Limit value for chromium for EU-fertilising products based on animal by-products

Scientific note from DCE – Danish Centre for Environment and Energy

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1 Background

The Agency for Green Transition and Aquatic Environment (SGAV) under the Danish Ministry of Green Transition (MGTP) has on July 7, 2025, asked the Danish Centre for Environment and Energy (DCE) at Aarhus University to make a scientific assessment of a new proposal for chromium limit-values in EU-fertilising products. DCA has previously assessed whether the limit values for chromium and vanadium set under the EU Fertilising Products Regulation are relevant in a Danish context (Krogh et al., 2022)

The background for the request is a new background report produced by Q-Lab Analytical Laboratory assessing the criteria that should be applied to animal by-products that can be used as components in CE-marked fertilising products under the EU Fertilising Products Regulation (2019/1009)[1][2] (Sfetsas et al., 2025)

One of the aspects described in the report from Q-Lab Analytical Laboratory concerns a limit value for chromium, including from residual products from the leather industry. The purpose of the criteria is to ensure that fertilising products are of good agronomic quality and do not pose a risk to human, animal, or plant health or to the environment.

SGAV expects to have the opportunity to comment on a draft of the upcoming delegated act on animal by-products under the EU Fertilising Products Regulation (2019/1009), in which limit values for, among other substances, chromium are expected to be set. In this context, SGAV requests DCA to review the limit values for chromium in EU fertilising products proposed by Q-Lab Analytical Laboratory. The response should include an assessment of the risks to soil-dwelling organisms, plants, and potential losses to the aquatic environment (groundwater and surface waters).

This reply is an expansion of the earlier assessment of limit values for chromium (Cr) and vanadium (Va) made in 2022 (Krogh et al., 2022). The new assessment focuses on the assessment made by Sfetsas et al. (2025) in a technical study and includes risks to both soil-dwelling organisms, plants, and potential losses to the aquatic environment (groundwater and surface waters).

In the earlier assessment by Krogh et al. (2022), it was concluded that the proposed limit value of **400 mg Cr/kg** for chromium in fertiliser products would not be acceptable, as the soil quality criteria are already exceeded in some agricultural soils. Furthermore, it was recommended that, as a minimum, the existing limit values of **100 mg Cr/kg** for sewage sludge and bio-ash should also apply to other types of fertilising products, including those containing by-products and recycled materials, until specific limit values have been established for these products.

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[1] https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A02019R1009-20241120

[2] https://circabc.europa.eu/ui/group/36ec94c7-575b-44dc-a6e9-4ace02907f2f/library/4fb33aed-a3fd-4ffe-86ad-7858fe2588dd/details

2 Estimation of maximum fertiliser application based on phosphate and nitrogen as a worst-case scenario

For the assessment of the proposed limit values, it is necessary to estimate the amounts that could potentially be applied to agricultural land. These estimates are often based on nitrogen (N) and phosphorus (P) application limits set in the Danish fertiliser use regulations (Ministeriet for Fødevarer Landbrug og Fiskeri, 2021).

For fertilisers with a phosphorus effect, a minimum content of 2% P in dry matter (DM) is assumed. At the same time, the maximum permitted application of phosphorus is set at 30 kg P/ha. This means that a maximum of 1500 kg DM/ha can be applied to the topsoil layer.

For organic fertilisers with a nitrogen effect, a minimum content of 2.5% N in dry matter is assumed (with a C/N ratio of approximately 16), and the maximum permitted application corresponds to 170 kg N/ha. This means that a maximum of 6800 kg DM/ha can be applied to the topsoil layer.

For organic fertilisers, these estimates imply that an application of up to 6800 kg DM/ha can be used as a worst-case scenario. In contrast, the annual application rate for inorganic fertilisers is normally below 2000 kg DM/ha.

