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Risk assessment of historical soil contamination with cyanides; origin, potential human exposure and evaluation of Intervention Values

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Abstract

This review on sources of cyanide (CN) soil contamination, behaviour of CN species and present environmental concentrations related to soils contaminated before 1987 was made so as to evaluate the current Dutch Intervention Values for CN and indicate their possible adjustment. Knowledge on ecotoxicological effects of CN species in soils is insufficient to derive Intervention Values; consequently, these have to be based on human exposure. Consumption of crops is the major contributing factor to the current soil Intervention Values. Recent plant physiological studies indicate that soil contamination will not lead to CN concentrations in crops which affect human health. Critical human exposure can occur via inhalation of free CN in ambient air, or after a one-time peak ingestion of soil contaminated with complex CN. For the time being 0.025 mg HCN per m^3 in soil air or in ambient air is suggested as a possible soil Intervention Value, equal to the Tolerable Concentration in Air. Further research is indicated to obtain a sound base for CN Intervention Values for soil. Consumption of untreated groundwater contaminated with ferrohexacyanide or thiocyanate can lead to critical exposure. The Tolerable Daily Intake will be reached with 0.075 mg total CN per dm^3, this concentration is one of the alternatives proposed as a possible Intervention Value for groundwater.

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Titel: **Risico beoordeling van historische bodemverontreiniging met cyaniden; oorsprong, potentiële humane blootstelling en evaluatie van Interventiewaarden**

Inleiding

Cyaniden algemeen voorkomen
Cyaniden (in dit rapport aangeduid als CN) omvatten een wijd spectrum van verbindingen welke de -C≡ N groep gemeen hebben. Verschillende cyaniden, bijv. cyanogene glycosiden, komen van nature voor, verschillende andere cyaniden, bijv. acrylonitriel, zijn man made (Homan, 1987). Cyaniden verschillen in reactiviteit, kunnen van origine giftig zijn, kunnen bij digestie vrij cyanide afgeven, of kunnen chemisch inactief blijven in het milieu of na opname door mens of dier. Cyaniden werden en worden op grote schaal gebruikt in de chemische industrie, ook kunnen zij gevormd worden als afval bijprodukt.
Het is meer dan twintig jaar geleden dat voor het laatst CN houdend afval gestort werd in Nederland. In principe is dus alle bodemverontreiniging met CN in Nederland historisch en heeft verder een lokaal karakter.
Het CN houdende stadsgasfabriek-afval (SGF afval)[1], ontstaan bij de produktie en reiniging van stadsgas en gestort in nabijheid van deze voormalige fabrieken, is de bron van het merendeel van de bodemverontreiniging met CN. Daarnaast is er de CN bodemverontreiniging door dumping van afval uit de metallurgische en fotografische industrie (MFI afval). CN in SGF afval is merendeels chemisch inactief, CN in MFI afval is daarentegen actief op het moment van storten. Hoewel niet vallend onder milieuregelgeving dient verder genoemd te worden het gebruik van alkali ferrohexacyanaat als anti-klonteringscomponent in strooizout voor wegen, van ammonium-ferri ferrohexacyanide in veevoer om besmetting van melk en vlees te verminderen van vee bij inname van ruwvoer verontreinigd met radioactief cesium, en van calciumcyanamide (gebruiksnaam kalkstikstof) als N kunstmest.

De Nederlandse regelgeving en CN
In de Wet op de bodembescherming worden twee op risico gebaseerde klassificatie-grenswaarden onderscheiden: Streefwaarden voor schone bodems en Interventiewaarden voor (historisch) ernstig verontreinigde bodems. De Interventiewaarde is gebaseerd op potentiële risico's van blootstelling aan bodemverontreiniging voor mensen en ecosystemen (Swartjes, 1999; VROM, 2000). Door gebrek aan kennis van de risico's op ecosystemen van CN, werd de huidige Interventiewaarde voor CN geheel gebaseerd op de humane blootstelling aan CN. Bij de schatting van de blootstelling werd een 'worst case' benadering gevolgd. Waarbij men zich realiseerde dat verschillende aannamen nader getoetst dienden te worden, met mogelijk een aanpassing van de Interventiewaarden in de toekomst (Berg van den, 1997). Uit een hernieuwde literatuurstudie is wederom geconcludeerd dat er nog onvoldoende informatie is voor ecotoxicologische risicobeoordeling van historische bodemverontreiniging met CN. Voor grondwater kan mogelijk een uitzondering gemaakt worden, indien men bij de

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[1] SGFs produceren verschillende soorten afval, in het onderhavige rapport heeft SGF afval altijd betrekking op het CN bevattende afval.

ecotoxicologische risicobeoordeling hiervan dezelfde maatstaf aanlegt als voor oppervlaktewater (Verbruggen et al., 2000). In het algemeen gesproken blijft de normgeving voor CN dus gebaseerd op de humane blootstelling aan CN.

Doel
De onderhavige studie richt zich op de potentiële blootstelling van de mens aan CN tengevolge van bodemverontreiniging met CN. Met het doel de huidige Interventiewaarden van CN (Tabel 1) te evalueren en aanpassing hiervan voor te stellen indien relevant. Ook zal nagegaan worden in hoeverre kennisleemten een inschatting van de potentiële menselijke blootstelling aan CN bodemverontreiniging bemoeilijken. Aangezien de schatting van deze blootstelling de basis vormt van de Interventiewaarden.

Methode
Bronnen van bodemverontreiniging met CN, de speciatie hiervan, en blootstellingwegen naar de mens zijn kritisch beoordeeld met behulp van literatuuronderzoek en door gesprekken en bijeenkomsten met onderzoekers, technische deskundigen en beleidsmedewerkers.
Gebaseerd op de verworven gegevens en nieuwe inzichten wordt de potentiële blootstelling van de mens aan CN van historische bodemverontreiniging geschat. Deze blootstelling wordt vergeleken met de aanvaardbare niveaus hiervan, met name met de Toelaatbare Dagelijkse Inname (TDI) en de Toelaatbare Concentratie in Lucht (TCL), zoals vastgesteld door het Centrum voor Stoffen en Risicobeoordeling (CSR) van het RIVM. De uitkomst van deze vergelijking wordt genomen als uitgangspunt voor de evaluatie van de huidige Interventiewaarden voor bodemverontreiniging met CN. Tevens wordt het belang van verder onderzoek, voorafgaande aan een mogelijke aanpassing van de Interventiewaarden, in beschouwing genomen.
De verwijdering van afval werd in het verleden niet systematisch geplanned en de verontreiniging van bodem en grondwater met bij industrieterreinen varieert in de regel sterk. Hier wordt in het onderhavige rapport geen rekening mee gehouden. Bij risico evaluaties is verondersteld dat waargenomen maximum concentraties over grote oppervlaktes voorkomen.

Tabel 1 De huidige Nederlandse Streef- en Interventiewaarden van CN in bodem en in grondwater (Berg van den, 1995; Swartjes 1999).

Verbinding	Streef-waarde bodem	Interventie-waarde bodem	Potentiële menselijke blootstelling aan CN door bodemverontreiniging	Streefwaarde grondwater	Interventie-waarde grondwater 1)
	mg CN/kg		aandeel door consumptie van plantaardige produkten	mg CN/l	
vrij CN	0.001	20	100%	0.005	1.5
complex cyanide	0.005	pH<5 650	g.g. 2)	0.01	1.5
		pH≥5 50	100%		
thiocyanaat	g.g. 2)	20	100%	g.g. 2)	1.5

1) Interventiewaarde gebaseerd op consumptie door een volwassene van ongezuiverd drinkwater 2 l/d met de veronderstelling dat na consumptie alle CN verbindingen opgelost in water reageren als vrij cyanide.
2) g.g. = geen gegevens of niet bepaald.

De huidige Nederlandse Interventiewaarden van CN

CN species
In de Nederlandse regelgeving worden drie verschillende groepen van CN onderscheiden, namelijk vrij cyanide, complex cyanide, en thiocynaat. Bij de regelgeving voor complex cyanide wordt onderscheid gemaakt tussen bodems met pH <5 en bodems met pH >5.

Humaan toxicologische grenswaarden
Er zijn betrekkelijk weinig humaan fysiologische en toxicologische gegevens van bovenstaande CN species. Daarom worden bij de afleiding van toxicologische grenswaarden onzekerheids-vermenigvuldigingsfactoren toegepast. De op deze wijze vastgestelde TDI is 0.05 mg CN/kg b.w./d voor vrij cyanide, voor vast en opgelost complex CN op 0.8 mg CN/kg b.w./d, en voor SCN op 0.005 mg CN/kg b.w./d. De TCL is vastgesteld op 0.025 mg HCN/m^3 (Meijerink, 1999). De internationaal vastgestelde Maximum Air Concentration (MAC) in werkplaatsen is 11 mg HCN/m^3.

Bodem Interventiewaarden
De huidige bodem Interventiewaarden van genoemde vormen van CN werden afgeleid met het CSOIL model. Opvallend hierbij is dat vrijwel 100% van de blootstelling volgens deze berekeningen veroorzaakt wordt door de consumptie van plantaardig voedsel (Tabel 1). Verondersteld werd dat de concentratie van CN in de plant gelijk is aan die in het bodem-poriewater, waarin een bepaalde fractie opgelost was van het in de bodem aanwezige CN (Berg vanden, 1995).

Grondwater Interventiewaarden
Bij de afleiding van de huidige grondwater Interventiewaarden werd aangenomen dat alle CN species, opgelost in grondwater, zich gedragen als vrij CN na opname door de mens. Hetgeen resulteerde in Interventiewaarden van 1.5 mg CN/l voor genoemde vormen van CN (Tabel 1).

Afval en stoffen met man-made CN in bodems

CN species en de belangrijkste componenten van in SFG afval
Complexe ijzercyaniden: Het vaste SFG afval wordt gekenmerkt door hoge concentraties van totaal CN; in de Verenigde Staten zijn concentraties van 10 g tot meer dan 20 g totaal CN/kg waargenomen (Theis et al., 1994) en in Nederland maxima van 50 g tot 80 g totaal CN/kg (Hoppener et al., 1983). Complex ijzerhexacyanide is het dominante cyanide species na de gasreiniging in SFG afval en blijft dit ook na storting op land. Meer dan 97% van het CN in SFG afval is aanwezig in de vorm van Pruisisch blauw, ferri ferrohexacyanide $Fe_4[Fe(CN)_6]_3$.
Thiocyanaat: SCN concentraties kunnen variëren van 0.3 g tot 26 g CN/kg (Hoppener et al., 1983; Wilson and Hudson, 1980).
Goed-oplosbare enkelvoudige cyaniden: In monsters SFG afval, met 24 - 45 g totaal CN/kg, waren goed-oplosbare enkelvoudige cyaniden [bijv. KCN, $Ca(CN)_2$] aanwezig in concentraties van 0.5 - 0.8 g CN/kg (Wilson and Hudson, 1980).
Vrij cyanide: Indien vrij cyanide aanwezig was in SFG afval kan aangenomen worden dat het hieruit verdwenen is door vervluchtiging (Theis et al., 1994); een andere veronderstelling is dat het weinige vrije cyanide, dat niet uit het ruw stadsgas verwijderd werd, in het gas bleef (Brettschneider, 1995).
Andere componenten: Andere componenten in SFG afval zijn: water ca. 20%; 30 - 50% zwavel, voornamelijk elementair S; ferri-oxide 10 - 20%; ferro-oxide 5 - 6%; zand en klei 4 -

8%; ammoniumsulfaat ca. 2%; kalk en gips samen ca. 2%; en in Amerikaans afval werden Cd, Cr, Cu, Ni, Pb, en Zn aangetroffen in concentraties van 0.002 – 0.008% (EEI, 1984; Hoppener et al., 1983).
pH: De pH in SFG afval en op daarmee verontreinigde terreinen kan variëren van 2 - 5. Het is niet duidelijk of de lage pH direct inherent is aan het afval, of dat deze een gevolg is van latere biologische en/of chemische omzettingen (Theis et al., 1994).

MFI afval
In de regel is MFI afval vloeibaar en werd het gemengd met vast afval, alvorens het gestort werd op vuilnisbelten of gebruikt werd bij de vereffening van terreinen. Afval uit de metaalverwerkende industrie kan het volgende bevatten: vrije cyaniden tot ca. 200 g CN/kg, merendeels NaCN; tot 25% cyanaten; en tot 30% barium (Lagas et al., 1982).
In de fotografische industrie kunnen zeer uiteenlopende vormen van CN gebruikt worden en in het verleden zijn deze ook gestort, zoals bijv.: ferri ferrohexacyanide; kalium ferrihexacyanide; acetonitrile; en natriumcyanide (Homan, 1987).

Niet-afval materiaal dat CN bevat
Om een gelijkmatige verdeling van wegenzout bij het strooien te verkrijgen wordt aan wegenzout natrium ferrohexacyanide $Na_4Fe(CN)_6$, of kalium ferrohexacyanide $K_4Fe(CN)_6$ toegevoegd als anti-klonteringmiddel (Ohno, 1996; Vries de, 1998). De totale CN concentratie is 10 - 60 mg CN/kg wegenzout, van dit cyanide is 2% - 5% in vorm van goed-oplosbare enkelvoudige cyaniden (Ohno, 1996; Brinkmann et al., 1997).
De eerste commercieel geproduceerde stikstof kunstmest was calciumcyanamid CaNCN (SKW, 1998). CaNCN wordt bij contact met het vocht in de bodem binnen enige dagen geheel omgezet in verbindingen die geen CN meer bevatten (Koning, 1965). CaNCN wordt tegenwoordig nog op bescheiden schaal gebruikt.
Om de besmetting met radioactief cesium (^{134}Cs en ^{137}Cs) van melk en vlees na het Chernobyl ongeval te verminderen of te voorkomen werd Pruisisch blauw toegediend aan vee of aan veevoer. Dit had als gevolg verspreiding van Pruisisch blauw bevattende mest in het milieu (Vandenhove et al., 2000).

Het gedrag en de concentratie van CN in de bodem

Vrij CN
De 'levensduur' van vrij cyanide in de bodem gebracht door het storten van afval is zeer beperkt. In het geval dat de vrij CN concentraties hoog zijn zal uitspoeling en emanatie overheersen. Ook zal vorming van complexe metaal-cyaniden plaats vinden, voornamelijk met ijzer en mangaan (Lagas et al., 1982; Keizer et al., 1995). Later en/of bij lagere concentraties zal het vrij cyanide ook biochemisch afgebroken worden (Fuller, 1985). Waarschijnlijk zal de concentratie van vrij cyanide in de bodem 6 à 10 jaar na storting niet meer verhoogd zijn. Vrijwel alleen ferri ferrohexacyanide en enige andere inerte complexe cyaniden zullen de aanwezige CN species zijn in historisch verontreinigde gronden. Uit deze species komt weinig vrij CN vrij. De maximale concentraties die gerapporteerd worden zijn 0.15 mg vrij CN/l in grondwater (Meeussen, 1992; Kjeldsen, 1999), en 1-2 mg HCN per m^3 in bodem- en omgevingslucht (Hoppener et al., 1983; Jans, 1999).

Complexe cyaniden
De 'levensduur' van makkelijk oplosbare complexe alkali-ferrohexacyaniden is beperkt daar deze omgezet worden in, en neerslagen worden als ferri ferrohexacyanide of mangaan

ferrohexacyanide. Laboratorium studies tonen aan dat opgeloste complexe metaalhexacyaniden ook in zekere mate afgebroken kunnen worden tot CO_2 en ammonium (Barclay et al., 1998; Hommelgaard et al., 1998). Ferri ferrohexacyanide en mangaan ferrohexacyanide zijn biochemisch vrijwel inactieve, stabiele verbindingen welke als zodanig in de bodem aanwezig blijven over vele decennia (Meeussen, 1992; Keizer et al., 1995).
De mobiliteit van ferrohexacyaniden in de bodem bij lage pH is waarschijnlijk beperkt tot verplaatsing in colloïdale vorm met inzijgend water over korte afstand in de bodem. De colloïden met complex CN zullen neerslaan op het oppervlak van structuurelementen in de bodem bij een verandering van de pH of wanneer de snelheid van de waterflux afneemt (Mansfeldt et al., 1998). Bij hoge pH waarden kan enig ferri ferrohexacyanide oplossen en met capillair opstijgend water getransporteerd worden naar het maaiveld. Vervolgens kunnen zo bevochtigde oppervlakken (Pruisisch) blauw gekleurd worden na verdamping van het water (Shifrin et al., 1996; Barclay et al., 1998).
De maximum CN concentratie aangetroffen in verontreinigde bodems als vast complex CN is 40,000 mg CN/kg, en als opgelost complex CN in verontreinigd grondwater 34 mg CN/l (Meeussen et al., 1992).

SCN
In het merendeel van de publicaties wordt vermeld dat weinig bekend is van het gedrag in het milieu van thiocyanaat of de effecten ervan (Stratford et al., 1994; Boening and Chew, 1999). Vorming van thiocyanaat onder anaërobe omstandigheden is mogelijk door reactie van vrij cyanide met zwavel of met zwavelverbindingen (Materassi et al., 1977; Newton, 1977).
Op enkele voormalige SGF terreinen in Nederland zijn analyses van thiocyanaat verricht. De gerapporteerde maximum thiocyanaat concentratie in grondwater is 32 mg CN/l (Brettschneider and Engelen, 1998). Niet gepubliceerde maximum waarden van thiocyanaat zijn 90 mg CN/l grondwater of ca. 30 mg CN/kg grond, en in aërobe bovengrond 7 mg CN/kg (Brettschneider, 1999). SCN wordt beschouwd als een zeer mobiele verbinding (Kd 1 tot 1.5), het gedrag ervan in anaërobe bodemlagen is vergelijkbaar met chloorionen (Brettschneider, 1999). In de overige literatuur wordt weinig aandacht besteed aan thiocyanaat op voormalige SGF terreinen en andere met CN verontreinigde locaties, alhoewel de (theoretische) aanwezigheid ervan door verschillende auteurs genoemd wordt. In het algemeen wordt SCN afgebroken tot S^{2-} en (waterstof)cyanaat HOCN, dat gehydrolyseerd wordt tot CO_2 en NH_3 (Stratford et al., 1994).

Enkelvoudige cyaniden en calciumcyanamide in de landbouw

Enkelvoudige cyaniden
Laboratorium proeven met NaCN, KCN and $Ca(CN)_2$ tonen dat CN^- bij lage concentraties in de bodem wordt omgezet tot NO_3^-, een stikstof voedingsbron voor planten. Hiervan uitgaande en gebaseerd op potproeven en enkele kleinschalige veldproeven werd aan enkelvoudige cyaniden een grote waarde toegedicht als N kunstmest, waarbij bovendien onjuist gerapporteerd werd dat dit al op praktijkschaal plaats vond (Fuller, 1985). Dit leidde tot de onjuiste interpretatie dat CN^-, als ook verbindingen waaruit CN^- vrijkomt niet phytotoxisch zijn (Hsu, 1994; Seijger, 1995; Wen et al., 1997). Echter, zoals hierna besproken wordt, tonen laboratorium proeven dat relatief lage concentraties van CN^- phytotoxisch zijn (Grossmann and Kwiatkowski, 1995). Zelfs natuurlijk voorkomende concentraties van vrij CN in de rhizosfeer kunnen toxisch zijn voor bepaalde planten (Schippers et al., 1990; Antoun et al., 1998). Met andere woorden enkelvoudige cyaniden zijn en zullen nooit op praktijkschaal gebruikt worden als plantennutriënt.

Calcium cyanamide

Calcium cyanamide wordt verkocht onder de naam kalkstikstof. Het is een stikstof-meststof met herbicidale nevenwerking. Dit laatste wordt veroorzaakt door het phytotoxische omzettingsprodukt (waterstof)cyanamide, dat binnen enkele dagen hydrolyseert tot ureum (Koning, 1965). Hetgeen hydrolyseert tot ammoniumbicarbonaat. Ureum en ammonium worden door de plant opgenomen en dienen als stikstofbron. Calcium cyanamide werd en wordt nog op praktijkschaal toegepast als N kunstmest.

Cyaniden in planten, phytotoxiciteit en CN species in plantaardig voedsel

Cyanogene planten

Een speciale groep planten, bekend als cyanogene planten, bevat CN in endogeen gevormde nitrielen. Meer dan 1,000 plant species in circa 100 families zijn cyanogeen en toxisch voor mens en dier (Conn, 1979; Eisler, 1991; Scheuer, 1992). Deze planten hebben namelijk het potentieel vrij cyanide af te geven bij beschadiging van hun cellen. Consumptie van cyanogene planten is alleen mogelijk na speciale bereidingswijzen waarmee vrij cyanide en de bronnen ervan verwijderd worden. Of CN concentraties in cyanogene planten verhoogd worden door bodemverontreiniging is niet bekend. Dit is echter van weinig of geen belang in aanmerking nemend dat zij zodanig bereid worden dat cyaniden altijd verwijderd worden voor consumptie van deze planten. Het is dus van geen belang verder aandacht te schenken aan cyanogene planten in verband met CN bodemverontreiniging.

Natuurlijke achtergrond concentratie vrij CN in planten

Begin tachtiger jaren werd ontdekt dat vrij cyanide een co-product is bij de synthese van ethyleen in de plant. Dientengevolge is endogeen gevormd vrij cyanide altijd aanwezig in alle planten. De concentratie ervan varieert van 0.05 – 0.5 mg vrij CN/kg vers gewicht, en is afhankelijk van plantensoort, groeistadium, en het deel van de plant. (Peiser et al., 1984; Manning, 1988; Yip and Yang, 1988; Grossmann, 1996).

Verhoogde concentraties vrij CN in planten

Vrij CN^- kan door de plant uit de bodemoplossing worden opgenomen, als chelaat verbonden aan een metaal (Wallace et al., 1971). Wat er na plantopname met het CN-chelaat in de plant gebeurt wordt niet vermeld.

Het is algemeen bekend dat verhoogde concentraties van vrij cyanide in de plant de respiratie en verschillende andere fysiologische processen onderdrukken. In algemene zin is gevonden dat een twee- tot viervoudige verhoging van de natuurlijke cyanide concentratie in planten phytotoxisch is (Grossmann, 1996 and 1998). De informatie met betrekking tot verhoogde vrij CN concentraties in de plant als gevolg van wortelopname van vrij CN is beperkt tot korte duur proeven met graszaailingen. Concentraties in de voedingsoplossing van 8 – 16 mg vrij CN/l brachten binnen vier dagen 50 - 80% reductie in de groei teweeg en leiden tot concentraties van 0.7 – 1.2 mg vrij CN/kg vers gewicht in de planten (Grossmann and Kwiatkowski, 1995). In historisch verontreinigde gronden zal het maximum dat de vrij CN concentratie in de bodemoplossing kan bereiken, waarschijnlijk niet hoger zijn dan dat hiervoor genoemd voor grondwater 0.15 mg vrij CN/l. Een op hierop afgestemde worst case schatting van de, ten gevolge van bodemverontreiniging, maximaal verhoogde concentratie in plantaardig voedsel is 1 mg vrij CN/kg vers gewicht.

Andere CN species
Weinig of geen informatie werd gevonden over andere species (dan vrij CN) met betrekking tot hun opname door en omzetting in planten, noch op hun effect op CN of SCN concentraties in de plant. Toxische concentraties voor mens of dier in niet-cyanogene planten worden niet gerapporteerd in de literatuur. In geval dat deze concentraties voorkomen zijn zij waarschijnlijk gekoppeld aan phytotoxiciteit en zieke planten, welke waarschijnlijk niet gebruikt worden voor consumptie.

Nieuwe overwegingen met betrekking tot CN Interventiewaarden

Natuurlijke achtergrond en CN concentraties in verontreinigde bodems en grondwater
Er zijn van nature verschillende CN bronnen in de bodem. Bijvoorbeeld wortels en resten van cyanogene planten, waaruit bij afbraak vrij en andere CN species vrijkomen. SCN kan vrij komen uit plantenresten van Cruciferae. Ook produceren verschillende bacterie genera vrij CN in de bodem. Tegelijkertijd worden CN species omgezet door bodemorganismen tot niet CN houdende verbindingen. Dit alles zal leiden tot een natuurlijk dynamisch evenwicht, waarbij CN species in de bodem aanwezig zijn maar niet accumuleren.
In de bestudeerde publicaties over CN verontreinigingen is de natuurlijke achtergrond van CN species in de bodem en grondwater veronachtzaamd. Een gefundeerde vergelijking van de concentraties van CN species in verontreinigde bodems met de natuurlijke achtergrond is dus niet mogelijk. Een oriënterende vergelijking (Tabellen 2 en 3) toont dat in verontreinigde SCN en complex CN de achtergrond concentraties respectievelijk tot 1E3 en tot 1E7 maal kunnen overschrijden. Dezelfde tabellen geven aan dat het onduidelijk is of de concentratie van vrij CN in historisch verontreinigde gronden de natuurlijke achtergrond overschrijdt. Dus een Interventiewaarde voor vrij CN in bodem of grondwater lijkt niet aan de orde te zijn alvorens zekerheid verworven wordt dat de natuurlijke achtergrond concentratie overschreden wordt op enige lokaties met historisch verontreinigde grond.

CN speciatie en oplosbaarheid in verontreinigde grond
Uit veldonderzoek blijkt dat vrijwel al het CN in historisch verontreinigde gronden aanwezig is als vaste complexe Fe en Mn hexacyaniden (Meeussen, 1992; Keizer et al., 1995; Staritsky et al., 1992). Dit is ook het geval in anaërobe waterverzadigde bodemlagen, waarin echter ook opgeloste thiocyanaten aanwezig kunnen zijn (Meeussen, 1992; Brettschneider et al., 1999). De complexe cyaniden in bodems zijn chemisch stabiel, afgezien van mogelijk beperkte omzettingen in andere onoplosbare complexe cyaniden. Er zijn geen formules ontwikkeld voor historisch verontreinigde gronden, waarmee de concentratie van opgelost hexacyanide of vrij CN in porie- of in grondwater afgeleid kan worden (Kjeldsen, 1999).
De huidige Interventiewaarden voor complex CN zijn verschillend voor bodems met $pH < 5$ en bodems met $pH \geq 5$. Deze afhankelijkheid van de pH is gebaseerd op de theoretische thermodynamische hogere oplosbaarheid van ferri ferrohexacyanide met toenemende pH (Meeussen, 1992). Echter zowel Meeussen als Keizer geven aan dat de oplosbaarheid en de concentratie van complex CN in grondwater niet alleen afhankelijk zijn van de bodem pH, maar ook van verschillende andere factoren zoals bijvoorbeeld de concentratie van Mn, hydrologie en de oplossings-kinetiek (Meeussen, 1992; Keizer et al., 1995). Er is dus geen duidelijke reden om een onderscheid te maken voor de Interventiewaarden van complex CN gebaseerd op alleen de bodem pH.

Vrij CN in lucht

Laboratorium data wijzen erop dat vrij CN gevormd wordt door fotodegradatie van opgelost complex CN (Meeussen et al., 1992). Geen informatie werd gevonden of fotodegradatie van opgelost complex cyanide en de daarop volgende emanatie van vrij CN een rol spelen onder veldomstandigheden. Overdag zal fotodegradatie plaats kunnen vinden aan het oppervlak van natte bodems of in plassen met stagnerend water. De schaarse gegevens van vrij CN in bodem- en omgevingslucht bij historisch verontreinigde gronden tonen dat concentraties van 1 - 2 mg vrij CN/m^3 kunnen voorkomen (Hoppener et al., 1983; Jans, 1999). Deze concentraties zijn 5 – 10 maal beneden de in werkplaatsen toegestane CN concentratie in lucht (MAC 11 mg HCN/m^3), echter zij overschrijden de toegestane concentratie in de overige lucht (TCA 0.025 mg HCN/m^3) met een factor 40 – 80. Er dient dus rekening gehouden te worden met de concentratie van vrij CN in de lucht bij de bodem Interventiewaarden. Met het oog op de regelgeving en/of de chemische analyse zal de voorkeur uitgaan een dergelijke Interventiewaarde te baseren op de concentratie van CN in bodem of in grondwater. Op het moment echter lijkt dit niet mogelijk daar er geen formularium bestaat waarmee de concentratie vrij CN in de lucht af te leiden is uit de CN concentratie in de bodem of in grondwater. Het ligt dus voor de hand om de Interventiewaarde te baseren op directe meting van de concentratie vrij CN in de omgevingslucht. Deze metingen kunnen ook vrij CN omvatten dat mogelijk vrijkomt door fotodegradatie uit natte bodems en/of stagnerend water aan het bodemoppervlak.

CN in plantaardig voedsel

De huidige Interventiewaarden voor CN zijn gebaseerd op de aanname van hoge CN concentraties in planten en voedsel tengevolge van bodemverontreiniging (Berg van den, 1995). Echter de concentratie van vrij CN zal in gezonde planten een lage phytotoxische grens niet overschrijden. Een hoge schatting van deze grens is 1 mg vrij CN/kg vers gewicht, hetgeen kan leiden tot een humane blootstelling van maximaal 9% van de TDI. Bodemverontreiniging met andere CN species leidt waarschijnlijk eerder tot phytotoxiciteit en verwerping van ongezonde planten als voedsel, dan tot voor de mens toxische concentraties in gezonde planten. De Interventiewaarde voor CN kan dus niet alleen op consumptie van plantaardig voedsel gebaseerd worden.

Potentiële humane blootstelling bij maximale historische bodemverontreiniging

Methode: De maximale humane blootstelling wordt geschat door de CSOIL default waarden voor bodemeigenschappen en menselijk gedrag (Swartjes, 1999) te verbinden met de maximum waargenomen concentraties van CN species in historisch verontreinigde gronden. Dit is gedaan voor de blootstellingroutes: inhalatie van HCN geëmaneerd uit de bodem; ingestie van bodemdeeltjes; en ingestie van ongezuiverd grondwater. Bovendien is de blootsteling van een kind geschat, tengevolge van een eenmalige piekinname van 5 gram gronddeeltjes (Calabrese et al., 1997; Kempchen, 2000).

Bodem: Vrij CN in omgevingslucht kan de TCA overschrijden en dan leiden tot overschrijding van de TDI. De blootstelling aan vrij CN via andere routes is verwaarloosbaar (een beperkte blootstelling via plantaardig voedsel kan mogelijk zijn, zie boven). Blootstelling aan de maximale concentraties van complex CN en van SCN leidt voor beide tot minder dan 0.1% van de TDI (blootstelling aan deze verbindingen via voedsel wordt verwaarloosbaar geacht, zie boven). Een uitzondering hierop is de zeer conservatieve schatting van de blootstelling van kinderen aan complex CN, 8.5 maal de toelaatbare acute inname, via een eenmalige piekinname van gronddeeltjes.

Grondwater: De maximale potentiële blootsteling via grondwater wordt geschat aan de hand van de consumptie van ongezuiverd grondwater, 2 l/d door volwassenen en 1 l/d door kinderen. Het berekende blootstellingrisico is het hoogst voor kinderen, namelijk: voor vrij CN 0.2 maal de TDI; voor complex CN 5 maal de TDI; en voor SCN 1,200 maal de TDI. De bestaande Interventiewaarde voor vrij CN lijkt niet noodzakelijk. Interventiewaarden voor de andere twee beschouwde CN species zijn noodzakelijk indien als criterium de consumptie van ongezuiverd grondwater wordt gebruikt.
Poriewater: Er zijn geen veldmetingen beschikbaar van CN species in poriewater, noch over een verband tussen de concentraties in poriewater en een daaruit voortkomende potentiële blootstelling van de mens. Met de huidige stand van kennis kan de Interventiewaarde dus niet gebaseerd worden op de concentratie van CN species in poriewater.

De spreiding van CN Interventiewaarden van 4 landen en maximale verontreiniging
Inventarisatie: Een internationale inventarisatie van Interventiewaarden viel buiten het kader van de onderhavige studie. Toch werd enige informatie doorgenomen over grenswaarden in België (Nouwen et al., 1999), Canada (CCME, 1997) en het Verenigd Koninkrijk (DOE, 1988; NTU, 1998).
Bodem: Alle grenswaarden van vrij CN en SCN liggen beduidend hoger dan de maxima welke zijn waargenomen in historisch verontreinigde gronden. De maximale concentratie van complex CN valt binnen de range van de gegeven grenswaarden (Tabel 2). Opvallend is dat de emanatie van HCN uit de bodem niet in beschouwing wordt genomen als een mogelijk potentieel risico, waaraan een grenswaarde gekoppeld dient te worden.

Tabel 2 CN species in de bodem, natuurlijke achtergrond, gerapporteerde maxima en grenswaarden.

CN species	Natuurlijke achtergrond	Maxima waargenomen in historisch verontreinigde bovengrond	Spreiding van de grenswaarden van 4 landen
	mg CN/kg grond		
Vrij CN	<0.005 – 1	0.045 [1)]	0.9 – 60
Complex CN	<0.005 –1.2	40,000	12 – 650
SCN	0.005	7	20 - ‘p.m.’ [2)]

[1)] Hoge schatting gebaseerd op maximum concentratie in grondwater.
[2)] ‘p.m.’ = genoemd maar niet beschouwd van belang te zijn.
Bronnen - Natuurlijke achtergrond: Beyer, 1990; Weuffen et al., 1990. Maxima: Meeussen, 1992; Brettschneider, 1999. Grenswaarden: Berg van den, 1995; Nouwen et al., 1999; NTU, 1998.

Grondwater: In de doorgenomen publicaties werd weinig of geen aandacht geschonken aan de consumptie van ongezuiverd grondwater en aan Interventiewaarden voor grondwater. De in België en Nederland afgeleide grenswaarden verschillen meer dan een factor 20 (Tabel 3). De maximale concentratie van vrij CN en van SCN in het grondwater van verontreinigde gronden ligt binnen de range van grenswaarden. De maximale concentraties van complex CN in het grondwater van verontreinigde gronden overschrijdt de Nederlandse grenswaarde.
Interventiewaarden: De grenswaarden van de drie genoemde landen en Nederland tonen een grote spreiding (Tabellen 2 en 3) en bieden geen basis voor een herziening van de Nederlandse Interventiewaarden.

Tabel 3 CN species in grondwater, natuurlijke achtergrond, gerapporteerde maxima en grenswaarden.

CN species	Natuurlijke achtergrond	Max. waargenomen in historisch verontreinigde grond	Huidige Nederlandse Interventiewaarden	Belgische grenswaarden
	mg CN/l grondwater			
Vrij CN	g.g.	0.15	1.5	0.07 1)
Complex CN	<0.01 – 0.02	34	1.5	
SCN	g.g.	90	1.5	n.v. 2)

1) Som van vrij CN + complex CN.
2) n.v. = niet vermeld in doorgenomen publicatie.

Kennisleemtes en de bepaling van CN Interventiewaarden

De belangrijkste kennis die ontbreekt om de humane blootstelling aan CN species in verontreinigde grond te bepalen is:
- duidelijke informatie over verhoogde concentraties van vrij CN in de omgevingslucht van verontreinigde gronden (bestaande informatie hierover is zo schaars dat een besluit om op deze factor een Interventiewaarde te baseren voortijdig lijkt);
- veld gegegevens of verhoogde concentraties voorkomen van vrij CN, complex CN, SCN of van andere potentieel toxische CN verbindingen in planten geteeld of van nature groeiend op met CN verontreinigde gronden;

Conclusies

Bodem

Het voorgaande toont dat de huidige Nederlandse Interventiewaarden gewijzigd dienen te worden. Deze waarden zijn namelijk gebaseerd op de aanname dat zeer hoge concentraties van vrij CN in planten kunnen voorkomen ten gevolge van bodemverontreiniging. De onderhavige literatuurstudie toont dat de inname van vrij CN, complex CN en SCN, via consumptie van plantaardig voedsel niet leidt tot overschrijding van de TDI. Hetzelfde geldt voor de blootstellingroutes ingestie en inhalatie van bodemdeeltjes. Uitgezonderd voor een eenmalige piekinname van grond door kinderen met een vrij extreme worst case schatting van 8.5 maal de toelaatbare acute inname van complex CN

Volgens berekeningen met gebruik van de CSOIL default waarden is inhalatie van omgevingslucht met door de bodem geëmaneerd HCN de enige blootstellingroute welke leidt tot overschrijding van de TDI/TCA. Het is nog niet mogelijk de concentratie van vrij CN in de omgevingslucht af te leiden uit bodemparameters. Ook zijn de heersende achtergrond concentraties onbekend, en verhoging door bodemverontreiniging valt mogelijk moeilijk te onderscheiden van verhogingen door het verkeer en andere antropogene bronnen. Zolang deze informatie ontbreekt is het mogelijk niet het juiste moment de concentratie van vrij CN in omgevingslucht te kiezen voor de definiëring van een bodem Interventiewaarde.

Grondwater

Consumptie van ongezuiverd met CN verontreinigd grondwater is van potentieel risico voor volwassenen en in sterkere mate voor kinderen. De maximum waargenomen concentraties van complex CN en SCN kunnen voor kinderen tot een blootstelling leiden van respectievelijk 2.8 en 1,200 maal de TDI. De maximale concentratie van vrij CN in grondwater leidt voor kinderen tot een blootstelling van 0.2 maal de TDI, hetgeen verwaarloosbaar is vergeleken bij de blootstelling aan complex CN en SCN.

Aanbevelingen

Bodem Interventiewaarden
Gezichtspunt 1: Aanvullend onderzoek is vereist om voldoende kennis te krijgen, waarmee nieuwe Interventiewaarden voor CN op gefundeerde wijze vast gesteld kunnen worden. Voordat de concentratie vrij CN in de omgevings- of in bodemlucht in aanmerking kan komen als een parameter voor een Interventiewaarde, is veldonderzoek nodig om informatie te verkrijgen over:
- HCN concentraties in bodem- en omgevingslucht op verontreinigde terreinen;
- HCN achtergrond concentraties in bodem- en stedelijke lucht;
- een betrouwbare, indien mogelijk eenvoudige, procedure om bodem geëmaneerd HCN te bepalen in het veld in omgevingslucht en/of in bodemlucht.

Alvorens te besluiten tot een Interventiewaarde voor complex CN, gebaseerd op een eenmalige piekinname van grond door kinderen, kan aangevoerd worden dat de acute ingestie limiet van complex CN nog te onzeker is en dat gewacht dient te worden op nieuwe informatie hierover.
Eventueel kan ook onderzoek gericht worden op Interventiewaarden voor CN species gebaseerd op hun concentratie in poriewater, en de link hiervan met humane blootstelling.
Gezichtspunt 2: Nieuwe Interventiewaarden voor CN dienen en kunnen gebaseerd worden op de huidige kennis en kunnen later altijd aangepast worden aan in de toekomst verworven nieuwe kennis. De huidige kennis biedt de mogelijkheid de Interventiewaarde te baseren op de boven de grond te meten HCN concentratie met de TCA als grenswaarde. Met andere woorden de Interventiewaarde van: 0.025 mg vrij CN/m^3. Deze Interventiewaarde geeft een short cut naar de blootstelling bij inhalatie en wordt niet gehinderd door het bestaande gebrek aan informatie betreffende het gedrag van CN species in de bodem en de emanatie van vrij CN uit de bodem. Een bijkomend voordeel van luchtmetingen in het veld is dat het uit opgelost complex CN (na fotodegradatie vrijkomende HCN) mogelijk emanerende HCN meegemeten wordt.
Verder is er de mogelijkheid een Interventiewaarde voor complex CN te stellen op 4.8 mg CN/kg grond gebaseerd op de vrij extreme worst case schatting van de blootstelling van kinderen bij een eenmalige piekinname van gronddeeltjes.

Grondwater Interventiewaarden
Zowel complex CN als SCN kunnen na consumptie van ongezuiverd grondwater leiden tot overschrijding van de TDI. Mogelijke nieuwe grondwater Interventiewaarden zijn voor complex CN 12 mg CN/l en voor SCN 0.075 mg CN/l. Beide species worden gezamenlijk geanalyseerd met de EPA 335.3 analyse van total CN. Dus een mogelijke nieuwe Interventiewaarde is 0.075 mg total(EPA) CN/l grondwater.
Bij de afleiding van de huidige Interventiewaarden, 1.5 mg CN/l voor elk van de CN species (Tabel 1), werd uitgegaan van een volwassene die twee liter ongezuiverd grondwater per dag consumeert, een TDI van 0.05 mg vrij CN/kg b.w./dag, en de aanname dat de CN species na ingestie reageren als vrij CN. Uitgaande van dit laatste zouden alle CN species samen de TDI van vrij CN niet mogen overschrijden. Aangezien total(EPA) CN alle CN species bevat ligt het voor de hand de huidige Interventiewaarde hierop af te stemmen en te vereenvoudigen tot 1.5 mg total(EPA) CN/l. Dit laatste kan, gezien de resterende onzekerheden over de

kwantificering van de toxiciteit van de CN species, eveneens beschouwd worden als een optie voor een nieuwe Interventiewaarde.
Een andere benadering is om voor de Interventiewaarde van grondwater de ecotoxicologische risico limieten voor oppervlakte water te gebruiken (Verbruggen et al., 2000). Deze benadering resulteert in de laagste Interventiewaarden voor vrij CN 0.031 mg CN/l en voor complex CN 0.029 mg CN/l, en de hoogste voor SCN 4.5 mg CN/l. Vereenvoudiging tot 0.03 mg total(EPA) CN/l is mogelijk.

