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Behaviour of heavy metals in soils

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Abstract

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Fractions of Zn, Cd, Cu, Pb, Fe and Mn extractable with water, a salt solution and dilute acid, and residual fractions were determined in soils with raised contents of heavy metals, near zinc smelters, along a river formerly discharging heavy metals, and in a sewage farm. Special attention was paid to the role of oxides of Fe and Mn in the binding of other heavy metals.
The theory of regular solid solutions was applied to exchange adsorption of ions in soil and some approximative equations of practical interest were derived. The possible role of hydrolysis and the adsorption of hydrolysis products was studied. Ion exchange in soil was described in terms of sites of high and low selectivity (two-site model) giving rise to a decreasing free enthalpy of adsorption with increasing surface coverage (Freundlich behaviour).
Cation-exchange experiments with Ca^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} on Winsum clay soil showed that heavy metals were subject to regular and selective (specific) exchange adsorption, and to superequivalent adsorption. A pronounced lowering of pH upon adsorption of heavy metals was assumed to be by desorption of weakly acidic protons or selective adsorption of hydrolysis products, in combination with a diminished acid-neutralizing capacity. Results may be of interest for environmental control of heavy metals.

Free descriptors: adsorption, ion exchange selectivity, regular solid solution, Freundlich isotherm, Langmuir isotherm, hydrolysis, ferric oxides, clay soil, waste water, environment.

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Samenvatting

Dit proefschrift beschrijft enkele aspecten van het gedrag van zware metalen in de bodem. Onder zware metalen worden die metalen verstaan met een relatieve dichtheid groter dan 5. Deze groep omvat zowel metalen die essentieel zijn voor plant en dier, zoals Fe, Mn, Cu, Zn, Mo en Co, de spoorelementen, als metalen waarvan niet bekend is of ze van belang zijn, zoals Hg, Cd en Pb.

De belangstelling voor de rol van zware metalen in de bodem kwam vroeger alleen van de zijde van hen die zich bezighouden met de bodemvruchtbaarheid, aangezien tekorten aan spoorelementen veel voorkomen in de landbouw. Meer recent ontstond belangstelling van de zijde van de milieuwetenschappen, aangezien zware metalen ook schadelijke effecten kunnen hebben op plant en dier als hun beschikbaarheid bepaalde drempelwaarden overschrijdt.

De oplosbaarheid in de bodem bepaalt in belangrijke mate de beweeglijkheid van zware metalen in het milieu en hun beschikbaarheid voor de plant en speelt daarom een belangrijke rol zowel bij het optreden van gebreksverschijnselen als bij de eventuele nadelige gevolgen van hoge gehalten in de bodem (bodemverontreiniging). De oplosbaarheid van zware metalen in de bodem hangt af van de pH, redoxpotentiaal, textuur en minerale samenstelling van de bodem, hoeveelheid en soort van organische verbindingen in de bodem en de bodemoplossing, onderlinge wisselwerking (concurrentie) tussen zware metalen, bodemtemperatuur, het vochtgehalte en de microbiologische activiteit.

Deze studie richt zich op het gedrag van Zn, Cd, Pb, Cu, Mn en Fe in de bodem; de resultaten kunnen bijdragen tot de kennis van de binding van zware metalen in de bodem en dus tot meer begrip van de oplosbaarheid en de beweeglijkheid van deze elementen in de bodem.

Transport en vastlegging van zware metalen in de bodem

Transport van zware metalen in de bodem kan plaatsvinden (a) in opgeloste (< 0.45 µm) of gesuspendeerde (> 0.45 µm) vorm, door de bodemoplossing, door middel van diffusie, of met de bewegende bodemoplossing mee; (b) door de plantewortel; en (c) gehecht aan, of opgenomen in (micro-)organismen. Alle metaalionen in de bodemoplossing gaan bindingen aan met watermoleculen of andere liganden, waarvan vooral organische verbindingen, zoals fulvo- en humuszuren, van belang zijn voor zware metalen.

Of een opgelost of gesuspendeerd metaalion in oplossing blijft, hangt af van (a) concentraties van het betrokken metaalion en van alle concurrerende ionen; (b) concentraties van liganden, in het bijzonder organische verbindingen met chelaterende eigenschappen; (c) pH, redoxpotentiaal en bodemtemperatuur; en (d) soort en aantal adsorptieplaatsen aan het oppervlak van de vaste fase.

Processen die een rol kunnen spelen bij de verwijdering van zware metalen uit de bodemoplossing zijn (a) opname in biologische systemen; (b) uitvlokken van gesuspendeerde deeltjes; (c) precipitatie of coprecipitatie, bijvoorbeeld met fosfaten of ijzeroxiden; (d) adsorptie; en (e) diffusie in een vaste fase (roosterpenetratie). Adsorptie kan plaatsvinden door elektrostatische aantrekking, bijvoorbeeld van het ion-ion of het ion-multipool type, London-van der Waals aantrekking, waterstofbinding, coördinatiebinding (ligandenomwisseling) of mogelijk ook chemische binding (chemisorptie).

Adsorptie van ionen aan geladen oppervlakken en uitvlokking van gesuspendeerde stof zijn waarschijnlijk het belangrijkst bij de initiële vastlegging van opgeloste en gesuspendeerde zware metalen in de bodem. Microbiologische omzetting van organisch materiaal kan leiden tot het weer vrijkomen van zware metalen. Op de lange duur kunnen zware metalen (a) specifiek adsorberen aan, of ingesloten worden in ijzer- of mangaanoxiden of andere mineralen; (b) diffunderen in mineralen, zoals zeolieten, veldspaten en mogelijk kleimineralen; of (c) stabiele precipitaten vormen, zoals bijvoorbeeld silicaten.

Gronden bij zinkfabrieken

De oplosbaarheid van zink in oppervlaktewater nabij een zinkfabriek bleek niet te worden bepaald door hydroxiden, carbonaten en fosfaten: in niet-zuur water voldeed zink aan de relatie

$$2(Zn^{2+}) + (H^{+}) = (OH^{-}) + (HCO_3^{-}) + 2(CO_3^{2-}) \qquad (4\text{-}5)$$

waarbij de ronde haakjes de concentratie in mol/l aangeven.

De gehalten aan Zn en Cd waren hoog in de bovenste 10 cm van de bodem (2000 en 25 mg/kg) en in de vegetatie (2000-7000 en 20-40 mg/kg) 1 km ten noordoosten van een zinkfabriek te Overpelt (België); de gehalten namen sterk af met de afstand tot de fabriek. Bladeren van berken (*Betula verrucosa*) bevatten beduidend meer Zn en Cd dan van eiken (*Quercus robur*) en esdoorns (*Acer campestre*). De gewichtsverhouding van Zn tot Cd in de vegetatie was gemiddeld 125 en in de bodem was dit 75, hetgeen erop wijst dat Zn beter wordt opgenomen door de plant dan Cd, of dat Cd beweeglijker is in de bodem dan Zn.

Gehalten aan zware metalen waren het hoogst in de bovenste 10 cm van de bodem, zoals te verwachten valt bij aanrijking vanuit de lucht, en namen sterk af met de diepte. De overeenkomst tussen de gehalten aan zware metalen en het gloeiverlies (organische stof) zou erop kunnen wijzen dat het adsorptiecomplex ten naaste bij verzadigd was met betrekking tot deze metalen. Onderlinge verschillen tussen de metaalgehalten als functie van de diepte zouden een gevolg kunnen zijn van een veranderde samenstelling van de neerslag vanuit de lucht of van verschillende beweeglijkheden van zware metalen in de bodem; daarbij zou de beweeglijkheid van Cd dan groter zijn dan die van Zn en Pb.

Resultaten van proeven met bodemmateriaal (A_1 horizon) verzameld op 1 km ten noordoosten van de zinkfabriek te Overpelt, wezen erop dat een deel van het zink in de bodemoplossing begeleid wordt door grote (> 48 Å) organische verbindingen en dat de oplosbaarheid van zink in de bodem wordt bepaald door adsorptie-desorptie en niet door een oplosbaarheidsprodukt van een zinkmateriaal.

Een betrouwbare schatting van de wateroplosbare fractie kan worden verkregen door bodemmonsters in evenwicht te brengen met gedemineraliseerd water in verschillende gewichtsverhoudingen en door de verandering in het metaalgehalte van de vaste fase te extrapoleren naar een verhouding van oplossing tot vaste fase van nul. Schattingen op deze wijze verkregen waren lager dan verkregen door percolatie van bodemmonsters.

Redoxpotentialen in met water verzadigde bodemmonsters bleken na ruim 2 maanden bepaald te worden door reductie van limonitische ijzeroxiden, met een oplosbaarheidsprodukt tussen dat van hematiet en goethiet. De toename in concentratie van Cd, Zn, Mn en Fe in de bodemoplossing was waarschijnlijk een gevolg van het vrijkomen van zware metalen geadsorbeerd aan, of ingesloten in limonitische ijzeroxiden, en van desorptie van zware metalen door Fe^{2+}. Het verdringend vermogen van Fe^{2+} was laag ten opzichte van andere tweewaardige kationen, in het bijzonder Zn^{2+}, in overeenstemming met de volgorde van chelaatstabilitiet van deze kationen.

Wateroplosbare fracties van Zn, Cd, Mn en Fe in Overpelt-grond lagen rond 1% of lager, terwijl Zn en Cd voor ongeveer 70% in zoutextraheerbare vorm waren, maar Fe en Mn voor minder dan 10%. Verdund zuur en Na-EDTA extraheerden bijna gelijke hoeveelheden Zn en Cd, maar Na-EDTA extraheerde beduidend meer Mn en Fe dan verdund zuur, hetgeen erop zou kunnen wijzen dat Mn en Fe voorkomen als gemengde oxiden in een moleculaire verhouding van Mn tot Fe van 0.14. Gewichtsfracties van Mn en Fe in gronden bij een zinkfabriek te Budel-Dorplein leken eveneens samen te hangen, in het bijzonder nabij de grondwaterspiegel. Zoutextraheerbare fracties van Zn, Cd en Pb waren hoog (50-60%) in deze gronden, maar van Cu, Mn en Fe waren ze laag (< 10%). De zuurextraheerbare fractie van Cu was hoger (40-60%) dan van Fe en Mn ($\leq$ 10%), hetgeen erop zou kunnen wijzen dat Cu, in tegenstelling tot Fe en Mn, grotendeels gebonden is aan organische stof in de bodem.

Een grond langs de Geul

De Geul is een kleine rivier die door de mijnstreek van La Calamine en Plombières (België) loopt, waar vroeger zink- en looderts werd gewonnen, en Nederland binnenstroomt in het zuiden van de provincie Limburg. De Geul voerde voorheen grote hoeveelheden Pb, Zn en Cd af, in opgeloste vorm of, vooral bij hoog water, gehecht aan gesuspendeerd materiaal. Het water van de Geul was vermoedelijk enigszins zuur, zoals blijkt uit de afwezigheid van kalkhoudende sedimenten langs de Geul ten zuiden van de samenkomst met de Sinselbeek. Dit zuur kwam waarschijnlijk vrij bij de oxidatieve verwering van sulfidische ertsen, in het bijzonder pyriet en marcasiet, in het Belgische stroomgebied van de Geul.

De korrelgrootteverdeling van een grond langs de Geul verliep regelmatig met de diepte en wees niet op discontinuïteiten in de afzetting van het bodemprofiel. De verdeling van de gewichtsfracties van Zn en Pb met de diepte in het profiel weerspiegelt waarschijnlijk de veranderende metaalgehalten van het gesuspendeerde materiaal dat door de Geul is afgevoerd in de loop der tijd. De hoge gehalten aan Zn (3620 mg/kg) en Pb (1330 mg/kg) in de 10-20 cm laag van het profiel hangen vermoedelijk samen met de mijnbouwactiviteiten in de jaren 1840-1880, toen de mijnbouw op haar hoogtepunt was, terwijl de toenemende metaalgehalten op 150-110 cm diepte wellicht de toename in mijnbouwactiviteit in de 14e en 15e eeuw weerspiegelen toen de bronsindustrie in het nabijgelegen Aken tot bloei kwam.

Niet-beschikbare (residuaire en zuurextraheerbare) fracties van Zn en Pb waren hoog (80-90%), mogelijk als gevolg van binding aan ijzeroxiden, of als gevolg van de aanwezigheid van stabiele mineralen, zoals silicaten of mogelijk sulfiden, aangevoerd door de Geul vanuit het Belgische stroomgebied. Als gevolg van de hoge gehalten aan Zn en Pb waren de zoutextraheerbare (omwisselbare) fracties toch nog van kwantitatieve betekenis: 10-20% van de kationenomwisselcapaciteit op 10-20 cm diepte was bezet met Zn^{2+} of Pb^{2+}. De toename in wateroplosbare en zoutextraheerbare fracties van Zn en Pb beneden de grondwaterspiegel bevestigde het vermoeden dat Zn en Pb voor een deel gebonden waren aan ijzeroxiden.

Vloeivelden van de gemeente Tilburg

Gronden in het oudste (50 jaar) gedeelte van het vloeiveldencomplex van de gemeente Tilburg werden bemonsterd en van deze monsters werden de dichtheid, het vochtgehalte, de gehalten aan Zn, Cu, Pb, Mn en Fe, en het gloeiverlies bepaald. Eén cyclus van bevloeiing met rioolwater werd in zijn geheel bijgewoond en gedurende 108 uur werden riool- en draineerwater regelmatig bemonsterd, gefiltreerd over een 0,45 µm-membraanfilter en geanalyseerd op opgeloste en gesuspendeerde vormen van Zn, Cu, Fe en Mn.

De afvoersnelheid van het draineerwater, gemeten bij de uitlaten van de draineerbuizen, en de variatie in pH en chloorconcentratie in het draineerwater als functie van de tijd na het begin van de bevloeiing (doorbraakcurve), toonden aan dat menging met capillair regenwater en grondwater van geringe betekenis was en dat het meeste draineerwater inderdaad gezuiverd rioolwater was. Gedurende perioden van herverdeling van water in de bodem kan mobilisatie van zware metalen optreden, misschien als gevolg van de afbraak van organische stof. Dit leidt tot een duidelijke 'piek' in het begin van de doorbraakcurven van de (gesuspendeerde) zware metalen in het effluent van de draineerbuizen.

Vergelijking van de concentraties van metalen in riool- en draineerwater toonde aan dat de capaciteit van de bodem om metalen te verwijderen uit het rioolwater afnam in de volgorde Fe (98%), Mn (92%), Zn (83%), Cu (55%), waarbij de door de bodem verwijderde fracties tussen haakjes zijn gegeven. Vanwege zijn grote affiniteit tot organische liganden kan Cu voor een deel voorkomen als ongeladen of negatief geladen complexen, hetgeen misschien de lage capaciteit van de bodem om Cu te verwijderen zou kunnen verklaren.

De totale hoeveelheden zware metalen die door de bodem zijn verwijderd in de loop van 50 jaar werden geschat aan de hand van metaalgehalten in de bodem en van metaalconcentraties in riool- en draineerwater. De schattingen stemden redelijk goed overeen voor Zn, Mn en Fe, terwijl de gegevens voor Cu erop wezen dat de capaciteit van de bodem om Cu te verwijderen vroeger groter was dan tegenwoordig.

Ionenwisseling en selectiviteit

De thermodynamische evenwichtsconstante voor een homovalente (A/B) omwisselreactie, $K^{o}_{A/B}$, wordt ingevoerd en een omwisselvergelijking wordt afgeleid:

$$(\bar{a}_A/\bar{a}_B) = K^{o}_{A/B}\,(a_A/a_B) \qquad (24)$$

Het opnemen van de verhouding van de activiteitscoëfficiënten van de ionen in de geadsorbeerde fase en in de oplossing in $K^o_{A/B}$, leidt tot een selectiviteitscoëfficiënt, $K_{A/B}$, die gewoonlijk wordt gebruikt om selectiviteit tussen ionen weer te geven en te meten.

De adsorptie van ionen aan een vast oppervlak wordt beschreven aan de hand van elektrostatische wisselwerking tussen het ion en het oplosmiddel en het ion en de vaste fase. Dicht bij het adsorberend oppervlak is het elektrische veld niet uniform, vanwege de aanwezigheid van discrete adsorptieplaatsen, en de veldsterkte kan hier zeer groot zijn. De diëlektrische constante van water, ongeveer 80 in de vrije oplossing, kan afnemen tot ongeveer 6 in het geval van volledige elektrische verzadiging. Bij grote elektrische veldsterkten zijn de meeste ionen geadsorbeerd in een Sternlaag en kleine verschillen in evenwichtsafstand tot het adsorberend oppervlak, bijvoorbeeld als gevolg van verschillen in hydratatiewarmte of polarizeerbaarheid, kunnen aanleiding geven tot aanzienlijke selectiviteit tussen ionen.

Ionenwisseling en adsorptievergelijkingen

De theorie van de binaire mengsels met een energie van menging ongelijk aan nul (reguliere mengsels) wordt toegepast op ionenwisseling om uitdrukkingen te verkrijgen voor de verhouding van de activiteitscoëfficiënten van ionen A en B in de geadsorbeerde fase, $\bar{f}_A/\bar{f}_B$. Hierbij wordt ervan uitgegaan dat tweewaardige ionen twee aangrenzende adsorptieplaatsen tegelijk bezetten op een regelmatig twee-dimensionaal rooster. Verscheidene benaderingen voor $\bar{f}_A/\bar{f}_B$ worden afgeleid van de exacte formules voor het reguliere mengsel door Guggenheim (1945). Deze vergelijkingen bieden de mogelijkheid om energie (en entropie) van menging op te nemen in omwisselvergelijkingen. De theorie van de reguliere mengsels toegepast op ionen kan van belang zijn voor mengsels van vaste stoffen, zoals van $CaCO_3$ en $ZnCO_3$ aan het oppervlak van calciet, en voor gelokaliseerde adsorptie (in een Sternlaag), bijvoorbeeld van zware metalen op oxideoppervlakken.

De Langmuirvergelijking

$$q = q_{\mathrm{max}} Kc/(1 + Kc) \tag{55}$$

wordt beschreven, en de invloed van een kleine hoeveelheid opgeloste stof, die niet aan de adsorptiereactie deelneemt, en van een variabele adsorptiecoëfficiënt (K) worden bediscussieerd. Het Langmuir-adsorptiemodel is niet van toepassing op ionenwisseling in gronden, maar (55) kan worden afgeleid als een benadering voor gewone omwisselvergelijkingen (24).

De Freundlich-adsorptievergelijking

$$q = kc^{1/n} \tag{65}$$

en de Rothmund-Kornfeld-vergelijking

$$q_A/q_B = k(c_A/c_B)^{1/n} \tag{71}$$

die kan worden beschouwd als een vorm van (65) die van toepassing is op ionenwisseling, worden ingevoerd en (71) wordt afgeleid als een benadering voor omwisselvergelijkingen gebaseerd op de theorie van de reguliere mengsels. Een energie van menging ongelijk aan nul kan een gevolg zijn van heterogeniteit van de adsorptieplaatsen in de bodem, maar de theorie van de reguliere mengsels neemt deze heterogeniteit, die karakteristiek is voor de bodem, niet expliciet in beschouwing.

Twee-plaatsen- en twee-soorten-modellen

Ionenwisseling in gronden kan worden beschreven met behulp van 'twee-plaatsen'- en 'twee-soorten'-modellen. Een twee-plaatsen-model beschrijft een systeem bestaande uit twee soorten kationen en twee soorten adsorptieplaatsen: hoge-selectiviteitsplaatsen die selectief zijn voor één van beide kationen en lage-selectiviteitsplaatsen die dit niet zijn.

Een 'gemiddelde' selectiviteitscoëfficiënt voor een A/B-omwisselreactie in een twee-plaatsen-systeem wordt als volgt gedefinieerd

$$K_a = (c_B/c_A)\Sigma q_i/\Sigma(Q_i - q_i) \qquad (87)$$

en er wordt aangetoond dat K_a afneemt met toenemende bezetting van het adsorberend oppervlak door het 'geprefereerde' ion. De Rothmund-Kornfeld- en Freundlich-vergelijkingen worden beide gekarakteriseerd door een afnemende adsorptiewarmte bij toenemende bezetting door het geprefereerde ion en kunnen worden afgeleid als benaderingen uit het twee-plaatsen-model. Er wordt aangetoond dat de coëfficiënten k en n in (65) en (71) een aanwijzing kunnen vormen voor de fractionele hoeveelheid hoge-selectiviteitsplaatsen en voor de verhouding van de selectiviteitscoëfficiënten voor hoge- en lage-selectiviteitsplaatsen.

Een twee-soorten-model beschrijft een systeem bestaande uit twee soorten kationen, waarvan er één stabiele complexen vormt met een ligand in oplossing en bestaande uit adsorptieplaatsen die niet selectief zijn voor één van beide kationen maar wel voor de geligandeerde complexen. De gemiddelde selectiviteitscoëfficiënt voor dit systeem neemt af met toenemende bezetting van het oppervlak door het complexvormende kation, evenals in het twee-plaatsen-model. Het twee-soorten-model is dan ook in verschijningsvorm niet of moeilijk te onderscheiden van het twee-plaatsen-model, en (65) en (71) kunnen ook worden afgeleid als benadering uit het twee-soorten-model. Kationen van zware metalen kunnen bindingen aangaan met ongeladen liganden, zoals thio-urea of ethyleendiamine, of met geladen liganden. Als tweewaardige kationen bindingen aangaan met monovalente anionen, zoals het glycine-ion, lijkt de ionenwisseling niet langer equivalent: de hoeveelheid kationen die uit de oplossing verdwijnt verschilt van de hoeveelheid kationen die door de vaste fase wordt afgegeven.

De adsorptie van hydrolyseprodukten zou ook aanleiding kunnen geven tot een schijnbare superequivalente adsorptie van kationen. De mogelijke rol van hydrolyse bij de adsorptie van zware metalen in de bodem is nog onderwerp van discussie, aangezien het dikwijls moeilijk is om onderscheid te maken tussen desorptie van protonen bij adsorptie van metalen en adsorptie van eerste hydrolyseprodukten, of een combinatie van beide processen.

In elektrische velden van hoge intensiteit kan de adsorptie van hydrolyseprodukten energetisch gunstiger zijn dan van de niet-gehydrolyseerde kationen als gevolg van de lagere adsorptiewarmte van de hydrolyseprodukten.

Selectieve adsorptie van hydrolyseprodukten kan aanleiding geven tot een schijnbare betrekking tussen de pH en de logaritme van de concentratie van het zware metaal, c_{hM},

$$2\ \mathrm{pH} + n \log c_{hM} = \text{constant} \qquad (122)$$

waarin n een functie is van de begin-pH en de buffercapaciteit van het systeem. De coëfficiënt n is gelijk aan 1 als, bij gelijkblijvende ionensterkte, de oplosbaarheid van zware metalen bepaald wordt door hydroxiden, carbonaten of silicaten, in evenwicht met CO_2 in de atmosfeer of vast SiO_2.

Een aantal gepubliceerde metingen die betrekking hebben op de adsorptie van zware metalen worden geïnterpreteerd met behulp van de modellen die in deze studie zijn afgeleid. Hierbij blijkt dat de selectiviteitscoëfficiënten die de omwisseling tussen zware metalen en alkali- of aardalkalimetalen beschrijven, over het algemeen hoog zijn bij lage bezetting door zware metalen of bij een hoge pH, en afnemen met toenemende bezetting door zware metalen of bij een afnemende pH tot waarden van circa 1.

Omwisselproeven

Een experimentele werkwijze wordt beschreven, die het mogelijk maakt een volledige omwisselisotherm te bepalen aan één grondmonster, door het monster herhaaldelijk in evenwicht te brengen met toenemende concentraties van het vereiste kation. Omwisselisothermen werden bepaald voor Ca^{2+} en Zn^{2+} aan Grundiet en voor Ca^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} en Pb^{2+} aan Winsum-kleigrond.

De adsorptie van component M aan een vaste fase werd gemeten als verlies van M uit de oplossing, en desorptie van component M^* als de hoeveelheid afgegeven door die vaste fase, d.w.z. als de toename van M^* in de oplossing. Omwisselisothermen waren niet eenduidig bepaald aangezien de 'verlies'- (adsorptie-) en 'toename'- (desorptie-)curven niet altijd samenvielen over het gehele omwisseltraject, hetgeen erop wees dat zware metalen betrokken waren in verschillende reacties: (a) gewone ionenwisseling, (b) specifieke ionenwisseling, en (c) superequivalente of 'overmaat'-adsorptie.

Ionenwisseling wordt gekenmerkt door het vrijkomen van equivalente hoeveelheden ionen bij adsorptie van ionen. Gewone (of: niet-specifieke of niet-selectieve) ionenwisseling heeft betrekking op selectiviteitscoëfficiënten van circa 1, en specifieke (of: selectieve) ionenwisseling op selectiviteitscoëfficiënten van circa 10 of groter. Superequivalente of overmaatadsorptie wordt gekenmerkt door het vrijkomen van minder dan equivalente hoeveelheden ionen bij adsorptie van ionen.

De resultaten tonen aan dat Zn^{2+}, Cd^{2+} en Cu^{2+} praktisch op voet van gelijkheid wedijveren om het grootste deel van de adsorptieplaatsen in Winsum-grond, terwijl Pb^{2+} een factor 2-3 wordt geprefereerd boven Ca^{2+}, mogelijk als gevolg van de kleinere gehydrateerde straal van Pb^{2+} in waterige oplossing. Adsorptie-desorptie hysterese, mogelijk als gevolg van herrangschikking van ionen in de geadsorbeerde fase of door condensatie van homoione kleiplaatjes, werd gevonden voor omwisseling van Pb^{2+} en Cu^{2+} tegen Ca^{2+}.

Er waren aanwijzingen dat Ca^{2+} (en Mg^{2+}) ook voorkwam in specifiek geadsorbeerde vorm in Winsum-grond, aangezien de onbehandelde grond een hoeveelheid zuurextraheerbaar calcium bevatte die niet kon worden toegeschreven aan calciet of apatiet (of dolomiet), en omdat bijna equivalente hoeveelheden Ca^{2+} (en Mg^{2+}) vrijkwamen bij de specifieke adsorptie van zware metalen. Maar er waren geen aanwijzingen dat calcium betrokken zou zijn in specifieke interacties tijdens de experimenten.

Gedrag van de pH

De pH van de grondsuspensies nam af bij de adsorptie van ionen van zware metalen aan homoione Ca^{2+}-grond, maar bleef vrijwel constant bij adsorptie van Ca^{2+} aan gronden bezet met ionen van zware metalen. Dit kon niet worden verklaard door de invloed van de toenemende zoutconcentratie op de pH ('zout-effect').

De betrekking

$$2\ \mathrm{pH} + \log hM = K \qquad (145)$$

gold zowel voor Zn en Cd waar de constante lag tussen 8 en 9, als voor Cu en Pb waar de constante lager was: 6-7. De resultaten van experimenten bij gelijkblijvende zoutconcentratie toonden aan dat (145) ook na een periode van 1-2 maanden gold voor Zn (K = 8,9) en Cu (K = 6,8). De geldigheid van (145) wijst erop dat een neerslag de pH bepaalt, maar de aanwezigheid van hydroxiden, carbonaten en silicaten (en ook fosfaten) bleek onwaarschijnlijk te zijn onder de omstandigheden van de experimenten. Daarom wordt verondersteld dat de verlaging van de pH een gevolg was van de desorptie van protonen of specifieke adsorptie van hydrolyseprodukten, of van de vorming van een 'oppervlakteneerslag' van hydroxiden of mogelijk ook silicaten. Een oppervlakteneerslag zou de pH kunnen bepalen als functie van de activiteit van de ionen van zware metalen in oplossing.

Uit de resultaten van adsorptieproeven bij gelijkblijvende pH (pH 7) bleek dat de hoeveelheid H^+ (mol/l) die vrijkwam bij adsorptie van Zn, gedeeld door de hoeveelheid specifiek geadsorbeerde Zn (mol/l), toenam van ongeveer 1 bij lage bezetting met Zn, tot ongeveer 2 met toenemende bezetting. Maar de adsorptie bij pH 7 behoeft niet gelijk te zijn aan die bij lagere pH, bijvoorbeeld doordat hydrolyse en de vorming van ongeladen oppervlaktecomplexen kan worden bevoordeeld bij pH 7.

Toediening van equivalente hoeveelheden Zn^{2+} of H^+ aan suspensies van Winsum-grond had hetzelfde effect op de pH tot 30-40 µeq/g, terwijl Cu^{2+} en H^+ hetzelfde effect op de pH hadden tot 40-50 µeq/g. Deze resultaten wijzen erop dat H^+, Cu^{2+} en Zn^{2+} wedijveren om dezelfde adsorptieplaatsen, die waarschijnlijk ongeveer 25% van de totale kationenomwisselcapaciteit uitmaken. Wanneer de adsorptieplaatsen bezet zijn met specifiek geadsorbeerde zware metalen kunnen ze ontoegankelijk zijn voor H^+, tot de pH laag genoeg is voor H^+ om doeltreffend te kunnen wedijveren met de zware metalen om deze plaatsen. De afname van de pH kan dus veroorzaakt worden door een relatief kleine hoeveelheid H^+, die is vrijgekomen bij de adsorptie van zware metalen, als gevolg van de verminderde buffercapaciteit van de grond.

Specifieke ionenwisseling en overmaatadsorptie

Specifieke ionenwisseling van ionen van zware metalen aan Winsum-grond (a) trad op bij lage bezetting door zware metalen, hetgeen aanleiding gaf tot een 'Freundlich'-gedrag; (b) was een snel proces, aangezien schudtijden van een paar uur tot verscheidene weken geen invloed hadden op de totale hoeveelheden geadsorbeerd; (c) ging gepaard met een daling van de pH, die groter was voor Pb en Cu dan voor Zn en Cd; (d) leek omkeerbaar te zijn voor zware metalen onderling, zoals bleek uit de resultaten van Zn-Cd omwisseling. De totale hoeveelheden specifiek geadsorbeerde zware metalen en de selectiviteitscoëfficiënten voor de specifieke omwisselreacties namen toe in de reeks

$$\mathrm{Cd} < \mathrm{Zn} < \mathrm{Cu} < \mathrm{Pb}$$

Overmaatadsorptie van zware metalen leek te worden begunstigd door lage pH en hoge concentratie van zware metalen, en nam toe met de tijd tot een maximum. Specifiek geadsorbeerde en in overmaat geadsorbeerde zware metalen konden niet worden verdrongen met Ca^{2+}, maar wel met verdund zuur.

Hydroxylgroepen in organische stof of aan het oppervlak van mineralen kunnen een belangrijke rol spelen bij de specifieke interacties van zware metalen in suspensies van Winsum-grond. Drie typen van associatie van tweewaardige kationen (M^{2+}) en oppervlaktehydroxylgroepen (Surf-OH) zijn denkbaar bij hoge pH

$$\mathrm{Surf\text{-}O^-}(\tfrac{1}{2}M^{2+}) \qquad (155)$$

waar de ronde haakjes aangeven dat de adsorptie in een diffuse laag plaatsvindt, en

$$\mathrm{Surf\text{-}O_2M} \qquad (156)$$

of

$$\mathrm{Surf\text{-}OMOH} \qquad (157)$$

waar adsorptie plaatsvindt in een Sternlaag. Bij lage pH vindt de adsorptie waarschijnlijk geheel plaats in een Sternlaag

$$\mathrm{Surf\text{-}OM^+} \qquad (158)$$

hetgeen zou leiden tot een toename van de anionenomwisselcapaciteit. Het type associatie kan afhangen van (a) ruimtelijke factoren, (b) aantal hydroxylgroepen per eenheid oppervlak van het adsorbens, (c) ladingsnulpunt van de hydroxylgroepen, (d) diëlektrische constanten van de vaste fase en de oplossing, (e) de pH van de oplossing, en (f) de affiniteit van het kation voor een oppervlaktegroep. Deze affiniteiten blijken de reeks van de eerste hydrolyseconstanten van de ionen van zware metalen te volgen, hetgeen erop zou kunnen wijzen dat de ionen hydrolyseren bij adsorptie om hun lading te verlagen en dus hun hydratatiewarmte te verlagen.

Specifieke ionenwisseling van zware metalen in Winsum-grond en de daling van de pH die daarmee gepaard gaat, kan worden toegeschreven aan specifieke adsorptie van ionen van zware metalen of eerste hydrolyseprodukten aan oppervlakte-hydroxylgroepen. Het tweede type adsorptie zou ook de schijnbare correlatie kunnen verklaren tussen de selectiviteitscoëfficiënten en de eerste hydrolyseconstanten.

Overmaatadsorptie kan een gevolg zijn van de vorming van monovalente oppervlaktecomplexen (158), en indien dat het geval zou zijn, zouden overmaatadsorptie en specifieke omwisseling nauw verbonden verschijnselen zijn. Overmaatadsorptie zou ook veroorzaakt kunnen worden door de vorming van tweewaardige oppervlaktecomplexen, vermoedelijk op een ander soort oppervlak ($Surf_a$)

$$Surf_a\text{-}OHM^{2+}$$

Een ligandenomwisselreactie tussen een oppervlakte-hydroxylgroep en een watermolecuul uit de binnenste hydratatiemantel van een ion van een zwaar metaal kan als volgt voorgesteld worden

$$Surf_a\text{-}OH + M(H_2O)_6^{2+} \rightleftarrows Surf_a\text{-}OHM(H_2O)_5^{2+} + H_2O \qquad (173)$$

mogelijk gevolgd door hydrolyse of de vorming van een oppervlakteneerslag

$$Surf_a\text{-}OHM(H_2O)_3(OH)_2 \qquad (175)$$

hetgeen een verklaring zou kunnen zijn voor de geldigheid van (145) bij adsorptie van zware metalen in Winsum-suspensies.

Contents

1 Introduction

The growing concern about the quality of the natural environment has stimulated an increasing interest in the occurrence and behaviour of heavy metals in soils and natural waters. The group of metals referred to collectively as 'heavy' metals includes all metals with a specific gravity (relative mass density) greater than 5. Alkali and alkaline earth metals fall outside this group (Weast, 1972). This study concentrated on Zn (80 ppm), Cd (0.2 ppm), Cu (70 ppm), Pb (16 ppm), Mn (0.1%) and Fe (5.0%), where the average mass fractions of the elements in the earth's crust from Goldschmidt (1954) are given in parenthesis. Thus Zn, Cu, Pb, and especially Cd, are trace constituents of most natural soils.

Historically, the interest in a number of heavy metals stems from soil fertility. Traces of Fe, Mn, Cu, Zn, Mo, and possibly Co, are known to be essential to plants, and also to man and animals. These elements are generally called micronutrients or trace elements, because of the small amounts in which they are required by plants. The group of trace elements includes also elements that are no trace constituents of soils, for example Fe, which is a major constituent of most soils. Other trace elements, which do not belong to the heavy metals, are B, Cl and Na. The role of trace elements in soils and agriculture was recently reviewed by Lisk (1972) and Sillanpää (1972).

Iron ranks fourth in abundance (5.0%) among the elements in the earth's crust, after O (46.6%), Si (27.7%), and Al (8.1%). But owing to its low solubility in aerated soils, its plant-availability is very low. Iron is essential to photosynthesis, since it is a component of chlorophyll.

Manganese has a very low solubility in non-acid aerated soils and plays a role in photosynthesis. It is a constituent of several enzymes that function in respiration. Among cereals, oats probably are the most sensitive to deficiency, often called 'grey speck' disease, after its symptoms.

Copper and zinc are also essential to plants, through the role they play in enzymic processes. In the Netherlands, copper deficiency became known as 'reclamation' disease (Du: ontginningsziekte). Molybdenum is essential to nitrogen fixing bacteria and hence to leguminous crops. Cobalt is also required for nitrogen fixation, since it is a component of vitamin B_{12}.

The detection of trace element problems in soils is often difficult, because of the resemblance of a number of deficiency symptoms, the large number of trace elements in soils, the complicated interactions (antagonisms) between the different elements, the different mechanisms of uptake (or exclusion) by plant roots, and the complicated role these elements play in physiological processes. Hidden trace element deficiencies are probably far more widespread than is generally estimated (Sillanpää, 1972).

Even in the most serious deficiency, the total amounts of micronutrients in soil generally far exceed the requirements of crops. But these elements are not available to the plant, because they are constituents of stable minerals, occluded by iron or manganese oxides, or specifically adsorbed by solid constituents of soil, including organic matter. The availability of trace elements is dependent on pH, redox potential, soil texture, mineral composition of the soil, amount and type of organic compounds in soil and the soil solution, competitive interactions between trace elements, soil temperature, moisture content, and microbiological activity.

All trace elements may have adverse effects on plants, if their availability in soils exceeds certain thresholds, which differ according to species of plant, soil and weather. Certain heavy metals, such as Hg, Pb, and Cd, which are probably not essential to plants or animals, are known to be hazardous to health, even at low concentrations.

The events at Minamata (Japan) in the 1950s showed the deleterious effect of Hg on human health. More than a hundred persons were seriously, about half of them fatally, affected by a diet consisting largely of shellfish caught in Minamata Bay, whose Hg contents were high because of discharge of waste Hg by a plastics factory.

In the early 1960s environmental Cd contamination was established as the cause of a bone disease (Itai-Itai disease) in Fuchu and other rural areas in Japan. The Cd had been taken up by rice grown on fields irrigated with Cd polluted water from rivers discharging mining wastes.

The events at Minamata and the Itai-Itai disease are rather exceptional, since acute poisoning by heavy metals is rare. Chronic exposure to raised levels of heavy metals in air, water and food is far more common, and may also harm human health. However, the possible (subclinical) effects of chronic exposure to raised levels of heavy metals are difficult to diagnose and still subject to discussion. The role played by Pb, Hg and Cd as environmental contaminants was reviewed extensively by Lagerwerff (1972).

Although the problem of heavy metals in soils is still largely one of deficiency, the present study pays particular attention to soils with relatively high amounts of heavy metals, since little research has been done on such soils in the Netherlands. Soils along highways, soils treated with certain types of sewage sludges, fertilizers (lime or phosphates), pesticides, fungicides or manure, or soils irrigated with contaminated water, and soils near mining or industrial centres, may all have raised contents of heavy metals. High contents of heavy metals in soils represent an environmental hazard since these metals may affect plants growing on these soils, and thus may reach man or animals. Surface contamination of crops by heavy metals, for example by sprinkling irrigation of sewage sludge, constitutes a source of direct contamination that becomes increasingly important.

As long as heavy metals remain tightly bound to solid soil constituents, and available contents remain low, there will generally be little effect on the environment. Grazing animals may ingest some soil particles with high contents of heavy metals, plants may take up some metals by direct contact between roots and solid soil constituents, and wind or water may transport soil particles to adjacent agricultural land, where the particles may become adhered to crops. Soil particles may also be transported to surface waters, where metals, associated with these particles, may become mobilized.

When soil conditions change in such a way that heavy metals go into solution, the raised heavy metal contents of soils impose a direct environmental hazard. The increasing availability of heavy metals in soil may then have adverse effects on plant growth. In addition, heavy metals may leach down to groundwater or to surface water, and hence reach man and animals through the drinking water. The hazard of a certain metal in a soil to plants growing on that soil depends on (a) plant species, (b) chemical form of the element in that soil, (c) occurrence of other elements, notably competing heavy metals, and of complexing ligands, and adsorption sites associated with the solid phase, (d) amount available in the soil, and (e) soil and weather conditions.

As in micronutrient deficiency, the problem of soil pollution, or contamination, by heavy metals is also complicated by the lack of simple correlation between the total amount of heavy metals in a soil and the possible adverse effects of heavy metals to plants growing on that soil, or the possible contamination of groundwater. Thus the environmental effects of heavy metals are governed by their mobility. The solubility relationships of heavy metals in soils play a major role in the mobility of these elements in the environment.

Under certain conditions, the solubility of heavy metals in soil may increase significantly. For example, a lowering of the pH of a soil may increase the solubility of heavy metals. Waterlogging of soils, followed by reduction, may increase solubility of Mn and Fe, and hence of all metals associated with manganic and ferric oxides under aerobic conditions (Jenne, 1968). Microbial decomposition of organic materials added to a soil, may result in the release of organic compounds that may complex with and dissolve heavy metals and hence increase the availability of these metals to plants, and possibly the amount of metals that reach the groundwater. Interactions of heavy metals in soils, in particular precipitation and adsorption reactions, have to be understood, before a prediction can be made on the effect of changing soil conditions on the mobility of heavy metals in the environment.

The chemistry of Fe and Mn in soils is rather involved, in particular the redox equilibria (Mulder, 1975). The behaviour of Hg in the environment was recently discussed by Frissel & Poelstra (1975), whereas the methylation of Hg was reviewed by Lexmond et al. (1976). The chemistry and the specific adsorption of Mo in Colorado soils were studied by Vlek (1975). The mechanisms of transport and accumulation of heavy metals in soils were summarized by Harmsen (1975).

In this study, I examined the behaviour of heavy metals in soils (a) through chemical extraction and total analysis of Zn, Cd, Pb, Cu, Mn and Fe in soils collected near zinc smelters, along a river discharging mining wastes, and at a sewage disposal farm, (b) through the development of models to describe the adsorption of heavy metals in soils, and (c) through exchange adsorption studies of Zn, Cd, Cu and Pb in clay soils. This group of heavy metals includes important micronutrients (Zn, Cu, Mn and Fe) and environmental contaminants (Pb and Cd). Fe and Mn were included in the 'field' research, but not in the adsorption experiments, since the solubility of Mn and Fe in aerated soils is very low.

The results of the present study may contribute to the knowledge of the binding of heavy metals in soils, and hence to the understanding of the factors that determine the mobility of these elements in soils. The adsorption and ion-exchange models developed in this study, may be helpful in predicting the possible effects of the addition of heavy metals or other elements to soils, and the effects of changing soil conditions on the mobility of heavy metals in soils.

2 Transport and accumulation of heavy metals in soils

An effective control of heavy metals in the environment is not possible without an understanding of the factors determining the mobility of heavy metals in soils. The transport and immobilization (retention) processes governing the behaviour of heavy metals in soils are not essentially different from those governing the behaviour of other cations. But heavy metals often occur in low concentrations in soils, they form stable complexes with a large number of (organic) ligands and they enter in specific adsorption reactions more readily than alkali and alkaline earth metals.

This review will give a brief outline of transport and immobilization processes involving heavy metals in soils. I have tried to avoid duplication of existing reviews on the same subject (e.g. Mitchell, 1955; Hodgson, 1963; Jenne, 1968, Sillanpää, 1972), although some overlap is inevitable. This review concentrates on some of the most important heavy metals: Zn, Cd, Ni, Co, Cu, Pb, Fe and Mn, of which Cd and Pb are the most hazardous to human health; Fe and Mn are included because they may markedly influence the availability of other heavy metals through surface sorption and occlusion (Jenne, 1968).

2.1 TRANSPORT OF HEAVY METALS IN SOILS

Transport of heavy metals in soils may occur (1) in dissolved or suspended form, (2) through plant roots, and (3) associated with soil (micro-)organisms. Transport of dissolved compounds may take place through the soil solution (diffusion) or with the moving soil solution (mass flow or convection). Leaching of clay and organic matter results in the migration of all the metals that are associated with these particles. Transport of volatile compounds through the gas phase may occur occasionally (e.g. dimethylmercury) but will be of minor importance for the metals under consideration. Transport through the solid phase is unlikely. Moreover, solid state diffusion or lattice penetration is a bonding mechanism rather than a transport mechanism. Ion uptake by plant roots may deplete the subsurface horizon and enrich the surface horizon by decay of leaves. That process is referred to as biological enrichment of the top soil and has been observed for Cu, Pb, and Zn (Mitchell, 1955). Heavy metals may become incorporated in or sorbed on micro-organisms, which in turn may contribute to the transport of the associated metals. Earthworms and other macro-organisms may help to translocate heavy metals by mechanical (or 'biological') mixing of the soil or by incorporating metals in their tissues. Although transport through plant roots and transport associated with organisms may be important under certain conditions, attention will be focussed here on transport through the liquid phase, since the majority of the metals enter the soil in dissolved or suspended form and virtually all interactions between heavy metals and solid constituents of soil occur at the solid liquid interface.

All metal ions in aqueous solution do coordinate with water molecules, but in the presence of suitable ligands, one or more water molecules in the inner coordination sphere (primary hydration sheath) of the aquo ion may be replaced by one or more ligands. This process is referred to as complex formation and differs from 'ion pair' formation in that the metal ion and the ligand both retain their primary hydration sheath in an ion pair. The ligands surrounding a metal cation in a metal ligand complex do create an electrostatic field around the central ion, which may produce an additional bonding effect, the 'ligand field stabilization energy' (Cotton, 1964). The stability constants of metal-ion complexes are tabulated extensively by Sillen & Martell (1964, 1971).

One of the most important inorganic ligands in natural waters, apart from H_2O itself, is OH^-. The hydrolysis reaction can be described either as the proton transfer from a hydrated metal ion to the surrounding water or as the coordination of the metal ion with one or more hydroxyl groups. Most cations of heavy metals hydrolyse quite readily in aqueous solutions and many polynuclear (multinuclear) hydrolysis products are known to occur (Hunt, 1963). These polynuclear hydrolysis products are larger than the unhydrolysed species and the metal ions are less hydrated because the interaction between the central metal ions and the coordinated water molecules is diminished. As a result, polynuclear hydrolysis products may be preferentially adsorbed onto solid surfaces (Stumm & Morgan, 1970, p. 474).

Organic ligands play a major role in soil water (and generally in natural waters), because organic ligands may form stable soluble complexes (chelates) with metal ions. A chelating agent containing more than one functional group is referred to as a multidentate complex-former. Metal chelates are characterized by the formation of more than one bond between the metal and functional groups of the complexing agent, so forming a ring structure incorporating the metal ion. The number of rings formed by one molecule of chelating agent with the metal ion, the size of the rings, the nature of the donor atoms, the effects of resonance stabilization and steric relationships determine the stability of a metal chelate (Lehman, 1963). The order of chelate stability for divalent transition metal cations does compare well with the 'Irving Williams' order for most chelates (Irving & Williams, 1953):

$$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

Comparison of this series with the common logarithms of the formation constants of the divalent-metal EDTA complexes, estimated from Sillen & Martell (1964, 1971) shows that these constants are in the predicted order: Mn(-13.8), Fe(-14.3), Co(-16.2), Ni(-18.6), Cu(-18.8), Pb(-18.0), Cd(-16.5) and Zn(-16.4), where Pb and Cd are included for reference. Ethylenediaminetetraacetic acid (EDTA) is one of the best known chelating agents and has been applied to soils as an extractant for heavy metals (Lindsay, 1972a). The Irving Williams order of chelate stability can be understood with the aid of ligand field theory (Cotton & Wilkinson, 1972, p. 596). The order of chelate stability of the divalent metal complexes also compares well with the order of electronegativities of the divalent heavy metals: Cu(1.9), Pb(1.8), Ni(1.8), Co(1.8), Fe(1.8), Cd(1.7), Zn(1.6) and Mn(1.5). The electronegativity is defined as "the power of an atom in a molecule to attract electrons to itself" (Pauling, 1960), hence electronegativity is a bond property rather than a property of isolated atoms.

There are indications that dissolved heavy metal cations in soil solutions are often to a large extent associated with organic ligands (Hodgson et al., 1966). Soluble organic compounds that may coordinate with metal ions, can be divided in (1) low-molecular organic substances, (2) fulvic acids, and (3) humic acids. The low-molecular organic substances ('non-humic' substances) include polysaccharides, proteins, peptides, amino acids, polyphenols and organic acids. This group of organic compounds comprises many ligands (e.g. organic acids such as citric acid and oxalic acid) that are known to form stable chelates with metal cations. Fulvic acids are defined as the fraction of organic substances which is soluble in both dilute acid and alkaline solution, whereas humic acids are defined as the fraction soluble in dilute alkaline solution, but precipitated upon acidification. The most common donor atoms in fulvic and humic acids are oxygen in carboxyl, hydroxyl, and carbonyl groups, nitrogen in amino and azo groups, and sulfur in sulfonic acid and sulfhydryl groups. Fulvic acids generally have a lower molecular weight than humic acids, and the total acidities of fulvic acids (900 to 1400 meq/100 g) are higher than those of humic acids (500 to 870 meq/100 g). The oxygen containing functional groups that contribute to the total acidity of humic and fulvic acids, include, in order of decreasing importance COOH, phenolic, alcoholic and enolic OH, and C=0 structures (Stevenson & Ardakani, 1972). The stability constants of metal fulvic-acid complexes are given by Schnitzer & Hansen (1970) for eight divalent metal cations at two pH levels and at two ionic strenghts (I)[1]. The order of stability of the divalent metal fulvic-acid complexes at pH 3.0 and I = 0.1 was:

$$Cu > Ni > Co > Pb > Ca > Zn > Mn > Mg$$

whereas at pH 5.0 and I = 0.1 the order changed t

$$Ni > Co > Pb > Cu > Zn > Mn > Ca > Mg$$

Thus, both the Cu and Ca complexes become less stable with increasing pH than the other complexes. The stability constants decreased strongly with increasing ionic strength, but the order of the stability constants did not change (as for increasing pH). At I = 0.1 the metal fulvic-acid complexes are assumed to be mononuclear, whereas at lower ionic strength polynuclear complexes occur, the fulvic acid to metal ratio decreasing with increasing pH.

The 'suspended' metals may be defined as those metals that are retained by a 0.45 µm membrane filter. This filter size is arbitrary, but in common use (Parker, 1972). The suspended metals are associated with suspended (colloidal) particles. The fraction of suspended metals includes metal humic-acid complexes, metals associated with inorganic

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[1] The ionic strength of a solution is expressed in mol/kg or in mol/l. In this study, which concentrates on metals in dilute aqueous solutions, it is assumed that 1.0 l of solution has a mass of 1.0 kg.

particles such as clays and iron hydroxides, with organic surfaces such as of bacteria, and with complex associations of organic and inorganic substances (sludges). The fraction of suspended metals may contribute more to the total transport of metals in surface waters than in soils; especially in soils with low contents of water, these particles may become immobilized more readily than in surface waters. However, transport of suspended matter does occur in soils as well, as is evidenced by the translocation of clay in soils (clay coatings) and the processes of podzolization and lateritization.

2.2 REMOVAL OF HEAVY METALS FROM SOLUTION

Whether a dissolved or suspended metal remains in solution, depends on (1) the aqueous concentration of the metal of interest and of all competing cations, notably the other heavy metals, (2) the aqueous concentrations of all ligands, notably chelating agents, capable of forming complexes with the metal of interest, (3) the pH and the redox potential, and (4) the nature and the amount of sorption sites associated with the solid phase. These sorption sites include all sites that may be occupied by simple cations, charged or uncharged complexes.

Most solids in natural waters possess electrically charged surfaces, giving rise to electrical double layers. The charge of the surfaces may arise from ionization of complex ionogenic groups on the surface of these particles. These surface charges are often dependent on pH, the net charge being positive at low pH and negative at high pH. This behaviour may be represented as

$$\text{Surf-OH}_2^+ \rightleftarrows \text{Surf-OH} + H^+ \rightleftarrows \text{Surf-O}^- + 2H^+ \tag{1}$$

where Surf-OH denotes a reactive surface group. Most hydrated oxides of Fe, Mn, Al and Si, but also organic surfaces, exhibit such amphoteric behaviour. The protolysis of functional amino and hydroxyl groups on organic surfaces may be represented as

$$R(COOH)NH_3^+ \rightleftarrows R(COO^-)NH_3^+ + H^+ \rightleftarrows R(COO^-)NH_2 + 2H^+ \tag{2}$$

where R denotes the organic matrix. For clay minerals and some other alumino-silicates, isomorphous substitutions of Al^{3+} for Si^{4+} in the tetrahedral layer, and Mg^{2+}, Fe^{2+}, or Zn^{2+} for Al^{3+} in the octahedral layer of the mineral, give rise to a net negative surface charge which is not dependent on pH. In most mineral soils, these substitution charges make up most of the negatively charged sorption sites.

One or more of the following processes may play a role in the removal of heavy metals from solution: (1) coagulation of suspended particles, (2) precipitation or co-precipitation, (3) adsorption, and (4) solid state diffusion (lattice penetration).

Incorporation of heavy metals in biological systems such as plant roots, micro-organisms or earthworms also results in the removal of heavy metals from soil solution, and although metals can still be transported through the soil profile, they can no longer take part in physicochemical interactions in the soil. However, a study of these mechanisms of removal of heavy metals from solution is beyond the scope of the present review.

2.2.1 Coagulation of suspended particles

Metals associated with suspended particles may be removed from solution through coagulation of the particles. The stability of suspended particles generally decreases with decreasing surface potential, and with decreasing double layer thickness. For particles with a pH dependent surface charge, the stability decreases when the pH approaches the point of zero charge (PZC), i.e. the pH value for which the surface potential equals zero. Specific adsorption, especially of heavy metal cations, on the surface of suspended particles may destabilize these particles by decreasing their effective charge, or may even reverse their surface charge.

Breeuwsma (1973) defines the point of zero charge as the pH for which the amount of H^+ adsorbed per unit area equals the amount of OH^- adsorbed per unit area, and then the PZC shifts towards lower pH, when H^+ is desorbed upon specific adsorption of heavy metals. Breeuwsma further defines the iso-electric point (IEP) as the pH for which the electrokinetic potential equals zero, and, therefore, the IEP shifts to higher pH, when specific adsorption of heavy metals results in a net increase in positive charge of the particle. Parks (1967), however, defines the PZC as the pH at which the solid surface charge from all sources is zero, and defines the IEP as the PZC arising from interaction of H^+, OH^-, the solid and the water alone, contrary to the convention adopted by Breeuwsma. Here the definitions of PZC and IEP as proposed by Breeuwsma have been adopted.

The thickness of the diffuse double layer decreases with increasing salt concentration and with increasing charge of the counterions. When suspended particles become less stable they tend to form aggregates (increasing collision efficiency) and subsequently they may settle. Although the charge of clay minerals is to a large extent independent of pH, the stability of suspended clay particles also decreases with increasing concentration of salt, due to compaction of the double layer. The processes of coagulation or flocculation may result in the occlusion (or coprecipitation) of heavy metals sorbed on the surfaces of the particles involved.

2.2.2 Precipitation or coprecipitation

Precipitation of the divalent heavy metals under consideration, is not expected to be an important immobilization mechanism, since most aqueous solutions are undersaturated with respect to known solubility products involving these heavy metals. These solubility products are not always known accurately, since the conditions prevailing in soils (e.g. alternating moisture levels, changing CO_2 and O_2 pressures) favour the formation of amorphous and poorly crystallized solid phases (Lindsay, 1972b). The freshly precipitated amorphous or poorly crystallized forms are often more soluble than the more stable crystalline forms formed upon ageing, by dehydration and rearrangement of the precipitates. Of course, all soluble salts will precipitate subsequently when a soil dries, but upon rewetting these salts will dissolve readily again. Only with extreme pollution, as near metal smelters (Buchauer, 1971), may precipitation of the discrete salts become significant. When fertilizers are added to soils containing heavy metals, and locally high concentrations of phosphates or other salts are present, heavy metals may precipitate, but these precipitates would dissolve again upon uptake of the nutrients from solution by plant roots. When lime is added to a soil, carbonates or hydroxides may precipitate, whereas also a 'solid solution' of heavy-metal carbonates and calcium carbonates may be formed in the lime solution interfacial layer, which may alter (lower) the solubility of the original salt.

Concentrations of heavy metals may be much higher near negatively charged surfaces than in the bulk solution, but since the concentrations of anions are lower near such surfaces, the solution probably remains undersaturated with respect to solubility products involving these ions. When the reactive surface groups (e.g. silanol groups), are considered as 'anions' ('silicate ions'), the product of the 'silicate activity' and the heavy-metal activity in the interfacial layer may exceed the solubility product of the solid phase corresponding to the true anion (heavy metal silicate). But generally the metals will retain their primary hydration water thus precluding chemical interactions with surface groups. When a soil dries, metals that are sorbed on oxide surfaces may lose part of their primary hydration water and form chemical bonds with one or more surface hydroxyls. This process may help to explain the relatively high contents of heavy metals in iron and manganese oxides in soils. Contrary to the divalent forms, the higher-valency forms (oxidized states) of Fe and Mn do form stable oxides, often occurring as coatings on clay and other minerals, indicating that these oxides are probably formed by adsorption of hydrolysed species onto these mineral surfaces. The term 'oxides' is used as a comprehensive term for oxides, hydrous oxides and hydroxides.

Precipitation and adsorption are interconnected phenomena in soils, since most precipitates are presumably formed by surface adsorption, followed by dehydration and rearrangement of the solid phase. Occlusion of adsorbed heavy metals in growing solid phases, such as the oxides of Fe and Mn has been suggested to be one of the most important mechanisms for immobilization of these heavy metals in soils (Jenne, 1968). Through the changing moisture and redox conditions in soils, the iron and manganese oxides remain in 'active' form and the occlusion of divalent cations in the oxides results in a net negative surface charge, thus enhancing the adsorption of other cations on the surface.

When submerged soils are drained off and the redox potential increases rapidly, the soil solution possibly becomes supersaturated with respect to iron or manganese oxides, and then coprecipitation of heavy metals with iron or manganese may become of importance. This type of coprecipitation is known to occur (Ng & Bloomfield, 1961, 1962), in fact it is an analytical chemical concentration method which has been applied successfully to water samples with very low heavy metal contents (Lebedinskaya & Chuiko, 1973), and this mechanism may in part explain the occlusion of heavy metals in iron and manganese oxides in soils.

2.2.3 Adsorption

Adsorption is a general term for the uptake of material (adsorptive) from a fluid by a condensed phase (adsorbent) at the surface of which the adsorbed species (adsorbate) accumulates. Heavy metals may be adsorbed as aquo cations, or in the form of cationic, anionic or uncharged complexes. If the adsorption of one or more ionic species is accompanied by the simultaneous desorption of an equivalent amount of other ionic species, this process is called ion exchange (also: exchange adsorption or equivalent adsorption). When upon adsorption of ions less than equivalent amounts of other ions are desorbed, or none at all, this process is called superequivalent or 'excess' adsorption (also: specific adsorption). The equivalent adsorption of ionic species does not alter the fixed charge of the solid surface, but the superequivalent adsorption of ionic species may alter the effective surface charge, provided the ionic species are tightly bound to the surface and may be considered as part of the adsorbent surface. The spatial distribution of free ionic charges near a solid surface gives rise to an electric double layer. One layer of this double layer is formed by the charges fixed to the solid surface (surface charges), and the other layer is formed by the ionic charges distributed more or less diffusely in the aqueous solution in contact with the solid. The ionic charges consist of an excess of counterions, opposite in charge to the surface charge, and usually a deficit of co-ions, of the same sign as the surface charge. The depletion of co-ions accompanying the adsorption of counterions on a charged surface is called negative adsorption or ion exclusion. Counterions and co-ions in immediate contact with the surface are said to lie in a Stern layer. The nuclei of ions that retain their primary hydration sheath are said to form an outer Helmholtz (or Stern) plane, and when they become dehydrated upon adsorption they are said to form an inner Helmholtz (or Stern) plane. Ions further away from the interface form a diffuse layer (also: Gouy Chapman layer or Gouy layer).

The adsorption capacity of a solid phase is defined as the amount of adsorbate needed to occupy all adsorption sites (per unit mass of adsorbent) and the ratio of the amount of adsorbed substance to the adsorption capacity is called the surface coverage or occupancy. The collection of all adsorption sites is sometimes referred to as 'adsorption complex'. The amount of cations that can be adsorbed exchangeably by a solid phase from a solution, at specified temperature, ionic strength and pH of the solution, and ionic species involved, is called the cation-exchange capacity (CEC) of that solid phase, commonly expressed in meq/100 g or in μeq/g of solid. In an analogous way an anion-exchange capacity (AEC) can be defined. The collection of negatively charged adsorption sites, associated with the solid phase of a soil, that take part in the exchange adsorption of cations, is called cation-exchange complex of the soil. The collection of all sites able to adsorb cations or anions by ion-exchange mechanisms is sometimes referred to as 'exchange complex'.

The terms 'chemisorption' and 'physisorption', which stem from the adsorption of gases on solid surfaces, have been used in soil science literature also to describe (specific) adsorption of ionic species in soils. Chemisorption (also: chemical adsorption, surface chemical or covalent bond formation, surface complex formation) is adsorption in which the forces involved are valency forces of the same kind as those operating in the formation of chemical compounds, whereas physisorption (also: physical adsorption or van der Waals adsorption) is adsorption in which the forces involved are intermolecular forces (van der Waals forces) which do not involve a significant change in the electronic orbital patterns of the species involved (Everett, 1972). The adsorption of ions on charged surface groups may thus be called chemisorption, since van der Waals forces generally play a minor part in the adsorption of these ions, whereas the forces involved (coulombic attraction) also operate in the formation of ionic bonds. The primary hydration sheaths of the ions generally preclude direct contact between the ionic species and the surface groups and thus preclude chemical bonding. Therefore neither chemisorption nor physisorption are well suited to describe the adsorption of ionic species in soils. One of the most important features of the adsorption of ionic species from aqueous solution is that the adsorption sites generally have a net (fixed) charge and hence the adsorption of one ionic species is accompanied by the simultaneous desorption of another ionic species. Another important feature is that the replacing power of one ionic species with respect to the other differs for different ions, especially when the ions lie in a Stern layer.

The forces involved in the adsorption of ionic species at charged surfaces may be classified as long-range forces, 'intermediate'-range forces, and short-range forces. All these forces are electrostatic in origin, since they are ultimately based on Coulomb's law of attraction between unlike charges, and repulsion between like charges. The long--range forces are of the ion ion type, and form the most important attractive forces between ions in a diffuse layer and a charged surface. They are unselective since they do not distinguish between different ions of equal charge. Negative surface groups, such as SiO^- groups, ionic species and coordinated ligands, may have permanent or induced dipole moments, or higher moments (such as quadrupoles or octupoles) but the attractive forces resulting from these charge distributions are not effective over a long range. But when ions approach the adsorbent surface, these attractive forces may become effective and may give rise to ion selective or ion specific phenomena: to differences in adsorption behaviour between different ionic species of equal charge. Forces that are effective over an intermediate range include ion dipole and ion induced-dipole interactions. The short range forces are of the dipole dipole type (orientation), the dipole induced-dipole type (induction), or of the 'oscillating' dipole type (dispersion). The attractive forces between neutral atoms or molecules resulting from dispersion interactions are often called London forces, whereas all three types of short range forces are collectively called London van der Waals forces or van der Waals forces. The induction and dispersion interactions depend on the polarizabilities of the elementary particles involved. The polarizability of an elementary particle is a measure of the ease with which a dipole moment can be induced in the particle. The polarizability increases with increasing mass, size and number of electrons in the outer shell of the particle (Margenau, 1939). Differences in polarizability may lead to ion-exchange selectivity, and the presence of polarizable ligands surrounding the central metal cation may enhance these differences in selectivity. The van der Waals forces may play a part in the adsorption of uncharged complexes, polynuclear hydrolysis products and heavy metal humic-acid or heavy metal fulvic-acid complexes. Complexes of heavy metals and organic ligands may also be adsorbed preferentially at the solid solution interface, because the apolar hydrocarbon parts of the organic ligands have low affinities for the polar aqueous phase. Oxides are generally strong adsorbents for hydrocarbons and this tendency increases with increasing chain length of the hydrocarbon group. Differences in ion solvent interactions, reflected in different enthalpies and entropies of hydration, and differences in ionic radii, may also result in ion selectivity, since they determine the distance of closest approach between the hydrated ion and the surface site. Taking into consideration that the dielectric constant of water decreases rapidly near most mineral surfaces, and given the nature of the short-range interactions, it can be understood that small differences in position of ions near the surface may result in large differences in selectivity between ions.