The Q-Lab background report (Sfetsas et al., 2025) discusses the use of wet blue leather-based products, a by-product of the leather industry, which supposedly offers significant agronomic benefits and efficiency when processed into fertilisers, aligning well with circular economy principles. The high collagen content in wet blue leather makes it a valuable nitrogen source. According to Sfetsas et al. (2025), vast differences in application rate has been documented for wet blue in the bibliography, ranging for example from 4-32 t/ha for common beans and 2.5-5 t/ha for peas. However, for their impact assessment in the technical study, Sfetsas et al. (2025) choose an application rate of 4 t/ha.

3 Investigation of Cr levels in Danish soils, fresh- and groundwater

3.1 Soils

The total content of heavy metals in Danish agricultural and natural soils was investigated in a monitoring programme conducted in 1992/93. This programme included samples taken from approximately half of the sites in the Danish Nitrate Monitoring Grid, in practice 393 sites, providing good geographical coverage of the country (Larsen et al., 1996). The numbers are not recent, but the average values are not expected to have increased much since 1992/93 (Bak and Elsgaard, 2025).

In the 1992/93 study, the following median concentrations of chromium in soil were found: **9.9 mg/kg** (overall median), **6.4 mg/kg** in sandy soils, **17.1 mg/kg** in clay soils, **10.7 mg/kg** in arable land, and **3.8 mg/kg** in natural soils. For arable land, concentrations vary between **3.0 and 31.4 mg/kg** (5. – 95. Percentile). Chromium concentrations in soils that had received sewage sludge were higher than in arable soils in general, with a median value of **12.3 mg Cr/kg**. Soil texture explained a significant proportion of the variation in chromium content (r^2 = 0.81). It can be noted that levels in agricultural soils in some other European countries can be substantially higher.

The main anthropogenic sources for Chromium reported in this study (Larsen et al., 1996) was: Wear and tear of chromium-treated surfaces (**13–100 t/yr**), Application of commercial fertilisers (**50–80 t/yr**), Livestock manure (**10–20 t/yr**), Agricultural lime (**10 t/yr**), Wear from paint (**10–20 t/yr**), Application of sewage sludge (**3 t/yr**), Disposal of municipal waste (**8 t/yr**) and Atmospheric deposition (**30 t/yr**). It can be noted that on country scale, atmospheric deposition gives a similar contribution as manure and lime together, i.e. 20-30 t/yr). On agricultural land, which constitutes 61 % of the Danish land area, the contribution from fertiliser, manure and lime are dominating. An average supply based on the numbers in (Larsen et al., 1996) is **3.44 mg/m²/yr**.

3.2 Fresh- and groundwater

The median value found in the NOVANA operational monitoring in streams is **0.12 µg/l,** and the 90 percentile is **0.28 µg/l (**Lassen et al, 2024). The median value for groundwater found in the groundwater monitoring (GRUMO) is below the detection limit (<DL), and the 90 percentile is **0.88 µg/l** (Boutrup et al., 2015).

3.3 Speciation, binding

Chromium is an essential trace element for many organisms and occurs in the soil environment primarily in trivalent or hexavalent forms, i.e. Cr(III) and Cr(VI), respectively. The oxidised form, Cr(VI), forms salts that are relatively mobile, whereas salts of the reduced Cr(III) form bind strongly, particularly to the organic fraction of the soil, but also to clay minerals and other negatively charged substances and are relatively insoluble at neutral pH. Cr(III). Cr(VI) is water-soluble, but is relatively easily reduced in the presence of organic matter. Cr(III) is considered the most common oxidation state in soils, but under specific conditions it can be oxidised to Cr(VI). Chromium bound to organic matter is only slightly affected by pH. Typically, only a relatively small fraction of the total chromium in soil is bioavailable to organisms (Larsen et al., 1996) (Bak and Elsgaard, 2025).

Figure 1 shows the pH dependency of the binding of Cr(III) and Cr(VI) in soil. It can be noted that within the typical pH range of agricultural soils, Cr is quite hard bound to soil.

