

Sewage Sludge Ordinance
- Klärschlammverordnung -
(AbfKlärV)*)

Of 15 April 1992

(Federal Law Gazette BGBl. I p. 912), as amended by Article 1 of the Ordinance of 6 March 1997 (Federal Law Gazette BGBl. I, p. 446), by Article 3 of the Act to Reform Nature Conservation and Landscape Management Law and Amend Other Statutory Provisions (*Gesetz zur Neuregelung des Rechts des Naturschutzes und der Landschaftspflege und zur Anpassung anderer Rechtsvorschriften*) of 25 March 2002 (Federal Law Gazette BGBl. I, p. 1193), by Article 2 of the Ordinance to Amend Requirements of Proof under Waste Management Law (*Verordnung zur Änderung abfallrechtlicher Nachweisbestimmungen*) of 25 April 2002 (Federal Law Gazette BGBl. I p. 1488), by Section 11 of the Fertiliser Ordinance (*Düngemittelverordnung*) of 26 November 2003 (Federal Law Gazette BGBl. I p. 2373), by Article 4 of the Ordinance on Simplifying the Monitoring under Waste Management Law (*Verordnung zur Vereinfachung der abfallrechtlichen Überwachung*) of 20 October 2006 (Federal Law Gazette BGBl. I p. 2298), by Article 19 of the Act to Reform Nature Conservation and Landscape Management Law (*Gesetz zur Neuregelung des Rechts des Naturschutzes und der Landschaftspflege*) of 29 July 2009 (Federal Law Gazette BGBl. I p. 2542) and by Article 9 of the Ordinance to Implement the Services Directive in the Field of Environmental Law and to Amend Environmental Law Provisions (*Verordnung zur Umsetzung der Dienstleistungsrichtlinie auf dem Gebiet des Umweltrechts sowie zur Änderung umweltrechtlicher Vorschriften*) of 9 November 2010 (Federal Law Gazette BGBl. I p. 1504).

On the basis of Section 15, sub-section 2 of the Waste Avoidance and Waste Management Act of 27 August 1986 (Federal Law Gazette I, p. 1410, 1501) and in agreement with the Federal Minister for Food, Agriculture and Forestry and with the Federal Minister for Health, the Federal Minister for the Environment, Nature Conservation and Nuclear Safety does hereby order, on the basis of Section 11, sub-section 2, sentence 3, sub-section 3, sentence 4 of this Act the Federal Minister for Environment, Nature Conservation and Nuclear Safety does hereby order:

*) This Ordinance serves to implement Council Directive 86/278/EEC of 12 June 1986 on the protection of the environment and in particular of the soil when sewage sludge is used in agriculture (Official Journal of the EC, no. L 181 p. 6).

Section 1

Scope

(1) This Ordinance must be observed by anyone who

1. operates waste-water treatment plants and surrenders or intends to surrender sewage sludge for application on agriculturally or horticulturally used soils,
2. applies or intends to apply sewage sludge on agriculturally or horticulturally used soils.

(2) The provisions under fertiliser law shall remain unaffected.

(3) The bodies concerned shall work towards ensuring that the limit values specified in this Ordinance are as far as possible not overstepped. The soil limit values specified in this Ordinance have been defined for the specific conditions of agricultural sewage sludge utilisation. It shall not be possible to derive general cultivation restrictions or restrictions of any other type from these values being attained or exceeded.

Section 2

Definition of terms

(1) Waste-water treatment plants shall be understood to mean plants for the treatment of waste water, irrespective of capacity and treatment type. Small-scale treatment plants shall be understood to be plants with several chambers for the treatment of domestic waste water with a sewage inflow of less than 8 cubic metres per day. Waste-water collection pits without any discharge outlet shall not be understood to mean waste-water treatment plants within the meaning of the Ordinance.

(2) Sewage sludge shall be understood to mean sludge, also de-watered or dried or treated in any other form, accruing from the treatment of waste water in waste-water treatment plants, including associated plants for further-reaching waste-water purification. Crude sludge shall be understood to mean sludge that is withdrawn in an untreated state from waste-water treatment plants. The de-watering of crude sludge shall not be considered as the treating of sewage sludge. Sludge accruing in small-scale sewage plants shall be understood to mean sewage sludge within the meaning of this Ordinance. Sewage sludge within the meaning of this Ordinance shall be deemed

to include sewage sludge composts and sewage sludge mixtures. Sewage sludge mixtures shall be understood to mean mixtures produced from sewage sludge and other suitable substances specified in Annex 2 Tables 11 and 12 of the Fertiliser Ordinance as last amended. Sewage sludge composts shall be understood to mean composted sewage sludge mixtures.

(3) Field forage within the meaning of this Ordinance shall be understood to be plant species grown on arable land and whose vegetative components are intended for feeding to animals. The growing of maize shall not be considered as field forage cropping within the meaning of this Ordinance.

Section 3

Conditions permitting application

(1) Sewage sludge may only be applied on agriculturally or horticulturally used soils in such a way that it does not adversely effect the common weal, and that the manner, quantity and time of application is geared to the nutrient requirements of the plants after allowing for the nutrients and organic substance available in the soil as well as for site-related and growing conditions. The application of sewage sludge shall moreover be subject to the provisions laid down in Fertiliser Law accordingly.

(2) Before applying sewage sludge on agriculturally or horticulturally used soils for the first time, the operator of a waste-water treatment plant shall undertake to have their content of lead, cadmium, chromium, copper, nickel, mercury and zinc analysed on the basis of soil analyses performed by a body appointed by the responsible authority.

(3) The soil analyses specified in sub-section 2 shall be repeated at intervals of 10 years. The responsible authority shall, in agreement with the responsible specialised agricultural authority, order that the soil analyses be repeated at shorter intervals if, on the basis of the result of sewage sludge and soil analyses conducted and after allowing for the application volume and for other causes of heavy-metal pollution, it must be feared that the values set down in Section 4, sub-section 8 will be exceeded. It shall be able to restrict the additional soil analyses to specific units of land and heavy metals.

(4) Sewage sludge may only be applied if the soil has been analysed in relation to its pH value, content of plant- available phosphate, potassium and magnesium. The costs of conducting this soil analysis shall be borne by the operator of the waste-water treatment plant.

(5) Sewage sludge may only be surrendered for application on agriculturally or horticulturally used soils or applied on such if samples of the sewage sludge are analysed at intervals of at the most six months by a body appointed by the responsible authority to establish the contents of lead, cadmium, chromium, copper, nickel, mercury and zinc, the sum of organic halogen compounds as adsorbed organically bound halogens (AOX), total and ammonia nitrogen, phosphate, potassium, magnesium as well as the dried residue, organic substance, basifying substances and the pH value. The responsible authority shall be able to extend the analysis to cover further constituents. It shall be able to reduce the interval between sewage sludge analyses down to two months. In doing so, it shall be able to restrict the analyses to specific heavy metals.

(6) Sewage sludge may only be surrendered for application on agriculturally or horticulturally used soils or applied on such if prior to the first time of application and thereafter at intervals of at most two years samples of the sewage sludge are analysed for the contents of the organic persistent pollutants

- polychlorinated biphenyls and
- polychlorinated dibenzodioxins and dibenzofurans.

Sub-section 5, sentence 3 shall apply accordingly. The analysis must be conducted by one of the bodies appointed by the responsible authority.

(7) The operators of waste-water treatment plants must conduct the sampling and analyses specified in sub-sections 2, 3, 5 and 6, or have such conducted, in accordance with the instruction contained in Appendix 1 of this Ordinance.

(8) In cases where sludge from small-scale treatment plants of an agricultural undertaking is applied on arable land owned by that undertaking, it shall not be necessary to observe the provisions contained in sub-sections 2 to 7. Before they are applied for the first time, sludges from such plants must be analysed for the parameters

specified in sub-section 5. The results must be submitted without delay to the responsible authority and to the responsible specialised agricultural authority.

(9) In respect of the application of sewage sludge from waste-water treatment plants for the treatment of domestic waste waters, municipal waste waters or waste waters with a similarly low level of pollution and with a capacity of less than 1,000 population equivalents, it shall, after an initial analysis under Section 2, be possible to dispense with the analyses specified in sub-sections 3 and 6. The analyses specified in sub-section 5 shall be performed at intervals of at most two years; the responsible authority shall be able to shorten the interval between analyses to six months or lengthen it to 48 months as well as extend the analysis to cover further constituents.

(10) In respect of small-scale treatment plants of individual households within the territory specified in Article 3 of the Unification Treaty, analyses under sub-sections 2 to 7 must only be performed up to 31 December 1998 upon the instruction of the responsible authority.