Other types of bonding that are effective over a short range include hydrogen bonding, coordinate bond formation or ligand exchange, and, of course, chemical bond formation between the adsorbate and the surface groups.

The hydrogen atom can form one covalent bond, and one bond, the 'hydrogen-bond', which is largely ionic in character and which is formed between the more negative atoms. Hydrogen bonds may play a part in the adsorption of organic ligands associated with heavy metals on oxide surfaces. The ability of hydrated heavy metal ions to form hydrogen bonds with surface groups may be correlated with the first hydrolysis constants of the heavy metals, since the hydrolysis reaction can be described as the proton transfer from a coordinated water molecule to a surrounding molecule, here a surface hydroxyl.

Coordinate bond formation or ligand exchange is of particular importance for transition metals (Cotton & Wilkinson, 1974). A coordinate bond between a heavy metal and a solid surface may be established by exchange of a ligand, such as H_2O, from the inner coordination sphere of the metal ion for a surface group, for example $-OH$ or $-NH_2$. These coordinate bonds may play an important part in the adsorption of uncharged complexes or in the superequivalent adsorption of ionic complexes.

Heavy metals generally have high affinities for adsorption sites associated with organic matter and oxide surfaces, and they have a high replacing power over alkali and alkaline earth metals. The selective uptake of heavy metals is sometimes referred to as 'specific' adsorption. The word 'specific' is used here to indicate that a phenomenon depends on the chemical properties of the ion rather than on its charge; in the latter case the word 'regular' may be used. These 'chemical' properties of an ion include its (hydrated) ionic radius, polarizability, ionization potential, electron affinity, electronegativity, enthalpy and entropy of hydration, hydrolysis constants and its ability to form coordinate bonds, among others. The term specific adsorption is sometimes used for all types of adsorption other than regular (low selectivity) ion exchange, and may thus refer to both high selectivity or superequivalent adsorption. Selectivity may also be due to steric factors, as in condensation of clay platelets: most divalent cations compete on an approximately even basis for the planar adsorption sites on clay minerals, but cations that become occluded ('sandwiched') between condensating clay platelets may become difficult to replace.

2.2.4 Solid-state diffusion

Solid-state diffusion (lattice penetration) into naturally occurring zeolites and into minerals that form 'open' surface structures in contact with aqueous solution, such as feldspars and freshly precipitated oxides, may be of some importance as a mechanism of immobilization of heavy metals in soils. Exchangeable divalent cations, as of Mg, Ni, Cu, Co and Zn, may become embedded, upon dehydration, in the 'hexagonal holes' in the surface of montmorillonite, and from there they may penetrate 'empty' positions in the octahedral layer and thus lower the layer charge of the clay mineral. This form of lattice penetration is known to occur, but would not be significant at temperatures and moisture conditions prevailing in soils (McBride & Mortland, 1974).

3 Survey of soils with raised contents of heavy metals

3.1 INTRODUCTION

The contents of heavy metals in non-polluted soils generally reflect those of the parent material from which the soils are formed (Mitchell, 1955). The content of trace elements in rocks and minerals (Goldschmidt, 1954) and soils (Swaine, 1955; Vinogradov, 1959) has been compiled in tables. The distribution of heavy metals in soil profiles is often rather uniform, although plant extraction and subsequent surface enrichment, (micro-)biological activity, leaching of colloidal and dissolved compounds and oxidation-reduction processes may lead to a redistribution of these elements in soil profiles. Unlike the total content of heavy metals, the 'available' metal content often decreases strongly with depth and may be correlated with pH, redox potential, contents of organic matter and clay, cation-exchange capacity and other factors. By 'available' is usually meant the availability to plants growing on that soil. In this chapter the available fraction is taken as the fraction that can be extracted with a near-neutral salt solution, such as $CaCl_2$ or $BaCl_2$. The available fraction, can be subdivided into a water-soluble and a salt-extractable fraction, where the latter is the fraction that can be extracted with a near neutral salt solution but not with water. The water soluble fraction includes easily soluble salts and the salt-extractable fraction consists of exchangeably adsorbed forms of the metal in question. The 'unavailable' fraction may be distinguished into an acid-extractable and a residual fraction. The acid-extractable fraction is the fraction that can be extracted with a 0.1 N HCl solution but not with a near neutral salt solution, and includes non-exchangeably adsorbed and organically complexed forms of the metal, Metals associated with oxides of Fe and Mn may dissolve to some extent in dilute acid, but, generally other extractants (reducing and complexing agents) are used to extract these metals from soils. For Mn, hydroquinone (0.2%) may be added to a near neutral salt solution to determine the fraction of 'active' Mn, which includes both the salt-extractable and the easily reducible (hydroquinone) fractions. In the same way 'free' iron and manganese oxides may be determined with a solution containing sodium dithionite (reducing agent), sodium bicarbonate (pH buffer) and sodium citrate (chelating agent). The residual fraction is the fraction that cannot be extracted from soil with dilute acid, and is found as the difference between the total metal content and the sum of the acid-, salt-, and water-extractable fractions. The total content of a certain metal in a soil sample is obtained by digesting the soil sample in a mixture of HNO_3 and $HClO_4$. Although quartz and some other minerals, such as chromite and zircon (Jackson, 1958, p. 273), do not dissolve in a mixture of HNO_3 and $HClO_4$, this treatment was assumed to be sufficient to bring all heavy metals of interest in solution. The residual fraction is thought to include heavy metals that are part of the structure of stable minerals and metals associated with insoluble oxides of Fe and Mn, and possibly Al and Si. The residual fraction is the most stable to weathering.

This chapter presents some data on the distribution and availability of Zn, Cd, Pb, Cu, Fe and Mn in soils with high contents of heavy metals. These soils can be grouped according to the main source of heavy metals: (1) soils near a zinc-smelter, (2) a soil along a river passing through an area of former zinc and lead mining, situated a few kilometres upstream, and (3) soils in a sewage farm where sewage water of domestic and industrial origin is put on the land. These groups represent the main sources of metal enrichment in soils: aerial fallout, polluted surface water, and sewage water and sludges.

3.2 MATERIALS AND METHODS

Analytical methods are mentioned briefly only, since most are routine procedures for plant and soil materials. Plant materials were dried for 48 hours at 70 °C, ground in a mortar, and digested in a 40:4:1 volume mixture of HNO_3, $HClO_4$ and H_2SO_4 (Schaumlöffel, 1960). Soil materials were dried at room temperature to constant weight, sieved over a 2-mm sieve, and digested in a 3:1 volume mixture of HNO_3 and $HClO_4$. Some H_2SO_4 was added to this mixture to prevent the formation of highly explosive perchlorates. No H_2SO_4 was added when Pb had to be determined, in order to prevent loss of Pb, in the form of $PbSO_4$, during digestion. Mn, Pb, Cd and Zn were determined by atomic absorption spectrophotometry (AAS) using an air-acetylene flame. An excess of La was added to samples in which Mn was determined to suppress possible interferences by Mg, Ca, Al, and Si. Iron was determined spectrophotometrically with o-phenanthroline in citric acid solution, to which p-methylaminephenol sulfate was added as a reducing agent. Copper was determined spectrophotometrically with zincdibenzyldithiocarbamate after extraction with CCl_4. Incidentally, Fe and Cu were also determined by AAS, using an air-acetylene flame.

In the shaking experiments increasing amounts of soil, ranging from 25 to 250 g, were added to 250 ml of demineralized water in polyethylene bottles and shaken continuously in a mechanical linear shaker. Cellulose dialysis bags, with an average pore diameter of 48 Å, were used to sample the solution, since centrifuging at 20 000 rpm and filtration did not give reproducible results. Besides the heavy metals, Mg was determined by AAS with an air-acetylene flame, and Na, K and Ca were determined by emission spectrophotometry with an air-acetylene flame for Ca and an air-propane flame for Na and K.

For the determination of water-, salt-, and acid-extractable metal fractions, 20 to 50 g of soil was mixed with 50 ml of purified quartz sand, put in a percolation tube, and closed at the lower end with glass wool and about 2 cm of quartz sand. The soils were percolated with 250 ml of a leaching solution by placing a flask upside down in the tube. To equilibrate, the soil was first saturated with the leaching solution and left standing for two hours. Then the cock was opened and the leachate was collected drop by drop in about two hours. Zinc and other metals were determined directly in the leachate by AAS after pH adjustment and matching the matrix of test and reference samples.

Sewage sludges were treated like the soils after drying and grinding in a mortar.

Sewage and drainage water were filtered over a 0.45-µm membrane filter. The filters were digested in an acid mixture of HNO_3, $HClO_4$ and H_2SO_4, including the addition of sodium nitrite in the last stage of digestion, to prevent the formation of insoluble manganese oxides. The filtrates (2 - 4 l) were evaporated to dryness in platinum crucibles on a water bath, and then dry-ashed in a furnace. The ash was dissolved in HCl and filtered into a volumetric flask. The filter paper was then ashed, dissolved in HF, and heated to dryness. The remaining material was dissolved in HCl, filtered, and added to the rest of the material in the volumetric flask. The initial concentrations were concentrated 20 to 40 times by this treatment.

3.3 SOILS NEAR ZINC SMELTERS

Soils were sampled near two zinc smelters, both in the 'Campine', an area of rather poor aeolic sands. The area stretches across the Dutch-Belgian border, in the Belgian Provinces of Antwerp and Limburg, and the Dutch Province of North Brabant. One zinc smelter is near Overpelt, Belgium, and the other is at Budel-Dorplein, the Netherlands.

There are several ways in which Zn and other metals may have reached the soils near the smelters. Exhaust fumes from the smelters do contain metal oxides which reach the soil either by direct precipitation or with rainfall. Zinc concentrates (enriched Zn ores) are stored in the form of finely ground powder, and dust may be blown directly to the soils close to the smelter. The solid wastes from the zinc smelter (sinters) are stored nearby and may contribute to the burden of heavy metals in soils and surface waters. Finally, the waste water produced by the smelters and the contact factories is acid (pH 1.0 - 1.5) and rich in dissolved metals. Most of these metals are precipitated as the respective hydroxides with a $Ca(OH)_2$ suspension, increasing the pH of the solution and often forming gypsum. Although appreciable amounts of heavy metals are precipitated in this way, the surface waters near the smelters are still rather rich in dissolved metals.

3.3.1 Zinc in surface waters around zinc smelters

The Dutch zinc smelter discharges its waste water in a fen, the 'Vogelpeel', where pH is low and zinc and cadmium concentrations[2] are high as can be seen from Table 1. The 'Tungelroysche Beek' is the brook discharging water from the fens around the smelter complex and Table 1 shows that pH increases downstream of the Vogelpeel fen (Sites 6 and 12). There is probably no solute transfer from the Vogelpeel fen to the neighbouring fen (upstream), the 'Vispeel', although the Tungelroysche Beek passes through both fens. Therefore it is likely that Zn and Cd reach the Vispeel fen solely by aerial fallout. The zinc and cadmium concentrations both decrease with increasing pH (Fig. 1) but a quantitative relationship is not easy to establish.

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[2] Mass concentration (mg/l) and substance concentration (mol/l) are both called 'concentration'. The relation between them is given by the molar mass (g/mol) of the particles involved.

Table 1. Zinc and cadmium in surface waters near the zinc smelter at Budel-Dorplein; estimated from Duijsens & Hoekstra (1973). The logarithm of the aqueous zinc concentration (mol/l) is denoted by log Zn.

Site	pH	Zn-conc (mg/l)	log Zn	Cd-conc (mg/l)
1. (Vispeel)	6.97	2.40	-4.44	< 0.10
2. (Vogelpeel)	4.34	84.40	-2.89	0.81
6. (Tungelroysche Beek)	5.60	39.25	-3.22	0.35
12. (Tungelroysche Beek)	6.44	8.26	-3.90	< 0.10

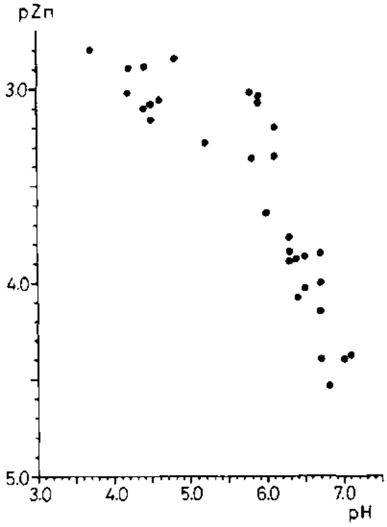

Fig. 1. Negative logarithm of concentration of zinc, pZn, in natural waters near the zinc smelter at Budel-Dorplein, plotted against pH.

It may be assumed that the relationship between the logarithm[3] of the zinc activity and pH is of the form

$$\log \mathrm{Zn} + 2\ \mathrm{pH} = K \qquad (3)$$

If so, the constant K would be about 9.3, for the data from the Vispeel fen, and for an ionic strength of about 0.02 (Kielland, 1937). Comparison of the value of 9.3 with values estimated from Sillen & Martell (1964, 1971) for different zinc salts, shows that the constant in Eq. 3 ranges from 11.5 for stable ZnO to 12.6 for amorphous $Zn(OH)_2$, so zinc oxides and hydroxides are probably too soluble to persist in solution. If $Zn_3(PO_4)_2$ be the solid phase, the total phosphate activity in solution would be about 0.6 mmol/l. No phosphate data for the Vispeel fen are available but this value seems rather high for

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[3] The logarithm to base 10 (common logarithm) may also be denoted by $\log_{10}$ (or lg) to avoid confusion with logarithms to other bases. In the presence study, only common logarithms, denoted by 'log', and natural logarithms (to base e), denoted by 'ln', are used.

natural waters (Parker, 1972) and therefore the solution is probably undersaturated with respect to phosphates too. If $ZnCO_3$ be the solid phase involved, the data for the Vispeel suggest that log CO_3^{2-} = -6.18 and log HCO_3^- = -2.82, where the logarithm of the solubility product of $ZnCO_3$, log K_{s0}, is taken as -10.84. The alkalinity, (Alk), is defined as

$$(Alk) = (OH^-) + (HCO_3^-) + 2(CO_3^{2-}) - (H^+) \qquad (4)$$

where round brackets denote concentrations (mol/l). At pH 7, the alkalinity is practically solely determined by the HCO_3^- concentration, hence

$$\log Alk \simeq \log HCO_3 = -2.77$$

where the symbol '≃' denotes[4] 'approximately equal to', and where the activity coefficient for HCO_3^- has been set at 0.9 (I = 0.02). The value obtained for the alkalinity, 1.70 mmol/l, is rather high, since Zn, which furnishes most of the alkalinity, is present at a much lower concentration: 0.04 mmol/l. The logarithm of the partial CO_2 pressure in equilibrium with $ZnCO_3$ is estimated to be -1.98 for the present system, corresponding to a volume fraction of 1 % CO_2, which is higher than in the atmosphere: 0.03 % CO_2. If CO_2 is produced in the Vispeel fen, as a result of metabolic activities, the average aqueous CO_2 concentration may be higher than the concentration in equilibrium with the atmosphere, through slow diffusion of CO_2 in water: the diffusion coefficient of CO_2 in H_2O is about 1.56 $cm^2 day^{-1}$ (Andrussow, 1969, p. 614). Although the solution may be supersaturated with CO_2, a value of 1 % seems rather high for a shallow fen like the Vispeel. The high alkalinity required and the supersaturation with CO_2 indicate that $ZnCO_3$ is not likely to determine Zn^{2+} and H^+ activities in solution.

If Zn reaches the Vispeel by aerial fallout, as ZnO or $Zn(OH)_2$, it may be assumed that the electroneutrality condition for the system can be represented as

$$2(Zn^{2+}) = (Alk) \qquad (5)$$

The zinc and pH data for the Vispeel show that in equilibrium with atmospheric CO_2

$$\log c^+ = \log (H^+ + 2\ Zn^{2+}) = -4.14$$

whereas

$$\log c^- = \log (OH^- + HCO_3^- + 2\ CO_3^{2-}) = -4.31$$

where c^+ and c^- denote the concentrations of cations and anions, respectively. The agreement between log c^+ and log c^- is rather good and confirms that the electroneutrality condition for the system can be represented by Eq. 5.

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[4] This symbol may also be used to denote 'asymptotically equal to', but this notion does not occur in the present study, so there are no grounds for confusion.

Little is known about the solubility of zinc silicates, but they may play a part in determining zinc solubilities in soil solutions (Lindsay, 1972a; Tiller & Pickering, 1974). Norvell & Lindsay (1970) estimated the log equilibrium constant for the formation of $ZnSiO_3$ in equilibrium with SiO_2 (quartz) to be -17.9, which yields a value of 10.1 for the constant in Eq. 3, suggesting that the solution is undersaturated with $ZnSiO_3$ as well, but the value of the equilibrium constant is uncertain.

It may be concluded that most common zinc minerals, with the possible exception of silicates, are too soluble to persist in the Vispeel fen, and that the relationship between dissolved zinc and pH is given by Eq. 5 in first approximation.

Table 1 shows that pH is very low in the Vogelpeel fen (Site 2), through the presence of H_2SO_4, and increases downstream of the Vogelpeel (Sites 6 and 12), mainly by mixing with other brooks that join the Tungelroysche Beek on its way to the River Meuse. The aqueous Zn concentrations decrease downstream of the Vogelpeel fen, mainly by dilution with other brooks, but sorption processes and sedimentation of colloidal particles, and possibly precipitation or coprecipitation may play a part in the removal of Zn from solution as well. The zinc concentrations at Sites 2, 6 and 12, exceed the estimated values for alkalinity, probably through the presence of other anions such as chlorides or sulfates, which have to be included in the electroneutrality conditions for the surface water at these sites.

Waste water from the zinc smelter at Overpelt (Belgium) is discharged in the River 'Dommel', a small river that enters the Netherlands Province of North Brabant a few kilometres downstream of the zinc smelter. Considerable amounts of zinc have been discharged in the course of time. Soils at Waalre (North Brabant), that were flooded regularly till 1940 with water from the Dommel, are much higher in acetic-acid extractable zinc (684 ppm) than soils that were not flooded (21 ppm). The soils rich in zinc are used as permanent pasture and the cultivation of arable crops on those soils is possible only after heavy liming: beets did not grow at all without liming (Ch.H. Henkens, 1961).

3.3.2 Heavy metals in soils and vegetation at Overpelt

Metal oxides in exhaust fumes of metal smelters can be carried large distances, according to weather conditions, height of emission and the size and chemical nature of the particles. Soils, grass and trees were sampled 1 - 2 kilometres north-east (NE) of the zinc smelter at Overpelt (Belgium), in the direction of the prevailing wind. Grass samples included leaves and stems, sampled over an area of several square metres, and leaf samples of trees were taken from the 'exposed' side of the trees, i.e. the side towards the smelter. Mass fractions of Zn in unwashed grass and tree samples were 2000 - 4000 ppm (grass) and 2000 - 7000 ppm (trees) 1 km NE of the smelter, and 800 ppm (grass) and 1000 - 4000 ppm (trees) 2 km NE of the smelter, and mass fractions of Cd were 20 ppm (grass) and 20 - 40 ppm (trees) 1 km NE of the smelter, and 10 ppm (grass) and 10-15 ppm (trees) 2 km NE of the smelter, thus showing a marked decrease in metal content with increasing distance to the smelter. The foliar accumulation of Zn and Cd differed for different trees: 1 km NE of the smelter (Fig. 2), birch trees (*Betula verrucosa*) contained Zn at 5000 - 7000 ppm and Cd at 30 - 40 ppm, whereas oak (*Quercus*

Fig. 2. Vegetation 1 km north-east of the zinc smelter at Overpelt. Photograph Rein Heij.

robur) and maple (*Acer campestre*) contained Zn at about 2500 ppm and Cd at 15 - 20 ppm. The differences between birch and oak were even more pronounced 2 km NE of the smelter, where birch contained Zn at about 4000 ppm and oak only at about 1000 ppm.

Buchauer (1973) studied the contamination of soil and vegetation around a zinc smelter in Palmerton, Pennsylvania, and reported foliar contents of Zn and Cd in birch (*Betula lenta*) to be consistently higher than in oak (*Quercus prinus* and *Quercus rubra*) and maple (*Acer rubrum*), whereas foliar metal contents were of the same order in oak and maple. In an earlier report, Buchauer (1971) suggested that 50 to 80% of foliar metals near a smelter were due to foliar intake rather than uptake from soil. Seedlings grown on a soil low in Zn (300 - 100 ppm) but exposed to high ambient levels of metal oxides, exhibited no signs of toxicity, even though contents of Zn and Cd in leaves (2120 and 38 ppm, respectively) were extremely high, but seedlings grown on a soil rich in zinc (2.0 - 0.2%) all died, whether they were exposed to high aerial loads of metal or not. Buchauer concluded that ambient metal oxides entering the leaves directly, possibly through the stomatal apertures, largely remain biologically inert, in contrast to metals entering via root uptake, which can produce immediate and significant toxic effects.

Little and Martin (1972) measured Zn, Cd and Pb contents in unwashed elm (*Ulmus glabra*) and hawthorn (*Crataegus monogyna*) leaves near a zinc smelter in Avonmouth, England, and metal contents were found to be consistently higher in elm leaves (about 4000 ppm 1 km east of the smelter) than in hawthorn leaves (about 2000 ppm 1 km east of the smelter). They assumed that elm leaves, being rough and hairy, were more effective in retaining surface deposits of aerial metals, whereas hawthorn leaves are shiny and smoother. Washing of elm leaves with a strong detergent solution in deionized water resulted in the removal of about 28% of foliar Zn and Cd, indicating that much of these metals penetrated the leaves. Although the aerodynamics of metal aerosols probably plays an important part in explaining the differences in foliar metal contents reported by Little & Martin (1972), the large differences in foliar metal contents between birch and oak, sampled from the same location NE of the zinc smelter at Overpelt, cannot be so explained, since both types of leaves are rather smooth. Denaeyer-De Smet (1970) also found high foliar contents of Zn (1300 ppm) in birch (*Betula verrucosa*) and low contents (169 ppm) in oak (*Quercus robur*) grown on soils high in Zn, and the author suggested that the difference was due to active exclusion of zinc by oak.

Aerodynamics of ambient metal oxides, direct uptake of aerosols through stomata, active uptake or exclusion by roots, transport of metals through cell walls, and amount and 'availability' of heavy metals in soils all help to determine foliar contents of metals, whereas root uptake probably largely determines toxicity.

Metal contents of topsoils (0 - 10 cm depth) 1 km NE of the zinc smelter at Overpelt averaged for Zn 1950 (80) ppm, Cd 25.0 (0.2) ppm, Pb 510 (16) ppm, and Cu 100 (70) ppm, where the average contents in the earth's crust (Goldschmidt, 1954) are given in parenthesis. The average metal contents of the earth's crust probably exceed the metal contents of the poor aeolic sands in the Overpelt area, but they are included for reference, to show that the heavy metal contents are high in these soils, the enrichment being most pronounced for Zn and Cd. Metal contents 2 km NE of the smelter averaged for Zn 320 ppm, Cd 5.3 ppm, Pb 140 ppm and Cu 28 ppm. All metal contents decreased with distance to the zinc smelter. The mass ratio of Zn to Cd in grass and trees averaged 125, and in soil 75, suggesting that the uptake of Zn by plant roots is favoured over Cd, or that Cd is more mobile in soil than Zn.

One soil profile 1 km NE of the zinc smelter, was sampled to 95 cm depth and analysed for Zn, Cu, Pb and Cd, and loss on ignition (Fig. 3). The soil was a weakly developed podzol as is reflected by the loss on ignition. All metal contents were highest in the surface 0 - 5 cm and decreased with depth, as would be expected with metal enrichment from aerial fallout. The similarity between the distributions of heavy metals and loss on ignition may indicate that the adsorption complex, which is mainly organic matter in these soils, is saturated with heavy metals. If indeed the composition of the adsorption complex be in equilibrium with the average composition of the soil solution, metals added to the soil would be no longer retained by the soil through adsorption mechanisms, and thus leach down to the groundwater. Only iron and manganese oxides may provide a 'sink' for heavy metals, but this mechanism of immobilization is slow.

Although differences between metals are small, Fig. 3 shows that Cu was most strongly accumulated in the topsoil, Cd most leached and Zn and Pb were intermediate. Assuming that the original contents of heavy metals in the parent material were small, as is suggested by the low values in the lower part of the profile, the order of mobility of the

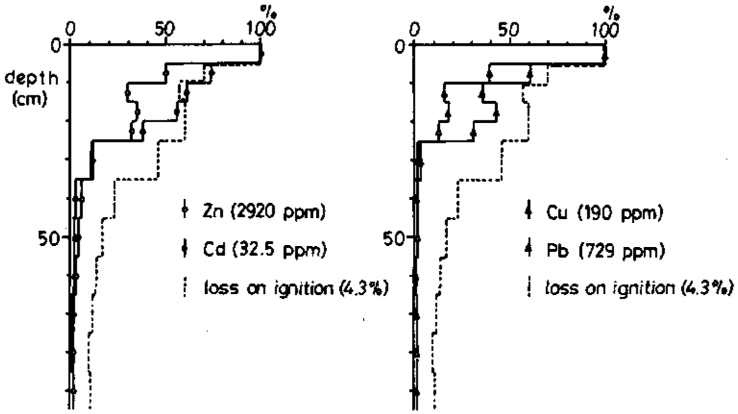

Fig. 3. Mass fractions of heavy metals and loss on ignition in a soil 1 km NE of the zinc smelter at Overpelt, plotted as percentage of their maxima with depth. Maxima are given in parenthesis; loss on ignition is expressed as percentage (g/100 g soil).

metals, expressed as the metal content in the 10 - 20 cm layer divided by the metal content in the 0 - 10 cm layer, reads Cd > Pb, Zn > Cu. From metal contents of surface soils determined at different distances from a mine dump near Littfeld, Germany (Ernst et al., 1974), the mobilities of the metals can be estimated to decrease in the order Cd > Zn > Cu > Pb. Lagerwerff et al. (1973) studied the accumulation of Cd, Cu, Pb and Zn in soil and vegetation near a smelter at Galena, Kansas. Comparison of contents of heavy metals extractable with 1 N HCl from uncontaminated soils, for instance protected by houses covering the sampling sites, and adjacent soils, exposed to aerial contamination, showed that the mobility of these metals decreased in the order Cu > Cd > Pb > Zn. If leaching with HCl and digestion in a mixture of HNO_3 and $HClO_4$ yield comparable results, the mobility of Cu would be higher in the Galena soils than in the Overpelt and Littfeld soils. The Cu contents in the soils studied by Lagerwerff et al. (1973) were lower (about 12 ppm) than in the other soils (200 - 600 ppm), and therefore the displacement of a small amount of Cu would have a much larger effect on the distribution of Cu in the Galena soils than in the other soils. But when the total contents of metals are low, the residual fractions are generally large and the metals may be expected to be almost immobile. Metal enrichment by aerial fallout will primarily result in an increase in 'available' metals and hence increase the mobility.

Elements such as Cu, which form stable complexes with organic matter may accumulate in A_1 horizons, thus showing a low mobility. But percolation of these soils with a solution containing organic ligands that form soluble complexes with Cu may leach large amounts of Cu, thus suggesting that Cu is mobile in soils. So the distribution of heavy metals with depth in a soil profile as presented in Fig. 3 is not sufficient as a measure of mobility of these elements in soils, and additional information is needed about the form in which the metals are present in the soil, and about leaching conditions.

3.3.3 Experiments with Overpelt soil

To obtain some information about the form in which zinc and other metals are present in soils near the zinc smelter at Overpelt, soils were sampled (A_1 horizon only) 1 km NE of the smelter, and subsamples were shaken with water in soil/water ratios ranging from 1.0 to 0.1. When a precipitate determines the zinc solubility, the zinc activities in all solutions eventually reach the same value, but when zinc is adsorbed by the soil, the zinc activity decreases with decreasing soil/water ratios. The zinc concentration inside a dialysis bag of average pore diameter 48 Å, in equilibrium with a soil solution, was taken as the concentration of 'dissolved' zinc. Part of the (organic) anions, associated with Zn^{2+} in the soil solution would not pass through the membrane wall, thus giving rise to Donnan equilibria. Aqueous zinc concentrations in the centrifugates decreased steadily with increasing frequency of rotation, but even at 20000 rpm for half an hour the zinc concentrations in the centrifugates were consistently higher, by a factor 1.4, than in the dialysates, suggesting that part of the zinc was associated with large (organic) anions not being removed from solution by centrifugation. A disadvantage of the use of dialysis bags was the time for equilibration: the concentration gradient between the inner and outer solution becomes zero at infinite time only.

The experiments were in several series that differed in equilibration times and soil/solution ratios. Soil samples were shaken at a frequency of about 100 cycles per minute in a linear shaker. Two different mechanisms seemed to control the kinetics of zinc solution (Fig. 4): a rapid increase during the first day followed by a much slower increase over several weeks. The rapid increase seemed to follow first order kinetics, probably due to solution of readily soluble salts and attainment of equilibrium between the solution inside the dialysis bag and the bulk solution. Afterwards the zinc concentration did not reach a constant value but continued to increase slowly perhaps by a slow solution, approaching zeroth order kinetics, but was more likely to be by breakdown of organic matter as a result of the shaking.

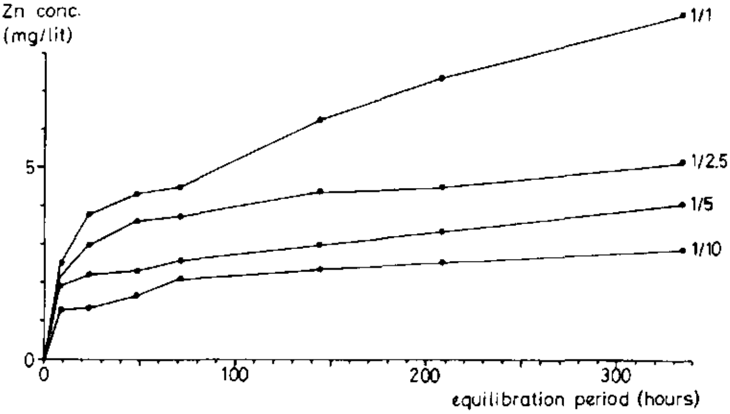

Fig. 4. Solution of Zn as a function of time, for different mass ratios of soil to solution: 1/1, 1/2.5, 1/5 and 1/10.

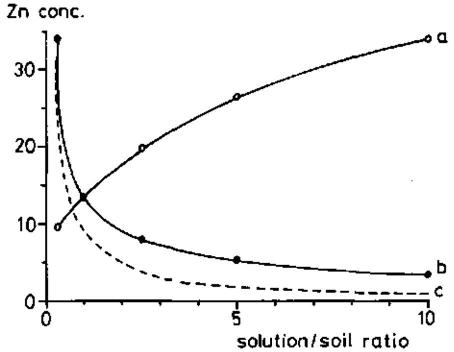

Fig. 5. The amount of Zn (mg/kg soil) dissolved during equilibration (Curve a), and the equilibrium concentrations (mg/l) of Zn in solution (Curve b) for different solution/soil ratios. The Zn concentrations for dilution of an initial amount of 9.5 mg/kg are plotted for reference (Curve c).

The zinc concentrations decreased with increasing solution/soil ratio, but less than by simple dilution of the amount initially in solution, as can be seen from Fig. 5. Data for the 'saturated' soil solution, corresponding to a solution/soil ratio of 0.3, have been included in Fig. 5. The total amount of zinc released per unit mass of soil increased with increasing water/soil ratio, perhaps by solution of one or more solid phases, increasing the zinc concentration either directly by releasing Zn associated with these solid phases or indirectly by desorbing exchangeably adsorbed Zn. The mean[5] concentrations of dissolved Zn in Fig. 5 clearly show the effect of dilution and therefore it may be assumed that the increase in dissolved zinc is caused by desorption of adsorbed Zn, rather than by solution of zinc minerals. Specific adsorption as complexes with organic matter may depend upon individual ion activities, thus releasing Zn and other metals upon dilution.

In addition to the 'shaking' experiments, Perspex tubes ('columns') were filled with soil material (A_1 horizon), taken 1 km NE of the smelter at Overpelt, saturated with demineralized water and left standing, to obtain the saturated soil solution and to examine the effect of lowering the redox potential on concentration of Zn and of other metals in solution. Each column contained a set of thin perforated tubes at intervals of 5 cm, through which the soil solution was sampled after 10, 36 and 61 days of equilibration at 10 depths. After acidification and filtration of the samples, Zn, Cd, Mn and Fe were measured in the filtrates by atomic absorption spectrophotometry (Table 2). One soil column consisted of 11 separate segments each 5 cm long and provided with a thin perforated tube. After equilibration for 63 days, redox potential, E_H, and pH were determined in each column segment. The mean value of the redox potential was 5 mV with a standard deviation of 34 mV. The negative logarithm of the electron activity, pe, was estimated to be 0.08 with a standard deviation of 0.58, from the relation pe = 16.92 E_H. Although the standard deviation of E_H was rather high (34 mV), this is not exceptional for soil samples (van Breemen, 1969). The mean value of the pH was 5.22, standard deviation 0.05. With the prevailing pH and E_H all O_2, NO_3^- and Mn^{IV} would be reduced (Takai &

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[5] 'Mean' stands for 'arithmetic mean', unless otherwise stated. In this sense, it is synonymous to 'average'.

Table 2. Metal concentrations (mg/l) of the soil solution of a soil 'column', after different periods of equilibration with demineralized water. All metal concentrations represent mean values for 10 depths. Values in parenthesis represent the relative change in concentration.

Element	Period of equilibration		
	10 days	36 days	61 days
Zn	30.5 (1.00)	33.1 (1.09)	33.5 (1.10)
Fe	4.91 (1.00)	6.04 (1.23)	6.38 (1.30)
Mn	3.97 (1.00)	4.20 (1.06)	4.27 (1.08)
Cd	0.334 (1.00)	0.343 (1.03)	0.345 (1.03)

Kamura, 1966), and virtually all Fe in solution would be present as Fe^{2+}, since the reaction

$$Fe^{3+} + e^- \rightleftarrows Fe^{2+} \tag{6}$$

has a log formation constant of about 13.02 (Sillen & Martell, 1964). The solution-reduction of ferric iron can be represented by

$$Fe^{III}(s) + e^- \rightleftarrows Fe^{2+} + 3\ OH^- \tag{7}$$

where $Fe^{III}(s)$ denotes Fe_2O_3 or FeOOH. With

$$\log K_{s0} = \log Fe^{3+} + 3\ pH - 42.00 \tag{8}$$

it follows that

$$\log Fe^{2+} + pe + 3\ pH = \log K_{s0} + 55.02. \tag{9}$$

Inserting $\log Fe^{2+} = -3.94$, i.e. neglecting an activity correction, pe = 0.08 and pH = 5.22 in Eq. 9 it follows that $\log K_{s0} = -43.22$, which is intermediate between $\log K_{s0}$ values listed for α-Fe_2O_3 (hematite), -42.5, and α-FeOOH (goethite), -44.0. So the increase in ferrous iron in solution was probably due to reduction of poorly crystallized hydrated ferric oxides, 'limonites' (van Breemen, 1969). Unlike Fe, aqueous Mn would not have increased by reduction of Mn^{IV}. If reduction of Mn^{IV} (manganite, pyrolusite) played a role, it would be initially, because as soon as the aqueous concentration of Fe starts to increase, redox potentials are too low for Mn^{IV} to persist. Zinc and cadmium were not involved in redox processes under the conditions prevailing in the soils and the aqueous concentrations were too low to be in equilibrium with the hydroxides, carbonates or phosphates. So the increase in aqueous Zn and Cd, as well as the increase in Mn would be caused by the reduction of Fe^{III}. The reduction of Fe^{III} may increase the aqueous concentrations of other metals either directly by releasing metals associated with ferric oxides, or indirectly by ion exchange. Because of the low ionic strength of the solution, $I \simeq 0.004$, the adsorption of monovalent cations was probably very small and the adsorption complex would be mainly saturated with divalent cations. If the increase of dissolved metals other than Fe^{2+} be due to desorption of adsorbed metals by Fe^{2+}, the preference of the adsorption complex for Fe^{2+} relative to the other divalent cations (R) may be estimated from

$$K_{Fe/R} = \bar{c}_{Fe}\ c_R/\bar{c}_R\ c_{Fe} \qquad (10)$$

where bars denote the adsorbed phase and where all concentrations are in meq/l. Calculations based on initial and final concentrations of Fe^{2+} of 0.176 and 0.228 meq/l (Table 2), on initial concentrations of R ranging from 1.5 to 2.0 meq/l, on a relative increase in concentrations of R of 10% (Table 2), and on cation-exchange capacities ranging from 4.2 to 5.6 meq/100 g soil, yield $K_{Fe/R}$ ranging from 0.04 to 0.09. Thus other divalent cations, mainly Zn^{2+}, are preferred by the adsorption complex, in qualitative agreement with the order of chelate stability

$$Zn^{II}\ (16.4),\ Cd^{II}\ (16.5) > Fe^{II}\ (14.3),\ Mn^{II}\ (13.8)$$

where Roman numerals indicate the oxidation state, and where log formation constants of the divalent metal-EDTA complexes are given in parenthesis. The low preference of the adsorption complex for Fe^{2+} relative to competing cations, such as Zn^{2+} and Cd^{2+} would be expected, since the adsorption complex was made up mainly of organic matter in the A_1 horizon of the soil. The assumption that the increase of aqueous metals other than Fe^{2+} was by ion exchange alone, simplified the situation. Also metals associated with ferric oxides will be released upon reduction and solution of these oxides, and therefore the selectivity coefficient (Eq. 10) may be somewhat closer to unity.

3.3.4 Extraction of heavy metals from Overpelt soil

Soil material from the A_1 horizon of a soil 1 km NE of the zinc smelter at Overpelt, was entered in a series of 8 percolation tubes and leached with different solutions: (a) demineralized water, (b) 1.0 N $CaCl_2$, (c) 0.1 N HCl, and (d) 0.1 N Na-EDTA, in such a way that 2 tubes were leached with Solutions a, b, c and d successively, the next 2 tubes with Solutions b, c and d, 2 tubes with Solutions c and d, and 2 tubes with Solution d only. The leachates were analysed for Zn, Cd, Mn and Fe, and samples from each percolation tube were digested in a mixture of $HClO_4$ and HNO_3 and analysed for the same metals (Fig. 6). A second series was analysed for Pb and Cu, in addition to the other metals, but leaching with EDTA was left out, and 1 M $BaCl_2$ was used instead of $CaCl_2$ (Fig. 7).

Water-soluble fractions of all metals were very low, generally below 1% of the total metal content, but would be important, since they form the most mobile part of the metal burden of soils. Since aqueous metals are in equilibrium with adsorbed metals, the composition of the water-extractable fraction depends on the leaching conditions. In a separate experiment, a soil column 1.00 m long, was percolated continuously (3.5 cm day^{-1}) with demineralized water and the Zn concentration in the leachate remained at

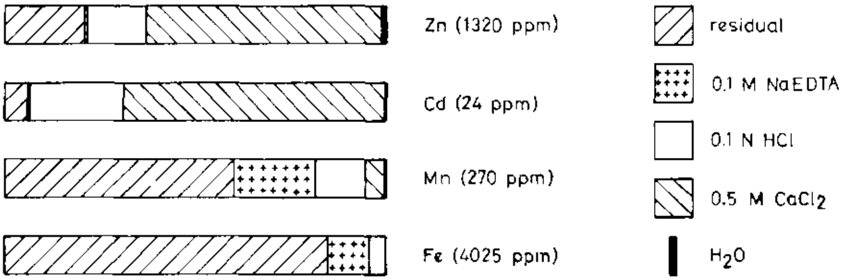

Fig. 6. Fractions of heavy metals extractable successively with water, salt, dilute acid and EDTA, and residual fractions in Overpelt soil (A_1 horizon). Total contents of metals are given in parenthesis.

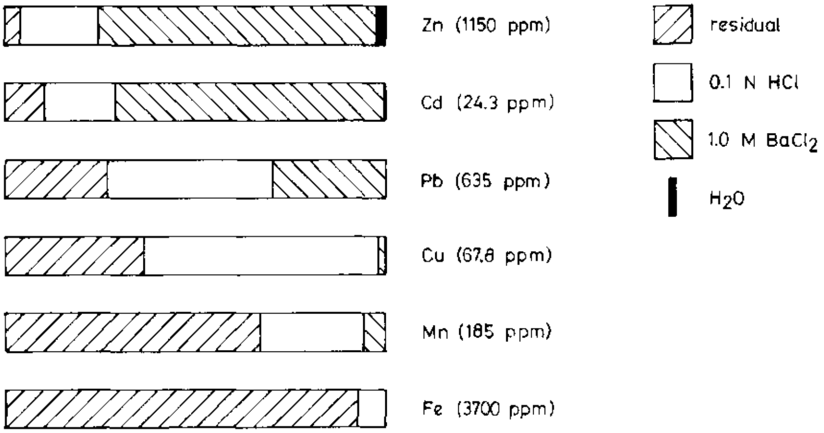

Fig. 7. Fractions of heavy metals extractable successively with water, salt and dilute acid, and residual fractions in Overpelt soil (A_1 horizon). Total contents of metals are given in parenthesis.

about 4 mg/l for several weeks, indicating a steady state for desorption of zinc from the soil. The same type of behaviour was observed in the shaking experiments, where Zn was released upon increasing the solution/soil ratio. This probably explains why there was more water-soluble Zn in Fig. 6 (1.6%) and Fig. 7 (2.5%) than obtained by extrapolation of Curve a in Fig. 5 towards the y-axis (0.6%). If detailed information about the water-soluble fraction be required, additional experiments like those described in Section 3.3.3 may thus be necessary.

The fraction of metals extractable with a near-neutral salt solution comprises 'reversibly' adsorbed forms of the metals, where 'reversibly' means that the metals are replaceable by excess $CaCl_2$ or $BaCl_2$. Since the majority of the adsorption sites in the soil would be in organic matter, a whole range of bonding energies may be expected, ranging from the low energies associated with electrostatic attraction to the high energies associated with the formation of chemical bonds between metals and functional groups of organic matter. Only metals adsorbed with low bonding energies would be extractable with a near-neutral salt solution, whereas metals associated with high energy sites would be extractable with a dilute acid only. Figure 6 shows that almost equal amounts of Zn and Cd were extracted by dilute acid and EDTA, suggesting that the acid-extractable fraction consists mainly of metals associated with high energy sites in organic matter. The acid-extractable fraction may further include some metals associated with solid phases, such as ferric oxides.

EDTA and HCl seem to be almost equally effective as extractant for Zn and Cd, but the amounts of Mn and Fe in the EDTA leachates exceed those in the HCl leachates. The log formation constants of the metal-EDTA complexes, Zn^{II} (16.4), Cd^{II} (16.5), Mn^{II} (13.8) and Fe^{III} (25.1), where Roman numerals indicate the oxidation state, show that the formation constants of the Zn^{II} and Cd^{II} complexes are of the same order and much lower than of the Fe^{III}-EDTA complex, in accordance with the high extracting power of EDTA for Fe^{III} in the soils. The formation constant of the Mn^{II}-EDTA complex is lower than of the Zn^{II} and Cd^{II} complexes and therefore the high extracting power of EDTA for Mn cannot be so explained. The log formation constant of the Mn^{III}-EDTA complex is 24.9 (Tanaka et al., 1965), which is of the same order as of the Fe^{III}-EDTA complex. The amount of Mn^{3+} in solution would be negligibly small, however, since at E_H 0.50 - 0.60 V, redox potentials commonly observed in oxidized soils, and pH about 5, $\log(Mn^{3+}/Mn^{2+})$ ranges from -16.8 to -15.1. The Mn^{III} state may be stabilized in solution by complexing anions such as $EDTA^{4-}$: $\log(Mn^{III}\text{-}EDTA^{-}/Mn^{II}\text{-}EDTA^{2-})$ is -5.4 and -3.7 at E_H 0.50 and 0.60 V, respectively (Tanaka et al., 1965). Although these values are considerably higher than those for the aquo ions, it seems unlikely that manganese was significantly extracted in the trivalent state. But Mn would be associated to a large extent with Fe in the solid phase, and by solution and complexing of Fe^{III}, Mn^{II} would be released and complexed by EDTA, even though the formation constant is relatively low. Figure 6 shows that, although the fraction was greater, the total amount of Mn extracted with EDTA was less (5.2 ppm) than of Fe (37.6 ppm), the substance ratio of Mn to Fe being 0.14.

The residual fraction would include metals associated with iron oxides, silicates and other stable minerals. Figures 6 and 7 show that about 70% of Cd and Zn was present in 'available' form, whereas only about 10% of each metal remained in the residue. In contrast to Zn and Cd, more than 90% of soil Fe could not be extracted with dilute acid or near neutral salt solutions, in accordance with the use of reducing and complexing agents in most iron extraction procedures for soils (Mehra & Jackson, 1960, McKeague et al., 1971). Part of the residual fractions of other metals, especially Mn, may consist of metals incorporated in the lattice of ferric oxides, present as concretions or as coatings on other minerals. Figure 7 shows that Pb and Cu were intermediate between Zn and Cd, on the one hand, and Fe and Mn on the other, indicating that these metals form strong bonds with organic matter, in agreement with the high log formation constants of the divalent metal-EDTA complexes of 18.0 (Pb) and 18.8 (Cu).

3.3.5 Heavy metals in Budel soils

Two soils near the zinc smelter at Budel were sampled with depth and analysed for Zn, Cd, Cu, Pb, Mn and Fe. Both soils had developed in sands of aeolic origin. The first soil was 1.4 km north-east of the smelter and showed no horizon differentiation at all,

Fig. 8. Soil profile and vegetation 1.4 km north-east of the zinc smelter at Budel-Dorplein. Photograph J.C. Dirven.

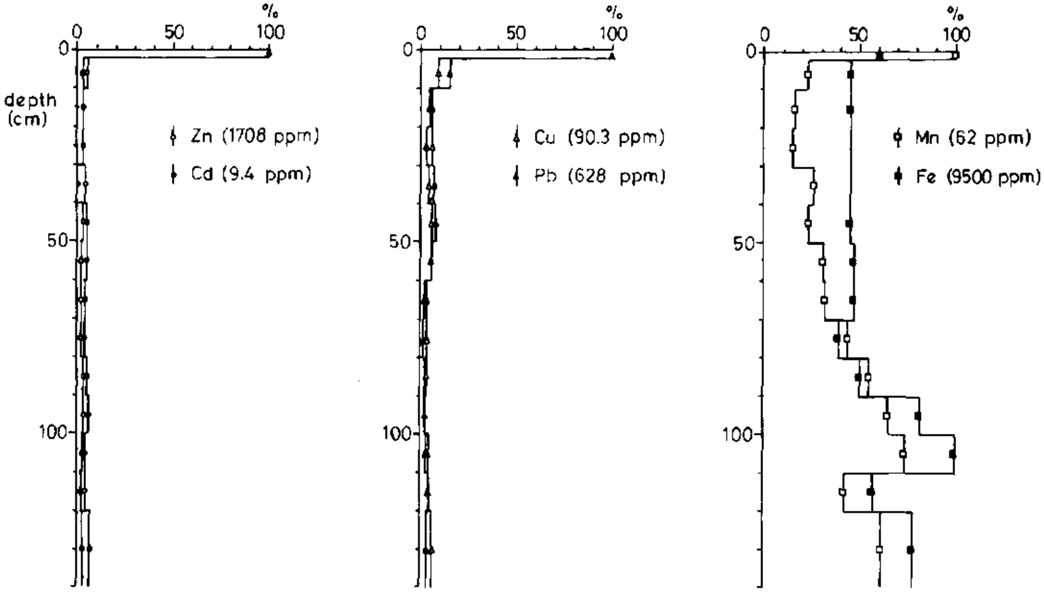

Fig. 9. Distribution of heavy metals in a sandy soil 1.4 km NE of the zinc smelter at Budel-Dorplein, plotted as percentage of their maxima. Maxima are given in parenthesis.

except for a 2-cm thick A_1 horizon; see Fig. 8. In the top 2 cm, Zn, Cd, Cu and Pb had strongly accumulated and were fairly constant below (Fig. 9). It might be more appropriate to express data per unit volume than per unit mass of soil, since differences in bulk density (volumetric mass) may be expected between the A_0/A_1 horizon and the mineral soil below 2 cm depth, but no reliable data on bulk density were available for the 0 - 2 cm layer of this soil. The distributions of Fe and Mn, which seemed to be correlated with each other, differed from the other metals and probably reflected the irregularity of the stratified parent material (Fig. 8), since Fe and Mn would be native in this soil, except for the top layer, where enrichment through aerial fallout, notably of Mn could have occurred. The redistribution of Fe and Mn at depth in the soil profile was probably due to the permanent watertable there. Organic compounds in groundwater and in water percolating from the surface, may serve as a source of energy for facultative anaerobic micro-organisms that use Mn^{IV} or Fe^{III} as electron acceptors in their metabolism, in the absence of sufficient O_2 or NO_3^-. The resulting increase in aqueous Mn^{2+} or Fe^{2+} would cause an upward (and possibly a downward) diffusion and could move considerable amounts of Mn and Fe in the course of time (Harmsen & van Breemen, 1975). The close correlation between Fe and Mn below one meter depth in the soil suggests that Fe and Mn occur as mixed oxides, Mn being incorporated in the ferric oxide lattice, as for the Overpelt soil.

The second soil, 1.3 km east of the smelter, was a well developed podzol with an A_1 horizon from 0-2 cm, an A_2 horizon from 2-20 cm and a B_{2h} horizon from 20-30 cm depth. This horizon differentiation is reflected in the distribution of Fe in the soil shown in Fig. 10, but not in the distribution of Mn or other metals. Figure 10 further shows that Zn, Cd, Pb, Cu and to some extent Mn, had accumulated in the top 2 cm of the soil, whereas Cd and possibly Pb had to some extent leached downwards. In the top layer, Mn and Fe seemed to be enriched by aerial fallout, but the high levels of Mn and Fe below 50 cm depth and the qualitative correlation between them probably reflect the native contents of the parent material.

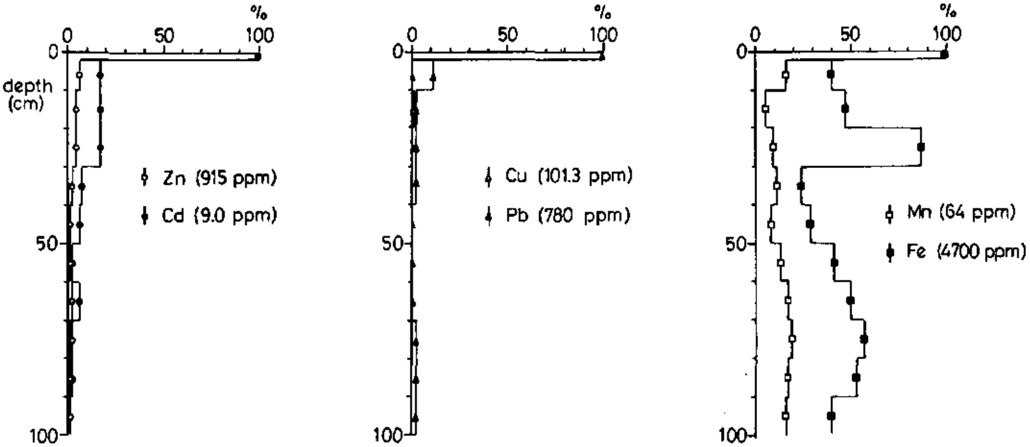

Fig. 10. Distribution of heavy metals in a podzol 1.3 km E of the zinc smelter at Budel-Dorplein, plotted as percentage of their maxima. Maxima are given in parenthesis.

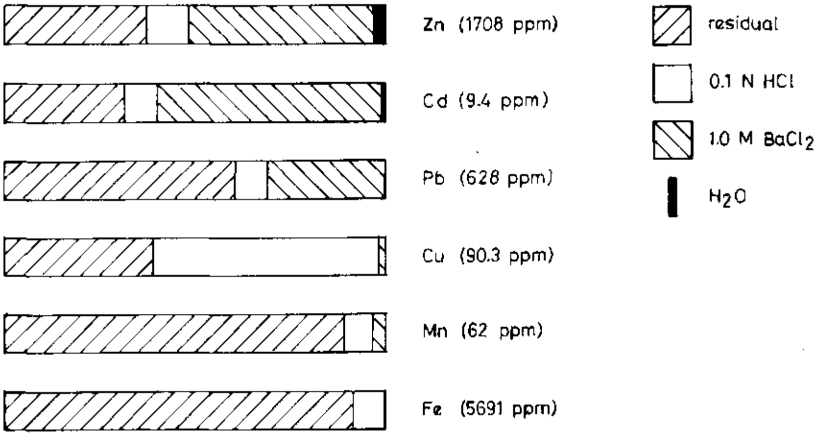

Fig. 11. Fractions of heavy metals extractable successively with water, salt and dilute acid, and residual fractions in a sandy soil near Budel (A_1 horizon). Total contents of metals are given in parenthesis.

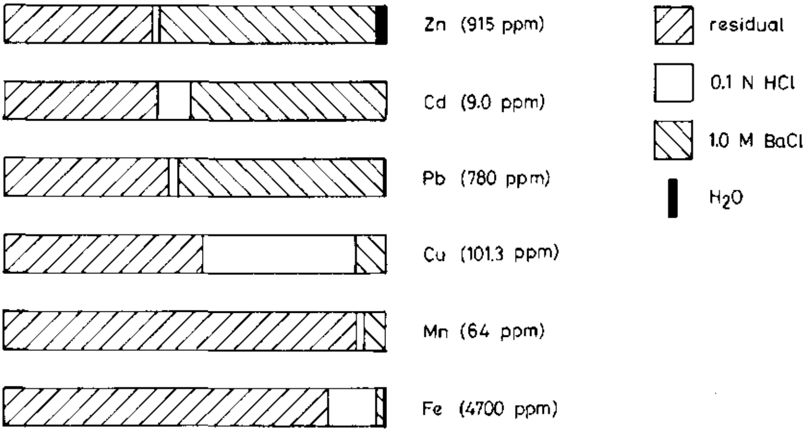

Fig. 12. Fractions of heavy metals extractable successively with water, salt and dilute acid, and residual fractions in a podzol near Budel (A_1 horizon). Total contents of metals are given in parenthesis.

Soil samples were extracted by different means: H_2O, $BaCl_2$ and HCl (Section 3.3.4). Results for the surface horizons of the 2 soils (Figs. 11 and 12) compare reasonably well with the Overpelt soil: 50 to 60% of Zn and Cd was in available form, about 10% in acid-extractable form, and 30-40% in residual form. About 90% of Mn and Fe was in residual form and less than 5% in available form, whereas Pb and Cu were again intermediate, but they differed from each other in that 30-55% of Pb was in the salt-extractable form and less than 10% of Cu, possibly indicating that Cu forms stronger bonds with organic matter.

When the composition of aerial fallout (exhaust fumes) remains constant, distributions of heavy metals with depth and chemical extraction data provide information about the mobilities of the elements in soil. Additional information about leaching, composition of the soil solution and chemical form of the heavy metals in soils is required to predict the long-term behaviour of these elements in soils. The chemical extraction data indicate that the high contents of available Zn, Cd and Pb in the soils at Overpelt and Budel do represent an environmental hazard.

3.4 A SOIL ALONG A RIVER DISCHARGING MINING WASTES

3.4.1 The River Geul

The Geul is a small river that rises near the German border in the Municipality of Eynatten, in the Belgian Province of Liège, then passes through the Moresnet area, where zinc and lead were formerly mined, enters the Netherlands in the south of the Province of Limburg and finally joins the River Meuse. Henri Chapelle (Belgium) is the highest point in the catchment area of the Geul, at 354 m above 'Amsterdam Ordnance Datum' (NAP), based on mean sea-level at Den Helder (Netherlands). Most of the ore deposits in the Moresnet area were centred along the Geul and its tributaries, and the Geul itself passes straight through the former mining centres of La Calamine and Plombières.

Discharges of the Geul vary from 0.5 to 20 m^3/s and average 3.5 m^3/s, as measured at the junction with the River Meuse. The discharges of the Geul at the Belgian-Dutch border are less, about a third of the discharges at the junction with the Meuse. At low water, the Geul is clear, but at high water it becomes turbid and muddy with a high content of suspended matter. Until recently, the Geul flooded regularly, mainly in winter, but also in summer, after heavy rain in the Belgian catchment area (about 1000 mm of rainfall per year).

The gradient of the Geul decreases quickly from about 20 m/km near Eynatten to about 5 m/km at the Dutch border and about 1.5 m/km near the junction with the Meuse. With the steep gradients the Geul did not form extensive alluvial deposits in Belgium: the river has incised a deep valley that widens as the Geul approaches the Netherlands. In the Netherlands, the Geul has formed about 1200 ha of alluvial soils (van den Broek & van der Marel, 1964). The Geul Valley is asymmetric: hill slopes on the western side are gentle, but slopes to the east are steeper, culminating in steep escarpments at the foot of the hills. In one of these escarpments, 'Heiman's Quarry', the Upper Carboniferous bedrock outcrops. Between the Dutch-Belgian border and Epen (Netherlands) the valley is 200 - 400 m wide. Old rivercourses and levees still witness the many changes in the course of this meandering fastest-flowing river of the Netherlands.

3.4.2 Metal contents of the Geul

The catchment area of the Geul and its tributaries coincides largely with the Moresnet mining region: all major ore deposits, except for those of the Welkenraedt-Eupen region, were within this area (Schneiderhöhn, 1941, p. 570). Mining in the Moresnet area started on a commercial scale in the 15th Century, when the brass industry moved to

Aachen (Germany). Mining activities reached their zenith in the 19th Century and continued till the middle of the 20th Century.

The Geul formerly discharged large amounts of Zn, Cd and Pb, by erosion and oxidative weathering of ore deposits, leaching of slag heaps and mine dumps, discharge of (acid) mine water and water used in the processing of ores (e.g. washing and flotation). The water of the Geul was probably slightly acid, as is evidenced by the complete absence of calcareous sediments along the Geul, upstream of the junction of the 'Sinselbeek' and the Geul. The Sinselbeek apparently had a higher pH, since alluvial deposits downstream of this junction are calcareous or partly decalcified (van den Broek & van der Marel, 1964). At first sight it may seem surprising that a river, draining off an area where the subsoil consists in part of limestone and dolomitic rock, would be slightly acid, but the acidity of the Geul is probably caused by the oxidation of sulfides, in particular the iron sulfides, marcasite, which oxidizes easiest, and pyrite (Lindgren, 1933). According to the amount of oxygen available, the following reactions may occur

$$Fe^{II}S_2 + 7O + H_2O \rightarrow Fe^{II}SO_4 + H_2SO_4 \qquad (11)$$

$$2\ Fe^{II}SO_4 + H_2SO_4 + O \rightarrow Fe_2^{III}(SO_4)_3 + H_2O \qquad (12)$$

$$Fe_2^{III}(SO_4)_3 + 6\ H_2O \rightarrow 2\ Fe^{III}(OH)_3 + 2\ H_2SO_4 \qquad (13)$$

whereas ferric hydroxide may dehydrate to form 'limonitic' ferric oxide: $Fe_2^{III}O_3.nH_2O$, with $0 < n < 3$. Ferric sulfate is a fairly strong oxidizing agent which attacks almost all sulfides. Sphalerite, for example, is oxidized according to

$$ZnS + 4\ Fe_2^{III}(SO_4)_3 + 4\ H_2O \rightarrow ZnSO_4 + 8\ Fe^{II}SO_4 + 4\ H_2SO_4 \qquad (14)$$

Sphalerite is also attacked by oxygenated waters

$$ZnS + 4O \rightarrow ZnSO_4 \qquad (15)$$

or may dissolve, when the solution contains sulfuric acid

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S \qquad (16)$$

The sulfuric acid produced by the oxidation of pyrite, marcasite or other metal sulfides, may be neutralized by calcite and dolomite, but generally the neutralization would be incomplete, and part of the sulfuric acid would remain in solution. The occurrence of large quantities of limonitic ferric oxides in the oxidation zone of zinc and lead ores confirms that the oxidation of iron sulfides may have been important in the acidification of surface waters in the area.

Weathering and erosion of ore deposits, at shallow depths or outcropping in the catchment area of the Geul, have contributed to the metal contents of the Geul, but also underground ore veins and beds, since these deposits are often associated with existing

Fig. 13. A zinc-tolerant ecotype of *Viola calaminaria*: a yellow violet that grows on certain unfertilized soils along the Geul (3-6 g Zn/kg soil) and locally on mine dumps or slag heaps (10-50 g Zn/kg soil) in the Moresnet mining area. The Ancient Romans used *Viola calaminaria* for ore-prospecting (Ernst, 1976). Photograph O. van Rootselaar.

fractures, fissures and solution holes, which play a role in the underground drainage of the area. The major part of the Zn and Pb content of the Geul, however, was due to mining activities: the exposure of sulfidic ore deposits to the influence of oxidative weathering, leaching of slag heaps and mine dumps, the discharge of waste water from ore processing, and mine drainage all contributed to the metal contents of the Geul. Annoyance caused by excess water in the mines was common in the area and pumping installations with a capacity of 6.5 million m^3/year were continuously in operation, but were often not sufficient to drain the mines (Engelen, 1976). A pumping capacity of 6.5 million m^3/year corresponds to about 20% of the yearly discharge of the Geul, so the contribution of mine drainage to the total amount of water discharged through the Geul was significant.

Mine waters contain large amounts of heavy metals: contents of Zn ranging from 10 to 1000 mg/l were reported by Pietsch (1956, p. 48), but most values fall in the range 10 - 100 mg/l. Zn contents of surface waters in mining areas are lower and generally fall in the range from 0.1 to 1.0 mg/l. In the River Saale (Germany) Zn contents averaged 0.15 mg/l, 10% of which was associated with colloidal matter, at low water levels, and 70% or more, at high water levels. In the River Neckar (Germany), contents of Zn ranged from 0.1 to 1.2 mg/l, averaging 0.4 mg/l (Pietsch, 1956, p. 48). The Zn content of the Elpe, a small river in a former Zn and Pb mining area in Westphalia (Germany) ranged from 1.6 to 5.9 mg/l in 1899, when the mines were still in operation. Recent determinations in the same river yielded a value of 0.04 mg/l upstream of the junction of the Elpe and a watercourse discharging water from zinc mines, which are now closed, and downstream of that junction values ranged from 0.2 to 0.4 mg/l (Ernst et al., 1974). These data compare well with recent data for the Geul: the Zn content of the Geul was of the order of 0.6 mg/l, and of different creeks and watercourses joining the Geul 0.04 - 0.06 mg/l (Dijkstra & Bot, 1968).

Metal contents of brooks and rivers discharging mine waters, decrease with increasing distance to the source, as a result of sorption and precipitation, sedimentation of suspended matter, and dilution with water low in metals. The 'dissolved' metal content of acid water generally is higher than of neutral or alkaline water, but not if the metals are associated with suspended matter. Therefore, at low water, the dissolved metal contents may be high, but only a small amount of metals will be associated with suspended matter. At high water, the sludge content of the river is high, due to surface run-off and by swirling up of bottom sediments. Hence the dissolved metal content is low, by dilution with rainwater, but the total metal content may be high, through the large amount of metals associated with suspended matter.