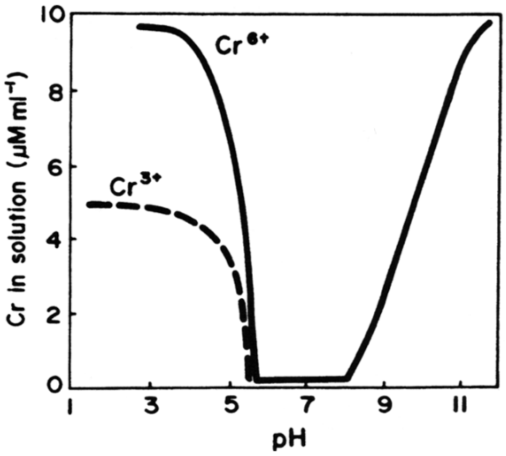

Figure 1. *The pH dependency of the binding of Cr(III) and Cr(VI) in soil (Kabata-Pendias & Pendias, 2001)*

3.4 Transformation of Cr(III) to Cr(VI)

Transformation between Cr(III) and Cr(VI) therefore has significant implications for the effects of chromium in soils.

There is no solid evidence that bacteria enzymatically oxidise Cr(III) to Cr(VI) as part of their metabolism, although the process may occur chemically (Liang et al. 2021). In contrast, a range of bacteria are capable of reducing the toxic Cr(VI) form to Cr(III) as part of their energy metabolism, in which Cr(VI) serves as a terminal electron acceptor. This reduction process generally requires anaerobic conditions and has been studied in facultative anaerobic bacteria such as *Shewanella* and *Aeromonas*, but it has also been observed in some aerobic *Pseudomonas* species (Kertesz & Frossard 2024).

The chemical transformation (oxidation) of Cr(III) to Cr(VI) primarily occurs in oxidising, well-drained and oxygen-rich soils with neutral to alkaline pH, especially where the content of manganese oxides is high. Manganese oxides are considered the most important natural oxidising agents for Cr(III) (Liang et al. 2021). Hexavalent Cr(VI) can, thus, be formed by oxidation of Cr(III) with molecular oxygen (O_2) and soil manganese oxides (MnO_2). Oxidation by O_2 alone is only relevant under strongly alkaline conditions (pH > 9). Consequently, manganese oxides are regarded as the dominant oxidants of Cr(III) in soils (Bartlett & James 1979), as illustrated by the overall oxidation reaction (Reijonen & Hartikainen 2016):

$$1.5\ MnO_2 + Cr(OH)^{2+} \rightarrow HCrO_4^{-} + 1.5\ Mn^{2+}$$

Experimental studies in agricultural soils show that oxidation of Cr(III) to Cr(VI) under normal cultivation conditions is limited. Reijonen & Hartikainen (2016) found that net oxidation of Cr(III) in oxic agricultural soils without the addition of extra manganese oxides was negligible, even when Cr(III) was added.

The results indicate that oxidation is governed by two opposing processes:

(1) oxidation of Cr(III) to Cr(VI) by manganese oxides, and
(2) simultaneous reduction of the formed Cr(VI) back to Cr(III) by soil organic matter (Reijonen & Hartikainen 2016).

3.5 Soil Quality Criteria for Chromium

Cr(VI) has a higher toxicity than Cr(III) and, therefore, normally also lower limit values. However, it is not always possible to distinguish between the different forms of chromium, and therefore a common value for total Cr is often used. There is a limit value of **30 mg/kg** for soils where sewage sludge can be applied[3], and a limit value for the content in sewage sludge and bioash set at **100 mg Cr/kg DM** (Miljø- og Fødevareministeriet, 2008, 2018). Furthermore, an ecotoxicological based soil quality criteria of **50 mg/kg** has been established based on effects on soil fauna (Larsen et al., 1996). A similar value can be used for plants.

Cr(VI) is far more toxic than Cr(III), with predicted no-effect concentration (PNEC) values reported **as 0.035 mg/kg** and **3.2 mg/kg**, respectively, in an ecotoxicological evaluation of chromium in mineral fertiliser products in Denmark (Sørensen et al. 2011).