Implicaties
De gegeven aanbevelingen lopen sterk uiteen. Namelijk van aanvullend veld onderzoek alvorens de huidige Interventiewaarden te wijzigen, tot verschillende alternatieven voor mogelijke nieuwe Interventiewaarden (Tabel 4). De laatsten kunnen in de toekomst gewijzigd worden met het beschikbaar komen van nieuwe kennis. Het valt buiten het doel en de scope van de onderhavige studie deze implicaties te bespreken, of een voorkeur-volgorde te geven aan de verschillende aanbevelingen, of een ervan te selecteren als de meest pragmatische.

Tabel 4 Mogelijke alternatieven voor nieuwe Nederlandse Interventiewaarden voor historische verontreinigde gronden gebaseerd op geschatte humane potentiële risico's; CN achtergrondconcentraties; en maximale CN concentraties waargenomen na 1990 op verontreinigde terreinen.

Parameter	Blootstelling-route	Mogelijke nieuwe Interventiewaarde	Achtergrond concentratie	Max. bij bodem-verontreiniging
Bodem				
vrij cyanide in omgevingslucht (door bodemverontreiniging)	inhalatie	0.025 mg CN/m^3 (TCA)	natuurlijk wereld gem.: 1.6E-4 tot 2.0E-4 CN/m^3; stadslucht: g.g. [1)]	2 mg CN/m^3
complex CN in de bodem	eenmalige piekinname van grond	4.8 g CN/kg	g.g.	40 g CN/kg
Grondwater				
complex CN in grondwater	consumptie ongezuiverd grondwater	12 mg CN/l	g.g.	34 mg CN/l
thiocyanaat in grondwater	consumptie ongezuiverd grondwater	0.075 mg CN/l	g.g.	90 mg CN/l
total(EPA) CN in grondwater	consumptie ongezuiverd grondwater	0.075 mg CN/l of 'nieuwe-huidige': 1.5 mg CN/l	mg CN/l: complex CN g.g. vrij CN g.g. SCN < 0.001	mg CN/l: complex CN 34 vrij CN 0.15 SCN 90

1) g.g. = geen gegevens.

Extended summary

Introduction

General occurrence of cyanides

Cyanides (indicated in this report as CN) comprise a wide range of chemicals, which have the C≡ N group in common. Some cyanides, e.g. cyanogenic glycosides, are formed naturally, while other cyanides are synthetic e.g. acrylonitrile (Homan, 1987). Cyanides, which differ widely in their reactivity, can be toxic by origin and may release free cyanides upon digestion or be considered chemically inert under general environmental, and specific human or animal physiological conditions. Cyanides were and are widely used in the chemical industry and can be formed as waste by-products.

In the Netherlands the last dumping of CN containing wastes took place 20 or more years ago. In principle, all soil contamination with CN is historical, and is generally restricted to small areas. The most widespread contamination with cyanides is from manufactured gas plants (MGP) wastes[2], in which cyanides are not used but inadvertently formed. Also common is contamination by wastes or spillage from cyanides used in metallurgical processes and photographic industries (MPI wastes). The CN in MGP waste is predominantly chemically inert, whereas in MPI wastes, most of the CN is chemically active at the moment of dumping. Although not subject to environmental legal restrictions, some applications of CN in the past and at present should be mentioned: alkali ferrohexacyanide as anti-caking amendment in road salt, ammonium-ferri ferrohexacyanide (AFCF) as a feed additive for cattle exposed to roughage contaminated by radio caesium to reduce contamination of milk and meat products, and calcium cyanamid as a N fertiliser.

The Dutch regulatory system and CN

In the framework of the Dutch Soil Protection Act two generic risk-based classification thresholds have been defined: the Target Value for clean soils, and the Intervention Value for (historically) seriously contaminated soils. The Intervention Value is based on potential risks to humans and ecosystems (Swartjes, 1999; VROM, 2000). Due to lack of knowledge about the risks for ecosystems, the derivation of the current CN Intervention Values has been based solely on human exposure-risks. Taking a worst-case approach for estimating potential human exposure led to the realisation that this approach would need future review, which would possibly lead to adjustments of the current CN Intervention Values (Berg van den, 1997). In a recent review study it was again concluded that information was still insufficient to determine ecotoxicological threshold values. An exception might be made for groundwater, when it is subjected to criteria applied to surface water (Verbruggen et al., 2000). In general terms, it can be concluded that the CN Intervention Values will be based for the time being on human-exposure risks.

Objective

This study focuses on the potential human exposure to cyanides due to historical CN soil contamination. The objective here is to evaluate the current Dutch Intervention Values of soil contamination by CN (Table 1), and if relevant to propose their possible adjustment. In

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[2] MGPs produce several kinds of waste; in this report MGP waste refers to CN-bearing waste from MGPs.

addition, a check will be made to see if gaps in knowledge on environmental occurrence and behaviour of CN hinder the derivation of potential human exposure to CN soil contamination.

Method
A literature review, discussions and meetings with researchers, technical and regulatory experts resulted in a study and critical assessment of CN soil contamination sources, CN speciation and pathways of CN leading to human exposure.
The potential human exposure to historical CN soil contamination is estimated from the data obtained and new insights gained. This exposure is compared with the tolerable levels of CN exposure as defined by RIVM's Centre for Substances and Risks Assessment (CSR - Dutch abbreviation) viz. the Tolerable Daily Intake (TDI) and the Tolerable Concentration in Air (TCA). The outcome of this comparison is taken as a base for the evaluation of the current Intervention Values of CN historical soil contamination. Also considered is the need for further research prior to a possible revision of the current Intervention Values.
The disposal of industrial wastes in the past was generally not systematically planned and CN contamination of soil and groundwater shows a large variation at most sites. No attention has been paid to this latter aspect. Namely for exposure estimates observed maximum contamination concentrations have been assumed to occur over large areas.

Table 1 Current Dutch CN Target and Intervention Values for soil and groundwater (van den Berg, 1995; Swartjes 1999).

Compound	Soil Target Value	Soil Intervention Value	Potential human exposure to CN soil contamination	Groundwater Target Value	Groundwater Intervention Value 1)
	mg CN/kg		Fraction due to vegetable consumption	mg CN/l	
free CN	0.001	20	100%	0.005	1.5
complex cyanide	0.005	pH<5 650	n.d. 2)	0.01	1.5
		pH≥5 50	100%		
thiocyanate	n.d. 2)	20	100%	n.d. 2)	1.5

1) Intervention Value based on consumption of untreated groundwater by adults at a rate of 2 litres per day, and on the assumption that cyanide compounds in drinking water can react as free CN.
2) n.d. = not determined and/or no data

Current Dutch Intervention Values for CN

CN species
With respect to the current Target Values and Intervention Values for CN the Dutch regulatory system distinguishes three separate forms of CN and two soil acidity (pH) categories for one of these forms, i.e. free CN; complex ironhexacyanides in soils with pH < 5 and pH ≥ 5 and thiocyanates.

Human toxicological threshold values
Human physiological and toxicological data are scarce for the CN species under consideration. For this reason, uncertainty multipliers have been used in the derivation of the Tolerable Daily Intake (TDI) and the Tolerable Concentration in Air (TCA). The TDI was set at 0.05 mg free CN/kg b.w. per day, for solid or dissolved complex CN at 0.8 mg CN/kg b.w.

per day, and for SCN at 0.005 mg CN/kg b.w. per day. The TCA was set at 0.025 mg HCN/m^3, while the international Maximum Air Concentration at workplaces is 11 mg HCN/m^3 (Meijerink, 1999).

Soil Intervention Values
The current soil Intervention Values were derived using the CSOIL model for the CN forms mentioned (Table 1). Striking is that according to the CSOIL calculations practically 100% of the human exposure to CN soil contamination is due to ingestion of vegetable food. It was assumed that CN concentrations in plants were equal to CN concentrations in soil-pore water, which contained a fixed fraction of CN present in the soil (van den Berg, 1995).

Groundwater Intervention Values
The current Dutch Intervention Values for groundwater have been based on the assumption that all CN species ingested by humans act as free CN. This results in an Intervention Value of 1.5 mg CN per litre for each of the three CN species considered, i.e. free CN, complex CN and SCN (Table 1).

CN containing waste and materials found in soils

CN species and main constituents in MGP waste
Complex iron cyanides: The solid MGP cyanide-bearing wastes are characterised by high total cyanide concentrations; levels of 10 g to more than 20 g total CN/kg have been observed in the United States (Theis et al., 1994) and in the Netherlands maxima of up to 50-80 g total CN kg (Hoppener et al., 1983). Complex ironhexacyanides are the predominant cyanide species in MGP waste after gas purification and remain predominant after weathering over long periods upon disposal on land. More than 97% of the cyanides present in these wastes are found in the form of Prussian blue, i.e. ferri ferrohexacyanide $Fe_4[Fe(CN)_6]_3$.
Thiocyanate: SCN concentrations are reported to range from 0.3 g to 26 g CN/kg (Hoppener et al., 1983; Wilson and Hudson, 1980).
Soluble simple cyanides: Samples of MGP waste, with 24 - 45 g total CN per kg, contained soluble simple cyanides [e.g. KCN, $Ca(CN)_2$] at concentrations of 0.5 - 0.8 g CN per kg (Wilson and Hudson, 1980).
Free cyanide: Free cyanide, if ever present in MGP wastes, would be expected to have been lost through volatilisation (Theis et al., 1994); probably the little free CN not removed from the crude gas remained in the gas (Brettschneider, 1995).
Other constituents: Other compounds in MGP waste: water, around 20%; 30 - 50% sulphur, mainly elemental S; ferri oxide, 10 - 20%; ferro oxide, 5 - 6%; sand and clay, 4 - 8%; ammonium sulphate, around 2%; lime and gypsum, collectively around 2%; concentraitions of 0.002 – 0.008% have been found for Cd, Cr, Cu, Ni, Pb, and Zn in American wastes (EEI, 1984; Hoppener et al., 1983).
pH: The pH in MGP waste and at contaminated sites ranges from 2 - 5. It is not clear whether the acidity of the wastes is a result of the manner in which they were generated or that the acidity was produced subsequently through biological and/or chemical reactions (Theis et al., 1994).

MPI wastes
MPI wastes are generally liquid and have often been dumped near the industrial site, or are added to solid wastes and dumped at waste disposal sites or used as landfills. Wastes from metal-processing operations may contain simple cyanides up to 200 g CN per kg, mostly as

NaCN, cyanates up to 25% and barium up to 30% (Lagas et al., 1982). A wide variety of compounds is used, having been dumped by the photographic industries; these include ferri ferrohexacyanide; potassium ferrihexacyanide; acetonitrile; and sodium cyanide (Homan, 1987).

Non-waste materials containing CN

To ensure uniform spreading road salt is commonly amended with an anti-caking agent sodium ferrohexacyanide $Na_4Fe(CN)_6$ (Ohno, 1996), or potassium ferrohexacyanide $K_4Fe(CN)_6$ (Vries de, 1998). Concentrations vary from 10 - 60 mg CN/kg road salt, of which 2% - 5% of the total CN is in the form of soluble simple cyanides (Ohno, 1996; Brinkmann et al., 1997).

The first commercially produced N fertiliser was calcium cyanamid (CaNCN), also called lime nitrogen (SKW, 1998). On contact with moisture, CaNCN is transformed in the soil within a few days into non-CN containing compounds (Koning, 1965). CaNCN is used today on a limited scale.

A counter-measure to reduce or prevent the contamination of products (milk and meat) from animals exposed to feed or grasslands contaminated with radioactive caesium (^{134}Cs and ^{137}Cs after the Chernobyl accident in 1986) was to incorporate Prussian blue in the animal diet (Hove et al., 1995). This resulted in the spread of Prussian blue (and caesium)-containing faeces in the agricultural environment (Vandenhove et al., 2000).

Chemistry and concentration of CN in contaminated soils

Free CN

The lifetime of dumped free CN and simple cyanides at high or low concentrations in the soil is limited. At high concentrations leaching and emanation of free CN will be dominant at first, with at the same time formation of metal hexacyanide complexes, generally with iron and or manganese present in the soil solution (Lagas et al., 1982; Keizer et al., 1995). Later, and/or at lower concentrations of free CN, biochemical breakdown will also take place (Fuller, 1985). Probably 6 to 10 years after contamination the concentrations of free CN in the soil will no longer be significantly increased.

Ferri ferrohexacyanide and several other inert complex cyanides will be the main CN species present in historically contaminated soils. Little free CN can be liberated from these species, and maximum reported concentrations are 0.15 mg free CN per litre in groundwater (Meeussen, 1992; Kjeldsen, 1999) and 1-2 mg HCN per m^3 in soil air or in ambient air (Hoppener et al., 1983; Jans, 1999).

Complex cyanides

The lifetime of easily soluble complex alkali ferrohexacyanides in the soil is limited since a reaction into and precipitation as ferri ferrohexacyanides or manganese ferrohexacyanides will occur. Laboratory studies indicate that dissolved complex metal-hexacyanides can also be broken down to some extent to CO_2 and ammonium (Barclay et al., 1998; Hommelgaard et al., 1998). Ferri ferrohexacyanides and manganese ferrohexacyanides are biochemically inert stable compounds which will remain in the soil for many years (Meeussen, 1992; Keizer et al., 1995).

The mobility of ferrohexacyanides in the soil at a low pH is probably limited to short-distance transport in colloidal form downward with the water fluxes in the soil. The complex CN colloids will precipitate during transport on the surface of soil structural elements with a change in pH, or when the velocity of the water flux deeper in the soil profile decreases

(Mansfeldt et al., 1998). At high pH values ferri ferrohexacyanide can dissolve and be transported with capillary rising water to the soil surface. Subsequently, wetted surfaces became stained (Prussian) blue on evaporation of the water (Shifrin et al., 1996; Barclay et al., 1998).
The maximum concentration of solid complex CN encountered in contaminated soil is 40,000 mg CN per kg, in contaminated groundwater 34 mg CN/l of dissolved complex CN (Meeussen et al., 1992).
Concentrations of complex CN in pore water (in the unsaturated zone) of CN contaminated soils are not reported in the literature reviewed. Laboratory experiments indicate that these concentrations are of the same order of magnitude as those found in groundwater at such sites. It should be noted that in these experiments dissolution of CN is likely to be better than in the field, while the breakdown and complexation of liberated CN is probably less than under field conditions.

SCN
Most publications on thiocyanate mention that little is known about its environmental effects or fate (Stratford et al., 1994; Boening and Chew, 1999). Its formation by reaction of free cyanide under anaerobic conditions with sulphur or sulphur-containing compounds is possible (Materassi et al., 1977; Newton, 1977). In the Netherlands thiocyanates have been measured at some former MGP sites. The reported maximum SCN concentration in groundwater is 32 mg CN per l (Brettschneider and Engelen, 1998). Still unpublished maximum thiocyanate concentrations of 90 mg CN/l groundwater have been indicated, with around 30 mg CN/kg soil indicated in anaerobic soil and 7 mg CN/kg soil in topsoil (Brettschneider, 1999). SCN is considered to be a very mobile compound (Kd 1 to 1.5); its behaviour in anaerobic soil layers without biological activity can be compared to that of chloride anions (Brettschneider, 1999). In the other articles reviewed little or no attention is given to thiocyanates at former MGP and other CN-contaminated sites, though their (theoretical) occurrence is mentioned by several authors. Generally, SCN is broken down to S^{2-} and (hydrogen)cyanate HOCN, which is hydrolysed to CO_2 and NH_3 (Stratford et al., 1994).

Simple cyanides and calcium cyanamid in agriculture

Laboratory experiments with NaCN, KCN and $Ca(CN)_2$ show that CN^- at low concentrations in the soil is converted to NO_3^-, a source of N for plants. Based on pot experiments and some small-scale field tests, simple cyanides were judged to have great potential as N fertilisers and were erroneously reported to be already used as such (Fuller, 1985). This led to further misinterpretations of CN^- and compounds which release CN^- as being non-phytotoxic (Hsu, 1994; Seijger, 1995; Wen et al., 1997). However, as discussed below, laboratory experiments show that CN^- is phytotoxic at relatively low concentrations (Grossmann and Kwiatkowski, 1995). Even natural occurring levels of free CN in the rhizosphere can be toxic to certain plants (Schippers et al., 1990; Antoun et al., 1998).
Calcium cyanamid is sold under the commercial name of lime nitrogen, a fertiliser with herbicidal effects. Its herbicidal effects are due to the phytotoxicity of the intermediate conversion product, hydrogen cyanamid, which is hydrolysed within a few days into urea. The last is hydrolysed to ammonium bicarbonate. Urea and ammonium are used by plants as a nitrogen source.

Cyanides in plants, phytotoxicity and CN species in vegetable food

Background concentrations
In the early 1980s free cyanide was discovered to be a co-product of the endogenous synthesis of the plant hormone, ethylene. Consequently, endogenously co-produced free cyanides are present in all plants; depending on species, growth stage and plant part at concentrations ranging from 0.05 to 0.5 mg free CN/kg fresh weight (Peiser et al., 1984; Manning, 1988; Yip and Yang, 1988; Grossmann, 1996).

Cyanogenic plants
A separate group of plants, called 'cyanogenic', contain CN in endogenously formed nitriles. More than 1000 plant species in about 100 plant families are cyanogenic and toxic to humans (Conn, 1979; Eisler, 1991; Scheuer, 1992). Specifically these plants have the potential to release free cyanide upon damage of their cells. Consumption of cyanogenic plants is only possible after special preparatory measures to remove free CN and its sources. It is not known if CN levels in cyanogenic plants are enhanced by soil contamination, but considering the special preparation before their consumption, it does not seem important and therefore no attention is given to this topic.

Free CN
Free CN^- can be taken up from the soil solution by plants, largely as a chelate linked to a metal (Wallace et al., 1971). Exogenously induced elevated free cyanide concentrations in plant tissues inhibit respiration and several physiological processes. In general terms, a two- to fourfold increase of the natural free CN concentration in plant tissues is stated to have phytotoxic effects (Grossmann, 1996 and 1998). The information retrieved on enhanced concentrations of free CN in plants induced by root uptake of free CN is limited to short-term hydroponic experiments with grass seedlings. Concentrations of 8 – 16 mg free CN/l in rooting media led within four days to growth reductions of 50 - 80% and concentrations of 0.7 – 1.2 mg free CN/kg fresh weight in plants (Grossmann and Kwiatkowski, 1995). Free CN concentrations in the soil solution of historically contaminated soils are estimated to reach a maximally much lower concentration, namely, the aforementioned maximum of 0.15 mg free CN/l observed in groundwater. Consequently, a worst-case estimate of free CN concentrations in vegetable food enhanced by soil contamination is 1 mg free CN/kg fresh weight.

Other CN species
Little or no information has been retrieved on other (than free) CN species, such as SCN and complex cyanides with regard to their uptake and conversion by plants, nor on their effect on CN or SCN levels in plants. Toxic levels of SCN and other CN species for humans or domesticated animals have not been reported in food or feed from cultivated non-cyanogenic plants. If such toxic levels occur, they will be coupled most likely to phytotoxicity and diseased plants, which will not be used as food.

New considerations on CN Intervention Values

Natural background and CN concentration in contaminated soils and groundwater
There are several natural sources of CN species in soils, e.g. roots and debris of cyanogenic plant species release free CN and intermediate CN-containing compounds upon decomposition. SCN can be released by plant material from Cruciferae. Also several bacteria strains produce free CN in soils. At the same time CN species are converted by soil organisms to non-CN species. The result will be a natural dynamic equilibrium in the soil in which CN species are present but do not accumulate.
In the CN contamination studies reviewed the CN natural background in the soil or groundwater has been ignored. Thus a well-founded comparison of concentrations of CN species in contaminated soils with background concentrations is not possible. An exploratory comparison (Tables 2 and 3) shows that SCN and complex CN can be present in contaminated soils at concentrations exceeding the natural background by a factor up to 1E3 and 1E7, respectively. The same tables indicate that it is uncertain if free CN concentrations in historically contaminated soils exceed the range of natural background concentrations. Consequently, an Intervention Value for free CN in soil or groundwater of historically contaminated soils does not seem appropriate prior to obtaining evidence that the natural concentration range is exceeded significantly at some historically contaminated sites.

CN speciation and solubility in contaminated soils
Field research shows that in soils practically all CN remaining from historical contamination is present as insoluble complex Fe or Mn hexacyanides (Meeussen, 1992; Keizer et al., 1995; Staritsky et al., 1992). This also applies to anaerobic water-saturated soil layers, though dissolved thiocyanates may be present in these layers too (Meeussen, 1992; Brettschneider et al., 1999).
The complex cyanides in soils are probably practically inert, apart from possible partial transformations from one to another insoluble complex cyanide. No relationships have been established for historical CN soil contamination from which the concentration of dissolved hexacyanide or free cyanide in pore water or in groundwater can be derived (Kjeldsen, 1999).
The current Intervention Values for complex CN differ in soils with $pH < 5$ and those with $pH \geq 5$. This dependence of the Intervention Value on the soil pH is based on the theoretical thermodynamical higher solubility of ferri ferrohexacyanide with increasing pH (Meeussen, 1992). However, both Meeussen and Keizer mention that the solubility of complex CN and its concentration in groundwater do not depend solely on soil pH, but on several other factors such as concentration of Mn, hydrological factors and dissolution kinetics (Meeussen, 1992; Keizer et al., 1995). Consequently, there is no strong argument to make a distinction in the Intervention Values for complex CN among soils based only on soil pH.

Free CN in air
Laboratory data indicate that free CN is liberated upon photodegradation of dissolved complex CN (Meeussen et al., 1992). No information has been found with indications that photodegradation of dissolved complex cyanides and subsequent enhanced emanation of free CN play a significant role under field conditions. During daytime photodegradation might occur at the surface of waterlogged, or moist, soils and in puddles with stagnant water.
The few available data of free CN in soil air and in ambient air in situations of historical CN soil contamination show that concentrations of 1 - 2 mg free CN/m^3 can occur (Hoppener et al., 1983; Jans, 1999). These concentrations are 5 - 10 times below the permissible CN concentration in air at workplaces (MAC) 11 mg HCN/m^3, but exceed the tolerable

concentration in air (TCA) of 0.025 mg HCN/m^3 by a factor of 40 - 80. Consequently, the concentration of free CN in ambient air should be taken into consideration for the Intervention Value of CN. From a regulatory and/or a soil analysis viewpoint, preference should go out to basing such an Intervention Value on CN concentrations in soil or in groundwater. However, this does not seem possible as at present a relationship between CN in soil and/or groundwater and free CN in air has not been identified.
It seems self-evident to consider the possibility of basing the Intervention Value for free CN directly on field measurements of the concentration of HCN in ambient air. Such measurements can include emanating free CN liberated by daylight from dissolved complex cynanides in soil moisture at the soil surface.

CN in vegetable food
The current Intervention Values for CN are based on the assumption of high CN levels in food, enhanced by soil contamination (van den Berg, 1995). However the concentration of free CN in healthy plants will not exceed a low phytotoxic ceiling. A high estimate of the non-phytotoxic maximum level is 1 mg free CN/kg fresh weight, which can lead to a human exposure of maximally 9% of the TDI. Soil contamination with other CN species will probably also not lead to levels toxic to humans, without plants being affected by phytotoxicity and rejected as food. Thus an Intervention Value for free CN and other CN species cannot be based on food consumption only.

Potential human exposure from maximum historical soil contamination
Method: The maximum human exposure is estimated by coupling the CSOIL default values for soil properties and human behaviour (Swartjes,1999) to the maximum concentrations of CN species observed in historically contaminated soils. This was done for the exposure routes of inhalation of soil emanated HCN, ingestion of soil particles and ingestion of untreated groundwater. In addition, the exposure was evaluated following a one-time peak soil ingestion of 5 g by children (Calabrese et al., 1997; Kempchen, 2000).
Soils: Free CN in ambient air can exceed the TCA and then lead to exceedance of the TDI. Exposure to free CN via other routes is negligible (limited exposure via food consumption being possible as mentioned above). Exposure to the maximum concentration of complex CN and SCN will lead to less than 0.1% of the TDI for both compounds (exposure to these compounds via food consumption is considered negligible as mentioned above). Except for a very conservatively estimated exposure of 8.5 times the tolerable acute intake of complex CN, possibly resulting from a one-time peak ingestion of soil by children.
Groundwater: To estimate the maximum potential exposure a consumption of 2 l per day of untreated groundwater is assumed for adults, and 1 l per day for children. The calculated exposure risk is highest for children, i.e. an exposure equal to 0.2 times the TDI for free CN; up to 5 times the TDI for complex CN; and up to 1200 times the TDI for SCN. An Intervention Value for free CN, as it currently exists, does not seem necessary. Intervention Values for the other two CN species are required when using consumption of untreated groundwater as a standard.
Pore water: No field information is available on CN species in pore water, nor on the correlation between pore water concentration of CN and the consequent potential exposure of humans to CN. To conclude, at this stage of knowledge CN Intervention Values cannot be based on the concentration of CN in pore water.

Range of CN Intervention Values in four countries and contamination maxima
Inventory: Although an international inventory of Intervention Values has remained outside the scope of this study, some publications at hand have been reviewed, these contained information on threshold levels in Belgium (Nouwen et al., 1999), Canada (CCME, 1997) and the United Kingdom (DOE, 1988; NTU, 1998).

Table 2 CN species in soils, natural background, reported maxima and threshold values.

CN species	Natural background in soils	Maxima observed in historically contaminated topsoil	Range of threshold values for four countries
	mg CN/kg soil		
Free CN	<0.005 – 1	0.045 [1]	0.9 – 60
Complex CN	<0.005 –1.2	40,000	12 – 650
SCN	0.005	7	20 - p.m. [2]

[1] High estimate based on maximum concentration in groundwater
[2] p.m. = risks mentioned but not considered to be of any importance
Sources - Natural background: Beyer, 1990; Weuffen et al., 1990. Maxima: Meeussen, 1992; Brettschneider, 1999. Threshold Values: Berg van den, 1995; Nouwen et al., 1999; NTU, 1998.

Soils: All the threshold values of free CN and SCN are much higher than the maxima observed in historically contaminated soils. The maximum concentration of complex CN observed in these soils is found within the depicted range of threshold values (Table 2).
It is striking to see that the emanation of HCN from contaminated soils is not considered to be a potential exposure requiring a threshold value.
Groundwater: Little or no attention is given to groundwater Intervention Values and the consumption of untreated groundwater in the reviewed publications. The derived groundwater threshold values for the Netherlands and Belgium differ by more than a factor of 20 (Table 3). The maximum free CN and SCN concentration observed in groundwater of contaminated soils are found within the depicted range of threshold values. The maximum concentration of complex CN of contaminated soils observed in groundwater exceed Dutch and Belgian threshold values.
Intervention Values: The threshold values of the three countries mentioned and the Netherlands show a wide range (Tables 2 and 3), and do not offer a base for revision of the Dutch Intervention Values.

Gaps in knowledge and determination of the CN Intervention Value
The most crucial knowledge lacking for determining the potential human exposure to CN species due to soil contamination seems to be:
- information on whether enhanced levels of free CN occur in ambient air at contaminated sites (in fact the existing information on this factor is so scant that it may be too premature to decide to base an Intervention Value on this factor);
- field information on whether enhanced levels of free CN, thiocyanate or other potentially toxic CN substances can occur in plants cultivated on soil contaminated with CN.

Table 3 CN species in groundwater, natural background, reported maxima and threshold values.

CN species	Natural background	Max. observed in historically soils	Current Dutch Intervention Values	Belgian threshold values
	mg CN/l groundwater			
Free CN	n.d.	0.15	1.5	0.07 1)
Complex CN	<0.01 – 0.02	34	1.5	
SCN	n.d.	90	1.5	n.c. 2)

1) Sum of free CN + complex CN

2) n.c. = not considered in reviewed publication

Conclusions

Soil

The current Dutch Intervention Values for soils have been based on the assumption that very high free CN levels in plant tissues can occur due to soil contamination. This review shows that this assumption is not correct and that consumption of vegetables does not lead to exceeding the TDI of any of the CN species. The same holds for the pathways' soil ingestion and inhalation of soil dust. Except for a one-time peak ingestion of soil by children, which very conservatively estimated may result in an exposure of 8.5 times the tolerable acute intake of complex CN. When calculated according to CSOIL default values, the only pathway leading to exceedance of the TDI/TCA is inhalation of ambient air containing soil-emanated HCN. It is not yet possible to predict the free CN concentration in ambient air from soil parameters. Present-day background concentrations are also largely unknown and concentration enhancement by soil contamination may be difficult to distinguish from enhancements by traffic, etc. As long as this information is lacking it may be premature to select the CN concentration in ambient air for the definition of a soil Intervention Value.

Groundwater

The consumption of untreated groundwater contaminated with CN can be a potential risk for adults and even more for children. The observed maximum concentrations of complex CN, and of SCN can lead to respective exposures of children of 2.8 and 1200 times the TDI. The observed maximum concentration of free CN in groundwater can lead to a maximum exposure for children of 0.2 times the TDI, which is negligible compared to that for complex CN and thiocyanate.

Recommendations

Soil Intervention Values

Viewpoint 1: Additional research is required to obtain sufficient knowledge to determine new Intervention Values for CN. Before the free CN concentration in ambient or in soil air can be considered as a parameter for an Intervention Value, field research will be needed to obtain information on:

- HCN concentrations in soil and ambient air at contaminated sites;
- HCN background concentrations in soil and urban air;

- a reliable, and if possible, simple procedure to determine soil-emanated HCN air in the field in ambient air and/or in soil air.

Before deciding on an Intervention Value for complex CN based only on a one-time peak ingestion of soil by children, it can be argued that the tolerable acute intake limit of complex CN is yet too uncertain, and that we will have to await new information on this. Research can also focus on Intervention Values for CN species based on their concentration in pore water and on establishing a link between this parameter and human exposure.

Viewpoint 2: New Intervention Values for CN have to be based on present knowledge and may be changed again later depending on newly acquired knowledge in the future. Present knowledge offers an opportunity to base the Intervention Values on the measured concentration of free CN in the air above the soil, with the TCA as the threshold level. In other words, the Intervention Value of 0.025 mg free CN/m^3 ambient air. This Intervention Value provides a short cut to inhalation exposure and is not hindered by the existing lack of information on the behaviour of CN species in the soil and on emanation of HCN from the soil. Another advantage is that it can include emanated free CN liberated by photodegradation of complex hexacyanides dissolved in moisture at the soil surface. An additional option is to set an Intervention Value for complex CN at 4.8 g CN/kg soil, based on the very worst estimation of the risk to children of a one-time peak ingestion.

Groundwater Intervention Values

Dissolved complex CN as well as SCN can, after consumption of untreated groundwater, lead to exceedance of the TDI. Possible new Intervention Values for groundwater are for complex CN 12 mg CN/l , and for thiocyanate 0.075 mg CN/l. Both species comprise part of the EPA 335.3 analysis of total CN, making a new Intervention Value of 0.075 mg total(EPA) CN/l groundwater also possible.

The current Intervention Values for groundwater, 1.5 mg CN/l for each CN species (Table1.1), were based on consumption of 2 l untreated groundwater per day by adults, a TDI of 0.05 mg free CN/kg b.w. per day, and the assumption that after ingestion all CN species would react as free CN. Extending this reasoning: all CN species taken together should not exceed the TDI for free CN. As total(EPA) CN includes all CN species, an obvious adaptation of the current Intervention Values for groundwater is to simplify these to 1.5 mg total(EPA) CN/l. This is evidently an option for a new Intervention Value, more so in view of the remaining uncertainties of the human toxicity of CN species.

A different approach is to use the ecotoxicological risks limits of surface water for the derivation of the Intervention Value of groundwater (Verbruggen et al., 2000). This approach results in the lowest Intervention Values for free CN 0.031 mg CN/l and complex CN 0.029 mg CN/l, and the highest for SCN 4.5 mg CN/l. Simplification to 0.03 mg total(EPA) CN/l is possible.

Implications

The recommendations diverge widely; i.e. from additional research prior to changing the Intervention Values to different alternatives for possible new Intervention Values (Table 4). These may be changed in the future as new knowledge becomes available. The decision on which of these options to choose will have large implications. It is beyond the objective and scope of the present study to discuss these implications and to rank the given recommendations, or to select one of these as being the most pragmatic.

Table 4 Possible alternatives for new Dutch Intervention Values for historical CN soil contamination based on estimated potential human risks; CN background data; and maximum CN concentrations observed after 1990 at contaminated sites.

Parameter	Exposure pathway	Possible new Intervention Value	Background concentration	Max. due to soil contamination
		Soil		
Free cyanide in ambient air (due to soil contamination)	inhalation	0.025 mg CN/m^3 (TCA)	natural global av.: 1.6E-4 to 2.0E-4 mg CN/m^3; urban air: n.d. [1)]	2 mg CN/m^3
complex CN in soil	one-time peak soil ingestion	4.8 g CN/kg	n.d.	40 g CN/kg
		Groundwater		
Complex CN in groundwater	drinking untreated groundwater	12 mg CN/l	n.d.	34 mg CN/l
Thiocyanate in groundwater	drinking untreated groundwater	0.075 mg CN/l	n.d.	90 mg CN/l
Total(EPA) CN in groundwater	drinking untreated groundwater	0.075 mg CN/lor ‘new-current’: 1.5 mg CN/l	mg CN/l: complex CN n.d. free CN n.d. SCN < 0.001	mg CN/l: complex CN 34 free CN 0.15 SCN 90

[1)] n.d. = not determined and/or no data

1. Introduction

Current Dutch Intervention Values of cyanides

Cyanides (CN) comprise a wide range of chemicals, which have the -C≡ N group in common (Table 2.1; Appendix 1 and 2). Some, for example, cyanogenic glycosides, are formed naturally endogenously in several plants; other cyanides are synthetic e.g. acrylonitrile. Industrial production of cynanides takes place by a catalytic reaction of ammonia and methane at elevated temperatures.
With respect to the current Target Values and Intervention Values of CN the Dutch regulatory system distinguishes three separate forms of CN and two levels of soil pH. Namely: free CN; complex ironhexacyanides in soils with pH < 5 and in soils with pH ≥ 5; and thiocyanates. The current soil Intervention Values derived with the CSOIL model for the three forms of CN mentioned (Table 1.1) are inconsistent in some respects with the knowledge about their toxicity and their behaviour. Striking is that according to the CSOIL calculations practically 100% of the human exposure to CN soil contamination is due to ingestion of vegetable food, which is assumed to have been contaminated during its growth through uptake of CN via its root system. In the effort to derive the current Intervention Values for CN it was recognised beforehand that the parameter values estimated for CN in CSOIL came close to a worst-case approach and deserved detailed review possibly leading to future adjustments (van den Berg and Roels, 1991; van den Berg, 1995; Kreule et al., 1995; van den Berg, 1997; Swartjes et al., 1998).

Table 1.1 Current Dutch Target and Intervention Values of CN soil contamination and major exposure route, as established with CSOIL (Berg van den, 1995; Swartjes, 1999).

Compound	Soil Target Value	Soil Intervention Value	Potential human exposure to CN soil contamination	Groundwater Target Value	Groundwater 1) Intervention Value
	mg CN/kg		Fraction due to vegetable consumption	mg CN/l	
Free CN	0.001	20	100%	0.005	1.5
Complex cyanide	0.005	pH<5 650	n.d. 2)	0.01	1.5
		pH≥5 50	100%		
Thiocyanate	n.d. 2)	20	100%	n.d. 2)	1.5

1) Intervention Value based on consumption of untreated groundwater by adults at a rate of 2 l per day, and on the assumption that cyanide compounds in drinking water can react as free CN.
2) n.d. = not determined and/or no data

Objective

This study focuses on the human exposure to all and any of the cyanides (indicated in this report as CN) due to historical CN soil contamination[3]. The objective is to evaluate the current Dutch Intervention Values of soil contamination by CN, and if relevant to propose their possible adjustment[4]. It will be checked if gaps in knowledge hinder the derivation of potential human exposure to CN soil contamination.

Method

A study and critical assessment is made of sources of CN soil contamination, its speciation and of the consequent dispersal, chemical transformation, and pathways of CN leading to human exposure. This is achieved by a literature review and discussions with researchers of plant physiological and environmental behaviour of CN and with environmental technologists confronted by soil or groundwater contamination with CN.

Several forms of CN come forward in this review. Emphasis is given to free CN, complex ironhexacyanides and thiocyanates in soils as current Intervention Values are based on these forms of CN. This is in line with common analysis of CN in soils and groundwater, whereby generally a distinction is made between: total cyanide EPA 335.3 (comprising free cyanide, thiocyanate and complex cyanide); total cyanide NEN 6655 (comprising free cyanide and complex cyanide, thiocyanates are not included); free cyanide NEN 6655; and thiocyanates NEN 6655 and ISO 10304-3. These and other analytical methods will not be discussed. Neither are the analytical methods reported with the quantitative CN data cited. Background information on this can be retrieved from the original publications to which is referred.

The human exposure to CN from historical soil contamination is estimated from the obtained data. This exposure is compared with the tolerable levels of CN exposure as defined by RIVM's Centre for (toxic) Compounds and Risks (Dutch acronym: CSR). The outcome of this comparison is taken as a base for the evaluation of the current Intervention Values of CN historical soil contamination. In case the maximum observed historical contamination of a CN species will not result in a potential exposure exceeding Dutch risk limits, an Intervention Value for this species is implicitly considered as superfluous and not needed.

The disposal of industrial wastes in the past was generally not systematically planned and CN contamination of soil and groundwater shows a large variation at most sites. No attention has been paid to this aspect. And for risk evaluations maximum concentrations are assumed to occur over large areas.

Also considered is the need of further research prior to a possible change of the current Intervention Values.

Close to the end of the review process a draft report was sent in December 1999 with a questionnaire to 20 experts in different fields of CN for comment (Appendix 5), and a workshop with experts was held in March 2000 (Appendix 6). Comments made on these occasions have been incorporated into the underlying report, finalising for this moment the evaluation and the recommendations with respect to the CN Intervention Values.

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[3] Soil contamination encompasses in this report : a) contamination of the soil, i.e. the soil matrix together with pore water; b) contamination of groundwater.

[4] In this report the evaluation of Intervention Values is limited to the behaviour of CN in the soil leading to exposure of men to CN. Toxicological threshold values have been derived by (CSR) RIVM (Meijerink, 1999). Intervention Values of CN are obtained subsequently by coupling human exposure to the toxicological threshold values.

Outline of the report

The outline of the report is as follows. In the introduction the objective, the current CN Intervention Values and method are presented (Chapter 1). Some background on CN sources, historical CN soil contamination, and Intervention Values is provided (Chapter 2). To show the complexity and different aspects of CN a critical overview is given of: sources of CN contamination (Chapter 3); concentrations and fate of CN in soils and groundwater (Chapter 4); existing indistinctnesses about the use of cyanides and cyanamids as fertilisers (Chapter 5); CN phytotoxicity and maximum CN concentrations in plants and vegetable food (Chapter 6). The last chapter is of special importance as current Intervention Values are determined by human intake of CN via vegetable food. Chapters 3 through 6 include past and recent findings as well as some new conclusions; readers not interested in this detailed account can neglect these chapters. Namely their contents are condensed (Chapter 7) into new considerations with respect to critical CN soil contamination levels and possible changes in the Intervention Values. The report ends with conclusions and recommendations for further research or possible changes of the current CN Intervention Values (Chapter 8).
The report contains seven appendices, the self-explanatory titles of these are given in the table of contents. Literature references have been placed at the end of the report.

2. Origin of CN and Intervention Values

2.1 CN and CN historical soil contamination

The origin of terrestrial life probably depended on the presence and reactivity of hydrogen cyanide and its derivatives. Paradoxically HCN and cyanides can be toxic to the majority of living matter. Viz. cyanide in its free form, as HCN or CN^- , is a potent and rapid-acting asphyxiant.

Cyanides are widely and extensively used in the manufacture of synthetic fabrics and plastics, in electroplating baths and metal mining operations. Processes in which cyanides are not used but are inadvertently formed, comprise: the production of cokes and gas from coal; power generation from fossil fuels; incineration of wastes. Cyanides differ widely in their reactivity, can be toxic by origin, may release free cyanides upon digestion or may be considered chemically inert under general environmental and human or animal physiological conditions. Soil contamination with cyanides is always anthropogenic, and is linked either to the use of cyanides or to processes in which cyanides are formed.

Table 2.1 Brief overview of main CN species (see Appendix 1 and 2)

Group name	CN species
Free cyanides	HCN, CN^-
Simple cyanides	alkali cyanides: NaCN, etc. metal cyanides: $Zn(CN)_2$, etc.
Complex cyanides	$K_2Zn(CN)_4$, $K_4Fe(CN)_6$, $KFe[Fe(CN)_6]$, $Fe_4[Fe(CN)_6]_3$, etc. dissolved: $Zn(CN)_4^{2-}$, $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, etc.
Cyanates	compound with positive charge linked to $-O-CN^-$
Thiocyanates	compound with positive charge linked to $-S-CN^-$
Cyanamids	H_2NCN, CaNCN, etc.
Nitriles (= organic cyano compounds R-CN)	acetonitrile CH_3CN, cyanogenic glycosides $R_1R_2C(OR_3)CN$, etc.