3.4.3 Zinc and lead in a soil along the Geul

Most cultivated soils along the Geul are used as pasture, presumably because of the periodic floodings of the Geul. The vegetation along the Geul is rich (Fig. 14), despite

Fig. 14. A view of the Geul near the site of sampling, photographed shortly after rainfall, which had raised the level of the Geul about one metre. Photograph O. van Rootselaar.

the high contents of Zn, Cd and Pb. It is thus difficult to draw conclusions about the environmental impact of heavy metals, solely on the basis of total contents of metals in soils, or even on the basis of 'available' metals, which appear to be high as well. The absence of aerial fallout, the favourable moisture conditions of the alluvial soils along the Geul, the higher cation-exchange capacity and high base saturation of these soils, and the more favourable nutrient status, both due to the mineral reserve and to the use of fertilizers, may all help to explain the differences between the wealthy vegetation along the Geul and the poor vegetation near zinc smelters. The high metal burden of these soils, however, would pose a danger if arable crops like sugar beets were grown (Henkens, 1961).

One high alluvial soil along the Geul, about 500 m from the Belgian border, was sampled to 230 cm depth; the grain size distribution of the soil is shown in Fig. 15. The soil becomes gradually more sandy with depth, but there seem to be no discontinuities in the soil profile, so the increasing sand content probably reflects the changing composition of sediments deposited by the Geul. The lower clay content in the top soil may reflect a changing composition of the Geul sediments, but may also be due to differential clay movement, as suggested by van Schuylenborgh et al. (1970) for a comparable soil profile along the Geul.

The total Pb and Zn contents as a function of depth are shown in Fig. 16. The question rises whether Zn and Pb entered the soil profile through surface infiltration of water high in dissolved metals, or in sediments, adhered to suspended matter. In the first case the metal enrichment is due to migration of Zn and Pb within the profile, and in the second case the distribution of these metals reflects the changing metal content of the Geul deposits. The Zn content of the soil averages 900 ppm to a depth of 150 cm, and the average enrichment equals 600 ppm over that depth, if the Zn content of the 'uncontaminated' soil material is 300 ppm, the value reached below 150 cm depth. When the bulk density (volumic mass) of the soil is taken to be 1.5 g/cm^3, the average Zn enrichment is estimated to be 1350 g/m^2. If 1.00 m of Geul water with a Zn content of 1.0 mg/l

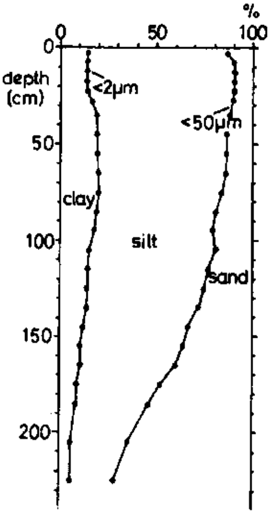

Fig. 15. Grain size distribution of a soil along the Geul: the mass fractions (%) < 2 µm and < 50 µm are plotted with depth.

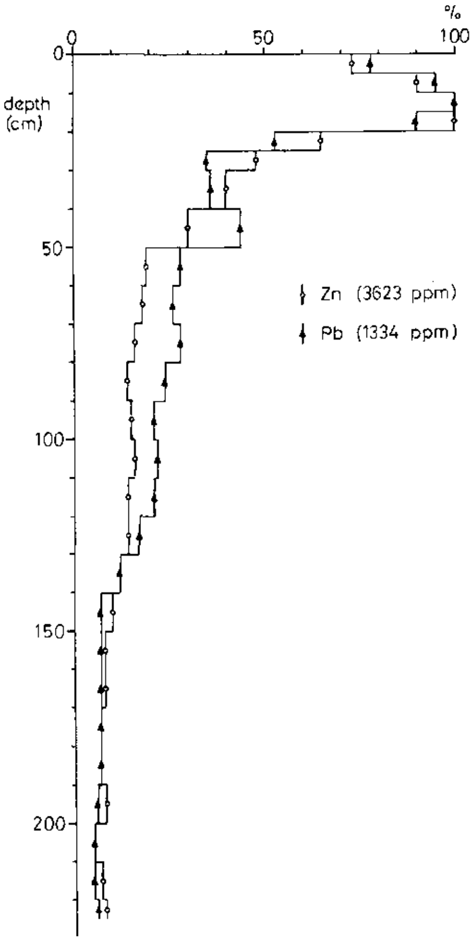

Fig. 16. Distribution of Zn and Pb with depth in a soil along the Geul, plotted as percentage of their maxima. Maxima are given in parenthesis.

percolated yearly through the soil, it would take 1350 years to produce the required enrichment. A total enrichment of 1350 g/m^2 is still a low estimate, since a reference level of 300 ppm Zn is rather high, and the Zn content of the surface layer of the present soil (3300 ppm) is low: Dijkstra & Bot (1968) reported values ranging from 3240 to 6000 ppm in surface horizons of floodplain soils. For uncontaminated soils and stream sediments in the wider surrounding, they reported contents of 35-135 ppm. A reference level of 300 ppm Zn for the alluvial soils of the Geul therefore probably represents the level of 'contamination' caused by natural weathering and erosion of ore deposits in the Belgian hinterland. An average concentration of dissolved Zn of 1.0 mg/l seems reasonable, although possibly somewhat high, since at high water the metal content of the Geul is low through dilution with rainwater or water from melting snow. An infiltration rate of 1.00 m/year is probably not excessive, since soils are already saturated with rainwater at the onset of flooding and most Geul water would run off the surface. Only in the lower situated basins of the floodplain would the water be left standing after the floodings and eventually infiltrate the soil or evaporate. But it would be difficult to decide whether the high metal contents of these soils are due to infiltration of dissolved metals or to sedimentation of clay particles rich in metals.

In conclusion, the metal enrichment of the soil is not likely to be due to surface infiltration of dissolved metals, since the time needed to reach the required accumulation is too long to neglect sedimentation processes. In addition, the rather similar distribution of Zn and Pb with depth would be difficult to explain, in view of differences in mobility between these metals. The distributions of Zn and Pb, at least partly, seem to follow the sedimentation pattern and thus reflect the changing content of heavy metals in suspended matter carried by the Geul. Metal contents of river bottom sediments are closely correlated with those of adjacent alluvial soils. Dijkstra & Bot (1968) investigated soils close to the soil profile under consideration, and reported mean values for Pb of 1600 ppm and for Zn 3700 ppm in floodplain soils, and for Pb 1400 ppm and Zn 3000 ppm in bottom sediments. In the Elpe Valley in Westphalia (Germany) Ernst et al. (1974) found a close correlation between Pb and Zn contents of soils 5 m from the river and stream sediments.

Part of the suspended matter in the Geul consisted of residual clays and loam released upon the processing of raw ore material. Mineralogical analysis of a comparable soil profile along the Geul, reported by van Schuylenborgh et al. (1970) shows that 43 - 48% of the clay minerals consist of smectites, 16 - 25% of kaolinites and only 29 - 36% of illites, suggesting that part of the clay minerals originate from solution of limestones and dolomites. Since the 'Vieille Montagne', a metasomatic ore body at La Calamine (Belgium), yielded about 2 million tons of 'calamine' ores (Klockmann, 1910), with a high residual clay content, which were all processed along the Geul, the contribution of these residual clays to the suspended matter carried by the Geul may have been considerable.

The pronounced accumulation of Zn and Pb in the upper 20 cm of the soil profile may be correlated with the increased Zn and Pb mining in the years 1840-1880, whereas the increase in metal contents, notably Pb, between 150 and 110 cm, may be correlated with the increased mining activities in the 15th and 16th Centuries. In the soil profile (Fig. 16) the Zn peak in the topsoil lies somewhat below the Pb peak, as is the case in the ore-production 'profile' (Fig. 17). Hence the decreasing metal contents in the upper 10 cm of the soil may represent the decreasing mining activities in the Moresnet area rather than migration of metals within the soil profile.

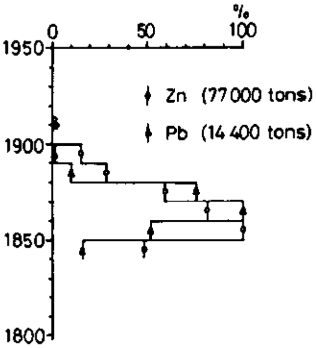

Fig. 17. Zinc and lead ore production data from Belgium for the period 1840 - 1913, plotted as percentage of their maxima. Maximum amounts produced in tonnes/year during 1850 - 1860 (Zn) and 1860 - 1870 (Pb) are given in parenthesis.

3.4.4 *Extraction of heavy metals*

Soil samples from 4 depths: 0 - 5, 15 - 20, 110 - 120, and 210 - 220 cm, were leached with 3 solutions: demineralized water, 1.0 M $BaCl_2$, and 0.1 N HCl, and analysed for total contents of metals, in the way described in Section 3.3.4 for Overpelt soil. All leachates were analysed for Zn, Cd, Pb, Cu, Fe and Mn by atomic absorption spectrometry. Figure 18 shows that Zn, Cd and Pb were strongly concentrated in the topsoil (0 - 20 cm), whereas Mn and Fe were fairly constant with depth. Copper was slightly concentrated in the topsoil, but total contents were low, owing to the low Cu content of Pb and Zn ores of the Moresnet area. The high Cd content of the topsoil confirms that Zn ores generally contain traces of Cd.

The cation-exchange capacity, determined with NH_4Cl as leaching solution, was esti-

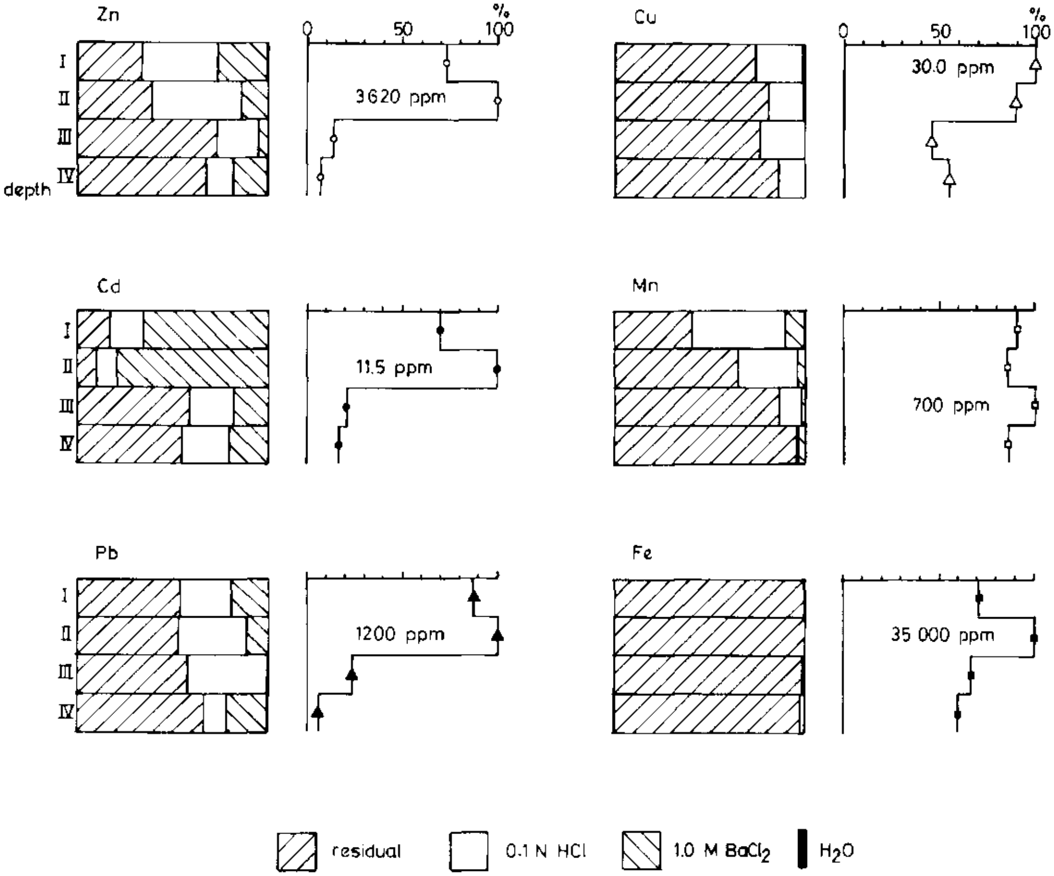

Fig. 18. Fractions of heavy metals extractable successively with water, salt and dilute acid, and residual fractions in a soil along the Geul; total metal contents are plotted as percentage of their maxima, which are indicated at the appropriate depths. Depths are indicated with Roman numerals: I (0 - 5 cm), II (15 - 20 cm), III (110 - 120 cm) and IV (210 - 220 cm). The watertable is between Layer III and IV.

mated to be 15 meq/100 g for levee soils, increasing to 23 meq/100 g for low-lying basin soils. The pH-H_2O of non-calcareous alluvial soils ranged from 5.4 to 6.0 and the pH-KCl (1.0 N) from 4.4 to 5.2, determined in 1:2.5 suspensions (van den Broek & van der Marel, 1964). In the top 5 cm of the profile, about 2.2 meq Zn^{2+} and about 0.2 meq Pb^{2+} were adsorbed exchangeably per 100 g soil, decreasing to 1.6 meq Zn^{2+} and 0.1 meq Pb^{2+} per 100 g at 15 - 20 cm depth. Hence the contribution of heavy metals to the cation-exchange complex ranged from 16 to 11% for the present soil. From data presented by Dijkstra & Bot (1968), the amounts of Zn^{2+} and Pb^{2+} exchangeably adsorbed can be estimated to be 0.10 - 0.25 meq Pb^{2+}/100 g and 1.2 - 3.9 meq Zn^{2+}/100 g, indicating that 10 to 20% of the exchange complex was saturated with Pb^{2+} and Zn^{2+}. Van den Broek & van der Marel (1964) observed discrepancies between the cation-exchange capacities determined with NH_4Cl and the sum of Na^+, K^+, Ca^{2+}, Mg^{2+} and Mn^{2+} for non-calcareous soils along the Geul, at Partij and Epen. These discrepancies, 13 - 17% of the CEC, may well be due to the occurrence of exchangeable Zn^{2+} and Pb^{2+}.

Figure 18 shows that Zn and Pb should be about equally mobile in the soil profile, but that Cd should be more mobile. This may be why the fractional content of Cd at 210 - 220 cm depth is higher than of Zn and Pb. These differences, however, may also reflect differences in the original metal contents of the suspended matter, during the deposition of the profile. The mass ratio of Zn to Cd in the upper 20 cm of the profile ranged from 316 to 321 and of Zn to Pb from 2.54 to 3.01. These ratios compare reasonably well with ratios estimated from data for the Elpe valley in Germany (Ernst et al., 1974): average Zn/Pb ratios of 2.3 and 1.9 and Zn/Cd ratios of 398 and 330, for brook bottom sediments and adjacent soils, respectively.

The availability of most metals, notably Zn and Pb, increased below the watertable in the Geul soil. At the time of sampling the watertable was at 190 - 200 cm depth. Samples from below that depth were all saturated with water and metal concentrations were measured in the soil solution, collected from these soil samples, and in water from the Geul; results are given in Table 3. Changes in the composition of the soil solutions, for instance by oxidation, may have occurred on the way from the site to the laboratory. Most metals, except for Zn, were present in very low concentrations, close to the detection limits. Figure 18 shows that there was a considerable increase in exchangeable Zn and Pb below the watertable, and also a slight increase in exchangeable Mn. The increased availability of these metals must, at least partly, be due to reduction and solution of ferric and manganic oxides. The extraction experiments were performed about

Table 3. Concentrations of metal species (mg/l) in the soil solution, sampled at 3 depths in a soil along the Geul. The permanent watertable was at 190 - 200 cm depth, at the time of sampling (October 1974). The concentration of Zn in Geul water is included for reference.

Depth (cm)	Zn	Cd	Cu	Pb	Mn	Fe
200 - 210	5.3	0.003	0.7	0.4	0.6	0.3
210 - 220	2.5	0.003	1.7	0.6	0.7	1.4
220 - 225	2.0	0.003	0.7	0.4	0.8	1.6
Geul	0.03					

Table 4. The amounts of heavy metals (mmol/kg) exchangeable with 1.0 M $BaCl_2$ and extractable with dilute-acid (0.1 N HCl) at two depths in a soil along the Geul. The watertable was at 190 - 200 cm depth at the time of sampling (October 1974).

Element	110 - 120 cm		210 - 220 cm	
	exch.	acid extr.	exch.	acid extr.
Zn	0.390	1.701	0.757	0.593
Cd	0.004	0.005	0.004	0.004
Pb	0.014	0.572	0.071	0.042
Cu	0.000	0.050	0.000	0.037
Mn	0.293	1.491	0.437	0.044
Fe	0.000	5.866	0.745	8.193

two months after sampling and the soil samples were stored under oxidizing conditions during that time. Therefore, the trend in Table 4 probably would have been more pronounced if the soils had been stored under field conditions. The availability of all elements increased below the watertable, and the amounts of Fe and Mn in exchangeable form exceeded the amounts of Pb and Zn in exchangeable form at 210 - 220 cm depth, whereas the amounts of Cd and Cu were negligible. The increased availability of Fe below the watertable is also reflected in the increased amount of acid-extractable Fe, possibly representing the amount of Fe^{II} that oxidized and precipitated during storage.

Stanton & Burger (1966a,b, 1967) showed that the Zn and Mn contents of ferruginous concretions in Orange Free State soils (South Africa) were higher than the contents of the surrounding soils. The authors suggested that the observed enrichment was due to association of Zn and Mn with iron oxides. Prabhakaran Nair & Cottenie (1971) evaluated the relationships between particle-size fractions, free iron oxides and trace elements statistically, and concluded that amorphous iron oxides probably retained a large proportion of Zn, Cu, Mn and Pb in the soils. Gadde & Laitinen (1974) showed that adsorption of heavy metals on oxides of Fe and Mn followed the order $Pb^{2+} >> Zn^{2+} > Cd^{2+}$, whereas adsorption by manganese oxides occurred already at pH 2, and by iron oxides at pH 4 and higher. The adsorption of heavy metals by goethite from dilute solutions (Grimme, 1968), started at pH 3 - 5, and at a given pH the adsorption followed the order Cu > Zn > Co > > Mn. White (1957) suggested that a large proportion of Zn in soils (30 - 60%) may be associated with iron oxides, but that also resistent minerals, such as ilmenite, may contain considerable amounts of Zn.

Mineralogical analysis of a soil profile along the Geul (van Schuylenborgh et al., 1970) showed that the clay fraction (12.6%) of the A_{12} horizon of the soil, contained 10.2% iron oxide, probably in the form of amorphous ferric hydroxides, whereas the sand and silt fractions contained only 1.1% iron oxide. Micromorphological studies on thin sections showed that the plasma of the soils consisted of a mixture of clay minerals and amorphous iron compounds, the skeleton grains consisted mainly of quartz, micas, feldspars and amphiboles. In the soils along the Geul, part of the residual metals are likely to be associated with oxides of Fe and Mn, but also the possible occurrence of zinc minerals, such as zincite, franklinite, willemite, hemimorphite or possibly sauconite, has to be considered. These minerals would not necessarily form in situ, but they may have been transported by the Geul. Microscopic examinations of samples from the banks of the Geul disclosed the presence of sphalerite grains (Dijkstra & Bot, 1968). The slow weathering and solution of stable zinc minerals, derived from ore deposits in the Belgian catchment area, may also help to explain the marked accumulation of Zn, Cd and Pb in the surface horizon along the Geul.

3.5 DISPOSAL OF SEWAGE ON LAND

3.5.1 Sewage farm near Tilburg

The growing population produces a continuously increasing waste. Indeed even the waste per person increases every year. In the past, municipal waste including residual sludge from sewage plants, has been dumped as land fill, incinerated, discharged into rivers, lakes or oceans, and to a limited extent composted or otherwise recycled. The surge of environmental concern in recent years has led to a more critical attitude towards the traditional methods of waste disposal, and has increased interest in spreading of municipal refuse and sewage sludge on agricultural land, thus utilizing the organic matter and nutrients in the refuse and sewage sludge. Sewage sludge spread on agricultural land may adversely affect the environment, since large amounts of nitrates may be leached into the groundwater, heavy metals, phosphates and other compounds may accumulate in the soil, and germination and plant growth may be inhibited. The feasibility of using land for waste disposal and for crop production needs closer study.

Untreated industrial and domestic waste water has been spread on land for about 50 years near the Town of Tilburg (Netherlands). The municipal sewage farm is situated on originally poor sandy soils with a high permeability and covers about 100 hectares. About 15 cm of sewage water was pumped on per month during the first thirty years and during the next fifteen years amounts increased to about 35 cm per month until 1971 - 1972, when a new sewage plant became operational. Since 1972, amounts were kept at about 20 cm per month. The sewage farm is under permanent pasture and until recently no fertilizers at all were applied to the land, although grazed intensively. Since 1970, the sewage water is first treated by screening of coarse substances and settlement of solids, before pumping on the land. This treatment removes part of the nitrogen from the sewage, thus necessitating a small application of nitrogen fertilizer twice yearly during the growing season.

The sewage water reaches the land through raised supply ditches, connected with the adjacent plots through simple inlet valves. Figure 19 shows schematically the situation of Plot east-12, in the oldest part of the sewage farm, which was selected for the present study. When the area was reclaimed, about fifty years ago, a system of tile drains was installed at a depth of 110 - 140 cm, with an average interval between drains of 14 m. Later new drains were laid in the old part of the sewage farm at a depth of 70 - 100 cm, such that the interval between drains now averages 7 m. Each plot is enclosed with soil ridges to prevent run-off of sewage water. The tile drains discharge into a lower system of discharge ditches, connected with a main discharge canal.

When large amounts of untreated sewage water are applied to soils, changes in the

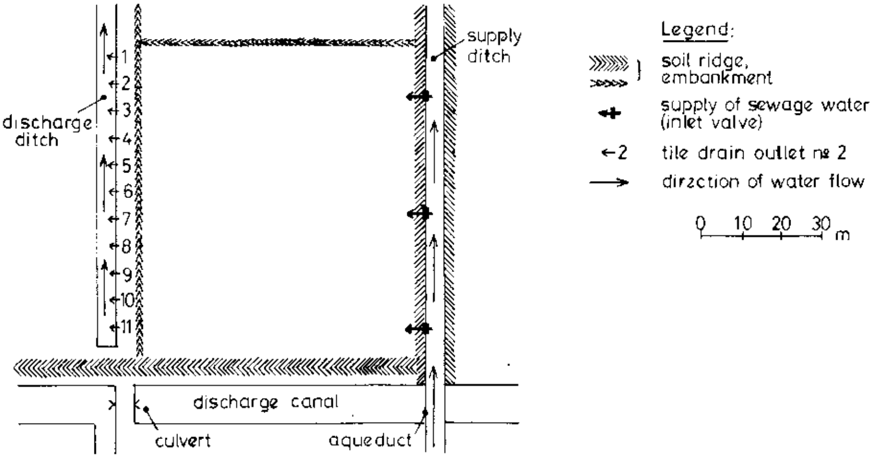

Fig. 19. Plan of Plot east-12 of the Tilburg municipal sewage farm.

natural environment have to be expected. Comparison of soils from uncultivated woodlands surrounding the sewage farm and soils of the oldest part of the sewage farm, shows a rise in pH-H_2O from 4.0 to 6.5 and a rise in loss on ignition from 2.9% (mass fraction) to 10.3% in the top 20 cm of the soils investigated (Beek & de Haan, 1973). The strong increase in loss on ignition, mainly caused by an increase in organic matter, illustrates the functioning of the soil and its vegetational cover as a 'sieve' for organic matter contained in the sewage water. The retention of these sewage sludges in the top layer of the soil plays an important role in the removal of heavy metals by the soil, in part because heavy metals are already strongly concentrated in these sludges with respect to the solution, but also because these sludges enhance the adsorption capacity of the soil. Since residence times of sewage water in these soils are generally short, ion exchange and other adsorption processes, rather than precipitation, must be a major process in the initial retention of dissolved heavy metals in these soils. Breakdown of organic matter by micro-organisms may release heavy metals. In this stage, precipitation or occlusion in growing solid phases, such as oxides (Fe, Al) or phosphates (Al, Fe, Ca), help in retention of heavy metals.

The efficiency of the soil in removing heavy metals from sewage water added to the soil can be estimated by comparing metal contents of sewage and drainage water. To interprete these correctly, it would be useful to know whether there were a direct relation between the amounts of metals in the sewage water and the drainage water, or whether part of the metals in the drainage water were soil-borne, being released by dissolving minerals or desorbed. Analysis of soil for heavy metals and comparison of these data with untreated soils near the sewage farm may help to indicate the filtering capacity of the soil.

3.5.2 *Soil analysis*

Two soils in Plot east-12 were sampled with depth and analysed for heavy metals and loss on ignition (Figs. 20 and 22); moisture content and bulk density were estimated in one soil (Fig. 21). Soil Til-1 was from near the discharge ditch, far from the sewage water inlets, as is reflected in lower contents of metals than in Soil Til-2. Soil Til-2 was a mixture of soil samples from several locations in the centre of the plot and was therefore more representative for Plot east-12.

The volume fractions of Soil Til-1 occupied by solid, liquid and gas phase 5 days after flooding are depicted in Fig. 21. The volume fraction of the soil occupied by the solid phase was estimated from bulk density data and specific gravities of the solid phase which ranged from 2.51 g/cm^3 in the top 10 cm, to 2.64 g/cm^3 in the lower part of the soil profile. The high porosity of the soil and the presence of a gas phase even below 80 cm depth point to a high permeability of the soil, as observed in the field.

Figures 20 and 22 show that all metals accumulated in the top 10 cm. Upon flooding with sewage water, redox potentials did not reach very low values, because of the presence of nitrates (denitrification) and the short periods of submersion. Ferric iron would not

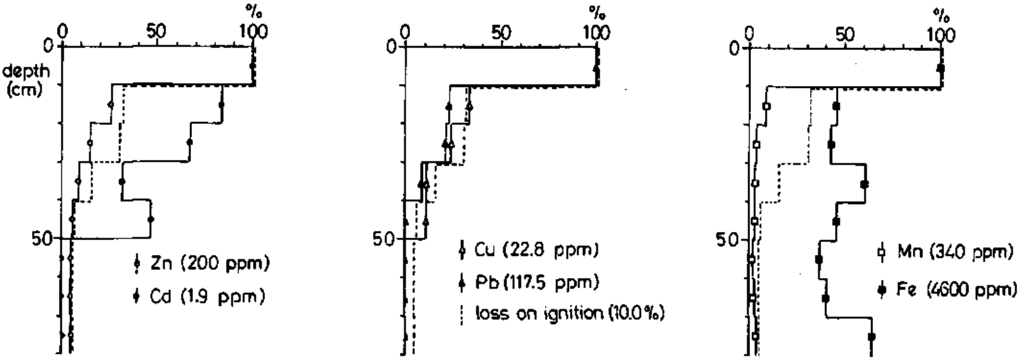

Fig. 20. Mass fractions of heavy metals and loss on ignition (broken line) plotted as percentage of their maxima with depth in Soil Til-1. Maxima are given in parenthesis, loss on ignition is expressed as percentage (g/100 g soil).

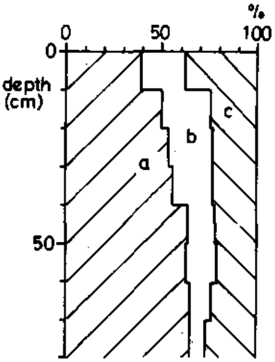

Fig. 21. Volume fractions of solid phase (a), gas phase (b) and liquid phase (c), with depth in Soil Til-1, 5 days after the start of flooding.

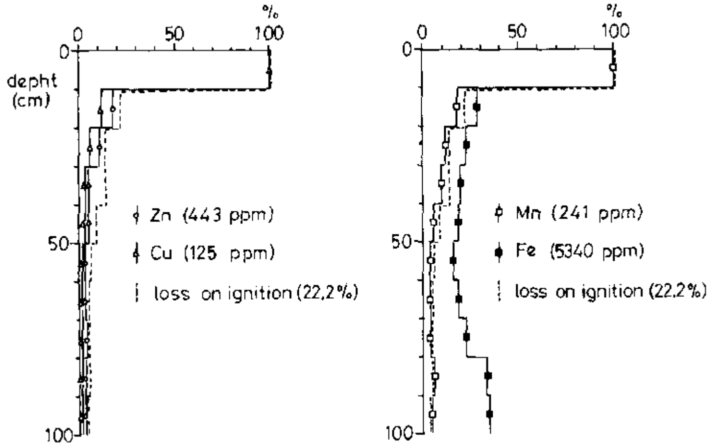

Fig. 22. Mass fractions of heavy metals and loss on ignition (broken line), plotted as percentage of their maxima with depth in Soil Til-2. Maxima are given in parenthesis, loss on ignition is expressed as percentage (g/100 g soil).

be much reduced, so there would be little movement of ferrous iron. Presumably the Fe distribution below 10 cm depth, and the differences in Fe content between Soils Til-1 and Til-2 represent the Fe content of the parent material. The contents of Zn, Cu, Pb (Fig. 20 only) and Mn plotted in Figs. 20 and 22 follow the loss on ignition quite closely, suggesting that these metals may be associated to a large extent with the organic fraction of the soil. If indeed heavy metals are held by the organic fraction of the soil, and if the conversion to other stabler forms be very slow, the retaining capacity of the soil for dissolved heavy metals could become saturated. The correlation between the loss on ignition and the heavy metal contents may also be because most metals reach the soil in suspended form, presumably associated with organic compounds.

3.5.3 *Experimental*

One cycle of irrigation of Plot east-12 with sewage water was observed from the onset of flooding on 11 November 1974 at noon, until the discharge of drainage water had declined sufficiently on 16 November at 1.00 AM. The plot was flooded by opening the inlet valves at the three inlet points (Fig. 19), and continued for about three hours. When the valves were closed again, the whole area embanked by the soil ridges, about 0.6 hectare, was submerged and it took between one and two days before the whole area dried up. The older drains at 1.10 - 1.40 m depth are numbered 2, 3, 4, 6, 8 and 10 in Fig. 19, and will be called deep drains. The newer drains 0.70 - 1.00 m deep, are numbered 1, 5, 7, 9 and 11, and will be called 'shallow' drains. Five drains, Numbers 2, 5, 6, 9 and 10 were sampled regularly, every two hours, for five days. The drainage water was collected at the outlets of the tile drains in plastic two-litre bottles or in graduated plastic buckets and rates of discharge were measured with a stop-watch.

The rate of discharge of the deep drains (2, 6 and 10) averaged 10.5 l/min during 108 hours and of the shallow drains (5 and 9) 10.1 l/min during that period. The total amount discharged by six deep and five shallow drains during 108 hours was thus estimated to be 737 m^3, corresponding to 12.3 cm of sewage water on an area of 0.6 hectare. This value is somewhat too low, however, since part of the water, especially during the first day, flowed directly into the discharge ditch, through the side of the ditch (through mole-holes). In addition, some lateral percolation towards adjacent parcels may have occurred.

At the onset of flooding, the shallow drains did not discharge any water at all, but the deep drains discharged water at a rate of about 1.0 l/min. That drainage was probably due to a fall in water level in the discharge canal, a few days before flooding, and to rainfall at that time. The water level had to be lowered in order to collect water at the outlets of the deep tile drains. At the end of the second and fifth day of sampling the water level in the discharge ditch rose temporarily above the level of the deep drain outlets, through rainfall near the sewage farm. About 80 mm of rain fell in the month before irrigation with sewage water. The beginning of November was rather dry, except for the 7th when about 10 mm of rain fell, and for the 12th and 13th, i.e. the second and third day of the period of sampling, when about 10 mm of rain fell in the two days; heavy rainfall started in the night of the 15th, at the end of the period of sampling.

After the samples had been collected, they were taken to a field laboratory where pH was measured with a portable pH-meter. Small subsamples of drainage water were filtered for analysis of phosphate fractions, reported elsewhere (Beek & Harmsen, 1977). Once a day, all samples were taken to the Laboratory of Soils and Fertilizers at Wageningen, where they were stored in a dark cold-storage chamber at 4 °C. In selected samples of two shallow drains (5 and 9) and two deep drains (6 and 10) the chloride content was determined. Selected samples from Drain 6, a deep drain, were filtered over a 0.45-μm membrane filter, and the filters (suspended fraction) and the filtrates (dissolved fraction) were both analysed for heavy metals.

3.5.4 Breakthrough curves of chlorides and pH

'Breakthrough curve' means the variation of a quantity (concentration or activity) in the drainage water collected at the tile drain outlets, as a function of time since the start of flooding. The average rates of discharge (l/min) of deep drains (2, 6 and 10) and shallow drains (5 and 9) are plotted in Fig. 23. The maximum rate of discharge from the shallow drains (about 50 l/min) preceded that from the deep drains (about 35 l/min). About 24 hours after the onset of flooding, the two curves intersected and the drains continued to discharge at a higher rate than the shallow drains.

The pH of sewage water was about 7.4, whereas the pH of drainage water varied between 6.0 and 6.1 (Fig. 24), presumably because of production of CO_2 in the soil by microbial decomposition of organic compounds. This may explain why the pH of the deep drains tends to be about 0.05 less than of the shallow drains: the residence time of the water discharged by the deep drains was longer and therefore more CO_2 was dissolved in the water discharged by the deep drains. The higher pH at the beginning of the breakthrough curves probably represented the pH of the capillary soil water. The pH of the deep drains was somewhat higher than of the shallow drains in the beginning of the

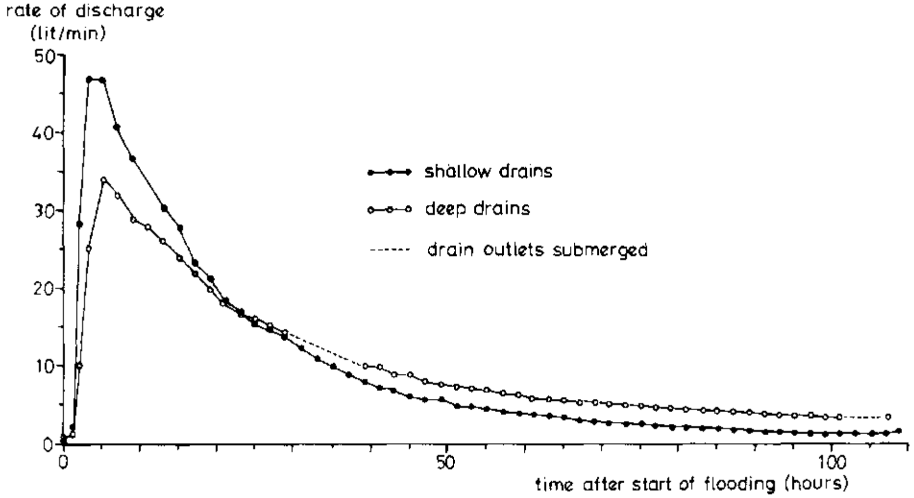

Fig. 23. Average rates of discharge of shallow and deep drains.

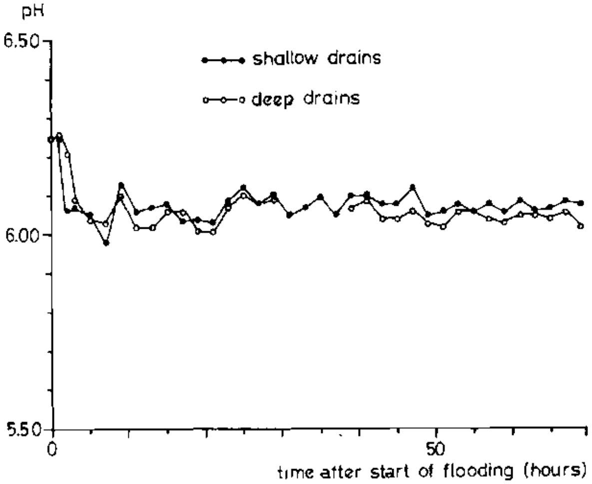

Fig. 24. Average pH of the effluent of shallow and deep drains.

breakthrough curves, but the two curves 'shifted' with respect to each other, because the peak discharge of the shallow drains was 1 - 2 hours earlier.

Mean concentrations of chloride (mg/l) of selected samples from shallow and deep drains are plotted in Fig. 25 for the first 24 hours after the start of flooding. Unfortunately the differences between the chloride concentrations of sewage water, capillary soil water and groundwater turned out to be rather small, and therefore Cl^- was not very suitable as a tracer for sewage water. Comparison of the concentrations of Na^+, K^+, Ca^{2+}, Cl^- and total phosphate in the present sewage water, and mean values reported else-

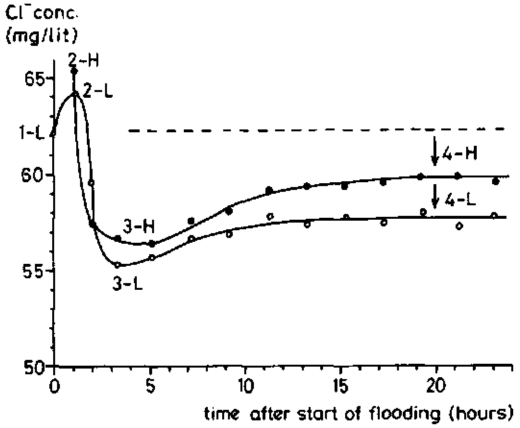

Fig. 25. Average concentration of chloride in the effluent of shallow and deep drains; the mean concentration of chloride in the sewage water (62.3 mg/l) is indicated with a broken line.

where (Beek et al., 1977), suggests that the sewage water was diluted: the relative concentrations range from 0.39 for Cl, 0.44 for Na, 0.49 for K, and 0.70 for Ca to 0.97 for total phosphates. These data also show considerable variations in the composition of the sewage water.

The chloride concentration of the drainage water remained important, however, for the interpretation of the breakthrough curves. Groundwater in Plot east-12 was composed of sewage water from preceding floodings and of rainwater, whereas mass flow or admixture with water from deeper layers or adjacent plots may have altered the composition of the groundwater as well. Concentration of chloride in capillary water exceeded that in groundwater and probably reached a maximum in the unsaturated zone. Concentrations in capillary water may be higher through evaporation of capillary water, or through redistribution and rearrangement processes involving chlorides, such as diffusion of chlorides from immobile to mobile water. Closer to the surface, the chloride concentration would be diluted by rainwater. The effluent discharged by the deep drains at the beginning of the flooding cycle (1-L, Fig. 25) seemed to be capillary water from the saturated zone. The concentration then increased, when mobile water of the unsaturated zone was replaced by infiltrating sewage water. The maximum concentration from the shallow drains (2-H, Fig. 25) was greater than that reached in the effluent of the deep drains (2-L, Fig. 25) probably because the latter was diluted by capillary water from the saturated zone or groundwater, both with less chloride. At the transition from Points 2 to 3, the chloride concentrations decreased, probably because mobile capillary water with low chloride contents (rainwater) reached the drains. The lowest chloride concentrations were reached 3 - 4 hours after the onset of flooding (3-L and 3-H, Fig. 25) and then the sewage water 'broke through' and the chloride concentrations started to increase again. The chloride level in the effluent from the shallow drains (4-H, Fig. 25) remained about 4% below the chloride level in the sewage water, through dilution with rainwater and possibly through diffusion of chlorides to immobile water. In the first day about 5 mm of rain fell, corresponding to about 4% of the amount of sewage water added, and tying in with the dilution of the chlorides in the shallow drains. The chloride level in the effluent of the deep drains was again 3 - 4% lower (4-L, Fig. 25), probably through the influence of groundwater or diffusion of chlorides to immobile water. Mixing of groundwater and capillary water with sewage water not only occurred with depth in the soil profile, but also with distance down the field, because the movement of the sewage water has a vertical and a horizontal component. The tile drains had been laid at depths of 70 and 110 cm, at the end of the plot with the supply ditch, and at depths of 100 and 140 cm, respectively, at the end with the discharge ditch, to encourage flow along the drains. Sewage water may enter the drains at one end of the field, and capillary water at the other, thus giving a mixed effluent at the tile drain outlets.

3.5.5 *Heavy metals in sewage and drainage water*

Samples of sewage and drainage water were filtered over a 0.45-μm membrane filter and analysed for Zn, Cu, Mn and Fe. Since procedures, notably for concentration, were laborious, samples from one drain only, a deep drain in the centre of Plot east-12, were selected for analysis; results are given in Figs. 26 - 29. Iron and manganese behaved quite similarly: the suspended fractions (> 0.45 μm) of both metals reached a maximum during the first hours after flooding, before sewage water broke through, and then remained fairly constant. The dissolved fractions (< 0.45 μm) of both metals were almost constant over the whole range and Mn was very low, about 0.01 mg/l. The behaviour of Zn and Cu was also quite similar, but they differed from Fe and Mn in that the maximum

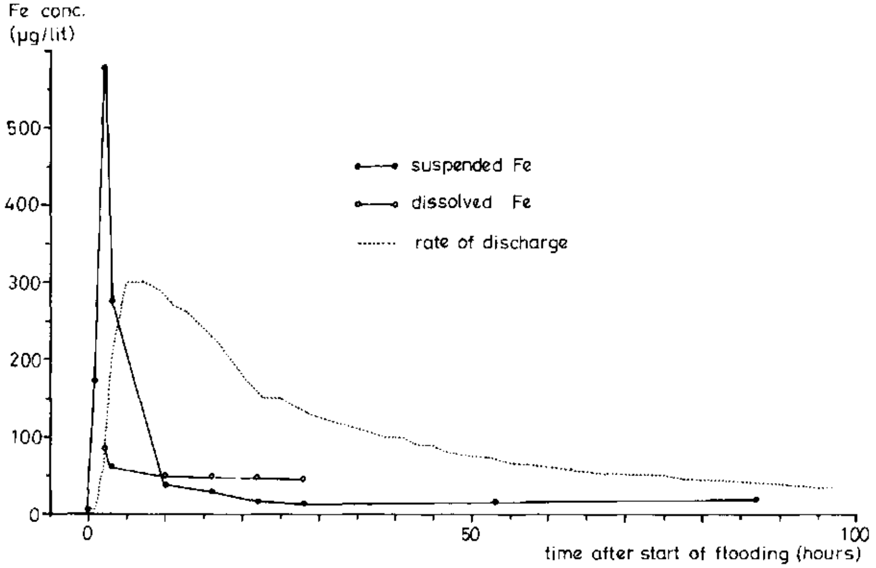

Fig. 26. Suspended and dissolved Fe in the effluent of Drain 6.

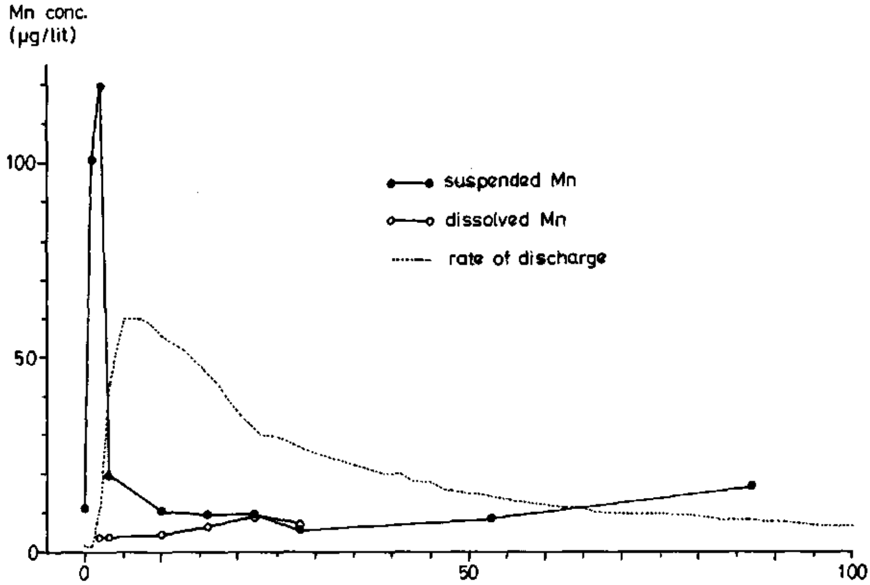

Fig. 27.

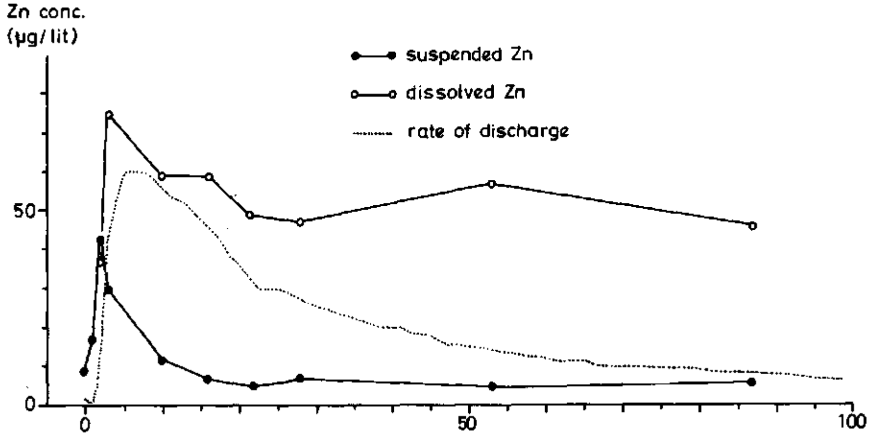

Fig. 28.

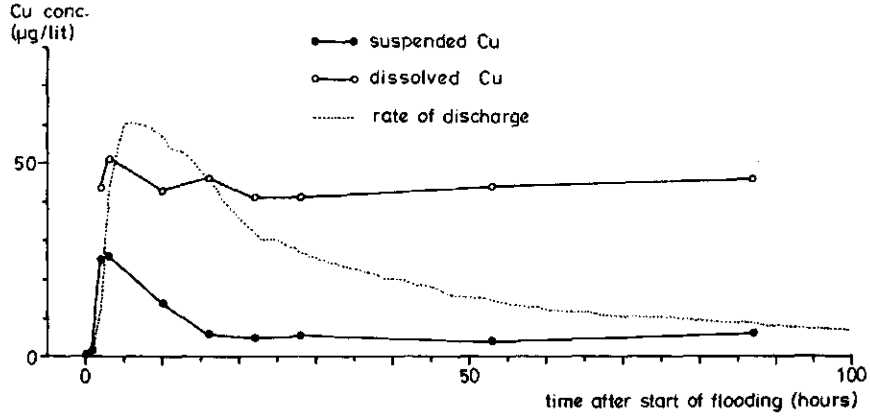

Fig. 29.

Figs. 27-29. Suspended and dissolved Mn (Fig. 27), Zn (Fig. 28) and Cu (Fig. 29) in the effluent of Drain 6.

concentrations in the suspended fractions were lower than in the dissolved fractions.

The suspended metals in the effluent of the drain during the first three hours after flooding did not come from sewage water, but from capillary water. The contents of suspended matter in drainage water were not determined quantitatively, but larger amounts of suspended matter remained on the filters used in phosphate analysis early in sampling than later. Part of this suspended matter may have been present in or near the tile drains, as was suggested by the presence of brown fibrous material, possibly clusters of filaments of *Sphaerotilus* spp. Iron reduction is not likely to a large extent, as is confirmed by the absence of iron accumulations around the drains. But some movement of Fe^{II} and Mn^{II} towards the drains may have occurred and may in part be responsible for the accumulation of these metals near the drains.

Comparison of the concentrations of Na^+, K^+, Ca^{2+} and Mg^{2+} in sewage and drainage water, presented elsewhere (Beek et al., 1977), shows that these cations were not retained by the soil, suggesting that the adsorption complex was saturated with respect to those ions. The cation-exchange complex could also be saturated with cationic heavy metals. The data presented in Table 5 suggest that the soil may have been nearly saturated with dissolved Cu and Zn, and that large differences in retention for the different metals may be expected.

Results for sewage water in Table 5 are split up into two series: the first series was 6 months after sampling and the second series 18 months. Comparison between the series indicates that part of the suspended metals was converted to dissolved form upon standing in the cold-storage chamber, probably by microbial decomposition of suspended matter. The drainage water was analysed for heavy metals 6 months after sampling, together with the first series of sewage water. Comparison of concentrations of suspended metals in the first series with those in the second series shows that conversion of

Table 5. Concentrations of heavy metals (mg/l) in sewage and drainage water and contents in sewage sludge (ppm) determined 6 months (Series 1) and 18 months (Series 2) after sampling (November 1974) at the sewage farm near Tilburg.

Element	Fraction	Sew. Water		Drain. Water	Ratio[1]	Sew. Sludge[2]
		series 1	series 2	series 1		series 1
Fe	susp	3.00	2.00	0.02		
	diss		1.00	0.05		
	tot		3.00	0.07	0.02	8400
Mn	susp	0.05	0.02	0.01		
	diss		0.22	0.01		
	tot		0.24	0.02	0.08	160
Zn	susp	0.35	0.06	0.01		
	diss		0.30	0.05		
	tot		0.36	0.06	0.17	970
Cu	susp	0.08	0.04	0.01		
	diss		0.07	0.04		
	tot		0.11	0.05	0.45	150

1. Total concentration in sewage water (Series 2) divided by total concentration in drainage water (Series 1).
2. Bottom sediment from the sewage supply ditch

suspended to dissolved forms apparently did not proceed to any large extent within 6 months. The high fraction of dissolved Mn is in agreement with literature data (Chen et al., 1974). Dissolved Fe contents of sewage water from November 1975 determined shortly after sampling, ranged from 0.24 to 0.30 mg/l (Beek, 1976). The ratios of Fe to Mn, Zn and Cu, respectively, in the suspended fraction of the sewage water after 6 months were close to the corresponding ratios in sludge from the supply ditch, in accordance with the close relation between them. From the Fe data in Table 5, the sludge content of the sewage water was estimated to be 0.36 g/l. Comparison of total metal contents in sewage and drainage water shows that the retaining capacity of the soil decreased in the order Fe (98%), Mn (92%), Zn (83%), Cu (55%). The lower capacity to retain Cu was not simply due to the high fraction of dissolved Cu, since 92% of Mn, which had a higher dissolved fraction, was retained. Possibly, dissolved Cu occurs to a large extent as uncharged or anionic complexes with organic ligands, through its higher affinity for organic ligands than Mn.

The question rises whether the total accumulation of metals in the soils in Plot east-12 is in accordance with the accumulation expected on the basis of metal contents of sewage and drainage water and total amounts of sewage water added. The amounts of metals retained by the soil (mg/l) during the flooding cycle in November 1974 can be estimated from the metal contents of sewage and drainage water given in Table 5. At the time of sampling the sewage water was diluted by heavy rainfall and the dilution factor is estimated to be 2.57 from the chloride concentration of the sewage water, 62.3 mg/l, and undiluted sewage water, 160 mg/l, reported by Beek et al. (1977). Hence the average amounts of metals retained by the soil can be estimated for diluted and undiluted sewage water, provided the retaining efficiency of the soil increases proportionally. If these retention data are representative for the past 50 years and if about 120 m^3 of sewage water has been added per m^2 during that period, the total amounts of metals accumulated in the soil can be estimated (Table 6). Granted the crudity of the calculations, the amounts of metals accumulated in the soil estimated from the retention data and from

Table 6. Retention of heavy metals in soil estimated from concentrations of metals in sewage and drainage water, and from metal contents and bulk density data of Soil Til-2.

	Zn	Cu	Mn	Fe
Total concn (mg/l)[1]				
sewage water	0.36	0.11	0.24	3.00
drainage water	0.06	0.05	0.02	0.07
Retention (mg/l)[2]	0.30-0.77	0.06-0.15	0.22-0.57	2.93-7.52
Amount retained (g/m^2)				
retention[3]	36-92	17-18	26-68	350-900
Soil Til-2[4]	77	20	41	630

1. Concentrations taken from Table 5.
2. Amount of metals retained by the soil per litre sewage water, estimated from the differences between the metal contents of diluted and undiluted sewage and drainage water.
3. Estimated from the retention data and from a total addition of 120 m^3 sewage water per m^2 in 50 years.
4. Estimated from metal contents and bulk density of Soil Til-2.

Soil Til-2 correspond reasonably well. The somewhat higher Cu accumulation estimated from Soil Til-2 suggests that the retaining capacity of the soil for Cu was higher in the past than would follow from the data in Table 5. Hence the adsorption complex may be saturated for cationic Cu.

4 Theoretical

4.1 INTRODUCTION

When aqueous concentrations of heavy metals are of the same order as of competing cations, adsorptive interactions are generally successfully described by the ion-exchange equations commonly used in soil science for alkali and alkaline earth metals (Bolt, 1967). At lower concentrations, however, heavy metals are often strongly preferred over alkali and alkaline earth metals, and this preference increases with decreasing coverage by heavy metals of the cation-exchange complex. At low concentrations, adsorption of heavy metals by soils is often described successfully by Langmuir or Freundlich adsorption equations. If, also at lower concentrations, heavy metals occur mainly as simple cations or cationic complexes, adsorption of these heavy metals would be expected to follow the common exchange equations rather than those particular adsorption equations. For the Langmuir adsorption equation is originally derived to describe the adsorption of gases on plane surfaces, and the Freundlich adsorption equation is an empirical relation, describing the adsorption of gases on solid gas interfaces and of dissolved components on solid-liquid interfaces. It is sometimes difficult to distinguish between the Langmuir and Freundlich adsorption equations on the basis of experimental data, in particular at low aqueous concentrations and at low surface coverage by the cations in question. The use of the Langmuir equation is sometimes preferred over the Freundlich equation since the former is based on a theoretical model, whereas the latter is empirical in nature. However, the model upon which the derivation of the Langmuir equation is based, does not hold for the adsorption of aqueous metals by soils, and therefore theoretically the only advantage of the Langmuir equation is that it predicts an adsorption maximum, whereas the Freundlich equation does not.

To account for the apparent contradiction between the adsorptive behaviour of heavy metals at high concentrations and in the trace region, it may be assumed that a small part of the heavy metals in aqueous solutions is present as (organic) complexes, that are adsorbed with high preference, or, if all heavy metals are present as simple cations, that there is a small fraction of adsorption sites with a high preference for aqueous heavy metals. Both assumptions yield the same result: the heavy metals are adsorbed with high preference at low concentrations and this preference decreases with increasing coverage by heavy metals of the cation-exchange complex. In the following sections of this chapter, regular ion-exchange equations, and the Langmuir and Freundlich adsorption equations will be discussed, and it will be shown that (1) the Langmuir adsorption equation can be derived from simple ion-exchange considerations, assuming that only one type of adsorption site is involved and that only simple heavy-metal cations take part in the exchange reaction ('one-site' model), whereas (2) the Freundlich adsorption equation can be interpreted as an approximative description of ion exchange involving one or more types of heavy-metal cations and one or more types of adsorption sites ('two-site' models). The derivation of the Freundlich equation as an approximation for exact equations, based on the two-site model will be discussed in some detail, since it gives an insight into the behaviour of heavy metals in natural soils.

4.2 ION EXCHANGE

Negatively charged adsorption sites associated with solid surfaces, as of clay minerals and oxides, are always compensated by equivalent amounts of positive charge in the form of protons or other cationic species. Therefore the adsorption of cationic species from aqueous solutions on solid surfaces commonly results in the simultaneous release of equivalent amounts of other cationic species; this process is called ion exchange or exchange adsorption. The collection of all negatively charged surface sites capable of adsorbing cations is referred to as cation-exchange complex and the total amount of these sites is referred to as cation-exchange capacity (CEC) expressed in μeq/g air-dry soil.

4.2.1 Thermodynamic equilibrium constant and ion-exchange equations

The adsorption of cation A on a soil which is initially in the homoionic B form can be represented as follows

$$A + \bar{B} \rightleftarrows \bar{A} + B \qquad (17)$$

where bars denote the adsorbed phase and where it is assumed that both cations are of equal valence (homovalent exchange). The thermodynamic equilibrium condition for Reaction (17) is

$$\Sigma \nu_i \mu_i = 0 \qquad \text{at constant } p,\ T \qquad (18)$$

where p denotes pressure, T temperature, and ν_i denotes the stoichiometric number of substance i, negative for reactants, positive for products, and μ_i the chemical potential of substance i. Thermodynamic quantities such as μ_i refer to electrically neutral species, and not to single ions. In ion-exchange reactions, however, both cations are associated with the same anion in solution and with the same adsorbent in the adsorbed phase. No distinction is here made between chemical potentials for single ions and neutral salts but, where ions are involved, only differences in chemical potentials referring to the same phase are considered. The thermodynamic equilibrium condition for Reaction 17 reads

$$-\mu_A - \bar{\mu}_B + \bar{\mu}_A + \mu_B = 0 \qquad (19)$$

where again bars refer to the adsorbed phase. This equilibrium condition can be transformed into an exchange equation with the aid of the Lewis equation, which reads

$$\mu_i = \mu_i^o + RT \ln a_i \quad (20)$$

where R is the gas constant, a_i is the relative activity of species i, and μ_i^o is the chemical potential of species i in the standard state of the system. The Lewis equation may also be considered as the definition equation of the relative activity. The standard state of a system is a chosen state in which all variables (p, T, composition) have specified values, and in which a_i equals unity. The standard state of an electrolyte solution is the hypothetical state in which the solute would exist at unit molarity and 1 atm pressure (and specified temperature) but would still follow Henry's law, i.e. behave 'ideally'. The standard state of the adsorbed phase is chosen as the homoionic adsorbent in equilibrium with an infinitely dilute solution of the ion of interest. In addition, it may be necessary to define the standard state of the solvent, and to specify the values of Galvani and Volta potential differences, dielectric constants, and others, in the standard state of the adsorbed phase. Substituting the appropriate chemical potentials in the equilibrium condition, it follows that

$$- \mu_A^o - \bar{\mu}_B^o + \bar{\mu}_A^o + \mu_B^o = RT \ln (a_A \bar{a}_B / a_B \bar{a}_A) \quad (21)$$

writing

$$\Sigma \nu_i \mu_i^o = \Delta G_{ads}^o \quad (22)$$

and

$$\exp (-\Delta G_{ads}^o / RT) = K_{A/B}^o \quad (23)$$

and substituting these expressions in the equilibrium condition it follows that

$$(\bar{a}_A / \bar{a}_B) = K_{A/B}^o \, (a_A / a_B) \quad (24)$$

where ΔG_{ads}^o is the change in free enthalpy accompanying the exchange reaction (the conversion of one mole of adsorbent from the homoionic B form to the homoionic A form) under standard conditions, and where $K_{A/B}^o$ is the thermodynamic equilibrium constant or 'selectivity' (exchange) constant for the A/B exchange reaction. Equation 24 may be referred to as an 'exchange' equation, since it relates the ratio of the ionic activities in the adsorbed phase to those in solution. When $\Delta G_{ads}^o = 0$, it follows that $K_{A/B}^o$ equals unity, which implies that there exists no preference for either A or B: the ratio of the activities in the adsorbed phase equals the ratio of the activities in the solution phase. When $\Delta G_{ads}^o < 0$ it follows that $K_{A/B}^o > 1$ and that A is preferentially adsorbed, whereas if $\Delta G_{ads}^o > 0$ it follows that $K_{A/B}^o < 1$ and then B is preferred over A by the adsorbent. The value of $K_{A/B}^o$ only indicates whether the adsorbent (resin, clay) discriminates between A and B ions, but does not indicate whether A or B are adsorbed at all.

The ion-exchange equation in the form of Eq. 24 is difficult to apply, since generally the activities of the ions are not known accurately. Therefore, the thermodynamic equilibrium constant may be replaced by a corrected selectivity constant, $K'_{A/B}$, according to

$$K'_{A/B} = K^{o}_{A/B}\ (\bar{f}_B/\bar{f}_A) \tag{25}$$

where $\bar{f}_A$ and $\bar{f}_B$ denote the activity coefficients of A and B in the adsorbed phase. The activity coefficient of species i in the adsorbed phase, $\bar{f}_i$, may be defined formally as

$$\bar{f}_i = \bar{a}_i/\bar{X}_i$$

where $\bar{X}_i$ denotes the substance (mole) fraction of species i in the adsorbed phase. The activity coefficient may also be defined as

$$\bar{f}_i = \bar{a}_i/(\bar{c}_i/\bar{c}^{o})$$

where $\bar{c}^{o}$ is a reference molarity, usually 1 mol/l. The activity coefficient of a single ion, however, is not a measurable quantity, only the ratio of the activity coefficients can be determined experimentally. Therefore it is more appropriate to define the ratio of the activity coefficients of A and B in the adsorbed phase according to

$$\bar{f}_A/\bar{f}_B = \bar{a}_A\bar{X}_B/\bar{a}_B\bar{X}_A \tag{26}$$

In ion exchange, the substance fraction of species i in the adsorbed phase is commonly expressed as the 'equivalent' fraction, e.g. for a system containing A and B ions, $\bar{X}_A$ is given by

$$\bar{X}_A = \bar{c}_A/(\bar{c}_A + \bar{c}_B) \tag{27}$$

where bars refer to the adsorbed phase and where concentrations are expressed in equivalents per litre (eq/l). Equation 24 can now be written as

$$\bar{X}_A/\bar{X}_B = K'_{A/B}\ (a_A/a_B) \tag{28}$$

where $\bar{X}_A$ and $\bar{X}_B$ denote the equivalent fractions of A and B in the adsorbed phase. Furthermore, a selectivity coefficient, $K_{A/B}$, may be defined according to

$$K_{A/B} = K'_{A/B}\ (f_A/f_B) = K^{o}_{A/B}\ (\bar{f}_B/\bar{f}_A)(f_A/f_B) \tag{29}$$

where f_A/f_B denotes the ratio of the activity coefficients of the ionic species in solution, which is defined as

$$f_A/f_B = a_AX_B/a_BX_A \tag{30}$$

where X_A and X_B denote the equivalent fractions of ions A and B in solution. Equations

24 and 28 now can be written as

$$\bar{X}_A/\bar{X}_B = K_{A/B}\ X_A/X_B \tag{31}$$

Since the present discussion is confined to homovalent exchange (Eq. 17), it is immaterial whether $\bar{X}_i$ and X_i are expressed as equivalent or mole fractions, but in case of heterovalent exchange, it is of importance.

Activity coefficients of ions in dilute aqueous solutions can be estimated with the Debye-Hückel equation (Garrels & Christ, 1965, p. 61). Once the ratio f_A/f_B is known for all X_A, the values of $K^o_{A/B}$, $\bar{f}_A$ and $\bar{f}_B$, may be estimated from ion-exchange experiments, according to a procedure described by Gaines & Thomas (1953). This procedure transforms ion-exchange isotherms into thermodynamically meaningful quantities, but yields no information about the factors underlying a possible variation in $K'_{A/B}$, i.e. in $\bar{f}_A$ and $\bar{f}_B$, with the surface composition of the adsorbent. Also, the procedure described by Gaines & Thomas does not predict the behaviour of $\bar{f}_A/\bar{f}_B$, so models have to be developed to predict this behaviour.