(11) Appointment as a body pursuant to sub-section 2, sub-section 5, sentence 1 and sub-section 6, sentence 3 shall be granted if the applicant is sufficiently qualified, independent and reliable and has the required technical equipment. The appointment shall be effected by the competent authority of the Land in which the applicant has established his business and shall be valid for the entire federal territory; if the applicant is not established in Germany, competence shall lie with the Land where the activity according to sub-sections 2, 5 and 6 is to be primarily conducted. The granting of an appointment may be subject to a proviso of revocation, to a time limit, specific conditions or obligations or to the proviso that obligations could be imposed subsequently. The competent authority may require an applicant who is engaged in activities beyond the regional level to present a valid DIN EN ISO/IEC 17025:2005 accreditation (available from Beuth-Verlag GmbH, 10772 Berlin, and archived in the German National Library in Leipzig) covering the parameters and methods of analysis set out in Annex 1 below. Procedures under this provision may be handled by points of single contact. The application for appointment as a body must be processed within a period of three months; Section 42a sub-section 2, sentences 2 to 4 of the Administrative Procedure Act (*Verwaltungsverfahrensgesetz*) shall apply.

(12) Accreditations of equivalent value issued by another Member State of the European Union or another Contracting Party to the Agreement on the European Economic Area shall be deemed equivalent to appointments pursuant to sub-section 2, sub-section 5, sentence 1 and sub-section 6, sentence 3. When an application for appointment pursuant to sub-section 2, sub-section 5, sentence 1 and sub-section 6, sentence 3 is processed, proofs furnished by another Member State of the European Union or another Contracting Party to the Agreement on the European Economic Area shall be deemed equivalent to national proofs if they evidence the applicant's compliance with the relevant requirements of sub-section 11, sentence 1 or with the requirements of the accrediting country which are essentially comparable as regards their purpose. Documents proving accreditation within the meaning of the first sentence above or other proofs pursuant to the second sentence above shall be supplied to the competent authority in their original form or as copies prior to the start of the activity. The applicant may be required to produce a certified copy or a certified German translation of a document.

Section 4

Application bans and restrictions

(1) It shall be prohibited on agriculturally or horticulturally used soils to apply crude sludge or sludge from waste-water treatment plants other than for the treatment of domestic waste waters, municipal waste waters or waste waters with a similarly low pollutant content.

(2) It shall be prohibited to apply sewage sludge on areas of land used for the growing of fruit and vegetables. On arable land also used for growing field vegetables it shall be prohibited to grow field vegetables in the year in which the sewage sludge is applied as well as in the year thereafter.

(3) On arable land used for growing field forage or for growing sugar beet, insofar as the sugar beet foliage is used as feedstuff, it shall only be permissible to apply sewage sludge prior to sowing and with subsequent deep-turn tillage. On land used for growing silo and green maize, the sewage sludge must be worked into the soil prior to sowing.

(4) It shall be prohibited to apply sewage sludge on permanent grassland.

(5) It shall be prohibited to apply sewage sludge on soils used for purposes of forestry.

(6) It shall be prohibited to apply sewage sludge on agriculturally or horticulturally used soils in nature conservation areas, national parks, national nature monuments, natural monuments, protected landscape elements and legally protected biotopes within the meaning of Section 30 of the Federal Nature Conservation Act

(*Bundesnaturschutzgesetz*) unless an exemption has been issued under Section 5.

(7) It shall be prohibited to apply sewage sludge on soils in Zones I and II of water protection zones as well as on soils in strips of land of up to 10 m in width alongside water bodies. Further-reaching regulations for water protection zones under the provisions contained in water legislation shall remain unaffected.

(8) It shall be prohibited to apply sewage sludge on agriculturally or horticulturally used soils if the soil analyses under Section 3, sub-section 2 or 3 show that the contents of the following heavy metals exceed at least one of the following values (milligrammes per kilogramme of dry matter):

lead	100
cadmium	1.5
chromium	100
copper	60
nickel	50
mercury	1
zinc	200

In the case of soils that are classified as light soils within the scope of soil rating and the clay content of which falls below 5 per cent or whose analysis under Section 3, sub-section 4 has shown a pH value of more than 5 and less than 6, it shall also be prohibited to apply sewage sludge insofar as the following values (milligrammes per kilogramme of dry matter) are exceeded for the heavy metals of cadmium and zinc:

cadmium	1
zinc	150

(9) It shall be prohibited to apply sewage sludge on agriculturally or horticulturally used soils insofar as for these soils it is the aim of proper management to achieve a pH target value of 5 or less or the analysis under Section 3, sub-section 4 produces a pH value of

5 or less. Soils with a pH target value in excess of 5 within the scope of proper management shall require a lime dressing with liming material if this value is not reached and prior to the application of sewage sludge. In calculating the quantity of lime, allowance must be made for the basifying components to be subsequently applied in the sewage sludge.

(10) It shall be prohibited to apply sewage sludge on agriculturally or horticulturally used soils if the sewage sludge analyses under Section 3, sub-section 6 show that the contents of the following organic persistent pollutants exceed at least one of the following values:

- polychlorinated biphenyls (PCB): in each case 0.2 milligrams per kilogram of sludge dry matter for component numbers 28, 52, 101, 138, 153, 180;
- polychlorinated dibenzodioxins/dibenzofurans (PCDD/PCDF): 100 nanogrammes of TCDD toxicity equivalents (in accordance with the calculation formula in Appendix 1) per kilogram of sludge dry matter.

(11) It shall be prohibited to apply sewage sludge on agriculturally or horticulturally used soils if the sewage sludge analyses under Section 3, sub-section 5 show that the sum of halogen organic compounds, expressed as the sum parameter AOX, exceeds 500 milligrammes per kilogramme of sludge dry matter.

(12) It shall be prohibited to apply sewage sludge to agriculturally or horticulturally used soils if the sewage sludge analyses under Section 3, sub-section 5 show that the contents of the following heavy metals exceeds at least one of the following values (milligramme per kilogramme of sludge dry matter):

lead	900
cadmium	10
chromium	900
copper	800
nickel	200
mercury	8
zinc	2.500

In the case of soils classified as light soils within the scope of soil rating and whose clay content is below 5 per cent or whose analysis under Section 3, sub-section 4 has revealed a pH value exceeding 5 and less than 6, the following values must be read in sentence 1 for cadmium and zinc:

cadmium	5
zinc	2.000

(13) When producing sewage sludge composts and sewage sludge mixtures, the pollutant values contained in sub-sections 10, 11, and 12 shall refer both to the sewage sludge and additives used prior to mixing as well as to the produced compost or mixture. When applying a mixture produced by using sewage sludge, a pollutant load resulting from the product of those pollutant contents permissible under sub-sections 10, 11 and 12 and the application quantity permissible under Section 6, sub-section 1 must not be exceeded.

(14) Sewage sludge may only be stored on or in the vicinity of the area of application insofar as such is necessary for the application.

Section 5

Exemption regulations

The responsible authority shall, in agreement with the responsible nature conservation authority, be able on a case-to-case basis to issue a permit for the application of sewage sludge on arable land in nature reserve, nature benchmarks, national parks, protected parts of the landscape and areas under Section 30 of the Federal Nature Conservation Act.

Section 6

Application quantity

(1) It shall be permissible within a period of 3 years to apply on those soils specified in section 1 no more than 5 tonnes of sewage sludge dry matter per hectare. Sewage sludge composts may be applied within a period of 3 years at a rate of up to 10 tonnes of dry matter per hectare if the pollutant contents of the sewage sludge compost do not exceed one half of heavy metal contents permissible under Section 4, sub-section 12 and one half of the contents of organic pollutants permissible under Section 4, sub-section 10.

(2) In the event of a mixture produced by using sewage sludge being applied, the application quantity permissible under sub-section 1 shall refer to the sewage sludge used and not to the mixture. The proportion of sewage sludge must be verified by the supplier and made known to the user. Section 4, sub-section 13, sentence 2 shall apply irrespectively hereof.

Section 7

Obligations to furnish verification

(1) At the latest two weeks before surrendering the sewage sludge, the operator of the waste-water treatment plant or an authorised third party shall give notice of the intended application to the authority responsible for the application area and to the specialised agricultural authority by submitting a carbon copy of the completed delivery note as per the specimen presented in Appendix 2 of this Ordinance.

(2) The operator of the waste-water treatment plant shall record on the delivery note the time at which the sewage sludge is surrendered and hand the delivery note to the forwarder. The delivery note must be held available in the vehicle during the period of transportation. The delivery and application of sewage sludge must be confirmed by the recipient.

