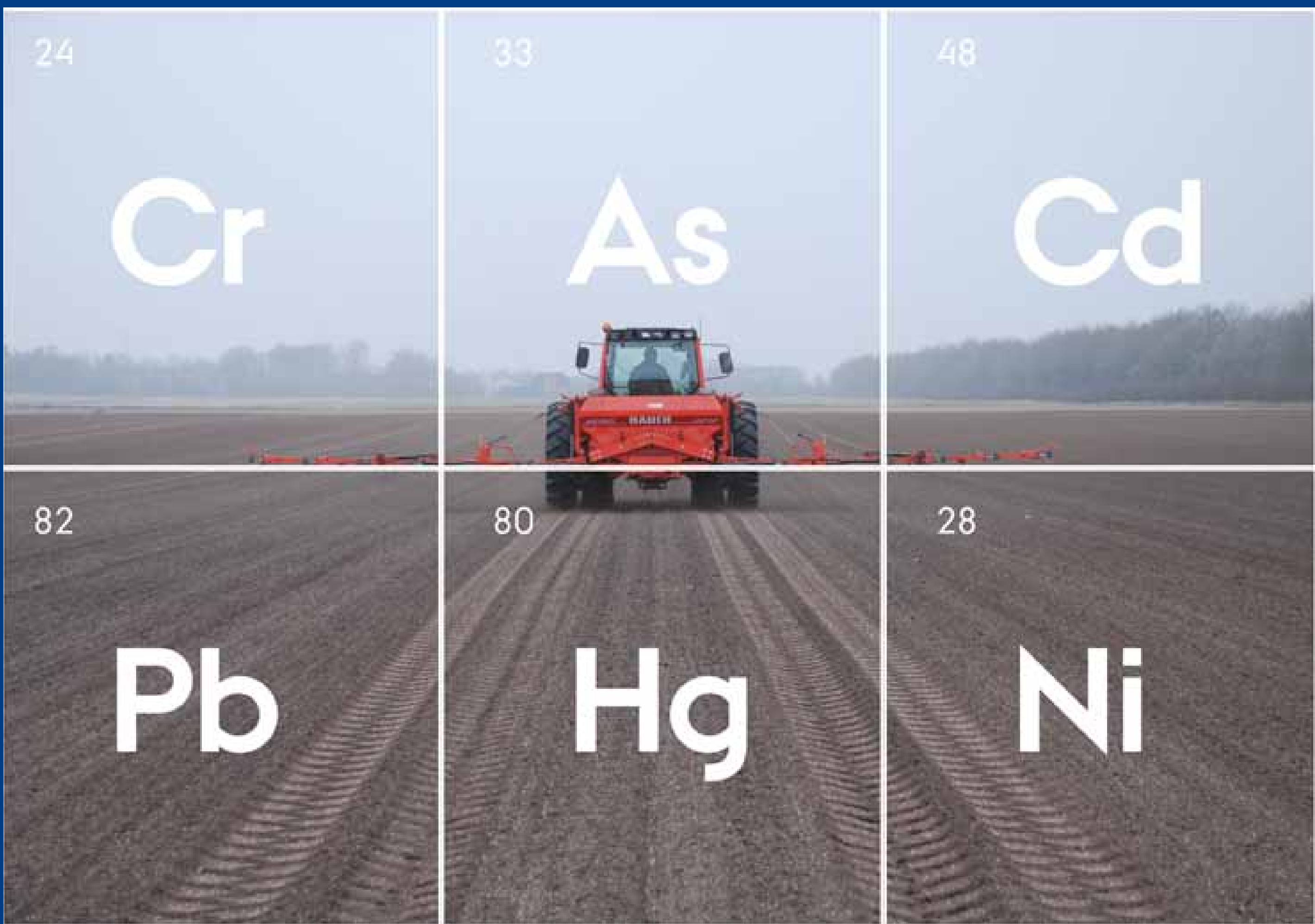
ECOTOXICOLOGICAL EVALUATION OF As, Cd, Cr, Pb, Hg AND Ni APPLIED WITH FERTILISERS IN DENMARK

INTERNAL REPORT NR. 111 · OCTOBER 2011

PETER SØRENSEN, JOHN JENSEN, JANECK SCOTT-FORDSMAND & BENT TOLSTRUP CHRISTENSEN

AARHUS UNIVERSITY



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Peter Sørensen [1), John Jensen [2), Janeck Scott-Fordsmand [2) & Bent Tolstrup Christensen [1)

[1) Department of Agroecology
Aarhus University
P.O. Box 50
8830 Tjele

[2) Department of Bioscience
Aarhus University
Vejlesøvej 25
P.O. Box 314
8600 Silkeborg

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Frontpage Photo: Henning C. Thomsen

The reports can be downloaded at www.agrsci.au.dk

Print: www.digisource.dk
ISBN 978-87-91949-93-7

Content

Preface

Mineral fertilisers contain a range of impurities that may be harmful to the environment if loads are too high. In EU it has been suggested to regulate the content of arsenic (As), cadmium (Cd), chromium (VI) (CrVI), mercury (Hg), nickel (Ni) and lead (Pb) in mineral fertilisers by setting cut-off values for these six metals. The content of environmentally harmful impurities in mineral fertilisers marketed in Denmark during 2006-2008 was reported by Petersen et al (2009). Subsequently, the Danish Plant Directorate commissioned an ecotoxicological evaluation of the six metals, As, Cd, Cr, Hg, Ni and Pb when applied to agricultural soils.

This report presents the results of the ecotoxicological evaluation and is filed as a deliverable to the Danish Plant Directorate under the ”Contract between Aarhus University and the Ministry of Food, Agriculture and Fisheries on the provision of research-based public-sector services, etc., at the Faculty of Agricultural Sciences for the period 2010 to 2013”.

Peter Sørensen has provided the scenarios for manure and fertiliser application at different Danish farm types and calculated the metal application with manures and fertilisers (Chapter 2). John Jensen and Janeck Scott-Fordsmand have provided the ecotoxicological evaluations of each of the six metals (Chapters 1 and 3 to 8). Chapter 9 gives a short ecotoxicological evaluation of other selected metals and PAH in mineral fertilisers, addressed in Petersen et al (2009).

Bent T. Christensen
October 2011

Abbreviations

BAF- Biological accumulation factor, i.e. the ratio between the concentration in biota and soil.
EC_{10} / EC_{50} – The Effective Concentration causing 10% or 50% reduction in the test endpoint, e.g. reproduction or growth.
HC_5 – The Hazardous Concentration for 5% of all species estimated by the use of Species Sensitivity Distributions (SSD). A theoretical value used as substitution for a no effect level for all species in an ecosystem.
LOEC- Lowest observed effect concentration, equals the lowest test concentration that differs statistically from the control.
MPA- Maximum permissible addition.
NOEC- No observed effect concentration, equals the highest test concentration that does not statistically differ from the control.
PEC- Predicted environmental concentration.
PNEC- Predicted no effect concentration. The PNEC is derived on the basis of the HC_5 or by applying an assessment/uncertainty factor to the lowest available NOEC or LC50 value. The size of the assessment factor depends on how many trophic levels that are covered by ecotoxicity studies.
SSD - Species Sensitivity Distributions. A statistical tool applied in ecological risk assessment.

Summary

Mineral fertilisers contain impurities of a range of metals, which have toxic effects on living organisms if concentrations are too high, and therefore applications to agricultural land should be regulated. New cut-off values for fertiliser concentrations of arsenic (As), cadmium (Cd), chromium (VI) (CrVI), mercury (Hg), nickel (Ni) and lead (Pb) have been proposed in EU. In this report typical agricultural applications of the six metals with fertilisers and animal manures are estimated under Danish conditions and metal application rates are estimated if fertilisers contain the proposed maximum concentrations. Ecotoxicological studies of the six metals are reviewed and metal concentrations in soil where no toxic effects on microbial processes, plants and invertebrates can be expected are assessed. Based on this, short- and long-term effects of fertilisers are evaluated.

It is concluded that there is no indication of short-term risk after one application of the six metals if the proposed cut-off values for fertilisers are used. If fertilisers contain the suggested cut-off concentration the annual load of the six metals via fertilisers and atmospheric deposition corresponds to less than 0.2 to 1.9% of the average background concentration in Danish agricultural soils.

An assessment of long term effects of the metal applications is based on previously established critical loads for the metals. A comparison with critical loads established for agricultural soils in the Netherlands and Denmark indicates that no long-term risk of As and Cd accumulation is anticipated when using the suggested cut-off values for fertilisers. However, a comparison with critical loads established for agricultural soils in the Netherlands indicates that long-term risks of total Cr, Ni and Pb accumulation cannot be ruled out in some of the most sensitive agricultural soils when using the new cut-off value for fertilisers. As the suggested regulation is only on Cr (VI) it is impossible to assess the effects on total Cr accumulation. For Hg a comparison with critical loads established for agricultural soils has not been possible as no suitable critical load for Hg has been identified.

It is noted that the maximal annual load of the six metals via fertilisers is lower than the anticipated annual load via maximal sewage sludge application in Denmark.

The suggested EU cut off values are not expected to cause serious environmental problems, but based on the information presented in this report it is recommended to reconsider the limits for Cr, Ni and Pb in mineral fertilisers.

In order to improve the assessment of the long-term risks of the metals it is recommended to develop and use more advanced steady-state models suited to fit Danish conditions in the future.

Dansk sammendrag

Økotoksikologisk vurdering af tilførslen af metallerne As, Cd, Cr, Pb, Hg and Ni med handelsgødning i Danmark

Handelsgødning indeholder metaller, der i høje koncentrationer kan være giftige for levende organismer. EU har på denne baggrund foreslået grænseværdier for indholdet af arsen (As), cadmium (Cd), chrom (VI) (CrVI), kviksølv (Hg), nikkel (Ni) and bly (Pb) i handelsgødning.

Med baggrund i EUs forslag til grænseværdier for metaller i handelsgødning er der gennemført en vurdering af, hvorvidt de tilførte metaller ved indførslen af disse grænseværdier vil kunne medføre en kortsigtet såvel som langsigtet risiko for jordbundsorganismer (mikroorganismer, fauna) og planter.

Der er opstillet otte typiske scenarier for anvendelse af handelsgødning og organisk gødning på danske landbrugsbedrifter. Beregnet tilførsel af metaller i de udvalgte scenarier er baseret på det gennemsnitlige indhold af tungmetaller i den organiske gødning samt et indhold af metaller i handelsgødning, som svarer til det maksimalt tilladte iflg. EU forslaget til grænseværdier. På denne baggrund er det beregnet, hvor høj metal koncentrationen vil være i jorden umiddelbart efter tilførslen af gødning. Denne koncentration er så sammenholdt med de koncentrationer i jorden, som bl.a. EU har vurderet er acceptable, såfremt uønskede effekter skal undgås. Ud fra en sådan simpel risikovurdering vurderes det ikke, at de enkelte metaller i en enkelt tilførsel af handelsgødning udgør en kortsigtet risiko for jordbundsorganismer og derved jordkvaliteten.

For at kunne vurdere, hvorvidt gentagne og årlige tilførsler udgør en langsigtet risiko, bør der optimalt set ske en sammenligning mellem de acceptable niveauer i jorden og den forventede langsigtede koncentration i jorden. Denne kan beregnes med dynamiske modeller, der også inddrager tab og bortførsel af metaller over tid. Sådanne modeller er under udvikling i en række lande, bl.a. Holland, men er ikke tilgængelige for danske forhold.

I stedet er det i denne rapport valgt at sammenholde det beregnede input af metaller fra gødning med etablerede såkaldte C*ritical Loads*. Critical Loads (CL) er den årlige deposition af metaller, som et økosystem kan tolerere på lang sigt, såfremt det er i ligevægt (hvilket mange økosystemer ikke er). Critical Loads har i mange år været et anerkendt redskab til at vurdere konsekvenserne af atmosfærisk deposition af metaller og især kvælstof og forsurende stoffer som svovl. Der findes ikke opdaterede CL for Danmark.

De Hollandske CL er derfor brugt i denne rapport, selv om det er anerkendt, at CL er økosystem- og jordtype afhængigt.

En sammenligning med de Hollandske CL viser, at for Pb, Ni og Cr vil den mulige tilførsel via gødning overstige de beregnede CL værdier, mens det for As og Cd ligger under de estimerede CL værdier for landbrugsjord. Der foreligger ikke CL værdier for Hg, og en vurdering af langtidseffekten har ikke været mulig.

En sammenligning af tilførslen af metaller med handelsgødning/husdyrgødning med den beregnede maksimale tilladte tilførsel af metaller via spildevandsslam i DK viser størst tilførsel med spildevandsslam.