4.2.2 Changes in chemical potential upon exchange adsorption

The standard chemical potential of species i in solution is a function of temperature, and includes translational (possibly rotational and vibrational), electronic and nuclear energy contributions, as well as energy contributions that arise from interactions of the ion with its surrounding, such as ion-solvent and ion-ion interactions. The standard chemical (or electro-chemical) potential of species i in the adsorbed phase, also includes energy contributions that arise from interactions with the solid surface, in particular the adsorption sites. Considerable changes in energies, that contribute to the standard chemical potentials, are to be expected when ions are adsorbed from aqueous solution by a solid adsorbent. In bulk solution, ions can move in three dimensions, but upon adsorption in a diffuse-double layer free translation is hindered, and, for adsorption in a non-localized monolayer, only two-dimensional translation is possible, whereas for localized adsorption, i.e. when ions are 'trapped' in 'potential wells' associated with the solid surface, no translation is possible at all. The loss of one or more translational degrees of freedom, however, is compensated by an increase in degrees of freedom associated with vibrational motion. The repulsive interactions between cations are negligible in an infinitely dilute solution, but in the adsorbed phase, where the particles are close together, these interactions may become significant, also by a lowering of the dielectric constant of the solution close to the solid surface. In the bulk solution, cations may have a primary hydration shell, consisting of a number of water molecules directly bonded to the cation, and a secondary hydration shell, consisting of water molecules that are held less strongly, by hydrogen bonds and ion-dipole interactions. Upon adsorption in a diffuse double-layer the ions remain largely hydrated, but in a Stern layer they lose part of their hydration water. The interactions between cations and anions in the bulk solution are replaced, upon adsorption, to a large extent by interactions with the surface sites. For cations these interactions may include, besides coulombic attraction, also hydrogen bonding, coordinate bonding or London-van der Waals interactions, which may notably be of influence when the adsorption of larger (organic) cations is considered.

It is possible to estimate some of the main energy changes for the A/B exchange reaction (Eq. 17), after some simplifications. The standard free enthalpy of exchange adsorption (Eq. 22) can be distinguished in three different terms:

$$\Delta G^o_{ads}(A/B) = \Delta G^o_{coul}(A/B) + \Delta G^o_{hydr}(A/B) + \Delta G^o_{spec}(A/B) \tag{32}$$

where $\Delta G^o_{coul}(A/B)$ denotes the change in free enthalpy from differences in coulombic attraction between the ionic species and the adsorption sites, $\Delta G^o_{hydr}(A/B)$ denotes the change in free enthalpy from differences in free enthalpy of dehydration of the adsorbing ions and of hydration of the ions being replaced, and $\Delta G^o_{spec}(A/B)$ includes changes in free enthalpy from differences in energies arising from specific interactions, such as hydrogen bonding or coordinate bonding.

The electrical work involved in bringing an Avogadro number, L, of unit charges, $z_i e$, where z_i is the charge number or valency of ion i and e is the charge of an electron, from the bulk solution up to a point at a distance x from the solid surface, equals $z_i F\psi(x)$, where Le = F, the Faraday constant, and where $\psi(x)$ is the (outer) potential difference at a distance x from the solid adsorbent surface. An expression for $\psi(x)$ is obtained by solving the Poisson-Boltzmann equation (Bockris & Reddy, 1970, p. 725) for the appropriate boundary conditions. The potential difference at the solid surface, $\psi(0)$, is a function of temperature, surface charge density, electrolyte concentration and dielectric constant of the solvent. When only two ionic species are involved in the exchange reaction, the coulombic contribution to $\Delta G^o_{ads}(A/B)$ takes the form

$$\Delta G^o_{coul}(A/B) = z_A F\psi(x_A) - z_B F\psi(x_B) \tag{33}$$

where x_A and x_B denote the equilibrium distances between A and B ions and the surface. The only ionic properties in this expression, are the charge numbers of the ions and the (hydrated) ionic radii, which determine the distance of closest approach between the ions and the adsorption site.

When the solid surface has a low electric field, i.e. when the electric field strength, $\frac{d}{dx}\psi(x)$, is smaller than 10^8 V/m, the relative dielectric constant of water, ε_w, remains approximately constant (about 80 at room temperature) near the surface. But in high electric fields $\varepsilon_w(x)$ may decrease sharply with decreasing distance to the solid surface. For $\frac{d}{dx}\psi(x) > 10^9$ V/m the first layer of water molecules adsorbed at the solid surface becomes electrically saturated, and $\varepsilon_w(x)$ may reach values as low as 6 in this layer. Through the (partial) electric saturation of the water molecules near the solid surface, $\psi(x)$ may decrease sharper with distance than would be expected for a constant dielectric constant. Hence small differences in equilibrium positions between ions may result in significant differences in $\Delta G^o_{coul}(A/B)$.

The Born expression for the free enthalpy of hydration is obtained from the work of discharging a sphere with radius r_i and charge $z_i e$ in vacuum plus the work of charging this sphere in water (Bockris & Reddy, 1970, p. 56)

$$\Delta G^{o}_{hydr} = -(z_i e)^2/8\pi r_i \varepsilon_o + (z_i e)^2/8\pi r_i \varepsilon_o \varepsilon_w \tag{34}$$

where ε_o is the permittivity of vacuum. The Born model does not take into consideration the variation in dielectric constant near the ion, and does not give an accurate description of the interactions between the central ion and the coordinated water molecules in the primary hydration shell, because of specific ion effects that contribute to the total hydration energy, e.g. ligand field stabilization energies for transition-metal cations. Therefore, it may be more convenient to take $r_i + 2r_w$ instead of r_i, where r_w is the radius of a water molecule (James & Healy, 1972), i.e. to confine the use of Eq. 34 to the secondary hydration shell only. In general this will be sufficient, since most ions retain their primary hydration shell upon adsorption.

The Born model of charging and discharging spheres may be applied to ions that move from the bulk solution ($\varepsilon_w \approx 80$) to the solid surface. When the relative dielectric constant of the solid, ε_s, is lower than ε_w, work must be done to replace part of the secondary hydration shell by the solid. If the dielectric constant of water remains constant near the solid surface, the change in free enthalpy of hydration upon adsorption of one mole of A and desorption of one mole of B is given by

$$\Delta G^{o}_{hydr}(A/B) = (z_A^2/x_A - z_B^2/x_B)(1/\varepsilon_s - 1/\varepsilon_w)e^2 L/32\pi\varepsilon_o \tag{35}$$

where the equilibrium distances of the ions to the surface, x_A and x_B, are assumed to be not smaller than $r_A + 2r_w$ and $r_B + 2r_w$, respectively (James & Healy, 1972). If the dielectric constant of water decreases near the solid surface, work must be done to replace part of the secondary hydration shell by surfacial water of low dielectric constant. If so, Eq. 35 becomes rather involved, since it is difficult to include ε_w as a continuous function of x in $\Delta G^{o}_{hydr}(A/B)$.

The only ionic properties in the expressions for $\Delta G^{o}_{coul}(A/B)$ and $\Delta G^{o}_{hydr}(A/B)$ are z_i and r_i, and no differences in exchange behaviour are to be expected between cations of equal charge and with equal hydrated radii. Ion exchange experiments described in Chapter 5 show that Ca^{2+}, Cd^{2+}, Zn^{2+} and Cu^{2+} compete on an almost equal basis for planar adsorption sites on clay minerals, suggesting that if adsorption occurs in a Stern layer, the hydrated radii of the cations involved are of the same order.

If adsorption takes place in a diffuse layer, i.e. for

$$x_i > r_i + 2r_w$$

the hydrated ionic radii are of minor importance.

If the ions involved in the exchange reaction differ in properties such as polarizability or the capability to form coordinate or hydrogen bonds, these properties have to be included in a specific interaction term, $\Delta G^{o}_{spec}(A/B)$. No general form can be proposed for this term: $\Delta G^{o}_{spec}(A/B)$ largely has the character of a 'remainder' term in which also the effects are included of a possible underestimation of $\psi(x)$, from the existence of discrete point charges on the solid surface instead of a continuous field spread out over the whole surface, and of a possible overestimation of the energy of hydration.

4.2.3 Theory of solid solutions applied to ion exchange

The theory of solid solutions assumes that particles of unequal size occupy different numbers of sites in a (hypothetical) lattice. Application of this theory to ionic species amounts to assuming that particles of unequal charge occupy different numbers of sites, not because of their ionic volumes, but because of their different charges. In order to simplify the formulae to be presented, the discussion will be confined to divalent cations, A^{2+} and B^{2+}, and it will be assumed that they are adsorbed on a regular two-dimensional array of sites presented by the surface of a mineral, i.e. each ion occupies two adjacent sites, and it will further be assumed that each site has four nearest neighbours. From the relation

$$nz_i = n\lambda_i + 2(z_i - 1) \qquad (36)$$

where n is the number of nearest neighbours of one site and z_i is the number of sites occupied by one particle (z_i equals the charge number of the ion), the number of sites adjacent to an A or B particle in the adsorbed state, $n\lambda_i$, can be calculated. For $n = 4$ and $z_i = 2$ it follows that $\lambda_i = 3/2$, i.e. each pair of sites has six nearest neighbours. The notion of λ_i is fundamental in the statistical thermodynamical treatment of mixtures by Guggenheim (1945), since it plays an essential role in the chance that, if one particular site is occupied by either an A or a B particle, a given neighbouring site is occupied by the same A or B particle, or by a different A or B particle.

If the energies of mixing are all zero, all configurations of A and B particles in the adsorbed phase have the same configurational energy and hence the same statistical weight, i.e. the arrangement of particles is completely random for zero energy of mixing; this situation is referred to as 'ideal solid solution' (ISS). When the energies of mixing are not zero, the statistical weight of the distinguishable configurations is also determined by the intermolecular energy; this situation is referred to as 'regular solid solution' (RSS). Then the intermolecular potential energy, W, for a given configuration of the system may be regarded as a sum of terms, each pair of neighbours contributing one term (Guggenheim, 1945). The contribution to the total potential energy by one pair of sites, one occupied by an element of A, the other by an element of B, is given by

$$w = w_{AB} - \tfrac{1}{2}w_{AA} - \tfrac{1}{2}w_{BB} \qquad (37)$$

where w_{AB} denotes the energy of interaction between unlike particles and w_{AA} and w_{BB} the energies of interaction between like particles. For adsorption of ions from solution, the repulsive interactions between ions may be described in first approximation by Coulomb's Law. If ionic species A and B differ in properties such as polarizability or number of water molecules in the inner coordination sphere, the 'effective' charge numbers, az_A and bz_B, where the parameters a and b are close to unity, may be slightly different from

z_A and z_B. Introducing the hypothetical 'effective' charges of ions A and B, az_Ae and bz_Be, the energy of interaction, w, for a system containing two divalent cations, A and B, may be represented as

$$w = \{4ab/x_{AB} - 2a^2/x_{AA} - 2b^2/x_{BB}\}\ e^2 \tag{38}$$

where x_{ij} denotes the interparticle distance. When $a = b$ it follows that $w > 0$ for

$$2/x_{AB} > 1/x_{AA} + 1/x_{BB}$$

and $w < 0$ for

$$2/x_{AB} < 1/x_{AA} + 1/x_{BB}$$

hence $w \neq 0$ for

$$x_{ij} = x_{ii} \neq x_{jj}$$

When the interparticle distances are all equal, $w < 0$ for $a \neq b$, since

$$2ab - a^2 - b^2 = -(a - b)^2 < 0$$

for all $a \neq b$. From these considerations it follows that, also for the divalent cations A and B, w may be positive or negative, according to the configuration of the particles and their molecular properties.

The energy of mixing for the present system ($n = 4$, $z_A = z_B = 2$) varies with the surface composition of the exchange complex

$$E_{mix} = 12\ w\ N\ \bar{\Xi}_A\bar{\Xi}_B/(1 + \beta) \tag{39}$$

where $N = N_A + N_B$, the total number of particles per unit mass of adsorbent, and $\bar{\Xi}_A$ and $\bar{\Xi}_B$ represent the 'corrected' equivalent fractions in the adsorbed phase

$$\bar{\Xi}_A = \lambda_AN_A/(\lambda_AN_A + \lambda_BN_B) \tag{40a}$$

and

$$\bar{\Xi}_B = \lambda_BN_B/(\lambda_AN_A + \lambda_BN_B) \tag{40b}$$

but for homovalent exchange these expressions reduce to the simple equivalent (or mole) fractions, and the notation $\bar{X}_i$ will be used instead of $\bar{\Xi}_i$. The quantity β (in Eq. 39) is obtained from the equation of quasi-chemical equilibrium for a binary mixture and is defined through

$$\beta = \{(1 - 2\bar{X}_A)^2 + 4\ \bar{X}_A\bar{X}_B \exp\ (2w/kT)\}^{\frac{1}{2}} \tag{41}$$

where k is the Boltzmann constant and T the temperature. It follows that β is a measure for the intermolecular interactions: for zero energy of mixing $\beta = 1$ and for non-zero energies of mixing $\beta \neq 1$. The activity coefficients of the ions in the adsorbed phase are given by

$$\bar{f}_A = \{\beta + \bar{X}_A - \bar{X}_B\}^3/\{(\beta + 1)\ \bar{X}_A\}^3 \tag{42a}$$

and

$$\bar{f}_B = \{\beta + \bar{X}_B - \bar{X}_A\}^3/\{(\beta + 1)\ \bar{X}_B\}^3 \tag{42b}$$

which may be inserted in Eq. 24 to yield an exchange equation for divalent cations based on the regular solid solution model. If 2w/kT is sufficiently small, exp (2w/kT) may be approximated by 1 + 2w/kT and β becomes

$$\beta \simeq (1 + 4\bar{X}_A\bar{X}_B\ 2w/kT)^{\frac{1}{2}} \tag{43}$$

which may be simplified to

$$\beta \simeq 1 + 2\bar{X}_A\bar{X}_B\ 2w/kT \tag{44}$$

where Taylor's approximation has been used. The symbol $\simeq$ denotes 'approximately equal to' (see Footnote 4). Inserting the simplified expression for β (Eq. 44) in the expressions for $\bar{f}_A$ and $\bar{f}_B$ (Eqs. 42a and b) the following relations are obtained

$$\bar{f}_A \simeq (1 + \bar{X}_B\ 2w/kT)^3/(1 + \bar{X}_A\bar{X}_B\ 2w/kT)^3 \tag{45a}$$

and

$$\bar{f}_B \simeq (1 + \bar{X}_A\ 2w/kT)^3/(1 + \bar{X}_A\bar{X}_B\ 2w/kT)^3 \tag{45b}$$

and insertion of these expressions for the activity coefficients in Eq. 24 results in an exchange equation of the form

$$\{(1 + \bar{X}_B\ 2w/kT)/(1 + \bar{X}_A\ 2w/kT)\}^3\ (\bar{X}_A/\bar{X}_B) = K^o_{A/B}\ (a_A/a_B) \tag{46}$$

which is valid for small values of 2w/kT only. Equations 45a and 45b can be transformed into

$$\ln \bar{f}_A = 3(2w/kT)\ \bar{X}_B^2 \tag{47a}$$

and

$$\ln \bar{f}_B = 3(2w/kT)\ \bar{X}_A^2 \tag{47b}$$

where the approximation $\ln (1 + x) \simeq x$ has been used, and where ln denotes the natural logarithm. In this form the activity coefficients are similar to those given by Lewis & Randall (1961, p. 284) for a binary mixture of equal sized particles with small but non-zero energies of mixing. The limiting behaviour of the exact formulae for the activity coefficients has to be investigated for $\bar{X}_A \to 0$ (Eq. 42a) and $\bar{X}_B \to 0$ (Eq. 42b). The Taylor approximation for $\beta(\bar{X}_A)$ for small values of $\bar{X}_A$ becomes

$$\beta(\bar{X}_A) \simeq 1 - 2\ \bar{X}_A\ \{1 - \exp\ (2w/kT)\} \tag{48}$$

and using this expression for $\beta(\bar{X}_A)$, it follows that

$$\lim\ (\bar{X}_A \to 0)\ \bar{f}_A(\bar{X}_A) = \{\exp(2w/kT)\}^3 \tag{49}$$

In an analogous way it is found that

$$\lim\ (\bar{X}_B \to 0)\ \bar{f}_B(\bar{X}_B) = \{\exp(2w/kT)\}^3 \tag{50}$$

and then the difference

$$|\{\exp(2w/kT)\}^3 - (1 + 2w/kT)^3| \tag{51}$$

where vertical bars denote the absolute value (modulus), represents the maximum deviation between the exact solution for the ratio $\bar{f}_A/\bar{f}_B$ (Eqs. 42a and b) and the approximate solution (Eqs. 45a and b). For $|2w/kT| \leq 0.25$ the relative errors in the approximative formulae are $\leq 10\%$.

In Fig. 30 the entropy of mixing, ΔS_{mix}, is plotted as a function of $\bar{X}_A$ for two values of 2w/kT; the curves of $\Delta S_{mix}/Nk$ for $2w/kT = +1.0$ and -1.0 are not exactly the same, but they coincide on the scale of Fig. 30. For values of $|2w/kT| \leq 0.25$ the curves practically coincide with the one for $2w/kT = 0$. The entropy of mixing is positive, reflecting that the number of accessible configurations increases with $\bar{X}_A$ to a maximum

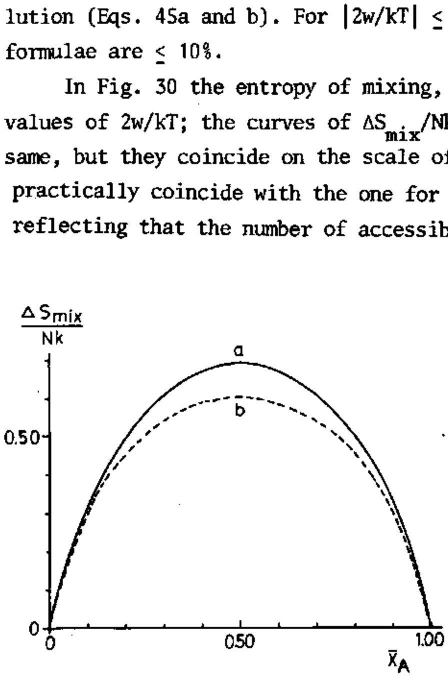

Fig. 30. Entropy of mixing as a function of substance fraction of A on the adsorbent surface for a binary mixture of equal-charged particles, A and B, for (a) $2w/kT = 0$ (Eq. 53) and (b) $2w/kT = \pm 1.0$ (Guggenheim, 1945, from Eq. 5.5).

at $\bar{X}_A = \bar{X}_B = \frac{1}{2}$. For athermal mixing this can be understood as follows: there are $(N_A + N_B)!$ ways of partitioning $(N_A + N_B)$ particles among $(N_A + N_B)$ sites. This number has to be corrected for the fact that N_A particles of category A are identical (not distinguishable) and N_B particles of category B are identical. Therefore the entropy of athermal mixing is found as (Lewis & Randall, 1961, p. 281)

$$\Delta S_{mix} = k \ln(N_A + N_B)!/N_A!N_B! \tag{52}$$

where N! denotes factorial N. With Stirling's approximation, which is valid for large N, Eq. 52 simplifies to

$$\Delta S_{mix}/(N_A + N_B)k = - \bar{X}_A \ln \bar{X}_A - \bar{X}_B \ln \bar{X}_B \tag{53}$$

For non-zero energies of mixing, the number of accessible configurations decreases, lowering the entropy of mixing.

The energy of mixing, E_{mix}, also has a maximum ($w > 0$) or a minimum ($w < 0$) for $\bar{X}_A = \bar{X}_B = \frac{1}{2}$, and Fig. 31 shows that

$$|E_{mix}(w = -a)| \geq E_{mix}(w = a) \tag{54}$$

where a is a positive number. For the ideal solid solution, the energy of mixing is zero

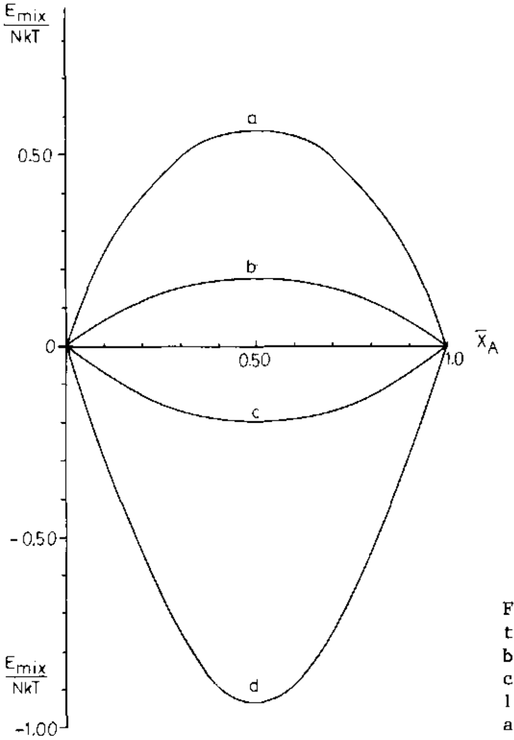

Fig. 31. Energy of mixing (Eq. 39) as a function of substance fraction of A on the adsorbent surface for a binary mixture of equal-charged particles, A and B, for (a) $2w/kT = 1.00$, (b) $2w/kT = 0.25$, (c) $2w/kT = -0.25$, and (d) $2w/kT = -1.00$.

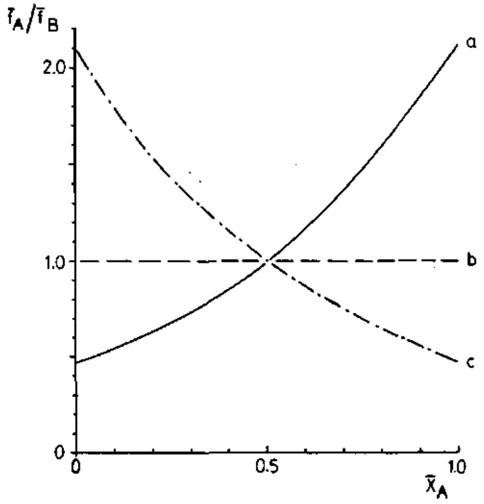

Fig. 32. The ratio of the activity coefficients of equal-charged particles in the adsorbed state (Eq. 42) for (a) 2w/kT = -0.25, (b) 2w/kT = 0, and (c) 2w/kT = 0.25.

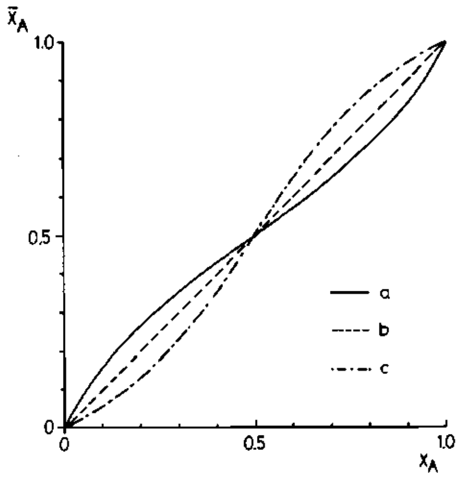

Fig. 33. Exchange isotherms for a binary mixture of equal-charged particles, based on Eq. 42 and $K^o_{A/B}$ = 1, for (a) 2w/kT = -0.25, (b) 2w/kT = 0, and (c) 2w/kT = 0.25.

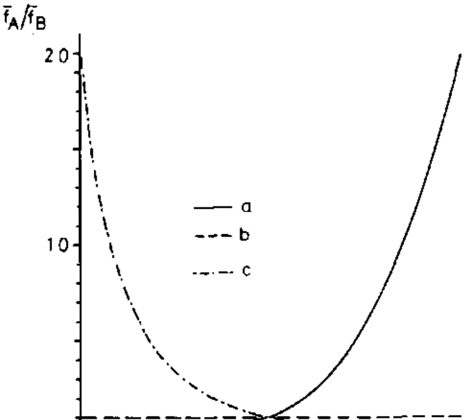

Fig. 34. The ratio of the activity coefficients of equal-charged particles in the adsorbed state (Eq. 42) for (a) 2w/kT = -1.0, (b) 2w/kT = 0, and (c) 2w/kT = 1.0.

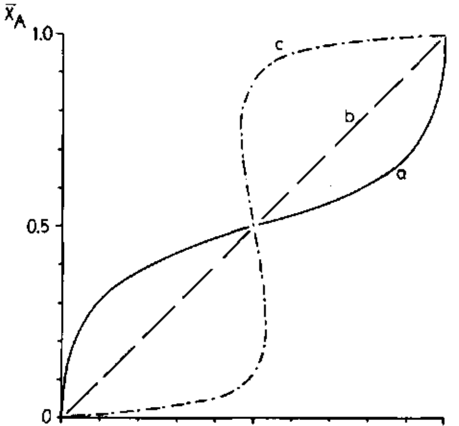

Fig. 35. Exchange isotherms for a binary mixture of equal-charged particles, based on Eq. 42 and $K^o_{A/B}$ = 1, for (a) 2w/kT = -1.0, (b) 2w/kT = 0, and (c) 2w/kT = 1.0.

by definition, and E_{mix} coincides with the x axis. Figures 30-35 are all based on the exact formulae for binary mixtures with non-zero energies of mixing as presented by Guggenheim (1945), and not on the approximative formulae derived from them in the present study, for small values of 2w/kT. The approximative formulae are presented only because they are more intelligible, as they do not contain β, and for future reference (Section 4.4.3).

In applying the theory of solid solutions to ionic species, expressions for $\bar{f}_A$ and $\bar{f}_B$ are obtained that cannot be verified experimentally. Therefore, only the ratio $\bar{f}_A/\bar{f}_B$ is plotted in Figs. 32 and 34. For athermal mixing the ratio $\bar{f}_A/\bar{f}_B$ equals unity for homovalent exchange; only for heterovalent exchange (e.g. Na^+/Ca^{2+}) the ratio differs from unity. The exchange isotherms for $K^o_{A/B} = 1$, corresponding to the activity coefficients in Figs. 32 and 34 are plotted in Figs. 33 and 35, respectively. The curves in Fig. 35, notably the curve for $2w/kT = +1.0$, look unfamiliar, but they are included because they show clearly the consequences for the present model of large values of $|2w/kT|$, even though they may not be likely to occur in soil systems. For $2w/kT = +1.0$ unlike particles will avoid contact with each other, due to the unfavourable energy conditions. Therefore, like particles will tend to form 'islands' in order to minimize contact between unlike particles. The curve for 2w/kT in Fig. 35 illustrates that, initially, it is difficult to bring A particles onto an adsorbent in the homoionic B form, since the homoionic form is energetically more favourable than a mixture. Entropy increases with mixing, however, and after the adsorbent has reached a critical composition ($\bar{X}_A \simeq 0.25$), the adsorbent starts to take up A particles 'spontaneously', thereby increasing $\bar{X}_A$ and decreasing X_A.

The exchange isotherms for $K^o_{A/B} = 1$ show what may be referred to as 'selectivity reversal': for $X_i < 0.5$ one type of cation is preferred over the other by the adsorbent, and for $X_i > 0.5$ the other is adsorbed preferentially. The Cu^{2+}/Ca^{2+} exchange isotherm on Bentonite clay determined at 25 °C by El Sayed et al. (1970), showed a type of selectivity reversal similar to Curve c ($2w/kT = +0.25$) in Fig. 33. The selectivity reversal disappeared at 50 °C, where it seemed that the Ca ion was slightly preferred over the Cu ion, for all X_{Cu}. Since a positive value for 2w/kT is likely to be a configurational effect, this effect could disappear when the temperature increases, by increasing thermal motion of the particles in the adsorbed state. El Sayed et al. (1970) suggest that 'the presence of islands of high charge density in the structure of the exchanger' provides a plausible explanation, but it is not clear why these islands would be destroyed upon raising the temperature, since charge density is a property of the solid adsorbent.

The formulae for binary mixtures (Guggenheim, 1945) as applied here to ion exchange, were developed and tested for uncharged particles of unequal size. However, the CEC of a soil, determined with a monovalent cation, is commonly approximately equal to the CEC, determined with a divalent or even a trivalent cation when the pH is not too high, e.g. below 7 (Papanicolaou & Overstreet, 1969; Carlson & Overstreet, 1967). Presumably divalent cations do occupy two adjacent adsorption sites at the same time. For the sake of simplicity the present discussion has been limited to homovalent cation exchange, but the theory of solid solutions is, of course, especially suited to account for differences in 'effective' size (charge) between cations. The regular solid solution theory also provides the theoretical framework to include non-zero energies of mixing in the ion-exchange equations. The regular solution theory may be of significance for solid solutions, such as of $CaCO_3$ and $ZnCO_3$, and for (localized) adsorption in a Stern layer, for instance the adsorption of heavy metals on oxide surfaces at high pH. When energies of mixing are close to zero, the ideal solid solution model may be a good approximation.

4.3 LANGMUIR ADSORPTION EQUATION

The Langmuir adsorption equation (or isotherm) was originally derived (Langmuir, 1918) to describe the simple adsorption of gas molecules on a plane surface having only one kind of elementary space, each of which could hold only one adsorbed molecule. It further assumed that the binding of a molecule on any one elementary space was independent of the binding on the remaining elementary spaces. When the Langmuir adsorption equation is applied to adsorption of ionic species in soils, one must remember that (a) adsorption sites with a net charge are never empty, but always associated with ionic species in solution to compensate the charge, (b) a whole range of adsorption sites is to be expected in soils, and (c) interactions among particles in the adsorbed phase cannot be ruled out and thus the free enthalpy of adsorption may depend upon the composition of the adsorbent. A derivation of the Langmuir equation for the adsorption of ionic species in soils, proposed by Ellis & Knezek (1972), does not explicitly consider that the adsorption sites are initially occupied by other ions and that the concentration of these ions in solution increases upon adsorption of the ionic species under consideration. Although application of the Langmuir equation to ion exchange in soils cannot be justified theoretically, there are at least two arguments in favour of it: (a) any type of adsorption reaction that approaches saturation with increasing concentration can be approximated with a Langmuir equation, and (b) all simple ion-exchange reactions reduce to the Langmuir equation at low coverage of the adsorption complex.

The Langmuir adsorption equation as used in soil science can be represented as follows

$$q = q_{max}Kc/(1 + Kc) \tag{55}$$

where q denotes the amount of component i adsorbed per unit mass of adsorbent, c is the aqueous concentration of component i, q_{max} is the adsorption maximum, and K is a constant, which is a measure for the binding strength of the adsorption site for component i. The Langmuir equation can also be written as follows

$$c/q = 1/q_{max}K + c/q_{max} \tag{56}$$

from which it can be seen that a plot of c/q versus c yields a straight line with an intercept of $1/q_{max}K$ and a slope of $1/q_{max}$. A plot of c/q versus c is generally referred to as a 'Langmuir' plot (Fig. 36). Any type of adsorption, characterized by

$$q(0) = 0$$

$$\frac{dq}{dc}(0) = q_{max}K$$

$$\lim(c \to \infty)q(c) = q_{max}$$

can be approximated with a Langmuir adsorption equation, which is the simplest mathemat-

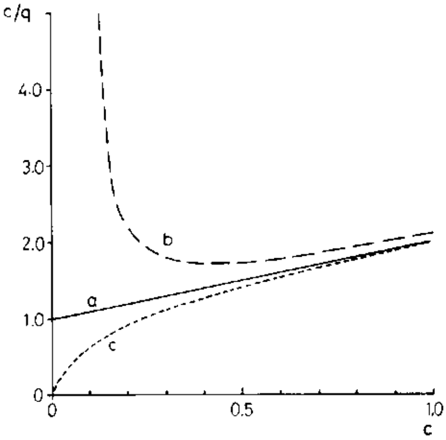

Fig. 36. Langmuir plot of (a) a regular Langmuir isotherm, (Eq. 56) for $q_{max} = K = 1$, (b) a Langmuir isotherm (Eq. 57) with $c = c_{app} - 0.10$, and (c) a Langmuir isotherm (Eq. 58) with $K(c) = 0.91(0.1 + c)/c$.

ical expression satisfying these requirements. Generally $q(0) = 0$ is satisfied for adsorption processes; only if a component is present in more than one form in solution, with one form taking part in the adsorption reaction, and one or more forms not taking part, it follows that $q(c_{app}) = 0$ for $c_{app} > 0$. If the apparent concentration of component i, c_{app}, includes a constant concentration of i in inactive form, c_{in}, and a variable concentration of i taking part in the adsorption reaction,

$$q = q_{max}K(c_{app} - c_{in})/\{1 + K(c_{app} - c_{in})\} \tag{57}$$

for $c_{app} \geq c_{in}$. Since in soils, a whole range of adsorption sites is to be expected, it is unlikely that K really is a constant. In general, K probably decreases with increasing surface coverage, and thus with increasing aqueous concentration, as long as the concentrations of competing ions in solution remain approximately constant. Assuming that $K(c)$ may be approximated by $n(m + c)/c$,

$$q = q_{max}n(m + c)/\{1 + n(m + c)\} \tag{58}$$

It is interesting to note that Curve c in Fig. 36 practically coincides with a curve of the form: $c/q = 2\sqrt{c}$, derived from a Freundlich isotherm $q = \frac{1}{2}\sqrt{c}$. If the adsorption sites are significantly non-uniform (heterogeneous), the Freundlich isotherm should give a better fit than the Langmuir isotherm.

The Langmuir equation can also be considered as an approximate ion-exchange equation, valid for low coverage only. The ion exchange equation describing homovalent exchange (Eq. 31) can be written as follows

$$q_A/q_R = K_{A/R}(c_A/c_R) \tag{59}$$

where the subscript R is used to denote all other competing ions of equal charge to ion A. With the aid of $q_R = Q - q_A$, where Q represents the exchange-adsorption maximum, the following expression can be derived

$$c_A/q_A = 1/Q(K_{A/R}/c_R) + c_A/Q \tag{60}$$

where $K_{A/R}/c_R$ is approximately constant for $c_R >> c_A$. From the ion-exchange equation describing monovalent-divalent exchange

$$q_A^2/q_R = K_{A/R}(c_A^2/c_R) \tag{61}$$

the following approximate expression can be derived

$$c_A/q_A \simeq 1/(QK_{A/R}/c_R)^{\frac{1}{2}} + c_A/2Q \tag{62}$$

Similarly, from the ion-exchange equation describing divalent-monovalent exchange

$$q_A/q_R^2 = K_{A/R}(c_A/c_R^2) \tag{63}$$

the following approximate expression can be derived

$$c_A/q_A \simeq 1/Q^2K_{A/R}c_R^2 + c_A/\tfrac{1}{2}Q \tag{64}$$

All these ion-exchange equations can be written as Langmuir adsorption equations, assuming that $c_A << c_R$. The advantage of the use of the Langmuir equation is that only c_A and q_A, calculated as loss from solution, have to be known, whereas for the application of ion-exchange equations, also the concentrations of competing ions and the adsorption maximum have to be known. For the correct interpretation of the constants in the Langmuir equation, the charge of the ion under consideration and of the major competing ions should be known.

4.4 FREUNDLICH AND ROTHMUND-KORNFELD ADSORPTION EQUATIONS

4.4.1 Freundlich adsorption equation

The Freundlich adsorption equation is an empirical relation between the amount adsorbed of substance i, and the aqueous concentration (or pressure, for gas adsorption), of the form

$$q_i = kc_i^{1/n} \tag{65}$$

where k and n are positive constants, n being > 1 in most cases of practical interest (Freundlich, 1922, p. 151 and p. 232). The Freundlich equation has been widely used in soil science to describe the adsorption of ionic and non-ionic species in soils. The Freundlich equation can also be written in the following form

$$\log q_i = \log k + (1/n)\log c_i \tag{66}$$

and it can be seen that, when experimental data follow a Freundlich isotherm, a plot of log q_i against log c_i should yield a straight line with a slope equal to 1/n and an intercept equal to log k; such a plot is referred to as a 'Freundlich plot'. Although the Freundlich equation is empirical, several authors have tried to give a theoretical derivation of the equation. Contrary to the Langmuir adsorption equation, which is based on an array of distinguishable, independent and equivalent sites, the derivations of the Freundlich equation are all based on the assumption of a decreasing free enthalpy or heat of adsorption with increasing surface coverage, due to surface heterogeneity or to particle interactions. For example, the Freundlich equation can be written as

$$Q\bar{X}_i = k\, a_i^{1/n} \tag{67}$$

where q_i has been replaced by the product of the adsorption maximum, Q, and the fractional surface coverage, $\bar{X}_i = q_i/Q$, and where the concentration c_i, has been replaced by the activity, a_i. This equation can be transformed into

$$nRT\ d\ Q\bar{X}_i = RT\ Q\bar{X}_i\ d\ \ln a_i \tag{68}$$

where both sides have been multiplied with RT. When the Freundlich equation in this form is compared with the Gibbs adsorption equation in the form

$$-d\gamma = RT\ Q\bar{X}_i\ d\ \ln a_i \tag{69}$$

where γ is the interfacial tension, it follows that for

$$-d\gamma = nRT\ d\ Q\bar{X}_i \tag{70}$$

both adsorption equations are equal (Trapnell, 1955, p. 118). Thus, assuming that the change in interfacial tension, which has the dimension of energy per unit area is proportional to the change in surface coverage, the Freundlich equation can be derived from the Gibbs equation. Other derivations of the Freundlich equation assume that the heat of adsorption decreases exponentially with increasing coverage, which also points to surface heterogeneity or to increasing interactions among adsorbed particles. For gas adsorption on initially empty surfaces, the decreasing heat of adsorption (or interfacial tension) with increasing coverage may be due to increasing interactions between adsorbed particles. For ion exchange, however, the surface is always covered with an equivalent amount of ionic species, and then non-zero energies of mixing may result in adsorption isotherms as described in Section 4.2.3 (Figs. 33 and 35), which indeed can be approximated with Freundlich equations over a limited range.

4.4.2 Rothmund-Kornfeld adsorption equation

An empirical equation that may be considered as a form of the Freundlich equation which applies to ion-exchange processes is the Rothmund-Kornfeld equation, which can be written as follows

$$q_A/q_B = k(c_A/c_B)^{1/n} \tag{71}$$

where the subscripts A and B refer to ionic species of equal charge. In this form the equation was found to hold for Ag/Na, K/Ag, Rb/Ag and Li/Ag exchange on permutite, for values of 1/n ranging from 0.39 to 0.69 (Rothmund & Kornfeld, 1918). The Rothmund-Kornfeld equation can also be written as

$$\log(q_A/q_B) = \log k + (1/n)\log(c_A/c_B) \tag{72}$$

and it can be seen that a log-log plot of experimental data that follow a Rothmund-Kornfeld isotherm should yield a straight line with slope 1/n and intercept log k; this is referred to as a 'Rothmund-Kornfeld plot'. The Freundlich equation may be considered as an approximation of the Rothmund-Kornfeld equation, valid for $q_A \ll q_B$ and $c_A \ll c_B$

$$q_A = k\ (q_B c_B^{-1/n})\ c_A^{1/n} \tag{73}$$

Therefore, a derivation of the Rothmund-Kornfeld equation also applies to the Freundlich equation for a limited range.

4.4.3 Derivation of the Rothmund-Kornfeld equation from the regular solid solution model

Comparison of the Rothmund-Kornfeld equation (Eq. 71), written as

$$\bar{X}_A/\bar{X}_B = k\ (a_A/a_B)^{1/n}$$

and the ion-exchange equation (Eq. 24), written as

$$\bar{f}_A\bar{X}_A/\bar{f}_B\bar{X}_B = K^o_{A/B}\ (a_A/a_B)$$

shows that Eq. 24 reduces to Eq. 71 if

$$\bar{f}_A/\bar{f}_B = (\bar{X}_A/\bar{X}_B)^{n-1}\ K^o_{A/B}\ k^{-n} \tag{74}$$

In the present study, such a relationship is derived from the equations presented in Section 4.2.3 for the regular solid solution model. Hence it is possible to derive the Rothmund-Kornfeld equation as an approximation for exchange equations based on the regular solid solution model.

A slightly different approach is described by Garrels & Christ (1965, p. 272 ff). These authors start form the approximate expressions for the activity coefficients as given in Eq. 47, which results in the following expression for the ratio of the activity coefficients

$$\bar{f}_A/\bar{f}_B \simeq \exp(1 - 2\ \bar{X}_A)3(2w/kT) \tag{75}$$

Then they use the following approximation for Eq. 75

$$\bar{f}_A/\bar{f}_B \simeq (\bar{X}_A/\bar{X}_B)^{-3(2w/kT)} \tag{76}$$

and thus they arrive at a 'Rothmund-Kornfeld' equation of the form

$$(\bar{X}_A/\bar{X}_B)^{1-3(2w/kT)} \simeq K^o_{A/B}\ (a_A/a_B) \tag{77}$$

A better approximation for Eq. 75, however, would be the following

$$\bar{f}_A/\bar{f}_B \simeq (2\bar{X}_B)^{3(2w/kT} \tag{78}$$

which would result in a slightly different exchange equation

$$\{\bar{X}_A/\bar{X}_B{}^{1-3(2w/kT)}\} \simeq K^o_{A/B}\ 2^{-3(2w/kT)}\ (a_A/a_B) \tag{79}$$

Figure 37 shows that Eq. 78 (Curve b) is a reasonable approximation for Eq. 75 (Curve a) for $\bar{X}_A$ values up to about 0.8, whereas Eq. 76 (Curve c) is approximative only for $\bar{X}_A$ close to 0.5. The use of Eqs. 47 and 75 for a derivation of the Rothmund-Kornfeld equation is also somewhat doubtful, since the activity coefficients as defined by Eq. 47 are already approximations, which stem from Eq. 42, through Eq. 45, and they are valid for small values of 2w/kT only.

A better approximation for the ratio of the activity coefficients, proposed in this study, is obtained directly from Eq. 45

$$\bar{f}_A/\bar{f}_B \simeq \{(1 + \bar{X}_B\ 2w/kT)/(1 + \bar{X}_A\ 2w/kT)\}^3 \tag{80}$$

and by first using the approximation

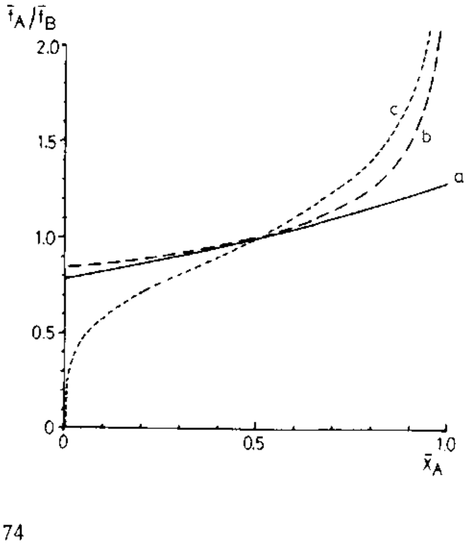

Fig. 37. Approximative equations for $\bar{f}_A/\bar{f}_B$ plotted as function of $\bar{X}_A$, for $3(2w/kT) = -0.25$. Equations 75 (a) and 78 (b) are derived in this study from Guggenheim (1945), and Eq. 76 (c) is from Garrels and Christ (1965).

$$1 + x \simeq \exp(x - \tfrac{1}{2}x^2)$$

and then, after rearrangement, the approximation

$$\exp(x) \simeq 1 + x$$

the ratio of the activity coefficients becomes

$$\bar{f}_A/\bar{f}_B \simeq (\bar{X}_A/\bar{X}_B)^{-3(2w/kT)\{1 - \frac{1}{2}(2w/kT)\}} \tag{81}$$

An even slightly better approximation for $\bar{f}_A/\bar{f}_B$ is obtained by taking the value of the first derivative of $\bar{f}_A/\bar{f}_B$, as given by Eq. 80, as a function of $\bar{X}_A/\bar{X}_B$ for $\bar{X}_A = \bar{X}_B = \frac{1}{2}$

$$d(\bar{f}_A/\bar{f}_B)/d(\bar{X}_A/\bar{X}_B) = -3(2w/kT)/\{1 + \tfrac{1}{2}(2w/kT)\} \tag{82}$$

and by writing

$$(\bar{f}_A/\bar{f}_B) \simeq (\bar{X}_A/\bar{X}_B)^{-3(2w/kT)/\{1 + \frac{1}{2}(2w/kT)\}} \tag{83}$$

which is very close to Eq. 81, because

$$1 - \tfrac{1}{2}(2w/kT) \simeq 1/(1 + \tfrac{1}{2}(2w/kT))$$

for 2w/kT sufficiently small. Introducing Eq. 83 in Eq. 24 then gives

$$(\bar{X}_A/\bar{X}_B)^{1 - 3(2w/kT)/\{1 + \frac{1}{2}(2w/kT)\}} \simeq K^{o}_{A/B}\ (a_A/a_B) \tag{84}$$

which is similar in form to the Rothmund-Kornfeld equation.

Experiments show that the exponent n in the Rothmund-Kornfeld and Freundlich equations is generally larger than unity. In terms of the regular solution models this implies that w is negative. Equations 76, 80 and 83 are plotted in Figs. 38 and 39 as function of $\bar{X}_A$ and $\bar{X}_A/\bar{X}_B$, respectively, for $2w/kT = -0.25$. Equation 80 (Curve a), which is derived from the exact solutions for $\bar{f}_A$ (Eq. 42a) and $\bar{f}_B$ (Eq. 42b) by Guggenheim (1945), becomes for $2w/kT = -0.25$

$$\bar{f}_A/\bar{f}_B \simeq \{(1 - 0.25\ \bar{X}_B)/(1 - 0.25\ \bar{X}_A)\}^3$$

whereas Eq. 83 (Curve b), derived from Eq. 80 by introducing the value of the first derivative for $\bar{X}_A = \frac{1}{2}$, becomes

$$\bar{f}_A/\bar{f}_B \simeq (\bar{X}_A/\bar{X}_B)^{0.43}$$

and Eq. 76 (Curve c), derived from Eq. 47 (Garrels & Christ, 1965), becomes

$$\bar{f}_A/\bar{f}_B \simeq (\bar{X}_A/\bar{X}_B)^{0.75}$$

Figures 38 and 39 show that Eq. 83 is a reasonable approximation for Eq. 80 for values of $\bar{X}_A$ between 0.1 and 0.8, whereas Eq. 76 is approximative only for $\bar{X}_A$ between 0.4 and 0.6. Figure 40 shows that Eq. 83 represents the tangent to Eq. 80 for $\log(\bar{X}_A/\bar{X}_B) = 0$. The exact solution for $\bar{f}_A/\bar{f}_B$ (Eq. 42) as derived by Guggenheim (1945) is also shown (Curve d) and it can be seen that Eq. 80 is a good approximation for Eq. 42 over the whole range of $\bar{X}_A/\bar{X}_B$. Figure 41 shows that Eq. 84 (Curve b)

$$\bar{X}_A/\bar{X}_B = (X_A/X_B)^{0.70}$$

is a better approximation for Eq. 46 (Curve a)

$$\{(1 - 0.25\ \bar{X}_B)/(1 - 0.25\ \bar{X}_A)\}^3(\bar{X}_A/\bar{X}_B) = (X_A/X_B)$$

than Eq. 77 (Curve c)

$$\bar{X}_A/\bar{X}_B = (X_A/X_B)^{0.57}$$

In conclusion, it is possible to derive the Rothmund-Kornfeld equation from the regular solid solution model, as an approximation which is valid for small, negative values of 2w/kT. The approximation is exact for $\bar{X}_A = \frac{1}{2}$, and good for values of $\bar{X}_A$ near $\frac{1}{2}$.

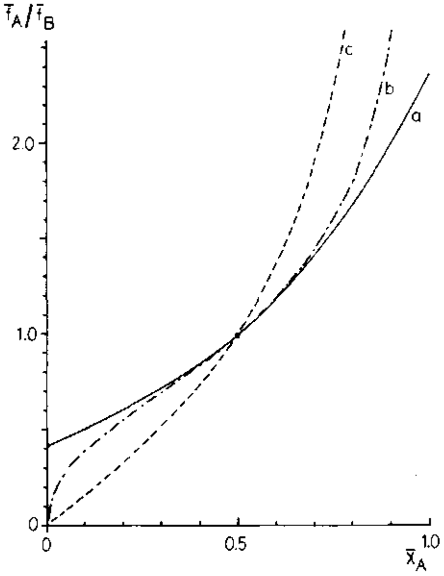

Fig. 38. Approximative equations for $\bar{f}_A/\bar{f}_B$ plotted as functions of $\bar{X}_A$, for 2w/kT = -0.25. Equations 80 (a) and 83 (b) are derived in this study from Guggenheim (1945), and Eq. 76 (c) is from Garrels & Christ (1965).

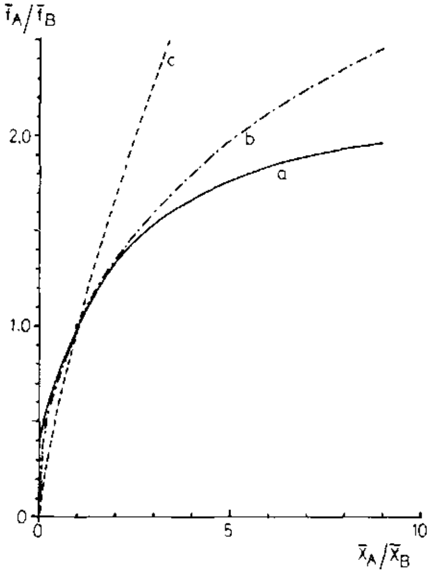

Fig. 39. Approximative equations for $\bar{f}_A/\bar{f}_B$ plotted as functions of $\bar{X}_A/\bar{X}_B$, for 2w/kT = -0.25. Equations 80 (a) and 83 (b) are derived in this study from Guggenheim (1945), and Eq. 76 (c) is from Garrels & Christ (1965).

Experiments show, however, that the Freundlich equation often applies at low coverage and breaks down at higher concentration. This is not necessarily in contradiction with the regular solid solution model, since the Freundlich equation may be considered as an approximation valid for small $\bar{X}_A$ only. Although non-zero energies of mixing, characteristic for the regular solid solution model, may to some extent reflect the non-uniformity of the adsorbent surface, the present derivation of the Rothmund-Kornfeld equation does not explicitly consider heterogeneity between adsorption sites. Sections 4.5 and 4.6 will consider this point in some detail, since surface heterogeneity is an important characteristic of most natural soils.

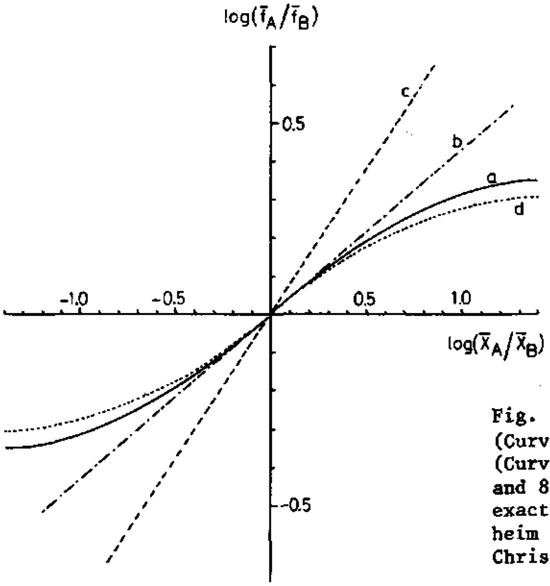

Fig. 40. Log-log plot of approximative equations (Curves a–c) and the exact equation for $\bar{f}_A/\bar{f}_B$ (Curve d), for $2w/kT = -0.25$. Equations 80 (a) and 83 (b) are derived in this study from the exact formulae, Eqs. 42a and b (d), by Guggenheim (1945), and Eq. 76 (c) is from Garrels & Christ (1965).

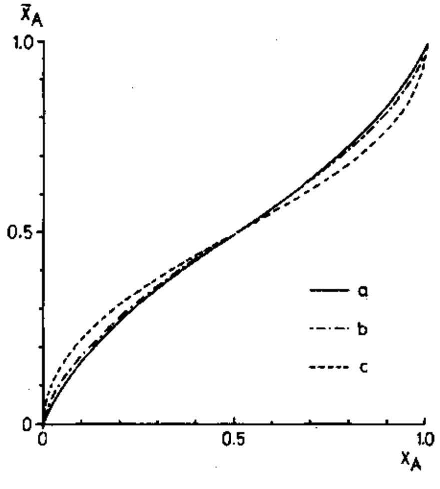

Fig. 41. Ion exchange isotherms derived from the regular solid solution model, calculated from Eq. 46 (a), Eq. 84 (b) and Eq. 77 (c), for $2w/kT = -0.25$, $K^o_{A/B} = 1$ and $f_A = f_B$ (liquid phase).

4.5 HETEROGENEITY

Most natural soils are heterogeneous media: they provide a whole range of adsorption sites with different bonding properties and they also contain a whole range of ionic and non-ionic aqueous complexes taking part in adsorption and possibly precipitation processes. Even clay minerals, such as illites, provide 3 different types of negative adsorption sites: (1) planar sites, associated with isomorphous replacements in the tetrahedral layer of the mineral, (2) edge sites, formed by the partly dissociated SiOH groups on the edges of the minerals, and (3) interlayer sites, generally occupied by K^+ ions that become occluded ('sandwiched') between the clay platelets. The planar sites may be further distinguished according to the number of nearest neighbours. Since the $Al^{3+} \rightarrow Si^{4+}$ replacement in the tetrahedral layer is incomplete, any one site may have 0 - 4 nearest neighbours. The degree of dissociation of SiOH groups on the edges of clay minerals may depend upon the extent of isomorphous replacements in the layer 'behind' the surface group. Phosphates or other anions that become specifically adsorbed on Al-OH groups on the edges of clay minerals may also provide negative adsorption sites. Thus clay minerals alone provide a whole range of adsorption sites; a heterogeneity which is even augmented by the presence of lattice imperfections and fractures.

Specifically adsorbed anions, oxides of Si and Mn, and, at high pH, also Fe and Al, often present as coatings on other soil constituents, aluminosilicates other than clay minerals, and organic matter, may all provide negative adsorption sites in soils.

Contrary to the conditions prevailing in most cation-exchange experiments, where most cations in solution are present as the simple aquo cations, cations in soil solutions often occur in complexed form. Heavy metals coordinate readily with organic ligands: up to 90% of these metals may be present as uncharged, anionic or cationic organic complexes. Coordination with organic ligands is especially important at high pH, where the solubility of aquo cations is generally low. Some of these heavy-metal complexes may be adsorbed with high selectivity, possibly by London-van der Waals forces, hydrogen bonding or due to steric factors.

It would be difficult to include all these factors in ion-exchange equations, but fortunately this is generally not necessarily, since in ion-exchange studies only differences between cations are observed and not absolute bonding energies. When the selectivity coefficient for two ionic species is the same for all types of adsorption sites, no site heterogeneity would be observed at all on the basis of ion-exchange experiments.

The simplest way to introduce heterogeneity explicitly into ion-exchange equations is by assuming that a soil is a mixture of two types of sites: one type being selective for a certain cation and the other type showing no selectivity for this cation. An ion-exchange model describing a system consisting of high-selectivity (h) sites and low-selectivity (l) sites, and two different cations (A and B), is hereafter referred to as a 'two-site' model.

Ion-exchange studies have shown that not the simple cation (A), but an ionic complex (AL) may be adsorbed preferentially. If there is a limited amount of a ligand (L), which coordinates with one of the two cations, a situation may arise like the two-site system. An ion-exchange model describing a system with one type of site and two species of cation (A and B), one of which is present in two forms (A and AL), that both take part in ion exchange, is hereafter referred to as a 'two-species' model. Although the two-site and two-species models are simplified models, they provide a basis for a better understanding of specific ion-exchange behaviour in soils.

4.6 TWO-SITE MODEL

The exchange equation for homovalent exchange (Eq. 31) may be written as

$$q/(Q - q) = K\,R \tag{85}$$

where $q = q_A$, the amount of A adsorbed per unit mass of adsorbent, Q is the cation-exchange capacity of the adsorbent, $Q - q = q_B$, the amount of B adsorbed per unit mass of adsorbent, $K = K_{A/B}$, the selectivity coefficient for the A/B exchange reaction, and $R = c_A/c_B$, the ratio of the aqueous concentrations, or activities, if $f_A = f_B$. For a system with more than one type of site, it follows that for each particular type of site, denoted by i,

$$q_i = K_i Q_i R/(1 + K_i R) \tag{86}$$

and the 'average' selectivity coefficient for the whole system is defined through the equation

$$K_a = R^{-1}\,\Sigma q_i/\Sigma(Q_i - q_i) \tag{87}$$

where the summation is over all types of site. In general K_a is considered to be a function of the surface composition, but under equilibrium conditions K_a may also be considered as a function of R. For a system consisting of two types of sites, low-selectivity sites (l) and high-selectivity sites (h), it follows from Eqs. 86 and 87 that

$$K_a = (K_l Q_l + K_h Q_h + K_h K_l Q R)/\{Q + (K_l Q_h + K_h Q_l)R\} \tag{88}$$

where $Q = Q_l + Q_h$, the cation-exchange capacity of the soil. With this expression for K_a, 'composite' exchange isotherms can be constructed (Figs. 42-43). The exchange isotherm for $Q_h/Q = 0.10$ (Fig. 43) is indicated with an arrow: this isotherm will be treated more fully in Figs. 44-46. Fig. 43 illustrates that, when K_h is sufficiently high, extrapolation of the straight part of the exchange isotherm towards the y axis yields a reasonably accurate estimate for Q_h/Q. Taking the first derivative of $K_a(R)$ (Eq. 88)

$$d\,K_a(R)/d\,R = -Q_l Q_h\,(K_h - K_l)^2/\{Q + (K_l Q_h + K_h Q_l)R\}^2 \tag{89}$$

it follows that for $K_h \neq K_l$

$$d\,K_a(R)/d\,R < 0 \tag{90}$$

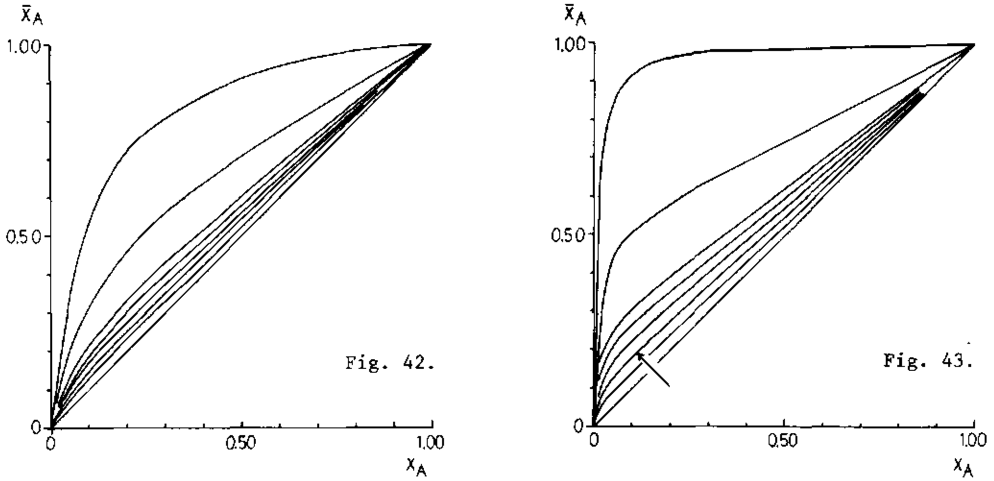

Fig. 42.

Fig. 43.

Figs. 42-43. A series of composite exchange isotherms derived from the two-site model (Eq. 88), for $K_l = 1$, $K_h = 10$ (Fig. 42) or 100 (Fig. 43), and $Q_h/Q = 0$ (bottom curve), 0.05, 0.10, 0.15, 0.20, 0.25, 0.50 and 1.00 (top curve).

for any R. This implies that K_a decreases with increasing R, from a maximum at $R = 0$

$$K_{max} = (K_l Q_l + K_h Q_h)/Q \tag{91}$$

to a minimum for $R \to \infty$

$$K_{min} = \lim(R \to \infty) K_a(R) = K_h K_l Q/(K_l Q_h + K_h Q_l) \tag{92}$$

It may be noted that K_{max} and K_{min} only depend on K_h, K_l and Q_i/Q, and not on the absolute value of Q. Figure 44 shows that K_a decreases rapidly with increasing R, from $K_{max} = 10.90$ at $R = 0$ to $K_{min} = 1.11$.

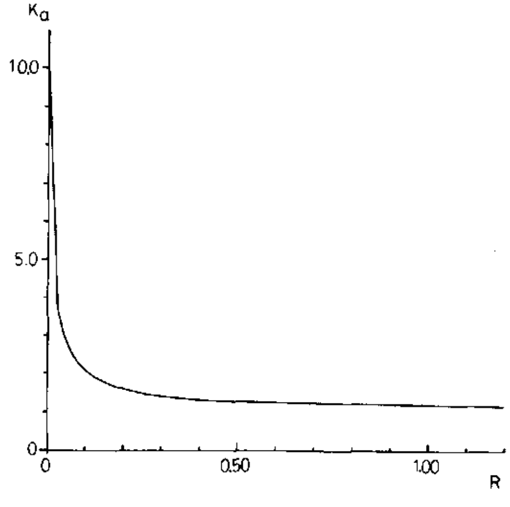

Fig. 44. The average selectivity coefficient derived from the two-site model (Eq. 88) for $K_l = 1$, $K_h = 100$, and $Q_h/Q = 0.10$.