(3) The recipient and the forwarder shall each retain a carbon copy of the delivery note, a further carbon copy shall be sent by the forwarder to the authority responsible for the waste-water treatment plant and to the authority responsible for the application area, the top copy to the operator of the waste-water treatment plant. The latter shall be required to preserve the top copy for a period of 30 years as from the time of hand-over and present such to the responsible authorities upon their request. In implementation of sub-sections 1 and 2 and of sentence 1, it shall be possible to use the facilities of electronic data processing.

(4) The obligations specified in sub-sections 1 to 3 shall also be effective if operators of waste-water treatment plants apply sewage sludge or have sewage sludge applied on their own property.

(5) The authority responsible for the application area shall, in consultation with the specialised agricultural authority, be able to dispense with the notifications under sub-section 1 in respect of specific waste-water treatment plants.

(6) Upon introducing sewage sludge into the territory in which the Waste Avoidance and Waste Management Act is in force, the obligations of the operator of the waste-water treatment plant under sub-sections 1 to 4 shall apply to the owner of the sewage sludge who introduces such or who has such introduced into the territory in which the Waste Avoidance and Waste Management Act is in force.

(7) Operators of waste-water treatment plants shall keep a register containing the following information:

1. volumes of sludge generated and the volumes of sludge supplied to agriculture (in tonnes of dry matter),
2. properties of the sewage sludges in accordance with Section 3, sub-section 5,
3. mode of treatment of the sewage sludges,
4. name and address of the recipients of sludges, plot- specific designation of the area of land on which the sludge is applied, arranged in the order of land-parcel number,
5. results of the soil analyses, broken down by plot and arranged in the order of land-parcel number.

The operators of waste-water treatment plants shall submit these details by 31 March of the following year for the previous calendar year to those authorities who are responsible for enforcing the Sewage Sludge Ordinance.

(8) The authorities responsible for enforcing the Sewage Sludge Ordinance shall submit to the responsible supreme Land authorities the details specified in sub-section 7, nos. 1 to 3 by 31 August of a following year for the previous calendar year. The Laender shall submit the collated data to the Federal Minister for the Environment, Nature Conservation and Nuclear Safety. The Federal Minister for the Environment, Nature Conservation and Nuclear Safety shall, on the basis of the details received from the Laender, draw up a summary report every four years, starting in 1991, for the Commission of the European Communities.

(9) The operators of waste-water treatment plants for the treatment of domestic waste waters, municipal waste waters or waste waters with a similarly low pollutant content

and with a capacity of less than 1,000 population equivalents shall be excluded from the obligations specified in sub-sections 1 to 7.

(10) The provisions of the Ordinance on the Furnishing of Proof, with the exception of Article 2 para. 1 no. 2 and Article 23 no. 2 thereof, shall not apply to the recovery of sewage sludges that are subject to the provisions of this Ordinance.

Section 8

Application schedule

The responsible specialised agricultural authorities of the Laender or third parties authorised by them shall be required each year to draw up an application schedule for those sewage sludges applied during the course of the calendar year.

Section 9

Administrative offences

An administrative offence within the meaning of Section 61, sub-section 1, no. 11 of the Closed Substance Cycle and Waste Management Act shall be deemed to have been committed by anyone who wilfully or negligently

1. contravenes Section 3, sub-section 4, sentence 1 by applying sewage sludge without the prescribed soil analysis,
2. contravenes Section 3, sub-section 5, sentence 1 or sub-section 6, sentence 1 by surrendering for application or by applying sewage sludge without the prescribed analysis,
3. contravenes section 3, sub-section 8, sentence 2 or 3 by failing to analyse sewage sludge or by failing to submit the results to the responsible authorities,
4. contravenes section 3, sub-section 9, sentence 9 by surrendering for application or by applying sewage sludge without the prescribed analysis,
5. contravenes section 3, sub-section 10 by failing to meet an enforceable order altogether, correctly or in good time,
6. contravenes Section 4, sub-section 1,2, sentence 1, sub-section 4 or 5, sub-section 6, first half of sentence 1, or sub-sections 7 to 11 by applying sludge,

7. contravenes section 4, sub-section 2, sentence 2 also in conjunction with sub-section 3, sentence 1, by growing the plants specified therein or by failing to subject the soil to deep-turn tillage,
8. contravenes Section 4, sub-section 3, sentence 2 by failing to work the sewage sludge into the soil prior to sowing,
9. contravenes Section 4, sub-section 12 by applying sewage sludge on agriculturally or horticulturally used soils,
10. applies sewage sludge mixtures in contravention of Section 4, sub-section 13, sentence 2,
11. contravenes Section 4, sub-section 14 by storing sewage sludge on or in the vicinity of the application area,
12. contravenes section 6 by applying more than the specified quantities of dry matter of sewage sludge, sewage sludge composts or a mixture produced by using sewage sludge,
13. contravenes Section 7, sub-section 1 by failing altogether or in good time to provide notification of application of sewage sludge,
14. contravenes Section 7, sub-section 2, sentence 2 failing to hold the delivery note available in the vehicle during the period of transportation,
15. fails to complete the delivery note presented in Appendix 2 of this Ordinance altogether, correctly or in full, or fails in contravention of Section 7, sub-section 3, sentence 2 to preserve a copy of the delivery note for a period of 30 years, or fails to present said delivery note for examination to the responsible authority upon its request,
16. contravenes Section 7, sub-section 7 by failing to keep the register altogether, correctly or in a complete state, or by failing to submit the information altogether or in good time.

Section 10

Entry into force, abrogation

This Ordinance shall enter into force on the first day of the third calendar month following that of promulgation. The Sewage Sludge Ordinance of 25 June 1982 (Federal Law Gazette I, p. 734) shall, at the same time, be abrogated.

The Bundesrat has given its consent.

Bonn, this 15th day of April 1992

The Federal Minister
for the Environment, Nature Conservation and Nuclear Safety
Klaus Töpfer

Appendix 1

Taking samples, preparing samples and analysing sewage sludge and soil

1 Sewage sludge

1.1 Taking samples

In respect of the sewage sludge analyses prescribed in section 3, the samples shall be taken in accordance with DIN 38414, Part 1 (issued in November 1986)¹⁾, the sewage sludge being in the state in which it is applied on agricultural areas of land.

In order to ensure representative analysis results, cumulative samples must be produced in the following manner:

Prior to the date set for the analysis, five litres of sludge must be taken from each of at least five different sewage sludge batches and mixed in a suitable vessel (e.g. of aluminium) to form the cumulative sample. Samples should, as far as possible, be taken at intervals of several days.

From the carefully mixed cumulative sample, a partial quantity shall be taken which is sufficient to ensure four parallel analyses for all of the prescribed analysis parameters.

The partial quantity shall be filled into a suitable, well-closing vessel (e.g. aluminium) and delivered immediately to the analysing body.

1.2 Preparing the sample

The sludge sample submitted for analysis shall undergo constant mixing immediately before a partial sample is taken. In the event of there being any risk of demixing, the partial sample shall be taken during the mixing process.

For all analysis parameters determined from the dry matter, a partial sample shall be taken that is at least sufficient to ensure four parallel analyses.

A partial sample shall also be taken for freeze-drying that is at least sufficient to conduct four parallel analyses in accordance with Sections 1.3.3.1 and 1.3.3.2.

Freeze-drying must be performed in such a way that evaporation losses of the substances to be analysed are avoided. In particular, it shall be ensured that the sample is unable to thaw during the freeze-drying process. Sewage sludges with a high water content should be partially de-watered by centrifuge prior to freeze-drying. The separated centrifugate is to contain no particles.

¹⁾ For the source of procurement, refer to Section 5.

1.3 Performing the analyses

When working with fresh and freeze-dried sewage sludge, it shall be necessary to observe the safety rules usually applicable to work carried out in microbiological laboratories²⁾. Provided the analysis results will not be influenced, it shall be possible to sterilise a partial quantity of the fresh or freeze-dried sludge for the relevant analyses (e.g. by heating the sample for a period of 30 minutes at 70° C).

For each analysis parameter, it shall be necessary to perform at least two parallel analyses and specify the result as the arithmetic mean of the two values. Equivalent methods shall be permitted.

1.3.1 Determination of the heavy metals, nutrients, pH value, dry residue, ignition loss and adsorbed organically bound halogens (AOX).

The prescribed analyses of these parameters shall be performed in accordance with the methods of analysis described in Table 1.

1.3.2 Determination of the basifying substances

I. Purpose and scope

The method shall be applicable to sewage sludges containing calcium and magnesium in basifying form (e.g. as oxide, hydroxide and carbonate).

II. Principle

The substance shall be rendered soluble with acid and the excess of acid back-titrated. The basifying substances shall be specified as % CaO.