På baggrund af ovenstående vurderes forslaget til nye grænseværdier for metaller i handelsgødning ikke at medføre et markant miljøproblem. Det bør dog overvejes om grænseværdierne for Ni, Cr og Pb kan reduceres.

Nyudvikling og anvendelse af dynamiske modeller til beregning af den langsigtede acceptable tilførsel af metaller under danske forhold vil kunne forbedre beslutningsgrundlaget.

1 Introduction

Mineral fertilisers contain impurities of a range of metals. The level of heavy metals depends on the geographical and geological origin of the fertiliser. All metals have toxic effects on living organisms if concentrations are too high. Furthermore, leaching and/or crop uptake may expose organisms outside the arable land itself. Applications to agricultural land via various sources like atmospheric deposition, organic fertilisers like sewage sludge and manure and mineral fertilisers should be minimised wherever possible. Cut-off values for concentrations of arsenic (As), cadmium (Cd), chromium (VI) (CrVI), mercury (Hg), nickel (Ni) and lead (Pb) in mineral fertilisers have therefore been proposed in EU (EU, 2009). In the present report the potential ecotoxicological impact of the new cut-off values have been evaluated under Danish conditions both in relation to short-term and long-term effects.

1.1 Ecotoxicological evaluation

In chapter 3-8, a short presentation of the ecotoxicological properties and observed effects to soil dwelling organisms are presented in order to evaluate the potential short- and long-term risk caused by metals in mineral fertilisers. Numerous ecotoxicological studies on metals have appeared during the last three or four decades. It is beyond the scope of this report to review all of these, so when available the ecotoxicity of the various heavy metals have been characterized by a reference to the official Risk Assessment Reports (RAR) produced by the European Commission under the framework of the REACH program for new and existing chemicals. Although some of these are not fully up to date, as they were released years ago, they all represent well-documented effect assessments covering the majority of relevant data at the time of release. The various EU-RAR have all established the so-called “PNEC values” (Predicted No effect Concentration), which is considered as soil concentrations that are protective for soil ecosystems and the species living herein. The PNEC are derived by either a simple application of an assessment or uncertainty factor to the lowest observed NOEC or EC10 value. The magnitude of the assessment factor depends on the quantity of data and the number of trophic levels covered by the collected ecotoxicity data (see Table 1.1.).

However, rather than making a PNEC assessment based on one single NOEC value, it is possible to use a statistical extrapolation method based on the species sensitivity distribution (SSD, Posthuma et al 2001). If the sensitivity distribution is proven for example log-normal, then it can be used to interpolate a theoretical soil concentration where 95% of all species within an ecosystem is un-affected by the chemical, or in other words where the soil concentration is hazardous for maximum of 5% of all species. This concentration is named the HC_5. Depending on the data an uncertainty factor between 1-5 is applied to the HC_5 in order to derive the PNEC (Table 1.1.). Alternatively national eco-toxicological based soil quality criteria or objectives can be used instead of the PNEC values established in the EU risk assessment reports.

Table 1.1. The assessment factors outlined for the terrestrial compartment as defined in the Technical Guidance Document for supporting the risk assessment of new and existing chemicals within the REACH programme in the EU (EU 1996).

Table R.10-10 Assessment factors for derivation of $PNEC_{soil}$

Information available	Assessment factor
L(E)C50 short-term toxicity test(s) (e.g. plants, earthworms, or microorganisms)	1000
NOEC for one long-term toxicity test (e.g. plants)	100
NOEC for additional long-term toxicity tests of two trophic levels	50
NOEC for additional long-term toxicity tests for three species of three trophic levels	10
Species sensitivity distribution (SSD method)	5 – 1, to be fully justified on a case-by-case basis (cf. main text)
Field data/data of model ecosystems	case-by-case

In combination with the predicted soil concentration, the PNEC value can be used to predict the short-term risk of metals to soil dwelling organisms and soil quality in general. The PNEC values are compared to the theoretical soil concentration after one application with mineral fertilisers assuming that the total load is homogenously mixed into the upper 20 cm of a top soil with a soil density of 1.5 kg/L. The background concentrations are neglected in this crude short-term risk evaluation, partly because it is anticipated that it is mainly the newly added metal that is available for soil organisms and partly because the ecotoxicological data often is expressed on the basis of the nominal soil concentration after spiking, i.e. also here neglecting the natural metal background concentration of the test soil.

In relation to protecting and maintaining the function of soils, the terrestrial toxicity studies have focused on three groups: microorganism (species/processes), plants (species) and invertebrates (species). For these species groups the information on effect and no-effect data were extracted and evaluated before use.

1.2 Potential long-term risk of metal applications

Long-term accumulation for contaminants in soils is an important issue especially for metals as these are not biodegradable. The long-term accumulation depends on the starting point, i.e. the current heavy metal concentrations, as well as the fluxes of metal from various sources in and out of the soil. Sources of input of metals to agricultural soils are dominantly fertilisers, animal manures and atmospheric deposition. The outflux of metals is primarily controlled by uptake in crops and subsequently removal via harvest and leaching/runoff via water flow. Thus, a long-term risk assessment should in principle be performed via advanced and dynamic models and/or by critical load models (that usually contain simple steady-state modelling).

In this report a provisional assessment of the long-term risk following repeated application of fertilisers have been made by comparing the estimated annual load from mineral fertilisers and atmospheric deposition with established critical loads of the metal in question. “The critical load of a metal can be calculated from the sum of tolerable outputs from the considered system in terms of net metal uptake and metal leaching. The critical load equals the net uptake by forest growth or agricultural products plus an acceptable metal leaching rate” (Reinds et al 2006)

Within the present context it has not been possible to develop or make references to advanced steady state models adjusted to Danish conditions as there generally was a lack of accessible and validated data. The data needed are crop uptake and removal rates, leaching and runoff values related to soil concentration, soil parameters (e.g. pH) and crop species. Such advanced models are currently being developed for some of the relevant metals in for example the Netherlands. Instead of these advanced steady state models, more simple critical load models have been used in this report to get an indication of the potential risk. Critical load models have generally large uncertainties as they, in line with other generic models, typically cover many different soil types and crops. Critical Loads for Denmark have been published for cadmium, mercury and lead back in 1998 (Bak and Jensen 1998). However, as these were based on preliminary guidelines and a first provisional attempt more emphasis have been laid in this report on the more recent set of critical loads developed in for example the Netherlands (Reinds et al 2006, Posch and de Vries 2009). Although the critical limit, i.e. the predicted no effect concentration (PNEC), may be different from the ones relevant for Denmark and the soil types are different compared to the Danish situation, they are nevertheless considered useful for a provisional and indicative assessment of the potential long-term risk of metals in mineral fertilisers.

Finally it should be emphasised that the provisional evaluation of potential risk of heavy metals in mineral fertilisers presented in this report does not include an assessment of the potential risk of long-term bioaccumulation in terrestrial food webs and does not consider the influence of soil types and ageing (sorption) upon the fate and toxicity of metals in soils as it would need a far more detailed assessment.

2 Application rates of As, Cd, Cr, Pb, Hg and Ni with mineral fertilisers and manures on Danish farm types

2.1 Introduction

Metals are applied to agricultural soils both in organic wastes and manures and in mineral fertilisers. The metal content of mineral fertilisers is significantly influenced by the fertiliser type. Similarly, the metal content of animal manure may vary with the livestock type and feeding practice. In the following the annual load of the metals As, Cd, Cr, Pb, Hg and Ni with mineral fertiliser and animal manure have been estimated for a number of Danish farm types. In Table 2.1 the selected farm typologies used in the inventory are listed. These were selected to represent farm types without animal production (both located on loamy soils) as well as farms with pig, cattle and poultry production. The expected fertiliser type used on these farms is indicated together with the mean concentrations of metals in the used fertilisers. The metal concentrations in fertilisers are based on the mean values measured in a survey of fertilisers used in Denmark reported by Petersen et al. (2009). As there is no specific information available of the fertiliser types used on different farm types, it is assumed that NS fertilisers are used on farms with animal production, NPK fertilisers are used on stockless farms, whereas NP based fertilisers are used as starter fertilisers for maize crops on cattle farms.

On average the farm type “cereal production on loamy soil” imports 49 kg N/ha in manure. However, part of these farms have no manure application at all and only apply mineral fertilisers, and a separate calculation for such farms is made as a reference. Farms without manure application do not necessarily apply P or NPK fertilisers every year, but in the long-term application of P equivalent to the export of P in crops is to be expected. A comparison of the measured mean concentration with the proposed EU maximum concentrations shows that for all other metals than cadmium, the concentration in the mineral fertilisers used in Denmark is generally well below the proposed EU cut-off value. For cadmium, all P-containing fertilisers have difficulties in fulfilling the maximum criteria as the mean concentration exceeds the proposed cut-off value by 46-86%.

Table 2.1. Mineral fertiliser types expected to be used on selected farm types, and their average content of As, Cd, Cr, Pb, Hg and Ni as reported by Petersen et al. (2009).

Farm type	Total area Ha	Fertiliser type	As	Cd	Cr**	Pb	Hg	Ni
					mg/kg			
Proposed EU cut-off values			60	3	2	150	2	120
Cereal production on loamy soil	180000	NPK	3.9	4.4	114	2.7	0.076	84
Cereal production without manure	*)	NPK	3.9	4.4	114	2.7	0.076	84
Pigs on loamy soil <1,4 LU/ha***	114000	NS	0	0.2	4.6	0.37	0.021	4
Pigs on sandy soil<1,4 LU/ha	156000	NS	0	0.2	4.6	0.37	0.021	4
Cattle on loamy soil, 1,4-2,3 LU/ha	37000	NP +NS	8.1	5.6	57	6.5	0.070	13
Cattle on sandy soil, 1,4-2,3 LU/ha	187000	NP +NS	8.1	5.6	57	6.5	0.070	13
Broiler (chicken)	12000	NS	0	0.2	4.6	0.37	0.021	4
Egg production	3600	NS	0	0.2	4.6	0.37	0.021	4

* No information available
** All data are for total Cr except the proposed cut-off value which is for Cr(VI).
*** LU = livestock units

For calculation of the typical current metal application with manures, the average concentration of metals in dry matter of different animal manure types are assessed (Table 2.2). Data is based on literature values collected by Petersen et al. (2009). These values are used in the following calculations. The composition of manure used on “cereal production farms” is assumed to be an average of pig and cattle manures.

Table 2.2. Average concentration of As, Cd, Cr, Pb, Hg and Ni in animal manure dry matter on different farm types assessed on basis of literature values collected by Petersen et al. (2009).

	As	Cd	Cr	Pb	Hg	Ni
			mg/kg DM			
Cereal production on loamy soil	1	0.35	7.3	3.9	0.3	11
Pigs on loamy soil <1,4 LU/ha	1	0.4	9.6	3.7	0.3	14
Pigs on sandy soil<1,4 LU/ha	1	0.4	9.6	3.7	0.3	14
Cattle on loamy soil, 1,4-2,3 LU/ha	1	0.3	5.0	4.1	0.3	7
Cattle on sandy soil, 1,4-2,3 LU/ha	1	0.3	5.0	4.1	0.3	7
Broiler (chicken)	4.5	0.5	8.8	3.7	0.3	8
Egg production	4.5	0.5	8.8	3.7	0.3	8

The application rate of manure on each farm type is based on nitrogen application rates reported in yearly farmer reports for 2002 (Kristensen, 2005). The metal application with animal manure is calculated from standard values for nitrogen, dry matter content and metal concentrations in dry matter from Table 2.2.

The metal content of fertilisers measured by Petersen et al. (2009) was not related to the nutrient content, but only to fertiliser types. The nutrient content of the different fertiliser types is variable. Therefore the fertiliser application rate is calculated from average N application rates on the farm types assuming average concentrations of 25% N in NS fertilisers, 20% N in NPK fertilisers and 18% N in NP fertilisers.

On cattle farms it is assumed that all maize crops (15% of area on loamy soils and 17% of area on sandy soils) receive NP starter fertilisers (18% P in fertiliser) at a rate of 15 kg P/ha, which is about the recommended rate (Knudsen, 2010).

2.2 Arsenic (As)

The annual application of As at the farm types is calculated to be 1.4 to 9.4 g/ha (Table 2.3.). The highest application is on farms with poultry production. Reported concentrations of As in poultry manure are very variable, and there may be significant differences between the content in manure from broilers and lay hens as a result of the differences in feed additives. However, no data was available to make such a distinction between poultry manure types. Arsenic in NS fertilisers is set to be zero as As was found to be below the detection limit in 38 out of 39 fertiliser samples (Petersen et al. 2009). The lowest application is calculated on pig farms, as no P or NPK fertilisers are expected to be used here.