In the Netherlands all soil contamination caused after 1987 has to be removed as ordained by the `Soil Protection Act', irrespective of the kind and degree of contamination (VROM, 1986). Consequently after 1987 contamination of soils by materials containing CN occurred only in accidental situations, or in situations where the potential CN soil contamination is very limited as for instance with road salt to which CN-compounds have been added to prevent coagulation during its storage . The last dumping of CN containing wastes happened 20 or more years ago. Concludingly with respect to CN soil contamination in the Netherlands can be spoken of CN ‘historical’ soil contamination.

The most widespread contamination with cyanides is from wastes formed in the past by gas production from coal. Also common is contamination by wastes or spillage from cyanides used in metallurgical processes and mining operations. The CN in the waste of gas plants is predominantly chemically inert, whereas in the other mentioned wastes most of the CN is chemically active at the moment of dumping, however this activity decreases with time.

2.2 Intervention Values in general

For soil contamination caused prior to 1987 the degree of contamination is judged in first instance by Target and Intervention Values. The Target Value reflects a concentration indicating a good soil quality. In case soil concentrations exceed the Target Value it is most likely that the soil has been contaminated. The Intervention Value indicates the concentration level above which the soil contamination is considered as serious. That is the concentration level whereby toxicological threshold values are reached for humans or for ecosystems. When the soil contamination exceeds the Intervention Value, further research has to be undertaken with respect to the actual risks at the site considered, e.g. site-specific human exposure and site-specific ecological risks. Based on this actual risk a decision is made on the urgency of soil remediation or of clean-up actions (Berg van den and Roels, 1991; Swartjes et al., 1998; Ferguson et al. (eds.), 1998; Ferguson and Kasamas (eds.), 1999; Swartjes, 1999).
For the Intervention Values the toxicological threshold value of a contaminant is just as important as the behaviour of a contaminant in the soil determining the exposure of humans and ecosystems. The toxicological threshold value Maximum Permissible Risk (MPR_{human}) of a contaminant is defined in accordance with the Dutch risk management policy (VROM, 1998b). Subsequently the human toxicological soil intervention value has been defined as the concentration of a contaminant in the soil which would result in a potential exposure equal to the MPR_{human} under standardised conditions. This potential exposure is calculated using the CSOIL model, encompassing all exposure pathways to humans in a residential situation including consumption of garden vegetables. For several contaminants the CSOIL calculations are subject to considerable uncertainty. For instance for five contaminants a Monte Carlo based analysis showed that the 95% confidence interval of the median value determined with CSOIL ranged from a factor 40 lower to a factor 100 higher for volatile contaminants. The largest part of the uncertainty stems from the estimation of the emanation of volatile species of contaminants from the soil and their inhalation by humans. If this pathway is not considered the 95% confidence interval ranges from a factor 10 lower to a factor 20 higher than the median value (Vissenberg and Swartjes, 1996).
The ecotoxicological soil intervention value has been defined as the contaminant concentration in the soil at which 50% of the ecosystem is threatened, the Hazardous Concentration 50 (HC50) (Denneman and Gestel, 1990).
As the Intervention Value the soil intervention value with the lowest contaminant concentration is taken, thus the most stringent of either the human toxicological or the ecotoxicological soil intervention value.
The Intervention Value is derived for a soil with 10% organic matter and 25% clay. For most contaminants a formularium has been developed to adjust the Intervention Value for soils differing in organic matter and clay content.
The Intervention Value for groundwater can be defined in relation with: the Intervention Value of the soil and supposing an equilibrium between the concentration in the soil and in groundwater; or the risk of consuming 2 litre per day of untreated groundwater; or the analytical detection limit.

2.3 Intervention Values of CN

The definition of critical levels for cyanides in soil/groundwater is internationally considered as a complex matter. There are differences in chemical behaviour between CN species, and in case of CN soil contamination a wide array of exposure routes has to be considered. There are, so far, no recommended safety levels for CN by the EC in water, air or soils, although the European Chemical Industry Council (CEFIC) is taking action in this direction (Korte and Coulston, 1998. p.125).

Exposure to CN from soil contamination is hard to fit in any scheme or model, because of its speciation which is quantitatively partly unknown and is effected by soil conditions. In the Dutch regulatory system it has been attempted to overcome this by distinguishing three separate forms of CN and two levels of soil pH. Namely: free CN; complex ironhexacyanides in soils with $pH < 5$ and in soils with $pH \geq 5$; and thiocyanates. As ecological data were considered to be inadequate to determine HC50 values for cyanides in soils, past and current CN Intervention Values have been based solely on the MPR_{human} and have been calculated with the exposure model CSOIL. The Intervention Values calculated in this way show considerable variation through time (Appendix 4), caused by changes in the estimates of MPR_{human} and of parameter values in CSOIL.

The current soil Intervention Values derived with CSOIL for the three forms of CN (Table 1.1) are inconsistent in some respects with the knowledge about their toxicity and their behaviour. Striking is that according to the CSOIL calculations practically 100% of the human exposure to CN soil contamination is on account of ingestion of vegetable food, which is assumed to have been contaminated due to uptake of free CN via its root system. The parameter values estimated for CN in CSOIL came close to a worst case approach. As was recognised beforehand this deserved detailed review, possibly leading to future adjustments of the Intervention Values for CN (Berg van den and Roels, 1991; Berg van den, 1995; Kreule et al., 1995; Berg van den, 1997; Swartjes et al., 1998).

The current groundwater Intervention Values are set for free CN, complex ironhexacyanides and thiocyanates (Table 1.1) and are based on consumption of 2 litre untreated groundwater per day. In addition to this a worst case is assumed in which all three forms of CN are acting in the human body identical to free CN (Berg van den, 1995).

No formularium has been developed yet to adjust CN Intervention Values for soils differing in organic matter and clay content.

The conclusion of a renewed ecological review-study is that there are still insufficient data to determine the ecotoxicological intervention value (HC50) for cyanides in soils or in groundwater (Verbruggen et al., 2000). Consequently soil and groundwater Intervention Values for cyanides will be derived directly from the MPR_{human}.

3. Synthetic CN-containing materials found in soils

3.1 General

A practically exhaustive review of (non-medical) industrial compounds, processes and human activities with potential for exposure to cyanides lists over fifty CN containing compounds (Homan, 1987). Both their production and use can lead inadvertently or accidentally to soil contamination. Fortunately safety measures are such that generally this has not occurred with most of these compounds. However when CN containing residues remain which can not be reused, conditions or policies can prevail under which they are dumped and lead to soil contamination.

In the past residues were dumped in the assumption that this would not cause any harm to the environment beyond the dumpsite. Soil contamination occurred also from CN containing wastes formed in specific industrial processes not using CN containing compounds. Such as in the case of the manufacturing of gas from coal where solid CN containing wastes were often dumped at the site of the plant or used as material for landfills.

In the following some background information is given on the processes leading to the most common of CN containing wastes encountered in contaminated soils and on some of their general characteristics.

Note: In this report waste always refers to CN bearing wastes unless stated otherwise. E.g. manufactured gas plants (MGPs) are producing several kinds of waste, in this report MGP waste refers to the CN bearing waste from MGPs.

3.2 Wastes from manufactured gas plants (MGPs)

MGP waste nomenclature

A variety of names is used for CN bearing wastes of MGPs, common ones are: iron oxide box waste, oxide box waste, MGP oxide box waste, and purifier waste. As stated above in this report the term MGP waste will be used.

Gas production and purification

Manufactured gas was made by the pyrolysis (heating in the absence of oxygen) of coal or oil or a mixture of the two. Manufactured gas was used amongst other for cooking and for illumination. From about 1850 to 1950 manufactured gas plants (MGP's) played a key role in the modernisation of the urban environment and nearly every town had one or more MGP's. Nowadays the traditional MGP's have completely disappeared as use is made from electricity generated by power plants. Pyrolysis of coal may play an important role again with in situ gasification of geological coal layers.

It is estimated that there were from 1,100 to 3,000 MGP's in the USA (Shifrin et al., 1996) and 234 in the Netherlands (Matthijsen, 1988). The crude gas from MGP's was a mixture of methane, carbon monoxide, hydrogen and low carbon number illuminants such as acetylene. Undesirable constituents such as ammonia, hydrogen sulphide, cyanides, and aspirated tars were removed at the MGP prior to distribution of the gas. The dumping of wastes from these steps is in many cases a primary factor for starting the cleanup of MGP sites, as it concerns rather volatile constituents from coal tar such as polyaromatic hydrocarbons, benzene, toluene, ethylbenzene and xylene (Shifrin et al., 1996).

Removal of hydrogensulphide and HCN from crude gas

General
The last step in a number of purification operations during the gas production process was generally the removal of sulphides and of cyanides from the crude gas by reaction with iron compounds. Depending on local circumstances and plant technology the source of iron used varied (for dry washing) from ferric oxide bound on wood chips (Shifrin et al., 1996) to bog ore which is an iron-bearing soil material (Hoppener et al., 1983), and iron oxide particles in scrubbers (Theis et al., 1994).

Bog ore
In the Netherlands as in many other countries bog ore was used in practically or all MGP plants. Prior to its use sodiumcarbonate is added to it or it is exposed to the NH_3 containing uncleaned gas in order to create alkalic conditions in which iron as $Fe(OH)_3$ reacts with the H_2S of the gas to Fe_2S_3 or FeS:

$2\,Fe(OH)_3 + 3H_2S \rightarrow Fe_2S_3 + 6H_2O$

$2\,Fe(OH)_3 + 3H_2S \rightarrow 2FeS + 6H_2O$

HCN was removed from the gas in this purification step as $Fe(CN)_2$ formed after reaction of HCN FeS and also with $Fe(OH)_2$ present from other reactions. Upon exposure of the waste to the air Prussian blue was formed:

$9\,Fe(CN)_2 + 1.5O_2 + 3H_2O \rightarrow Fe_4[Fe(CN)_6]_3 + 2Fe(OH)_3$

Bog ore was regenerated several times up till it contained so much sulphur that it could not be reused anymore.

Regeneration was commonly done by spreading the bog ore on the soil surface and adding water to it, ‘posterior regeneration’:

$Fe_2S_3 + 1.5\,O_2 + 3H_2O \rightarrow 2\,Fe(OH)_3 + 3\,S$

$FeS + 1.5\,O_2 + S + 3H_2O \rightarrow 2\,Fe(OH)_3 + 3\,S$

Regeneration of the bog ore was also done by adding a few percent air to the gas to be cleaned, after which cleaning of the gas and regeneration of the bog ore occurred instantaneous, ‘simultaneous regeneration’. This method was not used always as the added air lowered the caloric value of the gas produced.

Wet scrubbing methods
A deviating gas purification method, which was employed sparingly in the Netherlands on large plants, was the removal of cyanide from the gas by wet scrubbing through a strongly concentrated ferrosulphate solution, prior to the dry washing of hydrogensulphide. Two methods have been used in which the final remaining cyanides in the water differ. When the Bueb method was used, the remaining wastewater contained mainly poorly soluble compounds $Fe(CN)_2$ and ammonium ferro ferrohexacyanide $(NH_4)_2FeFe(CN)_6$ and some $(NH_4)_4Fe(CN)_6$ which is soluble. And when the Rutten method was used 80% of the cyanides was present as the soluble $K_4Fe(CN)_6$ and 20% as insoluble $Fe(CN)_2$ (Hoppener et al., 1983).

The main non-cyanogenic components of MGP waste

Sulphur

After its use for purification, in which the bog ore has been regenerated several times, S has accumulated in the bog ore, i.e. MGP waste, to levels of 30 - 50% by weight most of it in the form of elemental S. Generally all the solid MGP cyanide-bearing wastes, often indicated as (iron) ‘oxide box wastes’, have a total sulphur content in excess of 40% by weight (GRI, 1987 as cited by Theis et al., 1994).

Other constituents

Predominant other compounds of the used bog ore, i.e. MGP waste, are: water around 20%; ferri oxide 10 - 20%; ferro oxide 5-6%; sand and clay 4-8%; ammoniumsulphate around 2%; lime and gypsum together around 2% (Hoppener et al., 1983).

Concentrations of 20-80 mg/kg have been found for Cd, Cr, Cu, Ni, Pb, and Zn in American wastes (EEI, 1984 cited by Theis et al, 1994).

pH

The pH in MGP waste and at contaminated sites is in the range of 2 - 5. It is not clear whether the acidity of the wastes is a result of the manner in which they were generated or that the acidity was produced subsequently through biological or chemical reactions (Theis et al., 1994). In any case it is reported that under aerobic conditions due to the gradual oxidation of iron sulphide to iron sulphate and the eventual formation of sulphuric acid the pH of the soil at MGP sites is often as low as 2 to 4 (Shifrin et al., 1996). In a soil at a former German MGP site pH values from 2.8 - 3.4 are found in the 30 cm waste-deposition layer unto a depth of >1.45 m in the underlying soil (Mansfeldt et al., 1998). At a contaminated MGP site in the Netherlands pH values range between 1.5 - 3.5 at depths of 0.5 -1.0 m (Hoppener et al., 1983).

In groundwater pH values ranged from 5.6 – 7.6 at three sites of former MGPs (Meeussen, 1992. p.34).

The main cyanogenic compounds in MGP waste

Complex iron cyanides

The solid MGP cyanide-bearing wastes are characterised by high total cyanide concentrations; levels of 1 to >2% total CN have been observed in the United States (Theis et al., 1994) and in the Netherlands of up to 5 - 8% CN (Hoppener et al., 1983). Complex ironhexacyanides are the predominant cyanide species in MGP waste shortly after formation during gas purification and remain predominant after weathering over long periods upon disposal on land. More than 97% of the cyanides present in these wastes are in the form of ferri ferrohexacyanide, $Fe_4[Fe(CN)_6]_3$ with a striking blue colour. The last is caused by the charge transfer resonance between the ferrous and ferric oxidation states present in this ferri ferrohexacyanide complex (Homan, 1987). The blue colour is indicated as Berlin blue in German based idioms and as Prussian blue in Anglo-Saxon idioms. Ferri ferrohexacyanide is very insoluble, there are other somewhat more soluble Prussian blue species such as $KFe[Fe(CN)_6]$. Generally only attention is given to ferri ferrohexacyanide in the literature reviewed on MGP wastes and all observations on characteristics and behaviour of CN of MGP waste are generally contributed and related to ferri ferrohexacyanide, correctly or not. The same line is followed in this report unless other specifications are given.

Thiocyanates

Thiocyanates can only be formed to any significant extent at pH > 8.5; their formation is reported to occur at very high concentrations of ammonia in the MGP gas to be purified, whereby the role of ammonia may be in increasing the pH of the reaction medium (Shifrin et al., 1996). The following chemical reactions are reported to occur at regeneration of bog ore:

$2NH_3 + 2H_2S + 2Fe(OH)_3 \rightarrow 2Fe(OH)_2 + (NH_4)_2S_2 + 2\ H_2O$

$(NH_4)_2S_2 + HCN \rightarrow NH_4CNS$

As the number of times of regeneration increases the (ammonium)thiocyanate content decreases and the ironhexacyanide as well as the sulphur content of the used bog ore (the cyanide containing MGP waste) increases. For instance in case of posterior regeneration bog ore contained upon three times reuse 0.3% ammoniumthiocyanate (SCN concentration 1 g CN/kg), 8% ironhexacyanide and 32% elemental sulphur, after eleven times of reuse respectively 0.1% (SCN concentration 0.3 g CN/kg), 13%, and 47%.

Higher temperatures further enhance the formation of thiocyanate. Consequently by simultaneous regeneration of bog ore relatively more thiocyanates are formed and less ironhexacyanides (Hoppener et al., 1983).

In a UK study of MGP waste SCN concentrations ranged from 9 – 26 g CN/kg (Wilson and Hudson, 1980).

In India thiocyanate concentrations are reported in the range of 100 - 400 mg CN/l in wastewater from different carbon containing fuels used for domestic cooking and coke ovens (Paruchuri et al., 1990).

Soluble simple cyanides

In discussing analyses of MGP wastes several authors mention the presence of free CN. This probably as a consequence of the presence of simple alkali cyanides, e.g. KCN, which dissolve during the analytical procedure. In a UK study of MGP waste free CN concentrations ranged from 500 – 800 mg CN/kg (Wilson and Hudson, 1980). Correctly formulated the MGP waste contained soluble simple cyanides [e.g. KCN, $Ca(CN)_2$] at concentrations of 500 – 800 mg CN/kg, total CN concentrations ranged from 24,000 – 45,000 mg total CN/kg.

Free cyanide

Free cyanide if ever present in MGP wastes, would be expected to have been lost through volatilisation; no evidence of HCN or CN^- was found (Theis et al., 1994). Probably the little free CN not removed from the crude gas remained in the gas (Brettschneider, 1995. p.11).

Other forms of cyanide

Other forms of cyanide present in weathered wastes include ferrohexacyanides $Fe(CN)_6^{4-}$, $Cu(CN)_6^{3-}$ and unidentified species.

Concentrations of 20 - 80 mg/kg have been found for Cd, Cr, Cu, Ni, Pb and Zn in American wastes (EEI, 1984 cited by Theis et al, 1994). Also these elements can form several combinations with CN.

Biological life in MGP waste

Specific research of biological conversion of CN in MGP waste before or after its dumping has not been executed. In general it is remarked that microbes occur in MGP waste (Wilson and Hudson, 1980), and several authors report that the sulphur present in MGP waste is converted to sulphate which indicates activity of sulphur oxidising bacteria. MGP waste is thus not toxic to certain biological life and can support it to a certain degree probably.

3.3 Wastes from cyanides used in industrial processes

3.3.1 Metallurgic and photographic industry

Case hardening

Case hardening is the generic term applied to a number of surface treatments applied to metals which result in the production of a hard, wear resistant outer layer (case) around a core which retains the original properties. This is achieved by heating the metal in an appropriate gaseous atmosphere, liquid bath or solid pack. A typical bath contains about 30% sodium cyanide along with sodium chloride and sodium carbonate (Homan, 1987).
Heat treatment wastes from metal processing operations may contain according to Dutch analyses: simple cyanides up to 200 g CN/kg, mostly as NaCN; cyanates up to 25% and barium up to 30% (Lagas et al., 1982).

Electroplating

In electroplating a metal object is covered with a film of another metal to obtain more resistance to corrosion, or more hardness, or another appearance. Plating is often done in alkaline baths containing sodium or potassium cyanide at concentrations of 5 to 15%. Accumulation of carbonates derived from cyanide decomposition or absorption of CO_2 from air makes regeneration of the plating solution necessary, when this is not possible anymore the liquid has to be discarded (Homan, 1987).

Photography

A number of cyanide compounds are used for colour-photo prints, such as ferri ferrohexacyanides, potassium ferrihexacyanide K_3 $Fe(CN)_6$, etc. Ammoniumthiocyanate is used for colour film processing, and acetonitrile is used as a reagent and solvent in the photographic industry. Silver has been recovered from photographic films by reaction with aqueous sodium cyanide in vats (Homan, 1987).

Disposal

In the seventies methods to destroy cyanide in wastes from metallurgic and photographical industries were developed and applied (Roos and Schmidt, 1977). In the sixties and early seventies these (generally liquid) wastes were often dumped near the industrial site or were added to solid wastes and were subsequently hauled for disposal at waste disposal sites or used as landfills.

3.3.2 Mineral extraction and recovery

Gold or silver from ores can be extracted by leaching finely crushed ore with alkali cyanide solutions in which stable soluble cyanide complexes of these precious metals dissolve. Sodium, potassium, or calcium cyanides and cyanogen bromide, BrCN, have been used for this extraction process (Homan, 1987). The wastewater remaining after extraction of the gold

or silver CN-complexes contains around 0.05 % CN, most of which escapes as HCN into the atmosphere after storage in tailing ponds. Leakage of wastewater, or spills due to collapsing pond-dams leads to enormous immediate environmental as recently in Colorado (Young, 1992), in Guyana (IUCN, 1995) and in 2000 in Baia Mare, Romania. The cyanide gold recovery in its old-fashioned form by the mines near Bergama in Turkey has been forbidden by the highest court in Turkey in 1997 (Korte and Coulston, 1998).
Though internationally seen CN soil contamination (more in particular of river systems neighbouring the pond-site) linked to exploration of precious ores is `common’ no attention will be given to it with respect to national Dutch Intervention Values of soil contamination, as in the Netherlands no precious ores are found or have been processed.

3.4 Processing of cyanogenic crop products

Cyanogenic plants contain nitriles, which can release CN upon enzymatic reactions induced by rupture of plant cells (Appendix 1 and 2). Cassava (Manihot utilissima, Pohl) a (starch) root crop is probably the best known of these plants, it is widely cultivated in the semi- and humid tropics and used as food and feed for local consumption and for export. In situations where large bulk quantities of cassava are being processed CN is liberated by enzymatic action and wastewater has been found containing 200 mg CN/l (Siller and Winter, 1998). No further information has been retrieved of environmental pollution caused by release of CN upon processing of cyanogenic plants. Soil contamination from this source is likely to occur in several locations in tropical regions.
Cyanogenic crop products have never been processed on a large scale in the Netherlands, apart from the use of (already processed) cassava meal which is imported for incorporation in concentrate feed mixtures.

3.5 Non-waste materials

3.5.1 General

Apart from CN containing wastes, other CN containing materials may lead to enhanced CN concentrations in the soil or in soil-material. In this respect some data were found of the following CN containing materials: road salt and; one artificial fertiliser (calciumcyanamid); complex cyanides used for decontamination of radiocaesium contaminated feed; and tare-soil (Appendix 2).
No soil data were found linked to a formerly used CN containing herbicide formulation, amitrol mixed in a ratio of 1:1 with ammoniumthiocyanate, to control perennial weeds under planted trees as e.g. in orchards and windbreaks (Anonymous, 1981. p. 392).

3.5.2 Road salt

To maintain roads and highways in good condition during periods with frost and/or snowfall the use of road salt (NaCl) is a standard practice. In the Netherlands annual consumption of road salt varies depending on winter-weather conditions around 0.5 million tons and in the USA around 10 million tons. To ensure uniform spreading road salt is commonly amended with an anti-caking agent sodium ferrohexacyanide $Na_4Fe(CN)_6$ (Ohno, 1996), or potassium ferrohexacyanide $K_4Fe(CN)_6$ (Vries de, 1998); the concentration is in the order of 10 - 60 mg CN/kg road salt (Ohno, 1996; Brinkmann et al., 1997). It was observed in analyses of road salt used in the Netherlands that 2% - 5% of the total CN is in the form of free CN (probably alkali CN salts, dissolving to CN^- during chemical analysis), i.e. 0.5 - 1.5 mg free CN/kg salt (Brinkmann et al., 1997). In many cases road salt is mixed with sand and stored in large stockpiles at special storage facilities, or in smaller quantities at sites where icing of roads occurs more frequent or is more critical for the traffic. Soil and water contamination from road salt and its anti-caking agent will occur, where road salt is stored outdoors without cover, after its application on roads, and possibly also when stored in shacks or storage buildings when lacking adequate soil protection, or in situations when large quantities of salt are spilled.

3.5.3 Artificial fertiliser

In 1905 was the first artificial N fertiliser produced at a commercial scale through fixation of atmospheric N. It was in Italy by the 'Societa Italiana per la Fabricazzione dei Prodotti Azotati' which produced calciumcyanamid CaNCN also named lime nitrogen (SKW, 1998). Upon contact with moisture in the soil CaNCN is transformed within a few days into non-CN containing compounds (paragraph 5.1 and Appendix 1). Its handling is subject to some specific worker safety precautions, its agricultural use is further without any (environmental) restrictions [Martin and Worthing (eds.), 1997; BCPC, 1994].

3.5.4 Complex cyanides for livestock exposed to radiocaesium

A countermeasure to reduce or prevent the contamination of products (milk and meat) from animals exposed to feed or grasslands contaminated with radioactive caesium (^{134}Cs and ^{137}Cs) is to incorporate Prussian blue in some way in the animal diet. One way is to let cattle ingest two to three solid balls (boli) each 250 g, containing 15% ammonium linked Prussian blue compounds (85 g CN/kg boli), most of which is released in the rumen over period of 2 months. This was done routinely with 40,000 to 50,000 head of cattle in Belarus, Russia and Ukraine in the years after the Chernobyl accident in 1986 (Hove et al., 1995). Following further testing, ferrohexacyanide compounds were approved as a feed additive first in Germany and Norway, and subsequently also by Russia and the EC (EC, 1996 cited in Ratnikov et al., 1998).

The background of mentioned countermeasure is that Prussian blue compounds, as $NH_4Fe[Fe(CN)_6]$ (= ammonium-ferri ferrohexacyanide = ammonium ferric hexacyanoferrate = AFCF) and others (Appendix 1), bind caesium ions in exchange for a monovalent positive charge, whereas Prussian blue compounds are not converted in digestive processes or absorbed from the gastro-intestinal tract by the animal (Pearce, 1994). Hence the use of Prussian blue compounds will prevent or reduce caesium contamination of animal food products (milk and meat), but may result in the spread of Prussian blue (and caesium) containing faeces in the environment (Vandenhove et al., 2000). Possible effects of AFCF on pasture growth have been investigated (par. 6.2.5).

4. Concentration, behaviour and fate of CN in contaminated soils

4.1 General behaviour of CN

Simple cyanides releasing free cyanide

Water soluble simple cyanides, releasing free cyanide, are not absorbed or retained in soils. At high concentrations they are toxic and their fate will be determined by abiotic processes. At low concentrations free CN will be subjected to biochemical processes: under aerobic conditions free CN will be converted to carbon dioxide and ammonia; and under anaerobic conditions free CN will be converted to gaseous nitrogen compounds. In the deeper groundwater where biochemical activity is nil or low, free CN will be diluted and will be transported by groundwater movements.

Complex cyanides ions and dissociation to free cyanides

Complex cyanide ions show only very limited dissociation to free cyanides. Probably several of the complex-cyanide anions, as e.g. hexacyanoferrates, are physiologically practically inert and stay at low concentrations in solution in the soil.

The cyanides in MGP waste are predominantly in the form of ferri ferrohexacyanide. The dissolution of ferri ferrohexacyanide can be written as follows:

$Fe_4[Fe(CN)_6]_3\ (s) \leftrightarrow 4\ Fe^{3+} + 3\ Fe(CN)_6^{4-} + 3\ e^{--}$

Under aerobic conditions the evolving Fe^{3+} will precipitate as iron (hydr)oxide, e.g. $Fe(OH)_3$ (s). This results in the overall dissolution reaction

$Fe_4[Fe(CN)_6]_3\ (s) + 12\ H_2O \leftrightarrow 4\ Fe(OH)_3\ (s) + 3\ Fe(CN)_6^{4-} + 12\ H^+ + 3\ e^{--}$

Under anaerobic conditions little or no electron consuming agents are present, the evolving iron will partly remain in the reduced Fe^{2+} state and more reduced states of iron hydroxide will form, e.g. $Fe_3(OH)_8$. This results in the overall dissolution reaction:

$3\ Fe_4[Fe(CN)_6]_3\ (s) + 32\ H_2O \leftrightarrow 4\ Fe_3(OH)_8\ (s) + 5\ Fe(CN)_6^{4--} + 4\ Fe(CN)_6^{3--} + 32\ H^+$

The way that protons and electrons are involved in these dissolution reactions indicates that the solubility of ferri ferrohexacyanide depends on soil pH and on redox potential. From the respective overall reactions it appears that under aerobic conditions four hydroxyl ions are needed to dissolve one mole of $Fe(CN)_6^{--}$ and under anaerobic conditions about 3.5. This makes the solubility of ferri ferrohexacyanide extremely pH dependent, with a higher solubility at higher pH levels (Meeussen et al., 1994). In soils it is found that as the solubility of ferri ferrohexacyanides increases precipitation as manganese ferrohexacyanides may occur (Keizer et al., 1995)

SCN

Most publications on thiocyanates mention that little is known about its environmental effects or fate (Stratford et al., 1994; Boening and Chew, 1999).

SCN degrading bacteria have been isolated from soils, such as several Thiobacillus and Arthrobacter species. Some of these species when grown in specific growth media can use SCN as the only source of carbon and energy, and a few as the only source of S and/or N. Generally SCN is broken down to S^{2-} and (hydrogen)cyanate HOCN, which is hydrolysed to CO_2 and NH_3 (Stratford et al., 1994).

Laboratory tests show that the breakdown of SCN at concentrations of 2.6 mg CN/kg in soils is dominantly by bacteria and is enhanced in general by organic matter. In these tests breakdown was practically completely in 5 up to 10 days (Brown and Morra, 1993).
Much information is available about degradation of SCN in wastewater subjected to different treatments (Paruchuri et al., 1990), it will not be attempted to translate these findings to the behaviour of SCN under different soil conditions. However it can be remarked that SCN is considered to be a very mobile compound (Kd 1 to 1.5), its behaviour in anaerobic soil layers without biological activity can be compared to that of chloride anions (Brettschneider, 1999).

4.2 MGP cyanide bearing wastes

4.2.1 CN content of contaminated soils

The total cyanide content in MGP wastes is generally between 1 and 2% with a reported maximum of 8%. Of the total CN more than 97 % is in the form of complex ironhexacyanides and generally around 0.2% as thiocyanate (paragraph 3.2).
The total cyanide content found in Dutch soils contaminated with these wastes ranges from 0.003 - 4.0 % (TAUW, 1981; Meeussen et al., 1992). MGP cyanide compounds are very stable in soil as demonstrated by their presence at former MGP sites decades after cessation of MGP activities (Meeussen, 1992; Shifrin et al., 1996)

4.2.2 Solubility, mobility and brake down of ferri ferrohexacyanides

Water saturated zone

Concentrations of dissolved ironhexacyanide
In order to get insight in CN behaviour in different soils twelve sites contaminated with MGP cyanide bearing wastes were studied in the Netherlands. Six Holocene clayey soils with approximately pH 7 and groundwater at 1.2 m, and six Pleistocene sandy soils with approximately pH 4 and groundwater at 3.2 m. In general the distribution of cyanide in these soils was very heterogeneous, part of the soil samples was virtually clean. The maximum total cyanide concentration found in the contaminated soils varied from approximately 0.03% to 1% of the soil. Of each of the twelve sites the two highest concentrations of total dissolved cyanide concentrations, probably mainly $Fe(CN)_6^{4-}$, in groundwater were considered, they showed the following ranges:
- at the six Holocene disposal sites 0.5 - 34 (av. 11) mg CN/l;
- at the six Pleistocene disposal sites 0.5 - 2 (av. 1) mg CN/l.

It was concluded that in acidic soils the ferri ferrohexacyanides have a low solubility, concentrations found dissolved in groundwater at MGP waste disposal sites with acidic soils (pH 4) correspond well to concentrations as calculated from the equilibrium dissolution concentrations of ferri ferrohexacyanide. The concentrations dissolved in groundwater at non-acidic soil disposal sites (pH 7) were roughly 10 to 50 times higher but much lower than the calculated equilibrium concentrations of ferri ferrohexacyanide (Meeussen, 1992; Meeussen et al., 1994). (Of the CN in the soil below the groundwater around 0.5% is in a dissolved state maximally). The differences in pH between pleistocene and holocene soils are emphasised as being a likely cause of the higher maxima found at the holocene sites; though other possible factors are mentioned such as hydrology and contamination level. The

investigation focussed on the comparison of the sites. No quantitative information is given on the variation of the dissolved concentrations between different spots within each site.
A compilation of groundwater analysis data of former Dutch MGP sites shows a similar range, 0.001 – 40 mg total CN/l (Koning and Schöller, 1986. Appendix 1).

Groundwater transition zone

At likely undisturbed soil depths of 3 m precipitation of ferri ferrohexacyanide in concentrations of 100 to 400 mg CN/kg soil have been observed at groundwater level in acidic sandy soils previously overlain by a layer with disposed MGP waste at the surface. Probably precipitation occurred at this depth due to changes in pE (and pH). In non-acidic soils no accumulation of ferri ferrohexacyanide was observed at groundwater depth, which indicates that after dissolution no precipitation of $Fe(CN)_6$ anions occurred during leaching in the profile. The mobility of dissolved hexacyanoferrate is higher in these soils as also indicated by the higher concentrations in the groundwater (Meeussen, 1992; Meeussen et al., 1994; Meeussen et al., 1995).

Unsaturated zone

Field measurements
No field measurements of CN species in soil pore water were found in the literature.

Laboratory studies: solubility
Solubility of CN present in contaminated soils is studied by equilibrating soil samples with an excess of solution over relatively short periods, the effect of different pH values of these solutions is often investigated as well. In such laboratory studies a clear increase of the solubility of the ferri ferrohexacyanide in MGP waste with increasing pH values has been observed (Table 4.1). The dominant dissolved cyanide species in all the leachate samples is the hexacyanoferrate(II) ion $Fe(CN)_6^{4-}$. In the 8 day period the dissolution of the ferric ferrohexacyanide reached an equilibrium in some of the batch experiments in others not.

Table 4.1 Dissolution of cyanide complexes contained in different MGP wastes at different pH. (Based on: Theis et al., 1994.)

Batch 10 gram MGP waste per litre		pH 3	pH 7	pH 9
Waste description	Total CN in batch	Dissolved CN complexes after 8 days stirring		
Relatively little weathered, brown-orange colour	143 mg CN (1.4% CN in waste)	b.d.l.[1)]	1 mg CN/l (equilibrium)	16 mg CN/l (no equilibrium)
Weathered during some decades blue-black colour	248 mg CN (2.5% CN in waste)	b.d.l.[1)]	24 mg CN/l (no equilibrium)	64 mg CN/l (equilibrium)
Kd CN in waste l/kg		< 4E-5	7E-5 - 10E-3	10E-3 - 3E-3

[1)] below detection limit of 0.5 mg CN/l.

Judging from Table 4.1 a bigger fraction of the total CN dissolves from MGP waste weathered over a longer period of years. If the weathering causes this difference can not be concluded as the two different MGP wastes studied differ in several other aspects. The concentrations at pH 7 as observed in the laboratory batch experiments exceeded those observed in groundwater sampled at disposal sites (Theis et al., 1994).

In a laboratory experiment comparing a sample of relatively little weathered (pH 4; 21% moisture) with a sample of weathered (pH 2.1; 58 % moisture) MGP waste it was observed that more cyanide leached from the weathered sample, increasing from 7% at pH 6 to 49% of leached CN at pH 9 (Gould et al., 1989, cited by Shifrin et al., 1996). These lab findings are in line with those in Table 1. However no firm conclusions can be drawn of the effect of weathering due to sample differences, neither of the leaching under field conditions (where under aerobic conditions a decrease in pH is likely to occur over time with weathering).

The dissolution of cyanide in the unsaturated zone was measured in other laboratory tests by ‘equilibrating’ 20 g soil samples during 5 days with 80 ml 0.01 M $CaCl_2$ as an alternative soil solution. Of the acidic sites only a small part, 0.1 - 5 % of the total cyanide present in the soil samples dissolved; of the non-acidic soil samples 5 - 75% of the total cyanide dissolved. Total CN concentrations in the soil samples ranged from 0.03 - 21 g/kg and in the equilibrated extraction solutions from 0.16 - 15 mg/l (Meeussen, 1992 p.89; Meeussen et al. 1994; Meeussen et al., 1995).

According to theory ferri ferrohexacyanide is very soluble in non-acidic soils. The fact that it is still present in such soils several decades after disposal of MGP wastes can probably be attributed to one or more of the following phenomena:

- the slow dissolution kinetics of ferri ferrohexacyanide (Meeussen, 1992);
- the consumption of hydroxyl ions at dissolution resulting in acidic micro-conditions (Meeussen, 1992);
- the reaction of hexacyanoferrate anions or other dissolved ‘cyanic-anions’ with cations present in the soil solution to other cyanide-complexes with very low solubility at the reigning soil conditions as pH and pE (Bellomo, 1970).

The last mentioned phenomenon is likely to occur in MGP waste contaminated non-acidic ($pH > 5$) soils at rather low pE values ($pE < 10$) by reaction with Mn 2+ cations to manganese iron cyanide $Mn_2Fe(CN)_6$. One of the equilibria which is most likely to exist in these soils is (Keizer et al., 1995):

$$Mn_2Fe(CN)_6\ (s) + H_2O \leftrightarrow 2\,Mn^{2+} + Fe(CN)_6^{3--} + e^{--}$$
$$\text{Mn-oxide} + H_2O + e^{--} \leftrightarrow Mn^{2+} + 3\,OH^{--}$$

Precipitation of $Mn_2Fe(CN)_6$ in soils has also been calculated for other CN containing wastes dumped in landfills (Stiff et al., 1976 cited by Lagas et al., 1981 and 1982).

In laboratory batch experiments with 20 g samples of two non acidic (pH 5.7 and 6.8) contaminated soils (360 and 1090 mg total CN/kg dry soil) were equilibrated over a period of 12 weeks, after application of different quantities of NaOH at the beginning of the experiment. In the treatments with an initial rise of the pH to 8 - 10 the iron cyanide present in the soil dissolved to a large extent, however after some weeks cyanide precipitation occurred and after 12 weeks at the end of the experiment concentrations in the solution were in the range of 1.6 - 16 mg CN/l. It is concluded that in non-acidic soils the CN in the soil solution is not in equilibrium with ferri ferrohexacyanide (the visibly present Prussian blue) but possibly with forms of manganese iron cyanide (Keizer et al., 1995).

Brake down of dissolved ironhexacyanide; laboratory studies

The fate of soluble ironhexacyanide was studied by adding $K_4Fe(CN)_6$ to aerated suspensions of fine soil particles from two slightly contaminated MGP sites. Measurements showed that 1-10% of the dissolved ironhexacyanide was broken down to CO_2 and NH_3, the last was nitrified or escaped to the atmosphere when the pH of the suspension exceeded 8.2. It was not

certain whether the brake down was biotic or abiotic. A larger fraction 17% of dissolved ferrihexacyanide was broken down than from dissolved ferrohexacyanide. The findings indicate that under field conditions dissolved iron-complexed hexacyanide will be attenuated probably by natural brake down processes.
Also certain fungi present in MGP soils heavily contaminated with complex metal hexacyanides are capable to brake ironhexacyanides down and to use hexacyanides as their sole source of nitrogen under certain conditions (Barclay et al., 1998).

Capillary rise and soil surface bloom

An interesting phenomenon observed at some former MGP sites is the staining with a blue colour of surface soils, rocks, grasses and debris at the soil surface. At pH 7 to 8, some solid ferri ferrohexacyanide dissolves releasing ferric ions and hexacyanoferrate ions. Capillary action may transport these dissolved species to the soil surface, as residual moisture evaporates, they may precipitate again as Berlin blue, ferri ferrohexacyanide (Shifrin et al., 1996). Similar phenomena have been observed on the surface of playing fields in the UK (Howland, 1989 cited by Barclay et al., 1998).
Striking about both these situations is that apart from the blue colour no accompanying harmful or annoying phenomena are reported. In the first situation grass is growing and in the second situation children are playing, apparently in both situations undisturbed by (traces of) emanating HCN or by other forms of CN.

Mobility of colloidal ferri ferrohexacyanides particles

Detailed soil-profile observations in Germany (Mansfeldt et al., 1998) reveal that at in an acid soil (pH 2.9) ferri ferrohexacyanide from overlying MGP waste illuviated in underlying undisturbed soil horizons. This could be concluded from:
- present former (‘fossil’) root and earthworm channels (macropores), now coated with precipitated blue coloured ferri ferrohexacyanide colloidal particles.
- calculations to derive possible transport mechanisms of the total cyanides now present in the undisturbed underlying soil horizons.

Namely the amount of total cyanide present in soil layers below the disposal layer is around 150 g CN/m^2. It was estimated that it would take about 1000 years to transport this quantity of CN in a dissolved form; considering a net precipitation surplus in the region of the Ruhr of 300 mm/year and a dissolved iron hexacyanide concentration of 0.5 mg CN/l. As the disposal of MGP wastes started only 90 years ago it is concluded that colloidal transport of ferri ferrohexacyanide has taken place.
The extreme low pH values observed in the disposal layer (pH 2.8-3.4) and in the underlying soil (pH 2.8-2.9) are caused probably by the oxidation of sulphides present in the disposed MGP wastes. Another source might have been acid spilled during transports from a sulphuric acid plant in the vicinity to an acid tank located at about 100 m distance from the soil profile studied.
In the soil profile the mentioned macropores sandy loess layer (pH 2.9) end at 1.45 m depth at the transition into the underlying coarser glaciofluvial sand (pH 2.8; with a higher saturated hydraulic conductivity); in the last layer most cyanides have been precipitated (106 g CN/m^2). Probably due to the stagnation the colloidal transported cyanides (through the macropores) the cyanides precipitate in the underlying coarser sand layer. The acting as a sink for cyanides of this layer is rather caused by soil physical influences than by soil chemical differences (Mansfeldt et al., 1998).