III. Chemicals

III.1 Hydrochloric acid solution

$c(\text{HCl}) = 0.5 \text{ mol/l}$

III.2 Sodium hydroxide solution

$c(\text{NaOH}) = 0.25 \text{ mol/l}$

²⁾ Refer, for example, to Laboratory Safety. Preliminary recommendations for the handling of pathogenic micro-organisms and for the classification of micro-organisms and pathogens by the hazards occurring at the time of handling in: Federal Health Gazette 24, no. 22 dated 30 October 1981, 347-359.

III.3 Phenolphthalein solution

w (phenolphthalein) = 1 % in ethanol (w = 96 %)

IV. Standard laboratory equipment

V. Performance³⁾

V.1 Preparing samples

From the sample dried at 1050 C in accordance with DIN 38414, Part 2¹⁾ and comminuted and homogenised in accordance with DIN 38414, Part 7¹⁾ 2 g shall be weighed off to an accuracy 1 mg on an analysis balance, transferred to a 200 ml measuring flask and mixed with 100 ml of hydrochloric acid in accordance with Section III.1. The measuring flask shall be allowed to stand in the cold until the principle reaction is concluded. This shall be followed by a process of careful heating and boiling for 5 minutes in such a way that no hydrochloric acid losses occur. Once the dissolution process is concluded, the solution shall be cooled, topped up with water as far as the mark, shaken and filtered.

V.2 FOERSTER method

50 ml (A) of the hydrochloric filtrate (described in Section V.1) shall be pipetted into a 200 ml measuring flask and, after adding phenolphthalein solution specified in Section III.3, titrated with sodium hydroxide solution specified in Section III.2. The still weakly acidic solution shall be boiled to remove the carbon dioxide, with titration being continued until the onset of turbidity (consumed volume of alkali = x ml).

This shall be followed by cooling, topping up with water as far as the mark, shaking and filtration. Titration shall be completed in 100 ml of filtrate = 0.25 g substance (consumed volume of alkali = y ml).

VI. Calculation

The content of basifying substances w_{bas} in % CaO shall be calculated using the following formula:

$$w_{\text{bas}} = (A - 0.5 B) \cdot C = \left(50 - \frac{x}{2} - y\right) \cdot 1.402$$

$$B = (x + 2 y) \text{ (ml)}$$

- A: presence of hydrochloric acid solution in ml (factor 1.00)
- B: consumption of sodium hydroxide solution in ml (factor 1.00)
- x: consumption of sodium hydroxide solution until the occurrence of turbidity
- y: consumption of standard sodium hydroxide solution after completion of filtration

³⁾ Refer to method book volume II of VDLUFA "Analysis of fertilisers".

– C: conversion factors

C₁ = 1.402 for CaO

C₂ = 2.502 for CaCO₃

1.3.3 Determination of the polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF)

1.3.3.1 Determination of the polychlorinated biphenyls

I. Principles

The following method of analysis is suitable for the determination, prescribed for precautionary reasons under Section 6, sub-section 6, of the six selected PCB congeners in sewage sludge.

It is based on the Standards of DIN 51527 Part 1 (4)¹⁾, DIN 38407 Part 2 (DEV, F2, draft 1985)¹⁾ (5) and ISO/TC 190/SC3 N2 Rev. 3 (18) as well as on the results of interlaboratory tests conducted by the working party 2 under the auspices of COST 681 in the European Community (6, 7). Recent literature has also been included (8, 9, 10, 11, 13, 14, 15, 19).

The method describes tested procedures which may only be applied by analysts or under the supervision of analysts with experience in trace analysis using gas chromatography and who ensure that the necessary measures are taken for quality assurance and control (refer to Section IX).

It shall only be permissible to diverge from the prescribed work processes if the gas-chromatographic separation of the PCB congeners is adversely affected to a such an extent by disturbing co-eluent substances that any reliable identification/quantification is not possible. In these cases of exception, it may be worthwhile repeating prescribed purification processes or performing other additional purification methods. It may furthermore be necessary in this context to use a mass-spectrographic detector.

In order to separate PCB from some chlorinated hydrocarbons, such as p,p-DDT, dieldrin, heptachlor epoxide, HCH isomers and others, it shall, if necessary, be possible to use a silica gel separation column as an additional purification stage (refer, for example, to 15, 18, 19 and 21).

As the procedure described here is geared towards the limit values of the Sewage Sludge Ordinance, it shall be necessary to alter aliquoting and dilution volumes as well as the added amounts of internal standard when determining very low PCB contents.

II. Brief description

The freeze-dried sewage sludge sample shall be extracted with n-hexane in the Soxhlet extractor after adding internal standard. Any PCB congeners contained in the extract will be extensively freed from any disturbing companion substances by means of purification steps, separated by capillary gas chromatography and determined using the electron capture detector (ECD) - (refer to diagram in Figure 1).

III. Chemicals

All chemicals must exhibit a degree of purity which permits the determination of PCB components within the scope of the detection limit of the method. This must be verified by conducting regular blank tests and, if necessary, be guaranteed by implementing additional purification measures.

III.1 Solvents for residue analyses

n-dodecane, n-hexane and isopropanol, if necessary extensively purified, e.g. re-distilled through a high-performance distillation column.

III.2 Water, demineralised

III.3 Desiccant

III.3.1 Sodium sulphate, anhydrous

If necessary, the sodium sulphate must be purified and dried by heating to 550° C for at least two hours in a muffle furnace.

III.3.2 Magnesium perchlorate

III.4 Tetrabutyl ammonium hydrogensulphate (TBA)

III.5 Sodium sulphite

III.6 TBA sulphite reagent

3.39 g of tetrabutyl ammonium hydrogensulphate shall be weighed into a 100 ml measuring flask to an accuracy of 0.01 g, dissolved in demineralised water and topped up with water. The solution shall be extracted three times in a 250 ml separatory funnel with 20 ml of n-hexane and saturated with 25 g of sodium sulphite. The solution should not be preserved for a period exceeding one month.

III.7 Silver nitrate

III.8 Packing materials for column chromatography

III.8.1 Aluminium oxide

Aluminium oxide W 200, basic or neutral, Super 1 Woelm activity or equivalent, shall be dried for a period of 16 hours at 150° C or for a period of two hours at 400° C.

89 g of the dried aluminium oxide shall be mixed with 11 g of water and shaken in a closed flask until all lumps have disappeared. The mixture shall be preserved for a period of at least 16 hours in a closed flask before it is used for the first time.

III.8.2 Silica gel

Silica gel 60, 0.063-0.200 mm (70-230 mesh), e.g. Merck Quality No. 7754 or equivalent, shall be dried for a period of 16 hours at 200° C, cooled in the desiccator over magnesium perchlorate where it shall be kept for a maximum period of 14 days.

III.8.3 Silver nitrate/silica gel mixture

10 g of silver nitrate shall be dissolved in 40 ml of water and added in portions to 90 g of activated silica gel described in Section III.8.2. The mixture shall be shaken until all lumps have disappeared and then heated in the drying oven from 70° C to 120° C within a period of five hours.

The mixture shall be heated for 15 hours to 125° C for activation, cooled in the desiccator over magnesium perchlorate, filled into a brown flask where it shall be kept for a maximum period of 14 days.

III.9 Gases

III.9.1 Carrier gas

Helium or hydrogen, each with a volume percentage of $\geq 99,99$ %.

III.9.2 Auxiliary gases

Gas mixture comprising 95 parts by volume of argon and five parts by volume of methane; alternatively nitrogen, each with a volume percentage of $> 99,99$ %. Nitrogen, purified and oil-free for the concentration of small extract volumes.

III.10 Calibrating and reference substances

III.10.1 Individual PCB components

2,4,4'-Trichlorobiphenyl	PCB 28
2,2',5,5'-Tetrachlorobiphenyl	PCB 52
2,2',4,5,5'-Pentachlorobiphenyl	PCB 101
2,2',3,4,5,5'-Hexachlorobiphenyl	PCB 138
2,2',4,4',5,5'-Hexachlorobiphenyl	PCB 153
2,2',3,4,4',5,5'-Heptachlorobiphenyl	PCB 180
Decachlorobiphenyl	PCB 209 (internal standard)

Stock solutions shall be produced by dissolving the individual components in hexane to form a mixture with a content per component of, for example, 10 µg/ml . The working standards shall be produced by diluting the stock solution(s) with n- hexane in such a way that under the given gas-chromatographic conditions the electron capture detector shows a linear reading throughout the selected working range. In general, contents of 2 µg/l to 20 µg/l shall be adequate for this purpose.

An equally large amount of decachlorobiphenyl shall be added as the internal standard to all working standards. This amount should be rated in such a way that the signal measured for the internal standard in the linear working range is greater than the signal measured for the individual PCB components of the working standard with the highest PCB content. With a working range of 2 µg/l to 20 µg/l and an injection volume of 1-2 µl, a concentration of internal standard of 20 µg/l may be sufficient.