In ECHA's risk assessment for hexavalent chromium (Cr (VI)), the PNEC for soil is: **0.15 mg/kg WW** (wet weight) in acidic conditions and **0.006 mg/kg WW** under other conditions. For trivalent chromium (Cr(III)), PNEC values are **3.3 mg/kg WW** in acidic conditions and **62 mg/kg WW** under other conditions (ECHA, 2021).

The PNEC values are very low compared with the measured median concentration of **17.1 mg Cr/kg** in clayey soils and suggest caution regarding the relaxation of chromium application limits. The PNEC values are, however, not necessarily relevant under Danish conditions, where the **5th percentile** of chromium concentrations in soils on natural sites is already 1.3 mg/kg (Larsen et al., 1996). This means that plant species and communities in Denmark are already exposed to soil Cr concentrations of at least **1.3 mg/kg** at **95%** of monitored sites and therefore may already be adapted to these concentration levels.

3.6 Plants, water

Sfetsas et al. (2025) describe the content of Cr in the product based on blue leather as dominated by Cr(III). As described in section 1.3 (and figure 1), Cr in soil is quite hard bound in the pH range found in arable soils. For crops, it is expected that the application can be managed so the positive agronomic effects of the fertiliser use outweigh any negative effects of Cr addition to the soil, at least in the short run. The worry is therefore more the accumulation of

[3] BEK nr. 1001 af 27/06/2018

Cr in the soils and the consequences hereof if the land use at a later stage changes, e.g. to nature, which might lead to a decline in pH. A higher mobilization of Cr can affect the plant species of the coming nature area but may also lead to higher loading of surface- and groundwater. Cr limit values for soil fauna and plant species can be comparable (50 mg/kg), but some plant species might be even more sensitive (e.g. Kabata-Pendias & Pendias, 2001).

Limit values for Cr in soil water used in critical load calculations aimed at protecting groundwater and soil fauna are of similar size (**44 and 50 µg/l**) (Reinds et al. 2006) (Bak and Elsgaard, 2025). Danish limit values for freshwater are **3.4 µg/l** for Cr(VI) and **4.9 µg/l** for Cr(III). For drinking water, there is a limit of **20 µg/l** where the water enters the property.

4 Model, scenarios and parameters.

4.1 Model

More or less complicated models for metals in soil exist and have been used e.g. for calculating critical loads aimed at protecting soil, fauna and groundwater (Reinds et al. 2006). Here, we have used a very simple model for Cr in soil because calculations will be made for parameters estimated for a 'worst case' situation. The model architecture resembles the model used in the previously mentioned consultancy study by Q-Lab (Sfetsas et al., 2025). To ease comparison, the same units for parameters are used as in this study.

The model is an ordinary differential equation of form:

$$\frac{dC}{dt} = I - K_s \cdot C(t)$$

And solution:

$$C(t) = \frac{I}{K_s}(1 - e^{-K_s t}) + C(0) \cdot e^{-K_s t}$$

C(t): soil concentration of metal at time t
I: constant annual input rate (from fertiliser + atmospheric deposition), scaled to soil mass.
K_s * C(t): first-order loss term (leaching, plant uptake, etc.).

Where the first-order loss term, Ks, can be expressed as:

$$K_s = \frac{P}{\theta * Z * \left(1 + BD * \frac{K_d}{\theta}\right)}$$

K_s: soil loss constant (1/yr)
P: average annual percolation (cm/yr)
Z: soil mixing depth (cm)
BD: soil bulk density (g/cm^3)
K_d: soil-water partitioning coefficient (mL/g)
θ: soil volumetric water content (mL/cm^3)

Removal with crop uptake is omitted because the scale is expected to be a few percent of leaching (Salo et al., 2018)(Kabata-Pendias & Pendias, 2001). The model can calculate soil water concentrations, which can be used to assess risk to surface and drinking water because the concentration in the water percolating from the mixing layer is expected to be the same.

However, only a fraction of percolated Cr will reach groundwater and there will be a large dilution in streams. This is not part of the model, and it is therefore not possible to compare calculated soil water concentrations directly with limit values for freshwater or groundwater. Therefore, a limit value for soil water is used (cf. section1.5).

