Release of Al, however, is expected to remain the major source of buffering of incoming protons because it also provided the largest part of acid buffering under natural conditions (see chapter 4). Compositional fluctuations in the soil solution resulting from other causes than ongoing soil acidification are numerous and include chemical speciation, geochemical regionality, and short term temporal variability (chapter 6). They reduce the likeliness of detecting subtle changes in soil solution composition as a result of a changing proton load.

To really assess the development of the soil acidity status, which in my opinion is a capacity phenomenon related to the reactivity of the solid phase, older studies that analyzed a comparable parameter set are needed. The studies from the past that can be found in the literature (both scientific and the so-called grey reports) do not fit this purpose because they lack either a sufficiently large parameter set, or a sufficiently large number of sampling sites. At present, it is therefore hard to determine how the buffer capacity is exactly affected by the incoming proton load and subsequently also what an effective monitoring strategy would look like. To design such a monitoring strategy it is essential to determine the extent and rate of the capacity changes (total change in $ANC_{(s)}$) and the nature of these changes (in what reactive pool do they occur) in a regional perspective. In addition, the effect of an altered (relative and absolute) abundance of the various pools should be assessed (for instance, does the depletion of a reactive pool lead to large changes in the soil solution composition, or is the dissolution kinetics of feldspar large enough to keep the balance). Only when these phenomena are known in a quantitative way, development of a monitoring system with a limited parameter set to support environmental policy can be successful. Until that time the monitoring effort bears a scientific mark with a goal that is more aimed at understanding and quantifying the systematics and rates of soil acidification in a regional setting than at supporting and checking environmental policy. Soil acidification monitoring in this light amounts to keeping track of the changes in the $ANC_{(s)}$ in combination with specifying the developments of the different pools, including the soil solution and the CEC. The following approach can provide the necessary insight.

The most straightforward way to obtain the total $ANC_{(s)}$ is by analyzing total element concentrations of the solid phase. X-ray fluorescence spectrometry is an obvious choice because it is an easy and cheap analysis technique that provides multi-element data of this kind. However, the time scale at which this solid phase ANC changes measurably is larger than generally

considered acceptable or useful in a governmental monitoring setting. In the first, more scientific stage of monitoring therefore, total element analysis of the solid phase is deemed useful for two purposes: first, to define the total soil matrix and to appreciate the relative importance of the various reactive phases, and second, to use the results in a version of the historic approach implying re-analysis of the solid phase on a relevant time scale using the previous analysis as a reference. To assess developments in the composition of the total $\text{ANC}_{(s)}$, identification of the nature of the reactive phases is needed. For this purpose several types of extractions can be chosen, the 0.43 M HNO_3 used in this study gives an indication of the easily dissolvable phases. More specific information on the division of this pool over inorganic and organic forms is acquired by using extractants like oxalate (to extract amorphous Al and Fe) and pyrophosphate (to extract organically bound Al and Fe). A combination of these methods provides the necessary insight into the progressive acidification of the soil. The total element analysis of the solid phase is beneficent every 10 to 20 years, whereas for the monitoring of the reactive phases an interval of 5 years is more appropriate.

The time intervals for these measurements are inspired by the rather slow trends of the solid phase. The soil solution and the CEC, however, display much faster but generally reversible changes of composition, for instance as a result of seasonal or weather influences. These compositional fluctuations are sometimes of such magnitude that they not only affect media such as displaced soil solution and a weak extract like 0.01 M CaCl_2 , but also more robust media like the 0.43 M HNO_3 extract. To correctly interpret the 5 yearly analysis of reactive phases in the light of for instance extreme weather conditions, a selection of monitoring sites must at least be used for yearly, but preferably bi-monthly analysis of the soil solution. By characterizing the typical conditions in the fast reacting soil solution/CEC phase every year, deviating results in the analysis of the reactive phases can be explained. For this purpose I favour a weak extraction for several reasons. First, this medium only reacts to fluctuations of relatively large magnitude, which is what is of prime interest in this case. Second, this method of analysis keeps open the possibility to re-analyze samples either to check suspect or outlying data, or to use old samples in a subsequent monitoring round to preclude that a shift in analytical results remains unnoticed. Third, a weak extraction, although sensitive to the precise operational details, is much less prone to circumstances beyond control than is displaced soil solution. Common situations include discrepancies between the sampling rate and the rate at which soil solution can be displaced (which interferes with the need to displace soil solution within as short a time as possible), and samples being analyzed in another laboratory than the one in which displacement took place (which leads to longer time intervals between displacement and analysis of critical parameters). The lower sensitivity of a weak extraction to such situations satisfies the need for robustness of methodology that is quintessential in a monitoring setting because without the elimination of as much unwanted variation as possible every (soil) monitoring effort becomes futile.