Prior to extraction, the sewage sludge sample shall also be mixed with as much internal standard as is necessary for the signal measured for the internal standard in the measurement solution under Section V.2.1.2 or V.2.2 to be larger than the signal measured for the individual PCB components in this solution, however no more than ten times its magnitude. In the procedure described here, the addition of 500 ng of decachlorobiphenyl will produce a content in the measurement solution of 20 µg/l.

III.10.2 Technical PCB mixtures

Technical PCB mixtures shall be used for detecting the peak pattern and for assessing the separation capacity of the gas-chromatographic system. In addition to the individual products of Chlophen^R A30, A40, A50 and A60 or the corresponding Arochlor mixtures^R, a mixture of Chlophen^R A40 and A60, e.g. each in a concentration of 2 µg/ml, shall in particular be used for the above-mentioned purpose.

IV. Equipment

All equipment coming into contact with the sample and its solutions/extracts must exhibit a degree of cleanliness that permits determination of the PCB components within the scope of the

detection limit of the procedure. This must be verified by regular blank tests and, if necessary, ensured by performing additional cleaning measures.

IV.1 Standard laboratory equipment

IV.2 Freeze-drying system

IV.3 Capillary gas chromatography with electron capture detector (ECD)

IV.4 Gas-chromatographic separation column

Refer to DIN 51527 Part 1¹⁾, Section 5,3 (4) and DEV F2¹⁾, Section 7.2.2 (5).

IV.5 Columns for preliminary liquid-chromatographic purification

Glass columns of different lengths (e.g. 150 to 250 mm) with an inside diameter of 6 mm at the bottom tapering to a point with a length of approx. 40 mm and provided at the top end with a reservoir, e.g. 50 mm in length with 20 mm inside diameter.

With the separation columns described below, the elution behaviour of PCB's on the column must be checked regularly, however at least for each new batch of packing material, with a mixture of the six PCB components and decachlorobiphenyl.

IV.5.1 Aluminium oxide separation column

A chromatographic column of the type described in Section IV.5 shall be fitted with a glass-wool bung and filled with 2 g of aluminium oxide suspended in n-hexane (refer to Section III.8.1).

IV.5.2 Silver nitrate/silica gel separation column

A glass column of the type described in Section IV.5 shall be fitted with a glass-wool bung, filled with a 5 mm deep layer of anhydrous sodium sulphate, covered with 2 g of silver nitrate/silica gel mixture according to Section III.8.3 and above that a further 5 mm deep layer of anhydrous sodium sulphate. The column must be freshly prepared before each purification.

V. Preparing samples

V.1 Extraction

2 grammes of the sewage sludge freeze-dried and comminuted in an analysis grinder and homogenised in accordance with DIN 38414, Part 7 (3)¹⁾ shall be weighed to an accuracy of 1 mg into an extraction thimble (pre-cleaned if necessary), mixed with 500 ng of decachlorobiphenyl as the internal standard (refer to section III.10.1) and extracted in the

Soxhlet extractor with n-hexane (e.g. 70 ml). The duration of extraction shall be rated in such a way that about 80-100 extraction cycles take place. The extract shall, if necessary, be filtered, concentrated to about 5 ml by gentle distillation, if applicable by adding a little n-dodecane (e.g. 100 µl of a solution of 20 µg/µl n-dodecane in n-hexane), quantitatively transferred into a 10 ml measuring flask and topped up with n-hexane.

V.2 Purifying the extract

The following describes two equivalent modes of procedures for separating the PCB's from disturbing companion substances (refer to diagram in Figure 1).

- a) A two-phase procedure involving the removal of sulphur and sulphurous compounds by means of TBA and column chromatography with aluminium oxide.
- b) A single-phase purification process using a silver nitrate/silica gel separation column.

Both procedures will generally be sufficient for samples exhibiting only a low level of contamination.

V.2.1 Purification with TBA and aluminium oxide

V.2.1.1 Removal of sulphur and sulphurous compounds (22)

2 ml of the extract described in Section V.1 or, if

applicable, another suitable aliquot shall be mixed with 1 ml of isopropanol and 1 ml of TBA sulphite reagent and shaken vigorously for a period of at least two minutes. If no crystalline precipitation is formed thereafter, a sufficient number of 100 mg lots of sodium sulphite shall be added and shaken until such time as a crystalline precipitation is formed. After adding 5 ml of water, shaking must be continued for a further two minutes. The hexane phase shall be removed and the aqueous phase subsequently extracted twice with a little n-hexane. The combined organic phases shall be dried with sodium sulphate and filtered off. The sodium sulphate shall be washed twice with a little n-hexane and the entire n-hexane phase concentrated gently with nitrogen to 1 ml.

V.2.1.2 Aluminium oxide separation column

The n-hexane phase, concentrated to 1 ml in accordance with Section V.2.1.1, shall be quantitatively pipetted onto the aluminium oxide separation column prewashed with n-hexane and described in Section IV.5.1. The residue vessel shall be re-washed with 0.5 ml of n-hexane. The hexane shall be pipetted onto the surface of the packing when the meniscus of the solution has just commenced infiltration. This rinsing process shall be repeated a further twice. The column shall then, as described above, be eluted with 5 ml portions of n-hexane or a volume determined in accordance with Section IV.5. The eluate shall be gently concentrated at room temperature in the stream of nitrogen to approx. 3 ml and topped up with n-hexane to 5 ml in the measuring flask for GC analysis.

V.2.2 Purification with silver nitrate/silica gel

2 ml of the extract specified in Section V.1 or, if applicable, another suitable aliquot, shall be filled onto the silver nitrate/silica gel column prewashed with n-hexane and described in Section IV.5.2.

When the meniscus of the extract just starts to infiltrate the surface of the packing, 40 ml of n-hexane or another volume adequate for the complete elution of the PCB shall be added in portions onto the column. The entire eluate shall be gently concentrated to about 3 ml and topped up with n-hexane to 5 ml in the measuring flask for GC analyses.

VI. Gas chromatographic determination

The six PCB congeners in the purified extract shall be identified and quantified by means of capillary gas chromatography and electron capture detector. The separation capacity of the GC system must be optimised in such a manner to achieve an adequate dissolution of the components PCB 28 and PCB 31. In order to optimise the GC working conditions, refer to DIN 51527, Part 1¹⁾, Sections 9.3 and 10 (4), DEV F2¹⁾, Sections 7 and 10,4 (5), Beck and Mathar (8) as well as VDLUFA (10).

It is recommended to secure identification of the PCB components with two capillary separation columns of differing polarity. Furthermore, it must be ensured that no interferences occur between the PCB components 101 and o,p'-DDE or α -endosulphane as well as between PCB 138 and p,p'-DDT.

If, in addition to PCB, the sewage sludge sample also contains tetrachlorodiphenyl methanes (e.g. Ugilec 141), a large part of the corresponding isomers will also be found in the eluate of the separation column(s) and may disturb the identification or quantification of PCB component 153. In order to ensure the perfect quantification of this component, a mass-spectrometric detector should be used in this case (refer, for example, to 11, 15, 16, 17, 19).

VII. Calibration

The gas-chromatographic separation system shall be calibrated in the linear measurement range of the ECD. For this purpose, it shall be appropriate to use multi-component solutions as the working standards (refer to Section III.10.1).

The linear calibration functions of the individual PCB components shall be determined as follows in accordance with DIN 38402, Part 51¹⁾ (1) on the basis of at least 5 calibration concentrations distributed equidistantly throughout the working range:

The working standards doped with internal standard shall be injected in rising concentrations into the gas chromatograph under the same conditions prevailing at the time of the sample measurement. The j measurement values y_{iej} shall be put in proportion to the values measured for internal standard y_{iej} . The same shall also apply to the mass concentrations β_{iej} and β_{iej} on

which the measurement values are based. These proportions shall be used to calculate the calibration functions (1) on the basis of linear regression:

$$\frac{y_{ie}}{y_{le}} = m_{ii} \cdot \frac{\beta_{ie}}{\beta_{le}} + b_{ii} \quad (1)$$

Where:

y_{ie} value measured for PCB i during calibration; dependent on β_{ie} ; unit dependent on evaluation; e.g. peak

y_{le} value measured for internal standard l during calibration; dependent on β_{le} ; unit dependent on evaluation; e.g. peak

β_{ie} mass concentration of substance i in the working standard in $\mu\text{g/l}$

β_{le} mass concentration of the internal standard in $\mu\text{g/l}$

m_{ii} gradient of the calibration curve, unit without dimension

b_{ii} section of the calibration curve on the ordinate axis, unit without dimension

The calibration functions shall only apply to the concentration range covered by them. They are also dependent on the operating status of the gas chromatograph (refer to VDLUFA (9)) and must be checked at regular intervals. For routine operation, the calibration function must be adjusted once daily in the form of a two-point calibration.