4.2.3 Free cyanides from dissolved ferri ferrohexacyanides in groundwater without exposure to light

Thermodynamic calculations indicate that at thermodynamic equilibrium dissolved iron hexacyanide will have dissociated predominantly to free cyanide ($HCN_{(aq)}$ and CN^-). However in groundwater sampled at three different contaminated MGP sites it was found that of the total dissolved cyanides only a fraction of 0.5 to 2.8% dissociated to free cyanides under conditions without any light. The pH and pE of the groundwater sampled ranged respectively from 5.6 - 7.3 and 6.5 - 8.8; the concentrations of free CN from 0.01 - 0.15 mg CN/l, and of total dissolved from 1.7 - 11.4 mg CN/l. No effects are reported of pH and pE or of location on observed free cyanide concentrations (Meeussen et al., 1992; Meeussen, 1992. p.34).
A similar pattern can be observed in the CN concentrations and speciation found more recently at a former MGP site in the upper Midwest region of the USA where operations ended in 1947. Groundwater sampling (pH 6.5 to 8; pE 4 to 5) in 1997 showed that , the quantity of free CN ranged from < 0.002 to 0.016 mg CN/l. I.e. from 0.1 to 1.3% of the dissolved total cyanide which had concentrations up to 6 mg CN/l and consisted for 98 to 99% of dissolved ferrohexacyanide (Ghosh et al., 1999). In dissociation studies with potassium ferrohexacyanide 0.015 mg CN/l in deionized water it was found that after 200 days 1.2% dissolved to free CN^-. At equilibrium conditions 3 % to 5% of dissolved ferrohexacyanides dissociated to free CN at pH 6.5 to 6.7 (Gosh 1998 cited in Gosh et al., 1999).
A very low dissociated fraction has been observed in experiments with soluble ironhexacyanides, in which at pH 7, free cyanides ranged from 0.01 to 0.2% at equilibrium (Broderius, 1973 cited by Shifrin et al., 1996).
In groundwater from sites contaminated with ferric ferrohexacyanides only hexacyanoferrate ions were found, indicating that the speciation of cyanide is not determined by chemical equilibrium but by decomposition kinetics. In fact the decomposition rate of iron cyanide in soils is so slow that it makes iron cyanide kinetically stable and allows it to remain the predominant species in soils. Consequently water-soluble strong complexes present in the soil, such as ferrihexacyanides and ferrohexacyanides, do hardly or not release free cyanide. Model calculations show half lives of dissolved iron cyanide complexes to free cyanides of 100 to 1000 years in soils at pE >8 with pH >4.5 and in soils at pE <6 with pH of 6.5 to 7.5; and half lives of 1 to 10 years in soils at pE <6 and pH <5.5 (Meeussen et al., 1992; Meeussen, 1992, p.42).

4.2.4 Formation and presence of free cyanide in soil (no light exposure)

Total sulphur and soluble simple cyanides (free CN^- upon addition of water) contents of MGP wastes are respectively around 45% and 750 ppm, and in soil contaminated by MGP waste respectively around 10% and 15 ppm (15 mg free CN/kg soil) (Wilson and Hudson, 1980). This indicates that at maximum 10% of the soluble simple ‘free’ CN in the MGP waste has remained in the contaminated soil. In case of formation of new free CN from the MGP waste, this process is overshadowed by the processes which lower the concentration of free CN in this soil. (Further conclusions are not possible as no information on the history of the contamination or on the soil characteristics are given.)
In laboratory studies it was found that ammonium-ferri ferrohexacyanide mixed at rates up to 32 mg CN/kg soil did not result over a period of two years in any detectable CN^- in the soil.

In case any CN^- was released from dissolved ferrohexacyanide it did not persist in the soil in detectable quantities, a possible reason may be that many species of bacteria and fungi can metabolise CN^- and degrade it to harmless substances (Vandenhove et al., 2000).
No data have been found of free CN^-, or soluble simple cyanides present in the soil, apart from very few data on HCN in soil air and some on CN^- present in groundwater. For (historically) contaminated soils the following worst case estimate can be made with the assumption that the pore water in the (aerated) soil contains the same maximum free CN concentration as observed in contaminated groundwater, 0.15 mg free CN/l. Assuming 300 ml porewater per kg of dry soil material, the resulting maximum (worst case) concentration is 0.045 mg free CN/kg dry soil. Two of the conditions that have to be fulfilled in the worst case situation are: a) HCN flux to soil moisture equals HCN emanation to soil air and ambient air; b) absence of any soil life breaking down HCN, this absence is probably not caused by the CN pollution itself but by accompanying pollutants.

4.2.5 Formation and presence of free cyanide under conditions with light

When aqueous solutions are exposed to ultraviolet light photodegradation has been well established (Broderius and Smith, 1980, Leduc et al., 1984; Meeussen et al., 1989; Eisler, 1991; Shifrin et al., 1996): $Fe(CN)_6^{4-} + h\nu \rightarrow Fe(CN)_5^{3-} + CN^-$
Dissolved complex hexacyanide can decompose completely even when exposed to diffuse daylight, as observed in the laboratory with solutions containing ferrihexacyanide 0.1 mg CN/l, at pH 12. The complete decomposition in 4 days could have been caused by lowering the activities of the ferri ions by hydrolysis (Meeussen et al., 1989; Meeussen, 1992. p.18).
A hypothesis which has been brought forward is that (dissolved) hexacyanoferrate can be considered to be as toxic as free cyanide when exposure to light is likely to occur (Meeussen, 1992, p.43; Meeussen et al., 1992). Other reactions which have to be considered in actual situations are: emanation of HCN; decomposition of free cyanide by UV (Asmus and Garschagen, 1953 cited by Meeussen et al., 1989; Meeussen, 1992. p.19).
Exposure to light of soil moisture or groundwater with dissolved hexacyanoferrate can occur for instance in the following three situations.
1. During daytime any hexacyanoferrate ion present in residual moisture at the soil surface may degrade and evolve HCN; no information on possible or observed fluxes of HCN liberated by photodegradation could be retrieved from the literature.
2. Dissolved hexacyanoferrate in ground water or drainage water is transported to surface water and is then exposed to daylight. The resulting concentration of free cyanides in the surface water and ambient air will depend on hydrological, biochemical and atmospheric conditions.
3. Groundwater pumped up for use as drinking water, and stored in ponds or in transparent containers or in glass bottles.
The presence of free CN in water from contaminated sites upon exposure to light of this water seems certainly possible, no quantitative information on this phenomenon could be retrieved from literature searches.

4.2.6 Presence of free cyanide, HCN, in soil and ambient air

Field measurements of HCN in air
In general no efforts have been spent to verify the presence of HCN gas evolving from MGP waste in soils under field conditions. If it occurs the fate of HCN gas apparently is such that

its concentration remains unnoticed. Possibly by lack of evidence it is generally concluded that the forming of HCN gas from iron hexacyanide occurs at a very low reaction speed as compared to the rate at which free cyanide is used by soil organisms or at which HCN evaporates to the ambient air. Consequently accretion of free cyanide in the soil solution or of HCN gas from MGP waste in soils is considered as being unlikely to occur (Meeussen, 1992; Theis et al., 1994; Shiffrin et al., 1996).

Very few literature references were found of HCN gas measured at MGP contaminated sites. This lack of information is recognised also by others (CCME, 1997; Kjeldsen, 1999). Even though the theoretical presence of HCN gas at MGP sites is mentioned in several publications.

Levels of 1 - 2 mg HCN per m^3 soil-air were found above the phreatic level at a former MGP waste dump site with concentrations of 90 g total CN/kg soil; according to chemical equilibrium calculations concentrations would be approximately half a million times as high (Hoppener et al., 1983. p.110).

Levels of < 1.0 – 4.0 E-5 mg HCN/m^3 were observed in autumn 1999 in crawl-spaces and rooms of houses constructed on the premises of a former MGP in the Netherlands (IWACO, 1999).

A concentration of 2 mg HCN/m^3 in ambient air in a large excavation during soil cleaning operations at a former MGP site is said to have been measured (Jans, 1999). The source of this HCN can have been emanation from the soil without exposure to light, or from puddles at the surface of the excavation with HCN formed by photodegradation of dissolved ironhexacyanides.

Probably more HCN data can be found in archived documents in between analytical data of other contaminants obtained in surveys of former MGP sites.

Model calculations of free CN in air

United Kingdom. Model calculations using conservative assumptions based on dissociation findings of complex ironhexacyanides arrive at an ambient air concentration at a representative former MGP site of 0.077 mg HCN per m^3 (Shifrin et al., 1996). (Some of the conservative assumptions are: a MGP site of which the soil contains 5% pure oxide-box waste with 3.6% ironhexacyanide and 5 ppm free CN, which is constantly generated and emanated as HCN gas resulting in a mass flux of 0.058 µg HCN.cm^{-2}. s^{-1}, and at the soil surface ambient air with a mixing zone 1.5 m high and a wind speed of 5 m.s^{-1}.)

The Netherlands, VOLASOIL. VOLASOIL is a recently developed model to calculate air quality (Waitz et al., 1996). A first attempt will be made to estimate with VOLASOIL the concentrations of HCN in air as linked to concentrations of free CN in groundwater (Table 4.2). For the calculations the following inputs have been used:

- standard chemical and physical parameter values for free CN retrieved from the Hazardous Substance Data Bank (NLM, 1998);
- default values of CSOIL and VOLASOIL;
- weather conditions: no rain, wind speed m/s at 10 m height;
- groundwater table at 1.25 m;
- no conversion of free CN in the soil, nor conversion after emanation;
- VOLASOIL does not estimate concentrations in outdoor air, use is made of the VOLASOIL estimated concentration in indoor air and of a concentration-ratio outdoor air/indoor air of 1/100, based on CSOIL for outdoor air concentration at 1.5 m above the soil.

With respect to the results of the VOLASOIL calculations (Table 4.2) the following remarks can be made:

a) VOLASOIL calculations using as an input the maximum observed concentration of dissolved HCN in Dutch groundwater, i.e. 0.15 mg free CN/l. The resulting concentration in indoor air is less than 0.0025 mg HCN/m^3 (Table 4.2). That is more than 10 times lower than the Tolerable Concentration in Air (TCA of 0.025 mg/m^3, see paragraph 6.2), more than 30 times lower than the outcome of the UK worst case calculation, and around 500 times less than the maximum concentrations observed in open air in the Netherlands, 1 – 2 mg CN/m^3. The last observations indicate that for estimates of HCN in ambient air VOLASOIL is not very well suited. (The VOLASOIL estimate of HCN in soil air matches reasonably well with the few observed values, 1-2 mg HCN/m^3).
b) The concentration levels of free CN in groundwater, corresponding with TCA concentrations in indoor air, are according to VOLASOIL calculations 10 to 100 times higher than the maximum free CN concentration observed in groundwater (Table 4.2).

Table 4.2 VOLASOIL model calculations of HCN concentrations in air. 1)

Scenario	Soil texture	Groundwater	Soil air	Outdoor air	Indoor air
		mg free CN/l	mg HCN/m^3		
Max. observed free CN conc. in groundwater	Sand	0.15	0.86 2)	av. 4) 1.3E-5	0.0024
	Clay	0.15	0.86 3)		0.0002
Free CN conc. in indoor air equals TCA	Sand	1.6	9.1 2)	av. 4) 2.5E-4	0.025
	Clay	17.6	100 3)		0.025

1) Default values of CSOIL and VOLASOIL have been used for these calculations, see text.
2) At average depth of contamination 0.75 m.
3) At average depth of contamination 1.05 m.
4) Outdoor air concentration estimated with CSOIL ratio outdoor/indoor air, no distinction between soil texture.

Calculations based on estimates of HCN concentration in porewater were not made. VOLASOIL uses the concentration of volatile compounds in groundwater as input, concentrations in soil pore water are not included in the model.

Conclusion on HCN gas from CN soil contamination
The outcomes of all model calculations made diverge widely from the few available field data. A general conclusion is that the HCN gas concentrations in ambient air due to soil contamination are too complex to predict as too many soil factors are involved. The fore mentioned concentrations, 1 – 2 mg CN/m^3, will be considered as the maxima observed in Dutch soil and ambient air.

4.2.7 Thiocyanates in soils containing MGP wastes

In a UK sample of a soil contaminated by MGP waste a SCN$^-$ concentration was observed of 217 mg CN/kg (Wilson and Hudson, 1980). The sample contains 16% total S of which 14% elemental S, combined with other data in the document it indicates that the MGP waste comprises around 30% of the soil by weight. One other sample at the same site contained more complex CN and no SCN. Apparently at this site MGP waste is coupled only occasionally to presence of SCN. In soil samples from two other contaminated sites no SCN

was detected, even though one of these contained probably more than 30% MGP waste. Additional information on the history or on the situation of these contaminated sites is not given. By lack of this and considering the irregularity of the occurrence of SCN at these sites the 217 mg CN/kg is not taken as a representative (maximum) value for the SCN concentration in soils contaminated historically.
In the Netherlands thiocyanates have been measured at some former MGP sites. In soil layers above groundwater the highest thiocyanate concentration is around 7 mg CN/kg soil. In water saturated layers at depths between of 4 – 15 m the highest observed thiocyanate concentrations of holocene soils are around 90 mg CN/lgroundwater or around 30 mg CN/kg soil below the phreatic level. Aforementioned Dutch data were personally communicated (Brettschneider, 1999). In a specific area at a MGP site the reported maximum SCN concentration in groundwater is 32 mg CN/l (Brettschneider and Engelen, 1998).
Further little attention has been given in the literature to thiocyanates at former MGP sites, although their (theoretical) occurrence is mentioned by several authors.

4.2.8 Conclusions on cyanides in soils containing MGP wastes

The following conclusions can be drawn from the studies reviewed above.

CN content of soils
- The total cyanide content found in Dutch soils contaminated with these wastes ranges from 0.003 - 4.0 %.
- MGP wastes disposed in soils contain cyanides mainly > 97 % as ferri ferrohexacyanide;
- In all soils almost all cyanides present in disposed MGP wastes stay contained in these wastes and are still present as complex hexacyanides several decades after their disposal.

Solubility and concentration of ferrohexacyanide
- Concentrations of CN in pore water (dissolved compounds or free CN) in the unsaturated zone of CN contaminated soils are not reported in the literature reviewed. Laboratory experiments indicate that these concentrations are in the same order of magnitude as those found in groundwater at such sites. It has to be noted that in these experiments dissolution of CN is likely to be better than in the field, while the brake down and complexation of liberated CN is probably less than under field conditions.
- In acidic soils the cyanides from MGP waste are practically insoluble (probably other possibly more soluble forms of cyanide are converted upon dissolution to insoluble complex cyanates. The little dissolved cyanide is present as $Fe(CN)_6$ anions.
- At waste disposal sites on acidic (pleistocene) soils cyanides are present in groundwater as $Fe(CN)_6$ ions at maximum concentrations of 0.5 - 2 mg CN/l.
- In non-acidic soils the cyanides from MGP waste are soluble according to thermodynamic calculations, though dissolution in the field seems extremely slow. Probably dissolved forms of cyanide are almost totally converted to other insoluble complex cyanides. The little dissolved cyanide present is in the form of $Fe(CN)_6$ anions.
- At waste disposal sites on non-acidic (holocene) soils cyanides have been found present in groundwater as $Fe(CN)_6$ ions at maximum concentrations of 0.5 - 34 mg CN/l.

Mobility and precipitation of ferrohexacyanide
- In soils below MGP waste disposal layers some mobility of dissolved hexacyanoferrate is observed.

- In acidic soils dissolved $Fe(CN)_6$ can be precipitated at groundwater depth. (Concentrations of 100 - 400 mg CN/kg soil have been observed.)
- In non-acidic soils no indications of precipitation of dissolved hexacyanoferrate have been found, also not at groundwater depth. Mobility of dissolved hexacyanoferrate in these soils is comparatively higher.
- In acid soils eluviation of ferri ferrohexacyanides in colloidal form from disposal layers may be a dominant transport mechanism in the unsaturated zone. The colloidal transported cyanides will generally precipitate some meters deeper in the soil profile and form an illuviation horizon in which the cyanides accumulate. (Concentrations of about 100 mg CN/kg soil have been observed.) This phenomenon of colloidal transport has been given little attention, and has been studied thus far at only one soil profile in Germany.

Free CN

- Free CN in soils with MGP waste can theoretically occur upon dissociation of dissolved hexacyanoferrate, this dissociation is favoured by low pH values, whereas under these conditions the solubility of ferri ferrohexacyanide is very low (Meeussen, 1992. p.32/33,69).
- The maximum free CN concentrations were 3% of the dissolved hexacyanoferrate. Freely interpreted this would give rise possibly to 1 mg free CN/l at the MGP site where the highest dissolved total CN concentration in groundwater was found, 34 mg total CN/l. A concentration of 0.15 mg free CN/l is the maximum of the few measurements of free cyanide in CN contaminated groundwater (Meeussen, 1992. p.34).
- Based on the observed maximum free CN concentration in groundwater the estimated maximum concentration in aerated soil is 0.045 mg free CN/kg soil.
- (Available) Information of HCN gas in soil air or in ambient air at contaminated sites is extremely scarce, indications are that concentrations up to 2 mg/m^3 can occur.

Thiocyanate

- Thiocyanate can be present in the water saturated zone below the groundwater level, maximum concentrations are in the order of 90 mg CN/l or 30 mg/kg soil; above groundwater the maximum concentration is around 7 mg CN/kg soil.

4.3 Wastes from cyanides used in industrial processes

4.3.1 General

Total CN and CN forms

Liquid wastes from metal processing industries (MPI) may contain 2 - 50 % CN mainly in the form of simple alkali cyanides and cyanates (par. 3.3.1). Situations occurred in the past in which large volumes of these wastes were dumped, this was (mostly) done in co-disposal with other solid wastes. Soil and groundwater under such dumpsites became contaminated with CN. Concentrations encountered in groundwater show a wide range, with maxima up to 70 mg total CN per litre (Table 4.3).

Table 4.3 Total CN concentrations in groundwater under dump sites containing waste from metallurgic industries

Country	UK	NL	NL	NL
Reference	Stiff et al., 1976	Lagas et al., 1982	BKH, 1988	VROM, 1988
Dumpsite area	3.000 m^2	2.500 m^2	Inventory	Inventory
Waste origin	Heat treatment waste from 1961 to 1964	Heat treatment waste from 1956 to 1971	Metallurgic industry	Metallurgic industry
Waste quantity	4 ton of CN in 50 ton waste	1.8 ton of CN in 36 ton waste	Not specified	Not specified
Groundwater total CN mg/l	in 1975: max. 0.56	in 1978: max. 0.012	0.075 – 12	0.08 - 68

Cyanate and thiocyanate

In the publications reviewed very few quantitative data of cyanates and thiocyanates were found. Presence of cyanate has been reported in groundwater at concentrations of 2 -16 mg/l under the dumpsite in the Netherlands listed in Table 4.3; at pH < 6 cyanate brakes down to ammonium and carbondioxide (Lagas, 1981. p.13,17).

At the same site 2 - 4 mg thiocyanate/l was found. Its formation was also observed in British studies of similar wastes in containers, its formation by reaction of free cyanide under anaerobic conditions with sulphur or sulphur containing compounds is possible (Materassi et al., 1977 and Newton, 1977 cited by Lagas et al., 1981. p.13,17 and by Lagas et al., 1982).

4.3.2 Review of some studies

Dutch field studies

Soil field measurements

In a survey of the 0.8 ha premises of a former galvanic factory (located at Vlijmen, the Netherlands) CN concentrations measured in the upper 3 m of the soil ranged from 0.0001 - 27 g total CN/kg dry soil. The CN contamination within this soil volume of 24,000 m^3 is in patches, veins and planes with sharp boundaries as judged by the occurrence of Prussian blue. Probably concentrations in a large part of the soil volume mentioned are below the present Dutch Intervention Value 50 mg total CN/kg dry soil. The most accurate estimates of the soil volume with concentrations exceeding the present CN Intervention Value were respectively 4.000 m^3 without and 9,000 m^3 with taking the prediction error standard deviation into account, as concluded in a study comparing different survey procedures based on spatial variability studies (Staritsky et al., 1992).

In a residential quarter located at Vaassen on the premise of a former galvanic industry the Intervention Value is exceeded below the phreatic level in an area around a former cess-pool. Striking is that of the total CN measured in the water saturated soil 21 – 96 % is present as free CN (though free CN concentrations in groundwater and in air above groundwater are low as will be discussed later) (Table 4.4) (Raes et al., 1999).

Table 4.4 CN concentrations at most contaminated spots in a residential quarter at Vaassen on the premise of a former galvanic industry. (Source: Raes et al., 1999.)

Soil below phreatic level			Groundwater		Soil air	Indoor air
Boring	Total CN	Free CN	Total CN	Free CN	Free CN	
Number	mg CN/kg dry soil		mg CN/l		mg HCN/m^3	
1000	84	81	0.046	0.004	≤0.3 d.l. 1)	≤0.003 d.l.
1001	315	65	not analysed			
1002	86	39	not analysed			

1) d.l. = detection limit

Groundwater field measurements

At a disposal site in Deurne the Netherlands, where dumping of CN containing wastes was halted in 1971, groundwater at depths of 4-6 m, 11-13 m and 18-20 m was sampled at five spots in 1976 through 1980. The analysed total CN concentrations differed relatively little between the different depths, in 1976 both the minimum 0.006 mg/l and the maximum concentration 0.064 mg/l were found at 18-20 m depth. Over the years the average values found decreased sharply, viz. in 1976 0.03 mg/l, in 1977 0.02 mg/l and in 1978 through 1980 all values were lower than the detection limit 0.003 mg/l (Lagas et al., 1981. Appendix 2, p. 69). A possible explanation is that over the years the leaching of CN from the dumpsite decreases due to immobilisation of the CN, resulting in the decrease of the CN concentration in the groundwater by dilution and replacement with uncontaminated groundwater or by brake down of CN.

In the fore mentioned residential quarter at Vaassen groundwater was still contaminated in 1999, the maximum concentrations were 0.046 mg total CN/l and 0.004 mg free CN/l. Higher maximum concentrations, 2.3 mg total CN/l and 1.9 mg free CN/l, were observed here in a soil-clean-up pilot area after its leaching with acidified groundwater in order to remove other pollutants (Raes et al., 1999).

Disposal of liquid wastes by injection into infiltration pipes at the premise of the former factory at Vlijmen resulted in groundwater pollution with several contaminants to a depth of at least 72 m below the soil surface (Staritsky et al., 1992).

Air measurements in situ

In the aforementioned residential quarter at Vaassen on the premise of a former galvanic concentrations of CN in air were measured, twice at five different houses on 2 different dates in June 1999, both gaseous HCN and total CN in aerosols were determined. Concentrations of HCN in soil air were all below 0.3 mg/m^3 the detection limit, in the crawl space below the house and in the living room concentrations were below 0.003 mg/m^3 the detection limit. The concentration of total CN in aerosols in the crawl space and in the living room of the five houses was only in one house on one date equal to the detection limit 0.3 mg total CN in aerosols/m^3 indoor air. It is concluded that the observed CN concentrations in air do not indicate emanation of HCN from the contaminated soil and groundwater (Raes et al., 1999).

Dutch laboratory studies of CN leaching and breakdown (Lagas et al., 1982)

Experimental approach and set up. The behaviour of CN in heat treatment waste after co-disposal with domestic waste on sand was studied under controlled conditions in a column experiment in the laboratory (Lagas et al., 1982):
- CN as NaCN was mixed with salt to a concentration of the same order of magnitude as found in heat treatment wastes.
- 25 g CN contained in the salt was embedded in 50 cm high layer of domestic waste which was placed on top of a 60 cm high layer of sand all placed in a column.
- four of such columns were build with CN either placed low or high in the waste and with a permanent water level at 10 cm from the top (simulating a water saturated dumpsite) or at 20 cm above the bottom of the sand layer (simulating an unsaturated situation).
- the columns (radius 9 cm) were percolated with water at 10 mm per day during 7 months.
- the amount of NaCN placed in the columns corresponds to 1 ton CN per 1000 m2 comparable to quantities observed at dumpsites (Table 4.3)
- the percolate and the gas phase above the columns were collected over consecutive periods of two weeks and analysed.

Observation of Prussian blue. In the course of the experiment a blue colour developed in the domestic waste below the embedded CN. Chemical analysis indicated that the colouring was caused by the formation of ferri ferrohexacyanides.

Breakdown of CN. Over the experimental period of seven months between 72 to 82% of the cyanide was broken down, mostly to ammonium and organic nitrogen compounds; between 4 and 22% of the cyanide leached as free or complex iron cyanide and 4 to 11% remained in the landfill. Evaporation of HCN did not play a role. Of all the CN leached out over the 7 months roughly 90% was leached out within 6 weeks from the start of the experiment. Probably after that period most of the NaCN that was not leached out had been broken down or had formed less mobile compounds.

Leaching of CN. In the first weeks 80% or more of the total leached CN was present as free CN, later in the experiment the quantity total CN in the two weekly periods decreased with a factor of ten or more and the percentage of free CN in the leachate decreased to roughly 50%, other leached CN probably consisted mainly of iron(II)-cyanide. With a low water table the highest fraction of free CN was leached out, probably due to a shorter residence and contact time of the leachate on its way to the outlet of the column. More CN was leached out when the CN was embedded at a low level in the waste, thus closer to the outlet of the column, than when placed near the top of the waste.

Cyanate and thiocyanate. Cyanate and thiocyanate appeared to be absent in the leachate of the soil columns. Probably the redox potentials were not low enough for the formation of thiocyanate, while cyanate would have been hydrolysed to ammonium and carbondioxide at pH 5 of the leachate (Lagas et al., 1982).

United States of America studies

In soil column percolation studies it was found that:
- KCN and complex Fe(III)cyanide when dissolved in demineralised water are more mobile than when dissolved in landfill leachate;

- a high iron content in the soil increased the attenuation of the cyanides studied;
- in the soil columns a precipitate of $Fe_4[Fe(CN)_6]_3$ was found;
- probably a high soil pH increased the attenuation of the cyanides studied;

English studies

In studies with concrete containers of 5 m^2 it was found that approximately 95% of the CN added with the waste was broken down over a period of 4 years in the soil to ammonium and organic N compounds. For the landfill in Britain, listed in Table 4.3, it was calculated that probably part of the CN remaining in the soil had been precipitated as $Mn_2Fe(CN)_6$ (Stiff et al., 1976).

4.3.3 Conclusions on cyanides in soils containing MPI wastes

Inferred hypotheses

From the results of the reviewed field and lab studies the following can be postulated:
- more than 70% of NaCN and free cyanides will be broken down within 7 months after dumping;
- cyanides remaining in the waste after 7 months are mainly in the form of complex iron hexacyanide of which gradually a very low fraction will dissolve as hexacyanoferrate ions or other complex hexacyanide-metal ions;
- indications are that in 6 months after dumping the behaviour of most CN in these wastes will be comparable to that of complex ironhexacyanides in MGP waste;
- in the first weeks after dumping high concentrations of free CN can be built up in the groundwater below wastes containing simple cyanides. When reaching layers without biochemical activity these high CN concentrations can persist; probably free CN will gradually be converted into complex ironhexacyanides over time and precipitate as such.

Maximum concentrations

Data of historical contamination due to discarding of wastes by metal processing and photographic industries (MPI) are not easily accessible for the years after 1990; and to retrieve these falls beyond the scope of this report. The maximum concentrations reported in the studies above are: in soil total CN 27 mg CN/kg soil; in groundwater total CN 0.046 mg CN/l and free CN 0.004 mg CN/l; in ambient air free CN < 0.003 mg CN/m^3 (Staritsky et al., 1992; Raes et al., 1999).

4.4 Non-waste materials containing CN

The behaviour of anti-caking alkali ferrohexacyanide from road salt as observed and studied in three different situations will be looked into.

Studies in the USA of uncovered road salt storage (Ohno, 1990)

General

In a study of four uncovered storage facilities of road salt mixed with sand large monthly fluctuations were observed in the NaCl content of this stored material; probably decreasing concentrations are mainly due to leaching of the salt by rain whereas high concentrations probably coincide with refilling of the facilities in late summer and fall.

Field observations of CN in surface water
Within 30 meter of the stockpiles surface water in shallow wetlands were studied, and increased concentrations of dissolved complex hexacyanide were observed in these waters. Concentrations varied monthly at each site probably depending on hydrological conditions (fluctuating water volumes) and varying salt-concentrations during the year of the mix stored. The concentrations in the surface waters ranged from < 0.01 (detection limit) to 0.2 mg CN/l. In surface waters up slope from the salt deposits total CN concentrations were year round below the detection limit, indicating that CN found in surface waters near the facilities was leached from the stockpiles. (In the contaminated surface water the Cl/Na ratio was the same as in the stored salt, whereas the dissolved CN/Na ratio in the contaminated surface water varied from 0.2 to 0.8 of the ratio in the stored salt. Which indicates either lesser leaching of CN than of Na, sorption of dissolved CN to the soil during overland flow of the leachate or to suspended matter in the surface water, or degradation of CN.)

Laboratory studies of sorption of CN to soils
A laboratory study was conducted to investigate the sorption of sodium ferrohexacyanide to soil material at the four sites. Of each of these sites 25 g of air dry soil was shaken overnight with 25 ml of a road salt solution, containing 6 g Cl/l and 0.029 µg CN/mg Na. The fraction of CN sorbed ranged from 30 to 54%, the pH of the different soils ranged from 5.1 to 6.1, the soil with pH 6.1 showed the lowest sorbed fraction. After changing the pH of a soil with approximately one unit by adding acid or base the CN fractions sorbed respectively increased (max. sorbed 83% at pH 4.2) and decreased (min. sorbed 25% at pH 6.3).

Studies in the USA of effects from de-icing roadways (Paschka et al., 1999)

Runoff from salted roadways in Milwaukee (Wisconsin, USA) contained total cyanide ranging in concentration from < 0.01 to 0.13 mg CN/l, and in Edmonton (Alberta, Canada) ranging from 0.003 to 0.007 mg CN/l. The concentrations in Edmonton are lower which possibly can be ascribed to the use of a mixture of antiskid material and de-icing salt, containing relatively little salt. The runoff is discharged via sewer outlets on local streams, its further fate has not been studied.
In a study of the effect of application of de-icing chemicals on groundwater quality, monitoring samples were collected at eight sites over the years 1991 through 1997 by the U.S. Geological Survey. The sites are along large undivided highways with open drainage ditches and groundwater flow perpendicular to the roadway. Out of 265 samples total cyanide levels found are lower than 0.01 mg CN/l in 258 samples, approximately 0.01 mg CN/l in 6 samples, and 0.02 mg CN/l in 1 sample. It is concluded that there is no consistent evidence to date of cyanide contamination in the shallow aquifers at the sites studied.

Studies in the Netherlands at a road salt storage site (Fugro, 1995; Oranjewoud, 1993 and 1998; Vries de, 1998)

General
Studies have been made of soil and groundwater by cyanides under and close to a road salt storage shed (surface of the floor 4 m by 5 m) located at Séwei in Joure (the Netherlands).

The site of the shed is paved with bricks and in addition gutters have been constructed by which most of the rainwater is carried away. The phreatic level under the shed is at 1.10 m depth. Under the covered floor of this building blue coloured veins were observed in the soil above the phreatic zone indicating the presence of ferri ferrohexacyanide. Apparently the anti caking agent potassium ferrohexacyanide $K_4Fe(CN)_6$ dissolved and moved into the soil. It is not reported if this occurred prior to the construction of the shed and/or its floor, or in which way the transport from the stored salt and its anti caking agent occurred. Dissolved ferrohexacyanide reacted with Fe^{3+} present in the soil and precipitated as ferri ferrohexacyanide.

Concentration in the soil

Outside the shed and its extended roof the total CN concentrations observed in the 0.5 m top layer of the soil vary from < 0.1 to 0.2 mg CN/kg soil, except at one spot within 1 m distance from the entrance where 2.9 mg CN/kg soil has been measured.
Analyses of the soil under the floor of the shed showed:
- at depths up to 0.5 m:
from 0.3 mg to 61 mg total CN/kg soil (av. 32);
no free cyanides were observed;
thiocyanate concentrations ranged from < 1.2 (d.l.) at one spot to a maximum of 9 mg SCN/kg soil.
- deeper in the sandy soil up to 3.5 m depth:
generally higher total CN concentrations are found, with a maximum of 226 mg total CN/kg soil, than at depths up to 0.5 m;
no free cyanides were observed;
often higher thiocyanate concentrations are found, with a maximum of 13 mg SCN/kg soil, than at depths unto 0.5 m.
It is concluded that soil contamination with CN only occurs under the paved floor of the storage shed. In the studies no special attention is given to the higher CN concentrations in the soil at 3.5 m depth than at 0.5 m depth.

Concentration in groundwater

The concentrations of total CN in the groundwater at a depth of approximately 2 meter have been measured at one point under the shed and at 12 points at distances of 0.5 m up to 10 m from the shed.
The highest concentration 4.8 mg CN/l was found under the shed; at a distance of 2 m from the shed concentrations of 0.4 and 2.5 mg/l were found at two spots; at the other spots either closer to or farther away from the shed the concentrations ranged from 0.003 to 0.05 mg CN/l.
Free CN concentrations ranged from < 0.001 to 0.023 (av. 0.005) mg CN/l.
Thiocyanate was found only at one location 0.0014 mg SCN/l, at the other locations levels were below the detection limit of 0.001 mg SCN/l.

Mobility in the soil

With regard to the mobility of the CN in this soil (pH 6.4 to 8.6 and Eh -28 to +102) it is concluded:
- that in the topsoil where CN is in the form of precipitated ferri ferrohexacyanide the ferrohexacyanide concentration in the soil solution is governed by its solubility equilibrium. At the occurring pH > 6 the solubility is relatively high and CN is distributed to spots where no precipitated ferri ferrohexacyanide is present and/or it reprecipitates. The distribution of

dissolved ferrohexacyanide will be relatively fast as a low K_d value 0.1 l/kg is estimated for this layer.
- below the phreatic zone no precipitation of ferri ferrohexacyanide has occurred, here ferrohexacyanide ions are sorbed by ironhydroxides, which are positively charged at pH values below 8. In this layer the K_d is estimated at 1 to 5 l/kg, increasing with decreasing pH.

Study in the Netherlands of CN contamination of soils and of sewage sludge due to road salt use

Soils
A straightforward calculation shows that in case road salt containing 142 mg $K_4Fe(CN)_6$ per kg salt is applied during 14 days at 12 g/day on 1 m^2 soil with a density of 1.4 kg/m^3 that these applications may result in a contamination of 0.15 mg CN/kg soil if the potassium ferrohexacyanide is contained within a surface area of 1 m^2 in the top 5 cm of the soil (Brinkmann et al., 1997). Another aspect is that in the periods of thawing melted-snow-water with dissolved $K_4Fe(CN)_6$ will be dispersed and may concentrate in low-lying spots where consequently accumulation of $K_4Fe(CN)_6$ can occur. $K_4Fe(CN)_6$ may leach to deeper layers, it will also be converted to insoluble ferrohexacyanide complexes. In such low-lying spots accumulation can or will continue over the years that road salt has been and will be applied, and concentrations may well exceed 0.15 mg CN/kg soil.

Sludge
Sludge from urban wastewater treatments was sampled after winter periods during which road salt had been used. Dewatered sludge contained 17% - 30% dry matter in which CN concentrations ranged from 10 - 40 mg total CN/kg d.m.
Dewatering-water was not sampled, however similar water was obtained by centrifuging fermented wet sludge. This centrifugation-water concentration ranged from 0.01 - 0.02 mg dissolved CN/l. These concentrations are probably higher than in corresponding water emitted by the treatment installations (Brinkmann et al., 1997).

4.5 Groundwater, wastewater and sludge purification studies

There is a wealth of information of CN degradation-systems employed under anaerobic and aerobic conditions to remediate groundwater, wastewater or sludge contaminated with CN (BKH, 1988; Paruchuri et al., 1990; Koning de, 1995; Siller and Winter, 1998)
Two self-evident factors which come forward out of these studies are: CN brake down can be reduced or practically be inhibited due to (toxic) concentrations of CN species themselves or due to other contaminants. Practically all brake down of CN is biochemically activated, thus conditions need to be preferably such that microbiological life thrives.
Many data from these studies can certainly be interpreted in terms of possible brake down of CN in soils under a wide range of conditions. By lack of time this has not been attempted in the present study.

4.6 Mobility, breakdown, persistence and concentrations of CN in soils

Introduction

The reviewed studies focus generally in decreasing order of emphasis on concentrations of total CN in soil and groundwater, speciation and mobility of CN in soil and groundwater and lastly generally as a side point some observations are made on persistence in relation to speciation and brake down of CN.
Dutch studies of CN contamination at industrial disposal sites started in 1978 and consequently only historical contamination was studied as CN dumping had been halted in the early seventies. In a qualitative way the findings seem to indicate the following with respect to CN brought by human actions in soils.

Free CN

Persistence
The life time of free CN and of simple cyanides at high or low concentrations in the soil is limited. At high concentrations evolution of HCN gas will be dominant at first, with at the same time formation of metal hexacyanide complexes, generally with iron and or manganese present in the soil solution (Keizer et al., 1995). Later, and/or at lower concentrations of free CN, also biochemical brake down will take place (Lagas et al., 1982; Fuller, 1985).
Possibly is the biological activity in recently dumped wastes at a low level and may be hindered by adverse conditions (frost/low temperatures, very low pH, etc.), due to which decomposition of free CN will be at a low level in the first months.
In alkaline calcareous soils free CN^- levels at least up to 200 mg CN^-/kg soil are readily (biochemically) converted to ammonium and nitrate (Fuller, 1985). Reactions leading to dispersion as HCN gas to the atmosphere and to other conversions are indicated but not further considered.
Under anaerobic conditions 2 mg CN^-/kg soil has been suggested as a limit for effective brake down of CN^- under anaerobic conditions (Fuller, 1985).
Shortly after disposal of wastes containing simple cyanides leaching of free CN will occur. Studies following this over a period of several years in the field under or close to dumpsites have not been retrieved, neither data indicating if free CN from anthropogenic sources persists in deeper biochemically inactive soil layers.
Shortly after dumping of wastes containing simple cyanides, total CN and free CN concentrations in groundwater and in the soil solution can be higher than the concentrations measured in situations with historical contamination. This is indicated by concentrations of free CN in groundwater under a dumpsite which decreased to a level below the detection limit in the four years following their first measurement (the first measurement took place probably five years after the last dumping of CN containing wastes from metal processing industries) (Lagas et al., 1982).

Concentration in air
HCN gas emanating from disposal sites can probably lead to concentrations in the order of 1 mg HCN per m^3 soil-air; which may effect soil life and plants positively or negatively (Chapter 6).

HCN gas emanating from disposal sites will be diluted generally at the surface to much lower concentrations in the ambient air, possibly close to the site by a factor in the order of ≥ 10 to a concentration of $\leq$ 0.1 mg HCN per m^3.

Concentration in groundwater

The actual speciation of cyanide was measured in the groundwater (pH 5.6 - 7.6 and pE 6.5 - 8.5) at several MGP sites in the Netherlands. Results showed that in all cases the contribution of free cyanide to the total is negligible (Meeussen, 1992. p.34). Presently the concentration of free CN in groundwater at MGP sites will probably not exceed 1 mg CN/l, the maximum concentration observed in the field was 0.15 mg CN/l.

In an overview of contamination of Dutch groundwater observed at CN historical sites the uncertainty if free cyanide occurs or not is clearly brought forward, and it is concluded to assume that all cyanides in Dutch groundwater at contaminated sites are present as complex metal-cyanides (Koning de, 1995. p.19).

- field observations and measurements of free CN at contaminated sites show large differences with the estimates made by chemical model calculations. Apparently many soil-factors which are not included in these calculations play an important role.

Ferrohexacyanides

Persistence

Laboratory studies indicate that dissolved complex metal-hexacyanides are broken down to some extend to CO_2 and ammonium (Barclay et al., 1998; Hommelgaard et al., 1998).

The lifetime of easily soluble complex alkali ferrohexacyanides in the soil is limited as reaction to ferri ferrohexacyanides or manganese ferrohexacyanides will occur.

Ferri ferrohexacyanides and manganese ferrohexacyanides are biochemically inert stable compounds which generally precipitate in the soil after their formation and will remain there over many years (Meeussen, 1992; Keizer et al., 1995; Mansfeldt et al., 1998).

Mobility

- mobility of ferrohexacyanides in the soil at low pH is probably limited to short distance transport in colloidal form downward with the water fluxes in the soil. The complex CN colloids will precipitate during transport on the surface of soil structural elements as the velocity of the water flux deeper in the soil profile decreases or with a change of pH (Mansfeldt et al., 1998). These sedimentation processes are probably similar to illuviation of clay in soils where a texture B horizon is formed;
- at high pH values, probably only when situated at or near the soil surface without dissolved manganese, ferri ferrohexacyanides can dissolve and can be transported with capillary rising water to the soil surface where they precipitate again as the water evaporates, staining the wetted surfaces.

Concentrations

- it can be stated that the CN at sites of former MGP's will be present in groundwater and in the soil solution predominantly as complex hexacyanoferrate ions at concentrations from 0.5 - 34 mg CN/l. Free CN is present in groundwater and in the soil solution at levels of 0.5% - 3% of the dissolved hexacyanoferrate. The highest concentration of dissolved free CN observed in the field is 0.15 mg CN/l.

Thiocyanate and cyanate

- most publications on thiocyanates mention that little is known about its environmental effects or fate;
- in laboratory tests SCN at concentrations of 2.6 mg CN/kg soil is broken down almost completely within 10 days;
- at former MGP sites the highest thiocyanate concentration in soil layers above groundwater is around 7 mg CN/kg soil;
- at former MGP sites on holocene soils the highest observed thiocyanate concentrations are around 90 mg CN/l in groundwater at depths between of 4 – 15 m, or around 30 mg CN/kg soil;
- thiocyanate concentrations in soil and groundwater observed at a salt storage site at Séwei, the Netherlands, are lower than the maxima reported of former MGP sites;
- although possible presence of cyanate is mentioned several times in respect to wastes from MGP's and industrial activities presence of cyanate is never reported.