Table 2.3. Annual application rates of Arsenic (As) to soil on Danish farm types based on farm fertiliser reports from 2002 (Kristensen, 2005) and average measured concentrations in Danish mineral fertilisers (Petersen et al 2009).

Farm type	Animal manure					Mineral fertiliser				Total	From mineral fertiliser
	kg N/ha	kg N/ton	% DM	As mg/kg DM	As g/ha	kg N/ha	% N	As mg/kg	As g/ha	As g/ha	%
Cereal production on loamy soil	49	5.6	6.5	1	0.6	112	20	3.9	2.18	2.8	79
Cereal production without manure	0					149	20	3.9	2.91	2.9	100
Pigs on loamy soil <1,4 LU/ha	119	5.6	6.5	1	1.4	82	25	0	0	1.4	0
Pigs on sandy soil<1,4 LU/ha	118	5.6	6.5	1	1.4	68	25	0	0	1.4	0
Cattle on loamy soil, 1,4-2,3 LU/ha	154	5.3	9.1	1	2.6	67	25	8.1	0.23	2.9	8
Cattle on sandy soil, 1,4-2,3 LU/ha	168	5.3	9.1	1	2.9	76	25	8.1	0.26	3.1	8
Broiler (chicken)	97	26.9	57.8	4.5	9.4	89	25	0	0	9.4	0
Egg production	104	7.3	11.1	4.5	7.1	80	25	0	0	7.1	0

LU: livestock units.

2.3 Cadmium (Cd)

The application of Cd varies from 0.6 to 3.3 g/ha (Table 2.4). The highest application occurs on farms without animal manure application where significant applications of NPK fertilisers are expected. Cd application is mainly influenced by the amount of P or NPK fertiliser applied.

Table 2.4. Annual application rates of cadmium (Cd) to soil on Danish farm types based on farm fertiliser reports from 2002 (Kristensen, 2005) and average measured concentrations in Danish mineral fertilisers (Petersen et al 2009).

Farm type	Animal manure					Mineral fertiliser				Total	From mineral fertiliser
	kg N/ha	Kg N/ton	% DM	Cd mg/kg DM	Cd g/ha	kg N/ha	%N	Cd mg/kg	Cd g/ha	Cd g/ha	%
Cereal production on loamy soil	49	5.6	6.5	0.35	0.2	112	20	4.4	2.5	2.7	93
Cereal production without manure	0					149	20	4.4	3.3	3.3	100
Pigs on loamy soil <1,4 LU/ha	119	5.6	6.5	0.4	0.6	82	25	0.2	0.066	0.6	11
Pigs on sandy soil<1,4 LU/ha	118	5.6	6.5	0.4	0.5	68	25	0.2	0.054	0.6	9
Cattle on loamy soil, 1,4-2,3 LU/ha	154	5.3	9.1	0.3	0.8	67	25	5.6	0.16	1.0	17
Cattle on sandy soil, 1,4-2,3 LU/ha	168	5.3	9.1	0.3	0.9	76	25	5.6	0.18	1.0	17
Broiler (chicken)	97	26.9	57.8	0.5	1.0	89	25	0.2	0.071	1.1	6
Egg production	104	7.3	11.1	0.5	0.8	80	25	0.2	0.064	0.9	7

2.4 Chromium (Cr)

The application of total Cr varies from 15 to 85 g/ha (Table 2.5). Like for Cd the highest application rate is related to the application of fertilisers containing P, and the highest application normally takes place on farms without manure application.

Table 2.5. Annual application rates of chromium (Cr) to soil on Danish farm types based on farm fertiliser reports from 2002 (Kristensen, 2005) and average measured concentrations in Danish mineral fertilisers (Petersen et al 2009).

Farm type	Animal manure					Mineral fertiliser				Total	From mineral fertiliser
	kg N/ha	kg N/ton	% DM	Cr mg/kg DM	Cr g/ha	kg N/ha	%N	Cr mg/kg	Cr g/ha	Cr g/ha	%
Cereal production on loamy soil	49	5.6	6.5	7.3	4	112	20	114	63.8	68	94
Cereal production without manure	0					149	20	114	84.9	85	100
Pigs on loamy soil <1,4 LU/ha	119	5.6	6.5	9.6	13	82	20	4.6	1.9	15	12
Pigs on sandy soil<1,4 LU/ha	118	5.6	6.5	9.6	13	68	20	4.6	1.6	15	11
Cattle on loamy soil, 1,4-2,3 LU/ha	154	5.3	9.1	5	13	67	20	57	1.6	15	11
Cattle on sandy soil, 1,4-2,3 LU/ha	168	5.3	9.1	5	14	76	20	57	1.8	16	11
Broiler (chicken)	97	26.9	57.8	8.8	18	89	20	4.6	2.0	20	10
Egg production	104	7.3	11.1	8.8	14	80	20	4.6	1.8	16	12

2.5 Lead (Pb)

The application of lead varies from 2 to 12 g Pb/ha (Table 2.6). The load of Pb is mainly related to animal manure, and the application rate is hence highest on farms with animal manure, especially on cattle farms.

Table 2.6. Annual application rates of lead (Pb) to soil on Danish farm types based on farm fertiliser reports from 2002 (Kristensen, 2005) and average measured concentrations in Danish mineral fertilisers (Petersen et al 2009).

Farm type	Animal manure					Mineral fertiliser				Total	From mineral fertiliser
	kg N/ha	kg N/ton	% DM	Pb mg/kg DM	Pb g/ha	kg N/ha	%N	Pb mg/kg	Pb g/ha	Pb g/ha	%
Cereal production on loamy soil	49	5.6	6.5	3.9	2.2	112	20	2.7	1.51	3.7	41
Cereal production without manure	0					149	20	2.7	2.01	2.0	100
Pigs on loamy soil <1,4 LU/ha	119	5.6	6.5	3.7	5.1	82	20	0.37	0.15	5.3	3
Pigs on sandy soil<1,4 LU/ha	118	5.6	6.5	3.7	5.1	68	20	0.37	0.13	5.2	2
Cattle on loamy soil, 1,4-2,3 LU/ha	154	5.3	9.1	4.1	10.8	67	20	6.5	0.18	11.0	2
Cattle on sandy soil, 1,4-2,3 LU/ha	168	5.3	9.1	4.1	11.8	76	20	6.5	0.21	12.0	2
Broiler (chicken)	97	26.9	57.8	3.7	7.7	89	20	0.37	0.16	7.9	2
Egg production	104	7.3	11.1	3.7	5.9	80	20	0.37	0.15	6.0	2

2.6 Mercury (Hg)

The application of mercury varies from 0.1 to 0.87 g /ha (Table 2. 7). Like for Pb the load is mainly influenced by animal manure application.

Table 2.7. Annual application rates of mercury (Hg) to soil on Danish farm types based on farm fertiliser reports from 2002 (Kristensen, 2005) and average measured concentrations in Danish mineral fertilisers (Petersen et al 2009).

Farm type	Animal manure					Mineral fertiliser				Total	From mineral fertiliser
	kg N/ha	kg N/ton	% DM	Hg mg/kg DM	Hg g/ha	kg N/ha	%N	Hg mg/kg	Hg g/ha	Hg g/ha	%
Cereal production on loamy soil	49	5.6	6.5	0.3	0.17	112	20	0.076	0.0426	0.21	20
Cereal production without manure	0					149	20	0.076	0.0566	0.1	100
Pigs on loamy soil <1,4 LU/ha	119	5.6	6.5	0.3	0.41	82	20	0.021	0.0086	0.42	2
Pigs on sandy soil<1,4 LU/ha	118	5.6	6.5	0.3	0.41	68	20	0.021	0.0071	0.42	2
Cattle on loamy soil, 1,4-2,3 LU/ha	154	5.3	9.1	0.3	0.79	67	20	0.07	0.0020	0.80	0
Cattle on sandy soil, 1,4-2,3 LU/ha	168	5.3	9.1	0.3	0.87	76	20	0.07	0.0022	0.87	0
Broiler (chicken)	97	26.9	57.8	0.3	0.63	89	20	0.02	0.0089	0.63	1
Egg production	104	7.3	11.1	0.3	0.47	80	20	0.021	0.0084	0.48	2

2.7 Nickel (Ni)

The application rate of nickel varies from 14 to 63 g Ni /ha (Table 2.8). The application rate is highest where P-containing fertilisers are used and therefore highest on farms where no animal manure is used.

Table 2.8. Annual application rates of nickel (Ni) to soil on Danish farm types based on farm fertiliser reports from 2002 (Kristensen, 2005) and average measured concentrations in Danish mineral fertilisers (Petersen et al 2009) .

Farm type	Animal manure					Mineral fertiliser				Total	From mineral fertiliser
	kg N/ha	kg N/ton	% DM	Ni mg/kg DM	Ni g/ha	kg N/ha	%N	Ni mg/kg	Ni g/ha	Ni g/ha	%
Cereal production on loamy soil	49	5.6	6.5	11	6	112	20	84	47	53	88
Cereal production without manure	0					149	20	84	63	63	100
Pigs on loamy soil <1,4 LU/ha	119	5.6	6.5	14	19	82	20	4	2	21	8
Pigs on sandy soil<1,4 LU/ha	118	5.6	6.5	14	19	68	20	4	1	21	7
Cattle on loamy soil, 1,4-2,3 LU/ha	154	5.3	9.1	7	19	67	20	13	0	19	2
Cattle on sandy soil, 1,4-2,3 LU/ha	168	5.3	9.1	7	20	76	20	13	0	21	2
Broiler (chicken)	97	26.9	57.8	8	17	89	20	4	2	18	10
Egg production	104	7.3	11.1	8	13	80	20	4	2	14	11

2.8 The EU proposal for cut-off values in mineral fertilisers

The estimation of the heavy metal load on Danish agricultural farm land presented above in Table 2.3-2.8 is based on typical use of fertilisers containing the average level of metals in the manure as well as the mineral fertilisers. In order to evaluate the potential risk from using mineral fertiliser with the maximum content of metals according to the EU proposal on cut-off values, the same calculations are made with the same assumptions except that the average concentrations of metals in Danish mineral fertilisers are replaced by the proposed EU cut-off values (Table 2.9). This will typically increase predicted maximum load in the various scenarios depending on the relative use of mineral vs. organic fertilisers. The estimated maximum loads are used for further assessment in the risk assessment chapters for the various metals (Chapter 3-8).

In Table 2.9 metal applications by sewage sludge application are also estimated. The sludge application rate is based on a maximal allowable yearly dry matter application in Denmark of 10 t/ha/year. There are also restrictions in the sludge regulation of a maximum load of 30 kg P /ha/year. With a median P content in Danish sludge around 30 kg/ton this criteria will normally markedly reduce the application of sludge below the maximum. The need for P application will normally be covered by the sludge on farms where sludge is applied regularly.

Table 2.9. Total application rates (g/ha/year) of six metals from fertilisers to selected Danish farm types. Input of metal via manure is based on data from Table 2.2-2.8, i.e. mean estimated concentrations in Danish manure, whereas the input of metals via mineral fertilisers are based on a maximum content corresponding to the EU proposal for cut-off values (except for Cr**). For comparison the annual load via atmospheric deposition and sewage sludge are listed.

Scenarios	**As**	**Cd**	**Cr(tot)**	**Hg**	**Ni**	**Pb**
Cut-off values in fertilisers (mg/kg)	60	3	--**	2	120	150
Atmospheric depositions[1]	0.9	0.3	1.5*	--	2.9	8.5
Deposition via sludge[2]	70	6.3	133*	7.7	147	245
Cereal production on loamy soil	34.2	1.9	68.0	1.3	73.5	86.2
Cereal production on loamy soil without animal manure	**44.7**	2.2	**84.9**	1.5	**89.4**	**112**
Pigs on loamy soil <1,4 LU/ha	26.0	1.8	15.2	1.2	68.5	66.6
Pigs on sandy soil<1,4 LU/ha	21.8	1.6	14.7	1.1	60.0	56.1
Cattle on loamy soil, 1,4-2,3 LU/ha	22.9	1.8	32.5	1.5	59.0	61.5
Cattle on sandy soil, 1,4-2,3 LU/ha	25.9	2.0	36.3	**1.6**	66.1	69.3
Broiler (chicken)	36.1	**2.4**	20.4	1.5	70.1	74.5
Egg production	31.1	2.0	15.8	1.3	60.7	65.9

[1] Atmospheric deposition 2008 (Ellermann et al., 2010

[2]. The load is based upon a worst case scenario of an annual soil amendment with 7 tons of sewage sludge (dry weight) containing the median level of metals monitored in Danish sludge in the year 2005 (Miljøstyrelsen 2009)

* Deposition of total chromium

** Not relevant in this context as the EU cut-off value is for Cr (VI) and all other available data (manure and sludge concentrations and atmospheric deposition rate) are based on total chromium concentration. All the presented application rates for chromium is hence based on the use of average concentration in manure and mineral fertilisers as opposed to the other metals where the worst case situation, i.e. the cut-off value, for the mineral fertilisers is used.