VIII. Evaluation

VIII.1 Identification

The PCB congeners in the sample shall be identified by

comparing the retention times of the relevant peaks in the sample gas chromatograms with the reference solutions measured under the same conditions or with those of a gas chromatogram for the sample extract stocked up with the substances being sought (refer to DEV F2, Section 11.1 (5)). In this context, concurring peaks should, as far as possible, be observed on two capillary columns of differing polarity for the anticipated substance-specific retention times.

If any reliable identification of individual PCBs is not possible with two capillary columns, e.g. in the case of heavily contaminated samples or disturbance through tetrachlorodiphenyl methanes, it may be necessary to employ another detection method, e.g. mass spectrometry in the form of GC/MS coupling.

VIII.2 Quantification

The identified PCB congeners shall be quantified using the method of the internal standard. The mass concentration β_i of the PCB i in mg/kg in the sewage sludge sample shall be calculated on the basis of the following equation (2):

$$\beta_i = \frac{\frac{y_i}{y_l} - b_{ii}}{m_{ii}} \cdot \frac{M_l}{E} \quad (2)$$

Where:

- β_i mass concentration of the PCB congener i being sought in the sewage sludge sample in mg/kg
- y_i value measured for the congener i in the measurement solution; unit dependent on evaluation; e.g. peak
- y_l value measured for internal standard l (decachlorobiphenyl) in the measurement solution; unit dependent on evaluation; e.g. peak
- M_l mass of internal standard added to the sewage sludge sample in μg
- E weighed portion of sewage sludge sample in g
- m_{il}, b_{il} refer to equation (1)

IX. Quality assurance and quality control

The reliability of the results of this method must be ensured by employing suitable measures of quality assurance and quality control. Individual measures necessary are, for example, described in:

- American Chemical Society's Committee on Environmental Improvement (1983) (12)
- Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten (Association of German Agricultural Investigation and Research Institutes), Technical Group XI Environmental Analysis (1980) (9)
- Verband Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten (Association of German Agricultural Investigation and Research Institutes), Technical Group XI Environmental Analysis (1984) (10)
- Erickson (1986) (15)
- Laenderarbeitsgemeinschaft Wasser (Laender Working Group on Water) (1989) (20)

In performing measures of quality control conforming to the above-mentioned references, particular importance must, for example, be attached to:

- a) measuring at least one method blank reading for each analysis series,
- b) achieving high (> 80 %) and reproducible recovery rates for the PCB congeners, including the internal standard,
- c) monitoring and calibrating the efficiency of the measuring system (GC/ECD) by regularly measuring control standards (e.g. by keeping control cards),
- d) documenting all quality control measures in verifiable form and keeping them on record for a prolonged period.

X. Blank readings

At least one method blank reading must be measured per analysis series in order to check the examination method. For this purpose, the entire method is carried out without sample.

In the event of a significant blank reading being obtained, the values for calibration and sample measurement must be corrected if the blank reading cannot be further reduced by optimising GC separation or by purifying the chemicals and cleaning the equipment.

XI. Specification of results

The results shall be formed as the arithmetic mean from two separate determinations (extractions). In this context, the mass concentrations β_{ij} of the six PCB congeners shall be specified individually in mg/kg sewage sludge sample, rounded to 0.01 mg/kg.

XII. Analysis report

The report is to refer to this method and contain the following details:

- a) identity of the sewage sludge sample,
- b) information on preliminary sample treatment, storage and preparation,
- c) indication of complete mode of procedure (aliquoting, dilution, GC conditions),
- d) mode of procedure for identifying and quantifying the individual PCB's,
- e) specification of the results in accordance with Section XI,
- f) any divergence from the above-mentioned analysis method and indication of all the circumstances that may have influenced the analysis result.

1.3.3.2 Determination of polychlorinated dibenzodioxins and polychlorinated dibenzofurans

I. Principles

The following method of identification must be applied to the determination, prescribed for precautionary reasons under Section 3, sub-section 6, of selected PCDD and PCDF congeners in sewage sludge.

It represents an analysis concept and is made up in such a way to encompass the necessary and possible elements of an analytical method which, when followed and applied in laboratories experienced in trace analyses, will, in conjunction with the regular implementation of measures of quality assurance and control, provide results of sufficient reliability for the implementation of the Sewage Sludge Ordinance.

II. Brief description

The freeze-dried sewage sludge sample shall be mixed with ^{13}C -marked PCDD and PCDF standards and extracted with toluene. The added standards and any PCDD/PCDF congeners contained in the sample shall be extensively freed from disturbing companion substances, separated by capillary gas chromatography and then determined using mass spectrometry in accordance with the MID (multiple ion detection) technique, with the quantification process following the isotope dilution method.

III. Equipment and chemicals

All equipment coming into contact with the sample and its solutions/extracts must be free from PCDD and PCDF within the detection limit of the method. All chemicals must exhibit a degree of

purity that permit the mass-spectrometric determination of PCDD and PCDF within the detection limit of the method. This must be verified and ensured by means of regular blank tests.

III.1 Standard laboratory equipment

III.2 Gas chromatograph for capillary chromatography

III.3 Mass spectrometer with evaluation unit

III.4 Gas-chromatographic separation columns

- polar columns, e.g. SP 2331 or SP 2330, 60 m
- non-polar column, e.g. DB-5, 25 m

III.5 Separation columns/packing materials for multi-phase column chromatography

III.6 Calibration substances

For the quantification to be carried out using the isotope dilution method, use shall be made of a solution of ¹³C- marked PCDD and PCDF standards each of which contains a PCDD or PCDF isomer respectively per homolog group.

IV. Preparing samples (extraction and enrichment)

The various stages of the multi-stage sample preparation process may altogether differ at the qualified and experienced analysing bodies. This shall be permissible since the quality assurance and quality control measures accompanying the analysis guarantee the comparability of the results attained at the various analysing bodies. The following contains an example of a tried and tested mode of procedure (24) that is applied in many research laboratories⁴⁾:

50 g (also less in specific cases) of the freeze-dried and ground sample shall be mixed with the following ¹³C- marked PCDD's and PCDF's: 5 ng each of 2,3,7,8-tetraCDD, 2,3,7,8-tetraCDF, 1,2,3,7,8-pentaCDD, 1,2,3,7,8-pentaCDF, 1,2,3,6,7,8-hexaCDD and 1,2,3,4,7,8-hexaCDF as well as 10 ng each of 1,2,3,4,6,7,8-heptaCDD, 1,2,3,4,6,7,8-heptaCDF, octaCDD and octaCDF.

The sample shall then be extracted with toluene in the Soxhlet apparatus for 20 h. The toluene extract shall be concentrated to approx. 25 ml. In some cases, it will only be possible to

⁴⁾ Variants not necessitating the hazardous working substance benzene must be given preference over the procedure presented here insofar as the companion substances disturbing PCDD/PCDF analyses are sufficiently separated and the comparability of results is ensured.

concentrate the extract to about 40 ml since a gelatinous mass will have already been produced.

The extract shall then be diluted in benzene to 100 ml. In those cases in which the extract can only be concentrated to about 40 ml, benzene shall be added until a volume of 200 ml has been attained. The following values specified in parentheses refer to those samples that have been absorbed in 200 ml of benzene. 50 g (or 75 g) of aluminium oxide shall be filled into a chromatographic column (60 x 4 cm) and covered with a layer of 50 g of sodium sulphate. The extract shall be added onto the column and eluted with 300 ml (or 400 ml) of benzene and 300 ml (or 500 ml) of n-hexane/dichloromethane (98:2). The eluates shall be discarded. The PCDD/PCDF fraction shall then be eluted with 300 ml of n-hexane/dichloromethane (1:1). After changing the solvent to n-hexane, the samples shall be chromatographed on a "mixed" column of silica gel (2 g), silica gel/NaOH (5 g), silica gel (2 g), silica gel /H₂SO₄ (10 g), silica gel (2 g) and silica gel/AgNO₃ (5 g). 300 ml of n-hexane shall be used for the elution process. The eluate shall be concentrated to approx. 5 ml and then chromatographed on a column (30 x 2.5 cm) filled with S-X3 bio-beads, with cyclohexane/ethyl acetate (1:1) as the eluting agent. The fraction of 100-160 ml contains the PCDD/PCDF. It shall be concentrated to a few millilitres, transferred to a 3 ml test tube, the solvent shall be blown off in the nitrogen stream and the "residue" absorbed with approx. 50 µl of toluene. After carefully rinsing the wall of the test tube with the solvent, 5 ng of ¹³C₆-1,2,3,4-tetraCDD shall be added and the volume of the sample solution reduced to approx. 20 µl.