5. Cyanamids and simple cyanides in agriculture

5.1 Cyanamids

General

Cyanamids comprise compounds with $=N-C\equiv N$. They do not release free cyanides, although they have been included in the overview of cyanides “Reactions, processes and materials with potential for cyanide exposure” (Homan,1987).

Hydrogen cyanamid H_2NCN

Hydrogen cyanamid has plant physiological properties and is used as a herbicide, a desiccant, as well as a plant growth regulator. E.g. for early post emergence control of broad leafed weeds, as a desiccant before harvesting potatoes (BCPC, 1994. p.238/9).
In soils hydrogen cyanamid is converted to nitrogenous compounds which are readily taken up by plants. Hydrogen cyanamid in soils and its use on plants does not give residue problems (BCPC, 1994).
More recently hydrogen cyanamid is used as a growth regulator on fruit trees in warm climates. The lack of chilling resulting in erratic and uneven bloom (of e.g. peaches, almonds, cherries, grapes) can be overcome by application of the commercial product ‘Dormex’ (Powell et al., 1994).

Calcium cyanamid CaNCN

Calcium cyanamid has been produced commercially since 1905 and is sold under the name lime nitrogen, a fertiliser with herbicidal effects, it has also been used as a defoliant.
It is converted after its application with moisture to hydrogen cyanamid and lime. Its herbicidal effects are due to the phytotoxicity of the intermediate conversion product hydrogen cyanamid, which is hydrolysed within a few days into urea, the last is hydrolysed to ammoniumbicarbonate. Urea and ammonium are used by plants as a nitrogen source.

$CaNCN + H_2O + CO_2 \rightarrow H_2NCN + CaCO_3$
calcium cyanamid → hydrogen cyanamid

$H_2NCN + H_2O \rightarrow CO(NH_2)_2$
hydrogen cyanamid → urea

$CO(NH_2)_2 + 2H_2O \rightarrow (NH_4)_2CO_3$
urea → ammoniumbicarbonate

The way to use calcium cyanamid as a fertiliser and to take advantage of its herbicidal effects is to apply it before seeding. The optimum number of days to apply it before seeding vary from 3 to 10 days and depend on weather conditions, its application rate and on the crop to be sown or planted (Koning, 1965). In this way its herbicidal effect results in the death of emerging seeds and seedlings.
The use of calcium cyanamid has always been a small fraction of the total commercial N fertiliser consumption, its use was probably at its height in the 1950’s. Since then it decreased

as the spectrum of available herbicides increased. However from a research point there is a renewed interest in calcium cyanamid. In field trials is tested if calcium cyanamid will reduce the number of earthworms in some Dutch polder soils, in which under specific soil moisture/water table conditions an abundance of earthworms in the top soil causes an aggregation of soil particles intervening with the harvest of potatoes and onions. In these demonstration/ investigations application rates of 100 – 200 kg N/ha are used in (Ester, 1998).

Calcium cyanamid will have been converted within 2 weeks after its application to nitrogenous compounds, such as ammonium, nitrate and urea, which are common in all agricultural fields. Calcium cyanamid does not give residue problems in crop products or soils (BCPC, 1994). For fertilisation purposes an application of 50 kg N/ha at the time of seeding is common, which corresponds to 144 kg CaNCN/ha or about 50 mg CaNCN/kg soil. The proposed Dutch ecological intervention value for calcium cyanamid is 10 mg CaNCN/kg soil for a standard soil (Denneman and Gestel van, 1990). This level is exceeded when aforementioned routine N application is applied as calcium cyanamid.

5.2 Indistinctness about the potentials of simple cyanides as fertilisers

Laboratory experiments with simple cyanides (NaCN and KCN) show that these CN salts (probably applied at low rates) are converted in the soil into nitrates, which are used as a nitrogen source by plants. These experiments date as far back as 1906 and 1945 and were referred to again later without further details in conjunction with new results from laboratory and small scale field tests with calciumcyanide, hydrogen cyanamid and dicyanodiamid $C_2H_4N_4$ (Fuller, 1985). As mentioned before hydrogen cyanamid and also dicyanodiamid do not release free cyanide, however calciumcyanide dissociates in soil moisture to Ca^{2+} and free cyanide CN^-.

The impression was given that all above mentioned compounds would have great potential as N fertilisers, or were already used as such (Fuller, 1985). The brief descriptions coupled with (unjustified) emphasis on practical applications have led to quotations that simple cyanides which release free CN are used or have been used as fertiliser (Koning de, 1995); and also to misinterpretations that free CN and/or cyanides which release free CN are not phytotoxic (Hsu, 1994; Seijger, 1995; Wen et al., 1997). In chapter 6 further details about phytotoxic levels of free CN will be discussed. Here the remark will suffice that simple cyanides have never been and are not used as fertilisers, and that elevated levels of free CN (and hydrogen cyanamid and calciumcyanamid) can be phytotoxic. Even natural occurring levels of free CN in the rhizosphere can be toxic to plant pathogens and to some extent also to certain plants (Schippers et al., 1990; Antoun et al., 1998).

6. Cyanides in plants, phytotoxicity, and (non-)toxicity to humans[5]

6.1 General

6.1.1 Cyanogenic plants

A separate group of plants, named cyanogenic plants, is distinguished for their potential to release elevated concentrations of free cyanide upon damage of their plant cells. Cyanogenic plants contain CN in nitriles, which are formed endogenously as part of the nitrogen metabolism (Appendices 1 and 2). Elevated levels of nitriles are encountered in more than 1,000 of such plant species in about 100 plant families (Scheuer, 1992; Conn, 1979). The nitrile levels of cyanogenic plants vary between plant species and cultivars, are dependant of physiological stage and growing conditions, and in many species nitrile levels are only elevated in some plant parts (Jones, 1998). Nitriles in cyanogenic plants possess two main functions: plant defence; and a source of N for synthesis of amino acids (Griengl et al., 1997a and 1997b).

Nitriles are generally present as cyanogenic glycosides, and in some genera as glucosinulates or as cyanolipids. When the cellular structure is disrupted by injury free CN can be released probably upon catalytic hydrolysis of these nitriles. This occurs e.g. upon ingestion and digestion of cyanogenic (parts of) plants by man or animals (Eissler, 1991, Griengl et al., 1997). CN or SCN (e.g. in case of Brassica species) can be liberated at toxic levels which is a natural phenomenon of these plants. Among the cyanogenic plant species are the important tropical root crop cassava (Evered and Harnettt eds., 1988) and sorghum of which fodder can contain elevated cyanide levels in the form of nitriles (Pickrell et al., 1991). Internationally this represents the greatest source of cyanide exposure and toxicosis to man and animals [Ballantyne and Marrs (eds.), 1987]. Toxicosis has to be prevented either by growing cultivars with low levels of nitriles, or by processing these plants in a way that the nitrile levels are reduced before consumption.

It has to be stressed that CN present in cyanogenic plants is natural, endogenously formed, is not present as free CN in the plant and is not induced by elevated CN levels in the environment or soil.

Consumption of cyanogenic plant parts is always a cause for concern independent of exogenous CN sources, consequently nitrile levels and possible free CN content of cyanogenic plants will not be discussed in relation to CN soil contamination. (That processing of these plants may lead to soil and environmental contamination with CN is another matter; see paragraph 3.4.).

6.1.2 Natural formation, conversion and detoxification of free cyanides in (non-cyanogenic) plants

In the early 1980's free cyanide has been discovered to be a co-product of the endogenous synthesis of the plant hormone ethylene (Peiser et al., 1984; Yip and Yang, 1988). Ethylene plays an important role in the regulation of developmental phenomena in plants such as growth, senescence and ripening. Its biosynthesis is also strongly stimulated under stress

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[5] More details of the studies reviewed in this chapter are given in Appendix 3.

conditions, such as pathogen infection, wounding and drought (Siefert et al., 1995; Grossmann, 1996). Consequently in all plants endogenously co-produced free cyanides are present in some stage at low concentrations, depending on species, growth stage and plant part ranging from probably 0.05 to 0.5 mg free CN/kg fresh weight (Manning, 1988; Yip and Yang, 1988; Grossmann, 1996).

Natural co-produced free CN is rapidly conjugated by the enzyme β-cyanoalanine synthase (BCA-synthase) into β-cyanoalanine (BCA) which is further metabolised to asparagine. BCA-synthase appears to be ubiquitous in plants and appears to maintain free cyanide levels in natural healthy plants at non-toxic levels (Blumenthal-Goldschmidt et al., 1963; Blumenthal et al., 1968; Grossmann, 1996; Yip and Yang, 1988, Miller and Conn, 1980). Detoxification of cyanides when present in plants at low levels is also possible by transformation into thiocyanates mediated by rhodanese (Towill et al., 1978). This enzyme occurs far less commonly in plants, amongst others in Brassica and Sorghum species, in which species BCA-synthase is also present (Miller and Conn, 1980).

BCA-synthase is considered to be the key enzyme in the detoxification of free CN, its activity level can be higher in (non-cyanogenic) plants with relatively less sensitivity to CN (e.g. rice, Oryza sativa cv. Thibonnet) (Grossmann, 1998), and in cyanogenic plants it has very high activity levels (Miller and Conn, 1980). [Remark: with respect to rice and/or Oryza species some confusion exists about their being cyanogenic or not (Jones, 1998)].

6.1.3 Uptake mechanism of cyanides by plants

The chelating ability of free CN^- has been clearly proven by the increased uptake of trace metals and americium from the soil by young bean plants in pots to which NaCN was added during their growth. CN was taken up by these plants for a large part as a chelate linked to a metal (Wallace, et al.1971; Wallace et al. 1981).

No further data have been retrieved on the uptake mechanism of free cyanide or other CN species.

6.1.4 Range of effects of exogenous free CN on plants

Effects of natural exogenous free CN on plants

The effects of exogenous free cyanides, at natural levels, on plant growth are often not predictable. E.g. about 50% of the Pseudomonas strains isolated from potato and wheat rhizospheres are able to produce HCN in vitro (Schippers et al., 1990), and also 3% of 266 rhizobium and bradyrhizobium bacteria-species tested (Antoun et al., 1998). It has been shown that HCN produced in natural soil by rhizobacteria can efficiently suppress certain soil-borne plant diseases and promote growth of wheat, tobacco, cotton and cherry trees (Défago et al., 1990). There is also circumstantial evidence that microbial cyanide, may inhibit root and plant development. This postulated growth reducing effect of CN from rhizobacteria may only become apparent in the absence of parasitic plant pathogens that are suppressed by HCN (Schippers et al., 1990).

Phytotoxicity of free CN

Exogenously induced elevated (free) cyanide concentrations in plant tissues inhibited respiration (through iron complexation in cytochrome oxidase), ATP production and other processes dependant on ATP, such as ion uptake and phloem transport. Visual symptoms comprise leaf yellowing (chlorophyll damage), necrosis, senescence and plant death (Towill et al., 1978, cited by Eisler, 1991; Lieberei et al., 1996; Grossmann, 1996).

6.1.5 Effects of herbicide-induced elevated levels of endogenous free CN

In shoot tissue of various grasses increased levels of HCN were found upon treatment with auxin herbicides. E.g. quinclorac (3,7-dichloro-8-quinolinecarboxylic acid) can act on sensitive species as an auxin overdose and effect the phytohormonal system. In sensitive grasses growth inhibition, development of tissue chlorosis and necrosis of the entire plant is paralleled by an increase in ethylene biosynthesis and increased levels of co-produced cyanide, the last appears to be the phytotoxic agent. In sensitive dicotyledons the dominating effect is ethylene induced accumulation of abscisic acid resulting in growth inhibition and plant senescence (Grossmann, 1996; and 1998).

6.1.6 Non-toxicity to humans of free CN and thiocyanates in non-cyanogenic plants

Toxic effects for humans or domesticated animals of free CN, BCA (β-cyanoalanine) and SCN have not been reported in food or feed from cultivated non-cyanogenic plants (Ressler, 1999) and will probably not be induced by environmental CN contamination as long as exogenous CN remains below phytotoxic levels.

6.2 Quantitative information on effects of CN on plants

6.2.1 Introduction

It can be said that there is a scarcity of information on free CN and CN species with respect to effects of CN soil contamination on seed emergence, seedling vigour, CN uptake by plants, plant growth and phytotoxicity. The same can be said of the concentration of free CN and CN-species in different plant parts (leaf vegetables, edible tubers, edible grains and seeds) of plants exposed to high levels of exogenous CN. The little available diverse information on this has been categorised and is included in Appendix 3.

Based on Appendix 3 the most relevant information is presented below on: natural and phytotoxic CN levels in plants; seeds or plants germinating or growing in contaminated soil; effects of hydroponically added free CN to young grass plants. From this information estimates are made of maximum CN levels in plants exposed to CN soil contamination and of maximum non-phytotoxic free CN concentrations in root media.

6.2.2 Free CN levels in non-cyanogenic plants

Natural levels of free CN in plant tissue are highest in plant tissues which actively produce ethylene. Natural maxima reported for healthy plant tissue are in the range of 0.05 - 0.5 mg free CN/kg fresh weight (Yip and Yang, 1988; Tittle et al., 1990; Grossmann and Kwiatkowski, 1993 and 1995).

It is stated in general terms for non-cyanogenic grasses sensitive to auxin herbicides that (Grossmann and Kwiatkowski 1995; Grossmann 1996 and 1998):
- that natural free CN concentrations are around 0.1 – 0.4 mg free CN/kg f.w. (Table A3.7);
- that a two- to fourfold increase of the natural CN concentration can have phytotoxic effects;
- concentrations of more than 10 mg free CN/l in hydroponic rooting media led within four days to growth reductions of more than 50% and concentrations of 0.7 – 1.2 mg free CN/kg fresh weight in plants (Table A3.6).

In a study with bean plants which were hydroponically exposed during four days to free CN (2.6 mg free CN/l) a concentration of at maximum about 8 mg total CN/kg d.m., i.e. about 1.0 mg total CN/kg fresh weight, was found in plants subject to exogenously caused CN-phytotoxicity (Wallace et al., 1977) (Appendix 3 Table A3.2).

It is estimated from the foregoing information that in non-cyanogenic plants exogenously induced CN concentrations which do not cause phytotoxicity can go up maximally from 0.1 to 2 mg free CN/kg f.w. depending on plant species and cultivar. Whereby the upper estimate is very likely a factor two too high, no information is available to support or to justify a lower estimate.

In contaminated soils concentrations of free CN are estimated to reach maximally 0.15 mg CN/l, a factor 20 to 70 lower than in before mentioned hydroponic rooting media. Consequently a very worst case estimate of the maximum concentration in plants on contaminated soils is 1 mg free CN/kg f.w. (Table A3.6). At which concentration plants are most likely unhealthy, hampered in their growth and rejected for consumption.

6.2.3 Free CN in soil, effect on seed emergence

Free cyanides can have an inhibitory effect on emergence of seeds and/or on seedling vigour and survival. In laboratory studies the maximum concentration not effecting seed emergence was found to be 1 - 5 mg free CN/kg soil, depending on species and/or incubation time (Table 6.1). It is not noted if concentrations of free CN decreased during the incubation time, nor are any remarks made on seedling vigour and subsequent plant growth.

Table 6.1 Effects of free CN in (artificial) soil on seed emergence. *(Source: CCME, 1997.)*

Seeds of	Incubation time	NOEC	LOEC	EC_{25}	EC_{50}
	days	mg free CN/kg soil			
Radish	3	0.9	1.9	1.3	2.9
Lettuce	5	5	10	7	13

6.2.4 Seed coating with SCN effect on germination and mildew

Seed coating of wheat with respectively Na-, K- and NH_4SCN at concentrations of 1, 10, and 100 ppm (of these salts in the pelleting substance probably; this is not specified) had an accelerating effect on germination, and the seedling-root growth (Müller et al., 1988). The seed coating had also a delaying and/or severity decreasing effect on powdery mildew infestation of the seedlings growing in pots. This disease suppressing effect increased with increasing concentrations within the range of concentrations tested (Müller et al., 1988).

6.2.5 CN soil contamination, effect on plant growth and CN content

Laboratory studies

Bean plants and free CN
Exposure of growing bean plants to addition of 27 mg free CN/kg soil caused severe growth reductions within 7 days (Wallace et al., 1977 and 1981).

Rye grass and ammonium-ferri ferrohexacyanide $NH_4Fe[Fe(CN)_6]$ *(AFCF)*
The following study was executed to check possible effects of the use of the feed additive AFCF (par. 3.5.4) on pasture growth. Italian ryegrass (Lolium multiflorum) was seeded and grown for 310 days in pots with sandy soil material pH-$CaCl_2$ 5.2 to which AFCF had been added at a rate of 3.2 g CN/kg soil. Plants were harvested by cutting every third week, resulting in 14 harvests; fertiliser was applied after each harvest. The addition of AFCF to the soil had no effect at all on the growth and dry matter production of the Italian ryegrass (Vandenhove et al., 2000).

Rye grass and MGP waste
It was found that a 1% mixture of oxide-box wastes and soil produced a slight inhibitory effect on the growth of ryegrass. When more than 10% oxide-box waste was mixed into the soil the growth inhibitory effect became quite evident (Roberts and Gemmell, 1979). It was not diagnosed whether this phytotoxicity of MGP waste was due to cyanides or to other constituents or factors such as aluminium toxicity evoked possibly by the low pH of the waste.

Field studies and observations

Natural vegetation on CN contaminated shorelines
In 1980 plants were sampled which were growing at shoreline sites contaminated with CN from gold-mill effluents (main contamination occurred in the years 1900 - 1960, in 1978 contamination had been practically halted). The total CN levels in three of the four species studied show very clear increases due to past and/or relatively recent CN soil contamination. No cyanide was found in willows; in a herb named tansy (Tanacetum vulgare) cyanide concentrations varied and appeared to increase with increasing soil concentration; CN levels in arrow grass (Trigochin maritima) growing at contaminated areas showed small increases; dandelions (Taraxacum officinale) growing at contaminated sites showed clear increases in CN content (Table 6.2). In this field-survey-study the correlation between total CN levels in plants and soils did not show high statistical evidence (Howe and Noble, 1985). A likely cause is that the CN levels in the plants studied fluctuate around a maximum ceiling. For Taraxacum this is supported by the laboratory studies with Taraxacum officinale which after 3 days growth on a solution with 260 mg free CN/l showed the same (maximum?) level of 11.5 mg total CN/kg (f.w. or d.m.) (Appendix 3 Table A3.5). CN speciation in the soil and within the plants, plant growth/vigour and possible cyanogenic properties of the plants fell beyond the scope of this study. It is indicated in the study that the fraction of dissolved CN in the soil and in the plant after uptake is probably in the form of complex metal-CN ions (Lakin et al., 1974 cited in Howe and Noble, 1985). The last supposition is supported by the metal-CN chelate uptake observed in studies with bean plants (par. 6.1.3; par. A3.1.2 in Appendix 3). Conversion of complex metal-CN in the plant is not discussed in these studies.

Table 6.2 Total cyanide in plants[1) growing at CN contaminated shoreline sites. (Source: Howe and Noble, 1985.)

Soil, dry	Dandelion	Tansy	Arrowgrass	Willows
mg total CN/kg				
0.7 (uncontaminated control)	< 0.5	< 0.5	< 0.5	< 0.5
2.0	< 0.5	2.0	n.d.	< 0.5
11.3	10.3	7.6	4.5	< 0.5
16.2	11.3	3.8	1.2	< 0.5

1) No details about plants parts sampled, nor information if CN contents are on a fresh or dry matter basis.

Grass on ferri ferrohexacyanide contaminated soil
As mentioned in Paragraph 4.2.2 grass was observed with a blue taint due to capillary rise of dissolved ferri ferrohexacyanide from the soil. Apparently grass persists in this situation and is growing.

Revegetation of MGP landfills and use of MGP waste a herbicide
In the UK experience is that large landfills of MGP waste (spent oxide) are difficult or impossible to revegetate unless the waste is at least 3 metres below the finished surface (Wilson and Hudson, 1980; Wilson and Stevens, 1981).
In earlier days in the Netherlands MGP waste has been used as a ‘herbicide’ at or close by MGP sites (Koning de, 1995. p.14); no information is given of the cause of this phytotoxicity.

Conclusions on effects of CN in soil on plants

Free CN
Seed emergence tests show that 1 mg free/CN/kg soil has little or no harmful effects. Laboratory studies with growing plants indicate that addition of 27 mg free CN/kg soil is phytotoxic.

Complex cyanides
In laboratory studies addition of a (soluble complex hexacyanide) ammonium-ferri ferrohexacyanide at 3.2 g CN/kg soil did not effect plant growth at all. Field studies on soils contaminated by mine-effluent indicate that natural vegetation can persist on soils containing 16 mg total CN/kg. On soils contaminated by MGP waste growing grass has been observed with at times blue colouring due to capillary risen ferri ferrohexacyanide. On the other hand field observations show that in situations with very high, not specified, levels of MGP waste in the soil that revegetation is not possible; no information is given of the underlying cause of the observed phytotoxicity.
Presence of soluble metal-CN complexes result in uptake by some naturally occurring plants. On soils contaminated by mine effluent higher total CN contents in the soil are reflected in an irregular way in an increase of total CN concentration in plant material of some of the plant species of the natural vegetation. Maximum concentrations observed in these species show a range of 4 - 11 mg total CN/kg plant material (either f.w. or d.m.). Indications are that fore mentioned CN concentrations coincide with the ceiling of the non-phytotoxic maximum concentration in these plants, and that the total CN is present as complex metal-CN ions or other ‘non-free’ CN compounds.

6.2.6 Effect of elevated free CN in rooting solutions on plants

Laboratory studies

Dandelions

Young dandelion plants showed increased levels of total CN but easily survived exposure during three days to mine effluent containing 7-8 mg total CN/l. Exposure to solutions containing 0.26 mg free CN/l showed variable results, probably indicating increases of CN content in the leaves just below or up to the detection limit of 0.2 mg total CN/kg (f.w. or d.m.) (Howe and Noble, 1985) (Appendix 3 paragraph A3.2.1).

Bean plants

Exposure of bean plants during four days to solutions containing 2.6 mg free CN/l resulted in severe growth reduction and 8 mg total CN/kg d.m. in exposed plants (Wallace et al., 1977).

Potatoes

Some evidence has been presented that a concentration of 0.13 mg free CN/l will cause reductions in root growth of potato plants (Schippers et al., 1990).

Digitaria sanguinalis

Young Digitaria sanguinalis grass plants exposed during 75 hours to a hydroponic solution with KCN containing 21 mg free CN/l showed severe reduction in shoot weight (Grossmann, 1998) (Appendix 3, Table A3.9).

Barnyard grass

Young barnyard grass plants survived exposure during four days to a hydroponic solution with KCN containing 7.8 mg free CN/l however leaf chlorosis and a severe reduction in growth were observed, a two-fold higher concentration caused also fore mentioned symptoms and shoot tissue necrosis in addition (Grossmann and Kwiatkowski, 1995).

Water hyacinth

Water hyacinths showed leaf discoloration and died in the course of an eight day exposure to lab-prepared effluent solutions containing 9 mg free CN/l and other contaminating compounds (Granato, 1993).

Conclusions of effects of free CN in rooting-solutions on plants

These studies show that short time exposure (3 - 8 days) of growing plants to concentrations of 9 - 21mg free CN/l rooting-solution caused severe reductions in growth and/or plant death; no data are available over longer exposure periods. The data do not indicate clearly the maximum level of free CN in rooting-solutions which does not cause reductions in plant growth, a gross estimate of this is made: 0.1 - 1.0 mg free CN/l, probably depending on species.

Background concentrations are not known but concentrations of around 0.1 mg free CN/l are likely to occur naturally in soil pore-water, certainly locally in micro-spots and in the rhizosphere. These concentrations may probably be beneficial or antagonistic to plant growth depending on soil life, plant pathogenic organisms and plant species (Schippers et al., 1990; Défago et al., 1990).

6.2.7 Effect of elevated free CN in ambient air on plants

Some limited quantitative information has been retrieved on effects of elevated CN levels in ambient air on plant growth. Acute exposure of plants to 180 mg free CN/m^3 during five minutes is lethal (Lieberei et al., 1996). In this study the HCN containing air passed through separated leaves, and within less than 1 minute the HCN concentration in the leaf tissue corresponded to the HCN concentration in the gas mixture used for the exposure.
Other information is that HCN is not phytotoxic at concentrations usually evolved from gassing powders (sodium cyanide mixed with kaolin) used for fumigation of greenhouses (Key et al., 1977 and Worthing, 1979, cited by Homan, 1987), while these concentrations increase commonly to 200 mg free CN/m^3 as mentioned in another publication (Ballantyne, 1988). Also no phytotoxic effects are reported of experiments in which plants were exposed at intervals to air with 100 mg free CN/m^3 (Blumenthal et al., 1968).
Probably by preventing the entering of HCN plants can adapt to and survive ambient air with 200 mg free CN/m^3, whereas phytotoxic effects will occur upon entering of such air into plant tissues.

6.3 Conclusions

6.3.1 Free CN

Phytotoxicity
The following estimates have been made in the foregoing of maximum free CN levels which do not effect plant growth:
- seed emergence will be effected little or not by 1 - 2 mg free CN/kg soil;
- 0.2 mg free CN/kg soil does probably have little or no effect on plant growth [this value has been based on 0.2 l water (with 1 mg free CN/l) per kg soil, soil moisture 30 vol.%];
- 1 mg free CN/l in rooting media does probably have little or no effect on the growth of most plant species;
- maximum free CN concentration in ambient or in soil air which does not effect plant growth may be as high as 200 mg CN/m^3;
- in non-cyanogenic plants the maximum non-phytotoxic level - generally a factor two or three higher than the natural background concentration - may be as high as 2 mg or as low as 0.1 mg free CN/kg f.w. depending on plant species and cultivar.

From the scattered and scarce information an overview is made of the lowest observed concentrations leading to phytotoxicity, without specification of plant species tested and experimental conditions as exposure time, etc. (Table 6.3).

Table 6.3 Lowest observed free CN concentrations leading to phytotoxic growth reduction in certain plant species tested.

Soil		Nutrient solution		Plant	
mg CN/kg	Info	mg CN/l	Info	mg CN/kg fresh	Info
27	Table A3.2	2.6	Table A3.2	≤ 0.4	Table A3.8
1.3	Table A3.1 seed emergence	21	Table A3.9	≤ 0.3	Table A3.9

The concentrations in plants listed in Table 6.3 are for grasses. The only information retrieved on dicotylodons are from experiments with beans exposed to free ^{14}CN after which ^{14}C was measured in the plants (Wallace et al., 1977; Wallace et al., 1981; Table A3.2). Phytotoxicity was observed at levels less than 8 mg total CN/kg d.m. or at levels less than about 1 mg total CN/kg fresh weight.

Free CN in plants and food
Free CN does not accumulate in healthy plants, practically all free CN taken up by healthy plants is converted to asparagine, as long as no phytotoxic effects occur. As discussed (paragraph 6.2.2) it is assumed that in all (non-cyanogenic) vegetable plants and food from CN contaminated soils at maximum 1 mg free CN/kg vegetable food can occur (paragraph 7.6.1). Edible plant parts used, processing (drying, etc.) and food preparation are not considered by lack of information on the effect of these factors on the CN content of food.

6.3.2 Other CN species

Italian ryegrass grown in pots containing 3.2 mg CN/kg soil (as ammonium-ferri ferrohexacyanide) did not show any yield depression in any of the 14 harvests cut at three weekly intervals during one year (Vandenhove et al., 2000).
Field observations have been reported of grass growing on soils contaminated by ferri ferrohexacyanide from MGP. In some situations both soil and grass can show at times a blue colour from capillary risen ferri ferrohexacyanide (paragraph 4.2.2). Apparently in these conditions grass can grow and persist. On the other hand field observations show that in situations with very high, not specified, levels of MGP waste in the soil that revegetation is not possible; no information is given of the underlying cause of the observed phytotoxicity. Natural vegetation is reported to be growing on river banks in soils with total CN concentration ranging from 2 – 16 mg total CN/kg dry soil due to CN contamination dating from some years or decennia ago. In view of this span of time most or all CN in the soil will be present as complex CN compounds and/or some insoluble metal simple-cyanides. In this environment some plant species show increased total CN concentrations others not, no information is provided if some species are cyanogenic or not (Table 6.2).
No other information has been retrieved on other CN species (than free CN), such as SCN and complex cyanides with regard to their uptake and conversion by plants, to their environmental levels toxic to plants, nor on their effect on CN or SCN levels in plants. Consequently no estimates will be made of non-phytotoxic maximum CN levels, or of other CN species in plants due to soil contamination with other CN species. It can be concluded that complex cyanides at levels 3 mg CN/kg soil are not phytotoxic, at least not for Italian ryegrass.

The risk of soil contamination with other CN species to humans will be considered as negligible for the pathway soil ⇒ plant uptake ⇒ conversion and concentration in the plant ⇒ concentration in food products ⇒ human intake. Although this approach can not be fully justified it can be supported by the following argument. Toxic levels for humans or domesticated animals of free CN, complex CN and SCN have not been reported in food or feed from cultivated non-cyanogenic plants. And toxic levels will probably not be induced by environmental CN contamination as long as exogenous CN does not hamper or inhibit plant growth and remains below phytotoxic levels. Once the last occurs diseased plants may possibly show enhanced CN levels, however diseased plants are unlikely to be used for food.

7. Human exposure to historical CN soil contamination and Intervention Values

7.1 Background information

Policy and Intervention Values

The basic aim of the Dutch environmental policy is the protection of man, animals, plants, ecosystems and property. The concept of 'Maximum Permissible Risk' was introduced in 1988 as one of the standards to serve as a base for the practical decision making and execution of the environmental policy [VROM, 1988b; Ferguson et al (eds.), 1998; Ferguson and Kasamas (eds.), 1999; this report paragraph 2.2].

The ecotoxicological intervention value for soil contamination with CN (which is set equal to the HC50) could not be derived, by lack of information about effects of CN soil contamination on animals, plants and ecosystems (Verbruggen et al., 2000). Thus for soil contamination with CN only the risks of exposure of humans to CN are considered. The Intervention Value for soil contamination with CN is equal to the human toxicological intervention value. That is the concentration level of a contaminant in a soil which, under standardised conditions, will result in a potential exposure whereby the toxicological threshold values (MPR_{human}) are reached for men. Consequently the definition of human toxicological threshold values of CN species is just as important as the behaviour of a contaminant in the soil determining the potential exposure of men. The potential exposure is calculated using the CSOIL model, encompassing specific exposure pathways to men in a residential situation including consumption of garden vegetables (Figure 7.1) (Berg van den and Roels, 1991; Berg van den et al., 1993; Berg van den, 1997; Swartjes et al., 1998; Swartjes, 1999).

7.2 Human toxicological MPR and TCA of CN

General

Species considered

The following four CN species have been considered as most important for the human exposure to soil contamination by CN.

- Free CN, intake by humans can be amongst other via groundwater containing CN^- ions and HCN, or by inhalation of (traces of) HCN gas present in air.
- Ferri ferrohexacyanide, intake by humans will be mainly through ingestion of soil particles and by inhalation of soil dust.
- The ionic form of ferrohexacyanide, intake by humans will be mainly upon the use of untreated groundwater as drinking water (from a toxicological viewpoint this species is equivalent to alkali ferrohexacyanide).
- Thiocyanate, the main intake route is via ingestion of untreated groundwater.

RIVM's Centre for (toxic) Compounds and Risks (RIVM-CSR) determined the MPR, i.e. the tolerable daily intake (TDI), for the four mentioned CN species from the available toxicological information. Also the maximum tolerable concentration in air (TCA) was determined for HCN gas (Meijerink, 1999; Janssen et al., 1987; Vermeire et al., 1991). The TDI and TCA values are adjusted through time, corresponding to ongoing new insights. The current Intervention Values are based on the TDI values as defined in 1991 (Vermeire et al., 1991). In the present report only the TDI and TCA values as defined in 1999 will be discussed (Meijerink, 1999).

TDI, TCA and uncertainties

The TDI and TCA are of critical importance for the soil Intervention Value. For instance a factor two difference in the TDI or in the TCA results directly in a factor 2 difference in the soil Intervention Value. Human physiological and toxicological data are scarce for many contaminants including the CN species under consideration, also animal data are studied in order to obtain additional information to extrapolate the TDI and the TCA. Furthermore uncertainty factors (UF) can be used as a means to compensate for lack of information. For instance if there is no information on a 'no observed adverse effect level' (NOAEL) for humans of the compound considered an UF of 10 is used, and for sensitive human subpopulations an UF of 10. With the determination of the TCA of HCN gas in air both the UF's mentioned are applied to the 'low observed adversary effect level' (LOAEL) of HCN gas 2.5 mg CN/m^3. The TCA is set consequently at 0.025 mg CN/m^3.

In Table 7.1 an overview of the TDI and the TCA of the CN species mentioned is given, more extensive information on their determination is provided in a separate RIVM-CSR report (Meijerink, 1999). Some brief remarks are made in the next paragraphs.

Table 7.1 Human toxicological limits1) to CN exposure and background values. (Sources: Meijerink, 1999; Janssen et al., 1987; Vermeire et al., 1991; CN intake by smoker from: Carson and Baker, 1982 in Janssen et al., 1987.)

CN species	TDI			Intake in general 70 kg b.w.	Ambient air TCA	Workplace air MAC
	1 kg b.w.	child 15 kg b.w.	adult 70 kg b.w.			
	mg CN/day				mg CN/m^3	
Free CN	0.05	0.75	3.5	n.d. (2-pack-a-day smoker: 22 mg)	0.025	11
Ferri ferrohexacyanide, solid and/or dissolved1)	0.8	12	56	0.03	not applicable	
SCN	5E-3 1)	0.075	0.34 2)	2.3 2)	not applicable	

1) TDI values listed are for lifelong exposure, for free CN and SCN these values are equal to acute exposure. Acute exposure risk limit for complex CN is 1.6 mg CN/kg b.w. (see text).

2) 5E-3 mg CN = 0,011 mg SCN; 0.34 mg CN = 0.77 mg SCN; 2.3 mg CN = 5.2 mg SCN.

Free cyanide

Free cyanide taken in by humans at sub-toxic levels is excreted in a few days, mainly as thiocyanate with urine. Free cyanide and its human physiological conversion products do not accumulate in the human body, and are generally considered not be carcinogenic or mutagenic. Cyanide in substantial but sublethal intermittent doses can be tolerated for long periods, perhaps indefinitely (Eisler, 1991). Chronic intoxication exists and, in some cases, can be incapacitating. For example diets containing incomplete processed cassava retaining cyanogenic glycoside/hydrolysis products have been associated with the development of several degenerative neurological diseases in Africa (Tatake and Ressler, 1999). Also the

extra CN inhaled by smokers has been associated with several afflictions and disorders including tobacco amblyopia, Leber's optic atrophy and neuropathy (CCME, 1997).
The TDI of 3.5 mg free CN has been determined from animal NOAEL data with application of a UF of 100. The daily (intermittent) intake by a 2-pack-a-day smoker of 22 mg free CN as HCN exceeds the TDI, a possible confirmation of the preceding remarks on chronic effects of and human tolerance to sublethal doses of free CN.
The TCA of HCN gas of 0.025 mg CN/m^3 is a factor 400 lower than the permissible maximum air concentration in workplaces (MAC) (Table 7.1). As mentioned above an UF of 100 has been used with the determination of the TCA.

Ferri ferrohexacyanide

Most of the ferri ferrohexacyanide ingested by man is not absorbed from the gastrointestinal tract and is excreted directly. It is assumed generally that 0.01% – 0.4% of the total ingestion dissociates and releases free cyanide into the human body which causes the toxicity of ferri ferrohexacyanide (Verzijl et al, 1993; Magee et al., 1996; Meijerink, 1999). More soluble forms of ferri ferrohexacyanide (e.g. ammonium-ferri ferrohexacyanide, potassium-ferri ferrohexacyanide) release about two to three times as much free CN as equivalent total CN quantities of ferri ferrohexacyanide (Verzijl et al, 1993; Magee et al., 1996). Still more free CN will be released probably to the human body by soluble alkali ferrohexacyanides and ferrohexacyanide ions in water (Vermeire et al., 1991). The TDI of ferrohexacyanide ions is 56 mg CN/70 kg b.w./day, it has been based on a conservative interpolation of its release of free CN (Meijerink, 1999). The same TDI has been given to ferri ferrohexacyanide. With the remark that the TDI for ferri ferrohexacyanide is a very conservative, a worst case approximation, as it is not taken into account that the ferri ferrohexacyanide in the human body is only partially dissolving and releasing free cyanide (Baars, 2000).

Thiocyanates

The TDI for ionic thiocyanate (SCN^-) was determined at 0.34 mg CN/70 kg b.w./day, with the application of an UF of 10. The TDI is exceeded in general by an intake of 2.3 mg CN/70 kg b.w./day mainly through ingestion of Cruciferae vegetables containing glucosinulates which release SCN (Appendix 1; Meijerink, 1999).

The tolerable acute intake of CN species

In case of soil contamination generally only effects of lifelong exposure are considered. This approach is also followed in the CSOIL model. Consequently the TDI values have been derived for lifelong exposure and if relevant the accumulation of compounds in the human body is taken into account. Apart from accumulation a certain period will pass between the intake of a compound and its breakdown in or its excretion from the human body. The effects of this are superimposed on further intake, which is taken into account with the derivation of the TDI.
In addition to the current CSOIL model also more acute effects can be evaluated, e.g. a one time peak ingestion of 5 gram contaminated soil by children (Calabrese et al., 1997; Kempchen, 2000). To evaluate the risk of this it is necessary to have at one's disposal the risk factor of acute one time exposure to compounds. When this factor has not been determined an approximation is made using the TDI. Whereby it is recognised that the tolerable one time intake will be: a) approximately equal to the TDI for substances with a short residence time in

the human body (such as free CN and SCN) and; b) higher than the TDI for substances with a long residence time or with a slow conversion (such as complex CN) into toxic derivatives. Based on these considerations the tolerable acute intake of free CN and SCN has been set equal to the TDI, and of complex CN at 1.6 mg CN/kg b.w./d, that is a factor two higher than the TDI (Baars, 2000).

7.3 CSOIL model and validation of Intervention Values

7.3.1 General

The CSOIL model is based on and comprises (Berg van den, 1995; Swartjes, 1999):
- cause effect chains in several exposure pathways (Figure 7.1), the exposure via dermal uptake and showering is generally only considered for organic contaminants;
- inhaled soil dust and ingested soil particles are both considered as ingested soil particles;
- default values for human characteristics and behaviour;
e.g. for adults bodyweight 70 kg per person per day: consumption of 295 gram fresh vegetables, 0.83 mg retained inhaled-soil dust, 50 mg ingested soil particles;
e.g. for children bodyweight 15 kg per person per day: 0.31 mg retained inhaled-soil dust, ingested soil particles 150;
- default values for soil properties; e.g. soil density 1.5 kg/dm^3 and water content 20%;
- default values for contaminant specific parameters; e.g. a single transfer factor from soil to plant, a single Kd value in which differences in chemical forms of the same contaminant are generalised.

A possible future addition to the CSOIL model is the one time ingestion of a relatively large quantity of soil by children, namely 5 gram (Lijzen et al., 2000; paragraph 7.2). This acute exposure to CN contamination has been considered too in the present study.

It is difficult to validate Intervention Values, in most field situations not all (potential) exposure routes occur. E.g. only very seldom plant products are produced at contaminated sites, thus the situation to determine human exposure via consumption of seldom or never exists.

Thus generally speaking CSOIL calculations are subject to considerable uncertainty for several contaminants. For instance for five contaminants a Monte Carlo based analysis showed that the 95% confidence Interval of the median value determined with CSOIL ranged from a factor 40 lower to a factor 100 higher values for volatile contaminants. The largest part of the uncertainty stems from the estimation of the emanation of volatile species of contaminants from the soil and their inhalation by men. If this pathway is not considered the 95% confidence interval ranges from a factor 10 lower to a factor 20 higher values than the median value (Vissenberg and Swartjes, 1996).