The worst case application rates presented (in bold) in Table 2.9 can be used to calculate a generic concentration in soils after a single application event. Here it is assumed that the total load from fertilisers is homogenously mixed in the upper 20 cm of the top soil with a density of 1.5 kg/L. This predicted soil concentration is listed in Table 2.10 together with median soil concentrations reported for agricultural sites in Denmark (n=311) or separated into sandy soils (n=226) or loamy clay soils (n=167) (Bak et al., 1997).

Table 2.10. The median soil concentrations in Danish soil samples monitored in 1995 (Bak et al 1997) together with predicted load of metals per kg soil in one year by fertiliser application and atmospheric deposition (2008 data, Ellermann et al. 2010) assuming a uniform distribution in the upper 20 cm of a soil with a density of 1.5 kg/L.The input of metals via mineral fertilisers are based on a maximum content corresponding to the EU proposal for cut-off values (except for Cr).

	As	**Cd**	**Cr(tot)[1]**	**Hg[4]**	**Ni**	**Pb**
Median background concentration in agricultural soils (mg/kg)	3.6	**0.18**	10.7	0.036	5.7	11.3
Median background concentration in sandy soils (mg/kg)	2.6	0.13	6.4	**0.028**	2.9	10.5
Median background concentration in loamy clay soils (mg/kg)	**4.1**	0.22	**17.1**	0.047	**9.6**	**12.1**
Max. load from mineral fertilisers and atmospheric deposition[2] (mg/kg)	0.015	0.001	0.029	0.0005	0.031	0.04
Max. load from mineral fertilisers and atmospheric deposition[3] (%)	0.42	0.50	0.27	1.51	0.85	0.35

[1]All data are for total chromium as no information of the Danish background concentration is reported for Cr (VI)

[2] The area-based load (g/ha) of mineral fertilisers and atmospheric deposition recalculated to soil concentrations (mg/kg) for the worse case scenarios defined in Table 2.1-2.8.

[3] The weight-based load of fertilisers in percentage of the background concentration measured in the most relevant soil type according to the worst-case scenarios defined in Table 2.1-2.8 (in bold), i.e. the background concentration in loamy soils are used for comparison with maximum loads from scenarios on loamy soils (As, Cr, Ni and Pb), whereas the background concentration in sandy soils are used for comparison in the case Hg as the worst-case load was identified on the Cattle on sandy soil scenario. For cadmium the poultry scenario was the worst-case scenario. Here the median soil concentration in agricultural soils in general are used.

[4] As no recent information regarding the atmospheric deposition of Hg is available for Denmark, this has therefore been neglected, i.e. set to zero, in the present calculations.

3 Ecotoxicological evaluation of arsenic (As) in mineral fertilisers

3.1 Introduction

There are indications that arsenic is essential for some organisms although not all. However, a number of studies have shown that it is toxic to organisms at high exposure concentrations. The toxicity of arsenic to soil dwelling organisms depends on the exposure and on uptake, which again like other metals depends on the fraction available to organisms, termed the bioavailable fraction, which may constitute of one or more geological fractions. The toxicity is caused by various mechanisms and depends on the oxidation state of As, i.e as arsenite (As III) and arsenate (As V). As (III) reacts with sulphur groups and hence inhibits proteins, and As (IV) competes with phosphate and may hence for example uncouple the oxidative phosphorylation. Within organisms, methylation of arsenite to form monomethyl arsenic acid and dimethyl arsenic acid may occur. The methylated forms are generally less toxic and more easily excreted in the urine. This conversion in the environment and biota further complicates the toxic evaluation of As.

An effect assessment of As has been carried out by a few countries, including Denmark (Scott-Fordsmand and Pedersen 1995) and the Netherlands (Crommentijn et al 1997), but apparently no risk assessment report on EU level is available. There has most likely emerged new toxicity data in the literature since the assessment made in Denmark and The Netherlands back in the 1990's. However, as it is beyond the scope of this report to collect and evaluate new data to obtain PNEC values, the present risk assessment is based on the existing reviews.

3.2 Ecotoxicological data for soil dwelling organisms

Microbial processes

The no observed effect concentration (NOEC) or the EC10 values for microbial processes ranged from 50 to 374 mg As/kg, covering the various enzyme activities in soil. Toxicity to some essential pathways in these cycles may result of inhibition of the S- and P- cycling. The lowest NOEC was observed by Wilke (1988) who observed an NOEC of 50 mg As (III)/kg nine years after the addition. Tabatabai (1977) observed a 14% reduction in the urease activity at 37 mg As (III)/kg in a clay soil following 2 hours of exposure.

Plants

For plants the NOEC values ranged between 2 to 80 mg As/kg, based on few studies on agricultural crops. It was not possible from the data to see differences in toxicity between the two oxidation states, mainly due to lack of data. The NOEC values tended to increase with time, e.g. after one year the NOEC for ryegrass on a sandy soil was 2 mg/kg (LOEC was 10 mg As/Kg) whereas the NOEC after 3 years was 50 mg As/kg soil.

Invertebrates

Very few data are available regarding the effects of arsenic to soil invertebrates. The lowest NOEC is approximately 7 mg As/kg for the earthworm *Eisenia fetida*. Lee and Kim (2008) observed adverse effects on survival starting with 0.1 umol As/g soil which is equivalent to 7.4 mg As/kg soil, following 28 days of exposure. Effects on the DNA level measured by the COMET assay were observed at 98 mg As/kg following exposure to field contaminated soil (Button et al 2010).

Soil type dependency

The literature contains some information regarding differences in toxicity as dependent on soil type. For example, Cao et al (2009) showed that arsenate toxicity to wheat and lettuce depended on the soil type with EC10 values ranging from 78-270 and 20-150 mg As/kg, respectively, in various soil types. The As toxicity correlated with the extractable Fe concentration, but not with CEC or Organic matter or pH. However, no internationally accepted model is available relating soil characteristics with toxicity of arsenic for risk assessment purposes.

Bioaccumulation and secondary poisoning

Plants and invertebrates take up arsenic from the environment. The bioaccumulation factors are normally below 1 for invertebrates whereas plants can accumulate arsenic to higher concentrations which may cause food chain effects, e.g. Zhao et al (2009) and Su et al (2010). As no internationally accepted model is available for evaluating the risk of arsenic for secondary poisoning, it is neglected in this report.

3.3 Risk evaluation - Predicted No Effect Concentration (PNEC)

The Danish Environmental Protection Agency published back in 1995 a set of Soil Quality Criteria for metals (Scott-Fordsmand and Pedersen 1995). The Danish soil quality criterion for arsenic is 2.0 mg As/kg, which is comparable to the maximum permissible addition (MPA) of arsenic to soils in The Netherlands of 4.5 mg As/kg (Crommentuijn et al 1997). Since then much new evidence is likely to have been published in the open literature. It would hence be recommended to re-evaluate for example the Danish soil quality criteria. Nevertheless, for the use of risk assessment in this report a PNEC of 2.0 mg/kg is used.

3.3.1 Short-term risk evaluation

Based on the estimation of the total application (g/ha) of As through fertilizing of eight different agricultural management scenarios in Denmark (Table 2.3), a realistic worst case estimate of the soil concentration can be estimated. The maximum load of arsenic to agricultural land via fertilisers is estimated to be 44.7 g/ha (Table 2.9). The maximum application of arsenic was estimated for a scenario of cereal production without the use of animal manure. In this scenario mineral fertilisers accounted for 100% of the total arsenic input from fertilisers.

Assuming a mixing zone, i.e. ploughing depth, of 20 cm and a soil density of 1.5 kg/L the maximum load of arsenic corresponds to 0.015 mg As/kg soil in dry weight. This predicted environmental concentration (PEC) should be compared to the predicted no effect concentration (PNEC – see above) in soil in order to quantify the potential short-term risk (RQ = PEC/PNEC). In cases where the ratio (RQ) is below one, the potential short-term risk can be judged as acceptable.

PEC = 0.015 mg/kg
PNEC = 2.0 mg/kg
RQ = 0.008

The RQ of 0.008 is significantly lower than 1.0. This simplistic and generic risk assessment therefore demonstrates that the use of mineral fertilisers complying with the suggested maximum content of arsenic (60 mg As/kg fertiliser) apparently do not pose any short-term risk to soil dwelling organisms.

3.3.2 Long-term risk evaluation

For Swedish soils, Andersson (1992) showed that approximately 10-30% of the applied As were removed by crops or by leaching. Application rates in this study were approximately 10 times lower than the ones estimated in this report. As leaching and plant uptake of metals is highly dependent on e.g. the soil type, it is uncertain to what extend the Swedish data can be extrapolated to Danish conditions.

There is currently no estimation of long-term accumulation of arsenic in Danish soil. From Table 2.10 it can be seen that the load via mineral fertilisers containing arsenic up to the proposed cut-off value will - together with the average atmospheric deposition - correspond to approximately 1% of the median background concentration monitored in Danish agricultural soils. Furthermore, as shown in Table 2.9, the maximum load of arsenic via fertilisers, sums up to 64% of the worse case load of arsenic via amendment of agricultural soils with sewage sludge application.

Comparison with Critical Loads

The critical load derived for arsenic in the Netherlands (Reinds et al 2006) are 35-370 and 130-480 g/ha/year for various types of forests and agricultural soils, respectively. The estimated total load of arsenic from fertilisers (manure and mineral fertilisers) and atmospheric deposition in Denmark was 45.6 g/ha/year (Table 2.9), which is lower than the critical loads estimated for agricultural soils in the Netherlands. However, it should be highlighted that the critical load models are associated with uncertainty and are not derived for Danish conditions.

3.4 Conclusion

A generic risk assessment of arsenic in fertilisers reveals that there is no indication of short-term risk after one annual application. The annual load of arsenic via fertilisers correspond to less than 0.42% of the background concentrations in Danish agricultural soils and is lower than the anticipated annual load via maximal sewage sludge application. Furthermore, a comparison with critical load established for agricultural soils in the Netherlands indicates that no long-term risk of arsenic up to the suggested cut-off value in mineral fertilisers is anticipated. However, in order to improve the assessment of the long-term risks it would be recommended to develop and use more advanced steady-state models suited to fit Danish conditions.

4 Ecotoxicological evaluation of Cd in mineral fertilisers

4.1 Introduction

Cadmium is a naturally occurring element with ubiquitous distribution. There is no indication that cadmium in general is essential for organisms. On the contrary, there is strong evidence that it is toxic to most or all organisms at high concentrations. The toxicity is caused by various mechanisms, but a general mechanism as for other metals is the binding of Cd to proteins causing the proteins to lose their functionality. Cadmium interacts more specifically with other elements and induces specific responses in the organism such as metallothionein production.

The speciation of cadmium in soils may have influence on the toxicity. The majority of evidence indicates that, in the short-term, CdO is less available than soluble Cd^{+2} salts but that the differences in availability between both Cd^{+2} forms are not very pronounced. Soil properties influence Cd toxicity. The general trend is that toxicity increases in soil when mobility of Cd increases, i.e. as soil pH or soil organic matter decrease.

An effect assessment of cadmium has been carried out by a few countries including Denmark (Scott-Fordsmand and Pedersen 1995), the Netherlands (Crommentuijn et al 1997) and recently a risk assessment report on the European level was made within the framework of Council Regulation 793/93/EEC on Existing Chemicals. Data and methodologies from this EU risk assessment report for cadmium have been adopted in order to elucidate to what extend the proposed cut-off value for Cd in mineral fertilisers is sufficiently conservative to protect soil dwelling organisms.

4.2 Ecotoxicological data for soil dwelling organisms

A wealth of information is available on the ecotoxicity of Cd. The data quality of that information varies between source documents. Not all source documents provide complete background information of the toxicity test. The EU-RAR (Cd) (2007) has therefore conducted a quality and reliability test of all data. A first selection was made based on the reliability of the test results. Secondly, some test results were not taken into account to avoid overrepresentation of similar data. As an example, some tests provide data at different exposure times. In these conditions, only the data at the highest exposure time were selected. If various endpoints were derived from one test (i.e. reproduction, growth and mortality), only the most sensitive endpoint was included. Similar toxicity tests are reported in different source documents (i.e. using the same organism, endpoint, soil or water and test conditions). For these cases, the lowest value is selected or a geometric mean value is calculated.

In relation to protecting and maintaining the function of soils, the terrestrial toxicity studies have focused on three groups: microorganism (species/processes), plants (species) and invertebrates (species). For these species groups the information on effect and no-effect data was extracted, and evaluated before use.