It is convenient to write Eq. 88 in the form

$$K_a = K_{min}\,(K_{max}/K_h K_l + R)/(K_{min}/K_h K_l + R) \qquad (93)$$

If $K_a(R)$, which is a decreasing function of R, can be approximated by an equation of the form

$$K_a(R) \simeq k\,R^{-(1 - 1/n)} \qquad (94)$$

where $n > 1$, a Rothmund-Kornfeld equation of the form

$$\Sigma q_i/\Sigma(Q_i - q_i) \simeq k\,R^{1/n} \qquad (95)$$

would be obtained. Equation 94 can also be written in the form

$$\log K_a(R) = \log k - (1 - 1/n)\log R \qquad (96)$$

In Fig. 45 $\log K_a$ is plotted as a function of $\log R$, for the same values of K_i and Q_i as in Fig. 44. The tangent to the $\log K_a$ curve in the point of inflexion (broken line in Fig. 45) would be a reasonable approximation for $\log K_a$. Therefore, let it be assumed that k and $(1 - 1/n)$ in Eqs. 94-96 are determined by the coordinates of the point of inflexion and by the value of the first derivative in that point. The first derivative of $\log K_a$ as a function of $\log R$ is given by

$$d \log K_a/d \log R = -R(K_{max} - K_{min})/K_h K_l\,(K_{max}/K_h K_l + R)(K_{min}/K_h K_l + R) \qquad (97)$$

which is < 0 for all finite values of $\log R$ and $K_{max} > K_{min}$. From

$$d^2 \log K_a/(d \log R)^2 = 0 \qquad (98)$$

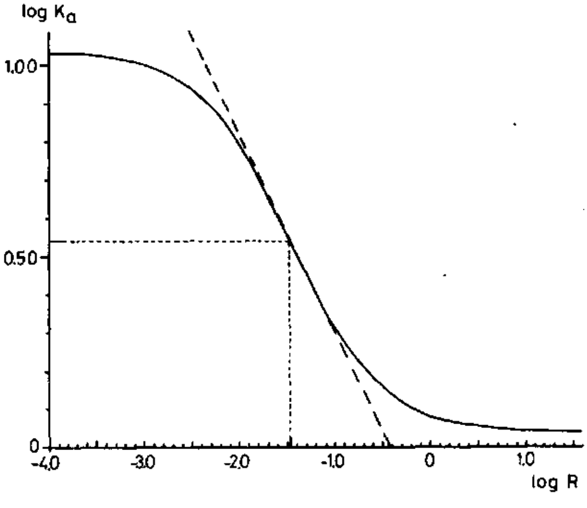

Fig. 45. The logarithm of the average selectivity coefficient (Eq. 88) for $K_l = 1$, $K_h = 100$ and $Q_h/Q = 0.10$. The broken line represents the tangent to the log K_a curve at the point of inflexion.

it follows that the point of inflexion is at

$$\log R = \log\{(K_{max}K_{min})^{\frac{1}{2}}/K_h K_l\} \tag{99}$$

and the value of the first derivative in this point, which is assumed to equal the exponent in Eq. 94, is given by

$$-(1 - 1/n) = -(K_{max} - K_{min})/(K_{max}^{\frac{1}{2}} + K_{min}^{\frac{1}{2}})^2 \tag{100}$$

and since $K_{max} > K_{min}$, it follows that $n > 1$. The value of the constant k in Eqs. 94-96 now follows from the coordinates of the point of inflexion

$$\log k = \log[K_{min}\{K_{max} + (K_{max}K_{min})^{\frac{1}{2}}\}/\{K_{min} + (K_{max}K_{min})^{\frac{1}{2}}\}] +$$

$$\{(K_{max} - K_{min})/(K_{max}^{\frac{1}{2}} + K_{min}^{\frac{1}{2}})^2\}\log\{(K_{max}K_{min})^{\frac{1}{2}}/K_h K_l\} \tag{101}$$

For example, for values of $K_l = 1$, $K_h = 100$, and $Q_h/Q = 0.10$ (Figs. 44 and 45) the point of inflexion is at $\log R = -1.46$ (Eq. 99), the first derivative in that point is -0.52 (Eq. 100) and the log of the constant k, determined from Eq. 101, equals -0.22. Insertion of these values in Eq. 96 gives

$$\log K_a = -0.22 - 0.52 \log R$$

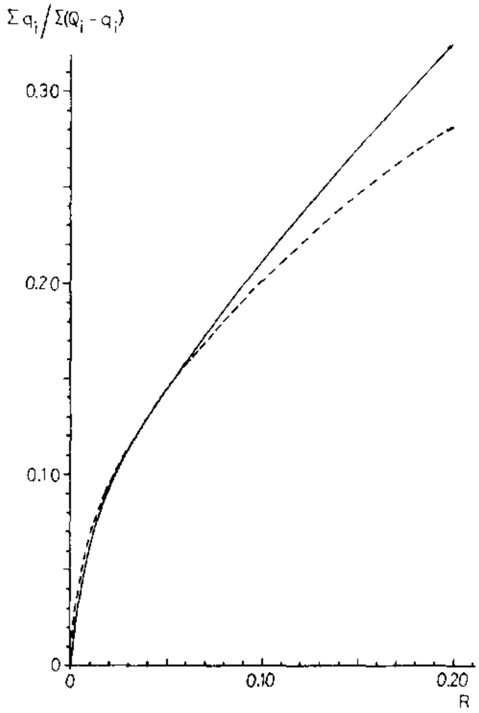

Fig. 46. Exchange isotherm calculated from Eqs. 87 and 88 (solid line) for $K_l = 1$, $K_h = 100$, and $Q_h/Q = 0.10$, and Rothmund-Kornfeld equation (broken line).

which results in a Rothmund-Kornfeld equation of the form

$$\Sigma q_i/\Sigma(Q_i - q_i) = 0.61\ R^{0.48}$$

In Fig. 46 this relation is plotted (broken line) alongside the exact calculation from Eqs. 87 and 88 for the appropriate values of K_i and Q_i/Q. Both curves practically coincide up to about 10% of A in solution, which is the range of interest for trace elements in soils.

When experimental data follow a Rothmund-Kornfeld equation (or a Freundlich equation) the values of the constant k and the exponent 1/n are then an indication for K_h, once K_l is known, and for the ratio Q_h/Q, if the specific exchange behaviour is caused by the presence of two types of sites, h-sites and l-sites. For a number of divalent cations, such as Ca^{2+}, Mg^{2+}, Zn^{2+}, Cd^{2+} and Cu^{2+}, the selectivity coefficients for low-selectivity sites (e.g. planar sites on clay minerals), will be close to unity. Once the constant k and the exponent 1/n are known, the selectivity coefficient K_h and the fraction Q_h/Q can

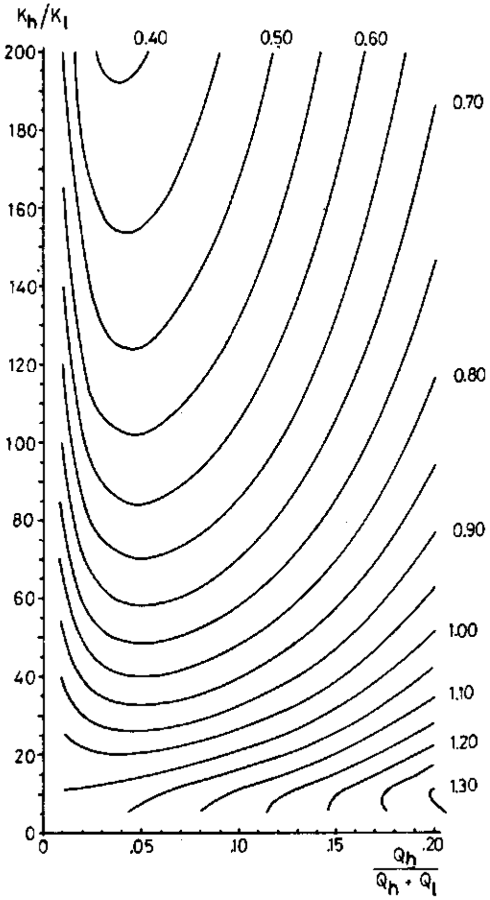

Fig. 47. Contour map of k, calculated from Eq. 101 for $K_l = 1$; solid curves represent equal values of k. Contours are drawn at intervals of 0.05.

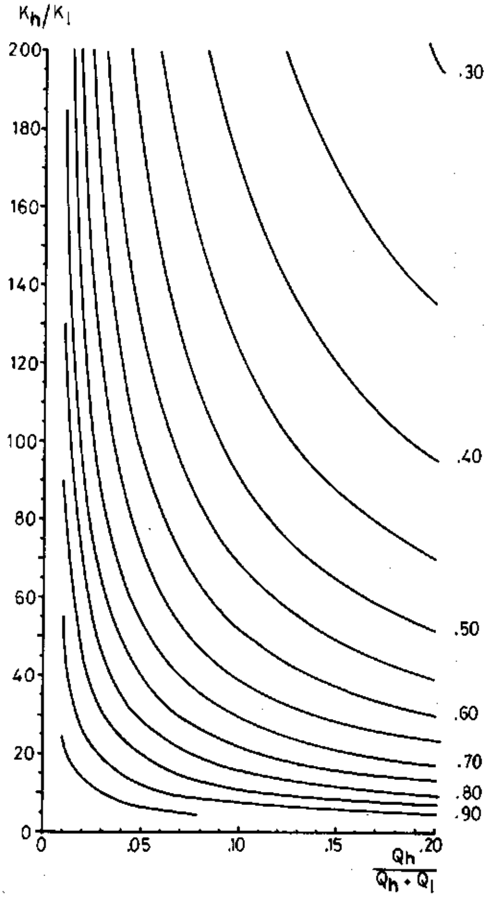

Fig. 48. Contour map of 1/n, calculated from Eq. 100 for $K_l = 1$; solid curves represent equal values of 1/n. Contours are drawn at intervals of 0.05.

be calculated from $k = k(K_h, K_l, Q_h/Q)$ (Eq. 100) and $1/n = 1/n(K_h, K_l, Q_h/Q)$ (Eq. 101), if K_l is known, as it generally is. One can also construct 'contour maps' of k and 1/n, plotted as functions of two variables, K_h/K_l and Q_h/Q, where the 'contours' represent equal values of k and 1/n. Examples of such contour maps are presented in Fig. 47-49. In Section 5.5, Zn/Ca adsorption data on Winsum soil will be presented in the form of a Rothmund-Kornfeld equation with $k = 0.45$ and $1/n = 0.42$, and thence Q_h/Q is about 8% and K_h is about 185, if $K_{Zn/Ca} = 1$ for the low-selectivity sites; this value of Q_h (about 20 μeq/g) is in good agreement with other estimates for Q_h presented in Chapter 5.

When the ion-exchange behaviour is governed by more than two selectivity coefficients, the situation remains essentially like the two-site model, although the formulae describing the exchange behaviour become very cumbersome for these 'multi-site' systems. In multi-site systems, the average selectivity coefficient also decreases with increasing surface coverage, and therefore the exchange equation of the system can always be approximated with a Rothmund-Kornfeld equation over a limited range. For many mineral soils notably for soils with a high clay content, a two-site model may be a good approximation, if the planar sites on the clay minerals can be classified as low-selectivity sites, and

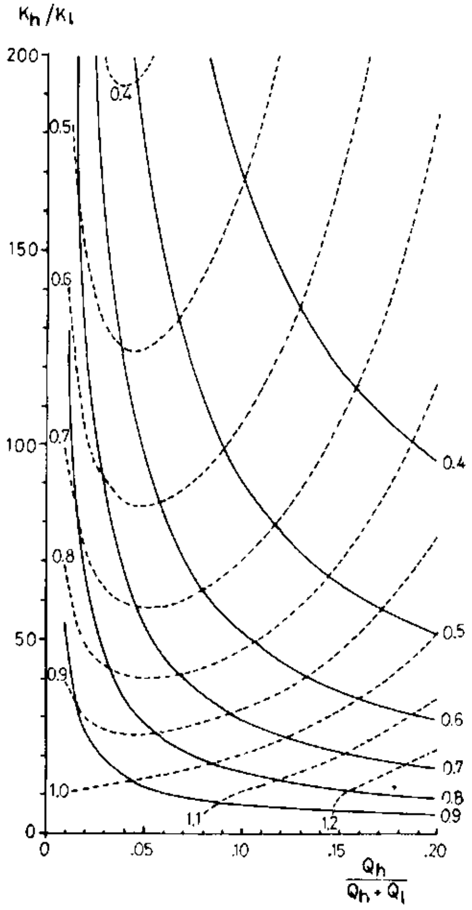

Fig. 49. Contour map of k (broken curves) and 1/n (solid curves) calculated from Eqs. 101 and 100 for $K_l = 1$. Contours are drawn at intervals of 0.10.

dissociated surface hydroxyl groups, e.g. SiOH groups on the edges of clay minerals, as high-selectivity sites. The experimental data presented in Chapter 5 may be interpreted in terms of such a two-site model.

The K^+/Mg^{2+} exchange on Winsum clay (fraction < 2μm) reported by van Schouwenburg & Schuffelen (1963) points to the existence of two or three types of sites with different selectivity coefficients. Van Schouwenburg & Schuffelen (1963) describe the K^+/Mg^{2+} exchange with a set of three 'Gapon' equations with different exchange coefficients, one for the planar sites, one for the edge sites, and one for the interlattice sites, i.e. planar sites between closely packed clay platelets. The Gapon equation for K/Mg exchange is given by (Gapon, 1933)

$$q_K/q_{Mg} = k_g \; c_K/c_{Mg}^{\frac{1}{2}} \tag{102}$$

where k_g is the Gapon coefficient for the K/Mg exchange reaction, and where the amounts adsorbed are in meq/g, and the concentrations in mol/l. The general validity of the Gapon equation is somewhat doubtful, however, and most monovalent-divalent exchange data, including those used by Gapon (1933) in his original treatment, can be described equally well (or better) by an exchange equation of the form

$$q_K^2/q_{Mg} = K'_{K/Mg} \; a_K^2/a_{Mg} \tag{103}$$

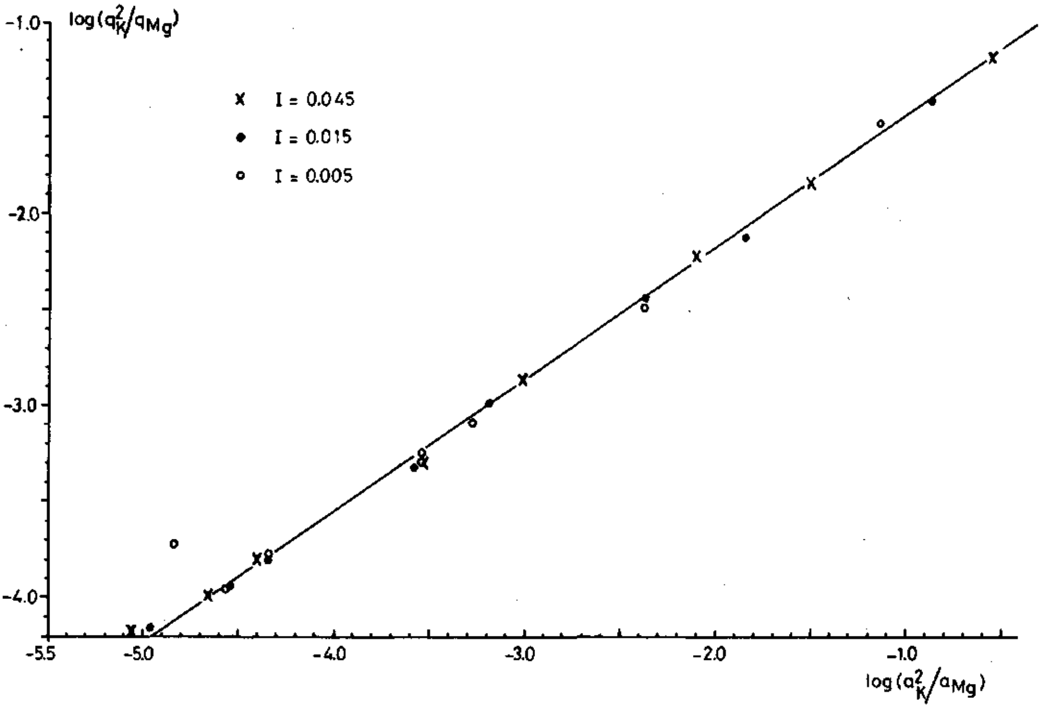

Fig. 50. Rothmund-Kornfeld plot of K/Mg exchange data measured on Winsum illite at different ionic strengths (estimated from van Schouwenburg & Schuffelen, 1963).

where $K'_{K/Mg}$ is the corrected selectivity coefficient (Eq. 28). A 'Rothmund-Kornfeld plot' (Fig. 50) of q_K^2/q_{Mg} against a_K^2/a_{Mg}, estimated from the data reported by van Schouwenburg & Schuffelen (1963), shows that the experimental points do fit a straight line

$$\log\,(q_K^2/q_{Mg}) = -0.70 + 0.71\,\log(a_K^2/a_{Mg})$$

corresponding to a Rothmund-Kornfeld equation of the form

$$q_K^2/q_{Mg} = 0.20\,(a_K^2/a_{Mg})^{0.71}$$

Ionic strength of the equilibrium solutions ranged from 0.045 (crosses) to 0.005 (open circles), but there seemed to be no influence of ionic strength on the exchange behaviour of K^+ and Mg^{2+}. The assumption of more than one type of site with different selectivity coefficients for K/Mg exchange seems to explain the observed exchange behaviour. The high preference of the interlattice sites for K^+ is due to steric factors and, when the clay platelets are occupied by K^+, and closely packed, the interlattice positions would be effectively inaccessible for Mg^{2+}, except perhaps for a few sites near the edges. Pretreatment of the Winsum soil with K^+ in order to cover all interlattice positions with K^+, might answer the question whether two (interlattice and planar sites) or three (also edge sites) types of sites are involved in the K/Mg exchange. The possible preference for edge sites (surface SiO^- groups) of K^+ ions may be because K^+ has a relatively small hydrated radius, e.g. the enthalpy of hydration of K^+ is -77 and of Mg^{2+} is -459 kcal/mol, based on the assignment of -261 kcal/mol to H^+ (Cotton & Wilkinson, 1972, p. 645), and therefore, K^+ may be adsorbed as the naked ion, whereas Mg^{2+} remains hydrated. The energy balance may be more favourable for

$$\text{Si-O}^-\{K^+\}$$

than for

$$\text{Si-O}^-\{Mg(H_2O)_n^{2+}\}$$

or

$$(\text{Si-O}^-)_2\{Mg(H_2O)_n^{2+}\}$$

because of the closer approach between $Si\text{-}O^-$ and K^+. Figure 50 offers no evidence whether two or three types of sites with different selectivity coefficients govern the exchange reaction; van Schouwenburg & Schuffelen (1963) suggest a three-site model with Q(interlattice) about 1%, Q(edge) about 5% and Q(planar) about 94% of the total CEC, which was determined to be about 450 μeq/g of clay, i.e. 200-225 μeq/g of Winsum soil. The K/Mg exchange data form a good illustration of specific ion-exchange behaviour, caused by site heterogeneity, since for K^+ and Mg^{2+} it is unlikely that ionic species, other than the simple aquo ions, are involved in the exchange reaction.

4.7 TWO-SPECIES MODELS

Cations in aqueous solution may coordinate with charged or uncharged ligands. For uncharged ligands, other than water, one or more water molecules from the inner coordination sphere of the cation are replaced by the ligands, but the charge of the liganded cation does not change. For charged ligands, the net charge of the aqueous complex may become negative, zero, or positive. Adsorption sites that are highly selective for liganded species may catalyse the formation of these complexes. When only a limited amount of these ligands, of the order of 1-10% of the CEC, is present in the system, the situation is rather like the two-site system. If the liganded cations have the same net charge as the aquo cations, the only way to distinguish experimentally between a two-species system and a two-site system is to identify the ligand of interest and to determine its concentration in the course of the exchange experiment. When the liganded cations have a different net charge, the exchange will no longer appear stoichiometric: the amount of cations lost from solution will differ from the amount of cations released by the solid phase. Therefore, apparent 'excess' or 'superequivalent' adsorption of divalent cations may be caused by adsorption of monovalent complexes.

4.7.1 Uncharged ligands

A model describing the selective adsorption of liganded cations (two-species model) has to deal with (a) 'regular' ion exchange involving the simple aquo cations, (b) the coordination of one of the cations with one or more ligands, and (c) the specific adsorption of the liganded species. If the charge of the liganded cations remains unaltered, these processes can be visualized as

$$A + \bar{B} \rightleftarrows \bar{A} + B \qquad (104a)$$

$$A + nL \rightleftarrows AL_n \qquad (104b)$$

$$AL_n + \bar{B} \rightleftarrows \overline{AL}_n + B \qquad (104c)$$

with the equilibrium constants

$$K_l = q_A a_B / q_B a_A \qquad (105a)$$

$$\beta_n = a_{AL_n} / a_A a_L^n \qquad (105b)$$

$$K_h = q_{AL_n} a_B / a_{AL_n} q_B \qquad (105c)$$

where β_n is called a cumulative or gross constant (Sillén & Martell, 1971). In the initial equilibrium situation, concentrations are as follows

$$c_A = 0, \qquad c_B = B, \qquad c_{AL_n} = 0, \qquad c_L = L,$$

$$q_A = 0, \qquad q_B = Q, \qquad q_{AL_n} = 0$$

Addition of a small amount of A to this system is followed by formation of AL_n, adsorption of A and AL_n, and desorption of an equivalent amount of B

$$c_A = A - x - y, \qquad c_B = B + y + z, \qquad c_{AL_n} = x - z, \qquad c_L = L - nx,$$

$$q_A = y, \qquad q_B = Q - y - z, \qquad q_{AL_n} = z$$

When activity coefficients are known, these concentrations may be inserted in the expressions for K_l, β_n, and K_h, which results in a system of 3 equations with 3 unknowns. These equations can be solved for x, y and z, but the formulae soon become rather cumbersome. The average corrected selectivity coefficient, K_a, for the overall A/B exchange reaction is defined by the equation

$$(q_A + q_{AL_n})/q_B = K_a\ (a_A + a_{AL_n})/a_B \tag{106}$$

which can be transformed into

$$K_a = (K_l + K_h\beta_n a_L^n)/(1 + \beta_n a_L^n) \tag{107}$$

If the activity coefficient of the uncharged ligands be unity,

$$K_a = \{K_l + K_h\beta_n(L - x)^n\}/\{1 + \beta_n(L - x)^n\} \tag{108}$$

and

$$d\ K_a/d\ x = -n\beta_n(K_h - K_l)(L - x)^{n-1}/\{1 + \beta_n(L - x)^n\}^2 \tag{109}$$

which is < 0, for $0 \leq x < L$ and $K_h > K_l$. Hence K_a is a decreasing function of x, from a maximum at $x = 0$ ($c_L = L$), i.e. for $c_A = 0$

$$K_{max} = (K_l + K_h\beta_n L^n)/(1 + \beta_n L^n) \tag{110}$$

to a minimum for $x \to L$ ($c_L \to 0$), i.e. for $c_A \gg L$

$$K_{min} = K_l \tag{111}$$

as for the two-site model.

Cremers & Pleysier (1973a, b) studied Ag^+/Na^+ exchange on montmorillonites in the presence of thiourea, $S{=}C(NH_2)_2$, which forms a stable complex with Ag^+; the stability constant of the three-coordinated complex is of the order of 10^{13}. The selectivity coefficient for the $Ag\{S{=}C(NH_2)_2\}_n^+/Na^+$ exchange reaction ranged from 10^3 to 5×10^3, whereas $K_{Ag/Na}$ in the absence of thiourea was about 1.5. Results of exchange experiments with ^{14}C-labelled thiourea indicated a coordination number of two for Ag^+ in the adsorbed state. Cremers & Pleysier suggested that the high affinity of the montmorillonites for the Ag-thiourea complexes be due to an increased polarizability of the liganded cations.

Peigneur (1973) studied the adsorption of heavy metals on montmorillonites in the presence of uncharged ligands. Selectivity coefficients for hM/Ca exchange were all about 0.8, where hM was Ni, Zn, Cd, or Co. In the presence of ethylenediamine (EDA), $H_2NCH_2CH_2NH_2$, selectivity coefficients were up to 400. The coordination number of $hM(EDA)_n^{2+}$ in the adsorbed phase was 3. The log β_3 values for the Ni, Co, Zn, and Cd complexes are about 18.3, 14.0, 12.9 and 12.3, respectively. Other uncharged ligands, such as cyclohexane-1,2-diamine and propane-1,2-diamine, had a similar effect on adsorption of heavy metals, but not as pronounced as EDA. These data show that the presence of uncharged ligands may result in specific ion-exchange phenomena, by selective uptake of the liganded species.

4.7.2 Monovalent ligands

Aquo cations may also coordinate with ligands that alter the net charge of the complex. For a system of 2 divalent cations and one monovalent ligand, the relevant reactions may be written as

$$A^{2+} + \overline{B^{2+}} \rightleftarrows \overline{A^{2+}} + B^{2+} \tag{112a}$$

$$A^{2+} + L^- \rightleftarrows AL^+ \tag{112b}$$

$$2AL^+ + \overline{B^{2+}} \rightleftarrows 2\,\overline{AL^+} + B^{2+} \tag{112c}$$

and the equilibrium constants become

$$K_l = q_A\, a_B/q_B\, a_A \tag{113a}$$

$$K_1 = a_{AL}/a_A\, a_L \tag{113b}$$

$$K_h = q_{AL}^2\, a_B/c_{AL}^2\, q_B \tag{113c}$$

which can also be considered as a system of three equations with three unknowns. Here the number of cations that become adsorbed (A), exceeds the number of cations released (B), through simultaneous adsorption of a number of ligand anions (L).

Siegel (1966) studied the adsorption of Zn^{2+} and $ZnGly^+$ complexes on ion-exchange resins and clays saturated with Na^+; 'Gly' denotes glycine, $CH_2(NH_2)COOH$. The log K_1 value for the $ZnGly^+$ complex was estimated to be 4.98 and the distribution coefficients

$$D_0 = q_{Zn}/c_{Zn}$$

and

$$D_1 = q_{ZnGly}/c_{ZnGly}$$

were about 10^4 and 4×10^3, respectively: the preference of the clays for the divalent cations is of the same order as for the monovalent complexes. The selectivity coefficient for the $ZnGly^+/Zn^{2+}$ exchange reaction may be represented by

$$K_{ZnGly/Zn} = D_1^2/D_0$$

and is estimated to be about 1600. An explanation for the enhanced uptake of $ZnGly^+$ would be the action of London-van der Waals forces on the organic ligand, and then one would expect the selectivity for the heavy metal amino acid complexes to increase with increasing chain length of the amino acid.

4.7.3 Possible role of hydrolysis

The positive change in free enthalpy accompanying the (partial) dehydration of an ion is smaller for a monovalent ionic complex than for a divalent ion. For large organic ligands this effect may be of minor importance, but for inorganic ligands such as OH^- and Cl^- this may be of prime importance. The adsorption of heavy metals by soils at near-neutral pH is often accompanied by a decrease in pH. The release of H^+ upon adsorption of heavy metals may be due to (a) selective uptake of heavy metals on sites that are initially occupied by H^+ (A/H exchange), (b) selective uptake of hydrolysis products of heavy metals on regular adsorption sites ($A(OH)_n/B$ exchange), or (c) selective uptake of hydrolysis products on sites that are initially occupied by H^+ ($A(OH)_n/H$ exchange). Since it is often difficult to distinguish experimentally between these mechanisms of adsorption, the role of hydrolysis in the adsorption of heavy metals is not yet clear.

James & Healy (1972) described the adsorption of hydrolysable metal ions at the oxide-water interface in terms of electrostatic ion-solid and ion-solvent interactions. The free enthalpy of adsorption, ΔG^o_{ads}, was assumed to be made up of a positive change in free enthalpy due to dehydration, ΔG^o_{hydr}, unfavourable to adsorption, and a negative change in free enthalpy due to coulombic attraction, ΔG^o_{coul}, favourable to adsorption. The authors further introduced a change in free enthalpy due to 'chemical' interactions, such as short-range attraction, hydrogen bonding or ligand exchange, and this contribution, ΔG^o_{chem}, was also assumed to be negative and thus favourable to adsorption.

The free enthalpy of (secondary) hydration is a function of the distance from the nucleus of the cation to the oxide surface, x_i, and further depends quadratically on the charge number of the ion, z_i. Other parameters in ΔG^o_{hydr} are the dielectric constants of (a) the solid, (b) the first layer of (electrically saturated) water molecules on the solid surface, and (c) the bulk solution. The change in coulombic free enthalpy is a function of x_i, depends linearly on z_i, and further on the surface potential, $\psi(0)$, the ionic strength of the solution and also the pH, for oxide surfaces. The influence of pH in the model of James & Healy (1972) is both through the surface potential, which becomes more negative with increasing pH, and through the activity of the first hydrolysis products which increases with increasing pH. They estimated the free enthalpy of adsorption of unhydrolysed and hydrolysed metal species at a distance

$$x_i = r_i + 2r_w$$

from the oxide surface, where r_i is the radius of the cation, and r_w is the radius of water, 1.38 Å. The equilibrium position of the ions, however, is not necessarily fixed at this distance, and therefore it is of interest to investigate the behaviour of the different contributions to the free enthalpy of adsorption as a function of the distance to the surface.

In Fig. 51 the free enthalpy changes accompanying the adsorption of Zn^{2+} and $ZnOH^+$ on an illite from a 0.01 molar $Zn(NO_3)_2$ solution are plotted as functions of the distance to the surface, for

$$x_{Zn} \geq r_{Zn} + 2r_w$$

and the equilibrium positions of the ions (free enthalpy minima) are indicated with vertical arrows; all curves are calculated from the formulae given by James & Healy (1972). The surface charge density of illite, σ, due to substitution charges, is assumed to be

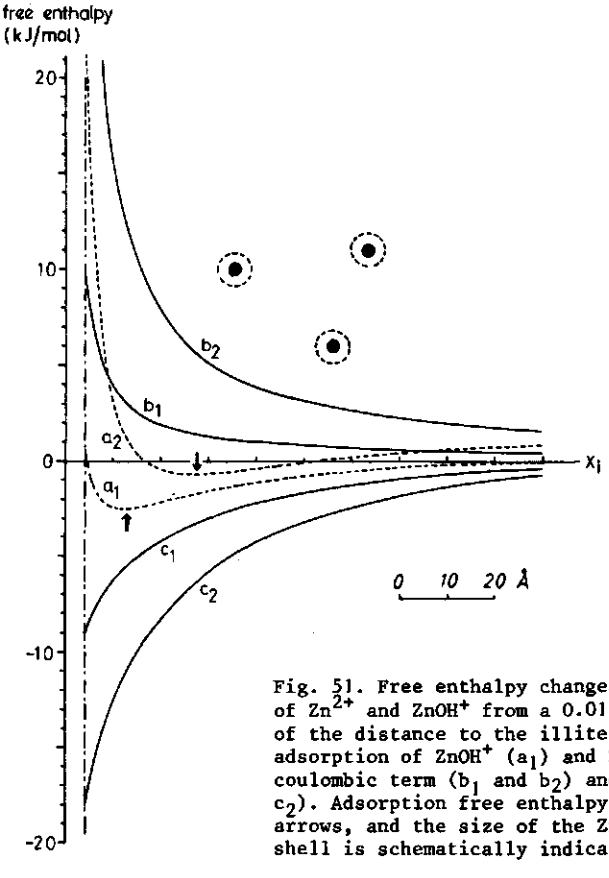

Fig. 51. Free enthalpy changes (kJ/mol) accompanying the adsorption of Zn^{2+} and $ZnOH^+$ from a 0.01 molar $Zn(NO_3)_2$ solution as function of the distance to the illite surface (Å). The free enthalpy of adsorption of $ZnOH^+$ (a_1) and Zn^{2+} (a_2) is separated into a coulombic term (b_1 and b_2) and a secondary hydration term (c_1 and c_2). Adsorption free enthalpy minima are indicated with vertical arrows, and the size of the Zn^{2+} ion with its primary hydration shell is schematically indicated for reference.

- 0.3 C/m^2, and the surface potential is then estimated to be -200 mV from the relation

$$\psi(0) = (2RT/F) \operatorname{arcsinh} \{\sigma/(8\ \varepsilon_o \varepsilon_w kT\ Lc)^{\frac{1}{2}}\} \tag{114}$$

where Lc is the number of ion pairs per m^3. Equation 114 shows that $\psi(0)$ is independent of pH and becomes less negative with increasing concentration, i.e. $|\psi(0)|$ decreases with increasing c. The dielectric constant of illite is estimated to be about 8 (Gast & Gast, 1959), which is much lower than the dielectric constant of water at 25°C. Figure 51 shows that the minimum free enthalpy of adsorption for $ZnOH^+$ is closer to the surface than for Zn^{2+}, but well outside

$$x_{Zn} = r_{Zn} + 2r_w$$

which is the closest approach of the nuclei of the cations to the surface, if they retain their primary hydration sheaths. The minimum for $ZnOH^+$ is also lower than for Zn^{2+}, since ΔG^o_{hydr} depends quadratically, and ΔG^o_{coul} linearly on the charge of the ion. Of course, Fig. 51 is incomplete since the effect of pH and free enthalpy changes accompanying hydrolysis are not considered, but it shows that under certan conditions the adsorption of monovalent hydrolysis products may be favoured over the unhydrolysed divalent cations.

4.7.4 Specific adsorption of hydrolysis products

Specific adsorption of first hydrolysis products may be described with a modified two-species model, which has to account for (a) regular ion-exchange on low-selectivity sites, (b) hydrolysis of one of the cations, (c) specific adsorption of hydrolysis products, and (d) buffering of the pH, by neutralization of H^+ released upon hydrolysis. Assuming that all exchange reactions take place on one type of site, the model can be represented by the following set of equations

$$A^{2+} + \overline{B^{2+}} \rightleftarrows \overline{A^{2+}} + B^{2+} \tag{115a}$$

$$A^{2+} \rightleftarrows AOH^+ + H^+ \tag{115b}$$

$$2AOH^+ + \overline{B^{2+}} \rightleftarrows \overline{2AOH^+} + B^{2+} \tag{115c}$$

$$2H^+ + \overline{B^{2+}} \rightleftarrows \overline{2H^+} + B^{2+} \tag{115d}$$

If there is only one type of adsorption site, the independent exchange equations (Eqs. 115a, c and d), form a complete description of all exchange reactions that can take place: from $K^o_{A/B}$ (Eq. 115a), $K^o_{AOH/B}$ (Eq. 115c) and $K^o_{H/B}$ (Eq. 115d), follow the other thermodynamic equilibrium constants by multiplication according to

$$K^o_{i/j} = K^o_{i/n}\ K^o_{n/j} \tag{116}$$

where

$$K^{o}_{n/j} = (K^{o}_{j/n})^{-1} \tag{117}$$

If there are two or three types of sites, the number of independent exchange equations needed to describe the system is doubled or tripled, since all exchange reactions take place on all types of sites. Since the formulae for the 'simple' one-site system, obtained by solving the 4 equilibrium constants belonging to Eqs. 115a-d for 4 unknowns, are already long (of the order of 10^3 km), it seems to be more appropriate to simplify Eqs. 115c and d further to

$$AOH^+ \rightleftarrows \overline{AOH^+} \tag{115c'}$$

$$H^+ \rightleftarrows \overline{H^+} \tag{115d'}$$

which are valid for small values of q_{AOH} and q_H only. It is further assumed that the sites highly selective for AOH^+ or H^+, do not select for the unhydrolysed cations. If H^+ is adsorbed mainly on neutral oxide surfaces, Eq. 115d' may be interpreted as a reaction of the type (see also Eqs. 1 and 2)

$$H^+ + L^- + FeOOH \rightleftarrows FeOOH_2^+\, L^-$$

where L^- denotes a monovalent anion. The simplified set of equations then yields the following set of equilibrium constants

$$K_l = q_A a_B / q_B a_A \tag{118a}$$

$$^{*}K_1 = a_{AOH} a_H / a_A \tag{118b}$$

$$K_h = q_{AOH} / a_{AOH} \tag{118c'}$$

$$b = q_H / a_H \tag{118d'}$$

where $^{*}K_1$ denotes the first hydrolysis constant and where b is related to the buffer capacity of the soil. In general the buffer capacity is a function of pH and the assumption that b is constant, is valid for a limited pH interval only. An essential feature of the present mechanism of adsorption is that the H^+ produced upon hydrolysis lowers the pH, and inhibits the hydrolysis further. Therefore, only a limited amount of AOH^+ is formed, and the average selectivity coefficient for the overall exchange reaction depends on the initial pH of the system and on the buffer capacity.

The behaviour of K_a as a function of $R = c_A/c_B$, will be illustrated with an example, for $A = Zn^{2+}$ and $B = Ca^{2+}$. The initial concentrations of the system are given by

$$c_{Zn} = q_{Zn} = c_{ZnOH} = q_{ZnOH} = 0$$

$$c_{Ca} = Ca_i \qquad q_{Ca} = Q$$

$$c_H = H_i \qquad q_H = bH_i$$

Then an amount of Zn is added to the system, and the final concentrations become

$$c_{Zn} = \Delta Zn - x - y \qquad q_{Zn'} = y$$

$$c_{Ca} = Ca_i + y \qquad q_{Ca} = Q - y$$

$$c_{ZnOH} = x/(K_h + 1) \qquad q_{ZnOH} = x\ K_h/(K_h + 1)$$

$$c_H = H_i + x/(b + 1) \qquad q_H = bH_i + x\ b/(b + 1)$$

where K_h (Eq. 118c') and b (Eq. 118d') are already introduced in the concentrations, replacing activities by concentrations. When the activities in the other equilibrium constants, Eqs. 118a and b are also replaced by concentrations, a system of two equations with two unknowns is obtained

$$K_l = y(Ca_i + y)/(Q - y)(\Delta Zn - x - y) \tag{119a}$$

$$^*K_1 = \{x/(K_h + 1)\}\{H_i + x/(b + 1)\}/(\Delta Zn - x - y) \tag{119b}$$

which can be solved for x and y rather easily. Thus a cubic equation in x is obtained, that can be solved analytically (Abramowitz, 1968, p. 17).

In Figure 52, log K_a is plotted as a function of log R, where K_a and R are defined

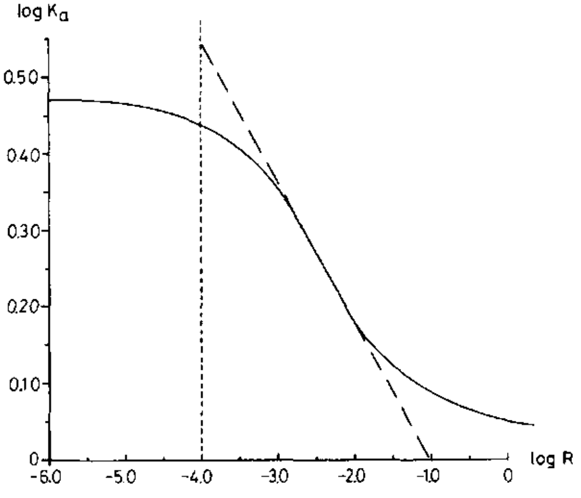

Fig. 52. A log-log plot of the average selectivity coefficient (Eq. 120) for the Zn^{2+}-$ZnOH^+$-Ca^{2+} system. The broken line represents the tangent at the point of inflexion, and the dotted vertical line indicates the detection limit for Zn.

by the equation

$$(q_{Zn} + q_{ZnOH})/q_{Ca} = K_a\ (c_{Zn} + c_{ZnOH})/c_{Ca} = K_a R \tag{120}$$

with the following data: $K_l = 1$, $^*K_1 = 10^{-9}$, $Ca_i = 5 \times 10^{-3}$ mol/1, $Q = 5 \times 10^{-3}$ mol/1, $K_h = 99$, $b = 99$, $H_i = 10^{-7}$ mol/1, and for ΔZn ranging from 5×10^{-8} to 5×10^{-3} mol/1. The curve in Fig. 52 behaves like the curve in Fig. 45 for the two-site model, and again the tangent to the log K_a curve at the point of inflexion seems a reasonably good approximation for log K_a. The vertical dotted line at log R = -4.0 indicates the detection limit for Zn, which is assumed to be about 5×10^{-7} mol/1 for atomic absorption spectrophotometry. With the use of certain scale expansion techniques, or the use of a 'graphite furnace', or possibly with polarographic methods, it may be possible to reach lower values. A detection limit is included in Fig. 52 to stress that below a certain value of log R it becomes irrelevant whether the tangent at the point of inflexion is a good approximation for log K_a, since below that threshold Zn can no longer be measured. The tangent at the point of inflexion is a reasonably good approximation for log K_a for log $R \leq -1.0$, thus for Zn concentrations lower than 5×10^{-4} mol/1. Figure 53 shows the amounts of Zn^{2+} and $ZnOH^+$ adsorbed, expressed as fractions of the total amount of Zn adsorbed, and plotted as functions of log R. It follows that the fractional contribution of q_{ZnOH} to the total amount of Zn adsorbed is highest at low Zn concentrations, and decreases with increasing log R. At log R = 0 only about 5% of the total cation-exchange capacity is occupied by $ZnOH^+$ and another 5% by H^+, which means that under the present conditions the errors made by neglecting the changes in c_{Ca} and q_{Ca} upon adsorption of $ZnOH^+$ and H^+ are very small over the whole range of log R in Figs.52 and 53. When H^+ is adsorbed on uncharged hydroxyl groups on oxide surfaces, the errors are even smaller, since then Eq.115d' would give the correct picture and Eq. 115d would be in error.

In Fig. 54 -log c_H is plotted as a function of log($c_{Zn} + c_{ZnOH}$), where $c_{Zn} + c_{ZnOH}$ represents the total Zn concentration, c'_{Zn}, and where the dotted line at log c'_{Zn} = -6.30 represents the detection limit of aqueous Zn. Since

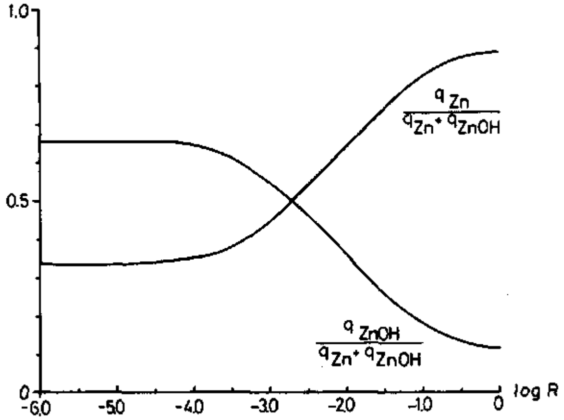

Fig. 53. Fractional contributions of Zn^{2+} and $ZnOH^+$ to the total amount of Zn adsorbed calculated from Eqs. 118-120.

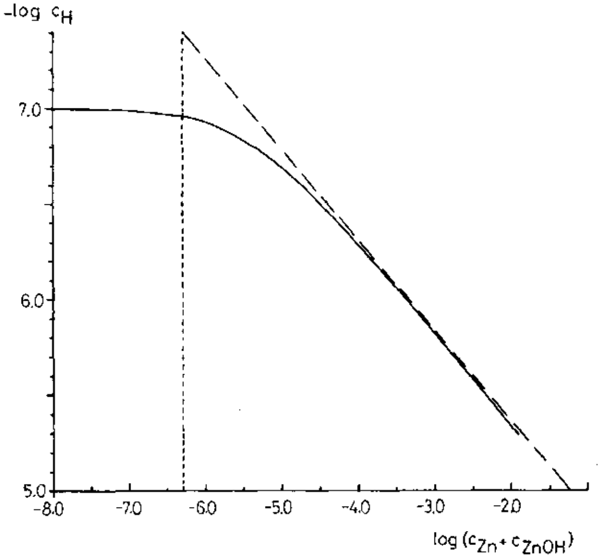

Fig. 54. A plot of -log c_H (solid line), calculated from Eqs. 118-120, as a function of the logarithm of the total Zn concentration. The dotted line indicates the detection limit for Zn and the broken line represents Eq. 122 for n = 0.95 and constant = 8.81.

$$pH = -\log a_H = -\log c_H - \log f_H$$

where the activity coefficient of H^+, f_H, ranges from 0.90 at I = 0.015 to 0.87 at I = 0.030 (Kielland, 1937) for the present system, it follows that

$$-\log c_H \approx pH$$

Hence pH decreases almost linearly with increasing log c'_{Zn}, and the broken line in Fig. 54, which represents the relationship

$$2pH + 0.95 \log c'_{Zn} = 8.81$$

is a good approximation for the pH curve, for log $c'_{Zn} > -5.0$. A relationship of the form

$$2pH + \log c'_{Zn} = \text{constant} \qquad (121)$$

generally points to the presence of a carbonate, hydroxide or silicate, controlling the aqueous Zn activity, but from the present treatment it may be concluded that a relationship of the form

$$2pH + n \log c'_{Zn} = \text{constant} \qquad (122)$$

may also be due to specific adsorption of first hydrolysis products. The coefficient n may be close to unity, as in Fig. 54, but in general n depends upon the initial pH of the system and on the buffer capacity: a higher value of n (n > 1) points to a lower buffer capacity, and a smaller value of n (n < 1) points to a higher buffer capacity.

Since the buffer capacity of the system under consideration is rather low, n would be smaller than unity in most soils.

4.7.5 Precipitation and ion exchange

The combination of regular ion exchange and precipitation of the hydroxide, carbonate or silicate results in an apparent selectivity coefficient that decreases with increasing concentration of the metal of interest. An apparent selectivity coefficient, K_{app}, may be defined by the equation

$$(q'_A + p_A)/q_B = K_{app}\, c'_A/c_B \tag{123}$$

where p_A denotes the amount of A lost from solution (mol/l) by precipitation, and where q'_A and c'_A include all A species adsorbed and in solution. Under suitable conditions, the behaviour of log K_{app} as a function of log R becomes similar to the behaviour of log K_a in Figs. 45 and 52, but the coefficient n in the relationship

$$2pH + n \log a_A = \text{constant} \tag{124}$$

is always 1.0 in the presence of hydroxides, carbonates, or silicates, if equilibrium with atmospheric CO_2 or solid SiO_2 exists.

4.8 SURVEY OF PUBLISHED MEASUREMENTS

Van der Weijden (1975) studied the adsorption of Zn and Cd at pH 7 and 8, on montmorillonite (CEC 0.70 meq/g) illite (CEC 0.39 meq/g) and kaolinite (CEC 0.12 meq/g), with radioactive tracers, ^{65}Zn and ^{112}Cd. A number of 25-ml samples of suspensions of 2 g clay (fraction < 2μm) in 0.001 molar $CaCl_2$ solution, were shaken for 10 days in polyethylene bottles in a waterbath at 25 °C, and the pH was adjusted regularly to 7 and 8, with HCl or $Ca(OH)_2$. It was noted that the pH of the suspensions decreased upon addition of Zn or Cd, and the largest drops in pH occurred in those samples where the initial Zn or Cd concentrations were highest, but this matter was not further investigated. From the data presented by van der Weijden (1975), the apparent selectivity coefficients, $K_{Zn/Ca}$ and $K_{Cd/Ca}$, can be estimated, from the relationship

$$K_{M/Ca} = \{M_1/(CEC - M_1)\}(Ca_o/M_o) \tag{125}$$

where M_1 denotes the amount of Zn or Cd lost from solution (meq/g) and M_o and Ca_o denote the aqueous concentrations (mol/l) of Zn or Cd, and Ca. Figures 55 and 56 show that $K_{Cd/Ca}$ and $K_{Zn/Ca}$ decrease with increasing Cd_o/Ca_o and Zn_o/Ca_o ratios, in agreement with the adsorption models discussed in Sections 4.6 and 4.7. At pH 7, both selectivity coefficients decrease for the different clay minerals in the order

illite > kaolinite > montmorillonite

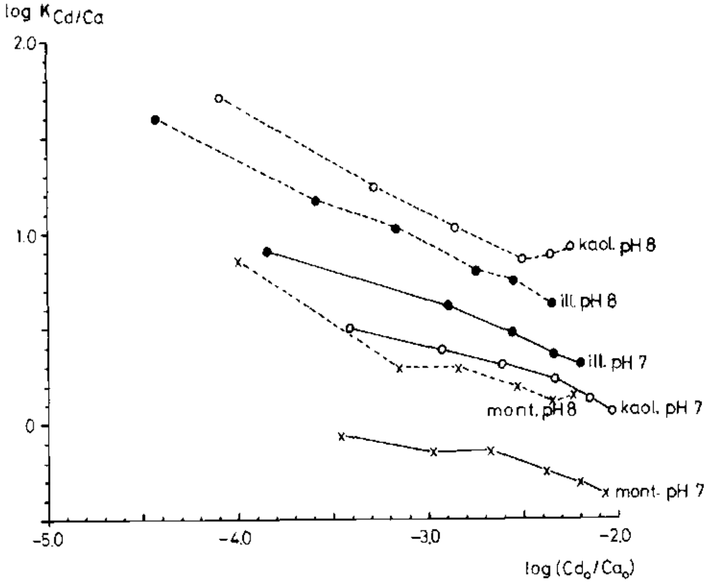

Fig. 55. The apparent Cd/Ca selectivity coefficient for kaolinite, illite, and montmorillonite, at pH 7 (solid lines) and 8 (broken lines), estimated from van der Weijden (1975).

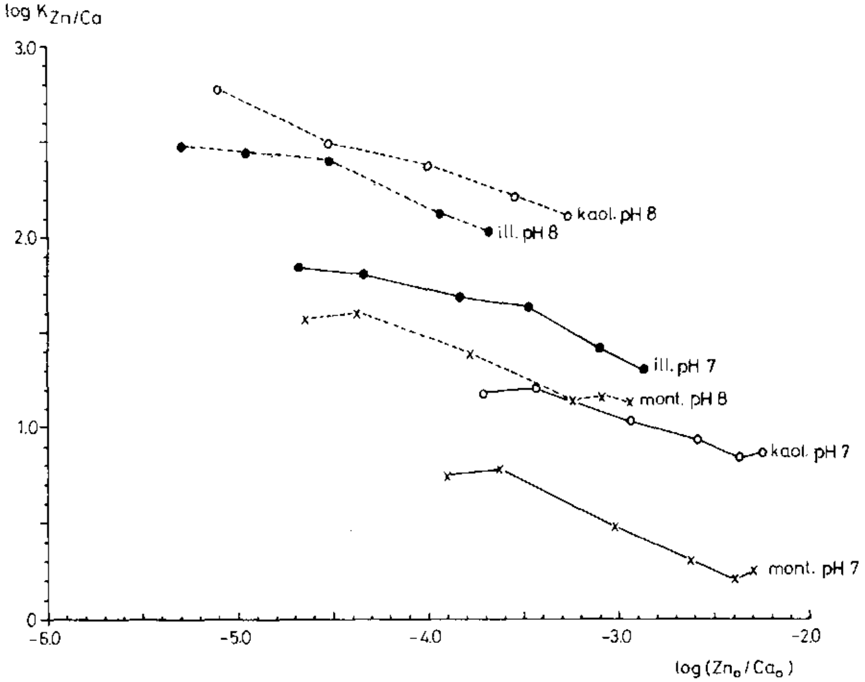

Fig. 56. The apparent Zn/Ca selectivity coefficient for kaolinite, illite, and montmorillonite, at pH 7 (solid lines) and 8 (broken lines), estimated from van der Weijden (1975).

whereas at pH 8 the order is

kaolinite > illite > montmorillonite

Hence the selectivity for Zn and Cd over Ca increases more rapidly with kaolinite than with other clay minerals. This suggests that the selectivity for Zn and Cd may be caused by pH dependent adsorption sites (surface hydroxyls), which make up a larger proportion of the CEC of kaolinite, due to the relatively small amount of substitution charges, which is also reflected by the low CEC of kaolinite: 0.12 meq/g. For montmorillonite the contribution of the substitution charges to the total CEC is much higher, as is reflected in the higher CEC of montmorillonite (0.70 meq/g), and this may help to explain the lower selectivity of montmorillonite for Zn and Cd than for Ca. At pH 7 the selectivity of montmorillonite for Ca is even higher than for Cd, with $K_{Cd/Ca}$ ranging from 0.9 to 0.4, suggesting that the substitution charges are selective for Ca. If the ratios of the activity coefficients be constant,

$$K_{Zn/Ca}(K_{Cd/Ca})^{-1} = K_{Zn/Cd} \tag{126}$$

(see also Eqs. 116 and 117). From the data plotted in Figs. 55 and 56 it can be estimated that at pH 7 $K_{Zn/Cd}$ ranges from 5, for kaolinite and montmorillonite, to 10, for illite, whereas at pH 8 $K_{Zn/Cd}$ ranges from 10, for montmorillonite, to 20, for kaolinite and illite. Hence the increase in selectivity for Zn is most pronounced for kaolinite, possibly through the large proportion of pH-dependent sites. The increase in selectivity and the differences between the clay minerals suggest that pH-dependent adsorption sites help to determine cation-exchange selectivity, whereas the differences in selectivity among Ca^{2+}, Cd^{2+} and Zn^{2+}, for these adsorption sites, may be due to differences in ionic properties, such as polarizability or free enthalpy of hydration. The lowering of the pH upon addition of Zn or Cd points to desorption of weakly acidic H^+, or to hydrolysis of Zn^{2+} or Cd^{2+}.

Sinha et al. (1975) studied the adsorption of Zn in some acid soils of Himachal Pradesh (India). The pH of the soil suspensions ranged from 5.0 to 6.4 and of the supernatant solutions from 6.8 to 7.9, so the soils were not very acid. Soil suspensions with 2 g of soil in 40 ml of water containing Zn at 2.5 - 30 mg/l were shaken for one hour in an end-over-end shaker. After centrifuging the samples, the pH of the supernatant solutions was measured and the solutions were analysed for Zn with atomic absorption spectrophotometry. Sinha et al. used the Langmuir adsorption equation to describe their experimental data and they estimated the adsorption maxima of the Langmuir equation to range from 3.8 to 10.9% of the CEC of the soils. Although the Langmuir adsorption maxima possibly refer to a particular type of adsorption sites, it is not likely that the remaining 90 - 95% of the CEC would not be accessible for Zn^{2+}. Therefore the physicochemical significance of these adsorption maxima is somewhat obscure. Sinha et al. suggested the following reaction

$$Si(OH)_4 + Zn^{2+} + 2H_2O \rightleftarrows Zn(OH)_2(crys) + SiO_2(amorph) + 2H_3O^+ \tag{127}$$

to account for the relationship

$$2\ \mathrm{pH} + \log \mathrm{Zn} = \mathrm{constant} \qquad (128)$$

It seems unlikely, however, that equilibrium would be established between a precipitate of $Zn(OH)_2$ in a matrix of amorphous silica, and aqueous Zn within one hour. The Langmuir adsorption equation is hardly applicable if Zn is precipitated, and also the interpretation of the 'adsorption' maxima is further obscured by the presence of a precipitate. The data presented by Sinha et al. are plotted in Fig. 57, without modification: they do not support the conclusion that Eq. 128 holds. The straight lines in Fig. 57 do represent the relationships

$$2\ \mathrm{pH} + 0.62 \log \mathrm{Zn} = 10.55 \qquad \text{(Curve a)}$$

$$2\ \mathrm{pH} + 0.51 \log \mathrm{Zn} = 10.82 \qquad \text{(Curve b)}$$

$$2\ \mathrm{pH} + 0.55 \log \mathrm{Zn} = 9.87 \qquad \text{(Curve c)}$$

$$2\ \mathrm{pH} + 0.91 \log \mathrm{Zn} = 6.68 \qquad \text{(Curve d)}$$

In the presence of $Zn(OH)_2$ all experimental data in Fig. 57 would conform to one straight line, parallel to the x axis. Therefore, it is more likely that the apparent relationships between the pH and log Zn are due to selective adsorption of first hydrolysis pro-

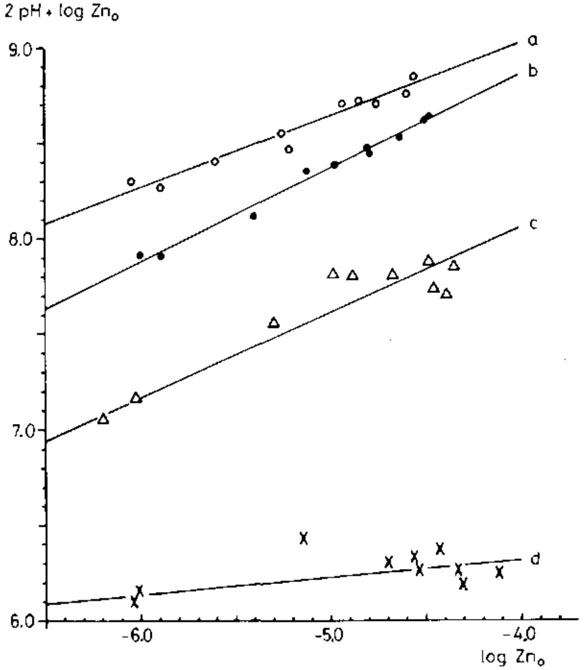

Fig. 57. Relationships between log Zn_o and pH for 4 Indian soils: (a) Palampur-I, (b) Pine forest soil, (c) Palampur-II, and (d) Dalhousie. Data from Sinha et al. (1975).

ducts, as discussed in Section 4.7.4, or to desorption of weakly acidic protons upon adsorption of Zn^{2+}.

Lagerwerff & Brower (1972) studied the exchange adsorption of Cd in 3 soils treated with chlorides of Al, Ca and Na. The soils used were a Cecil sandy loam, with CEC 59 μeq/g, pH 4.3, and kaolinite and vermiculite in the clay fraction, a Winsum clay loam, with CEC 205 μeq/g, pH 6.7, and predominantly illite in the clay fraction, and a Yolo silt loam, with CEC 184 μeq/g, pH 6.8, and montmorillonite, mica and chlorite in the clay fraction; the Yolo soil contained some $CaCO_3$. The CEC was measured at pH 7 with Cd^{2+} as indicator ion and 1 N HCl as extractant, and pH was measured in the natural soil as aqueous paste at liquid point. Samples of 5 g Cecil soil and 2 g Winsum and Yolo soil were first converted to the homoionic Ca-form, then equilibrated with 35 ml of the required solutions for 48 hours in a turnover-type shaker, and finally centrifuged off, after which the supernatant solutions were analysed for Cd and Ca by atomic absorption spectrophotometry. The coverage of the soils with Cd ranged from 0.14 to 1.6% of CEC. Lagerwerff & Brouwer described the Cd/Ca exchange by a Gapon equation of the form

$$Cd_s/Ca_s = k_g(Cd_o/Ca_o)^{\frac{1}{2}} \qquad (129)$$

where the subscripts 's' refer to the adsorbed phase (meq/g), the subscripts 'o' to the equilibrium solution (mol/l), and where k_g represents the Gapon exchange coefficient for the Cd/Ca exchange reaction. It may be noted that the Gapon equation can be written in the general form (Ermolenko, 1966, p. 137)

$$A_s/B_s = k_g(A_o^{1/z_A} B_o^{-1/z_B}) \qquad (130)$$

where z_A and z_B denote the charge numbers of the cations A and B. Commonly the Gapon equation is used only to describe monovalent-divalent cation exchange, e.g. Na^+/Ca^{2+} exchange. The theoretical model used by Gapon (1933) is unsatisfactory in some respects, but the derivation of a similar type of equation by Eriksson (1952) on the basis of the diffuse double layer theory provides a theoretical basis for the Gapon equation as well, as was shown by Lagerwerff & Bolt (1959). The mean values of the Gapon exchange coefficient for the 3 soils were 0.30 for Winsum, 0.35 for Yolo, and 0.13 for Cecil; the last value differs from the one given by Lagerwerff & Brower (1972) for Cecil, $k_g = 0.19$, because of an error in the calculation of the original value. From these values for k_g it may seem that the adsorption of Ca is favoured over Cd by the soils, but the Gapon exchange coefficient differs from the selectivity coefficient for the Cd/Ca exchange reaction, although the coefficients are both dimensionless. Also, the mean Gapon coefficients do not reflect the systematic variation of these coefficients with both the inital Cd concentrations and the $CaCl_2$ levels, a matter which was noticed by Lagerwerff & Brower, but not investigated. The selectivity coefficient for the Cd/Ca exchange reaction becomes in the present notation

$$K_{Cd/Ca} = (Cd_s/Ca_s)(Ca_o/Cd_o) \qquad (131)$$

and the relation to the Gapon exchange coefficient is given by

$$K_{Cd/Ca} = k_g \ (Ca_o/Cd_o)^{\frac{1}{2}} \tag{132}$$

The use of the selectivity coefficient is preferred over the Gapon coefficient, because K_{sel} is related to the thermodynamic equilibrium constant through the ratios of the activity coefficients, and also because K_{sel} is more widely used than k_g. Figures 58-60 show that $K_{Cd/Ca}$ decreases with increasing Cd_o, in accordance with the adsorption models discussed in Sections 4.6-4.7. The influence of $CaCl_2$ levels is less pronounced, although

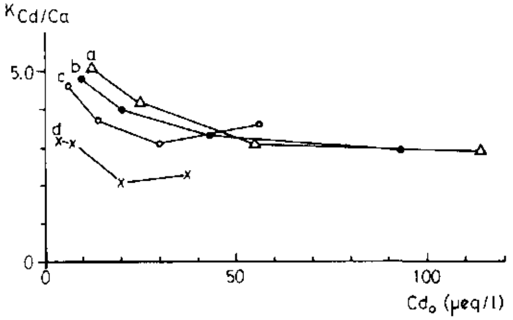

Fig. 58. $K_{Cd/Ca}$ as a function of Cd_o for Cecil sandy loam at 4 different $CaCl_2$ levels: (a) 47.1 meq/l, (b) 28.3 meq/l, (c) 14.3 meq/l, and (d) 1.5 meq/l. Calculated from Lagerwerff & Brower (1972).

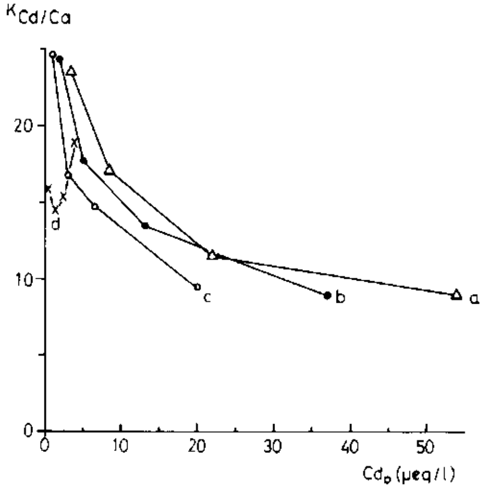

Fig. 59. $K_{Cd/Ca}$ as a function of Cd_o for Winsum clay loam at 4 different $CaCl_2$ levels: (a) 47.1 meq/l, (b) 28.3 meq/l, (c) 14.3 meq/l, and (d) 5.1 meq/l. Calculated from Lagerwerff & Brower (1972).

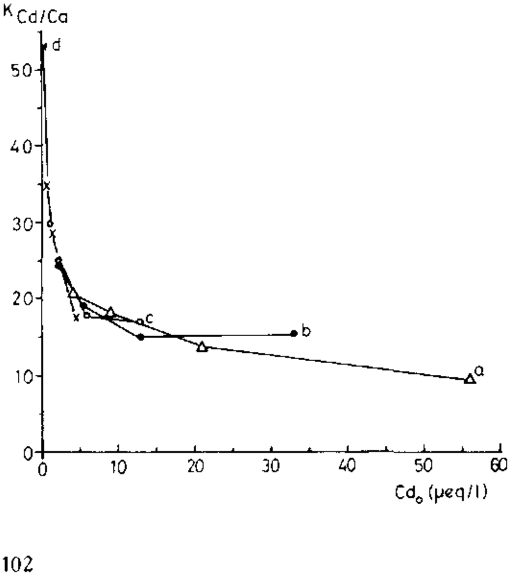

Fig. 60. $K_{Cd/Ca}$ as a function of Cd_o for Yolo silt loam at 4 different $CaCl_2$ levels: (a) 47.1 meq/l, (b) 28.3 meq/l, (c) 14.3 meq/l, and (d) 5.1 meq/l. Calculated from Lagerwerff & Brower (1972).

the preference for Cd seems to increase with increasing $CaCl_2$ level for Cecil and Winsum. The mean values of $K_{Cd/Ca}$ are 3.5 for Cecil, 16.1 for Winsum, and 22.6 for Yolo, and the selectivity for Cd seems to increase with increasing soil pH. Notably the Cecil soil, which has the lowest pH, shows a relatively low preference for Cd and also little variation in $K_{Cd/Ca}$. The pH of the equilibrium solutions ranged from 5.32 to 5.52 which means that in Winsum and Yolo pH has decreased considerably upon addition of Cd to the suspensions. In Figs. 61 and 62 the Cd/Ca exchange data are presented in the form of 'Rothmund-Kornfeld plots'; the experimental data fit straight lines reasonably well. Curve a in Fig. 61 represents the relationship

$$\log (Cd_s/Ca_s) = -0.14 + 0.77 \log (Cd_o/Ca_o)$$

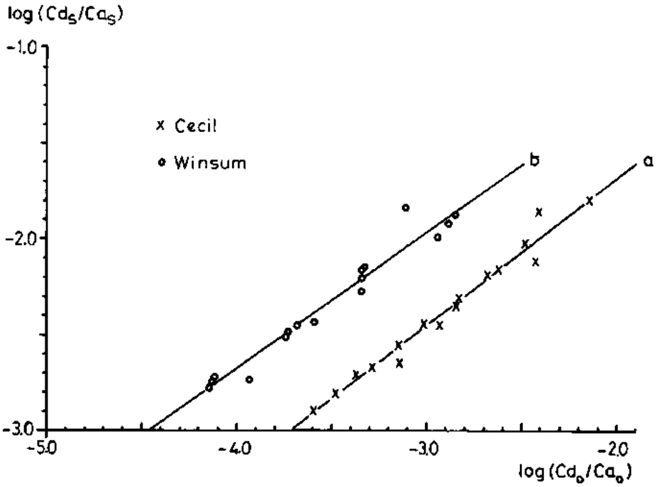

Fig. 61. Rothmund-Kornfeld plot of Cd-Ca exchange data for Cecil and Winsum soil. Data from Lagerwerff & Brower (1972).