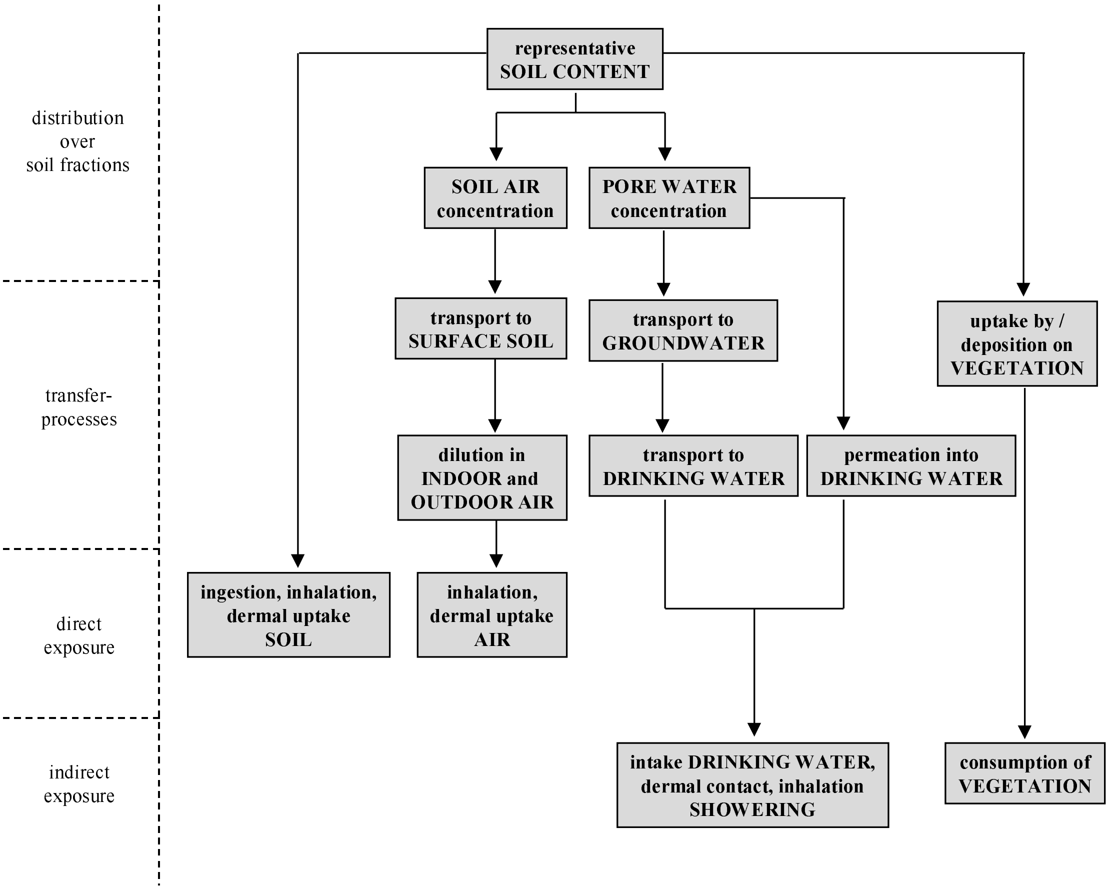

Figure 7.1 Exposure pathways in the CSOIL model (Swartjes et al., 1998).

7.3.2 CN

General

In the case of CN the available knowledge was insufficient for the estimation of several CSOIL input parameters and the determination of the current CN Intervention Values was based on adjusted CSOIL calculations. (Exposure via dermal uptake and showering was not considered, this exposure is only considered for organic contaminants.) The most important sources of uncertainty in the derivation of the current CN Intervention Values were the human toxicological risk limits (TDI an d TCA, see paragraph 7.2) and the contaminant specific parameters. Of the last were particular uncertain: the speciation and partition of the contaminant in the soil matrix, the ratio between the solid and solute phase, the ratio between solute and gas phase (Chapter 4); the transfer from soil to plant and; the fate of CN species after uptake by the plant (Appendix 3, and Chapter 6).

Field validation

Field validation of CSOIL calculations should comprise measurements at contaminated sites of contaminant concentrations in: soil, ambient air, soil dust in air, groundwater, and crop products in order to check the corresponding cause effect chains of human exposure to CN. Thus far this has not been done for historical soil contamination with CN. Even not for the transfer of CN from soil to plant, or of the CN concentration and speciation in food products, which dominated the human exposure pathway in the determination of the current Intervention Values.

7.4 Current CN Intervention Values in some countries

7.4.1 The Netherlands

Year of proposal and of approval
The human toxicological limits as determined in 1991 (Vermeire et al., 1991) form the basis for the current Intervention Values, which were proposed in 1989 (VROM, 1989) and legally formalised in 1994 (VROM, 1994).

CN species
The differences in environmental behaviour and in human toxicological risks of free CN, complex CN (i.e. practically insoluble complex CN species like ferri and other ferrohexacyanides), and thiocyanate were a reason to formulate Intervention Values for each of these three CN species separately (Table 1.1).

HCN in air is not taken into account in the current Intervention Values
In the 1989 proposal it was assumed that the emanation of free CN from soil contaminated with (historical) CN was negligible, consequently the TCA was not considered to have any relevance to CN (historical) soil contamination.

Free CN and thiocyanate in soil
The application of CSOIL to determine the exposure from CN soil contamination was difficult. Viz. some crucial CN-specific parameter values had to be estimated due to lack of relevant data and/or information. For instance both the fraction of CN present in the soil which is dissolved in porewater is unknown, as well as the transfer from CN dissolved in porewater to the plant, and its subsequent conversion in the plant. For free CN and for thiocyanate the assumption was made that all CN present in soils was dissolved in pore water of the soil, and that subsequently the concentration in the plant sap was equal to that in porewater. Accumulation of CN taken up by the plant was not assumed, neither breakdown of CN or its conversion to non-toxic compounds. The use of these worst case estimates (solubility and soil-plant transfer factors) for the calculation of the Intervention Values with CSOIL led to the 100% dominance of the plant consumption pathway for the human exposure, and led to the current Intervention Values listed in Table 1.1 (Chapter 1).

Complex CN in soil
The maximum concentrations of dissolved ferrohexacyanide concentrations in the groundwater of contaminated Dutch pleistocene soils (sandy soils, naturally with a $pH < 5.0$) are lower than those in the groundwater of contaminated Dutch holocene soils (clayey soils, naturally with a $pH \geq 5.0$) (Meeussen et al., 1994; this report 3.2.2). This finding was incorporated by setting pH-specific Intervention Values for complex cyanides, differences related to soil texture, hydrology, or to geo(morpho)logy were not considered.
For complex CN in soils with $pH \geq 5.0$ the same worst case solubility and soil-plant transfer factor were assumed as for free CN and thiocyanate described above. This resulted in the 100 % dominance of the plant consumption pathway for the human exposure, and the current Intervention Value of 50 mg CN/kg soil (Table 1.1).

Based on the assumed lower solubility of complex CN in soils with a low pH (paragraph 4.2.2) the current Intervention Value was set at a higher level for soils with pH < 5.0, namely arbitrarily at 650 mg CN/kg soil (Table 1.1).

Intervention Values for groundwater
The Intervention Values for groundwater are estimated from the CN intake via the consumption of untreated groundwater at a rate of 2 litre per (adult) person per day. Whereby it is assumed that all CN species present in groundwater act as free CN upon consumption as drinking water, consequently the CN Intervention Values for groundwater are the same for all CN species, 1.5 mg CN/l (Table 1.1) (Berg van den and Roels, 1991; Meeussen and Keizer, 1993).

7.4.2 Four other countries

General

An international overview of regulatory threshold values of CN soil contamination has not been an objective of this study. However in the course of this study some CN regulatory publications were reviewed. And as being very relevant, a brief description of the information contained in these publications is summarised below. The picture obtained in this way and given below is of course very incomplete and it has an at random character both in respect to the countries listed as to the publications reviewed of those countries. It has not been checked if these threshold values have obtained a legal status within the respective countries.

Belgium

A Belgian study (Nouwen et al., 1999) has been executed recently to derive Soil Remediation (threshold) Values, these are set at the TDI for oral ingestion or for inhalation. Values are derived for four different land use and corresponding exposure scenarios; the residential-with-gardens scenario will be considered here (Table 7.2). In some respects the derivation parallels the approach used for the current Dutch Intervention Values. Amongst others supposedly high increments of free CN in vegetables growing on soil contaminated by complex cyanides; as discussed before this is contradicted by plant physiological studies (Chapter 6 and Appendix 3). Thiocyanate is not included in the Belgian study.

Table 7.2 Belgian proposed Soil Remediation Values for CN species in soil and groundwater (Nouwen et al., 1999).

Species	Soil Remediation Value	Main exposure route (contribution %); and remarks
Free CN	5 mg free CN/kg soil	inhalation of HCN (99%); residential-with-gardens scenario
Complex CN	12 mg complex CN/kg soil	consumption of vegetables (99%); residential-with-gardens scenario
Sum of: free CN + dissolved complex CN	0.07 mg total CN/l groundwater	ingestion of untreated groundwater 2 l per day (100%); assumption dissolved complex cyanides act as free CN

Germany

In Germany concentration values have been derived for slight contamination of groundwater (SCG) which has no impact on groundwater quality, the concentration of the contaminant is close to the background value. The SCG is meant more as an quasi emission threshold value than as an environmental quality criteria. The SCG is only valid for groundwater close to the source of contamination (Röder et al., 1999).
For easily liberating free CN the SCG value is 0.005 mg CN/l.
For total CN the SCG value is 0.05 mg CN/l.

United Kingdom

Long term leaching tests over several months were executed with three samples of MGP waste. Linked to these ‘laboratory shaker tests’ the gases evolved over this period were analysed. The volatilised HCN collected was equivalent to maximally 0.3% of the soluble simple cyanides present in the sample (Wilson and Hudson, 1980). Based on this result worst case estimates have been made, the Department of the Environment (DOE) suggests correspondingly that 300 mg (dissolved) complex CN/kg soil could give rise to a toxic concentration of HCN in air within a 2 m deep trench (DOE, 1988).
In the UK Soil Guideline Values (SGLV) indicate concentration threshold levels of a contaminant, which when exceeded will normally trigger either remedial action or more detailed site-specific assessment of the risks. For soluble CN species SGLV’s have been derived by the Nottingham Trent University (Table 7.3) (NTU, 1998). For soluble complex CN in the soil the SGLV coincides with the worst case estimate made by DOE for the emanation of HCN, as mentioned above.

Table 7.3 UK Soil Guideline Values derived for soluble CN species (NTU, 1998).

CN species	Exposure	Soil Guideline Value	Remark
Soluble simple CN	acute one-time soil ingestion by child	60 mg 'free' CN/kg dry soil	
Soluble complex CN	acute one-time soil ingestion by child	indicative 300 mg soluble complex CN/kg dry soil	all soluble complex CN is assumed to transform rapidly into free CN
Soluble simple CN	chronic exposure in the residential-with-gardens scenario	615 mg 'free' CN/kg dry soil	
SCN	not considered	not considered, SCN relatively low toxicity	above certain levels SCN can lead to a red discoloration of water

Canada

In Canada Soil Quality Guidelines (SQG) are based on threshold values, these are for general guidance for the protection of human and environmental health. Site specific conditions should be considered in the application of these values; and the values may be applied differently in various jurisdictions. For human health SQG_{HH} and for environmental health SQG_E have been derived for free cyanide in the soil. In this derivation the emanation of free CN to soil air and to ambient air has not been considered. Consequently the exposure risk for humans is dominated by soil ingestion and for animal species by soil contact and dermal uptake of free CN (Table 7.4). The lower of the SQG_{HH} and SQG_E is taken as the SQG. The groundwater check for drinking water and for aquatic life are not calculated for free cyanide and should be addressed on a site specific basis (CCME, 1997).

Table 7.4 Canadian threshold concentrations and Soil Quality Guideline for free cyanide in soil (CCME, 1997).

	Exposure route	Threshold concentration mg free CN/kg soil
Human health	soil ingestion guideline	29
Human health	inhalation HCN in air	not considered
Environmental health	HCN in soil air	not considered
Environmental health	soil contact guideline	0.9
Environmental health	soil and feed ingestion guideline	11
SQG_{HH}		29
SQG_E		0.9
Soil Quality Guideline		0.9 [1)]

1) the lowest of the considered threshold concentrations has been selected.

7.4.3 Comparison of the Netherlands and four other countries

General

An international overview of regulatory threshold values of CN soil contamination has not been an objective of this study, neither an all encompassing comparison with Dutch Intervention Values. However in the course of this study some CN regulatory publications were reviewed, as mentioned in paragraph 7.4.2. As being relevant, a brief comparison of the threshold values presented in these publications is summarised below. The picture obtained in this way and given below is of course very incomplete and has an at random character both in respect to the countries listed as to the publications reviewed of those countries. It has not been checked if these threshold values have obtained a legal status, as is the case in the Netherlands.
With respect to the reviewed soil threshold values it is striking that (Table 7.5):
- only Canada has derived an environmental health threshold value, and then probably only for free CN, in the other countries ecological-risk information on CN is considered inadequate for derivation of threshold values;
- SCN receives attention probably only in the Netherlands;
- in the Netherlands and in Belgium practically non-soluble complex CN (ferri ferrohexacyanide) in the soil is considered and no attention is given to soluble complex CN, whereas in the United Kingdom soluble complex CN is considered and non-soluble not;
- only in the Netherlands and Belgium has the consumption of vegetables the largest contribution to the critical human exposure to one or more CN species;
- only in Belgium has the inhalation of free CN the largest contribution to the critical human exposure to free CN;
- the ‘general threshold values’ differ more than a factor 50 between the few countries considered, and are based on different assumptions with respect to: the environmental behaviour of CN species; the exposure pathways; the human health criteria;
- in situations with historical soil contamination with CN, the maximum concentrations of free CN, soluble complex CN, and SCN in the aerated top soil have been attenuated to levels far below the ‘general threshold values’ (Table 7.5 and Table 7.11).

Table 7.5 Overview of some ‘general-threshold values’ for CN soil contamination in four countries and their corresponding range.

CN species	NL	B	UK	Canada	Range
	mg/kg soil				
free CN	20	5	60[1]	0.9	0.9 - 60
complex CN	650 (pH<5) 50 (pH ≥ 5)	12	300 (soluble)	n.r.[2]	12 - 650
SCN	20	n.r.	‘p.m.’[3]	n.r.	20 - ‘p.m.’

[1] in fact soluble simple CN salts.
[2] n.r. = not referred to in publications reviewed.
[3] ‘p.m.’ = mentioned but risks not considered as important.

Little or no attention is given in the few reviewed publications to the consumption of untreated groundwater. For this scenario 'general-threshold values' have been derived in the Netherlands and Belgium for respectively three and two CN species. The 'general-threshold values' derived for groundwater contaminated by the same CN species differ more than a factor 20 (Table 7.6).

Table 7.6 'General-threshold values' for CN groundwater contamination in the Netherlands and Belgium.

CN species	NL	B
	mg CN/l	
free CN	1.5	0.07[1]
complex CN	1.5	
SCN	1.5	n.r.[2]

[1] sum of: free CN + complex CN

[2] n.r. = not referred to in publications reviewed.

7.5 New considerations with respect to CN Intervention Values

7.5.1 CN speciation and solubility in contaminated soils

Speciation

Field research shows that in soil layers with some biological activity practically all CN remaining from historical contamination is present as insoluble metal hexacyanides, such as ferri ferrohexacyanide and mangano ferrohexacyanide (Meeussen, 1992; Keizer et al., 1995; Chapter 3).

The same applies for anaerobic, water saturated soil layers with low biochemical activity. Though thiocyanates remain dissolved under these conditions and are consequently subject to transport by groundwater (Meeussen, 1992; Brettschneider, 1999; Chapter 3).

Solubility of complex cyanides and dissociation to free CN in relation to soil pH

General

The complex cyanides in soils are probably practically inert, apart from possible partial transformations from one into another insoluble complex cyanide. No relationships have been established for historical CN soil contamination from which the concentration of dissolved hexacyanide or free cyanide in pore water or in groundwater can be derived (Kjeldsen, 1999).

The concentration of dissolved ferrohexacyanide in groundwater of Dutch contaminated former MGP sites on holocene soils show higher maxima than on pleistocene soils [the holocene maxima are in 'average' 11 times higher (Paragraph 4.2.2)]. On both holocene and pleistocene soils maximum concentrations between 0.5 and 2 mg CN/l are common (Meeussen, 1992. p.102).

The current Intervention Values for complex CN differ between soils with pH < 5 and soils with pH ≥ 5. This dependence of the Intervention Value on the soil pH is based on the theoretical thermodynamical higher solubility of ferri ferrohexacyanide with increasing pH (Meeussen, 1992).

Indistinctnesses about and contra-indications of pH effects in the field
A pH dependence of the solubility of complex cyanides in the soil is ambiguous and to a certain extent contra-indicated by findings of both Meeussen and Keizer:
Meeussen (1992) stated at p.101/2:
”The results of the available data of the two highest total cyanide concentrations found in the groundwater on contaminated sites (former gasworks sites) indeed reveal a large contrast between the sites located on the higher sandy soils with a presumable pH of ca. 4 and the sites located on the lower, most clay, soils with a pH of ca. 7. Although the actual pH of the sites was not determined and may in some cases differ from the assumed pH level, and cyanide concentrations in the groundwater may also be influenced by different groundwater heights, different total amounts of cyanide present and different hydrological situations, the results are a strong indication for the existence of large differences in concentrations of dissolved cyanide between the alkaline and the acidic sites”.
The groundwater data considered by Meeussen were retrieved and selected by Meeussen from surveys for the presence of potentially hazardous substances on many former MGP sites, unfortunately these data do not contain information about pH or pE levels. The selected data show that on three clay soil sites the two highest CN concentrations in groundwater are significantly higher than those on the other three selected clay soil sites and than those on the six selected sandy soil sites. No follow up research has been executed to identify the causes of the higher two-highest-CN concentrations in groundwater on the respective three selected clay soil sites.
Meeussen (1992) follows at p.109 with:
“According to theory Prussian blue is very soluble in alkaline soils. The fact that this mineral is still present decades after having been dumped is due to slow dissolution kinetics. The concentrations leaching from contaminated alkaline soils are determined by the dissolution rate of Prussian blue”.
Apparently the effect of soil pH on the solubility of complex CN is masked by the low dissolution rate of the Prussian blue, possibly the solubility is mainly physically (contact-surface) determined.
Keizer et al. (1995) state that:
”In non-acidic soils (pH > 5) cyanide solubility might be governed by equilibrium with manganese iron cyanide $Mn_2Fe(CN)_6$ (s). The solubility constant for this mineral can vary between different soils, but an average value of –24 for log K_s is estimated for the two contaminated soils studied. Iron cyanide solubility in non-acidic soils depends on pH, redox potential and Mn-oxide solubility.”
(These conclusions were drawn from batch experiments (l/s weight ratio 10/1) with soil samples from two former MGP sites (pH-$CaCl_2$ > 5.7) which were equilibrated over a period of twelve weeks with 0.1 M NaCl solutions. With respectively no and two different additions of NaOH to investigate the effect of different pH (increases) on the cyanide speciation in non-acidic soils. The relative long equilibration period is possibly crucial for the results obtained.)

Conclusion

Both Meeussen and Keizer mention that an effect of soil pH on the solubility of complex CN and its concentration in groundwater is, or can be, masked by several other soil factors (Mn, hydrology, dissolution kinetics, etc.). It seems that an effect of the actual soil pH on the

solubility of complex CN in the soil or on the exposure to CN from soil contamination with complex CN has not been established. Consequently there is no strong argument to make a distinction in the Intervention Values for complex CN between soils based on soil pH.
The following seems a further justification not to formulate different CN Intervention Values for soils differing in pH. Field measurements show free CN concentrations in groundwater in the range 0.5% - 3% of the total dissolved CN concentration (Meeussen, 1992. p.34); either incidentally or not in the groundwater sample with the lowest pH the highest fraction of dissolved complex CN dissociated to free CN. This is in accordance with theoretical higher dissociation of dissolved complex CN to free CN at a lower pH (Meeussen, 1992; Paragraph 3.2.4). With respect to concentration of free CN in soils with a high pH, the theoretically higher solubility of complex CN is thus possibly counteracted by the theoretical lower dissociation of dissolved complex CN to free CN at a high pH.

7.5.2 CN natural background and concentrations in contaminated soils and groundwater

There are several natural sources of CN species in soils. E.g. roots and debris of cyanogenic plant species which release upon decomposition free CN and intermediate CN containing compounds, and Cruciferae releasing SCN (paragraph 6.1.1 and Appendices 1 and 2). Also several bacteria strains are producing free CN in soils (paragraph 6.1.4). At the same time CN species are converted by soil organisms to non-CN species. The result will be a natural dynamic equilibrium in the soil in which CN species are present but do not accumulate. The concentration of CN species will depend amongst others on soil properties, vegetation and season. In Appendix 2 some information is given on natural background concentrations of CN species. The information presented is rather scant as an overview of natural CN background concentrations fell clearly beyond the scope of this study.
In the CN contamination studies reviewed the possibility of CN natural background effects on the concentration of CN species in the soil or in ambient air has been practically categorically neglected. A well founded comparison of concentrations of CN species in contaminated soils with background concentrations is thus not possible. The result of an orientative comparison is presented in Table 7.7.

Table 7.7 Orientative comparison of natural background and concentrations of CN in historically contaminated soils.

	Top soil			Groundwater		
	Free CN	Total CN	SCN	Free CN	Total CN	SCN
	mg CN/kg soil			mg CN/l		
Natural background [1)]	<0.005 - 1	<0.005 – 1.2	around 0.005	n.d.	<0.01 – 0.02	n.d.
Contaminated soils maximum concentration [2)]	0.045	40,000	7	0.15	34	90

[1)] Additional information in Appendix 2.
[2)] Additional information in paragraph 7.5.6 and Table 7.11.

The most striking outcome of the orientative comparison is that concentrations of free CN in soil and groundwater in historically contaminated areas are most likely within the range of natural background concentrations. Whereby it has to be remarked that this conclusion is

uncertain due to lack of sufficient supporting data. An orientative comparison for free CN species in soil air has not been attempted by lack of information on the natural background in the publications reviewed.
As a conclusion it can be postulated that it is uncertain that free CN concentrations in historically contaminated soils fall beyond the range of natural background concentrations, which are not known to have any harmful effects. Consequently an Intervention Value for free CN in soil or groundwater of historically contaminated soils seems illogic and/or superfluous, until the contrary has been proven.

7.5.3 Free CN in air and CN Intervention Value

Emanation and concentration of free CN in air

Laboratory data indicate that free CN is liberated upon photodegradation of dissolved complex CN (Meeussen et al., 1992). No information has been found indicating if photodegradation of dissolved complex cyanides and subsequent enhanced emanation of free CN plays a role under field conditions. During daytime it might occur at the surface of waterlogged or of moist soils and in puddles with stagnant rainwater.
The few available data of free CN in soil air, and in ambient air in situations with historical CN soil contamination show that concentrations of 1 - 2 mg free CN/m^3 can occur (Hoppener et al., 1983; Jans, 1999). These concentrations are 5 - 10 times below the permissible CN concentration in air of workplaces (MAC), though they exceed the TCA by a factor 40 - 80.

Estimation of free CN in air with VOLASOIL

The calculations with the VOLASOIL model (paragraph 4.2.6 and Table 4.2) to estimate the concentration of CN in air using as input the free CN concentration in groundwater and default values for soil parameters show the following.
- For the maximum observed concentration of free CN in groundwater, 0.15 mg free CN/l, VOLASOIL estimates 0.9 mg HCN/m^3 in soil air at 1 m depth, which is relatively close to the range of observed maximum concentrations in soil air, 1 – 2 mg free HCN/m^3.
- VOLASOIL estimates of HCN in indoor air are more than a factor 10 lower for clayey than for sandy soils. No HCN field data are available to confirm or contradict these differences between clayey and sandy soils.
- VOLASOIL calculations for the maximum observed concentration of free CN in groundwater yield indoor air free CN concentrations of 0.0002 – 0.0024 mg HCN/m^3. Taking in consideration that ambient air concentrations have been observed of 1 - 2 mg HCN/m^3 and that related indoor concentrations should be higher than these VOLASOIL does not seem a good instrument to use at this stage to determine a relationship between free CN in groundwater and free CN in air.

Consequently at this stage is it not possible to estimate free CN concentrations in ambient air from VOLASOIL model calculations using measured CN soil data as input without further research and field validation of the VOLASOIL model for HCN.

Intervention Value for the risk of soil-emanated HCN in air

The concentration of free CN in ambient air can exceed the TCA, which should be taken into consideration for the Intervention Value of CN. From a regulatory and/or a soil analysis

viewpoint, it deserves preference to base such an Intervention Value on CN concentrations in soil or in groundwater. However this seems not possible as no studies exist of the relationship between CN in soil and/or groundwater and free CN in air.
The soil parameter HCN concentration in soil air can be measured directly. Although the link from measured HCN concentrations in soil air to ambient has not yet been established it gives at least an indication of the (worst case) maximum concentration of HCN in ambient air. Considered from this viewpoint the HCN concentration in soil air could possibly serve as a parameter for the Intervention Value, which logically would then be set at 0.025 mg HCN/m^3 in soil air equal to the TCA in ambient air. At this moment the range of HCN background concentrations in soil air is unknown. It is not unlikely that this range will overlap with 0.025 mg HCN/m^3, in which case this (ambient air TCA) concentration level in soil air can not be used in a simple way as a factor in the definition of the Intervention Value.
Considering the little available information about HCN in soil air and also about its interpretation in terms of HCN in ambient air its seems self-evident to consider the possibility to base the Intervention Value for free CN directly on field measurements of the concentration of HCN in ambient air. An advantage of such field measurements is that they comprise also emanating free CN, liberated by daylight from dissolved complex cynanides in soil moisture at the soil surface.

7.5.4 CN in plants

Cyanogenic plants

Cyanogenic plants contain CN in nitriles and are distinguished for their potential to release elevated concentrations of free cyanide upon damage of their plant cells. Consumption of cyanogenic plant parts is always a cause for concern, and precautions are always taken to reduce CN levels in food from such plants, independent of exogenous CN sources. Consequently there is no need to consider nitrile levels and potential free CN of cyanogenic plants in relation to CN soil contamination. Furthermore information on these points does not seem to exist.

Free CN transfer to and concentration in (non-cyanogenic) plants

By lack of information a worst case estimate was made of the transfer of CN in soils to plants for the determination in 1991 of current Intervention Value, 20 mg free CN/kg soil. With CSOIL parameter values used at that time this CN concentration in the soil resulted in a concentration in consumed roots and leaves of respectively 104 and 116 mg free CN/kg fresh weight. Although there are no field data available of enhanced CN levels in edible plant parts, there is substantial evidence that these high levels of free CN will not occur in (non-cyanogenic) plants. Namely laboratory tests with young plants indicate that, depending on plant species, non-phytotoxic maximum concentrations can range from 0.1 – 0.4 mg free CN/kg fresh weight in plant material. When these free CN levels are exceeded the growth of young plants will be hampered due to phytotoxicity. If this is overcome it can be supposed that the free CN level in the plant tissues is reduced to lower concentrations, so that the plants can develop into adult plants which will be harvested. The reduction of the free CN level in plants is possible by transformations of CN in the plant, mainly to asparagine.
CSOIL the default value for vegetable consumption is 0.295 kg/person/day. Considering the estimated maximum non-phytotoxic concentration in plants and food from CN contaminated

soils, 1 mg free CN/kg fresh weight (paragraphs 6.2.2 and 6.3.1), the resulting maximum intake is 0.295 mg free CN/person/day, which is 8.5% of the TDI.

Food produced on soils contaminated with thiocyanates and complex cyanides

Thiocyanate and complex cyanides uptake by plants
The uptake by plants of SCN and/or complex cyanides from contaminated soils is unknown. The risks to humans of consumption of food produced on such soils are to all likelihood negligible and will not be considered (paragraph 6.3.2).

Free CN coupled to presence of thiocyanate and complex cyanides
Soils containing complex cyanides and/or thiocyanates will also contain some free CN. As discussed above this free CN will lead to a maximum free CN intake of 8.5% of the human TDI.

7.5.5 Human toxicological critical CN levels and levels observed in soils

General

With respect to potential human exposure to CN soil contamination the following five main exposure routes can be distinguished: inhalation of HCN present in ambient or indoor air; consumption of untreated groundwater; consumption of vegetables; and ingestion of soil particles. For each of these main exposure pathways, which are the same as in CSOIL (Figure 7.1, paragraph 7.3), will be checked:
- if the critical CN concentration in soil or in groundwater corresponding to the TDI and TCA (Table 7.1) can be estimated;
- the ratio between the critical and the maximum[6] observed concentration in soil or in groundwater at sites with historical CN contamination.

This will be done for free CN, dissolved ferrohexacyanide, ferri ferrohexacyanide, and thiocyanate. The estimated critical concentrations corresponding to the TDI will be for adults with a body weight of 70 kg or for children with a bodyweight of 15 kg. Using the same default values as in CSOIL for human characteristics and behaviour, and for intrinsic soil properties (paragraph 7.3). In addition to the CSOIL model the one time ingestion of a relatively large quantity of soil by children, namely 5 gram, will be considered (Lijzen et al., 2000; paragraph 7.2 and 7.3.1).
The estimated critical concentrations are listed in Tables 7.7, 7.8 and 7.9. Most estimates of critical concentrations have been obtained in a straightforward way, only some deserve some further elaboration which is given below.
The ratio estimated critical concentration/maximum observed concentration is discussed below for all pathways and CN species considered.

Free CN (critical concentration estimates in Table 7.8)

HCN emanation from groundwater to ambient air
The calculation of the emanation of free CN from the soil with VOLASOIL has been presented before (paragraph 4.2.6). These calculations indicate that the emanation of free CN from groundwater leading to 0.025 mg CN/m^3 the TCA, requires 11 to 117 times the

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[6] Maximum observed concentrations are discussed in Paragraph 7.5.6

observed maximum free CN concentration in groundwater. As field measurements show that the TCA is exceeded at least at some sites, it can be concluded that with the current knowledge the concentration in groundwater is not a useful indicator for the free CN in air.

Ingestion of soil particles by children
The critical concentration of free CN in the soil resulting in the TDI via ingestion of soil particles by children is far beyond the observed maximum concentration, from an exposure point of view this pathway can be neglected.

Consumption of untreated groundwater
Consumption of untreated groundwater with the observed maximum free CN concentration will lead to an intake equal to 9% of the TDI for adults and for children of 20% of the TDI.

Consumption of vegetables (and phytotoxicity)
As discussed in paragraphs 6.2.2 and 6.3.1 a worst case estimate of enhanced free CN concentrations is 1 mg CN/ kg fresh weight in vegetable food from CN contaminated soils. Consumption of such food will result in an exposure equal to 8.5% of the TDI (paragraph 7.5.4).

Total ingestion
A summation of the potential exposure to free CN via ingestion (Table 7.8) will not lead to exceedance of the TDI not even for the observed maximum concentrations of free CN. It can be at maximum in the order of 10% of the TDI, mainly due to consumption of untreated groundwater.

Table 7.8 Human toxicological critical free CN concentrations in contaminated soil and ratio of critical to maximum observed concentrations.

Source	Critical exposure		Critical conc.	Observed max. conc.	Ratio critical/max.
	Pathway	Level			
Groundwater					
groundwater sandy soil	emanation, indoor inhalation	TCA	1.6 mg CN/l (VOLASOIL)	0.15 mg CN/l groundwater	11
groundwater clayey soil	emanation, indoor inhalation	TCA	17.6 mg CN/l (VOLASOIL)	0.15 mg CN/l groundwater	117
untreated groundwater	adult, consumption 2 l/d	TDI	1.75 mg CN/l	0.15 mg CN/l groundwater	12
	child, consumption 1 l/d	TDI	0.75 mg CN/l	0.15 mg CN/l groundwater	5
Soil					
soil	vegetable consumption, non-phytotoxic max. conc. ≤ 1 mg CN/kg fresh	≤ 8.5% of TDI[2)]	not applicable [2)]	0.045 [1)] mg CN/kg soil	not applicable [2)]
soil	Ingestion (child) (150 mg/d)	TDI	5E3 mg CN/ kg soil	0.045 [1)] mg CN/kg soil	1.1E5
soil	ingestion (child) one day maximum (5.000 mg/d)	t.a.i.[3)]	150 mg CN/ kg soil	0.045 [1)] mg CN/kg soil	3.3E4

[1)] Estimate of maximum concentration in dry top soil based on maximum concentration in groundwater (paragraph 7.5.6).

[2)] The maximum non-phytotoxic concentration in plantmaterial is 1 ≤ mg/kg f.w., this corresponds to ≤ 8.5% of TDI, a critical concentration is not reached for human consumption.

[3)] t.a.i. = tolerable acute intake

Complex CN (critical concentration estimates in Table 7.9)

Consumption of untreated groundwater
The critical concentration and the observed maximum concentration of dissolved ferrohexacyanide in groundwater indicate that the use of untreated groundwater as drinking water can lead to the exceedance of the TDI both for adults as for children.

Ingestion of soil particles by children
Average daily ingestion 150 mg soil particles/d The critical concentration of dissolved complex CN in the soil resulting in the TDI via ingestion of soil particles by children is a factor 500 higher than the observed maximum. For solid ferri ferrohexacyanide the maximum observed concentration is only a factor two lower than the critical concentration. This is partly caused by the very conservative TDI value for solid ferri ferrohexacyanide, which is the same as for dissolved ferrohexacyanide ions (paragraph 7.2; Baars, 2000).
One time maximum soil ingestion 5,000 mg soil particles/d For dissolved ferri ferrohexacyanide the maximum observed concentration is a factor 480 lower than the tolerable acute intake. For solid ferri ferrohexacyanide the maximum observed concentration is a factor 8.3 higher than the tolerable acute intake. This is partly caused by the very conservative TDI value for solid ferri ferrohexacyanide, which is the same as for dissolved ferrohexacyanide ions (paragraph 7.2; Baars, 2000).
Remark With the derivation of the TDI of solid complex CN (ferri ferrohexacyanide) two conservative assumptions have been superimposed, namely (paragraph 7.2; Baars, 2000):
- the TDI value for dissolved complex CN, i.e. ferrohexacyanide ions, is based on a conservative assumption;
- the simplification that all solid complex CN in the soil dissolves after inhalation or ingestion.

This ‘doubling’ of unrealistic premises results in the very conservative estimate of the tolerable acute intake of undissolved complex cyanides (ferri ferrohexacyanide) in contaminated soil. Based on this very conservative estimate a potential exposure exceeding the tolerable acute intake for children is possible after a one time peak ingestion of soil particles. As the quantity of ferri ferrohexacyanide which can be tolerated as a one-time intake is (probably much) higher than the tolerable acute intake (1.6 mg CN/kg b.w.; paragraph 7.2) it can be doubted if this ‘calculated critical potential’ exposure deserves any or much further attention for the derivation of an Intervention Value.
It can be remarked again that the one time peak soil ingestion by children is not included in CSOIL, though it is considered to incorporate this in a future version (Lijzen et al., 2000).

Consumption of vegetables
There are no data about the plant uptake of dissolved ferrohexacyanide neither about its conversion in the plant after uptake. Toxic levels in vegetable food are not expected (paragraph 6.3.2). With regard to human exposure this pathway will be considered as not relevant.

Table 7.9 Human toxicological critical concentrations of dissolved and solid complex CN in contaminated soil, and ratio of critical to maximum observed concentrations.

Source	Critical exposure		Critical conc.	Observed max. concentration	Ratio critical/max.
	Pathway	Level			
		Groundwater			
untreated groundwater	adult, consumption 2 l per day	TDI	28 mg CN/l	34 mg CN/l	1 /1.2
	child, consumption 1 l/d	TDI	12 mg CN/l	34 mg CN/l	1 /2.8
		Soil			
soil/vegetable	vegetable consumption; complex CN metabolism by plants no data, vegetable contamination probably irrelevant	TDI	n.d.; not relevant	40 g total CN/ kg soil	n.d.; not relevant
soil	soil ingestion (child) 150 mg/d	TDI	80 g CN/ kg soil	soluble complex 0.01 g CN/kg soil	8,000
				solid ferri ferrohexacyanide 40 g CN/kg soil	2
	soil ingestion (child) 5000 mg/d	t.a.i.1)	4.8 g CN/ kg soil	soluble complex 0.01 g CN/kg	480
				solid ferri ferrohexacyanide 40 g CN/kg soil	1/8.3

1) t.a.i. = tolerable acute intake

Thiocyanate (critical concentration estimates in Table 7.10)

Consumption of untreated groundwater

The critical concentration and the observed maximum concentration of dissolved thiocyanate in groundwater indicate that the use of untreated groundwater as drinking water can certainly lead to the exceedance of the TDI.

Ingestion of soil particles by children

The critical concentration of SCN in the soil resulting in the TDI via ingestion of soil particles at a rate of 150 mg/d by children is a factor 70 higher than the observed maximum concentration SCN concentration observed in top soil, according to a personal communication (Brettschneider, 1999). There is a factor two difference between the critical and the maximum observed concentration when the one day peak value of soil ingestion by children is considered. Also in this case a ‘doubling’ of worst cases is likely, namely the one day peak value of soil ingestion and the maximum observed thiocyanate concentration in top soil which is ‘worst case estimated’ (Brettschneider, 1999).

Consumption of vegetables

There are no data about the plant uptake of thiocyanate neither about its conversion in the plant after uptake, or about the phytotoxic concentration of SCN in plants. With regard to human exposure the pathway of SCN intake via consumption of vegetables is probably not relevant (paragraph 6.3.2).

Table 7.10 Human toxicological critical thiocyanate concentrations in contaminated soil and ratio of critical to maximum observed concentrations.

Source	Critical exposure		Critical conc.	Observed max. conc.	Ratio critical/max.
	Pathway	Level			
		Groundwater			
untreated groundwater	adult, consumption 2 l/d	TDI	0.17 mg CN/l	90 mg CN/l[1)]	1 / 529
	child, consumption 1 l/d	TDI	0.075 mg CN/l	90 mg CN/l[1)]	1/1200
		Soil			
soil/vegetable	vegetable consumption; SCN uptake by plants no data, probably not relevant	TDI	n.d.; not relevant	7 mg CN/kg soil [1)]	n.d.; not relevant
soil	soil ingestion (child) 150 mg/d	TDI	500 mg CN/kg	7 mg CN/kg [1)]	70
soil	soil ingestion (child) 5 g/d	t.a.i.	15 mg CN/kg	7 mg CN/kg [1)]	2

[1)] Personal communication (Brettschneider, 1999).
[2)] t.a.i. = tolerable acute intake.

Conclusions

Soil

The observed maximum levels of free cyanide, complex cyanide and thiocyanate in soils do not lead to exceedance of the human TDI via the pathways considered in CSOIL and the corresponding default values for human behaviour. In this respect these CN-soil parameters do not give any prospect for the definition of the Intervention Value.
However a one day peak value of soil ingestion by children, not (yet) included in CSOIL, may lead to exceedance of the tolerable acute intake. Viz. maximum solid complex CN concentrations of 40 g CN/kg soil have been observed, which would lead to exceedance of the tolerable acute intake by a factor 8.3. Based on this an Intervention Value for solid complex CN would be 4.8 g CN/kg soil. It has been remarked before that the estimate of the tolerable intake of solid complex CN is very conservative (paragraph 7.5.5).

Groundwater

With respect to human exposure to CN species in groundwater the levels of dissolved ferrohexacyanide and of thiocyanate in groundwater indicate an exceedance of the TDI upon consumption of 2 l per day of untreated groundwater. The soil-groundwater parameters seem useful for the definition of Intervention Values for these CN species or for total CN. It can be remarked that the maximum observed concentration level of free CN in groundwater is below that of any concern with respect to its use as drinking water.

7.5.6 Intervention Value based on maximum potential exposure

Maximum-exposure approach

The soil biochemical, physical, hydrological, plant physiological and agronomic processes of CN historical soil contamination are largely unknown. Thus it is not realistic to estimate via an ‘all-pathway-approach’ as in the CSOIL model, the soil Intervention Value for CN. Another approach is to look at the maximum environmental concentrations observed after 1990 in the Netherlands (i.e. 20 or more years since the last ‘environmental disposal’ of CN containing materials). By combining these maxima with default values for soil properties and human behaviour (as used in the conventional CSOIL model calculations) the potential maximum human exposure is estimated. This is done for the following exposure routes: inhalation of soil emanated HCN in ambient air; ingestion of soil particles, ingestion of vegetable products (crop consumption); and ingestion of untreated groundwater. The estimates obtained in this way are compared with the TDI and TCA values of the respective CN species.

Exposure via dermal contact with soil and water will not be taken into account (paragraphs 7..3.1/2). This exposure is for inorganic compounds a fraction of the first mentioned exposure routes.

The one time peak ingestion by children of 4.8 gram soil particles in one day will lead to an estimated exposure exceeding the tolerable acute intake for the situation with the maximum concentration of complex CN observed in contaminated soil. As discussed before the exposure and risk calculations in this situation lead to over-estimates, which provide a rather weak base for the Intervention Value (paragraph 7.5.5).

Maximum CN concentrations at contaminated sites

The maximum environmental concentrations observed at locations historically contaminated with MGP and MPI wastes and due to road salt are listed in Table 7.11. These maxima were not criticised by experts, and seem to be correct in general terms (Appendix 5, discussion point 2; Appendix 6, expert discussion).

Table 7.11 Maximum CN concentrations observed in wastes and in the environment after 1990 resulting from historical contamination.

Source	Waste	Soil (top soil 0-1m)			Groundwater			Ambient air
	total CN g CN/kg	total CN g CN/kg	free CN mg CN/kg	SCN mg CN/kg	total CN mg CN/l	free CN mg CN/l	SCN mg CN/l	free CN mg CN/m^3
MGP	80	**40** **0.01** 1,2)	**0.045** 2)	**7** 3,4) 27 3,4)	**34**	**0.15**	**90** 4)	**2**
MPI 5)	80	27	n.d.	n.d.	0.046	0.004	n.d.	< 0.003
Road salt	0.06	0.061	n.d.	n.d.	5	0.02	0.001	n.d.