Other demands that need to be satisfied to ensure interpretable monitoring data concern the choice of parameters and the analytical quality of the data. This study again confirms that understanding the intricacies of complex phenomena like soil acidification is impossible on the basis of a limited dataset. Two examples are the possible concealment of the significant contribution of S accumulation to acid buffering, and the erroneous interpretation of Al/BC ratios if DOC is not taken into account (see chapter 4). In my opinion the following parameters constitute the minimum for monitoring soil acidification: in the solid phase (once every 10 - 20

years) SiO_2 , Al_2O_3 , K_2O , Na_2O , CaO , MgO , Fe_2O_3 , MnO , P_2O_5 , and S; in the reactive extractions focus should be on Al, K, Na, Ca, Mg, Fe, Mn, P and S; and to trace the year to year fluctuations in a weak extraction at least pH, DOC, NO_3^- , NH_4^+ , SO_4^{2-} , Na, K, Al, Mg, Fe and Mn should be determined. An important realization in this respect is that modern analytical techniques often provide multi-element results, which makes the need for carefully selecting a small parameter set for financial reasons less pressing.

Paramount in obtaining good results for the parameters chosen is attention for important details in the measurement protocol. In the present study this included the displacement of the soil solution within 24 hours after sampling in combination with storage at 4°C in the dark to minimize chemical changes, the fast execution of the main sampling campaign to minimize short term temporal variation, and the careful preparation of composite samples of the displaced soil solution (done after displacement) and the solid phase (see appendix A for more details). Finally and although it may sound superfluous, a close watch is required of the quality and constancy of the analytical equipment used. Especially the constancy is quintessential in a monitoring setting, intra-laboratory and inter-annual variation (within the same laboratory) may easily overshadow important trends and fluctuations. To obtain a useful monitoring dataset, the protocol should include prescriptions on how to minimize these variations (e.g. re-analysis of samples of previous batches). Long term commitments with the selected laboratories must be made as changes of laboratory must be avoided.

Last but not least, the people interpreting the monitoring data should be aware of sources of variation other than acid deposition that can influence soil acidification data, such as geochemical regionality and short term temporal variability (for which a solution has been described above). This study proved that even within the poor Pleistocene sands geochemical regionality exists that is meaningful to the soil acidity status as well as to other environmental and geoscientific aspects of these sands. These regional patterns do not only exist in the solid phase, they also affect the reactivity of this phase and the composition and chemical speciation of the soil solution. It is noted that this geochemical regionality is of great importance to the interpretation of provincial soil monitoring results because it not only affects interprovincial patterns, it is also of consequence to the results of individual provinces as some patterns divide provinces in two geochemically distinguishable regions. The monitoring network of the province of Utrecht, for example, combines locations belonging to the Utrechtse Heuvelrug and to the Holocene influenced region. With a geochemical regionality that does not follow the provincial division of the country, and that cannot even be derived from the soil classification found on soil maps because these maps use morphometric pedogenic classification criteria that not necessarily reflect chemical variation, it is questionable whether provincial arrangement of the soil quality monitoring networks is appropriate. The interprovincial body involved in the monitoring activities should strive for a united effort in order to obtain a coherent dataset that does not suffer from interprovincial operational differences (e.g. different way and time of sampling, different parameter sets, different laboratories), and that can be interpreted meaningfully. Initially the dataset and the interpretation will be largely related to identifying and quantifying the changes in the soil acidity status in a regional setting, in later stages the dataset can probably be reduced and the interpretation will be limited to regularly checking the status of the pools that have been identified as essential.

7.2 Suggestions for future research

Besides implications for the practice of soil acidification monitoring, the present study also provides fertile ground on the basis of which further scientific research can be suggested. To some extent these suggestions are related to the first, more scientific stage of the monitoring effort. I would like to divide them into two categories. First, the concrete suggestions directly resulting from the data and interpretation in the present study, here the sample archive also advocated in a monitoring setting can serve its purpose again. Second, the more contemplative suggestions relating to the different approaches towards subjects like soil acidification found in the scientific community.