Microbial processes

The NOEC and EC10 values for microbial processes ranged from 3.6 to 3,000 mg Cd/kg (see Table 4.1), covering the processes involving the C, N, P and S compounds in soil. Toxicity to some essential pathways in these cycles may result in plant nutrient deficiencies or unacceptable losses of nutrients to the environment. The toxicity tests for soil microorganisms or processes often lack standardization, but data compilation shows that N_2-fixation is a likely candidate as the most sensitive of the soil microbial processes.

Plants

The NOEC and EC10 values from plant studies ranged from 1.8 to 80 mg Cd/kg (see Table 4.1). The studies generally report effects of Cd^{+2} salts on plant development in potted soil, using pot trials in greenhouse conditions. In most pot trials, cadmium is homogeneously mixed in the whole soil prior to plant growth. In total 20 different plant species were tested belonging to 9 different families and 9 different orders.

Invertebrates

The NOEC and EC10 values range for invertebrate studies ranged from 5 to 320 mg Cd/kg (see Table 4.1). The invertebrates tested belong to 3 different families and 3 different orders. The toxicity of Cd to adult invertebrates has been tested in the two available standard tests, i.e. the 14-day LC50 test using the earthworm *Eisenia fetida* (OECD 1984) and the ISO test (ISO, 1994) with the collembolan *Folsomia candida*. However, effects of Cd on the reproduction of soil invertebrates have rarely been tested in the lower exposure range, i.e. 1-10 mg Cd/kg. Three tests were found where Cd toxicity was measured below 10 mg/kg (Khalil et al., 1996, Spurgeon et al., 1994 and Parmelee et al., 1997). One of these tests showed Cd toxicity at 5 mg/kg (Khalil et al., 1996). Spurgeon et al (1994) found that cocoon production was unaffected at 5 mg/kg, but was reduced by 80% at 20 mg/kg. The NOEC value for cocoon production in this soil is the lowest NOEC value for soil fauna in the EU-RAR (Cd) (2007).

Table 4.1. Summary of Cd toxicity data (mg/kg) for the terrestrial environment as presented in EU-RAR(Cd) (2007). All the included data have been evaluated as reliable and are a result of a selection process.

	NOEC/EC10				
	Min.	HC5	Median	Max.	N
Microorganisms	3.6	3.6	50	3,000	21
Plants	1.8	2.5	10	80	41
Soil fauna	5.0	8.0	32	320	13

4.3 Risk evaluation - predicted No Effect Concentration (PNEC)

There are enough data from all three trophic levels (microbial processes, plants and invertebrates) to calculate the PNEC for soils by the assessment factor method using an assessment factor 10. The lowest NOEC value of 1.8 mg/kg was observed for plants. This yields a generic PNEC for soils of 0.18 mg/kg. However, rather than making a PNEC assessment based on one single NOEC value, it is possible to use the statistical extrapolation method based on the species sensitivity distribution (SSD, Posthuma et al 2001) as enough NOEC data are available in the case of cadmium covering information from a wide range of species and microbial processes. Selection on data quality slightly affects the value of HC5 depending on the selection criteria imposed. For the statistical SSD calculations EU-RAR (Cd)(2007) suggested to split the terrestrial data set in two groups: 1) microbial processes and 2) soil invertebrates and higher plants. The estimated HC_5 were 2.3 and 2.5, respectively, for the two sets of data. Based on a large set of argumentations EU-RAR (Cd)(2007) suggests to use an assessment factor ranging from 1 to 2 to encompass the uncertainties in deriving a PNEC for soils from the HC5. This results in an estimated PNEC for soils of 1.15 mg/kg, which is higher than the PNEC of 0.18 mg/kg for soils, when based on the application of assessment factors according to the recommendation in the risk assessment procedure under the REACH programme for new and existing chemicals. As a conservative approach, a PNEC of 0.18 mg/kg is used for further assessment in the present report.

Soil type dependency

Toxicity of cadmium to soil dwelling species is well known to vary with soil properties, which in principle justifies deriving soil type depending PNEC values. The pH of the soil dominates the solid-liquid distribution of Cd in soil. It is often assumed that the metal concentration in soil solution represents the toxic dose and, therefore, a correlation between metal toxicity and pH is to be expected. In comparison EU-RAR (Cd)(2007) did not find any correlation between the NOEC values and the content of clay in soil. It was also attempted to extract soil-type related relationships by using adsorption information to estimate the Cd in the soil solution, however there was no apparent relationship. Although it is known that toxicity of Cd depends on the soil type it is, however, at present not attempted to derive PNEC values that are soil type dependent or specified to specific Danish conditions.

Bioaccumulation and secondary poisoning

Cadmium intake by wildlife is probably most documented in shrews (*Sorex araneus*) because they may have a high Cd body burden (Hunter et al., 1989). Shrews have a high dietary Cd intake rate and feed on invertebrates active at the ground surface supplemented with soil dwelling macrofauna. Earthworms can be the major source of dietary uptake of cadmium in shrews (Ma et al., 1991).

Toxicity of Cd through secondary poisoning is assessed based on laboratory studies where organisms are exposed to variable Cd concentrations in their prey. A PNECoral can be calculated from such studies. In the EU RAR (Cd) (2007), a case study on Cd bioaccumulation in the lower food chain was made for the plant-insect-predator pathway. A soil with low content of cadmium was fertilized with fertiliser with high levels of cadmium. This resulted in higher cadmium content in soil and in wheat shoots. Aphids feeding on the wheat plants of the fertilized soil had 3 times higher cadmium concentrations than those feeding on the control plants. However, lacewings showed no significant accumulation of cadmium and no differences in larval performance were recorded. In summary EU-RAR (Cd)(2007), based on assessment of bioaccumulation and food web transfers, suggested a PNEC for soil of 0.8 mg/kg in order to avoid secondary poisoning in terrestrial food webs. This is higher than the conservative PNEC of 0.18 mg/kg suggested to be used for the risk assessment in this report (see above).

4.3.1 Short-term risk evaluation

Based on the estimation of the total application (g/ha) of Cd through fertilizing of eight different agricultural management scenarios in Denmark (Table 2.4), a realistic worst case estimate of the soil concentration can be estimated. The maximum load of cadmium to agricultural land via fertilisers is estimated to be 3.3 g/ha. The maximum current application of cadmium was estimated for a scenario of cereal production without use of animal manure. In this scenario mineral fertilisers accounted for 100% of the total cadmium input from fertilisers. In the case where a maximum content of 3 mg/kg in mineral fertilisers is imposed, the farm type of broilers becomes the scenario leading to the highest total load of cadmium to agricultural land with a maximum load of cadmium estimated to be 2.4 g/ha (Table 2.9).

Assuming a mixing zone, i.e. ploughing depth, of 20 cm and a soil density of 1.5 kg/L, the maximum load of cadmium corresponds to 0.001 mg/kg soil in dry weight. The predicted environmental concentration (PEC) should be compared to the predicted no effect concentration (PNEC – see above) in soil in order to quantify the potential risk (RQ = PEC/PNEC). In cases where the ratio (RQ) is below one, the potential short-term risk can be judged as acceptable.

PEC = 0.001 mg/kg
PNEC = 0.18 mg/kg
RQ = 0.006

The RQ of 0.006 significantly lower than 1.0. This simplistic and generic risk assessment therefore shows that the use of mineral fertilisers complying with the suggested maximum content of cadmium (3 mg Cd/kg) apparently does not pose any short-term risk to soil dwelling organisms.

4.3.2 Potential long-term risk evaluation

For Swedish soils, Andersson (1992) showed that approximately 20-50% of the applied cadmium were removed by crops or by leaching. Application rates in this study were approximately 7 times lower than the ones estimated in this report. As leaching and plant uptake of metals is highly dependent on e.g. the soil type, it is uncertain to what extend the Swedish data can be extrapolated to Danish conditions.

There is currently no estimation of long-term accumulation of cadmium in Danish soil. From Table 2.10 it can be seen that the load via mineral fertilisers containing cadmium up to the proposed cut-off value will - together with the average atmospheric deposition - correspond to approximately 0.5% of the median background concentration monitored in Danish agricultural soils. The load of cadmium via fertilisers sums up to be only 38% of the maximum load of cadmium via amendments of agricultural soils with sewage sludge (see Table 2.9).

Comparison with Critical Loads

The critical loads derived for cadmium in the Netherlands (Posch and de Vries 2009) are 38, 50 and 68 g Cd/ha/year for sand, clay and peat soil, respectively. The highest estimated total load of cadmium from fertilisers (manure and mineral fertilisers) and atmospheric deposition was 2.7 g/ha/year (Table 2.9), which is significantly lower than the critical loads estimated for soils in the Netherlands. However, it should be highlighted that such critical load models are associated with uncertainty and are furthermore not derived for Danish conditions. Critical Loads between 3.4 and 4.7 g Cd/ha/y has been published back in 1998 for various farm types in Denmark (Bak and Jensen 1998). These critical loads are still higher than the estimated total load of cadmium from fertilisers and atmospheric deposition for all of the scenarios in Table 2.9. It should, however, be mentioned that the Danish critical loads were based on preliminary guidelines and has to be considered as a first provisional attempt.

4.4 Conclusion

A generic risk assessment of cadmium in fertilisers reveals that there is no indication of short-term risk after one annual application. The maximum annual load of cadmium via fertilisers correspond to approximately 0.5% of the background concentrations in Danish agricultural soils and is significantly lower than the anticipated annual load via e.g. normal sewage sludge application. Furthermore, a comparison with critical load established for agricultural soils in the Netherlands and Denmark indicates that no long-term risk of cadmium up to the cut-off value in mineral fertilisers is anticipated. However, in order to improve the assessment of the long-term risks it would be recommended to develop and use dynamic steady-state models suited to fit Danish conditions.

5 Ecotoxicological evaluation of Chromium (Cr) in mineral fertilisers

5.1 Introduction

Chromium forms two major groups of compounds in soil, the trivalent (Cr^{3+}) and the hexavalent (Cr^{6+}). Whether it is present on one or the other form depends on the soil condition, and may even be fluctuating throughout a year.

There is evidence that Cr is essential for organisms although it is not shown for all groups of organisms. But there are also reports on high toxicity of chromium to organisms. The Cr uptake depends on the available fraction, termed the bio-available fraction, which is dependent on the oxidation state. The toxicity is caused by various mechanisms, but a general mechanism as for other metals is the binding of Cr to proteins causing the proteins to loose their normal biological functions. Due to similarities with trivalent iron, chromium may also affect the iron metabolism.

The number of toxicity data for soil organisms is scarce for chromium in the terrestrial environment and the majority of information is concerning the toxicity of chromium (VI). In the soil environment, it is likely that chromium (VI) will be reduced to chromium (III), and it is therefore also likely that such conversion have taken place in many of the toxicity tests.

An effect assessment of chromium has been carried out by a few countries, including Denmark (Scott-Fordsmand and Pedersen 1995), the Netherlands (Crommentuijn et al 1997) and recently in the Europena Union[1] within the framework of Council Regulation 793/93/EEC on Existing Chemicals (EU-RAR (Cr), 2005). In the latter the terrestrial effect assessment is mainly based on the data found in Crommentuijn et al (1997). Common for all assessments is a limitation with regards to the number of soil toxicity data. There has most likely emerged new toxicity data in the literature since the assessment made in Denmark and The Netherlands back in the 1990's. However, as it is beyond the scope of this report to collect and evaluate new data to obtain PNEC values, the present risk assessment is based on the existing reviews.

Within the present report, the EU risk assessment report (EU-RAR (Cr), 2005) for chromium forms the basis for the derivation of the PNEC value for soil as the data have been evaluated according to quality and relevance in trans-national European scenarios,

[1] The risk assessment was bound to the principles that are laid down in European Economic Community's (EEC) Regulation 1488/94 (EC 1994)

which is pertinent for an evaluation of EU-based cut-off values of Cr in mineral fertilisers.

5.2 Ecotoxicological data for soil dwelling organisms

Chromium (III) has generally been shown to be less toxic than chromium (VI) to soil organisms (Ueda et al. 1988). For chromium (VI), long-term toxicity data are available for three trophic levels (plants, earthworms and soil processes/micro-organisms), with plants generally being the most sensitive species.

Microbial processes

For microbial processes the toxicity studies mainly cover the initial exposure with trivalent chromium, with only a few studies covering the hexavalent form. The NOEC levels of trivalent chromium range from 10 to 260, while the NOEC levels for chromium (VI) range from 3 to 520 mg Cr/kg. Crommentuijn et al. (1997) reviewed the toxicity of chromium (III) to soil processes. The review included 51 results, covering arylsulphatase, nitrification, N mineralisation, phosphatase, respiration and urease. The test results ranged from 1.0 mg/kg dw to 3,332 mg/kg dw (both values being for arylsulphatase). All studies used soluble chromium (III) compounds mostly chromic (III) chloride. A final selection of data resulted in a set of 30 values, which were used for a statistical extrapolation method (SSD) to derive an HC5 value of 5.9 mg/kg (Crommentuijn et al (1997).