1) Soluble/dissolved complex CN.

2) Estimate based on: porewater concentration = maximum concentration in groundwater, and 300 ml porewater/kg top soil.

3) Lower value above groundwater; higher value below topsoil and below groundwater level.

4) Personal communication (Brettschneider, 1999); this SCN has not been included in the value of maximum total CN in groundwater in the respective adjacent column.

5) Wastes from metal processing and photographic industries.

The environmental maxima caused by MGP waste are the highest and seem in this respect the best values for estimating the maximum human exposure caused by historical soil contamination with CN.

Not all data required for the estimation of the maximum human exposure are available, by lack of field data some environmental maxima have been estimated:

- Concentration of free CN in soil 0.045 mg CN/kg dry soil; this worst case estimate assumes pore water with the same maximum free CN concentration as in groundwater 0.15 mg free CN/l and with 300 ml pore water per kg of dry soil material;
- Concentration of free CN in plant products 1 mg free CN/kg fresh plant material (paragraph 6.2.2).

- Concentration in plant products due to soil contamination of other CN species with toxic potential to humans is also unknown. The related possible risk to humans of other CN species in plants is assumed to be negligible (paragraph 6.3.2).

Estimated maximum potential human exposure via soil and crops

Using the CSOIL default values of human behaviour and the CSOIL cause effect chains the estimate of the maximum human exposure from CN historical contamination for adults is (Table 7.12):
- for free CN 40.6 mg free CN per person per day (40 mg via inhalation and 0.3 mg via consumption of vegetable products)(equal to 11.6 times the TDI);
- for complex CN negligible (0.002 mg CN via inhalation of soil dust, which is equal to 3.6E-5 TDI);
- for SCN negligible (3.5E-4 mg CN via inhalation of soil dust, which is equal to 0.001 TDI).

The estimated maximum human exposure from CN soil contamination is negligible for complex CN and SCN.
The exposure to free CN is a factor 12 higher than the TDI; 99 % is due to the inhalation of free CN in ambient air.

Table 7.12 Estimate of the maximum potential exposure of adults to CN from CN historical soil contamination in the Netherlands according to CSOIL cause effect chains.

Human intake, adult default value (per person per day)	Maximum value CN contamination	**Adult exposure estimate** (intake per person per day)
inhalation air 20 m^3	2 mg free CN/m^3 air	40 mg free CN
soil ingestion 50 mg	complex cyanide 40 mg CN/kg soil free cyanide 0.045 mg CN/kg soil thiocyanate 7 mg CN/kg soil	complex cyanide 0.002 mg CN free cyanide p.m. thiocyanate 0.00035 mg CN
vegetable consumption 0.295 kg fresh vegetable	1 mg free CN/kg fresh vegetable [1]	0.30 mg free CN
		Sum = Maximum total daily CN intake: **free cyanide 40.3 mg CN** (=12x TDI) **complex CN p.m.** (<0.001x TDI) **thiocyanate p.m.** (<0.001x TDI)

[1] No observation, high worst case estimate

Using the CSOIL default values of human behaviour and the CSOIL cause effect chains the estimate of the maximum human exposure from CN historical contamination for children shows roughly the same as for adults. Also for children only the estimated exposure due to the inhalation of free CN in ambient air exceeds the TDI, namely by a factor 21 (Table 7.13).

Table 7.13 Estimate of the maximum potential exposure of children to CN from CN historical soil contamination in the Netherlands according to CSOIL cause effect chains.

Human intake, children default value (per person per day)	Maximum value CN contamination	**Children exposure estimate** (intake per person per day)
inhalation air 7.6 m^3	2 mg free CN/m^3 air	15.2 mg free CN
soil ingestion 150 mg	complex cyanide 40 mg CN/kg soil free cyanide 0.045 mg CN/kg soil thiocyanate 7 mg CN/kg soil	complex cyanide 0.006 mg CN free cyanide 0.000007 thiocyanate 0.00011 mg CN
vegetable consumption 0.12 kg fresh vegetable	1 mg free CN/kg fresh vegetable [1)]	0.12 mg free CN
		Sum = Maximum total daily CN intake: **free cyanide 15.3 mg CN** (=21x TDI) **complex CN p.m.** (<0.001x TDI) **thiocyanate p.m.** (=0.005x TDI)

[1)] No observation, high worst case estimate

Intervention Values for soil

According to the current CSOIL pathways and default values the inhalation of free CN is the only exposure route with a maximum exposure exceeding the TDI, both for adults and children. Taking this in consideration a possibility would be to base the Intervention Value on the measured concentration of free CN in ambient air. With measurements the estimation of this parameter will not be necessary any longer, which is an advantage considering the fact that the estimation of the concentration of volatile species in the air is causing the largest uncertainties in the CSOIL derivation of the Intervention Values (Vissenberg and Swartjes, 1996).
When considering a possible one time peak ingestion by children of 5 gram soil particles in one day this will lead to an estimated exposure exceeding the tolerable acute intake for the situation with the maximum concentration of complex CN observed in contaminated soil. The corresponding soil Intervention Value for complex is 4.8 g CN/kg soil.
As discussed before the very worst case estimate of the tolerable acute intake of solid complex CN provides a rather weak base for this Intervention Value (paragraph 7.5.5).

Intervention Values for groundwater

The evaluation of the human CN exposure from groundwater is based on consumption of untreated groundwater at a rate of 2 litre per adult person per day, or for children 1 litre per day. Considering the measured maximum CN concentrations in groundwater its ingestion can give rise for adults to a maximum CN intake of (Table 7.11 and/or Table 7.14):
- 0.3 mg free CN per person per day, i.e. a factor 0.09 times the TDI;
- 68 mg CN as complex CN per person per day, i.e. a factor 1.2 times the TDI;
- 180 mg CN as SCN per person per day, i.e. a factor 529 times the TDI.

For children consumption of untreated groundwater can lead to ingestion of:
- 0.15 mg free CN per person per day, i.e. a factor 0.2 times the TDI;
- 34 mg CN as complex CN per person per day, i.e. a factor 2.8 times the TDI;
- 90 mg CN as SCN per person per day, i.e. a factor 1200 times the TDI.

Exceedance of the TDI due to groundwater consumption can occur for two CN species complex CN and thiocyanate, both for adults and for children. The groundwater Intervention Value has the lowest value when based on the TDI for children, for dissolved complex cyanide 12 mg CN/l and for thiocyanate 0.075 mg CN/l.
The maximum exposure due to ingestion of free CN with groundwater is negligible in comparison to the exposure by complex CN and thiocyanate, and free CN can be considered to be of no concern with respect to the Intervention Value of groundwater.
Photodegradation of dissolved complex CN to free CN can occur in case groundwater is exposed to daylight before consumption. A worst case assumption is that all complex CN is converted into free CN, in which case the TDI for children is reached by untreated groundwater originally containing complex cyanide at a concentration of 0.75 mg CN/l. It can be considered to propose this lower concentration as the Intervention Value of complex CN in groundwater.
Analysis of total CN in groundwater, according to the EPA 335.3 protocol, includes dissolved ferrohexacyanide and SCN. Consequently an attractive option is a groundwater Intervention Value of 0.075 mg total(EPA) CN/l, based on the low TDI value for children of SCN. A disadvantage of this Intervention Value based on total(EPA) CN is that groundwater with 0.075 to 0.75 mg total CN/l and without any or with a small fraction of SCN exceeds the Intervention Value for total(EPA) CN, whereas neither the Intervention Values for dissolved ferrohexacyanide and for SCN would be exceeded by such groundwater. The Intervention Value of 0.075 mg CN/l for total(EPA) CN can thus be too strict in some cases in the range of 0.075 – 0.75 mg total(EPA) CN/l.

Table 7.14 CN concentrations in untreated groundwater corresponding to TDI and observed maximum concentrations.

CN species	Unit	CN concentrations in groundwater corresponding to TDI		Observed maximum concentrations
		Adult 2 l/d	Child 1 l/d	
Free CN	mg CN/l	1.75	0.75	0.15
Dissolved ferrohexacyanide	mg CN/l	28 (1.75) [1)]	12 (0.75) [1)]	34
SCN	mg CN/l	0.17	0.075	90
Total(EPA) CN [2)]	mg CN/l	0.17 – 28	0.075 – 6	0.15 – 90

[1)] TDI based on the assumption that all complex CN is converted by photodegradation to free CN

[2)] Total(EPA) CN (EPA 335.3 protocol) comprises dissolved ferrohexacyanide, thiocyanate and free CN.

7.6 Gaps in knowledge and determination of the CN Intervention Value[7]

7.6.1 Questionaire

Information is limited about the speciation and behaviour of CN historical soil contamination in the environment and the corresponding potential exposure of man. In December 1999 a draft report has been sent to 20 CN experts with a questionnaire. In the last twelve major questions were defined addressing gaps in knowledge with respect to CN in soil, potential exposure to men, and the Intervention Values (Appendix 5). The information obtained was limited to the important suggestion to lower the maximum free CN concentration in healthy plants and food from 2 mg free CN/kg fresh weight to 1 mg free CN/kg fresh weight (Grossmann, 2000).
There remain thus several topics on which additional information is crucial either for the selection of CN Intervention Value(s) and/or for the quantification of the CN Intervention Value(s).

7.6.2 Tabular overview

A tabular overview of the remaining gaps in knowledge is given in Table 7.15, Table 7.16, and Table 7.17; respectively for free CN, dissolved ironhexacyanide and thiocyanate. The importance of the topics, listed in the tables, with respect to possible Intervention Values is obvious, as illustrated below for some topics.
Emanation of HCN from the soil An Intervention Value can be derived for the concentration of CN species in the soil, or in soil air corresponding to the TCA in case a quantitative relationship between these parameters would be known. It is also important to know if urban background levels of free CN in air or in soil air exceed (at times) the TCA or never.
Leaching, chemical fixation and biological breakdown of dissolved CN species Maximum levels of dissolved CN species in top soil can be derived from quantitative information on these processes. Consequently estimates can be made if the MPR can be exceeded by these maximum CN levels in the soil, and if the last are relevant with respect to the Intervention Values.
Conversion of CN species in plants; Phytotoxic levels in plant Qualitative information is available about conversion of free CN in plants to non-toxic compounds. In plant physiological laboratory studies with seedlings internal free CN toxicity levels have been established for several plant species, most of them Gramineae. More quantitative information of effects of CN species in soil on concentrations of CN species in adult consumable plants is needed to quantify human exposure via the plant consumption pathway.
Non-dissolved (‘insoluble’) complex cyanide is not considered as it is generally assumed to be inert material of which only a variable but always small dissolving fraction can (re)act. And complex CN though the main remnant of historical CN contamination is not by itself a reason of concern only the possible exposure to humans via the above mentioned three species.

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[7] Restricted to gaps in knowledge of environmental behaviour and of human exposure to CN. Gaps in knowledge and uncertainty factors with respect the derivation of the TDI and TCA of CN (paragraph 7.2) are not considered. Information on the last is provided in: Meijerink, 1999.

Several of the topics listed in Table 7.15, 7.16 and 7.17 have been mentioned in the publications reviewed, generally with a remark that little or no information is available quantitatively and or qualitatively.

For each topic has been noted in the tables if no or if some quantitative information has been retrieved, and the quantitative estimate made in the present report is presented. The estimates have been restricted to the few topics on which at least some quantitative information has been retrieved.

It is striking that in practically none of the reviewed publications any attention in a quantitative way has been given to human exposure due to SCN in top soil and/or in groundwater, neither to the behavior and fate of SCN in soil. This compound is considered rarely in surveys of CN contaminated sites. With the exception of recent surveys and recently initiated studies of SCN in groundwater at former MGP sites in a Dutch area (Brettschneider, 1999).

Table 7.15 Lacking information on free CN in soils for human exposure estimation

Topic	Information		Estimate	Section in report
	Level	Relevance for Interv. Value		
Background concentration levels				
urban air	none 1)	very high; f.d.2)	n.e. 3)	App. 2
soil air	none	very high; f.d.	n.e.	--
soil	none	low	n.e.	--
Abiotic processes in soils with enhanced levels 4)				
leaching	not quantified	medium	n.e.	4.3.2
chemical fixation (e.g. Fe or Mn ferrohexacyanide)	not quantified	high	n.e.	4.2.2
emanation	no field data	very high; f.d.	n.e.	4.2.4/5/6; 7.5.2/4
relationships quantifying CN processes (outside the lab)	attempts not successful	high; f.d.	n.e.	4.2.2/3/6; 5.5.1/2/4
Concentration levels in air due to enhanced levels in soils				
soil air	3 measurements	very high; f.d.	max. 1-2 mg/m^3	4.2.6; 4.3.2
ambient air (out- and inside houses)	very few measurements	very high; f.d. 5)	max. 1-2 mg/m^3	4.2.6; 4.3.2; 4.6
Biotic processes in top soils with enhanced levels				
biological breakdown	200 mg/kg soil readily	medium	n.e.	4.3.2; 4.6
toxic levels	not quantified	low	n.e.	--
Plants growing on soils with enhanced levels				
uptake from soil, soil-plant transfer factor	some lab studies	medium	n.e.	6.2.5/6; App. 4
conversion in plant	not quantified	high; f.d.	n.e.	6.1.2
minimum phytotoxic level in soil	lab studies on seed	medium	(1 mg/kg soil) 6)	6.2.3/5/6; App. 4
maximum phytotoxic level in plant	lab studies seedlings	very high; f.d.	max. 2 mg/kg f.w.	6.2.6; App. 4

1) none = no information found in publications reviewed.

2) f.d. = field data, noted in case field data are considered very relevant with respect to selection and derivation of Intervention Values.

3) n.e. = no estimate.

4) quantitative results have been published of the movement in 2 years of a plume of CN contaminated groundwater at one MGP site (Ghosh et al., 1999).

5) probably more information in contamination survey documents.

6) estimates in between brackets have not been used for human exposure calculations in this report.

In the literature (reviewed) also no attention is given to uptake by plants of dissolved ironhexacyanide or thiocyanate, apparently this is never considered as a potential source of human risk.
The most crucial knowledge or information, which is lacking to determine the potential human exposure to CN species due to soil contamination seems to be:
- the occurrence of enhanced levels emanation of free CN from contaminated soil and its concentration in ambient air (in fact the existing information on this factor provides to scant a base to determine if it should be considered or not, with respect to exposure to CN from contaminated soils);
- the occurrence of enhanced levels of free CN, thiocyanate or other potentially toxic CN substances in plants cultivated on soil contaminated with CN.

It deserves consideration to execute additional research in order to obtain more information on the fore mentioned points prior to the decision how to redefine the CN soil Intervention Values.

Table 7.16 Lacking information on dissolved ironhexacyanide in soils for human exposure estimation

Topic	Information		Estimate	Section in report
	Level	Relevance for Interv. Value		
		Background concentration levels		
top soil	none [1)]	low	n.e. [2)]	--
pore water	none	low	n.e.	--
Abiotic processes in soils with enhanced levels [3)]				
leaching	not quantified	medium	n.e.	4.2.2
relationships quantifying CN processes (outside the lab)	one site plume movement [3)]; no other successful attempts	high; f.d. [4)]	n.e.	4.2.2/3/6
		Biotic processes in top soils with enhanced levels		
biological breakdown	none	low	n.e.	--
toxic levels	none	low	n.e.	--
		Plants growing on soils with enhanced levels		
uptake from soil, soil-plant transfer factor	none	medium	n.e.	6.2.5/6; 6.3.2
conversion in plant	none	low	not increasing human risk	--
minimum phytotoxic level in soil	none	medium	n.e.	6.3.2
maximum non-phytotoxic level in plant	none	high; f.d.	negligible for human risk	6.3.2

[1)] none = no information found in publications reviewed.
[2)] n.e. = no estimate.
[3)] quantitative results have been published of the movement in 2 years of a plume of CN contaminated groundwater at one MGP site (Ghosh et al., 1999).
[4)] f.d. = field data, noted in case field data are considered very relevant with respect to selection and derivation of Intervention Values.

Table 7.17 Lacking information on SCN in soils for human exposure estimation

Topic	Information		Estimate	Section in report
	Level	Relevance for Interv. Value		
Background concentration levels				
top soil	none 1)	low	n.e. 2)	App. 2
pore water	none	low	n.e.	--
groundwater	none	medium	n.e.	--
Concentration levels at contaminated sites				
top soil	p.c. 3)	very high: f.d. 5)	max. 7 mg/kg	4.2.7/8; 7.5
pore water	none	low	n.e.	--
groundwater	one Dutch area 4)	high; f.d.	max. 90 mg/l	4.2.7/8
Abiotic processes in soils with enhanced levels				
leaching	not quantified	medium	n.e.	4.1
relationships quantifying CN processes (outside the lab)	none	high; f.d.	n.e.	--
Biotic processes in top soils with enhanced levels in soils				
biological breakdown	not quantified	low	n.e.	--
toxic levels	none	low	n.e.	--
Plants growing on soils with enhanced levels				
uptake from soil, soil-plant transfer factor	none	medium	n.e.	--
conversion in plant	none	medium; f.d.	not increasing human risk	--
minimum phytotoxic level in soil	none	low	n.e.	6.3.2
maximum phytotoxic level in plant	none	high; f.d.	negligible for human risk	6.3.2

1) none = no information found in publications reviewed.
2) n.e. = no estimate.
3) p.c. = personal communication.
4) probably more information can be found in documented surveys of contaminated sites.
5) f.d. = field data, noted in case field data are considered very relevant with respect to selection and derivation of Intervention Values.

7.7 Possible changes in Intervention Values or research first

7.7.1 Possible changes based on new considerations

Total CN in the soil

The human toxicological risk of sites with historical CN soil contamination is practically negligible at most sites, as presently practically all CN is present in the nearly harmless form of solid, biochemically inert, insoluble complex metal ferrohexacyanides (Chapter 4; Table 7.9; paragraph 7.5.7). The total concentration in the soil of this inert solid complex cyanide does not correlate with the risk of CN at such sites to humans. It is proposed not to base the intervention level on the total CN concentration in the soil. Although it can be considered to base this on the one time peak soil ingestion by children (see below).

Consumption of plant products

Plants grown on contaminated sites may possibly have increased CN contents. However, their free cyanide concentration remains low (possibly two or three times a low background level) as long as these plants have a healthy appearance and growth. Consumption of these plants does not lead to exceedance of the TDI (paragraph 7.5.5).
Also the concentration of complex CN and SCN in plant material remains probably below TDI levels (paragraph 6.3.2 and 7.5.5).
To all likelihood the consumption of CN contaminated plant products is thus of no importance in the determination of the Intervention Value. It is proposed not to consider this exposure pathway as long as (field) knowledge and field data of CN in plants do not indicate the need to take this pathway into account.

Ingestion of soil particles

According to CSOIL default values for human behaviour the intake of CN by humans via ingestion of soil particles from maximally contaminated sites is much less than the TDI (paragraph 7.5.6). At first sight this exposure seems to be of little or no concern. However when considering a possible one time peak ingestion by children of 5 gram soil particles in one day this will lead to an estimated exposure exceeding the tolerable acute intake in a situation with the maximum concentration of complex CN as observed in contaminated soil. The corresponding soil Intervention Value for complex CN is 4.8 g CN/kg soil; or 5 g total CN/kg soil as more than 97% of total CN consists of complex CN. As discussed before the very worst case estimate of the tolerable acute intake of solid complex CN provides a rather weak base for this Intervention Value (paragraph 7.5.5).

CN species in groundwater (paragraph 7.5.6)

Consumption of untreated groundwater containing the maximum observed concentration of free CN gives rise to an intake of 10 % of the TDI. It is proposed to neglect the human exposure due to free CN in groundwater, as the concomitant presence of dissolved ferrohexacyanide and/or SCN will cause a greater human risk.
Groundwater at sites with historical CN contamination can contain dissolved thiocyanate at concentrations which will lead upon consumption of untreated groundwater to a manifold exceedance of the TDI. High thiocyanate concentrations in groundwater can be expected in particular at former MGP sites with simultaneous regeneration of bog ore, and possibly also at some sites with MPI wastes.
Dissolved ferrohexacyanide can attain also concentrations in groundwater that consumption of this (untreated) groundwater may lead to an exceedance of the TDI. If photodegradation of dissolved complex CN to free CN is taken into consideration, then the concentration at which the TDI is exceeded is a factor 16 lower, i.e. 0.75 mg CN/l as complex CN.
Both complex CN and SCN can be included in the analysis of total CN. A possible Intervention Value is 0.075 mg total CN/l (Table 7.9). A disadvantage of this Intervention Value is that groundwater with a concentration between 0.075 and 0.75 mg total CN per litre which contains little or no SCN exceeds the Intervention Value for total, whereas its consumption would not lead to exceedance of the TDI of dissolved ferrohexacyanide neither of SCN (paragraph 7.5.6). However a groundwater Intervention Value 0.075 mg total CN/l may be acceptable, as in situations where the Intervention Value is exceeded the need for soil remediation will be determined only after more detailed further investigations.

Uncommon parameters for CN soil Intervention Values

In the foregoing it has been shown that Intervention Values for CN soil contamination can not be based on commonly used soil parameters. This is a reason to look at some ‘uncommon’ parameters thus far never used for Intervention Values. Namely: pore water, soil air, and ambient air.

CN species in pore water

Review of CN in pore water in Chapter 4 led to the conclusion (paragraph 4.2.8): ‘Concentrations of CN in pore water (dissolved compounds or free CN) in the unsaturated zone of CN contaminated soils are not reported in the literature reviewed. Laboratory experiments indicate that these concentrations are in the same order of magnitude as those found in groundwater at such sites. It has to be noted that in these experiments dissolution of CN is likely to be better than in the field, while the brake down and complexation of liberated CN is probably less than under field conditions.’ Thus it can be expected that under field conditions concentrations in pore water will be lower than found in laboratory experiments. Not any information is available on the correlation between pore water concentration of CN and the consequent potential exposure of humansto CN. It can be concluded that at this stage of knowledge CN Intervention Values can not be based on the concentration of CN in pore water.

Free CN in soil air

The soil parameter HCN concentration in soil air can be measured directly. Although the link from measured HCN concentrations in soil air to ambient has not yet been established it gives at least an indication of the (worst case) maximum concentration of HCN in ambient air. Concentrations in soil air of 1 - 2 mg free CN/m^3 have been reported (Hoppener et al., 1983; paragraphs 4.2.6 and 7.5.3). Thus the HCN concentration in soil air could possibly serve as a parameter for the Intervention Value, which logically would then be set at 0.025 mg HCN/m^3 in soil air equal to the TCA in ambient air. However at this moment the range of HCN background concentrations in soil air is unknown. It is not unlikely that this range will overlap with 0.025 mg HCN/m^3, in which case this (ambient air TCA) concentration level in soil air can not be used in a simple way as a factor in the definition of the Intervention Value. Considering the little available information about HCN in soil air and also about its interpretation in terms of HCN in ambient air its seems self-evident to consider the possibility to base the Intervention Value for free CN directly on field measurements of the concentration of HCN in ambient air.

Free CN in ambient air

Emanation of free CN from the soil (possibly including water puddles at the surface and/or groundwater) to the ambient air has been observed at some sites with historical CN soil contamination to lead to concentrations up to 2 mg free CN/m^3 exceeding the TCA 0.025 mg free CN/m^3. Whereas using the CSOIL parameter values inhalation of air containing 0.175 mg free CN/m^3 will lead to exceedance of the TDI.

To propose a soil Intervention Value based on the concentration of free CN in ambient air seems justified (paragraph 7.5.3). The proposed Intervention Value of free CN in the ambient air emanated from the soil is 0.025 mg free CN/m^3, equal to the TCA.

Possible new Intervention Values

It is proposed to limit possible new Intervention Values to one or more of those mentioned above in this paragraph, listed again in Table 8.1.
That is for soil a concentration of free CN in ambient air of 0.025 mg free CN/m^3 due to emanation of free CN from the soil, and possibly for complex CN 5 mg CN/kg soil.
And for groundwater complex CN at a concentration of 12 mg CN/l, thiocyanate at a concentration of 0.075 mg CN/l, and total CN at a concentration of 0.075 mg CN/l.

Analyses of CN coupled to Intervention Values

No attention has been given in this report to methods to determine CN. It is self-evident that analytical protocols are a part of and should be coupled to the proposed intervention levels. This is of particular importance for the determination of free CN in ambient air, which is effected by weather influences. It can be influenced too by atmospheric CN emissions from non-soil sources such as exhaust gases from cars and other fuel driven machines. The emanation of free CN from the soil to ambient air is further dependent on factors like of soil temperature and soil humidity, which determine chemical/physical processes and biochemical activity in the soil. The CN concentration in groundwater is dependent e.g. on soil temperature and groundwater dilution by fresh supplies (either by uprising or infiltrating water) which fluctuate in time.
Strictly spoken all these factors should be considered in protocols for determining and interpreting CN concentrations.

7.7.2 Proposal for research prior to changes in Intervention Values

The current state of knowledge of CN soil contamination is rather limited on several points related to human exposure. Most crucial in this respect are the limited information on: enhancement of the concentration of free CN in soil and ambient air due to soil contamination; the relation of the concentration CN species in the soil to the concentration of free CN in air; the effects of CN soil contamination on food crops and their products.
With respect to the concentration of free CN in air it is also necessary to obtain information about background levels in soil air and in ambient (e.g. urban) air. Possibly these concentrations show an overlap with the TCA and may complicate identification of the fraction of the total free CN in air, which can be ascribed to CN soil contamination.
It deserves serious consideration to obtain additional data and insights on the above points and their effects on human toxicological risks prior to changing the soil Intervention Values. In addition to this it should possibly be attempted to obtain sufficient data and insights on the ecotoxicological effects due to historical CN soil contamination prior to the proposal of new Intervention Values. With respect to plants it is reassuring to note that the lowest free CN concentrations with phytotoxic effects as observed in laboratory studies (paragraph 6.3.1 and Table 6.3) are at least a factor twenty higher than the maximum free CN concentration observed in soil or soil moisture (groundwater) at contaminated sites (Table 7.11). In other words actual maximum observed CN concentrations seem from a phytotoxicological point of

view not a cause of concern. It can be mentioned though that the scattered available information indicates that free CN background concentrations show large spatial variations (e.g. in the rhizosphere), are harmful to certain soil organisms while at the same time creating better conditions for other (soil) organisms and in certain situations also for plants (Chapter 6 and Appendix 3). Thus to determine the HC50 concentration will be complicated by opposite ecotoxicological effects of CN at ‘low to medium levels’ on different organisms. To formulate an opinion on this ecotoxicological point is beyond the scope of this report (Verbruggen et al., 2000).

8. Conclusions and recommendations

Conclusions

Soil

This review has shown the need for revising the current Dutch Intervention Values for soils. It is namely the Intervention Values that have been based on the assumption that very high free CN levels in plant tissues could occur due to soil contamination. This has been proven to be incorrect as neither phytotoxicity nor conversion to asparagine were taken into consideration. The free CN intake of humans via food from contaminated sites has now been estimated to comprise maximally 8.5% of the TDI. It is uncertain if this will occur as the maximum free CN levels in contaminated soils indicate that free CN in plants will attain concentrations which will cause much less than 8.5% of the TDI. Indications are that human risks by other CN species in plant tissues due to soil contamination are negligible. The consumption of vegetables is concluded as not leading to exceedance of the TDI for any of the CN species. The same holds for the pathways of soil ingestion and inhalation of soil dust, when calculated with the same default values for human behaviour as used in CSOIL. A new aspect is the one-time peak ingestion of soil by children. For this event a complex CN concentration of 4.8 g CN/kg soil will exceed the very conservatively estimated tolerable acute ingestion limit for complex CN. Complex CN concentrations up to 40 g CN/kg soil have been reported. Thus an Intervention Value for complex CN of 4.8 g CN/kg soil, may be considered.

In previous risk assessments the emanation of HCN from contaminated soil was not considered. However, observed maxima of the concentration of free CN in ambient air exceed the TCA. It can be concluded that the only CSOIL pathway which can lead to exceedance of the TDI/TCA is inhalation of soil-emanated HCN. It is not yet possible to predict the free CN concentration in ambient air from soil parameters. However, the upper limit of the maximum concentration of free CN in ambient air is indicated by the concentration in soil air. To select this parameter for the definition of an Intervention Value would be premature considering that its background concentrations are unknown and may be difficult to distinguish from enhanced concentrations. An alternative is to base the Intervention Value on the free CN concentration in ambient air. This may be possible as the global background concentration is clearly below the TCA, though there is little or no information on urban background values (Table 8.1).

Groundwater

The current Dutch Intervention Values for groundwater have been based on the assumption that all CN species ingested by humans act as free CN. This results in an Intervention value of 1.5 mg CN/l for each of the three CN species considered free CN, complex CN and SCN (Table 1.1). For the last species this results in a relative high Intervention Value concentration, considering that the TDI of SCN is ten times lower than the TDI of free CN. This review shows that the consumption of untreated groundwater contaminated with CN can be a potential risk for adults and even more for children. The observed maximum concentrations of complex CN, and of thiocyanate, can lead to respective exposures of children of 2.8 and 1200 times the TDI. The maximum concentration of free CN can lead after ingestion of groundwater to a maximum exposure of children equal to 0.2 times the TDI. This exposure can be considered negligible when compared to that for complex CN and thiocyanate.

Recommendations

Soil

Recommendations encompass two points of view: 1) need for additional research to obtain sufficient knowledge to determine new Intervention Values for CN, and 2) need to base Intervention Values for CN on present knowledge, realising that Intervention Values for CN may be changed again later depending on newly acquired knowledge in the future.
Viewpoint 1: Before the free CN concentration in ambient air or in soil air can be considered as a parameter for an Intervention Value, field research is needed to obtain information on:

- HCN concentrations in soil and ambient air at contaminated sites;
- HCN background concentrations in soil and urban air, and
- a reliable, and if possible, simple procedure to determine soil-emanated HCN in the field in ambient and/or in soil air.

Depending on the outcome, we will learn if soil contamination with CN has the potential or not to lead to a CN exposure exceeding the TCA and/or TDI.
Although all evidence indicates that enhanced concentrations of CN species in plants will never attain levels of unacceptable risk for men, it can be argued that there is not sufficient information to eliminate doubt on this point. Further research can be considered, e.g. to determine concentrations of free CN, complex CN and SCN in plant material at contaminated sites and to determine maximum non-phytotoxic concentrations of CN species in plant material.
Before deciding on an Intervention Value for complex CN based only on a one-time peak ingestion of soil by children, the tolerable acute ingestion limit of complex CN can be argued to as being too uncertain yet, and that we will have to wait for new information on this.
Research can also be focused on Intervention Values for CN species based on the concentration of these species in pore water and to establish a link between this parameter and human exposure.
Viewpoint 2: On the basis of present knowledge one option is to base the Intervention Values on the measured concentration of free CN in the air above the soil, with the TCA as the threshold level. In other words, the Intervention Value: 0.025 mg free CN/m^3 ambient air, provides a short cut to inhalation exposure and is not hindered by the existing lack of information on behaviour of CN species in the soil and on emanation of HCN from the soil. Another advantage is that it can include emanated free CN liberated by photodegradation of complex hexacyanides dissolved in moisture at the soil surface.
An additional option is to set an Intervention Value for complex CN at 4.8 g CN/kg soil, based on the very worst estimation of the risk of a one-time peak ingestion of soil by children.

Groundwater

Dissolved complex CN as well as SCN can lead after consumption of untreated groundwater to exceedance of the TDI. Possible new Intervention Values for groundwater are 12 mg CN/l for complex CN, and 0.075 mg CN/l for thiocyanate. Both species form part of the EPA 335.3 analysis of total CN. It is also possible to select this as a parameter for a new Intervention Value of 0.075 mg total(EPA) CN/l groundwater.
The current Intervention Values for groundwater, 1.5 mg CN/l for each CN species (Table1.1), were based on a consumption of 2 l untreated groundwater per day by adults, a TDI of 0.05 mg free CN/kg b.w. per day, and the assumption that after ingestion all CN species would react as free CN. Extending this reasoning, all CN species should, collectively, not exceed the TDI for free CN. As total (EPA) CN includes all CN species, an obvious adaptation of the current Intervention Values for groundwater is to simplify these to 1.5 mg

total(EPA) CN/l. The last point can also be considered as an option for a new Intervention Value in view of the remaining uncertainties of the human toxicity of CN species.
A different approach is to use the ecotoxicological risks limits of surface water for the Intervention Value of groundwater (Verbruggen et al., 2000). This approach results in the lowest Intervention Values, 0.031 mg CN/l for free CN and 0.029 mg CN/l for complex CN , and the highest, 4.5 mg CN/l, for SCN. Simplification to 0.03 mg total(EPA) CN/l is possible.

Implications
The recommendations diverge widely. Namely from additional research prior to changing the Intervention Values to different alternatives for possible new Intervention Values (Table 8.1), these may be changed in the future as new knowledge becomes available. The decision to choose one or more of these options will have large implications. It is beyond the objective and scope of the present study to discuss these implications and to rank the given recommendations, or to select one of these as being the most pragmatic.

Table 8.1 Possible alternatives for new Dutch Intervention Values for historical CN soil contamination based on estimated potential human risks; CN background data and maximum CN concentrations observed after 1990 at contaminated sites.

Parameter	Exposure pathway	Possible new Intervention Value	Background concentration	Max. due to soil contamination
Soil				
Free cyanide in ambient air (due to soil contamination)	inhalation	0.025 mg CN/m^3 (TCA)	natural global av.: 1.6E-4 to 2.0E-4 mg CN/m^3; urban air: n.d. [1)]	2 mg CN/m^3
Complex CN in soil	One-time peak Soil ingestion	4.8 g CN/kg	n.d.	40 g CN/kg
Groundwater				
Complex CN in groundwater	Drinking untreated groundwater	12 mg CN/l	n.d.	34 mg CN/l
Thiocyanate in groundwater	Drinking untreated groundwater	0.075 mg CN/l	n.d.	90 mg CN/l
Total(EPA) CN in groundwater	Drinking untreated groundwater	0.075 mg CN/l or ‘new-current’: 1.5 mg CN/l	mg CN/l: complex CN n.d. free CN n.d. SCN < 0.001	mg CN/l: complex CN 34 free CN 0.15 SCN 90

[1)] n.d. = not determined and/or no data

APPENDIX 1 Groups of cyanides and cyanogenic compounds

The chemical speciation of cyanides varies according to their source. The most common forms of cyanide in the environment are free cyanide, simple cyanides, complex cyanides, cyanogenic glycosides, and thiocyanates.

Free cyanides

Free cyanide refers to the sum of molecular HCN and the cyanide anion CN^-. The cyanide anion CN^- is in solution in equilibrium with HCN, and with simple or complex cyanides molecules.
HCN is a colourless, flammable liquid or gas that boils at 25.7 ^{0}C and freezes at -13.2 ^{0}C. HCN is extremely water soluble. HCN gas rarely occurs in nature, is lighter than air, and diffuses rapidly, its odour is not equally well detectable for all persons and is often associated with the odour of bitter almonds. [Note: in some publications (possibly only from the UK) free cyanides also include alkali metal CN salts (NTU, 1998), generally classified as simple cyanides, but dissolving in water to CN^- or free cyanide and an alkali metal ion.]

Simple cyanides

Simple cyanides typically refer to alkali water-soluble salts, such as NaCN, KCN, $Ca(CN)_2$ and $Hg(CN)_2$, but also include several cyanide salts of varying degrees of water solubility such as $Zn(CN)_2$, $Cd(CN)_2$, $Ni(CN)_2$, and AgCN. All simple cyanides ionise in water to release CN^- which, depending on pH will form HCN. [Note: in some publications (possibly only from the UK) free cyanides also include alkali metal CN salts (NTU, 1998), generally classified as simple cyanides, but dissolving in water to CN^- or free cyanide and an alkali metal ion.]

Complex cyanides

General

Complex cyanides are compounds in which the cyanide anion is incorporated into a complex or complexes, they differ in chemical and toxicological properties from simple cyanides. Some of these complexes can dissociate in weak acids to give free cyanide and a positive charge, while other metallo cyanide complexes require much stronger acidic conditions for dissociation. The least stable complexes include $Zn(CN)_4^{2-}$, $Cd(CN)_3^{1-}$ and $Cd(CN)_4^{2-}$, moderately stable complexes include $Cu(CN)_2^{1-}$, $Cu(CN)_3^{2-}$ and $Ni(CN)_4^{2-}$, the most stable complexes include the hexacyanoferrates $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$, Mn-Fe complexes, $Co(CN)_6^{4-}$, etc. (Meeussen, 1992; Keizer et al., 1995)

Iron hexacyanide forms.

Potassium ferrohexacyanide yellow prussiate of potassium $K_4Fe(CN)_6$.
Sodium ferrohexacyanide yellow, sodium hexacyanoferrate, prussiate of sodium $Na_4Fe(CN)_6$ used as anti-caking agent
Potassium-ferri ferrohexacyanide $KFe[Fe(CN)_6]$ slightly soluble Prussian-blue, can be present in the soil in a colloidal form (Mengel and Friedberg, 1991)
Ferri ferrohexacyanide $Fe_4[Fe(CN)_6]_3$ insoluble Prussian-blue present in MGP waste. Very low solubility at low pH values, higher solubility at pH 7 and higher (Meeussen, 1992).

Prussian blue $Fe_4[Fe(CN)_6]_3$ was shown to be the stable iron cyanide solid at higher pE conditions over the aqueous pE-pH range studied, while Turnbull's blue $Fe_3[Fe(CN)_6]_2$ was identified as the stable iron cyanide solid at lower pE values (Ghosh, 1999).
The class of iron-cyanide blue pigments may be described generically as $(MFe^{3+})Fe^{2+}(CN)_6$ where M may be potassium, sodium, or ammonium, or rare alkali metals lithium, caesium, rubidium. The fundamental basis for the colour is charge transfer resonance based on the presence of both ferrous and ferric oxidation states in the complex. The definition of Prussian blue compounds is imprecise and potassium ferrohexacyanide $K_4Fe(CN)_6$ and Cu, Co, Ni and Zn ferrohexacyanides are often also included in the group (Homan, 1987; Pearce, 1994).
Water-soluble K, Na and NH_4 linked with ferrihexacyanides and ferrohexacyanides, do not release free cyanide. However when aqueous solutions are exposed to ultraviolet light photodegradation of dissolved hexacyanoferrate ions has been well established (Leduc et al., 1982; Marrs et al., 1987; Eisler, 1991; Shifrin et al., 1996):

$$Fe(CN)_6^{4-} + h\nu \rightarrow Fe(CN)_5^{3-} + CN^-$$

Cyanates

Cyanates contain the OCN group. These inorganic cyanates, formed industrially by the oxidation of cyanide salts, hydrolyse in water to form ammonia and bicarbonate ion. In nature cyanate is presumably formed as an intermediate in the degradation of thiocyanates.

Thiocyanates

Thiocyanates contain the SCN group, and can be formed biochemically in nature from cyanides and sulphur-containing materials, they are relatively stable. Thiocyanates can be hydrolysed also by some soil bacteria to ammonia, carbondioxide and sulphide, the last is oxidised (Youatt, 1954; Paruchuri et al., 1990; Stratford et al., 1994). Thiocyanates also come about by decomposing of plant tissues containing glucosinulates. SCN is also contained in urine from mammals.

Cyanogen

Cyanogen $(CN)_2$ is an extremely toxic, flammable gas that reacts slowly with water to form HCN and other compounds; it is rapidly degraded in the environment. Cyanogen and its halide derivations are comparable in toxicity to HCN.

Cyanamids

Cyanamids comprise compounds with $=N-C\equiv N$.
Hydrogen cyanamid, H_2NCN, has plant physiological properties, and is used both as a herbicide, a desiccant (e.g. to induce wilting/loss of foliage) and as a plant growth regulator.
Calcium cyanamid, CaNCN, has been produced commercially since 1905 and is sold under the name lime nitrogen, a fertiliser with herbicidal effects, it has also been used as a desiccant.
In plants and soils the cyanamids mentioned are converted to nitrogenous compounds which are readily taken up, they do not give residue problems (BCPC, 1994. p.238/9).

Nitriles

General

Nitriles are defined as organic cyano compounds, $R-C\equiv N$, containing the cyanide group. They comprise a very wide and diverse range of chemical compounds, of which a few will be mentioned here.

Mononitriles, dinitriles and synthetic polymerised nitriles

Mononitriles CH_3CN (acetonitrile), C_2H_5CN, CH_2CHCN (compound which is the basis for acrylonitrile, vinyl cyanide), C_3H_7CN, etc.

Dinitriles $CH_2(CN)_2$, $C_2H_4(CN)_2$, $C_3H_6(CN)_2$, etc. These nitriles are comparatively innocuous in the environment, are low in chemical reactivity and are biodegradable.

Synthetic nitrile-polymers composed from e.g. acrylonitrile, propionitrile and succinonitrile vary in complexity and stability. These polymers can liberate free CN and toxic CN compounds, in addition the liberated non-nitrile part of the molecule may exert an independent or interactive toxicity.

Cyanogenic glycosides

Cyanogenic glycosides $R_1R_2C(OR_3)CN$ are special nitriles in that they will decompose to HCN and cyanide ions under appropriate conditions. They are found in several plants, more than 28 different cyanoglycosides have been measured in about 1,000 species of higher plants (Conn, 1979; Leduc, 1984). Decomposition takes place by enzymatic action promoted by crushing the plant followed by lengthy air drying; a processing method that has been used since historical times in many tropical regions to make cyanogenic plant parts edible.