Concrete suggestions based on the present study include an analysis of the nature of the reactive Al pool on a regional scale, a detailed analysis of the typical behaviour of the CaCl_2 extracts in soils that represent extremes in the soil spectrum, and a further analysis of the factors determining chemical speciation in the soil solution of acid sandy soils and the regional variability therein. The nature of the reactive Al pool is generally determined through extractions of the soil material that release a typical part of total Al and Fe such as pyrophosphate which extracts organic bound Al and Fe, or oxalate which extracts amorphous Al and Fe. Establishing the regional variation in the contribution of both reactive forms of Al (and Fe) is interesting for the assessment of the soil acidity status but it also provides additional insight in the factors determining the relative importance of both reactive forms of Al and Fe. The very mild extraction with 0.01 M CaCl_2 , generally used in the (agricultural) assessment of plant available amounts of nutrients, shows substantially different behaviour in acid sandy soils. On the one hand because of the large dilution effect it entails compared to the natural situation of these soils, and on the other hand because of the very low pH. Further assessment of the possibilities and limitations of the 0.01 M CaCl_2 extraction in soils of different composition will be useful. The chemical speciation of the soil solution shows a large amount of variation that can mainly be ascribed to the master variables pH and DOC in combination with the total amount of the components in solution. Speciation studies with advanced models such as the NICCA-Donnan model have been predominantly applied in laboratory studies, partly to validate model parameters and partly to assess the range in which the model accurately describes chemical speciation. Application of speciation modelling in regional exploratory studies such as this one, and assessing the dominant factors that determine chemical speciation regionally will benefit the insight in the most important model parameters as well as in the natural variability of these parameters. A final suggestion concerns the concept of using the subsoil as a proxy for the topsoil with respect to establishing trustworthy estimates of natural background values for environmentally important elements. Two recent studies have explored this concept and the results are promising. Further development of this concept would benefit environmental management by generating more realistic ideas about natural background values in the soil.

Finally, I would like to make two suggestions contemplating the methodology of (acidification) research. First, searching the literature for uninterpreted or raw data is often futile, many authors in the acidification research skip this obvious first step in the presentation of results. This complicates comparison of ones own data with older data, and estimation of concentrations beforehand, for instance to fine-tune analytical equipment. Research would benefit from a dedication to the presentation of the leading, uninterpreted data at the beginning of the *Results*

section. A second beneficial development could result from a closer cooperation between process and mechanism oriented research, and exploratory and regionally focussed research. Both scientific approaches have great value in themselves but are also limited in their scope because they work at quantifying phenomena on a confined scale. The results are often complementary, but not seldom this is only discovered by accident, for instance through chance cooperation between research groups. Deliberately pursuing such cooperation could lead to innovative research in which (acidification and other) processes can be quantified at various scales, thereby generating the most realistic picture of nature achievable with current knowledge.

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APPENDIX A

SAMPLING AND ANALYTICAL PROCEDURES

In this appendix a description is given of the procedures used in the field and in the laboratory. Relevant criteria for the choices made are given. In general, all procedures, techniques, and criteria discussed concern both the main and the seasonal sampling campaigns; exceptions are mentioned explicitly.

Sampling procedure

As mentioned in chapter 1, we decided to sample a selection of 92 locations used for soil acidification monitoring in the Dutch provinces of Groningen, Friesland, Drenthe, Gelderland, Utrecht, and Noord Brabant. These provinces were selected because they have operational soil acidification monitoring networks and because they hold areas of coniferous forest on Pleistocene sands. Chapter 1 also briefly mentions the fact that the sampling procedure for this thesis was to some extent based on the current practice in soil acidification monitoring (primarily the application of soil solution displacement by centrifugation), but for a large part adjusted to the needs of this study. To minimize chemical changes immediately after sampling, the general procedure was to take soil samples one day, keep the samples overnight at 4 °C in the dark and displace the soil solution by centrifugation the next day. A balance had to be struck between the effects of chemical changes in the soil samples immediately after sampling (necessitating displacement of the soil solution as quickly as possible) on the one hand and the short term temporal variability (necessitating a very short sampling period) on the other hand. The practical compromise meant two days fieldwork per week (Monday and Wednesday) and three days in the lab to displace and analyze soil solution and prepare the remainder of the samples for further analysis after the sampling campaign was completed.

Each location, of about 10,000 m², was divided into 6 equal sections in which a randomly located sample was collected at two depths (stratified random) with a so called Edelman hand auger. After the first boring a profile description was made and the two horizons to be sampled were chosen; the top horizon (usually the first 20 to 30 cm of the mineral layer starting below the litter layer) and a deeper horizon, usually a C or a BC horizon (mostly somewhere between a depth of 60 and 110 cm). A site and vegetation description was also made at each location. The 12 subsamples of 2 kg each were transported to the laboratory in separate poly-ethylene sampling bags as mixing of moist soil is undesirable, especially when done in the field. For the main campaign a total of 92 locations was sampled, resulting in 184 samples. For the seasonal campaign a subset of 20 locations was sampled on 8 occasions over a period of two years.