Plants

The toxicity studies on plants have been performed in various exposure media, as for many other metal studies. In the case of Cr the exposure condition can be very important for the stability of the oxidation state of Cr and hence for potential toxicity e.g. for plants aquaculture studies are often performed. The NOEC levels range from 50 to 5000 mg/kg for Cr (III) and 5 to 50 for Cr (VI).

Invertebrates

Very few studies are available regarding the toxicity of chromium to invertebrates and most of these are with earthworms, wherefore data generally are insufficient to cover the various physiological life-forms of soil invertebrates, e.g. soft- versus hard-bodied species. For the trivalent form the NOECs range from 32 to 320, whereas the lowest NOEC found in the studies with the hexavalent form was 2.0 mg Cr/kg.

Soil type dependency

Studies have shown that toxicity of chromium is dependent on the soil type. For example, Haanstra and Doelmann (1991) observed EC10 values ranging from 55 to 2800 mg

Cr/kg soil, depending on the soil type (and exposure time). Peat sand had the highest EC10 whereas sand and sandy-loam had the lowest. There are only few studies showing soil-type related toxicity, and no clear trend can be derived. Although it is known that toxicity depends on the soil type it is, however, at present impossible to calculate PNEC values that are soil type dependent or specified to specific Danish conditions.

5.3 Risk evaluation

The suggested cut-off value for chromium in mineral fertilisers are based on the level of Cr(VI). However, for comparison, the conclusion for Cr(III) from the EU risk assessment of chromium is included as well. Since chromium (III) adsorbs more strongly onto soil than chromium (VI), it is expected that in soils, chromium (III) would be less toxic than chromium (VI).

Chromium (III)

The available data for Cr (III) include studies with microbial processes, plants and soil invertebrates, which justify the use of an assessment factor of 10. The NOEC for chromium (III) to plants is of the order of 100 mg Cr/kg soil, with a NOEC of 32 mg Cr/kg soil being reported for earthworms. Applying an assessment factor of 10 to the lowest of these NOECs gives a PNEC for chromium (III) of approximated 3.2 mg Cr/kg dry soil. This value is lower than the HC5 value for soil processes of 5.9 mg/kg.

Chromium (VI)

For chromium (VI), long-term toxicity data are available for three trophic levels, i.e. plants, earthworm and soil processes/micro-organisms, with plants generally being the most sensitive species. No clear NOEC was determined for earthworms. However, the EC50 values are generally higher than those found in the plant experiments. The lowest NOEC from these studies is around 0.35 mg/kg dry weight for plants. According to the EU Technical Guidance Document (EU 1996), an assessment factor of 10 is appropriate wherefore the PNEC for soil can be estimated to 0.035 mg/kg dry weight.

However, the PNEC for Cr (VI) should be considered very tentative and conservative in nature as Cr (VI) is likely to rapidly be reduced to Cr (III) under the conditions found in most soils. Since Cr (III) is likely to be of much lower water solubility (and bioavailability) than Cr (VI), this would lower the potential for adverse effects on soil dwelling species.

5.4 Short-term risk evaluation

The risk evaluation of Cr is greatly complicated by the fact that Cr speciation is of high importance for the evaluation. Based on the estimation of the total application (g/ha) of Cr though fertilizing of eight different agricultural management scenarios in Denmark (Table 2.5), a realistic worst case estimate of the soil concentration can be estimated. The maximum current load of total Cr to agricultural land via fertilisers is estimated to be 85 g Cr/ha/y. Speciation of Cr is not taken into account in this estimate as it is based on analytical data on the total Cr content in Danish mineral fertilisers and manure. The maximum application of total Cr was estimated for a scenario of cereal production without the use of animal manure. By applying the suggested cut-off value of 2.0 mg Cr (VI)/kg a maximum load of 1.5 g Cr(VI)/ha can be estimated in the same scenario. Here it is assumed that the predominating speciation of Cr in mineral fertilisers is Cr (III). The PEC soil value based on the total Cr content in fertilisers is hence compared to the PNEC value for Cr (III), whereas the PEC soil value based on the suggested cut-off criteria for Cr (VI) in mineral fertilisers obviously is compared to the PNEC value for Cr (VI).

Assuming a mixing zone, i.e. ploughing depth, of 20 cm and a soil density of 1.5 kg/L the maximum load of Cr corresponds to soil concentrations of 0.06 mg total Cr/kg and 0.01 mg Cr VI/kg soil in dry weight, respectively. The predicted environmental concentration (PEC) should be compared to the predicted no effect concentration (PNEC – see above) in soil in order to quantify the potential risk (RQ = PEC/PNEC). In cases where the ratio (RQ) is below one, the potential short-term risk can be judged as acceptable.

PEC (Total Cr) = 0.06 mg/kg
PNEC (Cr III) = 3.2 mg/kg
RQ (Cr III) = 0.02

PEC (Cr VI) = 0.001 mg/kg
PNEC (Cr VI) = 0.035 mg/kg
RQ (Cr III) = 0.03

The RQ values of 0.02-0.03 are significantly lower than 1.0. This simplistic and generic risk assessment therefore shows that the use of mineral fertilisers complying with the suggested maximum content of Cr (2 mg Cr (VI)/kg) apparently does not pose any short-term risk to soil dwelling organisms.

5.4.1 Potential long-term risk

Long-term accumulation for contaminants in soils is an important issue especially for metals as they are not biodegradable. The EU risk assessment for Cr (EU RAR (Cr), 2005) has estimated the potential bioaccumulation based on a calculation showing that very little Cr (III)[2] is leaching from the soils. The model therefore predicted that all the added Cr will remain in the soil. There is currently no estimation of long-term accumulation of Cr in Danish soil. From Table 2.10 it can be seen that the load of total Cr via mineral fertilisers will, together with the average atmospheric deposition, correspond to 0.27% of the median background concentration monitored in Danish soils. Furthermore, the maximum load of total Cr (84.9 g/ha/y) via fertilisers sums up to be 64% of the load of total Cr via maximum amendment of agricultural soils with sewage sludge.

Comparison with Critical Loads

The critical loads derived for total Cr in the Netherlands (Posch and de Vries 2009) are 24-230 and 80-300 g/ha/year for forest and agriculture soils, respectively. The highest estimated total load of Cr from fertilisers (manure and mineral fertilisers) and atmospheric deposition was 86.4 g/ha/year (Table 2.5), which corresponds to the lower end of the critical loads estimated for soils in the Netherlands. However, it should be highlighted that such critical load models are associated with uncertainty and are furthermore not derived for Danish conditions.

5.5 Conclusion

A generic risk assessment of Cr in fertilisers reveals that there is no indication of short-term risk after one annual application. As the proposed EU cut-off value for Cr is for Cr (VI) and most other information is based in total Cr it is difficult to evaluate the potential risk to the soil environment of the proposed limit. A comparison with critical load established for agricultural soils in the Netherlands indicates that long-term risk of total Cr up to the level currently found in mineral fertilisers cannot be ruled out in some of the most sensitive agricultural soils. However, in order to improve the assessment of the long-term risks it would be recommended to develop and use more advanced steady-state models suited to fit Danish conditions.

[2] It is noted that the assumption is that there is a rapid reduction of Cr (VI) to Cr (III)

6 Ecotoxicological evaluation of lead (Pb) in mineral fertilisers

6.1 Introduction

There is no indication that Pb in general is essential for organisms. On the contrary there is evidence that it is toxic to most organisms. The uptake of Pb in biota depends like other metals on the fraction available for these, termed the bioavailable fraction, which may constitute of one or more geological fractions. The toxicity is caused by various mechanisms. One of the more dominating modes of action of is the binding of Pb to proteins, which may cause the proteins to loose their normal biological functionality.

As shown in EU-VRAR (Pb) (2008) the short-term effects of Pb in soil depend on the source, i.e. soluble forms are more toxic than the less soluble forms. Depending on the conditions prevailing in the soil, insoluble forms such as metallic Pb and lead oxides will slowly transform and may finally have similar availability as Pb^{2+} salts. Even metallic Pb in soils around shooting ranges corrodes to secondary minerals (Pb^{2+} precipitates) and can be mobilised to subsurface soils or taken up by organisms (Astrup et al., 1999, Xifra et al., 2002).

An effect assessment of Pb and Pb compounds has been carried out by a few countries, including Denmark (Scott-Fordsmand and Pedersen 1995) and recently a transnational risk assessment report (EU-VRAR (Pb), 2008) has been discussed at the European level. Data and methodologies from EU-VRAR(Pb) (2008) for Pb have been adopted in order to elucidate to what extend the proposed cut-off value for Pb in mineral fertilisers is sufficiently conservative to protect soil dwelling organisms.

6.2 Ecotoxicological data for soil dwelling organisms

In relation to protecting and maintaining the function of soils, the terrestrial toxicity studies have focussed on three groups: microorganism (species/processes), plants (species) and invertebrates (species). For these “groups” differences in toxicity between various species/processes have been observed both within the groups and between the groups. Below is a short description of the data, which form the basis for the derivation of the overall PNEC value for Pb in EU-VRAR (Pb)(2008).

Microbial processes

EU-VRAR(Pb) (2008) identified 18 useful NOEC or EC10 values on functional parameters. The functional parameters comprise C- and N-mineralization. The NOEC’s on functional parameters vary from 96 to 4144 mg Pb/kg.

Plant species
In EU-VRAR(Pb) (2008), 14 NOEC's were selected ranging from 65 mg Pb/kg for *Hordeum vulgare* (Barley) to 2,207 mg/kg for *Triticum aestivum* (wheat).

Invertebrates
In EU-VRAR (Pb) (2008), twelve NOEC or EC_{10} values are selected ranging from 130 mg Pb/kg for *Dendrobaena rubida* (earthworm) to 2207 mg Pb/kg for *Folsomia candida*. In cases where similar toxicity tests are reported in different source documents (i.e. using the same organism, endpoint, soil and test conditions) a geometric mean value is calculated.

Soil type dependent toxicity
It is known that the soil composition is important for the toxicity of Pb to soil organisms, e.g. Haanstra and Doelman (1991) showed that EC10 values for soil enzymes ranged from 276 to 2652 mg Pb/kg depending on the soil. However, EU-VRAR(Pb)(2008) judged that currently it was not possible to derive soil-type dependent PNEC values for Pb as there are currently no models available that on a solid scientific basis can relate toxicity of Pb in soils to abiotic soil factors. No attempt has therefore been made to derive soil type related PNEC values.

Ageing dependent toxicity
Based on studies where toxicity studies with freshly spiked soils, were compared to studies using soil from the field that was slowly contaminated due to historical emissions. Based on these studies a so-called leaching/ageing factor[3] of 4.2 was derived (EU-VRAR(Pb) 2008) meaning that the PNEC obtained by the use of simple laboratory studies needs to be multiplied by a factor of 4.2 in order to get a more field-realistic PNEC value for soil ecosystems.

Bioaccumulation and secondary poisoning
Bioaccumulation and secondary poisoning are major issues for Pb in higher terrestrial food chain, and further work is needed in this area. However, Pb does rarely concentrate from the soil into invertebrate organisms as reported bioaccumulation factors (BAF) typically are lower than 1. The BAF's are not significantly affected by the Pb concentration in the soil, but increased with decreasing the pH and CEC. A median BAF value for soil dwelling organisms on a wet weight basis is for example 0.10 $kg_{dw}/kg_{ww,}$ at pH 6.5 and 4 times higher at pH 4.5 (median of 101 BAF values). Bioaccumulation and secondary poisoning is important issues for Pb, and further work is needed in this area. However, in this specific assessment of Pb bioaccumulation has not been considered.

[3] Leaching/ageing factor approximates the impact that leaching and ageing is assumed to influence (reduce) the bioavilability of the metal.

6.3 Risk evaluation

In EU-VRAR(Pb) (2008) the generic $PNEC_{soil}$ was estimated at 166 mg Pb/kg. This value is based on a SSD estimate of HC5 and application of an uncertainty factor of 2. Furthermore, the final PNEC for Pb in soil estimated by EU-VRAR(Pb)(2008) includes an application of a subsequent leaching/ageing factor of 4.2, i.e. the PNEC value is increased by a factor of 4.2, as it is assumed that some of the Pb found in the environment are unavailable for uptake in organisms either due to leaching or adsorption to soil. The use of such a leaching/ageing factor may be questionable in relation to the risk assessment of fertilisers for which it must be assumed that the metals found as impurities in fertilisers will be available for uptake in organisms. On a longer term some of the applied Pb may leach and/or adsorb to the soil matrix.