V. Gas-chromatographic/mass-spectrometric analysis (GC/MS)

Identification and quantification of the 17 PCDD/PCDF congeners to be used for calculating the TCDD toxicity equivalent shall be performed by means of capillary gas chromatography and mass spectrometric detection. VDI Guideline 3499 (23) must be applied in performing this step.

VI. Quality assurance and quality control

The following statements shall apply in supplementation or amendment of the statements made in 1.3.3.1/IX.:

- a) Level and reproducibility of the recovery rates (WFR) of the ¹³C- marked PCDD/PCDF standards for the selected separation processes must be subject to regular checks, the WFR must be > 40 % for OCDD/OCDF, > 70 % for all other congeners.
- b) The efficiency of the measuring system (GC/MS) must be checked by means of regular measurements and calibrated (e.g. keeping of control cards).

VII. Specification of results

The results shall be formed as the arithmetic mean from two separate determinations (extractions). In doing so, the mass concentrations of the 17 PCDD/PCDF congeners to be used for calculating the TCDD toxicity equivalent shall be indicated individually in ng/kg of sewage sludge dry matter, rounded to 1 ng/kg. In order to calculate the sum of 2,3,7,8-TCDD-

toxicity equivalents (TE), the respective mass concentrations shall be multiplied by the following factors and the products added.

2,3,7,8-tetraCDD	1.0
1,2,3,7,8-pentaCDD	0.5
1,2,3,4,7,8-hexaCDD	0.1
1,2,3,6,7,8-hexaCDD	0.1
1,2,3,7,8,9-hexaCDD	0.1
1,2,3,4,6,7,8-heptaCDD	0.01
octaCDD	0.001
2,3,7,8-tetraCDF	0.1
1,2,3,7,8-pentaCDF	0.05
2,3,4,7,8-pentaCDF	0.5
1,2,3,4,7,8-hexaCDF	0.1
1,2,3,6,7,8-hexaCDF	0.1
1,2,3,7,8,9-hexaCDF	0.1
2,3,4,6,7,8-hexaCDF	0.1
1,2,3,4,6,7,8-heptaCDF	0.01
1,2,3,4,7,8,9-heptaCDF	0.01
octaCDF	0.001

The value gained in this way shall be used for checking the value to be verified under Section 4, sub-section 10 of this Ordinance.

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- (24) Hagenmaier, H., Brunner, H., Knapp, W., Weberruß, U., Institute for Organic Chemistry, University of Tübingen Untersuchungen von ausgewählten Böden und Pflanzen auf Dioxine und Furane. Research Report No. 107 01 010 on behalf of the Umweltbundesamt (Federal German Environmental Agency) Berlin. Tübingen 1988

2 Soil

2.1 Taking and preparing samples

The period after harvesting and before the next time of sewage

sludge application must be selected for sampling. One average sample must be taken from each uniformly farmed piece of land (e.g. plot, enclosure) covering an area of up to one hectare. On larger pieces of land, samples must be taken from parts of approximately one hectare in size, on land with uniform soil properties and identical form of management from parts of up to three hectares in size. At least 20 penetrations extending down as far as tilling depth shall be necessary for an average sample. The penetrations must be distributed evenly throughout the area.

The average sample shall be dried in the air, if necessary crushed, screened (< 2 mm), mixed and partial samples to DIN 38414, part 7¹⁾ reduced to grain size of 0.1 millimetre.

In order to accelerate drying, it shall be permissible to dry the samples in the drying oven at 40° C.

2.2 Performance of analyses

At least two parallel analyses must be conducted for each analysis parameter, with the arithmetic mean of the two values being specified as the result. Equivalent methods shall be permissible.

2.2.1 Determination of heavy metals

The air-dry average sample shall be used for digestion and determination of the heavy metals.

The samples shall be digested in accordance with DIN Standard 38414, Part 7 (issued in January 1983)¹⁾ (aqua regia digestion).

In the case of lead, cadmium, chromium, copper, nickel and zinc the measurements shall be performed in accordance with DIN Standard 38406, Part 22 (issued in March 1988)¹⁾, for mercury in accordance with DIN Standard 38406, Part 12 (issued in July 1988)¹⁾.

The results of the heavy metal determinations must be specified in milligrammes per kilogramme of dry matter (105° C).

2.2.2 Determination of plant nutrients

The contents of phosphate, potassium and magnesium available for plants shall be determined in the air-dry sample using the methods⁵⁾ customary in agricultural fertiliser counselling.

The results must be specified in milligrammes per kilogramme of dry matter (105° C).

2.2.3 Determination of the pH value

The pH value must be determined in accordance with DIN Standard 19684/Part 1 (1977)¹⁾.

Before each further sludge application, the pH value may be measured by means of a mobile method. Compared with the DIN method the difference in accuracy may account for a maximum of 0.2 pH units.

2.2.4 Determination of the clay content

The clay content shall be determined in accordance with DIN Standard 18123 (1983)¹⁾.

⁵⁾ Refer, for example, to VDLUFA publication series, issue 15 (refer to section 5).

3 Exceeding the limit values

Any of the contents permissible under Section 4, sub-sections 8,10, 11 and 12 shall be deemed to have been exceeded if the contents determined for

- the relevant heavy metal are more than 5 %
 - the relevant PCB congener are more than 25 %
 - halogen organic compounds (AOX) are more than 10 %
 - TCDD toxicity equivalents are more than 25 %
- higher than the relevant limit values.

4 Quality assurance and control

The analysing bodies shall undertake to ensure the reliability of the analysis results by taking suitable measures of quality assurance and quality control⁶⁾. This shall, for example, involve the successful participation in interlaboratory tests of the responsible Federal Land.

5 Notifications from expert bodies

The publications from expert bodies specified in Sections 1 and 2 are held on record in the archives of the German Patent Office in Munich. Publications issued encompass:

- the DIN standards published by Beuth Verlag GmbH Berlin and Cologne,
- the "Standard German Procedure for Water, Waste-Water and Sludge Analysis", of the Fachgruppe Wasserchemie (Water Chemistry Group) of the Gesellschaft Deutscher Chemiker (Society of German Chemists), published by Verlag Chemie, Weinheim/Bergstrasse,
- the Manual of Agricultural Investigation and Research Methods (method book), published by Verlag J. Neumann-Neudamm in Melsungen.

6 Other documents

Association of German Agricultural Investigation and Research Institutes (publisher): Analysis of sewage sludge and soil samples for their content of heavy metals and nutrients in accordance with the Sewage Sludge Ordinance of the Federal Government of 25 June 1982, VDLUFA publication series, issue 15, published by VDLUFA-Verlag, Darmstadt 1986.

⁶⁾ Refer, for example, to AQS - Analytical quality assurance. General recommendations of the Laender Working Group on Water for water, waste-water and sludge analysis. Published by: LAWA, E. Schmidt Verlag, Berlin 1989.