It has not been possible to establish a model for the possible transformations between Cr(III) and Cr(VI) that could be used based on generalised parameters for all soils or could be used for a 'worst case' situation. Calculations are therefore for total Cr, assuming the far greatest part of Cr in arable soils will be in the form of Cr(III). It could, however, be part of a risk assessment to acknowledge that, on some soils, a not negligible part of the total Cr content could be Cr(VI).

4.2 Scenarios and parameters

As described earlier, in general it is not desirable to allow an accumulation of Cr in soils that will lead to a rapid increase in soil concentrations to a level that will exceed soil quality criteria and / or will pose a risk to fresh- or groundwater if e.g. a future land use change would result in a decrease in soil pH and a higher mobility of Cr.

We have looked at different scenarios that could be used as a basis for setting a limit value for the Cr content in the applied product: i) zero accumulation in soils, ii) allowed accumulation up to a steady state value of 30 mg/kg, which is the limit for soils where sewage sludge can be applied. In addition, the expected concentrations in soil water have been calculated in a situation where afforestation will take place on former arable soils.

Because the idea is to have a single limit value applicable for all areas, calculations should in principle be made with 'worst case' parameters. There is, however, very large variation in soil- and other parameters, especially the Kd values, so in practice a set of parameters have been selected that are precautionary, but not 'worst case' in a strict sense. It should also be noticed that the selection has been for parameters there are 'worst case' concerning accumulation in soil, but not necessarily 'worst case' for soil water concentrations.

As described in section 1.2.1, there are several significant sources for Cr in soil and significantly higher levels of Cr in arable soils compared to soils in nature areas. Calculations are made for arable soils and for afforestation. Only inputs from air pollution and fertiliser are included in the mass balance because the application of the product is expected to use the N quota, and other sources of pollution will be less relevant for agricultural soils.

Parameters used are: P (average annual percolation): 20cm/yr, θ (soil volumetric water content): 0.3 mL/cm^3, Z (soil mixing depth) 20 cm, BD (soil bulk density) 1.7 g/cm^3, Kd (soil-water partitioning coefficient): 3000 mL/g, atmospheric Cr input: 0.16 mg/m^2/yr, maximum application of product: of 6800 kg DM/ha/yr. For calculation of soil accumulation, 'worst case' is the lowest starting point for soil concentrations, where the 5. Percentile based on monitoring data of 3.0 mg/kg has been used.

Calculations are especially sensitive to the Kd value used. Kd for Cr depends both on pH and organic content in soil. We have used the formula:

$\log \mathrm{Kd}\ (\mathrm{Cr(III)}) = 1.61 + 0.290\ \mathrm{pH} + 0.381 \log \mathrm{orgC}(\%)$ based on Eggen et al. (2022)

The value of 3000 reflects comparable low pH and high organic content for arable land, but is used as 'worst case' for risk to freshwater and groundwater.

In a long-term study with afforestation on former agricultural soils in Denmark, Ritter et al. (2003) have shown a decline in pH of around 1.5 units, both for oak and Norway spruce. For this situation, we have used a Kd value of 700 to test possible violations of limit values for soil water.

5 Results and conclusions

A calculation aimed at securing no accumulation of Cr on all areas where the product might be applied will allow (with 'worst case' parameters) a load of 0.19 mg Cr / m^2, which corresponds to an allowable content in product applied of 3.5 mg/kg if the application was the only input. In practice, it will be necessary to account for atmospheric input allowing practically no application on the most sensitive soils. Steady state soil water concentrations would be 1 µg/l, well below limit values.

Allowing accumulation up to a limit value of 30 mg/kg for soils, where sewage sludge can be applied, would allow a content in the product of 35 mg/kg. Steady state soil water concentrations would be 10 µg/l, which is still below limit values used for critical load calculations.

Afforestation lowering pH with 1.5 units would mean that soil water concentrations in a transition phase of some decades can go up to 43 µg/l, equalling the limit for protection of groundwater that has been used in critical load calculations.

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