The lowest NOEC of 65 mg/kg was observed for plants. As a large number of data was available for the three trophic levels, microorganisms, plants and soil invertebrates, the use of an uncertainty factor of 10 is appropriate. This leads to a PNEC estimation of 6.5 mg Pb/kg. As a conservative approach, this PNEC is used for further assessment in the present report.

6.3.1 Short term risk evaluation

Based on the estimation of the total application (g/ha) of Pb through fertilizing of eight different agricultural management scenarios in Denmark (Table 2.6), a realistic worst case estimate of the soil concentration can be estimated. The maximum current load of Pb to agricultural land via fertilisers is estimated to be 12 g/ha in the cattle manure on sandy soils scenario. In the case where a maximum cut-off value of 150 mg/kg in mineral fertilisers is imposed, the scenario of cereal production without use of manure becomes the scenario leading to the highest total load of Pb from fertilisers to agricultural land. Here the maximum load of Pb was estimated to be 112 g/ha (Table 2.9).

Assuming a mixing zone, i.e. ploughing depth, of 20 cm and a soil density of 1.5 kg/L the maximum load of Pb (112 g/ha) corresponds to 0.04 mg Pb/kg soil in dry weight. This predicted environmental concentration (PEC) should be compared to the predicted no effect concentration (PNEC) in soil in order to quantify the potential risk (RQ = PEC/PNEC). In cases where the ratio (RQ) is below one, the potential short-term risk can be judged as acceptable.

PEC = 0.04 mg/kg
PNEC = 6.50 mg/kg
RQ = 0.006

The RQ of 0.006 is significantly lower than 1. This simplistic and generic risk assessment therefore shows that the use of mineral fertilisers complying with the suggested maximum content of Pb (150 mg Pb/kg) apparently does not pose any short-term risk to soil dwelling organisms.

6.3.2 Potential long-term risk

For Swedish soils, Andersson (1992) showed that approximately 10-20% of the applied Pb were removed by crops or by leaching. Application rates in this study were approximately 3-5 times lower than the ones estimated in this report. As leaching and plant uptake of metals are highly dependent on e.g. the soil type, it is uncertain to what extend the Swedish data can be extrapolated to Danish conditions.

There is currently no estimation of long-term accumulation of Pb in Danish soil. From Table 2.10 it can be seen that the load via mineral fertilisers containing Pb up to the proposed cut-off value of 150 mg/kg will - together with the average atmospheric deposition - correspond to approximately 0.35% of the median background concentration monitored in Danish soils. The maximum load of Pb via mineral fertilisers sums up to be only 46% of the load of Pb via maximum amendment of agricultural soils with sewage sludge (Table 2.9).

The critical loads derived for Pb in the Netherlands (Posch and de Vries 2009) are 21, 30 and 47 g Pb/ha/year for clay, peat and sandy soils, respectively. The highest estimated total load of Pb from fertilisers (manure and mineral fertilisers) and atmospheric deposition was 120.5 g/ha/year (Table 2.9) if the new cut-off value in mineral fertilisers is used to define the maximum content of Pb. This load is markedly higher than the critical loads estimated for soils in the Netherlands. However, it should be highlighted that such critical load models are associated with uncertainty and are furthermore not derived for Danish conditions. Critical Loads between 7.8 and 21.0 g Pb/ha/y have been published back in 1998 for various farm types in Denmark (Bak and Jensen 1998). These critical loads are also lower than the estimated total load of Pb from fertilisers and atmospheric deposition for all of the scenarios in Table 2.9. It should, however, be mentioned that the Danish critical loads were based on preliminary guidelines and has to be considered as a first provisional attempt.

6.4 Conclusion

A generic risk assessment of Pb in fertilisers reveals that there is no indication of short-term risk after one annual application. The maximum annual load of Pb via fertilisers corresponds to 0.35% of the background concentrations in Danish agricultural soils and is significantly lower than the anticipated annual load via e.g. maximum allowable sewage sludge applications. A comparison with critical load established for agricultural soils in the Netherlands and Denmark indicates that there may be a long-term risk of the Pb accumulation associated with using the proposed cut-off value for Pb in mineral fertilisers. In order to improve the assessment of the long-term risks it would, however, be recommended to develop and use dynamic steady-state models suited to fit Danish conditions.

7 Ecotoxicological evaluation of mercury (Hg) in mineral fertilisers

7.1 Introduction

There is no indication that Hg in an essential element for organisms. On the contrary it is evident from numerous studies that it is toxic to most organisms. The toxicity of Hg to soil dwelling organisms depends on the exposure and on uptake, which again depends on the fraction available for these, termed the bioavailable fraction, which may constitute of one or more geological fractions. The toxicity is caused by various mechanisms depending on the oxidation state of Hg, i.e. Hg (I), Hg (II) or as organic Hg. Methyl-mercury was previously produced anthropogenic but is now primarily a result of methylation processes that converts mineral Hg to methyl-mercury in natural environments such as sediments and soils. Methyl mercury is readily and completely absorbed over membranes e.g. in the guts, skin or gills of organisms. After uptake it may form complexes with free cysteine and with proteins and peptides containing that amino acid. Due to its strong binding to proteins, methyl-mercury is not readily eliminated.

An effect assessment of Hg has been carried out by a few countries, including Denmark (Scott-Fordsmand and Pedersen 1995) and the Netherlands (Crommentijn et al 1997), but apparently no risk assessment report on EU level is available. New toxicity data has emerged in the literature since the assessment made in Denmark and The Netherlands back in the 1990's. However, as it is beyond the scope of this report to collect and evaluate new data to obtain PNEC values, the present risk assessment is based on the existing reviews.

7.2 Ecotoxicological data for soil dwelling organisms

Microbial processes

The NOECs for Hg range between 0.3 and 100 mg Hg/kg with adverse effects observed at soil concentrations as low as 1 mg Hg/kg. A wide range of enzymatic processes are covered combined with data on C and N metabolism (Scott-Fordsmand and Pedersen 1995).

Plants

Only a few studies are available for plants, with NOEC and EC10 values ranging from 1 to 50 mg Hg/kg soil. The toxicity (LOEC) values ranged from 1 to 250 mg Hg/kg. (Scott-Fordsmand and Pedersen 1995)

Invertebrates
For invertebrates the toxicity of Hg starts from below 1 mg Hg/kg, but very few data were reported. It is, however, clear that Hg is one of the most toxic metals to soil invertebrates (Scott-Fordsmand and Pedersen 1995).

Soil type dependency
There is not sufficient evidence on how toxicity of Hg may be soil type dependent, although soil type is known to affect the toxicity of many metals.

Bioaccumulation and secondary poisoning
Plants and invertebrates take up Hg from the environment, but the bioaccumulation factors are normally below 1 for invertebrates although plants can accumulate higher concentrations. Secondary poisoning may be very important for Hg but mainly for higher level organisms such as mammals and birds.

7.3 Risk evaluation

The Danish Environmental Protection Agency published back in 1995 a set of Soil Quality Criteria for metals (Scott-Fordsmand and Pedersen 1995). The Danish soil quality criteria for mineral Hg is 0.1 mg Hg/kg, which is lower than the maximum permissible addition (MPA) of mineral Hg to soils in The Netherlands of 1.9 mg Hg/kg (Crommentuijn et al 1997). Since then much new evidence is likely to have been published in the open literature. It would therefore be recommended to re-evaluate for example the Danish soil quality criteria. Nevertheless, for the use of a conservative risk assessment in this report a PNEC of 0.1 mg/kg is used.

7.3.1 Short-term risk evaluation

Based on the estimation of the total application (g/ha) of Hg through fertilizing of eight different agricultural management scenarios in Denmark (Table 2.7), a realistic worst case estimate of the soil concentration can be estimated. The maximum current application of Hg was estimated to 0.87 g/ha for a scenario of soils amended with manure from cattle on sandy soils. In the case where a maximum content of 2 mg/kg in mineral fertilisers is imposed, the farm type of cattle on sandy soils becomes the scenario leading to the highest total load of Hg from fertilisers to agricultural land with a maximum load of 1.6 g/ha (Table 2.9). This load of Hg corresponds to approximately 21% of the estimated worst case load of Hg from sewage sludge amendment.

Assuming a mixing zone, i.e. ploughing depth, of 20 cm and a soil density of 1.5 kg/L the maximum load of Hg corresponds to 0.0005 mg/kg soil in dry weight. The predicted environmental concentration (PEC) should be compared to the predicted no effect concentration (PNEC) in soil in order to quantify the potential risk (RQ = PEC/PNEC). In cases where the ratio (RQ) is below one, the potential risk can be judged as acceptable.

PEC = 0.0005 mg/kg
PNEC = 0.1 mg/kg
RQ = 0.005

The RQ of 0.005 significantly lower than 1 showing that the use of mineral fertilisers complying with the suggested maximum content of Hg (2.0 mg Hg/kg) apparently does not pose any short-term risk to soil dwelling organisms.

7.3.2 Potential long-term risks

For Swedish soils, Andersson (1992) showed that approximately 10% of the applied Hg is removed by crops and 5-10% by leaching. Application rates in this study were approximately 10 times lower than the ones estimated in this report. As leaching and plant uptake of metals are highly dependent on e.g. the soil type, it is uncertain to what extend the Swedish data can be extrapolated to Danish conditions. Using a Scandinavian iron-humus podzol (also present in Denmark), Schüter and Gäth (1997) estimated the leaching of Hg to be between 40-90% of all the added Hg, depending on the concentration in the soil and the rain input (here also using acid rain).

There is currently no estimation of long-term accumulation of Hg in Danish soil. From Table 2.10 it can be seen that the load via mineral fertilisers containing Hg up to the proposed cut-off value will correspond to approximately 1.5% of the median background concentration monitored in Danish agricultural soils. No data for atmospheric deposition of Hg have been identified. However, it is anticipated to be relatively low and not to have any major influence on the conclusions made in this report. The maximum load of Hg via fertilisers sums up to be only 21% of the load of Hg via maximum amendment of agricultural soils with sewage sludge.

Comparison with estimates of critical loads
No critical loads for Hg have been identified for e.g. the Netherlands or Denmark.

7.4 Conclusion

A generic risk assessment of Hg in fertilisers reveals that there is no indication of short-term risk after one annual application. The maximum annual load of Hg via fertilisers corresponds to approximately 1.5% of the background concentrations in Danish agricultural soils, which is relatively high compared to other metals evaluated in this report. The load via fertilisers is, however, markedly lower than the annual load via maximum sewage sludge application. A comparison with critical load established for agricultural soils has not been possible as no suitable critical load for Hg has been identified. In order to improve the assessment of the long-term risks it is hence recommended to develop and use dynamic steady-state models suited to fit Danish conditions.

8 Ecotoxicological evaluation of nickel (Ni) in mineral fertilisers

8.1 Introduction

Nickel is essential for the normal growth of many species of microorganisms and plants and several species of vertebrates as well. However, it is toxic for most organisms when exposure is sufficiently high. Changes in soil environmental conditions, changes in pH, redox potential or soil solution composition, e.g. due to natural weathering processes, may enhance mobility of Ni in soils.

An effect assessment of Ni has been carried out by a few countries, including Denmark (Scott-Fordsmand and Pedersen 1995), the Netherlands (Crommentuijn et al 1997) and recently on the European level in EU-RAR (Ni) (2008). Within the present report, the EU risk assessment for Ni forms the basis for the derivation of the PNEC value for soil as the data has been evaluated according to quality and relevance in trans-national European scenarios, which is pertinent for an evaluation of EU-based cut-off values of Ni in mineral fertilisers.

8.2 Ecotoxicological data for soil dwelling organisms

A substantial number of toxicity studies are available for all three trophic levels in soils, i.e. microorganisms or microbial processes, plants and soil dwelling invertebrates. For these groups differences in toxicity have been observed both within the groups and between the groups.

Microbial processes

Tests with microbial processes are multi-species test, in which the native soil microbial community is exposed. The selected NOEC or EC_{10} values for Ni comprised functional parameters (n=39), and microbial species (n=13) (EU-RAR(Ni), 2008). The functional parameters were based on the carbon cycle (n=27), nitrogen cycle (n=12), including denitrification and mineralization of specific substrates. Enzymatic parameters were also considered in the effects assessment, with 6 different enzymatic processes compiled in the database. NOEC or EC_{10} values range from 28 mg Ni/kg to 2491 mg Ni/kg.