Laboratory and Analytical Procedures

Soil solution displacement

The day after sampling, the moist soil samples were centrifuged as follows: an equal amount of each of the six individual samples from one depth was put in one of the 6 canisters (made of Delrin) used in the centrifuge (Heraeus Christ Cryofuge 8000). The canisters (diameter 8.5 cm, height 12 cm) were designed to hold about 500 to 700 g of soil in an upper reservoir. This reservoir was separated by a 0.45 µm cellulose-nitrate filter (supported by a teflon support filter) from the lower reservoir with a volume of about 150 ml. After centrifuging for 15 minutes at 3500 G at a constant temperature of 15 °C, the filtered soil solution was put in poly-ethylene bottles that were placed in a refrigerator until further analysis. Analysis of critical parameters like NH₄, NO₃, SO₄ and DOC was carried out within a day, subsamples for parameters measured by ICP (AES and MS) were acidified to pH=1 with

Appendix A

concentrated ultrapure HNO₃ and analyzed within two weeks. From each sample the moisture yield and the pH (solid state electrode, Sentron 1001 pH system) were recorded immediately after centrifugation.

General soil characteristics and a composite sample of the solid phase

A composite sample of the solid phase for each depth was assembled from a second part of the subsamples by putting an equal amount of soil (mostly about 50 g) from each sampling bag into a small plastic container. Of this composite sample two subsamples were taken to determine dry matter content and organic matter content. Dry matter content was determined by drying moist soil at 105 °C till constant weight. Organic matter content was determined by loss on ignition at 550°C. The remainder of the composite sample was dried at 40 °C, mixed and sieved over a 2 mm sieve. This <2 mm fraction was used for the remaining analyses.

Total element analysis of the solid phase

A 10 g subsample from the <2 mm fraction of the composite samples was ground to about 20 µm and pressed with wax to produce pressed-powder tablets (Herzog HSM-HTP). These tablets were analyzed for total element content with X-ray fluorescence spectrometry (Siemens SRS 3400, Rh tube, Compton correction applied for elements beyond the Fe absorption edge). This analysis was only done for the main campaign because the 20 locations sampled for the seasonal campaign are a subset of the 92 locations of the main campaign. In addition, it is highly unlikely that the composition of the solid phase will show short term temporal fluctuations, thus one analysis of the total element concentrations of the solid phase suffices.

X-ray diffraction analysis

An impression of the general mineralogical composition of the samples was obtained by XRD analysis (Philips, Cu tube, 3-73° 2Θ) on three grain size intervals (<8 µm, 0-50 µm, >250 µm) of a small selection of samples. The selection was based on the XRF results and covered the entire range of Al₂O₃ content present in the samples.

Extractions of the solid phase

The fraction <2mm is also used for two extractions, one with 0.01 M CaCl₂ and the other with 0.43 M HNO₃, both at room temperature. The CaCl₂ extraction was used as an approximation of the occupation of the cation exchange complex (Houba et al., 2000). The (rather mild) 0.43 M HNO₃ extraction (Otte et al. 2000) was used gain insight into the amount of readily reactive constituents such as freshly precipitated (hydr-)oxides. For both extractions 3 g of soil and 30 ml of extractant were mixed in 50 ml centrifuge tubes, shaken for 2 hours at room temperature in a mechanical table shaker at a frequency of 220 per minute, centrifuged (before centrifugation of the CaCl₂-extract the pH was measured in suspension), and the supernatant liquid was collected for further analysis. For the seasonal campaign, solid phase composite samples were stored until all sampling rounds were completed so that the extraction could be performed in one analytical batch, this in order to rule out interbatch differences as a source of variation.

Chemical analyses

An overview of all the analyses on the solid phase, the displaced soil solution and the extracts is given in table A. ICP analysis were performed in as little runs as possible to rule out multiple batches as a source of variation.

Table A

Overview of the different chemical analyses grouped per method.

Method	Parameters	Analytical technique
Dry soil	dry matter content organic matter content SiO ₂ , Al ₂ O ₃ , K ₂ O, Na ₂ O, CaO, MgO TiO ₂ , Fe ₂ O ₃ , MnO, P ₂ O ₅ , S, Zr, As, Ba, Bi, Br, Ce, Cr, Cs, Cu, Ga, Hf, La, Nb, Nd, Nd, Pb, Rb, Sb, Sc, Sr, Th, U, V, Y, Zn	oven (105°C) loss on ignition (550°C) XRF, pressed powder tablets*
Displaced soil solution	pH Dissolved Organic Carbon NH ₄ SO ₄ , NO ₃ , Cl, PO ₄ Al, K, Na, Ca, Mg, Fe, Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	TOC analyzer Spectrometry Ion chromatography ICP-AES ICP-MS
CaCl ₂ extract (0.01 mol l ⁻¹)	pH Dissolved Organic Carbon NO ₃ , NH ₄ , N _{tot} , PO ₄ , Na, K Al, Mg, Fe, Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	Organic carbon analyzer Segmented Flow Analyzer ICP-AES ICP-MS
HNO ₃ extract (0.43 mol l ⁻¹)	Al, K, Na, Ca, Mg, Fe, Mn, P, S Cd, Cu, Cr, Ni, Pb, Zn	ICP-AES ICP-MS