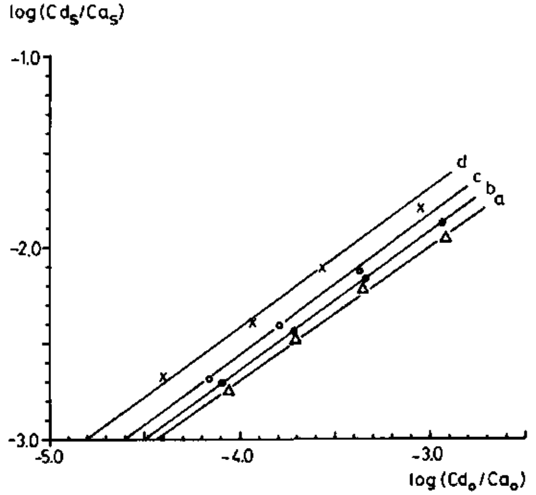

Fig. 62. Rothmund-Kornfeld plot of Cd-Ca exchange data for Yolo soil at 4 different $CaCl_2$ levels: (a) 47.1 meq/l, (b) 28.3 meq/l, (c) 14.3 meq/l, and (d) 5.1 meq/l. Data from Lagerwerff & Brower (1972).

and Curve b the relationship

$$\log (Cd_s/Ca_s) = 0.09 + 0.69 \log (Cd_o/Ca_o)$$

The mean of Curves a-d in Fig. 62 is given by

$$\log (Cd_s/Ca_s) = 0.23 + 0.70 \log (Cd_o/Ca_o)$$

and the experimental data of all soils can be described with a Rothmund-Kornfeld equation of the form

$$(Cd_s/Ca_s) = k\ (Cd_o/Ca_o)^{0.7}$$

Curves a, b, c and d, in Fig. 62 refer to $CaCl_2$ levels of 47.1, 28.3, 14.3 and 5.1 meq/l, respectively, and Fig. 62 shows that the selectivity for Cd decreases with increasing $CaCl_2$ level. The Yolo soil contained some $CaCO_3$ and pH should decrease with increasing $CaCl_2$ level: if equilibrium exists with atmospheric CO_2 the relation between pH and log Ca is given by

$$\log Ca + 2\ pH = 13.4$$

and it follows that pH = 8.0 at $CaCl_2$ = 5.1 meq/l (Curve d) and pH = 7.5 at $CaCl_2$ = 47.1 meq/l (Curve a). Hence Fig. 62 suggests that the selectivity for Cd increases with increasing pH. The decreasing selectivity for Cd with increasing $CaCl_2$ level may be due to an increasing fraction of $CdCl^+$ in solution. From $\log \beta_1 = 1.32$ (Hahne & Kroontje, 1973) it follows that at a $CaCl_2$ level of 5.1 meq/l the ratio $CdCl^+/Cd^{2+}$ equals 0.11, whereas at a $CaCl_2$ level of 47.3 meq/l the ratio equals 0.98, i.e. about 50% of the Cd in solution is in the form of $CdCl^+$. When monovalent complexes are not specifically adsorbed, the only consequence of the occurrence of $CdCl^+$ in solution is a lowering of the Cd^{2+} activity, since monovalent species will hardly be adsorbed by regular ion-exchange at concentrations of 1-10 µmol/l. If $CdOH^+$ complexes are adsorbed selectively, $CdCl^+$ must also be adsorbed selectively, since no differences are to be expected between $CdOH^+$ and $CdCl^+$ on the basis of electrostatic ion-solvent and ion-solid interactions, as discussed in Section 4.7.3. It may be concluded that the presence of $CdCl^+$ complexes cannot be neglected in explaining the Cd exchange in soils at different $CaCl_2$ levels.

In another paper, Lagerwerff & Brower (1973) reported the exchange adsorption of Pb in the same soils, and Fig. 63 summarizes their results in the form of a log-log plot of $K_{Pb/Ca}$ against Pb_o/Ca_o. It can be seen that $K_{Pb/Ca}$ decreases from values of the order of 2000 to about 40, with increasing Pb_o/Ca_o ratio. The overall Pb/Ca exchange can be described with a Rothmund-Kornfeld equation of the form

$$(Pb_s/Ca_s) = 1.58\ (Pb_o/Ca_o)^{0.36}$$

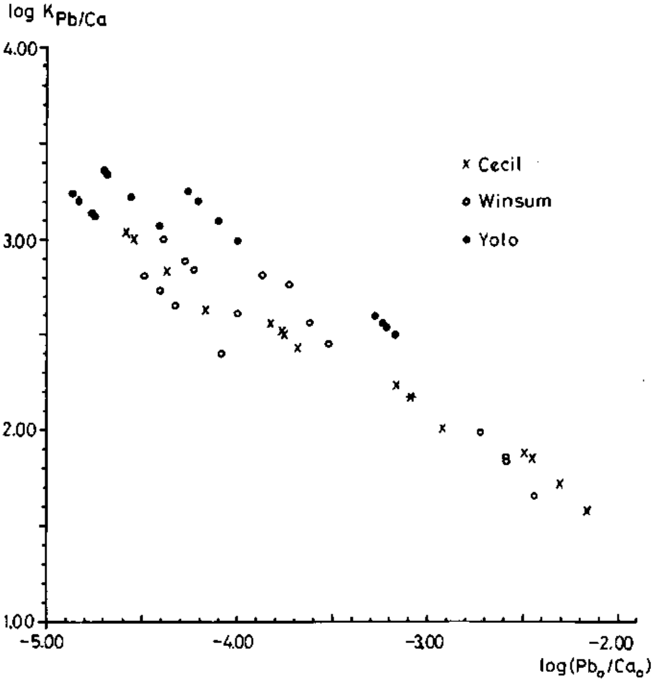

Fig. 63. Log-log plot of Pb-Ca exchange data for three soils: Cecil sandy loam, Winsum clay loam, and Yolo silt loam. Data from Lagerwerff & Brower (1973).

but the exchange data for each soil separately may be better described by a Gapon equation of the form

$$(Pb_s/Ca_s) = k_g\ (Pb_o/Ca_o)^{0.5}$$

The Gapon equation in this form may be considered as a special case of the Rothmund-Kornfeld equation, for $1/n = 0.5$. The mean values of the exchange coefficients were estimated to be 4.13 for Cecil, 4.97 for Winsum and 11.1 for Yolo (Lagerwerff & Brower, 1973). Using $\log \beta_1 = 0.88$ for the Pb-Cl system and $\log \beta_1 = 7.82$ for the Pb-OH system (Hahne & Kroontje, 1973) it follows that $PbCl^+_o/Pb^{2+}_o$ ranges from 0.04 at 5.8 meq Cl/l to 0.37 at 49.4 meq Cl/l, and $PbOH^+_o/Pb^{2+}_o$ ranges from 0.06 at pH = 4.96 to 1.45 at pH = 6.34. Hence, the occurrence of monovalent Pb complexes cannot be neglected in explaining the Pb/Ca exchange behaviour, since more than half the Pb in solution may occur in the form of $PbCl^+$ or $PbOH^+$.

Bittel & Miller (1974) studied the exchange adsorption of Pb, Cd and Ca on montmorillonite, illite and kaolinite. They concluded that the selectivity coefficients did not vary in a consistent manner over the 10-90% range of Pb^{2+} and Cd^{2+} surface coverage and they interpreted this as an indication that the adsorption sites were all similar and that there was little or no interaction between adsorbed ions. A closer look on the experimental data, however, shows that (a) a number of selectivity coefficients tend to decrease with increasing surface coverage of the 'preferred ion', and (b) some exchange experiments show adsorption-desorption hysteresis. Fig. 64 summarizes the experimental data in the form of plots of $K_{Pb/Ca}$, $K_{Ca/Cd}$ and $K_{Pb/Cd}$, as a function of fractional surface coverage, for the three clay minerals. The Pb-Ca exchange data (Fig. 64,

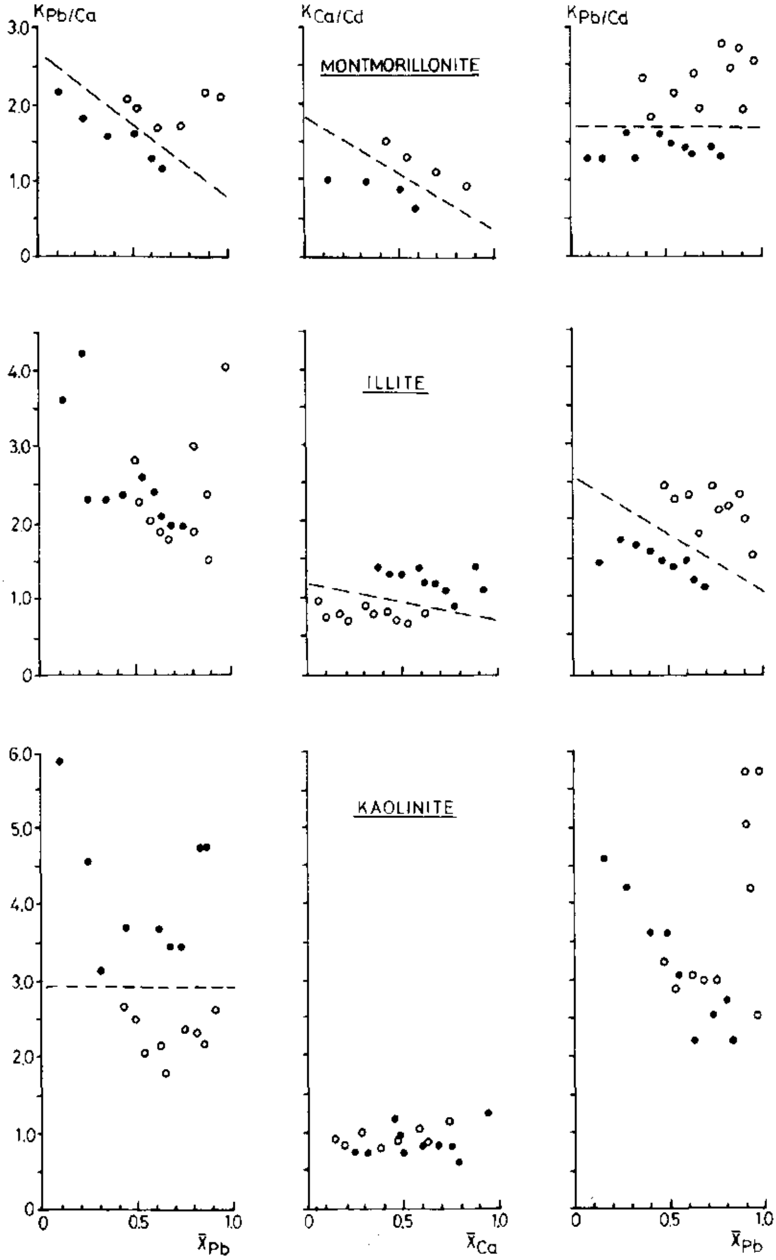

Fig. 64. Selectivity coefficients for Pb-Cd-Ca exchanges on three clay minerals as functions of surface composition. Data from Bittel & Miller (1974).

Column 1) are distinguished in Ca/Pb (open circles) and Pb/Ca (dots) exchange data, where the first ion in the notation 'A/B exchange' represents the ion being adsorbed and B is the ion initially present on the exchange complex, i.e. the ion being desorbed. For montmorillonite the values of $K_{Pb/Ca}$ referring to Ca/Pb exchange (mean value 7.90) are higher than for Pb/Ca exchange (mean value 1.52), whereas for kaolinite the situation is reversed: $K_{Pb/Ca}$ values for Ca/Pb exchange (mean value 2.28) are lower than for Pb/Ca exchange (mean value 4.00). The Ca-Cd exchange data (Fig. 64, Column 2) show that for montmorillonite the values of $K_{Ca/Cd}$ referring to Cd/Ca exchange (open circles) are higher, with a mean of 1.21, than for Ca/Cd exchange (dots), where the mean value equals 0.87, whereas for illite these trends are reversed and here the mean values are 0.79 and 1.23, respectively. The Pb-Cd exchange data (Fig. 64, Column 3) show that for montmorillonite and illite, the values of $K_{Pb/Cd}$ referring to Cd/Pb exchange (open circles) are higher, with means of 2.25 and 2.10, than for Pb/Cd exchange (dots), where the means are 1.39 and 1.54 for montmorillonite and illite, respectively. This adsorption-desorption hysteresis may be caused by precipitation or specific adsorption, or possibly by condensation of (homoionic) clay platelets. In montmorillonite, $K_{Pb/Ca}$ and $K_{Ca/Cd}$ tend to decrease with increasing $\bar{X}_{Pb}$ and $\bar{X}_{Ca}$, respectively, and in illite, $K_{Ca/Cd}$ and $K_{Pb/Cd}$ tend to decrease with increasing $\bar{X}_{Ca}$ and $\bar{X}_{Pb}$, respectively. Therefore the Pb-Ca-Cd exchange data show that adsorption-desorption hysteresis and also the surface composition of the adsorbent may determine the selectivity coefficient for a particular pair of cations. Figure 64 shows that $K_{Ca/Cd}$ is fairly constant for the three clay minerals, the means range from 0.90 to 1.04, but $K_{Pb/Ca}$ and $K_{Pb/Cd}$ increase in the order montmorillonite (1.71 and 1.76) < illite (2.28 and 1.80) < kaolinite (3.03 and 3.29), where the mean values of $K_{Pb/Ca}$ and $K_{Pb/Cd}$ are given in parenthesis. The variation in the selectivity coefficient with surface composition and the differences between clay minerals point to site-heterogeneity rather than to site-uniformity. Since the highest selectivity coefficients are on kaolinite, it is likely that (deprotonated) surface hydroxyls are at least partly responsible for the observed differences in selectivity between clay minerals.

Bittel & Miller (1974) compared their results with those of Lagerwerff & Brower (1972, 1973) and stated that, contrary to their own results, the adsorption of Ca was significantly favoured over Cd in the experiments of Lagerwerff & Brower. This observation is not entirely correct, since selectivity coefficients are compared with Gapon exchange coefficients. On the contrary the adsorption of Cd is significantly favoured over Ca, as can be seen from Figs. 58-60. The conclusion of Bittel & Miller, that exchange data obtained over a range of 0.14 to 1.6% of Cd^{2+} coverage may not be comparable to data where Cd^{2+} coverage varied from 7 to 94%, also applies to the reverse situation.

Maes (1973) studied monovalent-divalent ion exchange of Na^+ against Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+}, on montmorillonites and found no essential differences between the 4 divalent cations. Maes suggested that two types of sites be active in the exchange process: planar sites and pH-dependent sites, 'broken bonds', on the edges of clay minerals, which were assumed to be responsible for the preferential uptake of divalent ions at low divalent metal coverage of the exchange complex.

5 Cation-exchange experiments

5.1 INTRODUCTION

Cation-exchange experiments were set up after study of the literature discussed in Section 4.8. The apparent contradiction between the highly selective adsorption of small amounts of Cd and Pb on soils treated with $CaCl_2$, reported by Lagerwerff & Brower (1972, 1973), and the 'regular' (low selectivity) exchange behaviour of these divalent metals, reported by Bittel & Miller (1974), formed an open question.

The experimental procedure described by Lagerwerff & Brower was modified such that a complete exchange isotherm could be determined on the same soil sample by consecutive equilibrations with stepwise increasing concentrations of the required salt. Exchange isotherms, covering the whole range 1-99% surface coverage were obtained for Ca^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} on Winsum soil. The heavy metals were subject to both regular ion-exchange and specific interactions, the latter being strongly dependent on pH and time. These observations are of concern for the control of heavy metals in the environment: traces of heavy metals will be adsorbed highly selectively by most soils, and the efficiency of this process can be increased by increasing the pH of the soil, e.g. by liming. But the efficiency of the soil to immobilize heavy metals in this way, decreases with increasing amounts of heavy metals added to the soil.

Because of the strong time-dependency of one of the specific adsorption mechanisms, the efficiency of this process depends on the leaching conditions prevailing in soil: when the rate of leaching is high, efficiency approaches to zero, but when the rate of leaching is low, the efficiency of this mechanism of immobilization may become high. Iron and manganese oxides in soils may play a significant role in the uptake of heavy metals from soil solutions, but the efficiency of this process depends not only on pH and time, but also on redox conditions prevailing in soil: at low redox potentials (e.g. during waterlogging) the iron and manganese oxides dissolve and the associated heavy metals are released.

The discussion of these specific interactions will examine the influence of surface composition, salt concentration, pH and time. The experimental design did not prove the most straightforward to study the influence of these factors on the specific adsorption of heavy metals, since the influence of pH, equilibration times and possibly surface hydroxyl groups was not realized when the research was started. To simplify the discussion little attention will be paid to hypotheses considered during the research but rejected later. Attention will be concentrated on results most relevant to adsorption of heavy metals in soils.

5.2 MATERIALS AND METHODS

5.2.1 Soil materials

Two different clay soils were used in the experiments: Winsum and Grundite. Winsum soil is a marine clay collected 20-40 cm depth near the Village of Winsum (Groningen, the Netherlands). The soil contained about 45% clay (fraction < 2μm), the dominant clay minerals being illite and smectite (Breeuwsma, 1976). The carbon content of the soil was 0.6%, the cation-exchange capacity was about 200 μeq/g soil and the composition of the exchange complex averaged 40% Ca, 40% Mg, 15% K, and 5% Na. The soil contained 3,3% Fe (mass fraction), 0.23% Mn, 0.3% $CaCO_3$, and 0.10% P_2O_5. The pH-H_2O of the soil was 7.1 and the pH-KCl (1.0 N) 6.1, both in a suspension of 10 g soil and 25 ml solution. Grundite is an almost pure illite obtained from the Illinois Clay Cy, with a cation-exchange capacity of about 150 μeq/g. The pH ranged from 3.6 (0.1 N $CaCl_2$, $ZnCl_2$) to 4.9 (demineralized water); the soil contained gypsum.

The Grundite and Winsum samples are called soils rather than clays to stress that the complete soil was used in the experiments and not only a particular size fraction. Besides drying, the soil material was not prepared in any way before the experiments.

After the first tests, only Winsum soil was used because heavy metals in Winsum soil were subject to specific interactions not observed in Grundite, and these specific interactions seemed to be of more significance for the control of heavy metals in the environment than non-selective ion exchange.

5.2.2 Experimental procedure

The experiments to be described were of batch type, soil samples being first brought into homoionic form and then saturated with the cation to be studied by equilibrating the clay samples with stepwise increasing concentrations, thus yielding a complete adsorption isotherm on one soil sample.

One equilibration cycle consisted of the following steps. First 2.00 g soil were placed in 50 ml polyethylene high-speed centrifuge tubes of known weight. Then 35 ml aliquots of the required solution were pipetted in the centrifuge tubes, which were then weighed and clamped in a turnover-type shaker (14 rotations per minute) for a period of equilibration. After equilibration the samples were centrifuged for 30 minutes at 20,000 rpm (at 20 °C) and the supernatant was decanted into numbered polyethylene 50-ml bottles. After the pH of the solutions had been measured, they were acidified to pH 1.0. The numbered bottles were then stored in a dark cold-storage chamber at 4 °C. After weighing the tubes, the new solutions were pipetted into the tubes, which were weighed again. The soil sediments in the tubes were dispersed by a rotating plastic bar, connected to a mechanical stirrer. The tubes with the homogeneous clay suspensions were then placed in the turnover-type shaker to equilibrate again.

In a series of such cycles, the clay samples were saturated with the required cation by consecutive equilibrations with 0.1 N solutions of the chloride or nitrate of that cation. Then the excess salt was washed out by consecutive equilibrations with demineralized water, pH 5.4 - 5.7 and conductivity less than 1 μmho. When the conductivity of the supernatant solutions decreased no further, the homoionic clay samples were equilibrated with stepwise increasing concentrations of the cation to be studied. The cation used to bring the clay into the initial homoionic form will be referred to as M^*, and the cation introduced thereafter will be referred to as M, i.e. during the actual exchange experiment, M^* represents the metal which is released by the solid phase, upon adsorption of M. After coverage with M was assumed complete, the soil samples were treated with dilute acid to dissolve unexchangeable forms of M^*. Finally all the supernatant solutions were analysed for both M and M^*. In regular cation exchange, the adsorption, measured as loss from solution during the successive equilibrations, should equal the desorption, measured as the increase in M^* in solution.

5.2.3 Calculation procedure

Adsorption isotherms were calculated with the following data: the mass[6] of the empty centrifuge tube, w_t, and of the dry soil, w_s, with $w_t + w_s = w_d$, the mass of the centrifuge tube after an aliquot of 35 ml of the required solution was pipetted in the tube, $w_f(i)$, where i denotes the i-th equilibration cycle, and the initial concentration of M in this solution, before addition, $M_{in}(i)$, the mass of the tube after the supernatant solution was decanted, $w_e(i)$, and the concentrations of M and M^* in the supernatant solution, $M_o(i)$ and $M^*_o(i)$. The amount of M lost from solution per g soil during the i-th equilibration cycle was calculated from

$$\{w_e(i) - w_d\}M_o(i)/w_s + \{w_f(i) - w_e(i)\}M_{in}(i)/w_s - \{w_f(i) - w_d\}M_o(i + 1)/w_s \qquad (133)$$

and the amount of cations released per g soil from

$$\{w_f(i) - w_d\}M^*_o(i + 1)/w_s - \{w_e(i) - w_d\}\, M^*_o(i)/w_s \qquad (134)$$

In these calculations 1 g of solution was taken as equal to 1 ml of solution, which is not entirely correct, but the errors were less than 1% under the conditions of the experiment. Also, the possible exclusion of anions from the solution occluded by the soil sediment upon centrifuging was neglected. Errors made in this way were rather difficult to estimate, because the thickness of a diffuse double layer was not known, but the results of the adsorption experiments suggested that these errors were small too (Section 5.3).

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[6] Mass is generally determined by weighing. In common parlance, weight is often expressed mistakenly in mass units, since most weighing instruments convert units of weight (Newton, dyne) directly into units of mass (kg, g), by dividing the weight by the acceleration due to gravity (9.8 m/s^2).

5.2.4 Adsorption experiments

The adsorption experiments were in four series, differing in experimental conditions: (1) Zn/Ca and Ca/Zn exchange on Winsum and Grundite, (2) Cd/Ca, Ca/Cd, Zn/Cd and Cd/Zn exchange on Winsum, (3) Cu/Ca, Ca/Cu, Pb/Ca and Ca/Pb exchange on Winsum, and (4) a series of experiments designed to investigate the relation between the amounts of Zn, Cu, or H added to Winsum clay and the resulting change in pH of the soil suspension. Each adsorption isotherm of Series 1, 2 and 3 was determined in duplicate, each series consisting of eight centrifuge tubes, equal to the capacity of the rotor head of the high-speed centrifuge.

The first series of adsorption experiments was primarily designed to develop a satisfactory experimental procedure for the determination of adsorption isotherms on soil samples. Before the actual experiment, stock samples of Winsum and Grundite soil (0.5 kg each) were equilibrated with 0.1 N salt solutions in 10-litre bottles. Excess salt was washed out with demineralized water which was decanted regularly until the conductivity of the solution remained constant. Soluble forms of phosphate and carbonate in Winsum and gypsum in Grundite would so be removed. After this pretreatment, Winsum and Grundite samples, already in the homoionic calcium or zinc form, were once more treated with 0.10 N $CaCl_2$ or $ZnCl_2$ and once with demineralized water to wash out excess salt. Then the samples were equilibrated twice with 0.0001 N and 0.0003 N $ZnCl_2$ or $CaCl_2$, next three times with 0.0010 N, four times with 0.0030 N and five times with 0.0100 N $ZnCl_2$ or $CaCl_2$, pH values of all solutions are given in Table 7. Equilibration times were all 10 hours. After this treatment, the soil samples which were initially in the zinc form were equilibrated three times with 0.1 N HCl to remove possible acid-extractable forms of zinc.

In a separate experiment, the use of nitrates and chlorides was compared: a number of homoionic Winsum samples of 2.00 g each were equilibrated with one of the following solutions: 0.003 N, 0.010 N, 0.030 N or 0.100 N $ZnCl_2$ or $Zn(NO_3)_2$. After equilibration for 16 hours the supernatant solutions were analysed for Zn and Ca. In another experiment, a Zn/Ca adsorption isotherm was determined at constant ionic strength by equilibrating 16 samples of Winsum in the homoionic calcium form, ranging from 8.0 to 0.010 g, for 16 hours with 30 to 35 ml of 0.001 N $ZnCl_2$ with a pH of 5.3.

On the basis of the results, it was decided to continue experiments with Winsum

Table 7. pH of solutions added to the soils in the adsorption experiments; pH of demineralized water was 5.4 - 5.7.

Conc. (eq/l)	Series 1		Series 2			Series 3		
	$ZnCl_2$	$CaCl_2$	$Ca(NO_3)_2$	$Zn(NO_3)_2$	$Cd(NO_3)_2$	$Ca(NO_3)_2$	$Cu(NO_3)_2$	$Pb(NO_3)_2$
0.10	4.2	5.3	5.0	5.4	4.6	5.4	4.3	4.0
0.0001	5.5	5.4	5.4	5.4	5.3	5.4	5.2	5.0
0.0003	5.4	5.5	5.5	5.4	5.4	5.5	5.1	5.1
0.0010	5.4	5.4	5.1	5.1	5.1	5.2	5.1	4.8
0.0030	5.3	5.4	4.9	5.1	5.1	5.0	4.7	4.8
0.0100	5.0	5.3	4.9	4.7	4.8	5.2	4.6	4.6

soil only, since adsorption isotherms showed a specific behaviour, not observed on Grundite samples.

The second series of adsorption experiments was designed to obtain Cd/Ca, Ca/Cd, Zn/Cd and Cd/Zn adsorption isotherms on Winsum soil. To avoid failure to equilibrate through short equilibration times, the time of equilibration was set to 20 hours for all solutions. The soil samples were made homoionic by equilibrating the samples 4 times with a 0.10 N solution of $Ca(NO_3)_2$, $Cd(NO_3)_2$ or $Zn(NO_3)_2$, and excess salt was washed out by equilibrating 5 times with demineralized water. The samples were then equilibrated 2 times with 0.0001 N and 0.0003 N solutions, 3 times with 0.0010 N, 4 times with 0.0030 N and 5 times with 0.0100 N solutions of the required salt. Non-exchangeable forms of the metals were removed by equilibrating twice with 0.01 N HNO_3. The supernatant solutions were analysed for Zn, Cd and Ca.

The third series of experiments was designed to obtain the Cu/Ca, Ca/Cu, Pb/Ca and Ca/Pb adsorption isotherms on Winsum soil. Samples were equilibrated 5 times for 20 hours with 0.10 N solutions of $Ca(NO_3)_2$, $Cu(NO_3)_2$ or $Pb(NO_3)_2$, then 6 times with demineralized water, 2 times with 0.0001 N, 2 times with 0.0003 N, 3 times with 0.0010 N, 4 times with 0.0030 N and finally 10 times with 0.0100 N solutions of the required salts. Non-exchangeable forms of the metals were removed by equilibrating the soils twice with 0.01 N HNO_3 and twice with 0.10 N HNO_3. The supernatant solutions were then analysed for M and M^*.

Series 4 was designed to obtain further information about the pH dependency of aqueous Zn, Cu and H, in suspensions of Winsum soil. The design was different from the first three series. Winsum soil 5 g was equilibrated with 100-ml aliquots of $Ca(NO_3)_2$ of different concentrations in 200-ml polyethylene bottles. The bottles were provided with a magnetic bar, with a Teflon coating, and placed on a magnetic stirrer. With an automatic burette, the required solution, 0.10 N $Zn(NO_3)_2$, was added to the soil suspensions at a constant rate (1.00 ml in 70 minutes). The pH of the suspension was kept constant at a pre-set equilibrium value by automatic titration with a 0.10 N NaOH solution. After addition of a known amount of Zn, the suspension was centrifuged off, the clear supernatant decanted, and analysed for Zn. In another part of series 4, known amounts of Zn, Cu, or H, were added to clay suspensions consisting of 5 g of Winsum and 100 ml of 0.010 N $Ca(NO_3)_2$. The bottles were then left standing and the pH was measured daily. After several weeks, the solutions were centrifuged off and analysed for Zn or Cu, and for Na, K, Ca and Mg. Further details about these experiments will be given in Sections 5.9 and 5.10.

5.2.5 Analytical conditions

The metal concentrations in the acidified solutions were measured by atomic absorption spectrophotometry, and Ca also by emission spectrophotometry. All analyses were performed at least in duplicate and, where possible, two different dilutions of the same sample were measured. To obtain reliable values for the loss from solution of metals at the upper end of the adsorption isotherm, at values near saturation, 5-10 independent measurements of each sample were necessary to limit the standard deviations. All analytical procedures for the determination of metals were standard procedures and are not described in detail here. The fact that all adsorption isotherms were determined in duplicate and that the amounts of both the metal lost from solution, M_o, and the metal released by the soil, M_o^*, were measured, provided a check on the reliability and consistency of the data.

5.3 TREATMENT OF EXPERIMENTAL DATA

The amount of metal added (per g soil) to the soil suspension in one equilibration cycle is denoted by ΔM (μeq/g). Capital M is used to denote all metal species, including alkali and alkaline earth metals, whereas hM is used to denote exclusively the heavy metals, notably Cd, Zn, Cu, and Pb. The concentration of metal in the clear supernatant solution, after the suspension had been centrifuged off, is denoted by M_o and is also expressed in μeq/g soil. The amount of metal lost from solution during one equilibration cycle, calculated from ΔM and M_o (Section 5.2.3), is denoted by M_l (μeq/g).[7] The amount of metal released by a soil, initially in the homoionic M^* form, is denoted by M_r^* (μeq/g) and is calculated from the increase in solution of aqueous M^* upon addition of M to the soil suspension. Figures 65-71 show that

$$M_l \geq M_r^*$$

and the numerical value of the positive difference

$$M_l - M_r^*$$

is a measure for the amount of M apparently adsorbed in excess, denoted by M_{ex} (μeq/g). The amount of hM exchangeably adsorbed by the soil, hM_a (μeq/g), is estimated from

$$hM_a = hM_l - hM_{ex} \tag{135}$$

hence

$$hM_a = M_r^*$$

The fraction hM_a is further divided into an amount of hM adsorbed by non-specific or 'regular' adsorption mechanisms, hM_{ar} (μeq/g), and an amount of hM specifically adsorbed, hM_{as} (μeq/g). Therefore, for an adsorption experiment consisting of a single equilibration cycle, the following relations hold:

$$\Delta hM - hM_o = hM_l \tag{136}$$

$$M_r^* = hM_a = hM_{as} + hM_{ar} \tag{137}$$

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[7] Zn_l refers to a type of interaction, and denotes both the amount of Zn lost from solution during the i-th equilibration cycle, $Zn_l(i)$, and the cumulative amount, $\Sigma Zn_l(i)$, where the summation is over all equilibration cycles. The same holds for the other subscripts in this section.

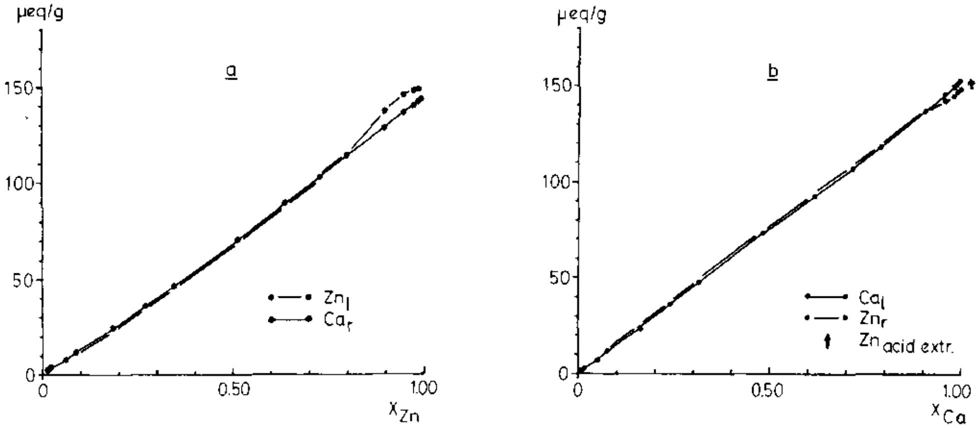


Fig. 65. Adsorption isotherms for Zn/Ca (a) and Ca/Zn exchange (b) on Grundite: loss of Zn and release of Ca (a) and loss of Ca and release of Zn (b) are indicated. The vertical arrow (b) denotes the amount of acid-extractable Zn.

where hM denotes the adsorbing heavy metal and M^* the metal being desorbed, and where all quantities are in µeq/g soil, i.e. aqueous concentrations multiplied by the solution/solid ratio in ml/g. For experiments consisting of more equilibration cycles the aqueous concentrations of hM and M^* have to be corrected for the amounts of metal occluded by the soil sediments in the centrifuge tubes during the preceding equilibration cycle.

Since the possible exclusion of anions from the solution occluded by the soil sediments in the centrifuge tubes is neglected in the calculation of M_l and M_r^*, the amount of M lost from solution may be underestimated, and the amount of M^* released may be overestimated. Figures 65-71 show, however, that

$$M_l \geq M_r^*$$

and therefore the exclusion was probably not of great importance, except possibly at concentrations below 10^{-3} N, but here the errors involved are relatively small, since salt levels are low, and do not affect the shape of the adsorption isotherms to a significant extent. Estimates of the anion exclusion effect indicate that the solution occluded by the soil sediments should be salt-free up to salt concentrations of 10^{-3} N; these estimates are based on the assumption that adsorption takes place in a diffuse double layer, however, and this is doubtful even at low ionic strength, because of specific adsorption.

Granted that the distinction between the different fractions is based on a phenomenological approach and that these different fractions do not necessarily coincide with particular bonding mechanisms or particular types of adsorption sites, the fractions will nevertheless be discussed briefly in terms of probable bonding mechanisms, hydration status of the ions, and types of sorption sites involved. The increase of M^* in solution is due to desorption of M^* upon adsorption of M (ion exchange), but may also include some M^* from dissolution of salts or release of specifically adsorbed M^*. Hereafter it will be

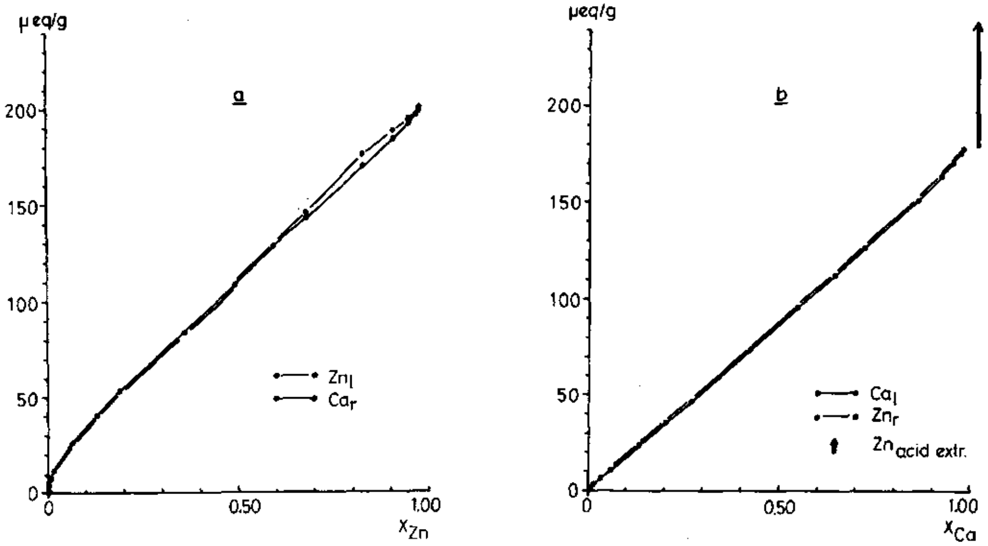


Fig. 66. Adsorption isotherms for Zn/Ca (a) and Ca/Zn exchange (b) on Winsum: loss of Zn and release of Ca (a), and loss of Ca and release of Zn (b) are indicated. The vertical arrow (b) denotes the amount of acid-extractable Zn.

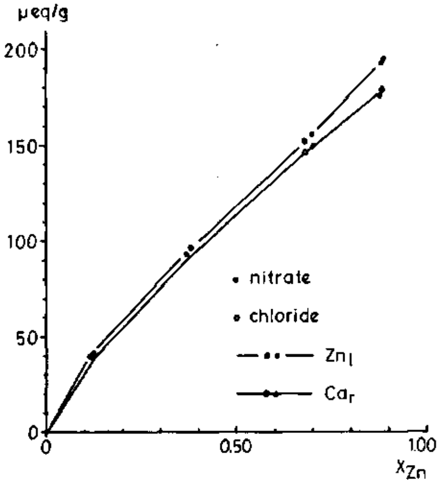


Fig. 67. Zn/Ca exchange on Winsum: comparison of chlorides and nitrates.

assumed that Ca may be considered as an indicator ion for 'regular' ion exchange. Although acid extractable forms of Ca occurred in Winsum soil, it is assumed that Ca did not take part in specific interactions or precipitation reactions under the conditions of the experiments. The apparent excess adsorption of heavy metals was confined to Winsum soils and occurred over the whole range of the adsorption isotherms. Figures 66a, 67, 68a, 70a and 71a show that

$$hM_1 \geq Ca_r$$

suggesting that in adsorption of hM on a soil, initially in the homoionic Ca form (hM/Ca exchange), heavy metals took part in specific interactions or precipitation reactions, resulting in apparent excess adsorption of heavy metals. In Ca/hM exchange it may seem that Ca was also adsorbed in excess, but it is assumed that Pb and Cu released, rather than Ca, took part in specific interactions, resulting in the loss of Pb and Cu from solution, not accompanied by an equivalent increase of other cations (Figs. 70b and 71b). For Zn and Cd Figs. 66b and 68b suggest that these ions did not take part in specific interactions upon desorption, or at least not to a measurable extent.

The apparent excess adsorption of heavy metals may be due to (a) specific adsorption of monovalent complexes, such as $hMCl^+$ or $hMNO_3^-$, or possibly hydrolysis products, provided H^+ released upon hydrolysis of hM did not result in an equivalent increase of Ca in solution, (b) precipitation of hydroxides, carbonates, silicates or phosphates, provided the (approximately) equivalent amount of H^+ released upon precipitation of hM did not result in an equivalent increase in aqueous Ca, and (c) specific adsorption of hM on sorption sites associated with oxide surfaces, thereby increasing the positive charge of the surface and resulting in an increase of the anion-exchange capacity of the soil.

Both specific and non-specific or regular adsorption of ionic species result in the release of an equivalent amount of cations by the solid phase, and therefore these types of adsorption may be referred to as 'ion exchange'. In non-specific interactions all divalent cations do compete on an almost equal basis for the adsorption sites and the attractive forces between the negatively charged sites and the cations are of the coulombic, ion induced-dipole or ion multipole type. As long as the cations remain fully hydrated, ion-exchange selectivity may be due to differences in hydrated radii or polarizabilities of the ionic species or to steric factors. When ionic species lose part of their (secondary) hydration sheath upon adsorption, selectivity may be due to differences in hydration energies or ionic radii. A relatively small difference between ions in free enthalpy of adsorption, of 1 kcal/mol, would result in a selectivity coefficient of about 5 (see Eq. 23). Therefore, a rearrangement of ionic species in the adsorbed phase resulting in a relatively small gain of energy, for example by ion induced-dipole interactions, may cause a significant selectivity between ionic species. Non-specific exchange adsorption is believed to be confined largely to the negatively charged planar sites on clay mineral surfaces and in general the adsorption process will be reversible, unless condensation of clay platelets occurs. The adsorption isotherm corresponding to completely non-selective ion exchange is a straight line ($K_{sel} = 1$) and it is assumed that the straight parts of the adsorption isotherms in Figs. 65-70 reflect this type of behaviour, whereas for Pb/Ca exchange the selectivity coefficient is about 2 (Fig. 71a).

Adsorption of ionic species caused by electrostatic attraction augmented by hydrogen bonding, coordinate bonding or London van der Waals bonding is considered to be specific exchange adsorption. The distinction between specific and regular exchange adsorption is vague: these types of adsorption could be called 'high-selectivity' and 'low-selectivity' ion exchange, respectively. It is assumed that specific adsorption occurs on negatively charged surface groups, notably on the edges of clay minerals, and possibly associated with organic matter.

The specific adsorption of heavy metals was confined to Winsum soil, occurred at

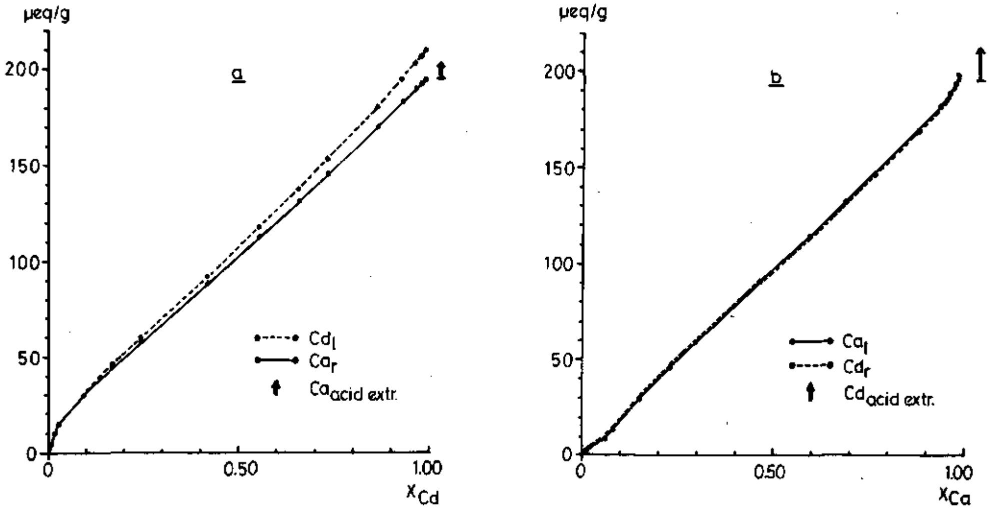


Fig. 68. Adsorption isotherms for Cd/Ca (a) and Ca/Cd exchange (b) on Winsum: loss of Cd and release of Ca (a), and loss of Ca and release of Cd (b) are indicated. Vertical arrows denote the amounts of acid-extractable Ca (a) and Cd (b).

low coverage of heavy metals, and the preference of the adsorption site for the cation decreased in the order

Pb > Cu > Zn > Cd > Ca

The cation-exchange capacity of the soil is denoted by Q (μeq/g), and the fraction of Q involved in specific adsorption is denoted by α, ranging from 0, in the absence of specific adsorption, to 1, when adsorption is all specific. The parameter α depends upon the type of cationic species involved in the adsorption process and on the pH of the system. The amount of a particular heavy metal that can be adsorbed specifically by 1 g of soil at a certain pH is given by αQ, whereas (1 - α)Q represents the 'regular' part of the cation-exchange capacity.

In Figs. 65-71 the cumulative amounts of metals lost from solution (M_l) and released by the solid phase (M_r^*) are plotted as a function of the equivalent fraction of the adsorbing ion in solution

$$X_M = M_o/(M_o + M_o^*) \tag{138}$$

Cation-exchange capacity of the soil could not easily be defined in a satisfactory way, through the apparent excess adsorption of heavy metals and the variable amount of heavy metals being specifically adsorbed, so M_l and M_r^* are not expressed as equivalent fractions in the adsorbed phase, but in amounts of substance (μeq) per g of soil. The data plotted in Figs. 65-71 represent mean values of duplicate determinations, which were equal to within 2%, except for Zn/Ca and Cd/Zn exchange on Winsum where they differed up to 4% and

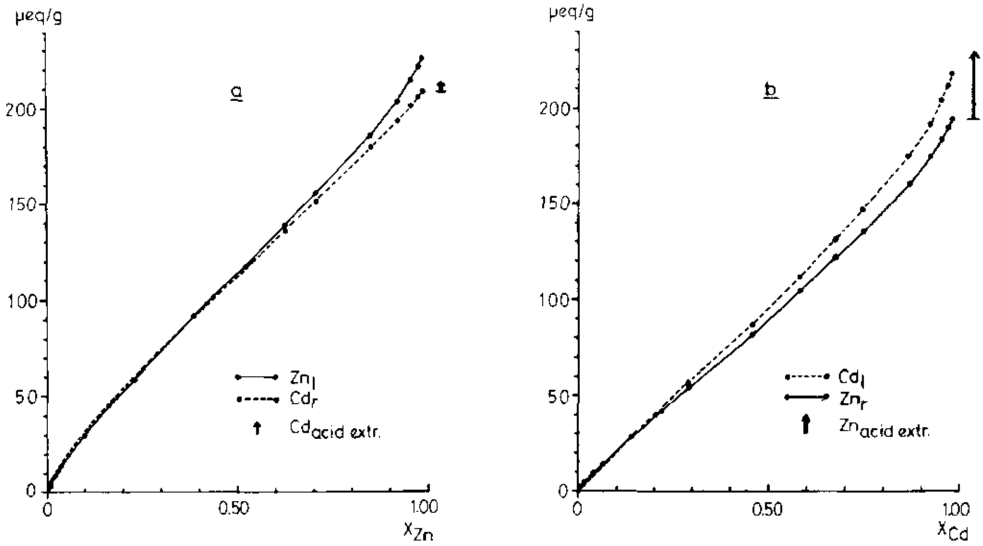


Fig. 69. Adsorption isotherms for Zn/Cd (a) and Cd/Zn exchange (b) on Winsum: loss of Zn and release of Cd (a), and loss of Cd and release of Zn (b) are indicated. Vertical arrows denote the amounts of acid-extractable Cd (a) and Zn (b).

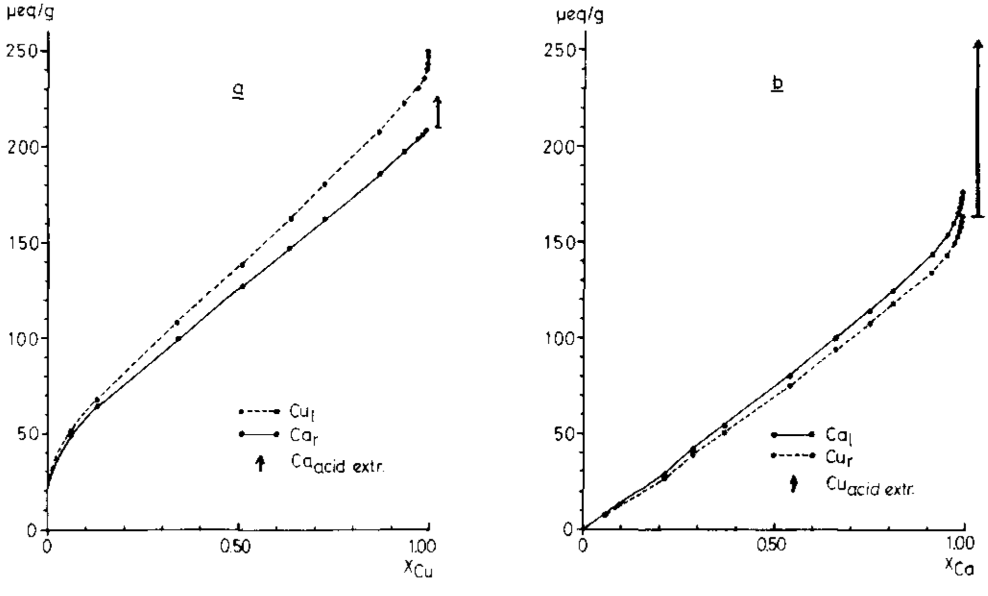


Fig. 70. Adsorption isotherms for Cu/Ca (a) and Ca/Cu exchange (b) on Winsum: loss of Cu and release of Ca (a), and loss of Ca and release of Cu (b) are indicated. Vertical arrows denote the amounts of acid-extractable Ca (a) and Cu (b).

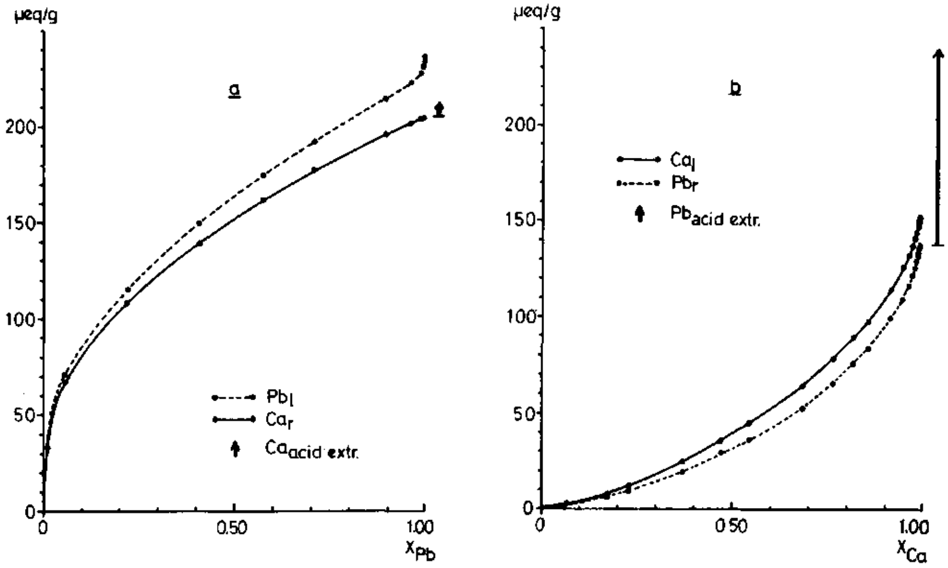


Fig. 71. Adsorption isotherms for Pb/Ca (a) and Ca/Pb exchange (b) on Winsum: loss of Pb and release of Ca (a), and loss of Ca and release of Pb (b) are indicated. Vertical arrows denote the amounts of acid-extractable Ca (a) and Pb (b).

Table 8. Cumulative amounts of cations lost from solution, released by the solid phase, and recovered upon treatment with acid. Type of exchange denoted by M/M*, where M is the metal being lost from solution and M* the metal released by the solid phase.

Soil	Exchange M/M*	M_l	M^*_r	$M^*_{ac.extr.}$	M^*_{total}
		(μeq/g)	(μeq/g)	(μeq/g)	(μeq/g)
Grundite	Zn/Ca	148.5	142.5	.[1]	
		148.1	144.0	.	
	Ca/Zn	154.6	148.8	4.5	153.3
		151.5	149.3	.	
Winsum	Zn/Ca	194.0	196.4	.	
		201.4	202.6	.	
	Ca/Zn	180.3	180.9	65.1	246.0
		177.3	181.5	.	
	Cd/Ca	201.74	188.43	7.42	195.85
		218.09	201.86	8.58	210.44
	Ca/Cd	199.26	195.27	17.89	213.16
		198.73	196.56	19.43	215.99
	Zn/Cd	226.59	208.64	4.69	213.33
		226.30	208.64	4.41	212.74
	Cd/Zn	222.19	194.45	35.22	229.67
		214.27	194.47	.	
	Cu/Ca	248.37	210.32	22.19	232.51
		251.73	210.04	22.56	232.60
	Ca/Cu	178.53	164.44	88.62	253.06
		175.67	163.64	93.07	256.71
	Pb/Ca	238.39	206.72	15.46	222.18
		235.89	204.88	15.43	220.31
	Ca/Pb	152.43	137.05	100.36	237.41
		152.46	139.59	100.98	240.57

[1] Not determined.

for Cd/Ca exchange on Winsum where they differed up to 8%.

The total amount of cations released by the soil consists of an amount desorbed through regular ion exchange and an amount desorbed upon treatment with dilute acid Table 8). The amount of acid-extractable metal represents the total amount of metal retained by the soil by mechanisms other than regular ion exchange,

$$M(\text{acid extr}) = M_{ex} + M_{as} \tag{139}$$

Table 8 shows that, except for Zn/Ca exchange on Winsum, the total amount of heavy metals lost from solution was very close to the sum of the amount of heavy metals released by regular exchange and the amount desorbed upon treatment with dilute acid. The presence of a small amount of acid-extractable Ca indicates that some Ca was present in precipitated or coprecipitated form in the soil, possibly as carbonates or phosphates, or possibly in specifically adsorbed form; there were no indications, however, that Ca was precipitated, coprecipitated or specifically adsorbed under the conditions of the experiments.

5.4 REGULAR ION EXCHANGE

The Zn/Ca and Ca/Zn exchange on Grundite shown in Fig 65 is reversible, and the selectivity coefficient for the exchange reaction is close to unity. The apparent excess adsorption of Zn in Fig. 65a is probably due to lack of equilibrium or to analytical error: the absence of an appreciable amount of acid-extractable Zn indicated that Zn was not specifically adsorbed by Grundite. The absence of specific interactions in Grundite may have been due to the absence of certain constituents such as organic compounds or manganese oxides, but was probably due also to the low pH of the Grundite soil: pH was 4-5 in Grundite as against 5-7 in Winsum. Grundite seemed very suitable for ion exchange studies through the virtual absence of specific interactions. But specific interactions seemed to be of more significance for the control of heavy metals in soil than non-specific ion exchange interactions, and therefore experiments were continued with Winsum alone.

The ion-exchange behaviour of Zn, Cd, Cu and Pb on Winsum is shown in Figs. 66-71. All adsorption isotherms, except for Ca/Zn and Ca/Cd exchange, show deviations between the 'loss' and 'release' curves. To investigate whether the apparent excess adsorption of heavy metals might be by adsorption of monovalent $hMCl^+$ complexes, zinc chlorides and nitrates were compared, but no differences were found (Fig. 67) and also longer equilibration times did not result in the disappearance of the apparent excess adsorption. An isotherm determined at constant ionic strength ($I = 0.0015$) showed the same behaviour as in Fig. 67. The Zn_l curve in Fig. 66 should probably lie slightly above the Ca_r curve, as in Fig. 67. The presence of acid-extractable Zn (Table 8; Fig. 66b) suggests that Zn would be subject to specific interactions, not reflected in Fig. 66a. This is confirmed by the Zn_l curves in Figs. 67 and 69a, and was also observed in the experiment performed at one ionic strength.

The amounts of heavy metals specifically adsorbed (Table 9) were obtained by extrapolating the straight part of the hM/Ca exchange isotherm towards the y axis, which

Table 9. Amounts of cations specifically adsorbed, αQ, non-specifically adsorbed, $(1-\alpha)Q$, and apparently adsorbed in excess, ΣM_{ex}, by Winsum soil, estimated from Table 8 and Figs. 65-71.

Cation	αQ (μeq/g)	$(1-\alpha)Q$ (μeq/g)	ΣM_{ex} (μeq/g)
Cd^{2+}	15	185	15
Zn^{2+}	20	180	30
Cu^{2+}	45	160	40
Pb^{2+}	60	145	35

yields a reasonable estimate, if the selectivity coefficient for the specific adsorption reaction is sufficiently high. Values for Pb were obtained in essentially the same way, by extrapolating the 'regular' part of the adsorption isotherm to the y axis (cf. Figs. 74-75). The excess amounts adsorbed were estimated from the difference between hM_1 and Ca_r^* at 100% coverage and from the amounts of acid extractable heavy metals given in Table 8. Although αQ and $(1 - \alpha)Q$ differed considerably for different species, Q was almost constant, ranging from 200-205 μeq/g (Table 9). Hence some of the adsorption sites were selective for Cu and Pb but not for Zn or Cd.

The calcium ion is considered to be an indicator for non-specific adsorption in Ca/hM exchange, and for ion exchange in hM/Ca exchange. Therefore, the apparent excess adsorption of Ca in Figs. 70b and 71b is assumed to be by loss from solution of Cu and Pb upon desorption rather than by loss of Ca from solution. For Zn/Cd and Cd/Zn exchange the Cd_1 (Fig. 69a) and Zn_r (Fig. 69b) curves are considered to be representative for non-selective exchange behaviour, since there were no indications that Zn (compare Fig. 66b) or Cd (compare Fig. 68b) were lost from solution upon desorption.

Figures 65-71 show that the values of the selectivity coefficients for the non-specific ion exchange reactions involving Ca, Zn, Cd and Cu ions were close to unity, whereas for Pb/Ca and Ca/Pb exchange, they were about 2 and 1/3, respectively (Figs. 74 and 75). The selectivity coefficient describing the non-specific exchange adsorption of M onto a soil initially saturated with M^* will be denoted by K^{ar}_{M/M^*}, whereas for specific exchange adsorption the selectivity coefficient will be denoted by K^{as}_{M/M^*}. The value of K^{ar} for the hM/Ca exchange reaction can be estimated from

$$\log (hM/Ca)_{ar} = \log K^{ar}_{hM/Ca} + \log \{X_{hM}/(1 - X_{hM})\} \tag{140}$$

where $(hM/Ca)_o$ has been replaced by the ratio of the equivalent fractions in solution. Assuming that the amount of Ca released represents the amount of hM exchangeably adsorbed, and considering that the amount of hM specifically adsorbed should be subtracted from Ca_r and Q, it follows that

$$(hM/Ca)_{ar} = (Ca_r - \alpha Q)/(Q - Ca_r) \tag{141}$$

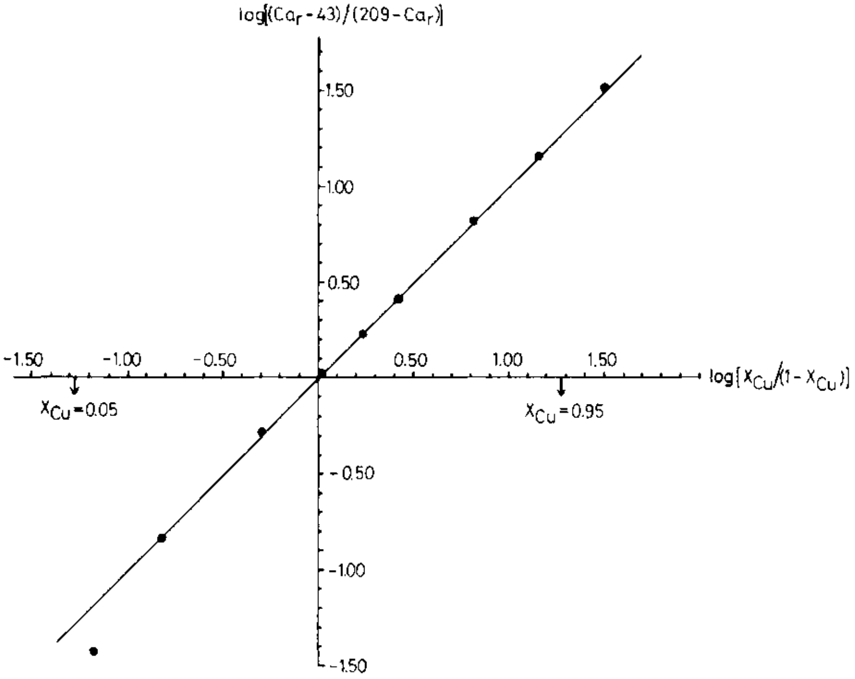


Fig. 72. Cu/Ca exchange on Winsum: log-log plot of $(Cu/Ca)_{ar}$ against $(Cu/Ca)_o$ (Eqs. 140-141).

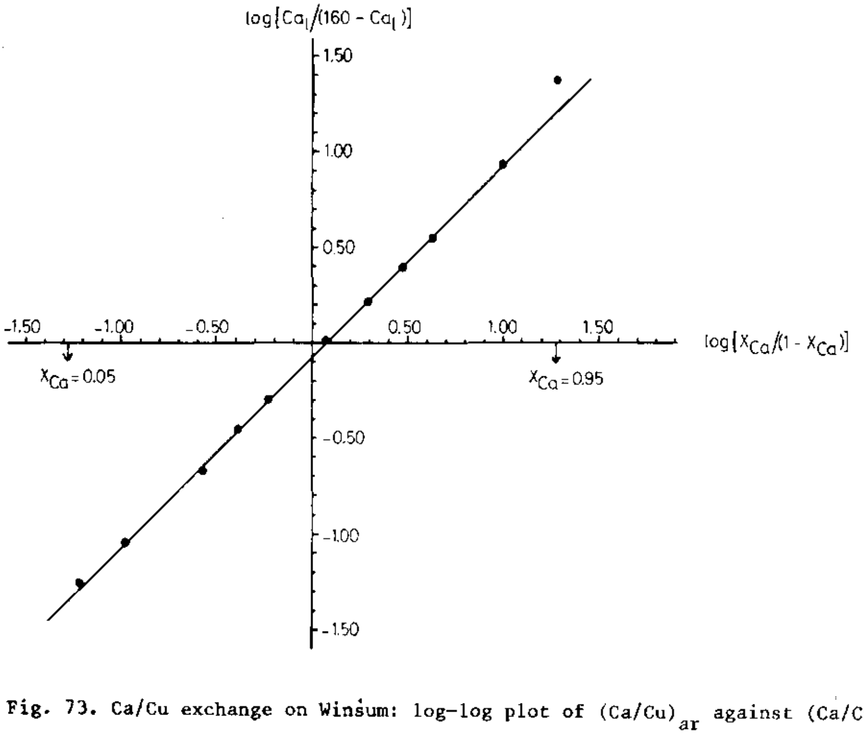


Fig. 73. Ca/Cu exchange on Winsum: log-log plot of $(Ca/Cu)_{ar}$ against $(Ca/Cu)_o$ (Eq. 142).

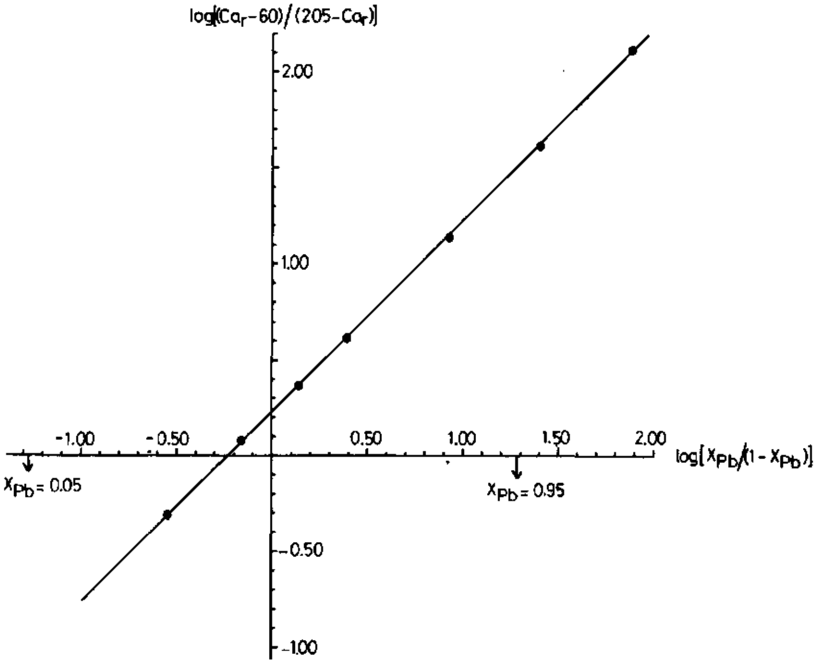


Fig. 74. Pb/Ca exchange on Winsum: log-log plot of $(Pb/Ca)_{ar}$ against $(Pb/Ca)_o$ (Eqs. 140-141).