Plants

In the EU risk assessment report (EU RAR (Ni), 2008) data from the open literature were evaluated and combined with a specific Ni research program. A total of 68 individual high quality $L(E)C_{10}$/NOEC values (for 11 different species) were available for the assessment. The values range from 11.0 mg Ni/kg (*Lycopersicum esculentum*) to 1127 mg Ni/kg for (*Hordeum vulgare*).

Invertebrates
In EU RAR (Ni) (2008) a total of 37 individual NOECs (for 6 different species) are available ranging from 36.4 mg Ni/kg (*Folsomia candida*) to 1140 mg Ni/kg (Eisenia *fetida*).

Soil type dependency
Toxicity of Ni is well known to vary with soil properties. In EU-RAR (Ni) (2008) results from 16 soils (pan-European soils having contrasting properties) were evaluated for the relationship between soil physico-chemistry and Ni toxicity. The toxicity data from these studies were then tested by regressions between the EC10 values and the soil parameters, and the relationships were used to extrapolate between soil types. The CEC (cation exchange capacity) showed the best correlation with the toxicity values. Although it is known that toxicity depends on the soil type it is, however, at present not attempted to derive PNEC values that are soil type dependent or specified to specific Danish conditions.

Ageing
Most toxicity experiments are performed with soil to which a soluble Ni salt is added. This is typically not the situation in the field. At EU level, tests were therefore performed in order to estimate an ageing factor. Based on test with microorganisms, plants and invertebrates ageing studies over 1.5 years were conducted using soils with different pHs (3.6-7.7). An empirical model predicts almost no ageing effect up to pH 6 and an ageing factor of 2 at pH 7.0 and 3 at pH 7.5. These ageing factors have been taken into account when estimating the PNEC values (increasing the PNEC) in EU-RAR(Ni) (2008).

8.3 Risk evaluation

In EU-RAR(Ni) (2008) the toxicity data above were modelled for ageing and normalized towards typical physico-chemical conditions occurring in typical EU soils. The different scenarios (Sweden, Greece, The Netherlands, Denmark and Germany) were selected to provide *examples* of typical conditions covering a wide range of physico-chemical conditions (pH between 3.0 and 7.5; CEC between 2.4 and 36 cmol/kg, clay between 7 and 46%) occurring in EU soils. In this exercise both agricultural (arable soil and grassland) and natural soils (woodland and forest) of different textures were selected: sandy, loamy, clay and peaty soils. Based on the toxicity data presented above for microbial processes, plants and soil invertebrates, HC_5 values for each group of organisms could be extrapolated. The PNEC values were then derived by applying an uncertainty (assessment) factor of 2 to the HC_5 values. The PNECs derived for various soil type scenarios are presented in Table 8.1.

Table 8.1. The PNECs derived for various soil type scenarios in the EU Risk Assessment Report (EU-RAR (Ni) 2008).

Scenario	PNEC
Agricultural acid sandy soil (Sweden)	4.25
Agricultural loamy soil (The Netherlands)	49.6
Agricultural peaty soil (The Netherlands)	93.1
Natural acid sandy soil (Germany)	12.5
Natural clay soil (Greece)	96.1
Natural & agricultural soil (Denmark)	23.5

The PNEC of 23.5 mg/kg for the Danish soils is based on the use of statistical extrapolations (SSD) and is markedly higher than the generic PNEC of 1.1 mg Ni/kg, which could be estimated using an assessment factor of 10 on the lowest NOEC (11.0 mg Ni/kg for *Lycopersicum esculentum*). The impact of soil type and ageing would then be neglected. In this report a conservative estimate of the PNEC of 1.1 mg/kg is used as a worst case estimate for further assessment and risk evaluation.

8.3.1 Short-term risk evaluation

Based on the estimation of the total application (g/ha) of Ni through fertilizing of eight different agricultural management scenarios in Denmark (Table 2.8), a realistic worst case estimate of the soil concentration can be estimated. The maximum current load of Ni to agricultural land via fertilisers is estimated to be 63 g/ha/y (Table 2.8). This load is estimated for the scenario of cereal production where mineral fertilisers account for 100% of the Ni input from fertilisers. In the case where a maximum content of 120 mg/kg in mineral fertilisers is imposed, the same farm scenario leads to a maximum total load of Ni from fertilisers to agricultural land of 89.4 g/ha/y (Table 2.9).

Assuming a mixing zone, i.e. ploughing depth, of 20 cm and a soil density of 1.5 kg/L the maximum load of Ni from mineral fertilisers corresponds to 0.03 mg/kg soil in dry weight. The predicted environmental concentration (PEC) should be compared to the predicted no effect concentration (PNEC) in soil in order to quantify the potential risk (RQ = PEC/PNEC). In cases where the ratio (RQ) is below one, the potential short-term risk can be judged as acceptable.

PEC = 0.03 mg/kg
PNEC = 1.1 mg/kg
RQ = 0.03

The RQ of 0.03 is significantly lower than 1. This simplistic and generic risk assessment therefore shows that the use of mineral fertilisers complying with the suggested maximum content of Ni (120 mg Ni/kg) apparently does not pose any short-term risk to soil dwelling organisms.

8.3.2 Potential long-term risk

The risk assessment of Ni in EU (EU RAR (Ni), 2008) has estimated the potential accumulation based on a modelling approach defined in the EUSES (European Union System for the Evaluation of Substances). This large scale generic model shows that leaching and run-off can amount for up to 80% of the added Ni, but various models provide different results. In the EU risk assessment it was also calculated that a steady state can take up to 1500 years, depending on the input. A new advanced model is currently under development, but at present it is not considered feasible to derive steady state concentrations of Ni in agricultural soils.

There is currently no estimation of long-term accumulation of Ni in Danish soil. From Table 2.10 it can be seen that the load of Ni via mineral fertilisers containing Ni up to the proposed cut-off value in the EU will, together with the average atmospheric deposition, correspond to approximately 0.85% of the median background concentration monitored in Danish soils. The maximum load of Ni via mineral fertilisers, sums up to 61% of the maximum load of Ni via sewage sludge (Table 2.9).

Comparison with critical loads

The critical loads derived for Ni in the Netherlands (Reinds et al 2006) are 27-1700 and 30-770 g/ha/year for various types of forests and agricultural soils, respectively. The estimated total load of Ni from fertilisers (manure and mineral fertilisers) and atmospheric deposition was 89.4 g/ha/year (Table 2.9). This it is still in the lower range of the critical loads estimated for agricultural soils in the Netherlands although the critical load of the most sensitive soils is exceeded by a factor of three. However, it should be highlighted that the critical load models are associated with uncertainty and are furthermore not derived for Danish conditions.

8.4 Conclusion

A generic risk assessment of Ni in fertilisers reveals that there is no indication of short-term risks after one application. The annual load of Ni via fertilisers corresponds to approximately 0.85% of the background concentrations in Danish agricultural soils and is lower than the anticipated annual load via maximum sewage sludge application. A comparison with critical loads established for agricultural soils in the Netherlands indicates that long-term risks of Ni up to the cut-off value in mineral fertilisers cannot be ruled out in some of the most sensitive agricultural soils. However, in order to improve the assessment of the long-term risks it would be recommended to develop and use more advanced steady-state models suited to fit Danish conditions.

9 Ecotoxicological evaluation of non-regulated metals and PAH in mineral fertilisers

The previous chapters presented an ecotoxicological evaluation of a number of metals typically mentioned, analysed and suggested to be regulated in mineral fertilisers. However, as mineral fertilisers are natural products reflecting the natural content of soil constituents, other metals will naturally occur as well. This chapter sums up the potential ecotoxicological risk associated to a number of these. Focus is on the constituents analysed and reported in Petersen et al (2009). These include: Cobalt, fluoride, molybdenum, selenium, vanadium, thallium, titanium and uranium. Overall area-based loads are, however, available only for a small sub-set of these metals, i.e. copper, zinc, cobalt, selenium and vanadium. As the load of copper of zinc predominantly will be through the use of organic fertilisers, like manure or sewage sludge, these are excluded from the current assessment.

Generally the ecotoxicological information regarding the non-regulated metals reported in Petersen et al (2009) is very limited, especially when it comes to ecotoxicity towards soil dwelling species. Table 9.1 lists the existing soil quality criteria found in Canada, The Netherlands and Denmark. Many of these are derived on a limited set of data and often date 10 or 20 years back. However, as it is beyond the scope of this report to compile or generate ecotoxicity data these are the most useful data for an evaluation of the potential risk of rare metals in mineral fertilisers.

Based on an estimated area-based load of metals, the expected worst case increase in soil concentration after use of mineral fertilisers can be calculated. These are the result of one year of soil amendment neglecting as well out-flux from leaching and plant uptake as well as the potential risk of long term accumulation as a result of multiple applications. The latter is a consequence of the lack of available critical loads for these metals.

Table 9.1. Existing soil quality criteria (SQC, mg/kg) found in Canada and Denmark together with Maximum Permissible Addition (MPA) from The Netherlands (NL). In cases where land-use or soil-type dependent criteria exist, the most sensitive is presented. The SQC used for further assessment is presented in bold.

Constituents	SQC (Canada)[1]	MPA (NL)[2]	SQC (DK)[3]
Cobalt	40	**24**	---
Fluoride (inorganic)	**200**	---	---
Molybdenum	5	253	**2.0**
Selenium	1.0	**0.11**	1.0
Thallium	1.0	**0.25**	0.5
Titanium	---	---	---
Uranium	**23**	---	---
Vanadium	130	**1.1**	---

[1] Canadian Soil Quality Guidelines for the Protection of Environmental and Human health (accessible from www.ccme.ca)
[2]RIVM report 601501 001, Crommentuijn et al 1997.
[3] Scott-Fordsmand and Pedersen 1995.

Table 9.2. A crude short-term risk assessment of three metals based on a comparison of the estimated increase in soil concentration (PEC), after one year of soil amendment with mineral fertilisers, with the lowest soil quality criteria listed in Table 9.1.

Constituents	Dose kg/ha	PEC[1] mg/kg	Limit value[2] mg/kg	RQ[3]
Cobalt	2.0	0.0007	24	<0.001
Selenium	0.2	0.00007	0.11	<0.001
Vanadium	27	0.009	1.1	0.008

[1] Calculated on the basis of the area-based load and a homogenous distribution in the upper 20 cm of a soil with a density of 1.5 kg/L
[2] The lowest soil quality criteria taken from Table 9.1
3 RQ = PEC/limit value

As mentioned above, area-based loads of only three of the listed metals are available for Danish scenarios. A quantitative assessment is therefore restricted to these metals as presented in Table 9.2. The calculations in Table 9.2 show that there are no short-term risks of the applications of cobalt, selenium and vanadium with fertilisers.

Qualitative assessments of the remaining substances are presented below.

Fluoride: The concentration in mineral fertilisers is measured in g/kg indicating a relative high load to arable land. The soil quality criterion is on the other hand relative high, i.e. 200 mg/kg, indicating a relative low toxic potential to soil dwelling species.
Molybdenum: The concentration in mineral fertilisers is measured in the lower mg/kg range indicating a relative moderate load to arable land. The lowest soil quality criterion is 2.0 mg/kg, indicating a moderate toxic potential to soil dwelling species.
Thallium: The concentration in mineral fertilisers is measured in mg/kg indicating a relative moderate load to arable land. No soil quality criterion has been identified.
Uranium: The concentration in mineral fertilisers is measured to be as high as 150 mg/kg in Phosphorous fertilisers indicating a relative high load to arable land. The lowest soil quality criterion is 23 mg/kg, indicating a moderate toxic potential to soil dwelling species.
Titanium: The concentration in mineral fertilisers is measured in µg/kg indicating a relative low load to arable land. The lowest soil quality criterion is 2.0 mg/kg, indicating a moderate toxic potential to soil dwelling species.
Polyaromatic Hydrocarbons (PAH): The concentration in mineral fertilisers is measured in µg/kg indicating a low load to arable land. The existing Danish soil quality criterion is 1.0 mg/kg, indicating a moderate toxic potential to soil dwelling species.

On the basis of the quantitative and qualitative short term assessments presented above the following conclusions can be made:

- Based on a quantitative risk assessment no unacceptable short-term risk of cobalt, selenium and vanadium to soil dwelling species is anticipated.
- Based on a qualitative risk assessment no unacceptable short-term risk of fluoride, molybdenum, thallium, titanium, and PAH to soil dwelling species is anticipated.
- Based on a qualitative risk assessment it is uncertain to what extend the relative high levels of uranium observed in phosphorous fertilisers could pose a long-term environmental risk.
- The potential risk of copper and zinc in mineral fertilisers has not been assessed as it is anticipated that the load from organic fertilisers like manure or sewage sludge by far exceed the load from mineral fertilisers.
- Critical load of the metals included in this chapter has not been established and therefore the long-term risk of potential accumulation in the soil environment cannot be assessed.

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