*The accuracy of this method for major oxides was checked and found to be excellent by re-analysis of 26 samples using glass beads.

The exact brands and types of analytical instruments are:

XRF	: Siemens SRS 3400, Rh tube, Compton correction for elements beyond the Fe absorption edge
XRD	: Philips, Cu-tube, 3-73° 2θ
TOC analyzer	: Shimadzu TOC 500
Spectrophotometer	: Perkin Elmer Lambda 1
Ion chromatograph	: Dionex Qic analyzer
Segmented Flow Analyzer	: Skalar
Organic Carbon Analyzer	: Skalar
ICP-AES	: Perkin Elmer Optima 3000
ICP-MS	: Perkin Elmer Elan 6000 (main campaign), VG Plasmaquad 2+ (seasonal campaign)
pH	: Sentron 1001 pH system, solid state electrode

CURRICULUM VITAE

Op 3 april 1971 ben ik geboren te Koudekerke. Mijn VWO diploma behaalde ik in 1989 aan de Christelijke Scholengemeenschap Walcheren (CSW) te Middelburg. In datzelfde jaar begon ik met de studie Milieuhygiëne aan de Landbouwniversiteit in Wageningen, waar ik in het tweede jaar koos voor de specialisatie Bodemkwaliteit. Tijdens de afstudeerfase heb ik me breed georiënteerd door te kiezen voor twee afstudeerprojecten en twee stages. Het eerste afstudeerproject was een onderzoek naar de koperopname in de tijd door de regenworm *Lumbricus rubellus* in afhankelijkheid van kopergehalte, pH en vochtgehalte van de grond. Ik heb dat onderzoek gedaan tussen mei en november 1993 aan de vakgroep Bodemkunde en Plantevoeding. Van januari tot juni 1994 volgde het tweede afstudeerproject, uitgevoerd bij de vakgroep Bodemkunde en Geologie. Het was een geochemische studie met als onderwerp het natuurlijk voorkomen van zware metalen en andere elementen en hun bronnen van variatie in de Nederlandse sedimenten tot ongeveer 100 meter diepte. Direct aansluitend, van juli 1994 tot januari 1995, volgde een buitenlandse stage bij de Hebrew University of Jerusalem alwaar ik, in het kader van een nieuw te ontwikkelen reinigingstechniek voor afvalwater, heb gewerkt aan de invloed van de pH op de adsorptiecapaciteit voor zware metalen van het watervarentje *Azolla filiculoides*. Ter afsluiting van mijn studie heb ik gekozen om een aantal maanden, van maart tot en met juli 1995, mee te lopen bij het ingenieurs- en adviesbureau TAUW Milieu BV. Ik heb daar enerzijds een werkdocument Chloorfenolen opgesteld, en anderzijds een organisatiekundige analyse gemaakt van de werkelijke implementatie van deze werkdocumenten op de werkvloer. In augustus 1995 behaalde ik Cum Laude mijn ingenieurstitel. In december van datzelfde jaar ben ik bij de onderzoeksgroep van prof. Schuiling begonnen met het promotieonderzoek waarvan dit proefschrift het resultaat is. Mijn vrije tijd bracht ik tot voor kort voornamelijk door met boeken, kranten, CD's, mijn trompet, en mijn hardloopschoenen. Sinds de geboorte van Camiel is daar iets bijgekomen dat ook meteen het leeuwendeel van mijn vrije tijd opslokt.

‘Waarom zei je nou dat je dat wel wilt doen?’ vroeg ze, nadat ze de eerste zijstraat waren overgestoken.
‘Ik moet toch een baan hebben?’ antwoordde hij korzelig.
‘Maar toch niet in de wetenschap?’
‘Wat doet dat er nu toe, of je een baan hebt in de wetenschap, of ergens anders.’
‘Ik dacht dat je ook de pest aan de wetenschap had.’
‘Aan mensen die er status aan ontlenen, ja! Die denken dat het belangrijk is!’

(uit Het Bureau van J.J. Voskuil)