Figure 1

Diagram of PCB determination in sewage sludge

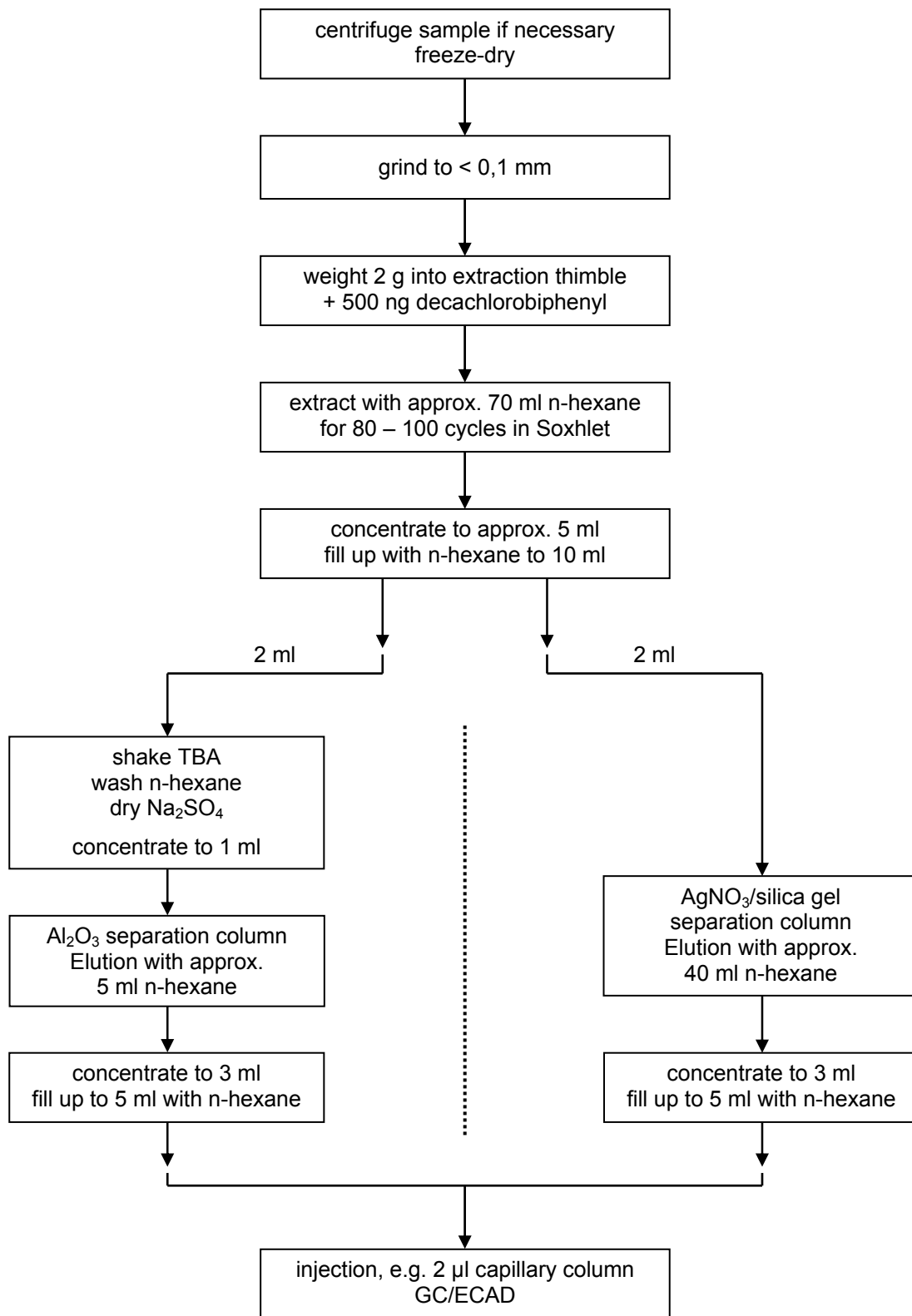


Table 1
Methods of analysing sewage sludge

No.	Parameter	Analysis method(s) ¹⁾	Matrix/sample preparation
1	pH value	DIN 38414, Part 5 (issued September 1981)	Original sample
2	Dry residue	DIN 38414, Part 2 (issued November 1985)	Original sample
3	Ignition loss (organic substance)	DIN 38414, Part 3 (issued November 1985)	Dry residue
4	Total nitrogen	DIN 19684, Part 4 (issued February 1977) (distillation method)	Original sample
5	Ammonia nitrogen	DIN 38406, Part 5 (issued October 1983)	Original sample
6	Lead	DIN 38406, Part 6 (issued May 1981) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
7	Cadmium	DIN 38406, Part 19 (issued July 1980) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
8	Calcium	DIN 38406, Part 3 (issued September 1982) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
9	Chromium	DIN 38406, Part 10 (issued June 1985) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
10	Potassium	DEV method E 13 (5th delivery 1968) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
11	Copper	DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
12	Magnesium	DIN 38406, Part 3 (issued September 1982) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
13	Nickel	DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
14	Phosphorus	DIN 38414, Part 12 (issued November 1986) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
15	Mercury	DIN 38406, Part 12 (issued July 1988)	Aqua regia digestion ²⁾
16	Zinc	DIN 38406, Part 8 (issued October 1980) DIN 38406, Part 22 (issued March 1988)	Aqua regia digestion ²⁾
17	Adsorbed, organically bound halogens (AOX)	DIN 38414, Part 18 (issued November 1989)	Dry residue

¹⁾ For sources of procurement, refer to Section 5.

²⁾ of the dry residue according to DIN 38414, Part 7 (issued January 1983)¹⁾.

Appendix 2

Waste-Water Treatment Plant

Name and address of the operator: _____ Place: _____

Date: _____

Tel.: _____

Fax: _____

Delivery Note
according to Section 7 of the Sewage Sludge Ordinance (AbfKlärV)

This delivery note must be preserved by the operator of the waste-water treatment plant for a period of 30 years.

Name and address of the user:

In the month(s) of 20..... we shall be

- surrendering
- applying
- instructing _____ to delivery/apply
(Name and address of the authorised third party)

_____ m³ of sewage sludge with a dry substance content of _____ % (this corresponds to a volume of _____ t of dry matter) at land parcel no. _____, communal district of _____, size _____ (in hectares).

Present soil use: _____

The soil analysis dated _____ (Analysis no.: _____)

- showed that the permissible contents of heavy metals were not exceeded.
- showed that the permissible contents of heavy metals were partially exceeded.

The sewage sludge has been treated as follows:

- biologically chemically thermally been in long-term storage
- decontaminated other treatment _____

The sewage sludge analysis dated _____ (analysis no.: _____)

showed that the permissible pollutant contents were not exceeded.

showed that the permissible pollutant contents were partially exceeded.

The soil-/sewage sludge analyses produced the following results:

1) Soil:

pH value _____

Soil type within the meaning of Section 4, sub-section 8 or 12 of the Sewage Sludge Ordinance (AbfKlärV) _____

The soil on average contains:

mg/100 g dry matter	
Phosphate (P ₂ O ₅):	
Potassium oxide (K ₂ O):	
Magnesium (Mg):	
mg/kg dry matter	
	Maximum contents in accordance with Section 4, sub-section 8 of the Sewage Sludge Ordinance (AbfKlärV)
Lead:	100
Cadmium:	1,5 (1 in accordance with section 4, sub-section 8, sentence 2)
Chromium:	100
Copper:	60
Nickel:	50
Mercury:	1
Zinc:	200 (150 in accordance with section 4, sub-section 8, sentence 2)

2) Sewage sludge:

The sewage sludge has the following pH value: _____

The sewage sludge on average contain:

	a) Nutrient contents in the fresh substance in %	b) Nutrient contents in the dry substance in %
Organic substance:		
Total nitrogen (N):		
Ammonia nitrogen (NH ₄ -N):		
Phosphate (P ₂ O ₅):		
Potassium oxide (K ₂ O):		
Calcium oxide (CaO):		
Magnesium oxide (MgO):		

mg/kg sludge dry matter (m_T)

	Limit values in accordance with Section 4, sub-section 11 and 12 of the Sewage Sludge Ordinance (AbfKlärV)	
Lead:	900	
Cadmium:	10	(5 in accordance with section 4, sub-section 12, sentence 2)
Chromium:	900	
Copper:	800	
Nickel:	200	
Mercury:	8	
Zinc:	2500	(2000 in accordance with section 4, sub-section 12, sentence 2)
AOX:	500	

mg/kg sludge dry matter (m_T)

	Limit values in accordance with Section 4, sub-section 10 of the Sewage Sludge Ordinance (AbfKlärV)	
PCB ¹⁾ no.		
28:	138:	0,2 mg PCB/kg m _T per component
52:	153:	
101:	180:	

ng TE/kg m_T

PCDD, PCDF ²⁾ :	100 ng TE/kg m _T
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Confirmation is hereby given that the above-specified sludge from our waste-water treatment plant may be utilised in accordance with the Sewage Sludge Ordinance of 15 April 1992 (Federal Law Gazette I p. 912) and in accordance with the guideline introduced by the responsible Supreme Land Authority relating to the utilisation of sewage sludge in agriculture dated

(Signature of the operator of the waste-water treatment plant)

¹⁾ Systematic numbering of the PCB components in accordance with the rules of the International Union for Pure and Applied Chemistry (IUPAC).

²⁾ According to the calculation prescribed in Appendix 1 of the Sewage Sludge Ordinance (AbfKlärV).

Confirmation of Surrender
according to Section 7, sub-section 2, sentence 1 of the Sewage Sludge Ordinance
(AbfKlärV)

Today we have surrendered _____ m³ of sewage sludge with a dry substance content of ____ %,
this corresponding to _____ t dry matter, in accordance with the above specifications.

(Signature of the operator of the waste-water treatment plant)

Confirmation of sewage sludge application
according to Section 7, sub-section 2, sentence 3 of the Sewage Sludge Ordinance
(AbfKlärV)

Today I have applied the above-specified sewage sludge which was surrendered to me by _____
_____ on _____.

The application volume permissible under Section 6 of the Sewage Sludge Ordinance is not exceeded.

(Signature of the recipient/farmer)

(The form is required with 6 carbon copies.)