Cyanolipids

All cyanolipids occur exclusively in seed oils of the plant family Sapindaceae, and so far known all are esters of mono- or dihydroxynitriles (Scheuer, 1992).

Glucosinulates

Glucosinulates are commonly found in Cruciferae, they do not contain a C≡N group but yield mustard oils (thiocyanate and isothiocyanate containing compounds) as degradation products (Scheuer, 1992).

β-cyanoalanines

In seeds of the cyanogenic legume common vetch (Vicia sativa L.) levels of γ-glutamyl-β-cyanoalanine (γ-gluBCA) and of BCA are found at levels of respectively 4,000 - 9,000 and 1,000 – 2,500 mg/kg, which levels are considered too high for human consumption. Consumption is possible after proper processing, e.g. in households by cooking the seeds in water and subsequent decantation of this water with the dissolved toxins (Ressler et al., 1997). Presence of γ-gluBCA is restricted to some vetch species, it does not occur in all vetch species. Common vetch which accumulates γ-gluBCA shows an atypical metabolism of HCN not shown by other vetches (Ressler et al., 1969; Blumenthal et al., 1968).

Isocyanides

Isocyanides comprise cyano-isomers which are unique in respect that they are stable compounds in which carbon is bonded to a single atom: R-N=C, they do not contain a -C≡N group. They occur naturally in the marine and terrestrial environment, some are used as antibiotics and of these some are produced by chemical industries (Scheuer, 1992). Another commercially produced isocyanate is methylisocyanate it can be formulated as a soil fumigant (Dazomet and others) and is mainly used to control nematodes. In 1984 leakage of methylisocyanate at a production plant near Bhopal (India) caused a large accident.

APPENDIX 2 Natural occurrence and/or background concentrations of cyanides

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A2.1 Soil, air and water

Soil

CN background concentration
In 6 geo-soil provinces in Lower Michigan a total of 218 samples were taken at depths varying from 0 to 24 m The detection limits in the study varied from 0.005 to 0.3 mg CN/kg soil. In 29 of these CN concentrations were above the detection limits, most of these in the sand and in the clay provinces of the `Huron-Erie Lobe'. In the respective sand province the average concentration was 0.43 mg CN/kg soil with a maximum concentration of 1.2 mg CN/kg soil (Kessler-Arnold and O'Hearn, 1990). No information is provided on the CN speciation neither on causes of the differences in concentration between the soils sampled.
CN background concentration of Great Lakes (USA) sediments is reported to be < 0.1 mg/kg soil (moderately polluted 0.1-0.25 mg/kg soil) (Beyer, 1990).
A background value of 0.7 mg total CN/kg is reported in a study focussing on contaminated shorelines in a gold mining region in South Dakota, USA (Howe and Noble, 1985).
A default value given of the background in soils of the USA is for free cyanides 1 mg/kg soil and for complex cyanides 5 mg/kg soil (Beyer, 1990).
In a study of the composition of tare-soil of harvested root crops in the Netherlands samples of 9 depositories were analysed. All or most of the thiocyanate has been formed from glucosinulates present in plant parts of the crop. The average values of the depositories show the following range (Lamé and Keijzer, 1998): free cyanide from <1 (d.l.) to 1.6 mg CN/kg d.m.; thiocyanate from <0.3 (d.l.) to 2.3 mg CN/kg d.m.
In German arable land thiocyanate concentrations are around 0.005 mg CN/kg dry soil (Weuffen et al., 1990).

Table A2.1 CN background concentrations in soils (references see text).

Sample information	Free CN	Total CN	Not specified CN	SCN
	mg CN/kg soil dry			
Lower Michigan 0-24 m depth, 218 samples	n.d.	n.d.	av. 0.43 (<0.005 – 1.2)	n.d.
Great Lakes sediments	n.d.	n.d.	<0.1	n.d.
South Dakota	n.d.	0.7	--	n.d.
USA default	1	5	--	n.d.
Root crop tare soil, Netherlands	<1 – 1.6	n.d.	--	<0.3 – 2.3
Arable land, Germany	n.d.	n.d.	--	around 0.005
Above observed range in soils	<0.005 – 1	<0.005 – 1.2	see total CN	around 0.005

Air and emission to the atmosphere

HCN

In a study of the atmospheric chemistry of HCN general tropospheric background concentrations are reported of 1.6E-4 - 2.0E-4 mg HCN/m^3. The annual terrestrial global emission to the atmosphere coupled to this atmospheric concentration is about 4E8 kg HCN (Cicerone and Zellner, 1983). The corresponding average background terrestrial emission to the atmosphere can be estimated at about 2.7 mg HCN/m^2/year (the earth's land surface is 1.49E8 km^2). The emission is both from biological and anthropogenic sources of which no quantification can be given.
Background concentration levels in the Netherlands observed in the crawl space and in a room of a residential home are < 1.0E-5 mg HCN/m^3 air (IWACO, 1999).
The background concentration of modern society is influenced by exhaust gasses from cars, these contain maxima from 500 - 10.000 mg CN/m^3 (Cicerone and Zellner, 1983; Eisler 1991).

SCN

In a survey executed in 1988 of thiocyanate in fertilisers the following 'background' concentration in ambient air in a garden was found: in September 4E-5 mg CN/m^3, in December no thiocyanate or no sampling; above a heap of cattle manure in September 3E-4 mg CN/m^3, in December no thiocyanate or no sampling; in the cattle barn 1E-4 - 2E-4 mg CN/m^3 in September and December.

Water

Rainwater, free CN

No data on HCN concentrations or presence of HCN in rain are found. It may be noted that 'Contrary to extrapolations from information in several popular handbooks, HCN is not very soluble in water when low partial pressures (<1 torr) are in question' and that consequently rainout of HCN (leading to wet deposition) appears to be negligible (Cicerone and Zellner, 1983). Considering the background concentration in air the corresponding background concentration in rainwater will be extremely low.

Groundwater, free CN

The recently in Germany derived threshold value derived for free CN, and dissolved CN compounds which are easily dissociable to free CN, in contaminated groundwater without affecting its ecological or its quality for human consumption is 0.005 mg CN/l (Röder et al., 1999).

Surface water, total CN

Total cyanide concentrations in surface waters (Thuerkow et al., 1990):
- uninhabited watersheds covered with grasslands and forest 0.0007 - 0.002 mg CN/l (max. 0.005);
- rivers central and Western Canada max. 0.006 mg/l;
- industrial areas 0.02 mg/l.

Groundwater, total CN

In Wisconsin a total CN of 265 groundwater samples has been collected near a highway; total CN concentrations are lower than 0.01 mg CN/l in 258 samples, approximately 0.01 mg CN/l in 6 samples, and 0.02 mg CN/l in 1 sample. It is concluded that there is no consistent evidence of cyanide contamination in the shallow aquifers at the sites studied. In other words the background concentration in the study area is in average <0.01 mg total CN/l and shows a range from <0.01 – 0.02 mg total CN/l.

A recent German threshold value derived for total CN in contaminated groundwater without affecting its ecological or its quality for human consumption is 0.05 mg CN/l (Röder et al., 1999).

Surface water, thiocyanate

Concentrations in surface water of ionic SCN were found to be in a range of 0.0003-0.003 mg/l, concentrations increase with increasing water temperature and biological activity (growth, multiplication, death and decay) in the water (Thuerkow et al., 1990).

Groundwater, thiocyanate

In groundwater at 20 m depth SCN^- concentrations of 0.0013 mg/l, this is in excess of the expected values probably due to the presence of micro-organisms in the pump installation (Thuerkow et al., 1990).

A2.2 Fertilisers (Weuffen et al., 1990)

All mineral fertilisers contain more thiocyanate than soil, concentrations are in the range of 0.02 mg CN/kg (potassiumchloride, ammoniumnitrate/lime mixture, sodiumnitrate) to 0.04 mg CN/kg (ammoniumsulphate, superphosphate).

In cattle dung 3 mg CN/kg d.m., in liquid cattle manure 24 mg CN/kg d.m.

A2.3 Micro-organisms, fungi and algae.

Hydrogen cyanide production may occur in green and blue-green algae during nitrate metabolism (Leduc et al., 1982).

A2.4 Plants

Elevated cyanide (nitrile) levels are encountered in more than 1,000 species in 100 plants families, the cyanides are generally present in the form of cyanoglycosides or cyanolipids (Scheuer, 1992). The cyanide containing plant parts vary per type of cyanogenic plant, e.g. young leaves of tropical Gramineae, nuts of some Prunus species, the seeds (beans) of some legumes, all plant parts of cassava.

Most of these plants - cassava, sweet potatoes, and young leaves of Gramineae as sorghum, sudan grass, johnson grass - occur in mediterranean, subtropical and tropical climates. In temperate climates cyanides (nitriles) occur in flax (linseed), vetches and in the kernel of the pits of stone fruits (cherry, peach, plums).

The levels of total cyanide (in this case nitriles) in mentioned plants range from 20 to 2.500 mg CN/kg fresh weight. The total CN content differs between different plant parts, the highest level has been reported for the growing point of bamboo with a maximum of 8.000 mg CN/kg fresh weight (Towill et al., 1978).

The consumption of cyanogenic forage grasses by range animals in non-temperate climates is common. And indicative values of health set levels have been derived from the following permissible intake rate by ruminants (Pickrell et al., 1991): approximately 0.5 mg cyanide per kg b.w./hr; all diet contains 20 mg cyanide per kg.
Data of CN in non-cyanogenic plants are scarce, as well as data on CN uptake by plants from the soil (Appendix 3). About the conversion of CN in the plant after uptake little or nothing has been published.
[Note. In the CSOIL calculations executed to obtain the current Intervention Value a phytotoxic ceiling to the CN levels in plant tissues was not considered and the following CN levels in plants corresponding to the human TDI were used toe determine the soil Intervention Value of CN.
- Free cyanides (17.4 mg/kg soil) in plants: leaves 116 mg/kg fresh weight; roots 104 mg/kg fresh weight.
- Thiocyanates (3.84 mg/kg soil) in plants: leaves 25 mg/kg fresh weight; roots 23 mg/kg fresh weight.
- Complex cyanides (4.54 mg/kg soil) in plants: leaves 30 mg/kg fresh weight; roots 27 mg/kg fresh weight.

The underlying report shows that these calculated levels in plant tissues are unrealistically high.]

A2.5 Animals

Some random information found as a by-product of the soil-CN literature review is presented here, the information is of course far from complete.
Hydrogen cyanide production may occur in hepatopancreas of mussels (Vennesland et al, 1981).
Permissible intake of free CN liberated upon consumption of cyanogenic forage grasses by ruminants approximately 0.5 mg cyanide per kg b.w./hr, all diet contains 20 mg cyanide per kg (Pickrell et al., 1991).
See also paragraph 3.5.4.

A2.6 Human beings

See: Meijerink, 1999; and paragraph 7.2.

APPENDIX 3 Effects of elevated levels of cyanides on plants

In this appendix an overview is given of results reported in diverse studies directed at, or touching upon, effects of elevated CN levels on plants. A summary with some conclusions has been presented as part of Chapter 5 of this report.

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A3.1 Uptake of free cyanides from soil and its effects

A3.1.1 Laboratory studies

Seed emergence

Free cyanides can have an inhibitory effect on emergence of seeds and/or on seedling vigour and survival (Table A3.1).

Table A3.1 Effects of free CN in (artificial) soil on seedling emergence. (Source: CCME, 1997.)

Species	Days	NOEC	LOEC	EC_{25}	EC_{50}
		mg CN/kg soil			
Radish	3	0.9	1.9	1.3	2.9
Lettuce	5	5	10	7	13

Generally speaking the effects of HCN at low concentrations germination, seedling and plant growth can be inhibitory to or promoting germination, seedling, root and plant growth. Variations occur depending both on ecological and environmental factors and on plant species and varieties. The underlying processes are in many cases not unequivocally clear and general conclusions can not be drawn (Towill et al., 1978, cited by Eisler, 1991).

MGP wastes

It was found that a 1 % mixture of oxide-box wastes and soil produced a slight inhibitory effect on the growth of ryegrass. When more than 10% oxide-box waste was mixed into the soil the growth inhibitory effect became quite evident (Roberts and Gemmell, 1979). It was not diagnosed whether this phytotoxicity of MGP waste was due to cyanides or to other constituents or factors such as aluminium toxicity evoked by the low pH of the waste.

Studies with bean plants

Scope of the studies and limitations with respect to information on CN

Cyanide ions have the ability to form chelate-type complexes with several metals, as e.g. Al, Co, Cu, Fe, Ni, Ti and Zn. Two publications were found in which effects of CN on uptake and transport of these trace metals by bean plants (Phaseolus vulgaris) is reported (Wallace et al., 1977; Wallace et al., 1981). Both studies do not aim to establish information on the phytotoxicity of exogenous CN and its uptake by plants. However some information on this can be derived, although this is done with the following reservations:

- An uncertainty in the published results of the respective studies is that it is not indicated if the amounts of NaCN added to the pots are expressed on gram dry or on gram moist soil; it is assumed here that they are expressed on dry soil. (This may underestimate the concentration in the (dry) soil by about 40%. It may lead to an estimate of a 40% too low concentration level of CN at which toxic effects occur, and an overestimation of the transfer from CN to plants by about 40%.)
- As a source of CN NaCN labelled with ^{14}C was used. And the analysis of the uptake of CN was done via analysis of ^{14}C in the plant. However it does not provide any information about conversion of CN in the plant. This is a crucial point as it may be that part of or all CN taken up by plants is converted in the plant to non-harmful compounds. In which case human exposure to CN contaminated soils via the consumption of plant products does not take place at all or at a lower level than indicated by the plant-uptake of CN.
- NaCN was added to well growing bean plants, so no conclusions on effects of CN present in the soil (or culture solution) from the time of seeding onwards can be drawn.

Results with respect to CN

In the first study with bean plants (Phaseolus vulgaris) growing in pots and culture-solutions it appeared that (Wallace et al., 1977):

- CN severely decreased plant growth at the concentrations tested compared to the control treatment (Table A3.2);
- CN chelated the metals mentioned above, and increased their uptake and movement through the plant;
- the quantity of ^{14}C present in the plants was somewhat lower than the equivalent of the increased uptake of trace metals. Possibly some ^{14}C was lost from plants by drying before analysis or after its uptake some ^{14}CN was converted in the plants and part of this ^{14}C was emitted as $^{14}CO_2$ upon plant respiration.

A CN^- uptake by the plants equalling 8 mg CN^-/kg d.m. is coupled to a plant dry weight of 70 % of the control. Assuming a 15 % dry weight of the plants it indicates that a level of 1.2 mg CN^-/kg fresh is phytotoxic. (This level may be lower considering possible conversion of free CN in the plant to less toxic substances.) Occurrence of phytotoxicity at this concentration level of free CN in the plant supports later findings with other plants presented in A3.2.2.

Table A3.2 Growth reduction of and CN uptake by bean plants after application of NaCN to soil or culture-solution. (Source: derived from Wallace et al., 1977.)

CN^- in growth medium	Period with CN in growth medium	Plant dry weight as compared to control [1]	CN^- uptake by plants	Transfer factor CN^- plant/soil [3]	Transfer factor CN^- plant/solution [3]
	Days	%	µg total CN uptake/g d.m. [2]		
27 µg CN/g soil	11	60	n.d.	n.d.	n.d.
53 µg CN/g soil	11	35	n.d.	n.d.	n.d.
27 µg CN/g soil	7	50	35	1.3	0.2 [4]
53 µg CN/g soil	7	25	100	1.9	0.7 [4]
2.6 µg CN/ml solution	4	70	8	n.d.	3.1
13 µg CN/ml solution	4	70	20	n.d.	1.5

[1] Quantitative conclusions about growth reduction by CN^- not possible, as initial weight of plants has not been reported.

[2] All plants suffer severe growth depression, caused by CN^- uptake, mainly after its chelation with cations in the soil. Chemical speciation, conversion or breakdown of CN in the plant unknown

[3] Transfer factor is based on analyses of ^{14}C transfer, no information about conversion or not of CN in the plant after uptake.

[4] Calculation based on the assumption of 0.4 ml soil solution per g of soil with all NaCN present as CN^- in the soil solution.

In the second study the effects of several chelating agents on the uptake of ^{241}Americium from soil by bean plants (Phaseolus vulgaris) growing in pots were tested. NaCN, labelled with ^{14}C, was added at concentrations of 27 and 53 µg CN/g soil. Seven days later plants were harvested and analysed. ^{241}Am uptake was increased clearly by CN on the two soils studied (Yolo and Hacienda loam). Also in this experiment plant growth was reduced by CN, more in Yolo loam than in the Hacienda loam possibly due to the higher pH, and more by the highest CN concentration tested (Table A3.3).

The studies clearly proved the chelating ability of free CN^- by the increased uptake of trace metals and americium; the CN uptake mechanism by plants is probably for a large part as a chelate linked to a metal.

Based on the ^{14}C analyses the Transfer Factor of CN from soil to plant has been calculated and is presented in Table A3.2. For the following reasons these estimates can not be used as Transfer Factors for CN in case of soil contamination: exposure time of the plants to CN only 4 to 7 days; plants not healthy effected by CN phytotoxicity; (CN not determined in plants). Consequently CN levels in plants due to soil contamination have to be derived from other information.

Table A3.3. Growth reduction of growing bean plants 7 days after application of NaCN to soils. (Source: Wallace et al., 1981.)

CN in growth medium	Soil type	Plant dry weight as compared to control [1]
		%
27 µg CN/g soil	Yolo pH 5.9	42
53 µg CN/g soil	Yolo pH 5.9	36
27 µg CN/g soil	Hacienda pH 7.5	45
53 µg CN/g soil	Hacienda pH 7.5	10

[1] Quantitative conclusions about growth reduction by CN not possible,
as initial weight of plants has not been reported.

Effects of natural exogenous free CN on plants

The effects of exogenous free cyanides, at natural levels, on plant growth are often not predictable. E.g. about 50% of the Pseudomonas strains isolated from potato and wheat rhizospheres are able to produce HCN in vitro (Schippers et al., 1990), and also 3% of 266 rhizobium and bradyrhizobium bacteria-species tested (Antoun et al., 1998). It has been shown that HCN produced in natural soil by rhizobacteria can efficiently suppress certain soil-borne plant diseases and promote growth of wheat, tobacco, cotton and cherry trees (Défago et al., 1990). There is also circumstantial evidence that microbial cyanide, may inhibit root and plant development. This postulated growth reducing effect of CN from rhizobacteria may only become apparent in the absence of parasitic plant pathogens that are suppressed by HCN (Schippers et al., 1990).

A3.1.2 Field studies and observations

Field studies and observations

Natural vegetation on CN contaminated shorelines in South Dakota USA
In 1980 plants were sampled which were growing at shoreline sites contaminated with CN from gold-mill effluents (main contamination occurred in the years 1900 - 1960, in 1978 contamination had been practically halted). No cyanide was found in willows; in a herb named tansy (Tanacetum vulgare) cyanide concentrations varied and appeared to increase with increasing soil concentration; CN levels in arrow grass (Trigochin maritima) growing at contaminated areas showed small increases; dandelions (Taraxacum officinale) growing at contaminated sites showed clear increases in CN content (Table A3.4). In this field-survey-study the correlation between total CN levels in plants and soils did not show high statistical evidence (Howe and Noble, 1985). The total CN levels in three of the four species studied show very clear increases due to past and/or relatively recent CN soil contamination. CN speciation within these plants, plant growth/vigour and possible cyanogenic characteristics fell beyond the scope of this study.

Table A3.4. Total cyanide in plants[1) 2)] *growing at CN contaminated shoreline sites. (Source: Howe and Noble, 1985.)*

Soil, dry	Dandelion	Tansy	Arrowgrass	Willows
mg CN/kg				
0.7 (uncontaminated control)	< 0.5	< 0.5	< 0.5	< 0.5
2.0	< 0.5	2.0	n.d.	< 0.5
11.3	10.3	7.6	4.5	< 0.5
16.2	11.3	3.8	1.2	< 0.5

1) No details about plants parts sampled, nor information if total CN contents are on a fresh or dry matter basis.
2) No information if some of these plant species are cyanogenic.

Residential gardens on the premises of a former galvanic factory in the Netherlands
In a residential quarter at Vaassen on the premise of a former galvanic CN was determined in samples composed of green material from ≥ 8 different garden plants mixed together. There is no conclusive evidence of uptake of CN from the soil by these plants (Raes et al., 1999).

Herbicidal use of MGP wastes
In earlier days in the Netherlands MGP waste has been used as a ‘herbicide’ at or close by MGP sites (Koning de, 1995. p.14); no information is given on the cause of this phytotoxicity.

A3.2 Uptake of free cyanides from solutions and its effects

A3.2.1 Gold mill effluent

Water hyacinths

A rather rudimentary study of free cyanide removal from gold mill effluent, containing 9 and 19 mg free CN/l, was executed by growing water hyacinths during 8 days outside in large containers through which a continuous flow passed of a surrogate effluent solution prepared in the laboratory. It was observed that CN removal was doubled by the presence of waterhyacinths as compared to the untreated controls. During the experiment the waterhyacinths showed chlorophyll, leaf discoloration and died (Granato, 1993). The deleterious effects of CN on the plants seem in accordance with the studies described above. Other factors such as presence of thiocyanates (14 and 23 mg/l), and presence of dissolved Cu, Zn and Fe may also have played a role. Thiocyanates were not taken up from the effluent by the waterhyacinths.

Dandelions

A laboratory study showed clear increases of total CN content in dandelion leaves after the roots of young plants (harvested from non-contaminated sites) had been placed in NaCN containing solutions during three consecutive days (Table A3.5). One of the conclusions was that young dandelion plants easily survive actual mine-effluent concentrations from 7 - 8 mg total CN/l; if such concentrations cause reductions in growth was not reported. (Howe and

Noble, 1985). In the mine effluent a large fraction of the CN is probably in other chemical forms than free CN^-.

Table A3.5 Total cyanide in leaves of young Dandelion plants[1) 2)] *after 3 days growth on NaCN containing solutions, on mine water, and on mine effluent. (Source: adapted from Howe and Noble, 1985.)*

Culture solution during 3 days		Dandelion leaves
Origin and characteristics	CN mg/l	mg total CN/kg
mine water total CN	0.5 (total)	0.0[3)]
mine effluent total CN	7 – 8 (total)	2.2
NaCN lab. Prepared solution	0.26 (free)	0.2[3)]
NaCN lab. Prepared solution	2.6 (free)	0.2[3)]
NaCN lab. Prepared solution	260 (free)	11.5 (phytotoxicity??)
NaCN lab. Prepared solution	2,600 (free)	373.9 (plants dying)

[1)] No information if total CN contents are on a dry matter or fresh weight basis.
[2)] No information if Dandelion is a cyanogenic plant species.
[3)] No information on detection limit

A3.2.2 Nutrient solutions

Beans

Exposure of growing bean plants during four days to rooting solutions containing 2.6 and 13 mg free CN/l caused severe growth reductions and led to increased CN concentrations in plants (Table A3.2).

Dandelions

If exposure of young dandelion plants during three days to rooting solutions containing 0.5 mg free CN/l resulted in increases of CN content in the leaves is not clear (the detection limit, possibly 0.2 mg total CN/kg was not reported) (Table A3.5). The young dandelion plants survived exposure during three days to solutions containing 7-8 mg free CN/l though the plants showed increased levels of total CN. A cyanide level of 5,000 mg/l in the culture solution had lethal effects on the young Dandelion plants, in these plants the concentration of total CN in the leaves had risen after 3 days to 374 mg total CN/kg (Howe and Noble, 1985).

Phytotoxicity of CN and CN levels in young plants

Manifold determinations of free CN background levels and of phytotoxicological levels of free CN in plant tissue of young plants were done in the studies leading to the conclusion that accumulation of free cyanide derived from ethylene biosynthesis, was the main herbicidal mechanism in quinclorac sensitive Gramineous species. In these studies plants were grown to the 2nd or 3rd leaf stage, after selection of uniform plants for the experiment, plants were hydroponically exposed for about 4 days to NaCN or to quinclorac depending on experimental treatment. At the termination of the experiments free CN was determined in shoot tissue (Grossmann, 1996 and 1998; Grossmann and Kwiatkowski, 1995). The results (Tables A3.6 through A3.9) give much information about phytotoxicological levels of CN in root-solutions and of phytotoxicological levels of free CN in plant tissue (of young plants not grown on CN containing media from seeding or emergence on).

In Grossmann, 1998. (p.712 fig. 4) a linear relationship between CN content in shoot tissue and reduction in shoot fresh-weight is shown for large crabgrass (Digitaria sanguinalis.

The following findings are additional to those listed in the mentioned tables A3.6 through A3.9.

- Exposure of isolated barnyard grass shoots [Echinochloa crus-galli (L.) P. Beauv.] to free cyanide 21 mg/l via the vascular system led after 5 days application to a 30% reduction in shoot fresh weight, with symptoms of chlorosis (chlorophyll break down) and subsequent necrosis of the leaves. Indicating that at this concentration level free CN is phytotoxic (Grossmann and Kwiatkowski, 1995. p.155, I30 value).
- The HCN production (as compared to control treatment plants) in rice shoot tissue during quinclorac treatment was estimated to be 240-fold lower than that in barnyard grass. This correlates well with the difference in sensitivity of both plants species to the herbicide quinclorac (Grossmann, 1998. p715.).

Table A3.6 Cyanide content and growth reduction and/or phytotoxic effects of free cyanide during 4 days in root medium of 2nd leaf stage barnyard grass (Echinochloa crus-galli). (Source: Grossmann and Kwiatkowski, 1995. p.157, fig.5A.)

Free CN in rooting medium	Free CN in shoot	Shoot fresh weight	
mg CN/l	mg CN/kg fresh weight	mg/shoot	% 1)
0	0.31	69	100
7.8	0.75	48	70
10.4	0.73	45	65
13.0	1.17	36	52
15.6	1.20	35	51

1) Relative as compared to control plants. Not relative to initial shoot weight which would indicate fresh weight loss or gain at the end of the experiment.

Table A3.7 Free CN content in shoot tissue and reduction in fresh weight of different Gramineae (3rd leaf stage) after hydroponic root treatment with quinclorac 100 μM for 75 hours. (Source: Grossmann, 1998. p.714, fig.6.)

Species	Control plants	Treated plants	
	free CN mg/kg fresh weight		% decrease in fresh weight 1)
Oryza sativa	0.16	0.16	20
Echinochloa hispidula (resistant biotype)	0.20	0.15	11
Brachiaria platphylla	0.44	1.62	60
Echinochloa crus-galli	0.25	0.89	69
Echinochloa colonum	0.10	0.49	76
Setaria viridis	0.07	0.39	73
Echinochloa hispidula (susceptible biotype)	0.10	1.86	86
Digitaria sanguinalis	0.11	1.72	92

1) Relative as compared to control plants. Not relative to initial shoot weight which would indicate fresh weight loss or gain at the end of the experiment.

Table A3.8 Background and 'toxic' free CN levels 1) in 2nd leaf stage barnyard grass (Echinochloa crus-galli), 4 days treatment. (Source: adapted from Grossmann and Kwiatkowski, 1995. p.154, fig.2.)

Treatment	Free CN mg/kg fresh	Chlorophyll mg/g fresh	Relative growth 2)
Background	0.2 3)	1.0	245 %
10 μM quinclorac	0.4	0.8	155 %
100 μM quinclorac	0.7	0.7	90% (10% decrease in weight)

1) toxic CN levels measured after four days hydroponic exposure of roots to quinclorac; observed chlorophyll and growth reducing effects are ascribed to free CN.

2) relative growth (fresh weight) = shoot weight of 14 days old plants including 4 days exposure / shoot weight of 10 days old plants at start of exposure.

3) relatively high free CN concentration which can be attributed possibly to cyanogenic properties.

Table A3.9 Tissue cyanide content and reduction of shoot weight of Digitaria sanguinalis (2nd leaf stage + 75h. hydroponic treatment). (Source: Grossmann, 1998. p.712, fig. 4.)

Hydroponic treatment[1)]	Digitaria sanguinalis	
	free CN mg/kg f.w.	Shoot weight %
Control	0.11	100
Picloram	0.15	85
Dicamba	0.17	73
MCPA	0.18	68
α-naphtaleneacetic acid	0.19	63
KCN at 21 mg CN/l	0.28	52
Quinmerac	0.34	29
Quinclorac	0.68	11

1) Hydroponic treatments consisted of root-exposure to herbicides at concentrations of 100 µM and KCN at 21 mg CN/l

A3.3 Effects of elevated levels of free cyanide in air

In a refined plant-physiological experiment studying the effects of exogenous HCN on non-cyanogenic plants an air stream containing 180 mg CN/m^3 was passed through illuminated leaves of sunflowers and corn. Within five minutes photosynthesis was completely blocked, leaves yellowed visibly, more than 90% of the chlorophyll was lost. Photosynthesis remained totally impaired after this five minute exposure, whereas respiration and transpiration of the leaves remained unchanged during and after exposure, in this respect destruction of cell metabolism was not complete. The same exposure to CN of non illuminated leaves led to somewhat less damage (Lieberei et al., 1996).

Field information is that HCN is not phytotoxic at concentrations usually evolved from gassing powders (sodium cyanide mixed with kaolin) used for fumigation of greenhouses (Key et al., 1977 and Worthing, 1979, cited by Homan, 1987), while these concentrations increase commonly to 200 mg free CN/m^3 as mentioned in another publication (Ballantyne, 1988). This information is contradictory with the results of the fore mentioned plant-physiological experiment, a possible explanation may be that in greenhouses with gassing powders the stomata of the exposed plants close as the HCN concentration in the air gradually increases. Also no phytotoxic effects are reported of experiments in which plants were exposed at intervals to air with 100 mg free CN/m^3 (Blumenthal et al., 1968).

A3.4 Conclusions

The conclusions of cyanides and plants are presented as part of Chapter 4 and 5 in this report.

APPENDIX 4 Dutch CN Intervention Values as proposed through time

The CN Intervention Values have changed over time. This is due to uncertainties inherent to the two main factors determining the CN Intervention Values:
- the humane toxicity and harmfulness of CN, expressed by the Tolerable Daily Intake (TDI) and the Tolerable Concentration in Air (TCA) of CN, which determination is based on available toxicological information and either or not coupled to uncertainty factors;
- the human exposure to CN from soil contamination, which determination is based on human behaviour and on CN contaminant behaviour in the soil relevant to pathways from soil to men.

The values estimated for the TDI, the TCA and for the exposure of humansto CN from the soil are particular uncertain in case of CN and have been adapted to new insights through time. As a consequence the Intervention Values for CN show clear differences through time (Table A4.1 through Table A4.3). The underlying causes of these differences vary, a common cause is the insufficient knowledge about the sub-lethal effect-concentrations of CN and about the behaviour of CN in the soil.

The insufficient knowledge about the soil-behaviour can be ruled out by basing the Intervention Values directly on CN concentrations in groundwater and in ambient air. The main determinants of the Intervention Values coupled to these parameters are: the human toxicological threshold values TDI and TCA; the consumption by humansof untreated contaminated groundwater; and the inhalation by humansof contaminated ambient air.

A complicating factor is that there is an effect of soil conditions on CN concentrations in groundwater and in ambient air. The CN concentration in groundwater is dependent e.g. on soil temperature and groundwater dilution by fresh supplies (either by uprising or infiltrating water) which fluctuate in time. The emanation of free CN from the soil in ambient air is dependent e.g. of soil temperature and soil humidity, determining chemical/physical parameters, biochemical activity in the soil, weather conditions, etc. Thus these factors should be considered strictly spoken in protocols for determining and interpreting CN concentrations.

Table A4.1 CN Intervention Values proposed through time for the soil.

CN species in soil	VROM, 1989	Berg van den and Roels, 1991	Berg van den, 1995 Current Intervention Values	Köster, 2001 (this report) alternatives
	Intervention Values mg CN/kg soil			
free CN	100	12	20	r.c. [2]
complex CN	500	12	650 when soil pH<5	r.c. or research or 4,800
			50 when soil pH ≥5	
SCN	n.c.c. [1]	2	20	r.c.

[1] n.c.c. = not considered as criterion.

[2] r.c. = rejected as criterion.

Table A4.2 CN Intervention Values proposed through time for groundwater.

CN species dissolved in groundwater	Berg van den and Roels, 1991	Berg van den, 1995 Current Intervention Values	Köster, 2001 (this report) alternatives
	Intervention Values mg CN/l		
free CN	8	1.5	r.c. [2]
complex CN	8	1.5	12 [3]
SCN	1.5	1.5	0.075 [4]
total(EPA) CN	n.c.c. [1]	n.c.c. [1]	0.075 [5] or 1.5

[1] n.c.c. = not considered as criterion.

[2] r.c. = rejected as criterion.

[3] [4] [5] The groundwater Intervention Value can be based on total(EPA) CN solely, or on both complex CN and SCN separately.

Table A4.3 Free CN concentrations in air proposed through time for the Tolerable Concentration in Air and proposed as (soil) Intervention Value.

	mg free CN/m^3 in ambient air	
Tolerable Concentration in Air	0.2 (Vermeire et al., 1991)	0.025 (Meijerink, 1999)
Intervention Value	n.c.c. [1] (Berg van den, 1995)	further research or 0.025 (Köster, 2001, this report)

[1] n.c.c. = not considered as criterion.

APPENDIX 5 Questionnaire and list of experts commenting on 1999 draft report

A draft report (dated 10-12-1999) was sent with a questionnaire to 20 experts in different fields of CN for comment. Comments made have been incorporated in the present report.

QUESTIONNAIRE

List of discussion points, items and questions
(related to draft proposal of new Dutch Soil Intervention Values, as put forward in draft report “Evaluation of Dutch Intervention Values of historical soil contamination with cyanides”.) (The Chapters, Paragraphs and Tables to which is referred below can be found in fore mentioned draft report dated 10-12-1999)

1. Intervention Values in the Netherlands apply to historical soil contamination only, dumping of CN occurred 20 or more years ago (Chp. 1).
The following questions refer to historical CN soil contamination.

2. Maximum contamination levels at present in the Netherlands are listed in Table 6.5.
Question: are the concentrations presented in Table 6.5 indeed the maxima. If not which higher concentrations have been measured recently; preferably with some info on contamination origin and literature reference.

3. I retrieved only a few measurements of free CN in soil air or ambient air at contaminated sites. These indicate maxima both in soil air and in ambient air of 2 mg free CN/m^3 (Par. 3.2.4; Par. 3.3.2).
Question: additional data; preferably with some info on contamination origin and literature reference.

4. I did not retrieve field validated algorithms or models relating:
a) total CN in the soil to CN species concentrations in groundwater (Par. 3.2.2; Par. 3.2.4; Par. 6.5.1); a possible exception is prediction of low concentrations of dissolved complex CN in soils with pH < 4.
b) total CN in the soil to free CN in soil air or in ambient air (Par. 3.2.4);
c) CN species dissolved in groundwater or in pore water (in water unsaturated zone) to free CN in soil air or in ambient air.
Question: can present available soil models contribute to the determination of CN Intervention Values.

5. Maximum free CN levels in plant material from healthy plants are 2 mg CN/kg fresh weight (Par.5.3; Par. 5.2.3).
Question: is this correct for (non-cyanogenic) plants and food.

6. I did not retrieve any field data or laboratory data of increased free CN concentrations in edible plants or food due to CN soil contamination.

Data given in Appendix 4 refer to: grass species grown in the laboratory (Grossman); non-edible plant parts of bean plants grown in the laboratory (Wallace); non-edible plants of the natural vegetation in the field with determination of total CN (Howe).

Question: additional data; preferably with some additional info on contamination origin and literature reference.

7. Question: is the following inferred hypothesis correct: “It is most unlikely that healthy (non-cyanogenic) edible plants or food will contain free CN at concentrations exceeding 2 mg CN/kg fresh”. (Par.5.3; Par. 5.2.3).

8. I did not retrieve any field data of increased concentrations of toxic CN species in edible plants or food due to CN soil contamination.
Question: additional data; preferably with some additional info on contamination origin and literature reference.

9. Human toxicological limits (TDI and TCA) have been determined by CSR of RIVM (Table 6.1; Par. 6.2; App. 3). They are not a topic for discussion of the present query. Though remarks can be made.

10. With respect to an Intervention Value relevant for unsaturated top soil my conclusions are:

a) the only pathway by which the maximum permissible exposure (MPR) i.e. TDI of CN species can be exceeded is: inhalation of free CN in ambient air (Par. 6.5.2; Par. 6.5.4;Par. 6.5.5);
b) the maxima observed at contaminated sites 2 mg free CN/m^3 exceed the TCA of 0.025 free CN/m^3 (Par. 3.2.4; Par. 3.3.2).

As there have been no relationships validated between soil-CN parameters and free CN in ambient air (also not in soil air) I propose as the CN Intervention Value 0.025mg free CN/m^3 in ambient air (Par. 6.5.2; Par. 6.6.1).
Question: are you in support of/neutral to/against this proposal. In case you are opposed to it can you suggest other options.
[**Remark:** I do not make any suggestions on a protocol how to measure free CN in ambient air. There is abundant literature on measurement of gases emanating from the soil and related inhalation-exposure to humans (amongst others radon gas)].

11. With respect to an Intervention Value for groundwater both dissolved ferrohexacyanide and thiocyanate can occur at concentration levels leading to exceedance of the TDI in case of consumption of 2 litre per day of untreated groundwater; the maximum observed levels of free cyanide do not lead to exceedance of the TDI (Par. 6.5.4; Par. 6.5.6).
The dissolved ferrohexacyanide and thiocyanate can be determined together analytically as total CN according to the EPA 335.3 analysis. By coincidence it is possible to base the Intervention Value for groundwater on total CN, without a large range of concentrations in which this criterion is too strict (Par. 6.5.6). The proposed Intervention Value for groundwater is 0.17 mg total CN/l (Par. 6.5.6; Chapter 7).
Remark: this proposed Intervention Value is much stricter than the present Intervention Value which is for all CN species 1.5 mg CN/l (Table 1.1)
Question: are you in support of/neutral to/against this proposal. In case you are opposed to it can you suggest other options.

Question: is further research on CN required before new Intervention Values can be proposed (par. 6.6.2).

12. Some other points and conclusions of no, or only of indirect, relevance to the proposed Intervention Values are the following:

12a) Simple cyanides have never been used as fertilisers and never will be used as such (Par. 4.2).

12b) With respect to CN Intervention Values a differentiation between soils based only on differences in pH can not be supported by present knowledge (Par. 6.5.1).

12c) Effects of CN soil contamination on cyanogenic plants are with respect to human exposure of no importance (Par. 5.1.1). As 'CN-precautions' have to be taken with cyanogenic food or feed increased CN levels by soil contamination do not seem to pose specific risks; no information was retrieved if CN levels will indeed increase by soil contamination.

12d) Natural occurring low concentrations of free CN and possibly other CN species have toxic effects on some species and promoting effects on others (Par. 5.1.4). Natural background concentrations in soils will vary between (micro)spots in the soil and have not been determined. There is no information available to determine or estimate the HC50 concentration of any CN species in soils (Par. 6.6.2; Chapter 5; Appendix 4).

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APPENDIX 6 Programme and list of experts participating in the 28-03-2000 workshop

A draft report (dated 20-03-2000) was discussed in a workshop on 28-03-2000. Comments made during the workshop have been incorporated in the present report.

PROGRAMME CYANIDE MEETING soil and groundwater Intervention Values
RIVM -- Dinsdag 28 maart 2000 -- 09.15 - 12.15

09.15 Koffie

Inleidende presentaties

09.30 Welkom
Annemarie van Wezel, Voorzitter (RIVM/CSR. Bilthoven)
09.35 'n Schets uit de praktijk, 12 gasfabrieklocaties op een rij
Roland Somers (V&S Milieu Adviseurs. Tilburg)
09.55 Wetenschappelijke bepaling CN Interventiewaarden
Heko Köster (RIVM/LBG). CN normen in de tijd; CN voorkomen en gedrag in de bodem; blootstelling van de mens; voorstel Interventiewaarden bodem en grondwater; kennisleemten.
10.25 Koffie
10.40 Toxicologische grenswaarden CN
Bert-Jan Baars (RIVM/CSR). Humaan toxicologisch
Eric Verbruggen. (RIVM/CSR). Ecotoxicologisch
11.00 Effecten van de voorgestelde normen voor de praktijk
Peter de Vries (The Three Engineers. Deventer)
Plenaire discussie
11.20 Voorkomen/afbraak CN in bodem en grondwater (aëroob, anaëroob) en lucht
11.30 Is de wetenschappelijke onderbouwing van de Interventiewaarden (Köster, 2000) juist en compleet
11.40 Beoordeling CN bodemverontreiniging aan HCN in omgevingslucht (bron: emanatie uit de bodem), bodemlucht of aan CN in de bodem en/of grondwater
11.55 Zijn de huidige en/of de nieuw voorgestelde CN normen voor grondwater te scherp/te soepel; totaal CN, of complex CN en SCN afzonderlijk
12.10 Wijzigen Interventiewaarden nu, of later na verder CN onderzoek, of niet
12.20 Afsluiting

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