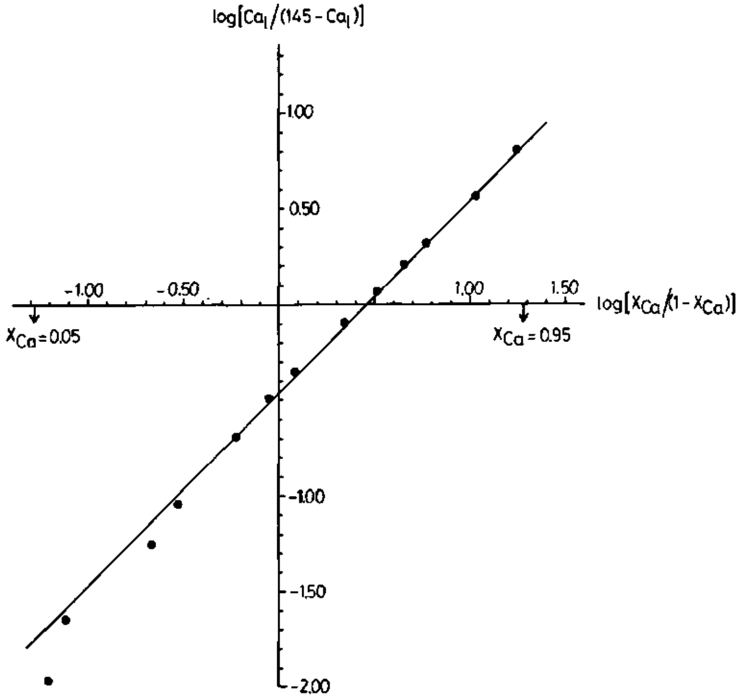


Fig. 75. Ca/Pb exchange on Winsum: log-log plot of $(Ca/Pb)_{ar}$ against $(Ca/Pb)_o$ (Eq. 142).

In this way $K^{ar}_{Cu/Ca}$ (Fig. 72) and $K^{ar}_{Pb/Ca}$ (Fig. 74) were estimated to be 1.00 and 1.73, respectively, and αQ and $(1 - \alpha)Q$ 43 and 166 µeq/g for Cu, and 60 and 145 µeq/g for Pb. For Cu/Ca exchange a value of 43 µeq/g for Cu specifically adsorbed was also obtained by extrapolation of the regular (straight) part of the Ca_r curve in Fig. 70a towards the y axis, but for Pb/Ca exchange the selectivity coefficient for regular exchange had to be estimated from a log-log plot, before αQ could be estimated from Fig. 71a. For Ca/hM exchange K^{ar} can be estimated from

$$\log [Ca_1/\{(1 - \alpha)Q - Ca_1\}] = \log K^{ar}_{Ca/hM} + \log \{X_{Ca}/(1 - X_{Ca})\} \tag{142}$$

In this way $K^{ar}_{Ca/Cu}$ (Fig. 73) and $K^{ar}_{Ca/Pb}$ (Fig. 75) were estimated to be 0.83 and 0.35, respectively, and $(1 - \alpha)Q$ 160 µeq/g for Ca/Cu and 145 µeq/g for Ca/Pb exchange. These selectivity coefficients show that Cu and Pb were subject to adsorption-desorption hysteresis

$$K^{ar}_{Cu/Ca}K^{ar}_{Ca/Cu} = 0.83$$

and

$$K^{ar}_{Pb/Ca}K^{ar}_{Ca/Pb} = 0.61$$

whereas in the absence of hysteresis these products would equal unity. This hysteresis could be caused by rearrangement and reorientation of the metals in the adsorbed phase: when the metals would be able to approach the adsorption site (centre of negative charge)

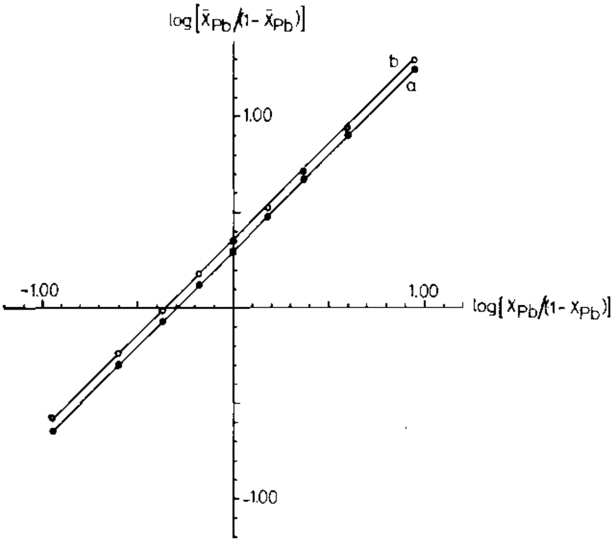


Fig. 76. Hypothetical Pb/Ca exchange on a soil: log-log plot of $\bar{X}_{Pb}/1-\bar{X}_{Pb}$ against $X_{Pb}/1-X_{Pb}$, for (a) $K^{ar}_{Pb/Ca} = 2$ for all sites, and (b) $K^{ar}_{Pb/Ca} = 2$ for 85% and 5 for 15% of the adsorption sites.

Table 10. Crystal ionic radii (Weast, 1972), entropies of hydration, S^o_{hydr} (Garrels & Christ, 1965), enthalpies of hydration, ΔH^o_{hydr} (Cotton & Wilkinson, 1972), and equivalent conductances, λ^0 (Gast & Gast, 1960), of some ionic species.

Cation	Radius (Å)	S^o_{hydr} (cal/deg.mol)	ΔH^o_{hydr} (kcal/mol)	λ^0 ($\Omega^{-1}cm^2/eq$)
Cu^{2+}	0.72	-23.6	-502	54.3
Zn^{2+}	0.74	-25.5	-489	53.8
Cd^{2+}	0.97	-14.6	-432	53.9
Ca^{2+}	0.99	-13.2	-377	59.6
Pb^{2+}	1.20	5.1	-354	71.3

closer, this would result in an increase in coulombic attraction and possibly an energy gain by ion induced-dipole or ion multipole interactions. The hysteresis may be caused by a fraction of the adsorbed metals only. When, for example, $K^{ar}_{Pb/Ca}$ equals 2 and when 15% of adsorbed Pb rearranges into a more favourable energy state such that K^{ar} for these rearranged ions becomes 5, then the mean value of $K^{ar}_{Pb/Ca}$ for all ions becomes 2.26 (Fig. 76). The selectivity coefficient for Pb/Ca exchange being larger than unity may be explained by entropies and energies of hydration, and equivalent conductances of the different metal ions. Table 10 shows that Pb^{2+}, which has the largest ionic radius, has the highest entropy and enthalpy of hydration (smallest absolute values), and also the highest equivalent conductance. The larger the absolute values of the entropy and energy of hydration, and the smaller the equivalent conductance, the larger the hydrated radius of the ion. The hydrated ionic radius of Pb is thus presumably smaller than of the other ions, albeit the ionic radius of Pb is larger. Hydrated radii of ions only influence the exchange behaviour, if adsorption occurs in a Stern layer to a significant extent. Lack of differences in selectivity between Ca and Cd on the one hand and Cu and Zn on the other suggests that above a certain 'threshold' hydration, divalent cations behave alike. But also another property of Pb, such as the polarizability could be responsible for the higher selectivity.

5.5 FREUNDLICH BEHAVIOUR

The hM/Ca adsorption isotherms on Winsum soil (Figs. 66a, 67, 68a, 70a and 71a) all show, at low hM coverage of the adsorption complex, Freundlich behaviour: the apparent selectivity coefficient for the hM/Ca exchange reaction decreases with increasing hM coverage. As an illustration of this behaviour, a set of Zn/Ca adsorption data on Winsum soil at constant ionic strength (I = 0.0015) is plotted in Fig. 77, for low Zn coverage of the adsorption complex. When these data are plotted log-log, they fit a straight line up to about 10% coverage of the adsorption complex. When the logarithm of the amount of Zn lost from solution divided by the total amount of Zn lost from solution at saturation (240 µeq/g) is plotted as a function of log Zn_o, a Freundlich isotherm of the form

$$Zn_1/240 = 15.4\ (Zn_o)^{0.47}$$

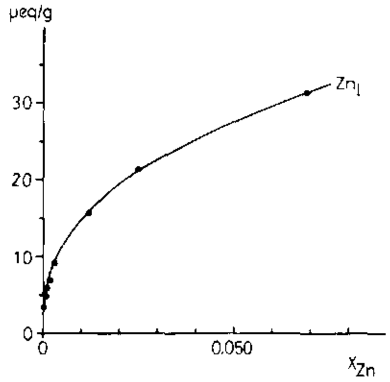


Fig. 77. Zn/Ca exchange on Winsum at constant ionic strength (0.0015): loss of Zn from solution in the trace region ($X_{Zn} < 0.10$).

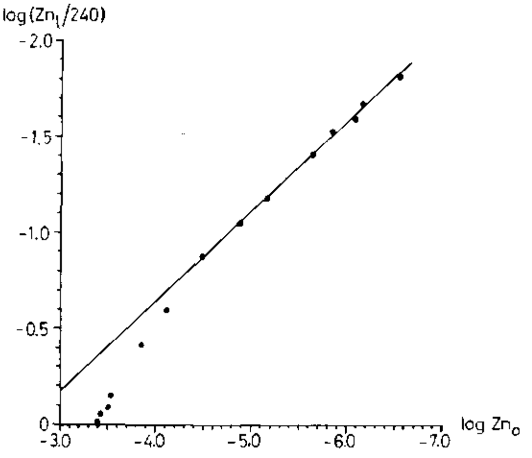


Fig. 78. Zn/Ca exchange on Winsum at constant ionic strength (0.0015): log-log plot of $Zn_1/\Sigma Zn_1$ against Zn_o (Freundlich plot), where ΣZn_1 denotes the amount of Zn lost from solution at saturation (240 μeq/g).

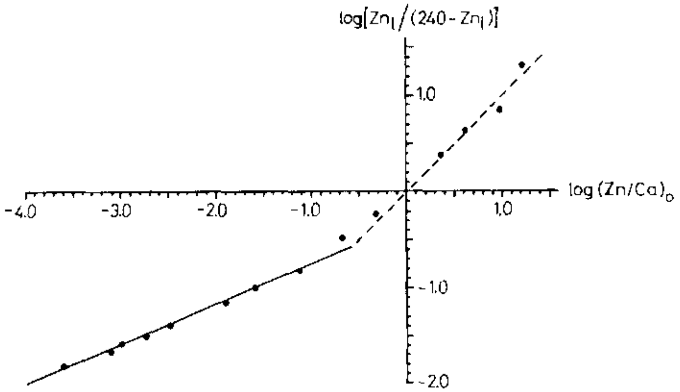


Fig. 79. Zn/Ca exchange on Winsum at constant ionic strength (0.0015): log-log plot of $Zn_1/(\Sigma Zn_1 - Zn_1)$ against $(Zn/Ca)_o$ (Rothmund-Kornfeld plot), where ΣZn_1 denotes the amount of Zn lost from solution at saturation (240 μeq/g).

is obtained (Fig. 78). A plot of log Zn_o/Ca_o against log $\{Zn_1/(240 - Zn_1)\}$ yields a Rothmund-Kornfeld isotherm of the form (Fig. 79)

$$Zn_1/(240 - Zn_1) = 0.45(Zn/Ca)_o^{0.42}$$

The experimental points fit the Freundlich and Rothmund-Kornfeld isotherms almost equally well, because of the small changes for Ca in the composition of the adsorption complex and the solution. In the Rothmund-Kornfeld plot the experimental points at Zn coverage above 10% approach the broken line in Fig. 79, representing an ion exchange reaction with $K_{sel} = 1$. In this respect a Rothmund-Kornfeld plot is superior to Freundlich plot: the transition from specific exchange adsorption to regular ion exchange is recognizable as a conformation of the experimental data to a straight line with a slope of unity, and the logarithm of the selectivity coefficient of the regular exchange reaction is obtained as the intercept of this straight line with the y axis. At low coverage by the ion of interest, the Freundlich isotherm is more universally applicable than the Rothmund-Kornfeld isotherm, since only the concentration of the adsorbing cation and the loss from solution have to be known.

The simplest way to explain Freundlich behaviour is to describe the adsorption of heavy metals on Winsum in terms of a two-site model (Section 4.6). Since other specific interactions reduce phenomenologically to the two-site model, the representation of experimental data by a Freundlich or a Rothmund-Kornfeld plot does not yield information about the nature of the specific interactions responsible for the specific behaviour. Therefore the values of the constants and exponents are difficult to interpret, although they do provide an empirical basis for comparison of the different heavy metals.

5.6 BEHAVIOUR OF pH

The behaviour of pH in Fig. 80 shows the influence of the salt concentration ('salt effect'): at high salt concentrations H^+ is released and pH is low (pH = 3.6 at 10^{-1} N salt) whereas at lower salt concentrations less H^+ is released and pH is higher (pH = 4.6 - 4.7 at 10^{-4} N salt). Since pH of the $ZnCl_2$ solutions tended to be slightly lower than of the $CaCl_2$ solutions, it may be concluded from Fig. 80 that the behaviour of pH upon Zn/Ca and Ca/Zn exchange was the same within experimental error.

In the supernatant solutions of the Winsum samples pH decreased upon Zn/Ca exchange, but remained, after an initial increase, almost constant upon Ca/Zn exchange; this be-

Fig. 80.

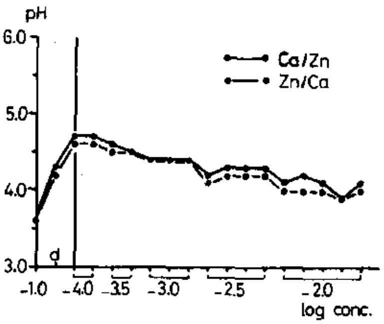
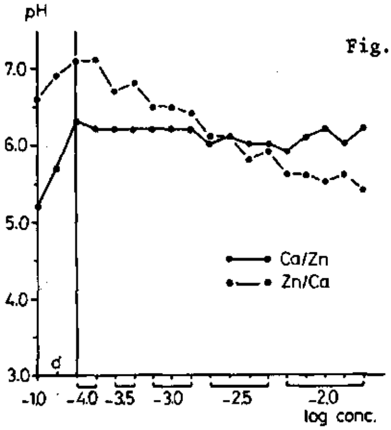


Fig. 81.



Figs. 80-81. Zn/Ca and Ca/Zn exchange on Grundite (Fig. 80) and Winsum (Fig. 81): behaviour of pH as a function of the concentration of the solution added (eq/l); 'd' denotes demineralized water. The vertical line separates the stage of covering the soil with the inital cation (left) from the stepwise coverage of the homoionic soil with the cation to be studied (right).

haviour could not be accounted for by the salt effect. Since the first hydrolysis constant of Zn^{2+} is larger ($\log {}^*K_1 = -9.1$) than of Ca^{2+} ($\log {}^*K_1 = -12.8$), the relation of hydrolysis of Zn^{2+} with the observed pH behaviour was tested. The amount of H^+ taken up by the soil from solution upon Zn/Ca adsorption was estimated from the initial pH of slightly acidified $ZnCl_2$ solutions added to the soil (pH_i) and the final pH of supernatant solutions after equilibrium was established (pH_f), and from the Zn activities in both solutions, where activity coefficients for Zn^{2+} were estimated from Kielland (1937); $ZnOH^+$ activities were estimated from the relation

$$\log ZnOH^+ = (9.1 - \log Zn^{2+}) - pH \qquad (143)$$

The amount of H^+ taken up by 2.00 g of soil from 35 ml of solution per equilibration cycle then equals (in µeq H^+/g soil):

$$\{(10^{-pH_i} - 10^{-pH_f}) + (10^{\log ZnOH_f} - 10^{\log ZnOH_i})\}\ 1.75 \times 10^4 \qquad (144)$$

where it is assumed that $ZnOH^+$ is not adsorbed. The cumulative amount of H^+ taken up during 17 successive equilibrations was thus estimated to be 1.5 µeq/g, which is negligible compared to an acid-neutralizing capacity of about 30 µeq H^+/g of soil per unit pH. Moreover, the cumulative amount of H^+ taken up from solution upon Ca/Zn exchange was estimated to be of the same order, about 1.0 µeq/g, and for Ca/Zn exchange no decrease in pH was observed at all, neither due to the salt effect, nor to uptake of H^+ from solution. Therefore, the pronounced lowering (about 1.65) of the pH upon Zn/Ca exchange cannot be by the salt effect and uptake of H^+ from solution alone: an additional mechanism, involving Zn ions, has to be introduced to account for the observed behaviour of the pH.

To test whether the addition of small amounts of Zn to suspensions of Winsum soil would indeed lower the pH of the solutions, 2.5-ml aliquots of $Zn(NO_3)_2$ 0.10 N were added with an automatic burette at a rate of 0.036 ml/min to rotating suspensions of 5 g of untreated Winsum soil and 100-ml $Ca(NO_3)_2$ solutions of increasing concentrations: 0.001 N ($pH_i = 7.30$, $pH_f = 6.36$), 0.010 N ($pH_i = 6.81$, $pH_f = 6.14$), and 0.100 N ($pH_i = 6.45$, $pH_f = 5.94$), where initial and final pH of the suspensions are given in parenthesis; the pH of the rotating suspensions equalled the pH of the supernatant solutions to within 0.05. The decrease in pH is plotted for the different suspensions in Fig. 82 as a function of the amount of $Zn(NO_3)_2$ added per g of soil. The amount of H^+ in solution increased almost linear with the amount of Zn^{2+} added, whereas the total amount of H^+ released was greatest in the suspension with the lowest Ca concentration and the highest initial pH.

The behaviour of pH upon Cd/Zn and Zn/Cd exchange on Winsum soil is shown in Fig. 83. In both systems pH followed similar courses and was probably determined by the salt effect, although specific interactions involving Zn, Cd or H could also contribute to the observed behaviour. Figures 84, 85 and 86 all show essentially the same picture: upon hM/Ca exchange pH decreased, about 1.5 to 2.0 whereas upon Ca/hM exchange pH remained fairly constant, between 6.0 and 6.5 for Cd, and between 5 and 6 for Cu and Pb. These data suggest that specific interactions involving heavy metals and H were, at least partly,

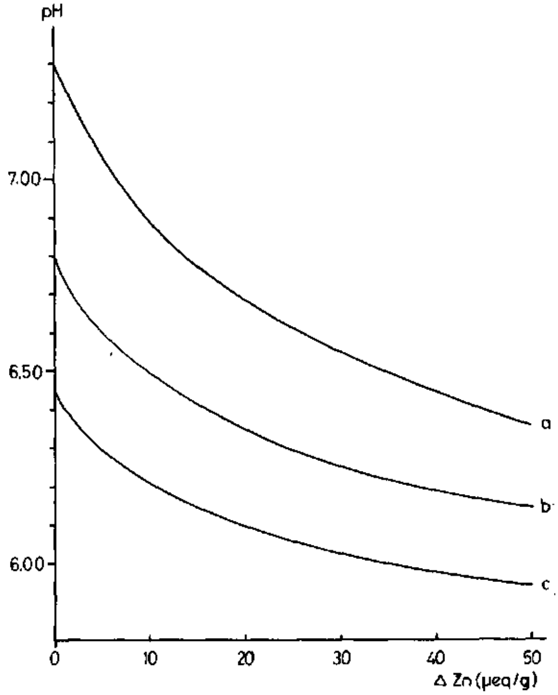


Fig. 82. Behaviour of pH upon addition of Zn to suspensions of Winsum soil in (a) 0.001 N, (b) 0.010 N, and (c) 0.100 N $Ca(NO_3)_2$ solutions.

Fig. 83.

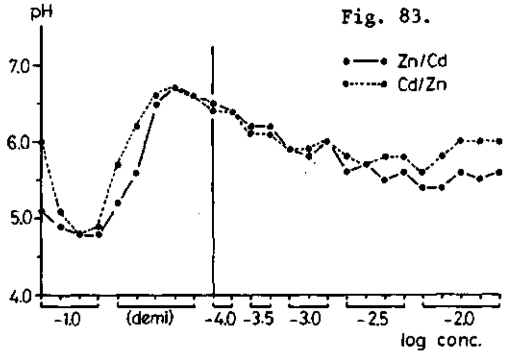
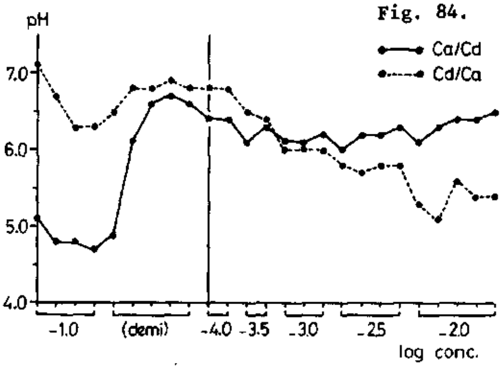


Fig. 84.



Figs. 83-84. Zn/Cd and Cd/Zn (Fig. 83) and Cd/Ca and Ca/Cd (Fig. 84) exchange on Winsum: behaviour of pH as a function of the concentration of the solution added (eq/l); 'demi' denotes demineralized water. The vertical line separates the stage of covering the soil with the inital cation (left) from the stepwise coverage of the homoionic soil with the cation to be studied (right).

responsible for the behaviour of pH in the supernatants.

To investigate whether pH of the supernatant solutions was influenced indeed by specific interactions involving H and heavy metals, relationship between pH and logarithm of activities of aqueous metals was tested. When a solution is in equilibrium with hydroxides, carbonates, or silicates, a relation of the form

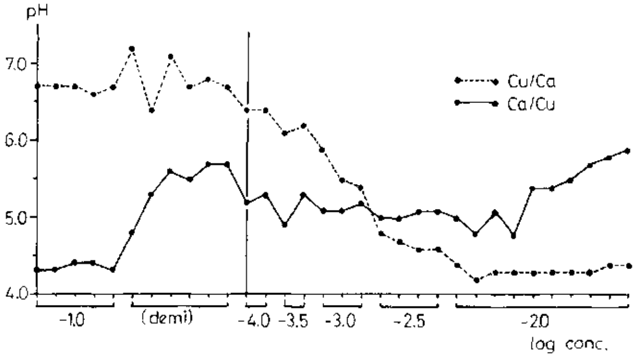


Fig. 85. Cu/Ca and Ca/Cu exchange on Winsum: behaviour of pH as a function of the concentration of the solution added (eq/l); 'demi' denotes demineralized water. The vertical line separates the stage of covering the soil with the initial cation (left) from the stepwise coverage of the homoionic soil with the cation to be studied (right).

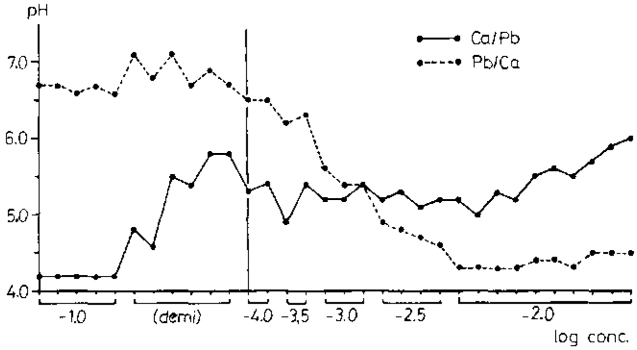


Fig. 86. Pb/Ca and Ca/Pb exchange on Winsum: behaviour of pH as a function of the concentration of the solution added (eq/l); 'demi' denotes demineralized water. The vertical line separates the stage of covering the soil with the inital cation (left) from the stepwise coverage of the homoionic soil with the cation to be studied (right).

$$2\ \mathrm{pH} + \log \mathrm{hM} = K \qquad (145)$$

where K is a constant, should hold, but also specific adsorption of heavy metals or first hydrolysis products of heavy metals, may result in a relationship between log hM and pH (Section 4.7.4). In Figs. 87-91 the relationship 2 pH + log M is plotted for all metals for all adsorption experiments on Winsum soil. The data are plotted for each equilibration cycle, the concentrations (eq/l) of the solutions added being indicated on the x axis, to establish a possible correlation with the salt concentrations. Activity coefficients for aqueous activities of metal ions were estimated from Kielland (1937). For hM/Ca exchange (Figs. 87a, 89a, 90a and 91a) 2 pH + log Ca decreased over the whole range, with increasing hM coverage, whereas 2 pH + log hM remained, after an initial increase, almost constant. For Ca/hM exchange (Figs. 87b, 89b, 90b and 91b) 2 pH + log Ca increased with increasing Ca coverage, whereas 2 pH + log hM remained almost constant over the whole

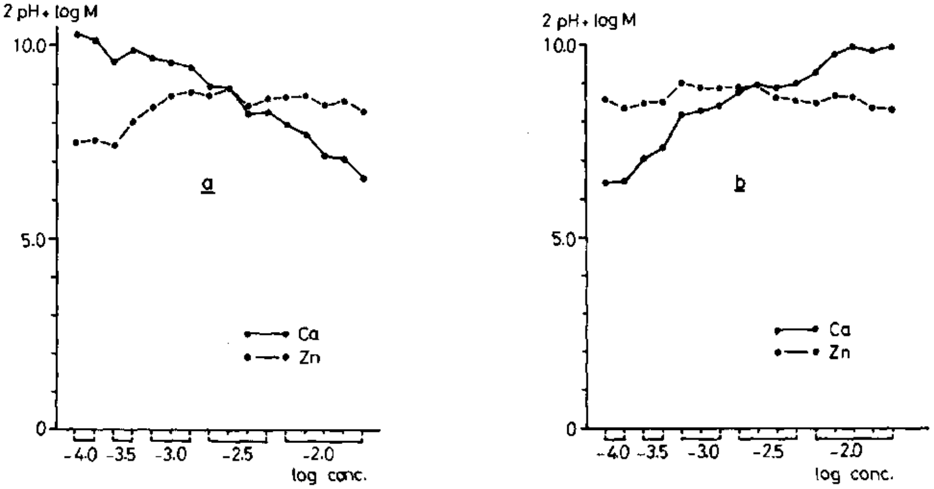


Fig. 87. Zn/Ca (a) and Ca/Zn exchange (b) on Winsum: 2 pH + log M plotted for Zn and Ca with increasing concentration (eq/l) of Zn (a) and Ca (b) of the solutions added.

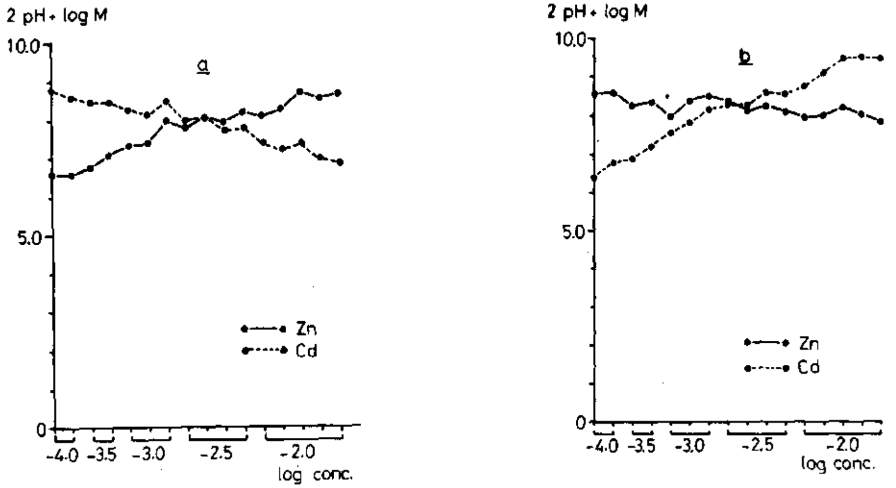


Fig. 88. Zn/Cd (a) and Cd/Zn exchange (b) on Winsum: 2 pH + log M plotted for Zn and Cd with increasing concentration (eq/l) of Zn (a) and Cd (b) of the solutions added.

range of coverage. Upon Zn adsorption on Cd soil (Fig. 88a) none of the relationships was constant, but upon Cd/Zn exchange (Fig. 88b) 2 pH + log Zn was almost constant: the behaviour of 2 pH + log Cd (Fig. 88b) was similar to the behaviour of 2 pH + log Ca (Fig. 87b).

From Eq. 145 it follows that

$$\mathrm{pH} + \log \mathrm{hM} = K - \mathrm{pH} \qquad (146)$$

increases with decreasing pH, as for hM/Ca exchange on Winsum. Hence the aqueous activi-

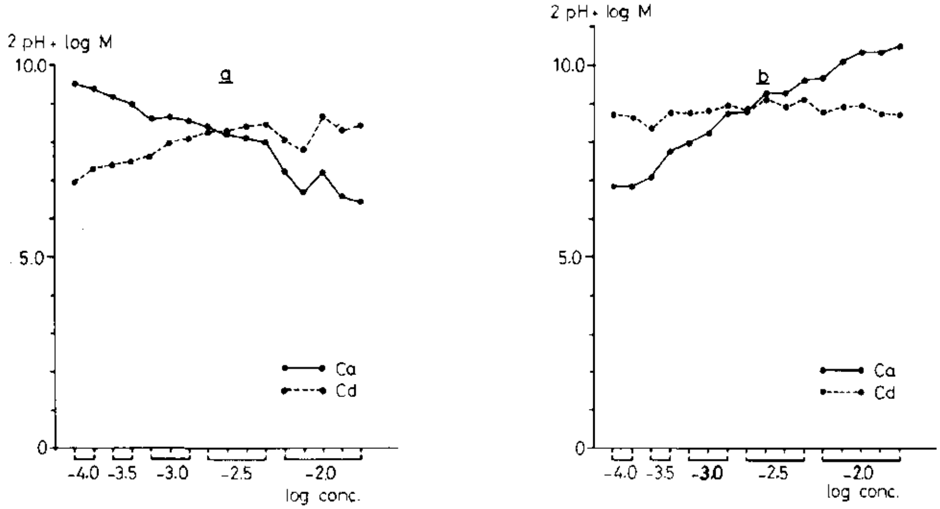


Fig. 89. Cd/Ca (a) and Ca/Cd exchange (b) on Winsum: 2 pH + log M plotted for Cd and Ca with increasing concentration (eq/l) of Cd (a) and Ca (b) of the solutions added.

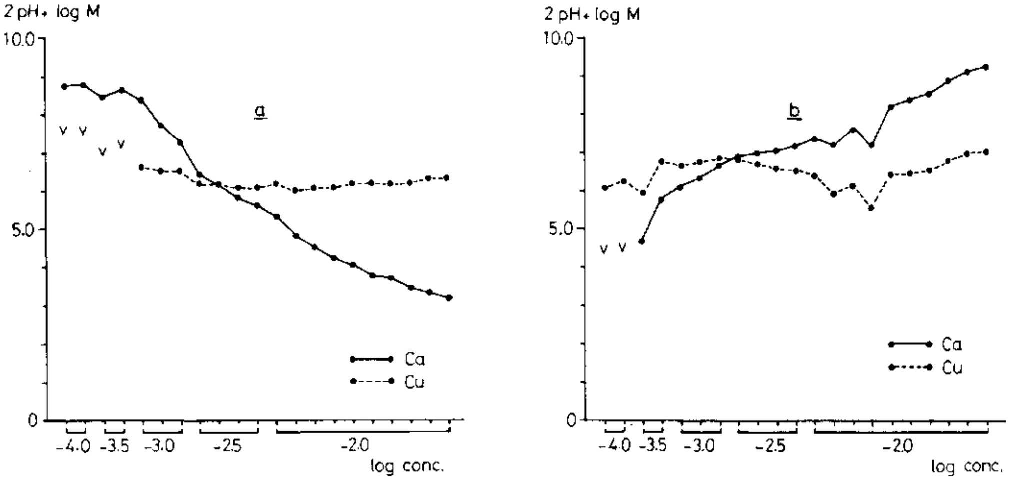


Fig. 90. Cu/Ca (a) and Ca/Cu exchange (b) on Winsum: 2 pH + log M plotted for Cu and Ca with increasing concentration (eq/l) of Cd (a) and Ca (b) of the solutions added. The symbol 'v' denotes that Cu (a) or Ca (b) were not present in detectable amounts.

ties of the first hydrolysis products of the heavy metals, $hMOH^+$, would also increase with decreasing pH, because

$$\log hMOH = \log {}^*K_1 + pH + \log hM \qquad (147)$$

where ${}^*K_1$ is the first hydrolysis constant. Figure 92 shows that the activities of the first hydrolysis products of all metals increased with increasing equivalent fraction of heavy metals in solution, indicating that specific adsorption of first hydrolysis pro-

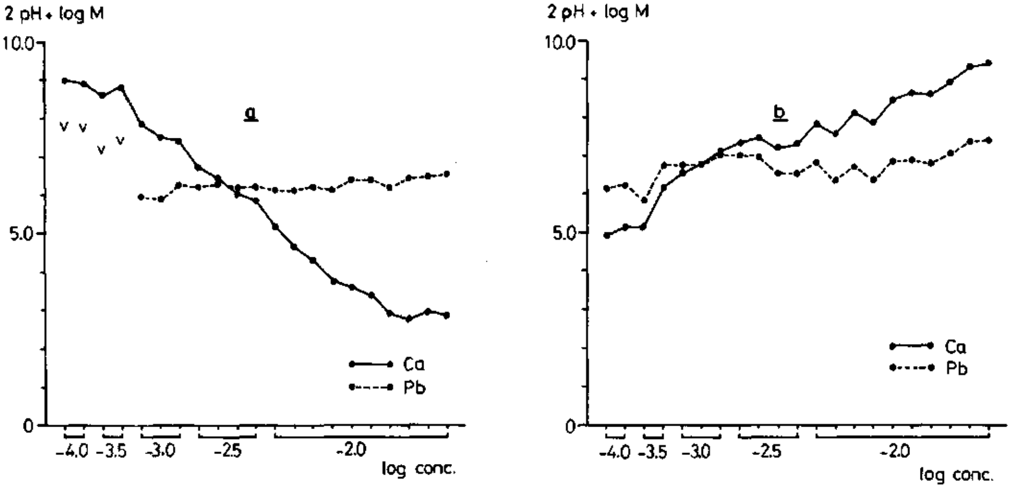


Fig. 91. Pb/Ca (a) and Ca/Pb exchange (b) on Winsum: 2 pH + log M plotted for Pb and Ca with increasing concentration (eq/l) of Pb (a) and Ca (b) of the solutions added. The symbol 'v' denotes that Pb was not present in detectable amounts.

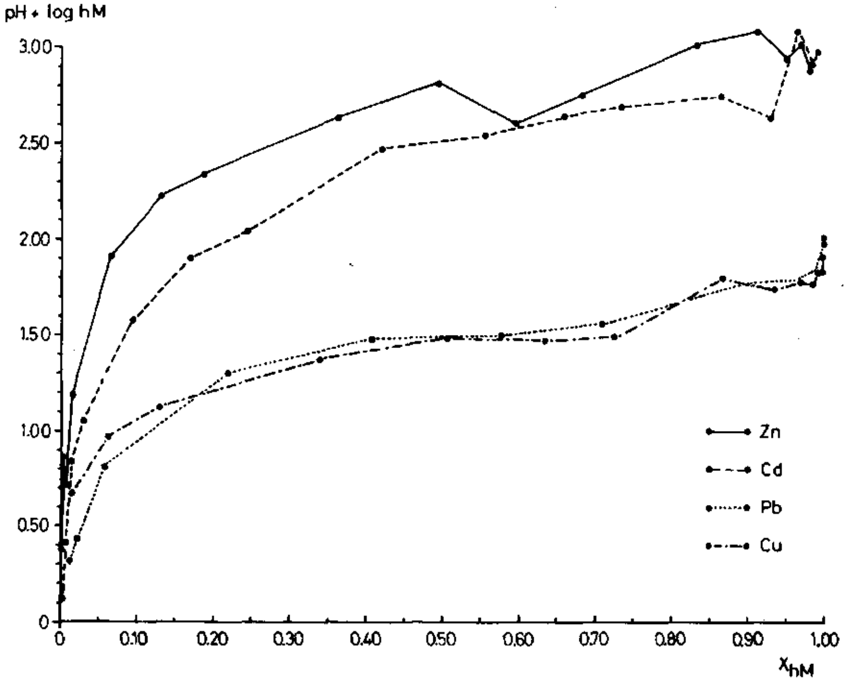


Fig. 92. hM/Ca exchange on Winsum: pH + log hM plotted for Zn, Cd, Cu and Pb with increasing X_{hM}.

ducts would be possible, even though pH decreased sharply with increasing X_{hM}. Figure 92 shows too that Zn and Cd on the one hand, and Cu and Pb on the other behaved quite like.

5.7 PRECIPITATION OF HEAVY METALS

Almost all precipitates of heavy metals, likely to occur in soils, have a bearing on pH of the soil solution: hydroxides (Eq. 148), carbonates (Eq. 149), and silicates (Eq. 150), all result in Eq. 145 to hold under equilibrium conditions, if the soil solution is in equilibrium with atmospheric $CO_2(g)$, for carbonates, and with $SiO_2(s)$, for silicates.

$$hM^{2+} + 2H_2O \rightleftarrows hM(OH)_2 + 2H^+ \tag{148}$$

$$hM^{2+} + H_2O + CO_2(g) \rightleftarrows hMCO_3 + 2H^+ \tag{149}$$

$$hM^{2+} + H_2O + SiO_2(s) \rightleftarrows hMSiO_3 + 2H^+ \tag{150}$$

The precipitation of phosphates also affects pH, but the relationship between pH and log hM is more complicated for phosphates.

The constants in the relation

$$2\ pH + \log M = K \tag{151}$$

may be estimated from the data listed in Table 11 and

$$2\ pH + \log M = \log K_{s0} + 28.0$$

for hydroxides, and

Table 11. First hydrolysis constants, $^*K_1$, and solubility products, K_{s0}, for hydroxides, carbonates and phosphates of some elements, estimated from Sillén & Martell (1964, 1971). All values refer to room temperature, atmospheric pressure and zero ionic strength.

Element	Hydrolysis	Hydroxide		Carbonate		Phosphate
	$\log {}^*K_1$	$\log K_{s0}$	2 pH + log M	$\log K_{s0}$	2 pH + log M	$\log K_{s0}$
Ca	-12.7	- 5.2	22.8	- 8.3	13.4	-28.7
Mg	-11.7	-10.8	17.2	- 7.5	14.2	-27.2
Cd	- 9.4	-14.0	14.0	-11.2	10.5	-32.6
Zn	- 9.1	-15.4	12.6	-10.8[1]	10.9	-32.0
Cu	- 7.4	-18.8	9.2	- 9.6[2]	12.1	-36.9
Pb	- 7.8	-18.2	9.8	-13.0	8.7	-42.0

1. $\log K_{s0} = -9.8$; 2 pH + log Zn = 11.9 (Crocket & Winchester, 1966).
2. $Cu_2(OH)_2CO_3$ (malachite) $\log K_{s0} = -33.8$; 2 pH + log Cu = 8.0 and $Cu_3(OH)_2(CO_3)_2$ (azurite) $\log K_{s0} = -46.0$; 2 pH + log Cu = 8.5.

$$2\ \mathrm{pH} + \log M = \log K_{s0} + 21.7$$

for carbonates, where it is assumed that

$$2\ \mathrm{pH} - \log CO_3^{2-} = 21.7$$

Since

$$2\ \mathrm{pH} + \log M = \log K_{s0} + K \tag{152}$$

a solution is undersaturated with respect to the salt in question when

$$2\ \mathrm{pH} + \log M < \log K_{s0} + K \tag{153}$$

Figures 87 and 89-91 show that the relation 2 pH + log M varied between 8 and 9 for Cd and Zn, and between 6 and 7 for Cu and Pb, which is 2 - 3 less than in Table 11, based on equilibrium with carbonates or hydroxides, so the soil suspensions were undersaturated with respect to these salts. Much uncertainty exists about solubility constants in soil systems: solid phases may be present in different forms, ranging from amorphous to well crystallized, they may be hydrated or not, they may contain impurities through coprecipitation, occlusion of adsorbed species, solid state diffusion or solid solution formation, and they may be coated with oxides of Si, Fe, Al or Mn. Therefore care has to be taken in applying data obtained from well-defined and pure systems to soil suspensions and the data compiled in Table 11 are to be seen as approximative only. Nevertheless, it is unlikely that hydroxides or carbonates would precipitate from undersaturated solutions, even in soil systems. Electroneutrality requires that Eq. 151 also holds for mixed salts with the general formula

$$M(CO_3)_{x/2}(OH)_{2-x}$$

where x varies between 0 and 2. Of course, x may vary as the reaction proceeds, and this would result in a variation of the constant in Eq. 151, but one would not expect that the constant of a mixed hydroxide carbonate would drop below the lowest value for either the hydroxide or the carbonate. Only for Cu is the value lower for the mixed salts malachite (8.0) and azurite (8.5) than for the hydroxide (9.2), but it is unlikely that such stable salts would be formed within the short time of the experiments. For carbonates the question must be posed whether equilibrium exists with atmospheric CO_2: the partial pressures of CO_2 were not measured directly, but Winsum samples equilibrated several days with demineralized water yielded a value of about 11.1 for log Ca + 2 pH, whereas addition of small amounts of $CaCO_3$ to the soil suspensions raised values to 12.8 - 13.4, close to those expected on the basis of the solubility product of $CaCO_3$ in equilibrium with atmospheric CO_2 (Table 11). Although carbonates were present in the soil in small amounts (0.3%, as calcite) they appear of no influence on pH of the suspensions. Possibly carbonates in Winsum (probably calcite or dolomite) were coated with more insoluble compounds such as silica.

Aqueous concentrations of total phosphates were measured separately in a number of Winsum suspensions and found to range from 0.2 to 0.4 μmol/l. The presence of Zn had no influence; there even seemed to be a slight tendency to increase with increasing Zn concentrations, possibly by a lowering of the pH. Upon treatment with dilute acid the aqueous phosphate concentration did increase, but less than would be expected from simple calcium phosphates: there appeared to be no correlation at all between Ca and P-total. Samples of Winsum soil that were equilibrated for 6 days with demineralized water yielded the following results: pH = 7.30, log (P-total) = 6.51, and log Ca = 3.74, where log (P-total) represents a concentration and log Ca an activity (activity coefficient 0.90). From these data the log (PO_4^{3-}) concentration was estimated to be -11.80 and the log solubility constant for the simple phosphate, $Ca_3(PO_4)_2$, was estimated to be -34.8, which is far below the value given in Table 11. The log solubility constant for hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, was estimated to be -121.6, which is close to the range of values given by Wier et al. (1971): -116.4 to 120.5. The soil suspensions were not analysed for fluoride, but some fluoride may be present in the soil, since the Winsum soil was reclaimed from the sea, and sea-water generally contains fluorides. Some of the OH^- in the apatite would have been replaced by F^-, in the Winsum soil. Precipitation of phosphates probably played no part at all in the Winsum suspensions under the conditions of the experiments, and possibly the solubility of phosphates was determined by phosphate minerals with the generalized formula: $Ca_{10}(PO_4)_6(OH,F)_2$ perhaps with some Mg or Na substitution for Ca and some substitution of carbonate for phosphate (Chien & Black, 1976). The solubility of phosphates may also be influenced by interactions with a solid phase: chemisorption of phosphates on iron or aluminum oxides.

The solubility constants of silicates are not known accurately, but the soil suspensions certainly contain $Si(OH)_4$ in solution, probably between 10^{-3} and 10^{-2} mol/l, and precipitation of heavy metal silicates might thus be possible. In the pH range of interest, 5 to 7, less than 1% of the total amount of aqueous silica is present as $SiO(OH)_3^-$, whereas $SiO_2(OH)_2^-$ is virtually absent. If the affinity of the heavy metals for the negatively charged silanol group is large, it is more likely that heavy metals react with surface silanol groups associated with silicate minerals, than with aqueous silica, because surface silanol groups tend to be more negatively charged in the pH range of interest; e.g. silica has its PZC at a pH of about 2, whereas surface silanol groups on the edges of clay minerals may have a PZC at slightly higher pH but still well below pH 5.

In conclusion, precipitation reactions are unlikely to occur in Winsum suspensions, because the solutions remain undersaturated with respect to known solubility products of hydroxides, carbonates, and phosphates. Furthermore, the precipitation of silicates from solution is unlikely, since negatively charged silanol groups associated with silicate minerals are present in the system. Also, a precipitation reaction would not be reversible, Zn/Cd (Fig. 69a) and Cd/Zn (Fig. 69b) exchange. Precipitation of hydroxides, carbonates or silicates would result in an equivalent increase of H^+ in solution, which would result in an almost equivalent increase in divalent cations, which is inconsistent with the observed apparent excess adsorption of cations from solution. The specific behaviour of heavy metals and the behaviour of the pH cannot be explained satisfactorily by precipitation, including of silicates, and therefore specific adsorption reactions must be responsible.

5.8 SPECIFIC ADSORPTION

5.8.1 General

Specific interactions were detected as (a) highly selective exchange adsorption of heavy metals at low coverage of the adsorption complex, and (b) a discrepancy between the amounts of cations lost from solution and released by the soil.

The specific exchange adsorption of heavy metals at low coverage had the following characteristics: (a) the process was very rapid, (b) approximately equivalent amounts of Ca were released upon adsorption of hM, (c) the process was accompanied by a lowering of the pH, the decrease being larger for Pb and Cu than for Cd and Zn, (d) the process appeared reversible for heavy metals among themselves, as was suggested by Zn/Cd (Fig. 69a) and Cd/Zn (Fig. 69b) exchange, and (e) the total amounts of heavy metals preferentially adsorbed (Table 9) as well as the selectivity coefficients for the specific adsorption reaction, followed the order

$$(Ca) < Cd < Zn < Cu < Pb$$

The specific interaction referred to as apparent excess adsorption was characterized (a) by a loss of heavy metals from solution, not accompanied by an equivalent increase in other cations, whereas the amount of hM_{ex} was recovered upon treatment with acid, (b) by a relation between pH and activity of heavy metals of the form

$$2\ pH + \log hM = K$$

to hold, and (c) by absence of the process to measurable extent at low hM coverage, which might be due to a lowering of pH, the increase in salt concentration, or to the increase of heavy metals both in the adsorbed phase and in the solution. It might also be a kinetic effect, the times being too short for the excess adsorption to occur to a measurable extent.

Since precipitation was unlikely to account for the observed specific interactions, specific adsorption on mineral surfaces or organic matter could be responsible for much of the observed behaviour. The composition of the hydroxylated mineral and organic surfaces changes with pH, H^+ being potential determining ion, according to Eqs. 1 and 2. The type of association between heavy metals and surface hydroxyl groups may depend on steric factors, the number of hydroxyls per unit area, the point of zero charge of the surface hydroxyls, pH of the solution, and affinity of a cation for a surface hydroxyl. These affinities appear to follow the order of the first hydrolysis constants of the divalent cations, so that first hydrolysis products rather than unhydrolysed species could be adsorbed, or that metals in the adsorbed state could hydrolyse to diminish their positive charge and thus their enthalpy of hydration.

The cation-exchange capacity of clay soils is mostly made up of sites on the planar surfaces of clay minerals (mainly illites in Winsum), the charge of these sites being independent of pH. The CEC is further made up of silanol groups on the edges of clay minerals, sites associated with organic compounds, oxides of Fe, Al, Mn and Si, and other minerals (such as carbonates or phosphates), and also phosphates adsorbed on iron or aluminum oxides; the charge of these sites is generally dependent on pH. The points of zero charge of oxide hydroxyls may differ considerably: silica (pH_{PZC} = 2), manganese oxides (pH_{PZC} = 2 - 5), aluminum oxides (pH_{PZC} = 5 - 9), and iron oxides (pH_{PZC} = 6.5 - 9), where it may be recalled (Section 2.2.1) that the specific adsorption of metals on oxide surfaces may result in a shift in PZC.

5.8.2 Specific exchange adsorption

The specific or selective exchange adsorption of heavy metals was a rapid process and resulted in the release of approximately equivalent amounts of counterions, mainly Ca^{2+} and H^+ in initially homoionic Ca soils.

To explain the sharp decrease in pH upon adsorption of heavy metals, it is suggested that heavy metals and H^+ compete for the same sites (at pH 7 - 6), possibly silanol groups, and that the observed lowering of the pH is, at least in part, due to reduction of the acid-neutralizing capacity of the soil in the pH range of interest, and only partly to release of H^+ upon adsorption of heavy metals. The acid-neutralizing capacity of Winsum soil is rather large, about 30 μeq/g in the pH range from 7 to 6, but in the presence of specifically adsorbed heavy metals the reactive sites would be inaccessible for H^+ until the pH is low enough for H^+ to compete effectively with hM^{2+} or $hMOH^+$ for the sites of interest. Therefore, the release of a relatively small amount of H^+ might result in a large lowering of the pH, by the diminished acid-neutralizing capacity of the soil.

The great variety in surface hydroxyls, notably the variation in PZC and surface charge density, and the presence of organic matter combined with the different affinities of the cations for the sites, is thought to be responsible for the differences in amounts of cations specifically adsorbed and the differences in selectivity. The affinity of the cations for the adsorption sites followed the order of the first hydrolysis constants (Table 11): only Pb and Cu deviated from the observed exchange behaviour (Table 9; Figs. 70-71), but the differences between the log $^*K_1$ values for Pb and Cu are small and their exact values are uncertain. The differences in amounts specifically adsorbed (αQ in Table 9) thus reflect that ions with larger hydrolysis constants are specifically adsorbed on more sites than ions with lower constants.

To account for the release of Ca^{2+} upon adsorption of heavy metals it may be assumed that the sites of interest are initially occupied by Ca^{2+} or that H^+ released upon adsorption of heavy metals is neutralized on sites initially occupied by Ca^{2+}. Since it is plausible that heavy-metal ions and H^+ compete, at least in part, for the same sites, it may be assumed that some of these sites are initially occupied by Ca^{2+}. Calcium ions may be adsorbed in a Gouy (diffuse) layer and this type of association may be denoted as

$$2\ \text{Surf-O}^{-}(\text{Ca}^{2+}) \quad (154)$$

or

$$\text{Surf-O}^{-}(\tfrac{1}{2}\text{Ca}^{2+}) \quad (155)$$

where Surf-O^{-} denotes a dissociated surface hydroxyl group and where round brackets denote that adsorption takes place in a Gouy layer. There are indications, however, that Ca^{2+} may also be adsorbed in a Stern layer. Breeuwsma (1973), for example reported that Ca^{2+} was adsorbed on hematite at pH $\geq$ 6.5, whereas the PZC, determined in the presence of chlorides of Li^{+}, K^{+} and Cs^{+}, was situated at pH 8.5. If Ca^{2+} is adsorbed in a Stern layer, the following types of associations are conceivable

$$\text{Surf-O}_2\text{Ca} \quad (156)$$

or

$$\text{Surf-OCaOH} \quad (157)$$

at high pH, probably well above 7, and

$$\text{Surf-OCa}^{+}(\text{L}^{-}) \quad (158)$$

at lower pH, possibly about 7, where L^{-} denotes a monovalent anion. Although the nature of the association of Ca^{2+} with dissociated surface groups is not known, it will be assumed that adsorption at pH 7 and lower is mainly in a Gouy layer, denoted by Eq. 155.

The specific exchange of heavy metal ions on these sites may be visualized as follows

$$\text{hM}^{2+} + 2\ \text{Surf-O}^{-}(\text{Ca}^{2+}) \rightleftarrows \text{Surf-O}_2\text{hM} + \text{Ca}^{2+} \quad (159)$$

$$\text{hM}^{2+} + \text{Surf-O}^{-}(\tfrac{1}{2}\text{Ca}^{2+}) \rightleftarrows \text{Surf-OhMOH} + \text{H}^{+} + \tfrac{1}{2}\text{Ca}^{2+} \quad (160)$$

Both mechanisms account for the release of Ca^{2+} upon adsorption of hM^{2+}, whereas the second mechanism would also account for the experimentally observed correlation between the selectivity coefficients for the specific exchange reaction and the first hydrolysis constants. With respect to Eq. 160, it is possible that first hydrolysis products are adsorbed, i.e. that hydrolysis takes place in solution before adsorption

$$\text{hM}^{2+} + \text{Surf-O}^{-}(\tfrac{1}{2}\text{Ca}^{2+}) \rightleftarrows \text{hMOH}^{+} + \text{H}^{+} + \text{Surf-O}^{-}(\tfrac{1}{2}\text{Ca}^{2+}) \rightleftarrows \text{Surf-OhMOH} + \text{H}^{+} + \tfrac{1}{2}\text{Ca}^{2+} \quad (161)$$

or that hydrolysis takes place after the heavy metals are adsorbed

$$\text{hM}^{2+} + \text{Surf-O}^{-}(\tfrac{1}{2}\text{Ca}^{2+}) \rightleftarrows \text{Surf-OhM}^{+} + \tfrac{1}{2}\text{Ca}^{2+} \rightleftarrows \text{Surf-OhMOH} + \text{H}^{+} + \tfrac{1}{2}\text{Ca}^{2+} \quad (162)$$

In either case, the adsorption sites act as catalyst for the hydrolysis reaction.

Although silica has its PZC at pH about 2, dissociation of surface hydroxyls does not occur to a significant extent until a pH of 4 - 5 (Schindler et al., 1976; Iler, 1975), whereas at pH 7 about 10% of the reactive surface hydroxyls is dissociated, i.e. negatively charged. When only about 10% of the surface groups is dissociated, it is unlikely that adjacent groups are dissociated, by electrostatic repulsion between the negatively charged surface groups, and for silica even at pH 7 less than 1 surface hydroxyl per 100 Å ^{2} would be dissociated, if the number of hydroxyls on the silica surface range from 5 to 6 per 100 Å ^{2}. Under these circumstances it is more appropriate to write Eq. 159 as

$$hM^{2+} + Surf\text{-}O^-(\tfrac{1}{2}Ca^{2+}) + Surf\text{-}OH \rightleftarrows Surf\text{-}O_2hM + \tfrac{1}{2}Ca^{2+} + H^+ \qquad (163)$$

at high pH, or as

$$hM^{2+} + 2\ Surf\text{-}OH \rightleftarrows Surf\text{-}O_2hM + 2\ H^+ \qquad (164)$$

at lower pH, whereas the same, of course, holds for Eq. 160.

Silanol groups associated with silica coatings on minerals, and those on the edges of clay minerals, may have a slightly higher PZC than pure silica; for illites by the presence of lower charged Al^{3+} ions in the adjacent octahedral layer and by isomorphous substitutions of lower charged cations for Si^{4+} in the tetrahedral layer and possibly for Al^{3+} in the octahedral layer. Measurements reported by Maes (1973) on montmorillonite showed that the contribution of dissociated silanol groups on the edges of the clay minerals ('broken bonds') to the total negative charge of the clay amounted to about 200 μeq/g at pH 3.9 and 300 μeq/g at pH 5.8, the total cation-exchange capacity of the montmorillonite being 1000 - 1100 μeq/g of clay, measured with Na^+ as the indicator ion, thus excluding specific adsorption effects. No data are available for illite, but it may be assumed that the contribution of dissociated surface hydroxyls to the total CEC of Illite is considerable too. In conclusion, adsorption according to Eqs. 159, 163 or 164 may result in the release of 0, 1 or 2 H^+ ions, whereas adsorption according to Eq. 160 may result in the release of 1 or 2 H^+ ions per hM^{2+} adsorbed.

Winsum soil has a high acid-neutralizing capacity in the pH range of interest (7 - 5): about 30 μeq H^+ per pH unit. The neutralization of acid may proceed according to one of the following reactions

$$Surf\text{-}OCa^+ + H^+ \rightleftarrows Surf\text{-}OH + Ca^{2+} \qquad (165)$$

$$Surf\text{-}O^-(\tfrac{1}{2}Ca^{2+}) + H^+ \rightleftarrows Surf\text{-}OH + \tfrac{1}{2}Ca^{2+} \qquad (166)$$

$$Surf\text{-}OH + H^+ \rightleftarrows Surf\text{-}OH_2^+ \qquad (167)$$

where it is assumed that the surface complexes represented by Eqs. 156 and 157, are not of quantitative significance at pH < 7. It will be difficult to establish experimentally whether neutralization of acid proceeds according to Eq. 166 or to a combination of Eqs. 165 and 167, even if the net increase in positive surface charge (anion-exchange capacity), and the concentrations of H^+ and Ca^{2+} would be known with sufficient accuracy. In general, however, the amount of H^+ released upon adsorption of heavy metals will not be known accurately, and it will be difficult to decide whether Ca^{2+} is released by hM^{2+} or by H^+.

The adsorption reactions (Eqs. 159-164) do not yield information about the mechanism of association of heavy metals with surface sites. The high selectivity for the different cations suggests, however, that the ions lose at least their secondary hydration sheath, since it is difficult to explain the observed selectivity by fully hydrated ions. The observed correlation with the first hydrolysis constants seems to favour the type of adsorption described by Eq. 160. It may also be assumed, however, that this correlation is more or less fortuitous and that first hydrolysis constants are a measure for the ability to form hydrogen bonds or that they are correlated with the polarizability or another property that may cause selectivity between ions.

5.8.3 Apparent excess adsorption

Apparent excess adsorption is thought to be a specific adsorption of heavy-metal ions on one ore more types of undissociated surface hydroxyls. Two mechanisms could be of significance: (a) desorption of weakly acidic protons by divalent-metal ions, followed by the formation of monovalent surface complexes, and (b) ligand exchange (coordinate bonding) involving surface hydroxyl groups and water molecules in the inner coordination sphere of heavy-metal ions, resulting in the formation of divalent surface complexes.

The first mechanism may be visualized as

$$\text{Surf-OH} + hM^{2+} \rightleftarrows \text{Surf-OhM}^{+} + H^{+} \qquad (168)$$

where the positive surface charge will be compensated by anions in solution. The formation of these monovalent surface complexes may also result from the neutralization of acid according to (compare Eqs. 159 and 160)

$$\text{Surf-O}_2\text{hM} + H^{+} \rightleftarrows \text{Surf-OhM}^{+} + \text{Surf-OH} \qquad (169)$$

or

$$\text{Surf-OhMOH} + H^{+} \rightleftarrows \text{Surf-OhM}^{+} \qquad (170)$$

and would also be favoured by high hM^{2+} concentrations

$$\text{Surf-O}_2\text{hM} + hM^{2+} \rightleftarrows 2\ \text{Surf-OhM}^{+} \qquad (171)$$

Hence if the increase in positive surface charge is caused by the formation of monovalent surface complexes (Eqs. 168-171), specific exchange adsorption and apparent excess adsorption would be closely related phenomena.

It may also be assumed that excess adsorption is independent of specific exchange and that it occurs on a different type of sites, 'a sites', (second mechanism)

$$hM^{2+} + Surf_a\text{-}OH \rightleftarrows Surf'_a\text{-}OHhM^{2+} \tag{172}$$

possibly followed by hydrolysis

$$Surf_a\text{-}OHhM^{2+} \rightleftarrows Surf_a\text{-}OHhMOH^+ + H^+ \rightleftarrows Surf_a\text{-}OHhM(OH)_2 + 2H^+ \tag{173}$$

Although it will be difficult to distinguish experimentally between the two mechanisms of excess adsorption, except for the $Surf_a\text{-}OHhM^{2+}$ product, there is a basic difference: in Eq. 168 hM^{2+} replaces a weakly acidic H^+ from a Surf-OH group, whereas in Eq. 172 H^+ released upon adsorption of heavy metals would be from hydrolysis of heavy metals in the adsorbed state. In Eq. 172, ligand exchange results in the formation of a coordinate bond between the heavy metal and 1 or more surface hydroxyls. The ligand exchange reaction involving 1 surface hydroxyl may be as follows

$$Surf_a\text{-}OH + hM(H_2O)_6^{2+} \rightleftarrows Surf_a\text{-}(OH)hM(H_2O)_5^{2+} + H_2O \tag{174}$$

and the hydrolysis of the heavy metal

$$\begin{aligned} Surf_a\text{-}(OH)hM(H_2O)_5^{2+} &\rightleftarrows Surf_a\text{-}(OH)hM(H_2O)_4OH^+ + H^+ \\ &\rightleftarrows Surf_a\text{-}(OH)hM(H_2O)_3(OH)_2 + 2\,H^+ \end{aligned} \tag{175}$$

Through their electronic structure, a number of heavy metals, notably the transition metals, form coordinate bonds quite readily. The formation of the $Surf_a\text{-}hM(OH)_2$ may be referred to as 'surface precipitation', and would occur from solutions that are undersaturated with respect to the pure hydroxides. Because surface precipitation would be confined to the adsorption sites, a surface precipitate would not form a continuous phase, unless the number of adsorption sites per unit area would be large enough to allow a surface precipitate to form a monolayer.

The proposed mechanism of surface precipitation would be in qualitative agreement with the observation that oxides, notably of Fe, in soils often occur as coatings on other minerals. Since Fe^{3+} and Al^{3+} occur in 6-fold coordination with oxygen in oxides, the ligand exchange between $hM(H_2O)_6^{2+}$ ions and surface hydroxyls of these oxides seems feasible sterically. But the occurrence of Zn^{II}, Cu^{II} and Pb^{II} in 4-coordination with oxygen in their respective oxides, and differences in size between the heavy metals indicate that the steric structure of a possible 'surface precipitate' would be different from the pure oxides. A ligand exchange reaction would probably be a slow process, also because of steric distortions of the heavy metals involved. The suggestion that coordinate bonds are formed between hydrated heavy metals and surface hydroxyls associated with iron or aluminum oxides would be in agreement with the observation that heavy metals in soils often become occluded by iron oxides.

The adsorption mechanisms, specified through Eqs. 168-170 and 172-173, both give rise to a pH effect: the adsorption of heavy metals with increasing hM concentration in solution lowers pH, whereas a decrease in hM concentration in solution, once the surface phase were formed, would increase pH. This predicted behaviour of pH fits in with the behaviour of the pH in the Winsum suspensions: upon hM/Ca exchange, pH decreased over the whole range, whereas upon Ca/hM exchange pH first remained fairly constant, presumably because a surface phase tended to 'buffer' the pH, and then pH increased, when hM concentrations in solution became very low. If the activity of the surface precipitate, $\mathrm{Surf_a\text{-}OHhM(OH)_2}$, be constant, adsorption of heavy metals by Eqs. 172-173 would give rise to the relation of Eq. 145, whereas the activity of $\mathrm{Surf_a\text{-}OHhMOH^+}$ would vary with $\mathrm{hM^{2+}}$ and $\mathrm{H^+}$ activities. The behaviour of pH in the Winsum suspensions and the results of experiments to be discussed in Section 5.10 suggest the validity of Eq. 145. Although these results support the assumption of a surface precipitate regulating the pH, they cannot be considered as conclusive of whether adsorption proceeds through Eqs. 172-173 or not, since other types of surface phases may play a role as well, or the apparent relation between the pH and log hM may be incidental.

5.9 ZINC ADSORPTION AT CONSTANT pH

To obtain more information about the mechanism of specific exchange, an experiment was designed to determine the amount of $\mathrm{H^+}$ produced per amount of $\mathrm{Zn^{2+}}$ adsorbed. The pH of a number of Winsum soil suspensions was kept at a pre-set equilibrium value during addition of known amounts of Zn (ΔZn) to the suspensions from an autoburette, and acid produced upon addition of Zn was automatically neutralized by titration with a 0.10 N NaOH solution. A series of samples were treated in this way, centrifuged off and analysed for Zn ($\mathrm{Zn_o}$), after known amounts of Zn had been added to each soil sample. In Fig. 93 Zn lost from solution ($\mathrm{Zn_l}$), is plotted as a function of $\mathrm{Zn_o}$. The solid line in Fig. 93 is drawn by hand through the experimental points, and the broken line represents non-specifically adsorbed Zn ($\mathrm{Zn_{ar}}$), estimated from

$$\mathrm{Zn_{ar}}/\{(1-\alpha)Q - \mathrm{Zn_{ar}}\} = \mathrm{Zn_o}/\{\mathrm{Ca_o(in)} - \mathrm{Zn_o}\} \tag{176}$$

where $(1 - \alpha)Q$ has been set at 180 µeq/g, $\mathrm{Ca_o(in)}$ at 0.010 N, and $K^{ar}_{\mathrm{Zn/Ca}}$ equal to unity. In Fig. 94 the substance ratio of the amount of NaOH added to the suspension (µmol/g) divided by the amount of Zn specifically adsorbed (µmol/g)

$$n = \Delta\mathrm{NaOH}/(\mathrm{Zn_l} - \mathrm{Zn_{ar}}) \tag{177}$$

is plotted as a function of $\mathrm{Zn_o}$. The substance ratio n increased from about 1.0 at low Zn concentrations to 1.3 - 1.4 at higher Zn concentrations. This suggests that at first one $\mathrm{H^+}$ is produced upon the adsorption of one $\mathrm{Zn^{2+}}$; then, possibly by a second mechanism of adsorption, about 2 $\mathrm{H^+}$ are released per $\mathrm{Zn^{2+}}$ adsorbed.

Figures 93-94 do not represent an equilibrium situation: when addition of NaOH was

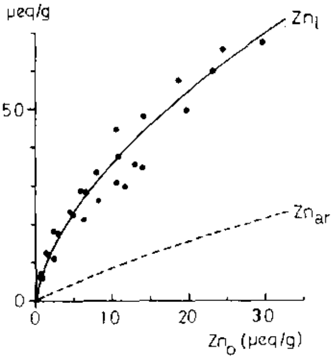


Fig. 93. Zn/Ca exchange on Winsum at constant pH: loss of Zn from solution. Zn_{ar} is estimated from Eq. 176.

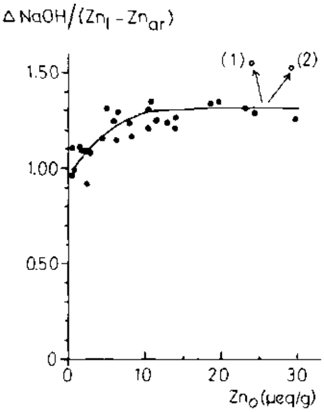


Fig. 94. Zn/Ca exchange on Winsum at constant pH: the ratio of the amount of NaOH added (μmol/g) to the amounts of Zn specifically adsorbed and adsorbed in excess (μmol/g). Points 1 and 2 indicate the direction of change if titration with NaOH (1) or equilibration (2) continued.

continued after stopping the addition of Zn, the suspension continued to produce acid. Although both (Zn_l - Zn_{ar}) and ΔNaOH increased upon continuing the titration with NaOH, the latter increased more rapidly and the net result was an increase in n to about 1.6 (Fig. 94, Point 1). When both the addition of Zn and NaOH were stopped simultaneously and the suspension was left standing for 48 hours, pH decreased from 7.08 to 6.72, and the amount of (Zn_l - Zn_{ar}) decreased: Zn_o increased, such that n increased to about 1.6 (Fig. 94, Point 2). The equal value of n in the two cases may be coincidence, since there was no evidence that either case was an equilibrium.

The wide scatter of the data, inexplicable by natural variation in samples, remains unsatisfactory. In other experiments too the combined electrode used for pH measurements became unstable in soil suspensions upon prolonged standing: when the electrode was left in contact with the suspension for more than 2-3 hours, readings became unreliable. The instability of the electrode may have been due to specific adsorption of certain hydrolysis products of Fe, Si or Al, on the electrode surface, but this was not further investigated. On the other hand, there was little doubt about the total amounts of NaOH and Zn added to the suspensions, and also the final Zn concentrations were measured independently, whereas sometimes pH was measured independently with 'fresh' electrodes. It may be noted that the type of adsorption taking place at pH 7.1 may differ from the type of adsorption at lower pH values, in that hydrolysis and formation of Surf-O_2Zn or Surf-OZnOH would be favoured over formation of Surf-OZn^+ complexes.

5.10 ADSORPTION AT CONSTANT SALT CONCENTRATION

In the experiments discussed so far, salt concentrations were not constant during adsorption and no equilibrium was reached for specific adsorption of heavy metals. Therefore, an experiment was designed in which (a) increasing amounts of Zn, Cu or H were added to suspensions of untreated Winsum soil in $Ca(NO_3)_2$ solutions, (b) the total salt concentrations were kept constant, (c) pH was measured regularly for several weeks, in both the clear supernatant solutions and the rotating suspensions, and (d) all solutions were analysed for Ca, Mg, Na, K and Zn or Cu after the experiment had been stopped and the suspensions centrifuged off. A series of 11 samples each of 5 g Winsum soil was equilibrated with 100-ml aliquots of $Ca(NO_3)_2$ 0.01 N in polyethylene bottles, and then a 10-ml aliquot of $Ca(NO_3)_2$ 0.10 N was added to the first bottle, 9 ml $Ca(NO_3)_2$ and 1 ml $Zn(NO_3)_2$ 0.10 N to the second bottle, up to 10 ml of $Zn(NO_3)_2$ to the last bottle. To another series of Winsum suspensions $Cu(NO_3)_2$ was added instead of $Zn(NO_3)_2$, and to a third series an acid $Ca(NO_3)_2$ solution, containing HNO_3 at 0.10 eq/l, was added to obtain an acid titration curve at approximately constant salt concentration. In addition, a few duplicates of the Zn and Cu series were prepared, to study the behaviour of pH and metal concentrations if equilibration continued.

Figure 95 shows the behaviour of pH as a function of time for soil suspensions to which from top to bottom increasing amounts of Zn were added and decreasing amounts of Ca; pH of supernatant solutions and rotating suspensions appeared to be equal within experimental error. The effect of added Zn on pH is easily detected: the initial rapid

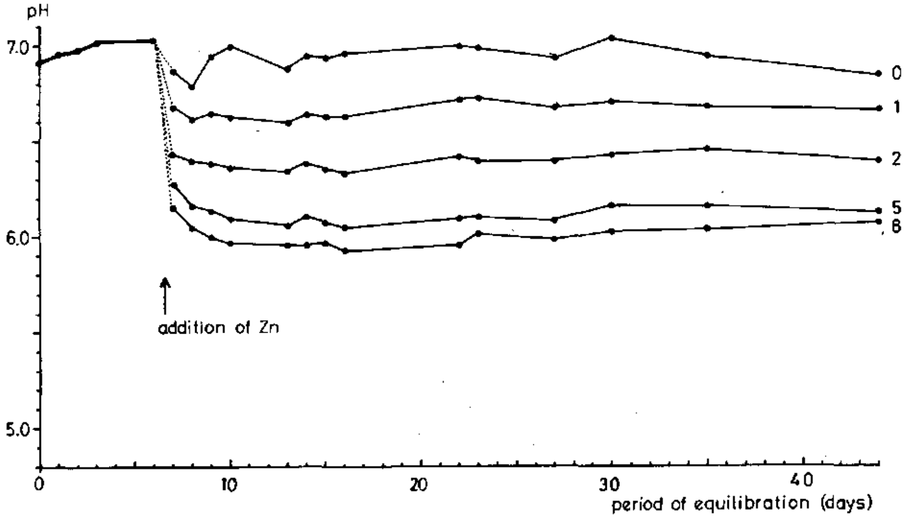


Fig. 95. Zn adsorption on Winsum soil at constant initial salt concentration: behaviour of pH upon prolonged equilibration. 0, 20, 40, 100 and 160 μeq Zn, and 200, 180, 160, 100 and 40 μeq Ca were added per g soil to Numbers 0, 1, 2, 5 and 8, respectively.

decrease in pH is assumed to be due to specific exchange by Eqs. 159 or 160, upon which Ca^{2+}, Mg^{2+} and H^+ are released, whereas the continuing decrease in pH may be due to adsorption by Eqs. 163-164 or 168, and the final slight increase in pH might be by solution of Al-compounds or rearrangement of Zn in the adsorbed phase resulting in the uptake of H^+ (e.g. Eqs. 169-170). In Fig. 96 the behaviour of pH of the copper series is shown: pH fell much lower than of the Zn series, the initial rapid decrease of pH did not continue, but remained constant for Numbers 5 - 8, or was even followed by an increase for Numbers 1 - 4. The behaviour of pH suggests that Cu had a much higher affinity for the adsorption sites, and indicates that initially 'too much' acid was produced, such that the initial adsorption reaction was followed by rearrangement of Cu^{2+} and uptake of H^+. Comparison of Curves 1 and 2 in Figs. 95 and 96 shows that the Cu and Zn curves approach closely, two weeks after addition of Cu and Zn, suggesting that both metals eventually occupy the same adsorption sites, although they react in different ways with the soil in the initial stage of the adsorption process. The effect of addition of acid to the soil suspensions is shown in Fig. 97: also pH of the acid series shows an initial rapid decrease, followed by a slow increase. Although the acid titration curve of the soil changed with time, the shape of the curve did not change much (Fig. 98). Addition of equivalent amounts of Zn^{2+} or acid to Winsum suspensions had the same effect on pH up to 30 - 40 µeq/g, whereas Cu and acid yielded the same result up to 40 - 50 µeq/g (Fig. 99). These results suggest that H^+, Cu^{2+} and Zn^{2+} compete for the same adsorption sites, which make up at least 30 - 50 µeq/g of the cation-adsorption capacity of Winsum soil. Figure 100 shows that pH + log hM increased with increasing X_{hM} for both Zn^{2+} and Cu^{2+}, whereas Eq. 145 held for Zn^{2+} (K = 8.9) and Cu^{2+} (K = 6.8). Since hM activities increased 100 to 1000 fold

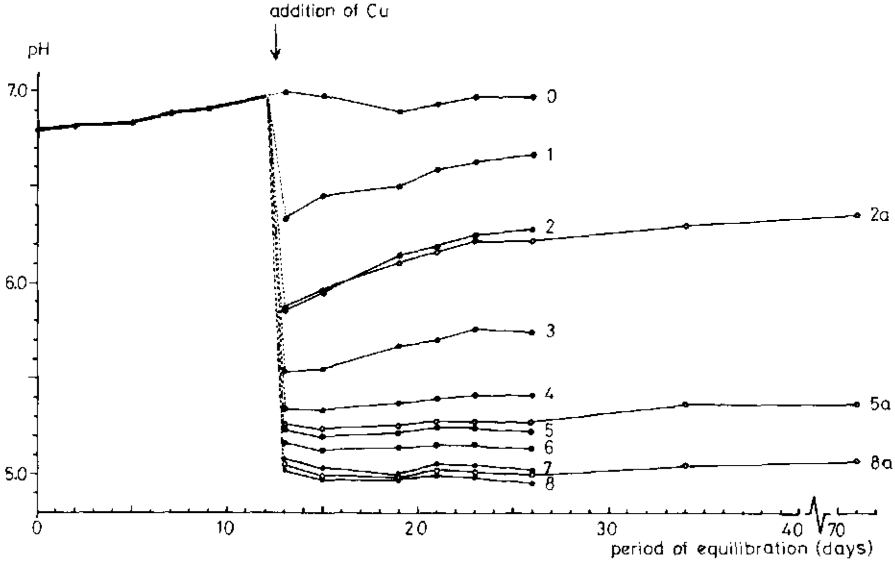


Fig. 96. Cu adsorption on Winsum soil at constant initial salt concentration: behaviour of pH upon prolonged equilibration. 0-160 µeq Cu and 200-40 µeq Ca, with intervals of 20 µeq, were added per g soil to Numbers 1-8; Numbers 2a, 5a and 8a are duplicates of 2, 5 and 8.

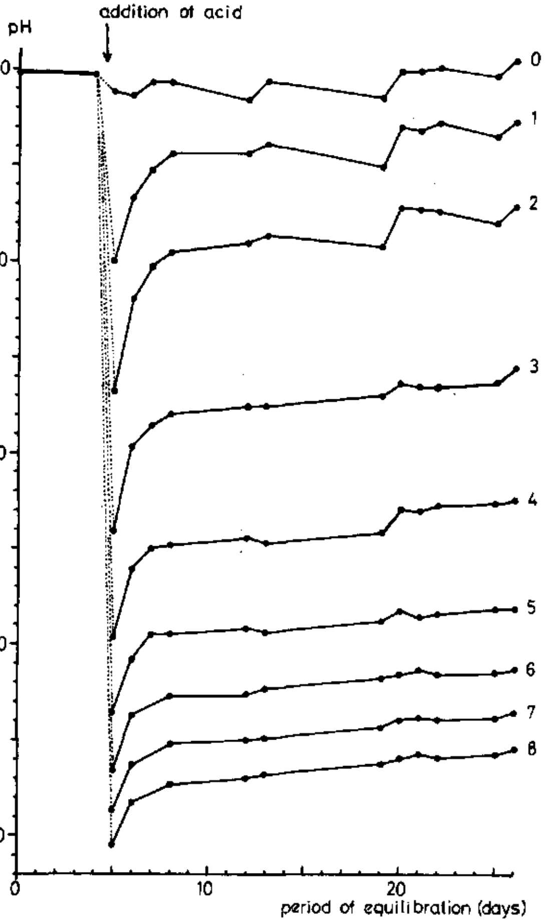


Fig. 97. H adsorption on Winsum soil at constant initial salt concentration: behaviour of the pH upon prolonged equilibration. 0-160 µeq H were added per g soil to Numbers 1-8.

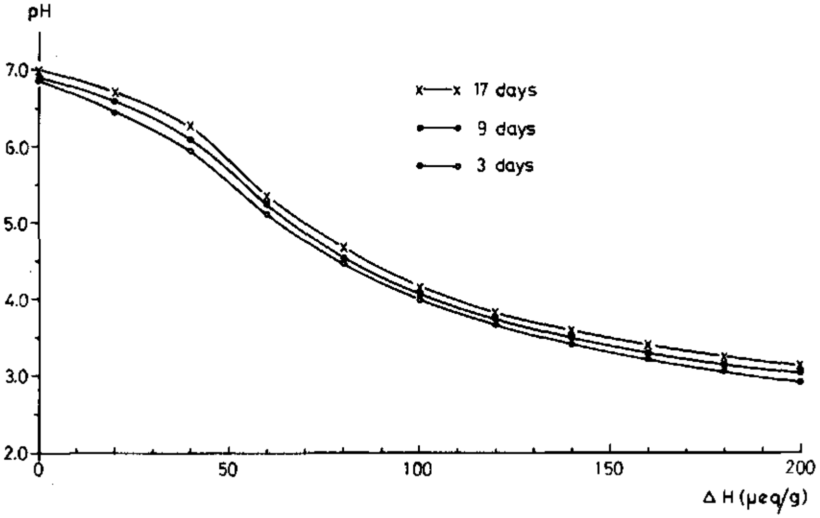


Fig. 98. pH of Winsum suspensions as a function of amounts of H added (µeq/g), at different times after the addition of acid.

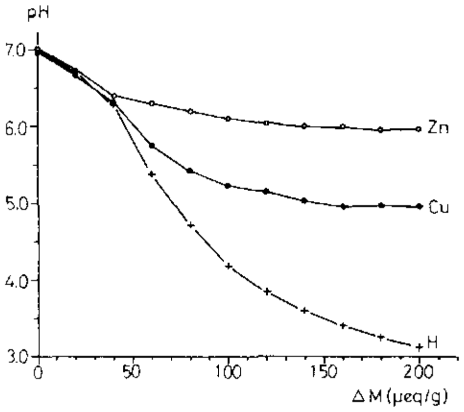


Fig. 99. pH of Winsum suspensions as a function of the amounts of Zn, Cu or H added, 16-17 (Zn), 14 (Cu) and 15-16 days (H) after the addition of the required solutions.

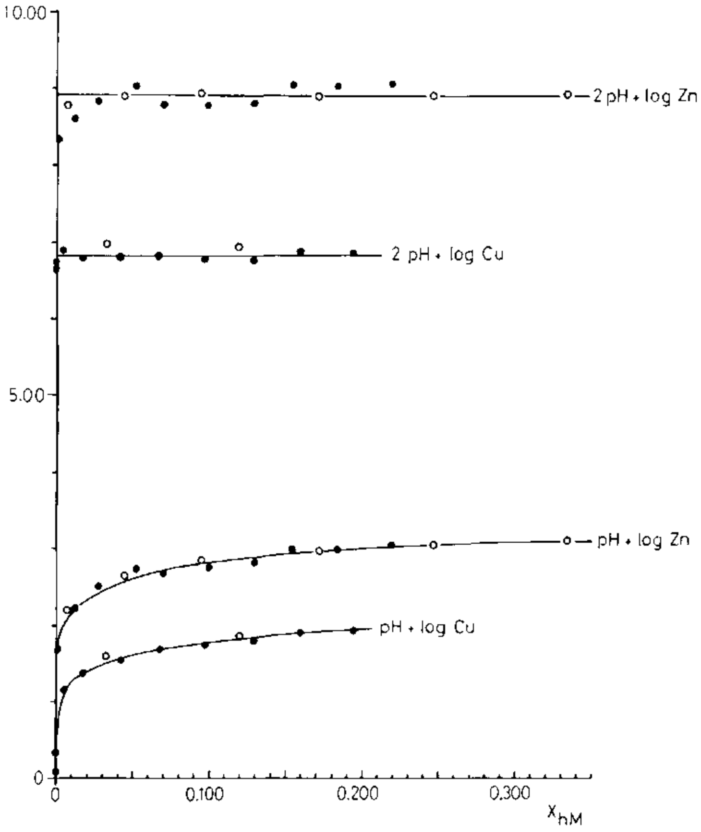


Fig. 100. Zn and Cu adsorption on Winsum soil at constant initial salt concentration: 2 pH + log hM and pH + log hM plotted for Zn and Cu as a function of X_{hM}. Equilibration periods for Zn were 44 (●) and 57 days (o), and for Cu 26 days (●) and 71 days (o).

and the H activity 10 to 100 fold in the Zn and Cu series, it is unlikely that the relationship between pH and log hM is fortuitous: the validity of Eq. 145 points to the presence of a surface precipitate, with a constant activity, determining pH as a function of hM activity in solution.

After the experiments were stopped, the solutions were also analysed for Mn and Al, but these elements were not present in detectable amounts. Alkali metals were present in low concentrations and were approximately constant in all samples, Na^+ at about 0.3 μeq/ml and K^+ 0.8 μeq/ml, which indicates that Zn^{2+} or Cu^{2+} were not adsorbed at interlattice sites, otherwise the K^+ concentration would have increased. The sum of the cations in solution, however, decreased upon addition of Zn^{2+} or Cu^{2+} (Fig. 101), where

$$X_{hM} = hM_o/(Ca + Mg + hM)_o \tag{178}$$

The loss of salt from solution is explained as an increase of the net positive charge of the solid phase, by excess adsorption of Zn or Cu. Since Zn_{ex} and Cu_{ex} were measured as loss of divalent cations from solution (μeq/g), the actual amounts of Zn and Cu adsorbed in excess are not known, as long as the type of adsorption is not known exactly. If the net positive charge of the solid surface increases one equivalent per mole of divalent cation adsorbed, as in $Surf\text{-}OhM^+$ or $Surf_a\text{-}OHhMOH^+$, the amount of hM^{2+} adsorbed in excess (μeq/g) would equal twice the amount of salt lost from solution (μeq/g), assuming that the neutralization of H^+ released upon adsorption of hM^{2+} results in an equivalent increase of Ca^{2+} and Mg^{2+} in solution. If the charge of the surface increases two equivalents per mole of divalent cation adsorbed, as in $Surf_a\text{-}OHhM^{2+}$, the amount of heavy metals adsorbed would equal the amount of salt lost from solution. The sum of the cations decreased also in the H series, but not as much as in the Zn and Cu series. The H_{ex} curve

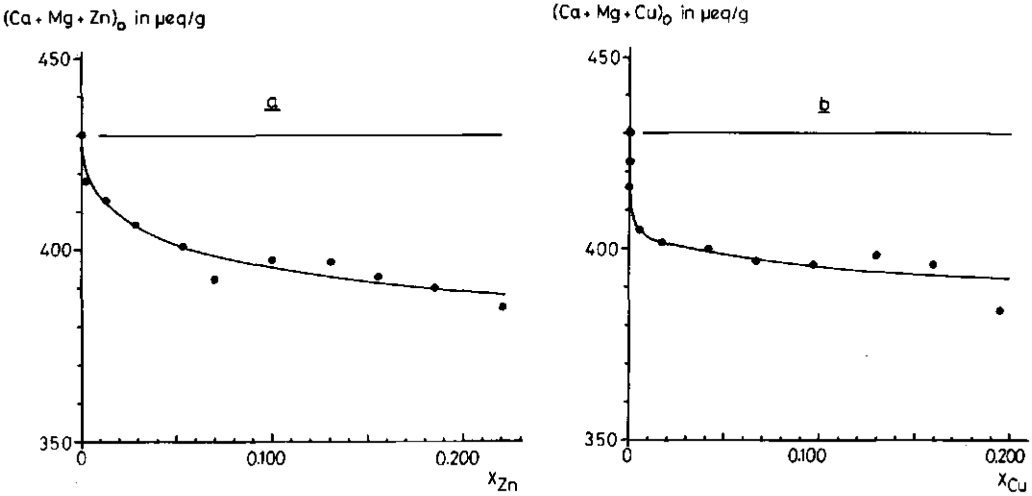


Fig. 101. Zn (a) and Cu (b) adsorption on Winsum soil at constant initial salt concentration: loss of salt from solution measured as the sum of divalent cations in solution, after 44 (a) and 26 (b) days of equilibration.

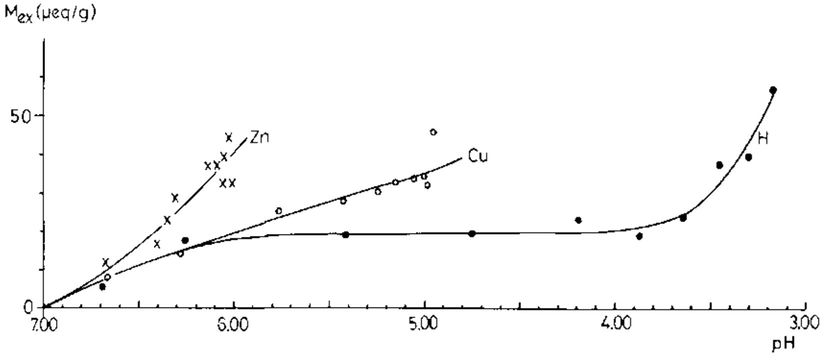


Fig. 102. Zn, Cu and H adsorption on Winsum soil at constant initial salt concentration: amounts adsorbed in excess, measured as loss from solution (μeq/g) as a function of pH.

(Fig. 102) suggests that there was only a limited number of surface hydroxyls that could be positively charged by H^+ in the pH range 6-7, whereas in the range 4-6 no more such sites were available for H^+. The excess adsorption of H^+ was probably due to a reaction of the type (compare Eqs. 1 and 2)

$$\text{Surf-OH} + H^+ \rightleftarrows \text{Surf-OH}_2^+ \tag{179}$$

If hM^{2+} and H^+ both interacted with the same surface hydroxyls, hM^{2+} would adhere to an uncharged adsorption site, probably by a ligand-exchange reaction, to yield the $\text{Surf}_a\text{-OHhM}^{2+}$ product. Figure 102 shows that H_{ex} was about 20 μeq/g, whereas almost twice as much Zn and Cu were adsorbed in excess, hence H_{ex} and hM_{ex} were of the same order in μmol/g. A limited number of reactive sites for excess adsorption would explain why almost equal amounts of Zn and Cu (30 - 40 μeq/g) were adsorbed in excess. If hM^{2+} and H^+ interacted with different sites, hM^{2+} could be adsorbed as a monovalent surface complex, whereas the H^+ then released could further increase the positive charge of the surface. It seems unlikely, however, that a surface hydroxyl that can be positively charged with H^+ would not react with hM^{2+} at all, and that sites that react with hM^{2+} to form positively charged surface complexes would not react with H^+. So the reactive sites in the excess adsorption of hM^{2+} and H^+ seem at least partly the same for both types of ions.

The curve for total amount of Zn lost from solution, after a period of 44 days (Fig. 103), estimated from Eq. 136, shows again the Freundlich behaviour, resulting from the simultaneous occurrence of specific and non-specific adsorption reactions. The amount of Zn adsorbed in excess is calculated from

$$Zn_{ex} = (Ca + Mg)_o^{ref} - (Zn + Ca + Mg)_o \tag{180}$$

where Ca_o^{ref} and Mg_o^{ref} represent the amounts present in the reference sample (Number 0 of each series) where only Ca is added. The amount of Zn exchangeably adsorbed can be estimated from Eq. 135, but the further distinction between Zn_{as} and Zn_{ar} requires an estimate of the regular part of the cation-exchange capacity, $(1 - \alpha)Q$. In Zn adsorption on Winsum

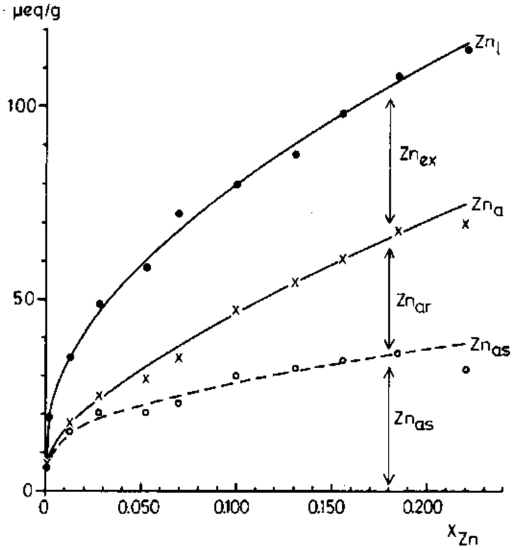


Fig. 103. Zn adsorption on Winsum soil at constant initial salt concentration after 44 days of equilibration. Zn_{ex} was estimated from Eq. 180, as loss of cations from solution (Fig. 101), and Zn_{ar} from Eq. 181.

soil $(1 - \alpha)Q$ was estimated to be 180 μeq/g, 4% of which was estimated to be occupied by Na^+ and K^+, if the selectivity coefficient for monovalent to divalent cations equal unity. If the selectivity coefficients for all divalent cations equal unity, Zn_{ar} can be estimated from

$$Zn_{ar} = X_{Zn}\ (1 - \alpha)Q \tag{181}$$

where $(1 - \alpha)Q$ here represents the 'available' part of the regular cation-exchange capacity, i.e. the part not occupied by Na^+ and K^+. The amount of Zn specifically adsorbed can now be estimated from

$$Zn_{as} = Zn_a - Zn_{ar} \tag{182}$$

For low X_{Zn}, the estimated values of Zn_{as} are not very sensitive to $(1 - \alpha)Q$, which varies between fairly strict limits for the different metals. So the broken line in Fig. 103 probably represents a reasonably accurate estimate for Zn_{as}. Specific exchange of Zn^{2+} would lead to an equivalent increase of Ca^{2+} and Mg^{2+} in solution. Hence it is of interest to estimate how much each ion contributes to the total release of cations upon adsorption of Zn^{2+}, since this may yield information about the Mg/Ca ratio on the adsorption sites involved in the specific adsorption process. The amount of Mg desorbed upon the specific adsorption of Zn is calculated from

$$Mg_{ds} = Mg_o + Mg_{ar} - (Mg_o + Mg_{ar})^{ref} \tag{183}$$

where the superscript 'ref' refers to the reference sample, and the amount of Ca desorbed is calculated from

$$Ca_{ds} = Ca_o + Ca_{ar} - \Delta Ca - (Ca_o + Ca_{ar} - \Delta Ca)^{ref} \tag{184}$$

where it is assumed that the increase in Mg and Ca in solution is solely due to desorption of adsorbed forms of Mg and Ca, and not to solution of salts, such as apatite or dolomite. From Eqs. 183 and 184, and from

$$\Delta Ca + \Delta Zn = \text{constant} \tag{185}$$

for all samples in the Zn series, and with

$$\Delta Zn^{ref} = 0 \tag{186}$$

it follows that

$$(Mg + Ca)_{ds} = Zn_{as} \tag{187}$$

From the experimental data, the substance ratio $(Mg/Ca)_{ds}$ ranged from 0.7 to 1.0, whereas $(Mg/Ca)_o^{ref}$ was close to 0.2, suggesting that Mg was preferred over Ca by a factor 3 - 5 by the adsorption sites involved in the specific adsorption of Zn. The preference for Mg over Ca was expected from the first hydrolysis constants analogous to the heavy metals. Although the ratio $(Mg/Ca)_{ds}$ represents a rather rough estimate of the Mg/Ca ratio in the adsorbed phase, these observations suggest that Mg and Ca are also specifically adsorbed by the adsorption sites that make up αQ. The suggestion that Ca and Mg may enter into specific adsorption reactions involving surface hydroxyls is supported by Breeuwsma (1973), who reported specific adsorption of Ca and Mg on hematite, and by James & Healy (1972) and Iler (1975), who reported specific adsorption of Ca on silica. Extrapolation

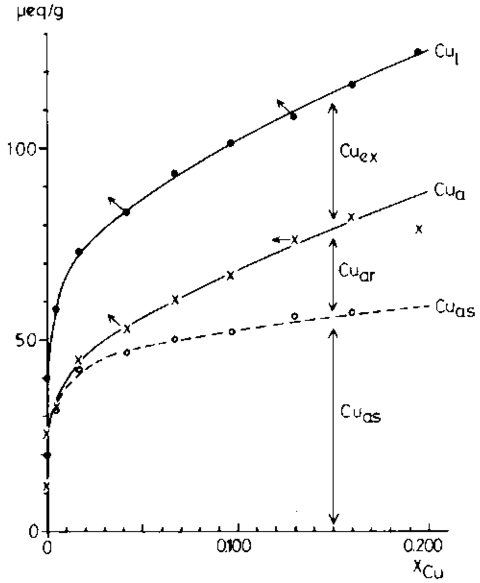


Fig. 104. Cu adsorption on Winsum soil at constant initial salt concentration after 26 days of equilibration. Cu_{ex} and Cu_{ar} were estimated from Eqs. 180 and 181, with Cu instead of Zn.

of the straight parts of the Zn_a and Zn_{as} curves in Fig. 103 towards the y axis both yield values of about 20 μeq/g, which is equal to the value for αQ, estimated from Figs. 66a and 67 and Table 9, but Fig. 103 suggests that this estimate for αQ may be too low, the actual value being closer to 30 - 40 μeq/g. The ratio Zn_{ex}/Zn_{as} varied between 1.0 and 1.9, and averaged 1.3 for the whole Zn series. If the excess adsorption of Zn resulted in the formation of monovalent surface complexes, the ratio Zn_{ex}/Zn_{as} would be less than 1.0, unless the release of H^+ resulted in an additional increase in positive charge of the solid surface. Therefore, the fact that Zn_{ex} exceeds Zn_{as} would point to the formation of divalent surface complexes.

In Fig. 104, Cu_{ar} is estimated under the same assumptions as Zn_{ar} in Fig. 103; the 'available' part of (1 - α)Q is estimated to be 156 μeq/g for Cu. Extrapolation of the Cu_a and Cu_{as} curves towards the y axis yields an estimate of about 45 μeq/g for αQ, equal to the value obtained from Fig. 70a and Table 9, but Fig. 104 shows that the actual value of αQ may be closer to 50 - 60 μeq/g. The ratio $(Mg/Ca)_{ds}$ varied between 0.5 and 0.8 in the Cu series and averaged 0.6, pointing to a somewhat lower preference for Mg over Ca in the Cu series than in the Zn series, but possibly the larger αQ in the Cu series included a number of adsorption sites with a lower Mg/Ca ratio. The ratio Cu_{ex}/Cu_{as} varied between 0.6 and 1.0, and averaged 0.7, less than in the Zn series, since Cu_{as} was greater than Zn_{as}, and Cu_{ex} and Zn_{ex} were of the same order. For both Zn and Cu, the ratio hM_{ex}/hM_{as} remained fairly constant in all samples, suggesting a relation between the two mechanisms of adsorption. If both types of adsorption occurred on the same sites, and if monovalent surface complexes were formed, the ratio of uncharged to monovalent surface complexes would be close to zero and almost equal in both the Zn and Cu series. If specific exchange and excess adsorption occurred on different types of adsorption sites, and if divalent surface complexes were formed, the ratio of uncharged to divalent surface complexes would remain fairly constant, of the order of unity. The preference of hM^{2+} for both types of adsorption sites would be of the same order and would not vary to a large extent with pH or hM_o. The data in Fig. 104 refer to an equilibration period of 26 days, and the arrows indicate how the curves changed when equilibration continued for

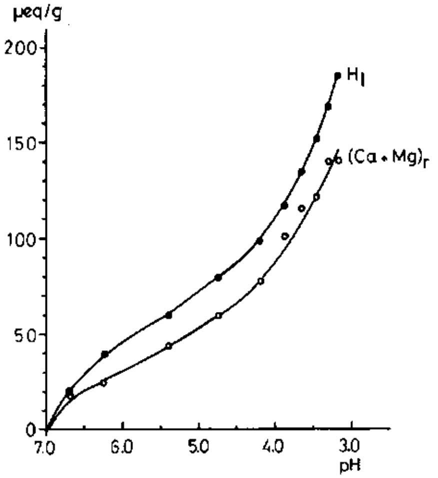


Fig. 105. H adsorption on Winsum soil at constant initial salt concentrations: loss of H and release of Ca and Mg plotted as a function of pH after a two weeks equilibration period.

another 44 days: both Cu_{ex} and Cu_{as} increased, but Cu_{ar} decreased, by a lowering of Cu_o upon prolonged equilibration.

The amount of H lost from solution in Fig. 53 was estimated from the initial and final pH, and the amounts of Ca and Mg released were estimated from

$$(Ca + Mg)_r = (Ca + Mg)_o - (Ca + Mg)_o^{ref} \qquad (188)$$

where ΔCa was the same for all samples, only ΔH increased in the present adsorption series. Figure 105 shows that the loss of H^+ from solution was largely accompanied by an equivalent increase of Ca^{2+} and Mg^{2+} in solution, the amount of H_{ex} (Fig. 102) being of the order of 20 μeq/g between pH 6 and 4.

5.11 SUMMARY OF SPECIFIC INTERACTIONS

A complete set of equations describing the specific interactions referred to as 'specific exchange adsorption' and 'excess adsorption' has to account for (a) specific exchange resulting in the release of one mole H per mole hM adsorbed, followed by specific exchange resulting in the release of two moles of H per mole hM adsorbed, and (b) specific adsorption resulting in an increase in net positive charge of the surface of one or two equivalents per mole hM adsorbed. Three mechanisms describing the specific interactions of heavy metals with Winsum soil have been suggested in the present study and will be summarized briefly.

The first mechanism considers specific exchange involving two neighbouring surface hydroxyls at the time

$$\text{Surf-O}^-(\tfrac{1}{2}Ca^{2+}) + \text{Surf-OH} + hM^{2+} \rightleftarrows \text{Surf-O}_2hM + \tfrac{1}{2}Ca^{2+} + H^+ \qquad (163)$$

$$2\ \text{Surf-OH} + hM^{2+} \rightleftarrows \text{Surf-O}_2hM + 2\ H^+ \qquad (164)$$

to account for the release of one and two moles of H respectively, followed by excess adsorption

$$\text{Surf-OH} + hM^{2+} \rightleftarrows \text{Surf-OhM}^+ + H^+ \qquad (168)$$

$$\text{Surf-O}_2hM + hM^{2+} \rightleftarrows 2\ \text{Surf-OhM}^+ \qquad (171)$$

which are favoured by high hM concentration, and

$$\text{Surf-O}_2hM + H^+ \rightleftarrows \text{Surf-OhM}^+ + \text{Surf-OH} \qquad (169)$$

which is favoured by low pH, and where Eqs. 171 and 169 may be referred to as rearrangement processes as well.

The second mechanism considers specific exchange involving first hydrolysis products or specific exchange followed by hydrolysis of the adsorbate

$$\text{Surf-O}^-(\tfrac{1}{2}\text{Ca}^{2+}) + \text{hM}^{2+} \rightleftarrows \text{Surf-OhMOH} + \tfrac{1}{2}\text{Ca}^{2+} + \text{H}^+ \tag{160}$$

$$\text{Surf-OH} + \text{hM}^{2+} \rightleftarrows \text{Surf-OhMOH} + 2\ \text{H}^+$$

followed by excess adsorption

$$\text{Surf-OH} + \text{hM}^{2+} \rightleftarrows \text{Surf-OhM}^+ + \text{H}^+ \tag{168}$$

or uptake of H^+ by hydrolysed surface complexes

$$\text{Surf-OhMOH} + \text{H}^+ \rightleftarrows \text{Surf-OhM}^+ \tag{170}$$

both processes resulting in a net increase in positive charge of the surface.

The third mechanism of specific interaction considers specific exchange, followed by a ligand exchange reaction (coordinate bond formation) involving a presumably different type of surface hydroxyls

$$\text{Surf}_a\text{-OH} + \text{hM}^{2+} \rightleftarrows \text{Surf}_a\text{-OHhM}^{2+} \tag{172}$$

possibly followed by hydrolysis of the adsorbate

$$\text{Surf}_a\text{-OHhM}^{2+} \rightleftarrows \text{Surf}_a\text{-OHhMOH}^+ + \text{H}^+ \tag{173}$$

or 'surface precipitation'

$$\text{Surf}_a\text{-OHhMOH}^+ \rightleftarrows \text{Surf}_a\text{-OHhM(OH)}_2 + \text{H}^+ \tag{173}$$

where the subscript 'a' is introduced to distinguish the present surface hydroxyls from those involved in the specific exchange reactions. The process of excess adsorption would be favoured by low pH and high hM^{2+} activity. In Table 12, the different surface complexes discussed in this section are summarized with a brief indication of the mechanism of adsorption involved.

Whether hydrolysis plays a part in adsorption of metals on oxides is still an open question: Iler (1975), for Ca^{2+} on SiO_2, Schindler et al. (1976), for Fe^{3+}, Cu^{2+}, Cd^{2+} and Pb^{2+} on SiO_2, and Hohl & Stumm (1976), for Pb^{2+} on Al_2O_3, favoured the first mechanism of adsorption, whereas Gadde & Laitinen (1974) described the adsorption of Pb^{2+} on hydrous ferric oxide as a specific replacement of weakly acidic protons by Pb^{2+} or $PbOH^+$, and James & Healy (1972) described the adsorptive behaviour of Fe^{3+}, Cr^{3+}, Co^{2+} and Ca^{2+} on SiO_2, as a specific adsorption of first hydrolysis products.

The apparent relation between ion-exchange selectivity and first hydrolysis constants suggests that hydrolysis plays a role in the adsorption process, whereas the validity of

$$2\ \text{pH} + \log \text{hM} = K \tag{145}$$

Table 12. Some characteristics of surface complexes.

Surface complex	Mechanism of adsorption[1]	Net charge	Number of H^+ released
Surf-O_2hM	spec.exch.	0	0, 1, 2
Surf-OhMOH	spec.exch./hydrol.	0	1, 2
Surf$_a$-OHhM$(OH)_2$	lig.exch./hydrol.	0	2
Surf-OhM$^+$	spec.exch.	+1	0, 1
Surf$_a$-OHhMOH$^+$	lig.exch./hydrol.	+1	1
Surf$_a$-OHhM^{2+}	lig.exch.	+2	0

1. Specific exchange, hydrolysis, ligand exchange.

for the Cu and Zn series, points to the presence of some kind of a surface precipitate, responsible for the observed relationship between pH and log hM. It is difficult, however, to distinguish experimentally between the first and second mechanism of adsorption. Whether divalent surface complexes may be formed would also depend on the dielectric constant of solvent and oxide, and on PZC and structure of the oxide surface. Grimme (1968) proposed the formation of a Surf-Fe$(OH)_2$Cu^{2+} complex, whereas Healy et al. (1968) suggested the Surf-SiOHCo^{2+} complex as a possibility, to explain the adsorption of Co^{2+} on SiO_2. The different types of adsorption would not be mutually exclusive: in soils, with a whole range of adsorption sites, different types of adsorptive interactions could occur simultaneously.

Summary and conclusions

Metals with a relative mass density greater than 5 are collectively called 'heavy' metals. This group includes metals that are essential to plants and animals (Fe, Mn, Cu, Zn, Mo and Co), called micronutrients or trace elements, and metals that are not known to be essential, such as Hg, Cd and Pb. Historically, the interest in heavy metals stemmed from soil fertility, since micronutrient deficiencies were widespread in agriculture. More recently, interest arose also from environmental science, since heavy metals may have adverse effects on plants or animals, if their availability exceeds certain thresholds.

The solubility of heavy metals in soil largely determines their mobility in the environment and their availability to plants, and hence plays a major role in both micronutrient deficiencies and soil pollution. The solubility of heavy metals in soils depends on pH, redox potential, texture and mineral composition of the soil, amount and type of organic compounds in soil and the soil solution, competitive interactions between heavy metals, soil temperature, moisture content and microbial activity.

This study concentrates on the behaviour of Zn, Cd, Pb, Cu, Mn and Fe in soils, and the results may contribute to knowledge of binding of heavy metals in soils, and hence to understanding of solubility and mobility of these elements in soils.

Transport and immobilization of heavy metals in soils

Transport of heavy metals in soils may occur (a) in dissolved (< 0.45 µm) or suspended (> 0.45 µm) form, through the soil solution, by diffusion, or with the moving soil solution, by mass flow; (b) through plant roots; and (c) with soil (micro-)organisms. All metal ions in aqueous solution coordinate with water molecules or other ligands, of which organic ligands, such as fulvic and humic acids, are of major significance for heavy metals in soils.

Whether a dissolved or suspended metal remains in solution depends on (a) aqueous concentration of the metal of interest and of all competing metals; (b) aqueous concentrations of ligands, notably organic compounds with chelating properties; (c) pH, redox potential and soil temperature; and (d) nature and amount of sorption sites associated with the solid phase. Processes that may play a role in the removal of heavy metals from solution include (a) incorporation in biological systems; (b) coagulation of suspended matter; (c) precipitation or coprecipitation; (d) adsorption; and (e) solid-state diffusion. Adsorption may be through electrostatic attraction, e.g. of the ion ion or ion (induced-)multipole type, London van der Waals attraction, hydrogen bonding, coordinate bonding (ligand exchange) or possibly chemical bonding.

The main mechanisms governing the initial immobilization of dissolved or suspended heavy metals in soils probably include adsorption of ionic complexes on charged surfaces and coagulation of suspended matter. Mirobial decomposition of organic matter may result in the release of heavy metals, which may then become adsorbed by inorganic soil constituents. In the long term, heavy metals may become specifically adsorbed by or occluded in iron, manganese or other oxides, incorporated in stable minerals through solid-state diffusion, or form stable precipitates, for instance silicates.

Soils near zinc smelters

Solubility of Zn in natural waters around a zinc smelter was not likely to be determined by hydroxides, carbonates or phosphates. In non-acid waters, Zn fulfilled the relation

$$2(Zn^{2+}) + (H^{+}) = (OH^{-}) + (HCO_3^{-}) + 2(CO_3^{2-}) \tag{4-5}$$

where round brackets denote concentrations in mol/l.

Mass fractions of Zn and Cd were high in topsoils (2000 ppm and 25 ppm) and vegetation (2000-7000 ppm and 20-40 ppm) 1 km north-east of a zinc smelter at Overpelt (Belgium), and fell off sharply with distance to the smelter. Leaves of birch (*Betula verrucosa*) contained significantly more Zn and Cd than oak (*Quercus robur*) and maple (*Acer campestre*). The mass ratio of Zn to Cd in vegetation averaged 125 and in soil 75, hence uptake of Zn is favoured over Cd, or Cd is more mobile in soil than Zn. Mass fractions of heavy metals were highest in topsoils, as would be expected with metal enrichment from fallout, and decreased markedly with depth. The similarity between the distributions of heavy metals and loss on ignition (organic matter) may indicate that the adsorption complex was nearly saturated with heavy metals. Differences between distributions of heavy metals with depth may reflect a changing composition of aerial fallout, or different mobilities of heavy metals or soluble complexes of heavy metals with organic compounds; the mobility of Cd being greater than of Zn and Pb.

Experiments with surface soil (A_1 horizon), collected 1 km north-east of a zinc smelter at Overpelt, indicated that a considerable part of Zn in soil solution was associated with large (> 48 Å) organic compounds, and that the solubility of Zn was determined by adsorption-desorption rather than by precipitation-solution relationships. A reliable estimate of the water-soluble fraction of heavy metals in soil can be obtained by equilibrating soil samples with demineralized water in different mass ratios and by extrapolating the change in metal content of the solid phase to zero solution/soil ratio. Estimates thus obtained were lower than by percolation of soil samples with demineralized water.

Redox potentials in soil samples that were equilibrated for 9 weeks with demineralized water, appeared to be determined by reduction of 'limonitic' ferric oxide, the solubility product being intermediate between hematite and goethite. The increase in aqueous concentrations of Zn, Cd, Mn and Fe upon submergence was probably due to release of heavy metals adsorbed on or occluded by limonitic ferric oxides, and to desorption of heavy metals by Fe^{2+}, the replacing power of Fe^{2+} over other divalent cations, notably

Zn^{2+}, being quite low, in agreement with the order of chelate stability of divalent heavy metals.

Water-soluble fractions of Zn, Cd, Mn and Fe in Overpelt soil were about 1% or lower, whereas Zn and Cd were about 70% salt-extractable, and Fe and Mn less than 10%. Dilute acid and Na-EDTA extracted almost equal amounts of Zn and Cd, but Na-EDTA extracted more Mn and Fe, indicating that Mn may be associated with ferric oxides, the substance ratio of Mn to Fe being 0.14. Mass fractions of Mn and Fe in soils near a zinc smelter at Budel-Dorplein (Netherlands) seemed to be correlated below 30-70 cm depth, in particular near the permanent watertable, pointing to the occurrence of mixed oxides of Fe and Mn. Salt-extractable fractions were high for Zn, Cd and Pb (50-60%), but low for Cu, Mn and Fe (< 10%). The acid-extractable fraction of Cu was higher (40-60%) than of Fe and Mn ($\leq$ 10%), suggesting that Cu is, contrary to Fe and Mn, largely associated with organic matter in soil.

A soil along a river discharging mining wastes

The Geul is a small river that passes through La Calamine and Plombières (Belgium), where Zn and Pb were formerly mined, and enters the Netherlands in the south of the Province of Limburg. The Geul formerly discharged large amounts of Pb, Zn and Cd, in dissolved form or adhered to suspended matter (at high water), and the water was slightly acid, as evidenced by the absence of calcareous sediments, probably through oxidative weathering of sulfidic ores, notably pyrite and marcasite, in the Belgian catchment area.

The grain-size distribution of a soil along the Geul revealed no discontinuities in the deposition of the soil profile, and the mass fractions of Pb and Zn with depth probably reflect the changing metal contents of suspended matter carried by the Geul. The high contents of Zn (3620 ppm) and Pb (1330 ppm) in the 10-20 cm layer of the soil may be correlated with mining activities from 1840-1880, when mining was at its zenith, whereas the decreasing metal contents at 110-150 cm depth may reflect the rise in mining in the 14th and 15th Centuries, when the brass industry moved to Aachen.

Unavailable (residual and acid-extractable) fractions of Zn and Pb were high (80-90%), possibly due to association with ferric oxides, or to the presence of stable minerals, such as silicates or sulfides, carried by the Geul from the Belgian catchment area. Because of the high contents of Pb and Zn in this soil, the salt-extractable (exchangeable) fractions were significant: 10-20% of the cation-exchange complex in the 0-20 cm layer was covered with Zn^{2+} or Pb^{2+}. The increased availability (fractions extractable with water and salt) of Zn and Pb below the watertable suggested that Zn and Pb were in part associated with ferric oxides.

Soils in a sewage farm

Soils in the oldest part (50 years old) of the municipal sewage farm near the Town of Tilburg (Netherlands) were sampled and analysed for bulk density, moisture content and mass fractions of Zn, Cu, Pb, Mn and Fe, and loss on ignition. One cycle of flooding with sewage water was attended, and sewage and drainage water were sampled regularly for

108 hours, filtered (0.45 μm membrane filter) and analysed for suspended (> 0.45 μm) and dissolved (< 0.45 μm) Zn, Cu, Fe and Mn.

The rate of discharge of drainage water, measured at the outlets of the tile drains, and the variation in pH and concentration of chloride in the drainage water as a function of time since the onset of flooding (breakthrough curves), suggested that admixture with capillary (rain)water and groundwater was of minor significance and that most drainage water was indeed purified sewage water. During periods of redistribution of water in soil, mobilization of heavy metals may occur, possibly associated with microbial decomposition of organic matter. This is observed as a pronounced peak early in the breakthrough curves of the (suspended) heavy metals, before the sewage water 'breaks through' in the effluent of the drains. Comparison of concentrations of metals in sewage and drainage water showed that the retaining capacity of the soil decreased in the order Fe (98%), Mn (92%), Zn (83%), Cu (55%), where the fraction retained is given in parenthesis. Because of its high affinity to organic ligands, Cu may occur to a large extent as uncharged or anionic complexes, which may in part explain the low retention of Cu. The total amounts of heavy metals retained by the soil were estimated from mass fractions of metals in soil, and from concentrations of metals in sewage and drainage water. Granted the crudity of the calculations, the estimates compared reasonably well for Zn, Mn and Fe, whereas data for Cu suggested that the retaining capacity for Cu was larger in the past than at present.

Ion exchange selectivity

The thermodynamic equilibrium constant for a homovalent (A/B) exchange reaction is introduced, and an ion-exchange equation is derived:

$$(\bar{a}_A/\bar{a}_B) = K^o_{A/B}\ (a_A/a_B) \tag{24}$$

Inclusion of the ratio of the activity coefficients of the ions in the adsorbed phase in $K^o_{A/B}$ yields a corrected selectivity coefficient, $K'_{A/B}$, and inclusion of the ratio of the activity coefficients of the ions in the liquid (aqueous) phase in $K'_{A/B}$ results in a selectivity coefficient, $K_{A/B}$, which is commonly used in ion-exchange studies to measure selectivity between ions. Equation 24 can be written in slightly different form through the introduction of $K'_{A/B}$ or $K_{A/B}$, but models have to be developed to predict the behaviour of the activity coefficients upon ion exchange.

The adsorption of ions onto a solid surface is described in terms of electrostatic ion-solvent (hydration-dehydration) and ion-solid interactions (coulombic attraction and possibly specific interactions). A non-zero change in free enthalpy accompanying an ion-exchange reaction may be due to differences between ions in equilibrium distance to the solid surface. Close to the adsorbent surface, the electric field is high and non-uniform, because of the presence of discrete adsorption sites, and the dielectric constant of water, about 80 in bulk solution, may decrease as low as 6, for complete electric saturation. In high intensity electric fields, small differences in equilibrium position between ions, for instance due to different (hydrated) radii or different polarizabilities, may result in significant selectivity between ions.

Ion exchange and adsorption equations

The theory of binary mixtures with non-zero energies of mixing (regular solid solutions) is applied to ion exchange to obtain expressions for the ratio of the activity coefficients of ions A and B in the adsorbed phase, $\bar{f}_A/\bar{f}_B$. It is assumed that divalent ions occupy two adjacent sites on a (hypothetical) regular two-dimensional array of sites. Several approximative equations for $\bar{f}_A/\bar{f}_B$ are derived from the exact formulae for the regular solid solution model by Guggenheim (1945). These equations may be of practical interest since they provide the theoretical basis for the inclusion of non-zero energies (and entropies) of mixing in ion-exchange equations. The regular solid solution theory may be of significance for solid solutions, as of $CaCO_3$ and $ZnCO_3$, and for localized adsorption (in a Stern layer), as of heavy metals on oxide surfaces at high pH.

The Langmuir adsorption equation

$$q = q_{max}Kc/(1 + Kc) \tag{55}$$

is described, and the influence of a small amount of solute, not taking part in the adsorption reaction, and of a variable adsorption coefficient (K) are discussed. The Langmuir adsorption model does not apply to ion exchange in soils, but Eq. 55 can be derived as an approximation for regular ion-exchange equations, such as Eq. 24.

The Freundlich adsorption equation

$$q = kc^{1/n} \tag{65}$$

and the Rothmund-Kornfeld equation

$$q_A/q_B = k(c_A/c_B)^{1/n} \tag{71}$$

which may be considered as a form of Eq. 65 that applies to ion exchange, are introduced and Eq. 71 is derived as an approximation for ion-exchange equations based on the regular solid solution model. Non-zero energies of mixing may reflect to some extent heterogeneity of adsorption sites in soils, but the regular solid solution theory does not explicitly consider this heterogeneity, which is characteristic for soils.

Two-site and two-species models

Ion-exchange in soils may be described in terms of 'two-site' or 'two-species' models. A two-site model describes a system of two species of cations and two types of adsorption sites: 'high selectivity' sites that are selective for one of the cations and 'low selectivity' sites that are unselective for either of them. An average selectivity coefficient for a two-site system is defined

$$K_a = (c_B/c_A)\Sigma q_i/\Sigma(Q_i - q_i) \qquad (87)$$

and it is shown that K_a decreases with increasing surface coverage of the 'preferred' ion. The Rothmund-Kornfeld and Freundlich equations, both characterized by a decreasing heat of adsorption with increasing surface coverage of the preferred ion, are shown to serve as approximative equations for the two-site model. It is shown that the coefficients k and n in Eqs. 65 and 71 form an indication for the fractional amount of high selectivity sites and for the ratio of the selectivity coefficients for high and low selectivity sites.

A two-species model describes a system of two species of cations, one of which forms stable complexes with a ligand in solution, and adsorption sites that are non-selective for the simple cations, but selective for the liganded complexes. The average selectivity coefficient for this system decreases with decreasing concentration of ligands in solution, i.e. with increasing surface coverage of the complexing cation, as in the two-site model. The two-species model thus reduces phenomenologically to the two-site model and the derivation of Eqs. 65 and 71 also holds for the two-species model.

Heavy metal cations may coordinate with uncharged ligands, such as thiourea or ethylenediamine, or with charged ligands. If divalent cations coordinate with monovalent anions, as of glycine, ion exchange no longer appears equivalent: the amount of cations lost from solution differs from the amount of cations released by the solid phase.

The adsorption of hydrolysis products might similarly result in an apparently superequivalent uptake of cations. The possible role of hydrolysis in the adsorption of heavy metals in soils is subject to discussion, since it is often difficult to distinguish between desorption of weakly acidic protons upon adsorption of heavy metals, and adsorption of first hydrolysis products, or a combination of these processes. In high intensity electric fields, the adsorption of hydrolysis products may be favoured over the unhydrolysed species, by the lower hydration energy of the lower charged species. Selective adsorption of hydrolysis products may give rise to an apparent relationship between the logarithm of the aqueous concentration of heavy metal, log c_{hM}, and pH

$$2\mathrm{pH} + n \log c_{hM} = \text{constant} \qquad (122)$$

where n depends on the initial pH and the buffer capacity of the system. The coefficient n equals 1 if, at constant ionic strength, the solubility of heavy metals in solution is determined by hydroxides, carbonates or silicates, in equilibrium with atmospheric CO_2 or solid SiO_2.

Some published measurements on the adsorption of heavy metals are interpreted in terms of the models derived in this study, and it is shown that selectivity coefficients describing the exchange adsorption of heavy metals against alkaline earth or alkali metals in soils are generally high at low coverage of heavy metals or high pH, and decrease with increasing coverage of heavy metals or decreasing pH, to the order of unity.

Cation-exchange experiments

An experimental procedure is described by which a complete cation-exchange isotherm can be determined on one soil sample by consecutive equilibrations with stepwise increasing concentrations of the required salt. Exchange isotherms were determined for Ca^{2+} and Zn^{2+} on Grundite and for Ca^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+} and Pb^{2+} on Winsum clay soil.

Adsorption of component M onto a solid phase was measured as loss of M from solution, and desorption of component M^* as the amount released by that solid phase, i.e. as the increase of M^* in solution. Exchange isotherms were not uniquely defined since 'loss' (adsorption) and 'release' (desorption) curves did not always coincide over the whole range of coverage, indicating that heavy metals took part in different adsorptive interactions: (a) regular exchange adsorption, (b) specific exchange adsorption, and (c) superequivalent or excess adsorption.

Equivalent exchange adsorption or ion exchange is characterized by the release of an equivalent amount of ions upon adsorption of ions. Regular (or: non-specific or non-selective) ion exchange refers to selectivity coefficients of the order of unity, and specific (or: selective) exchange adsorption to selectivity coefficients of the order of 10 or more. Superequivalent or excess adsorption is characterized by the release of less than equivalent amounts of ions upon adsorption of ions.

Results indicate that Zn^{2+}, Cd^{2+} and Cu^{2+} compete with Ca^{2+} on an approximately even basis for the majority of the adsorption sites in Winsum soil, presumably planar sites on clay minerals, whereas Pb^{2+} is favoured by a factor 2-3 over Ca^{2+}, possibly because of the smaller hydrated radius of Pb^{2+} in aqueous solution. Adsorption-desorption hysteresis, possibly by rearrangement of part of the ions in the adsorbed phase, or by condensation of a fraction of the homoionic clay platelets, was observed for Cu^{2+} and Pb^{2+} against Ca^{2+}.

There were indications that Ca^{2+} (and Mg^{2+}) also occurred in specifically adsorbed form in Winsum soil, since the untreated soils contained an amount of acid-extractable Ca, which could not be correlated with calcite or apatite (or dolomite), and because almost equivalent amounts of Ca^{2+} (and Mg^{2+}) were released upon specific adsorption of heavy metals. But there were no indications that Ca would be involved in specific interactions under the conditions of the experiments.

Behaviour of pH

The pH of soil suspensions decreased upon adsorption of heavy-metal ions on homoionic Ca^{2+} soil, but remained fairly constant for adsorption of Ca^{2+} on soils covered with heavy-metal ions. This behaviour of pH could not be explained by the 'salt effect': the influence of the increasing salt concentration on pH.

The relation

$$2\mathrm{pH} + \log hM = K \qquad (145)$$

held for both Zn and Cd, where K ranged from 8-9, and for Cu and Pb, where K was lower:

6-7. Results of experiments performed at constant salt concentration showed that Eq. 145 held for Zn ($K = 8.9$) and Cu ($K = 6.8$) after an equilibration period of 1-2 months too. The validity of Eq. 145 would suggest that a precipitate govern pH, but precipitation of hydroxides, carbonates, phosphates or silicates was unlikely under the conditions of the experiments. Therefore the lowering of pH upon adsorption of heavy metals was probably by desorption of weakly acidic protons or specific adsorption of hydrolysis products, or by formation of a 'surface precipitate' of hydroxides or possibly silicates. A surface precipitate could determine pH as a function of the activity of heavy-metal ions in solution.

Results of adsorption experiments at constant pH (pH 7), suggest that the amount of H^+ released, divided by the amount of Zn specifically adsorbed, increased from close to 1 at low coverage by Zn, to about 2, with increasing coverage. But the adsorption at pH 7 may be different from that at lower pH in that hydrolysis and the formation of uncharged surface complexes may be favoured at pH 7.

Addition of equivalent amounts of Zn^{2+} or H^+ to Winsum suspensions had the same effect on pH up to 30-40 μeq/g, whereas Cu^{2+} and H^+ yielded the same result up to 40-50 μeq/g. These results suggest that H^+, Cu^{2+} and Zn^{2+} compete for the same adsorption sites, which would make up about 25% of the cation-exchange capacity of Winsum soil. When the reactive sites are occupied by specifically adsorbed heavy metals, they may be inaccessible for H^+ until pH is low enough for H^+ to compete effectively for the sites of interest. Hence the decrease in pH may be caused by a relatively small amount of H^+ released upon adsorption of heavy metals, because of the diminished acid-neutralizing capacity of the soil.

Specific exchange adsorption and excess adsorption

Specific exchange adsorption of heavy-metal ions on Winsum soil (a) occurred at low heavy-metal coverage of the adsorbent, resulting in a Freundlich-type behaviour; (b) was a rapid process, since equilibration times ranging from a few hours to several weeks did not affect the amounts adsorbed in this way; (c) was accompanied by a lowering of the pH, the decrease being larger for Pb and Cu than for Zn and Cd; (d) seemed reversible for heavy metals among themselves, as suggested by results of Zn-Cd exchange experiments; and (e) the total amounts of heavy metals specifically adsorbed and the selectivity coefficients for the specific exchange reactions followed the order

$$\mathrm{Cd} < \mathrm{Zn} < \mathrm{Cu} < \mathrm{Pb}$$

Apparent excess adsorption of heavy metals would be favoured by low pH and high concentration of heavy metals, and increased with equilibration time up to an adsorption maximum.

Heavy metals specifically adsorbed and adsorbed in excess could virtually not be displaced by Ca^{2+}, but were recovered upon treatment with dilute acid.

Hydroxyl groups associated with organic matter or mineral surfaces may play an important part in specific interactions of heavy metals in suspensions of Winsum soil.

Three types of association of divalent cations (M^{2+}) and surface hydroxyls (Surf-OH) are conceivable at high pH

$$\text{Surf-O}^-(\tfrac{1}{2}M^{2+}) \tag{155}$$

where round brackets denote that adsorption occurs in a diffuse layer, and

$$\text{Surf-O}_2\text{M} \tag{156}$$

or

$$\text{Surf-OMOH} \tag{157}$$

where adsorption occurs in a Stern layer. At low pH adsorption would all be in a Stern layer

$$\text{Surf-OM}^+ \tag{158}$$

resulting in an increase in anion-exchange capacity (superequivalent adsorption). The type of association may depend on (a) steric factors, (b) number of surface hydroxyls per unit area of adsorbent, (c) point of zero charge of the surface hydroxyls, (d) dielectric constants of solid and solution phase, (e) pH of the solution, and (f) affinity of a cation for a surface group. These affinities appear to follow the order of the first hydrolysis constants of the heavy-metal ions, suggesting that the ions would hydrolyse upon adsorption to diminish their positive charge and hence their enthalpy of hydration.

Specific exchange adsorption of heavy metals on Winsum soil and the simultaneously occurring decrease in pH may be explained by specific adsorption of metal ions or first hydrolysis products on surface hydroxyls. The second type of adsorption would also account for the apparent correlation between hydrolysis constants and selectivity coefficients.

Excess adsorption may be by formation of monovalent surface complexes (Eq. 158), and, if so, excess adsorption and specific exchange would be closely related, or by divalent surface complexes, on a presumably different type of sites ('a' sites)

$$\text{Surf}_a\text{-OHM}^{2+}$$

A ligand exchange reaction (coordinate bond formation) between a surface hydroxyl and a water molecule of the inner coordination sphere of the heavy-metal ion may be represented as

$$\text{Surf}_a\text{-OH} + \text{M(H}_2\text{O)}_6^{2+} \rightleftarrows \text{Surf}_a\text{-OHM(H}_2\text{O)}_5^{2+} + \text{H}_2\text{O} \tag{173}$$

possibly followed by hydrolysis or the formation of a 'surface precipitate'

$$\mathrm{Surf_a\text{-}OHM(H_2O)_3(OH)_2} \qquad (175)$$

which might explain the validity of Eq. 145 upon adsorption of heavy metals in Winsum suspensions.

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