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Project HORIZONTAL Validation Report

Validation of a horizontal standard for the determination of Kjeldahl nitrogen in soils, sludge and treated biowaste in a European Intercomparison Exercise

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Summary

Project HORIZONTAL is interdisciplinary aiming at a harmonisation and horizontal standardisation of test procedures, in particular for sludge, soils and biowastes. In the context of this standardization project, a series of draft technical specification were designed upon an extensive desk study, fine-tuned after expert consultations and finally validated in international intercomparisons exercise.

This report summarises the work performed within the validation study of the draft standard for the determination of Kjeldahl nitrogen in soils, sludge and treated bio-waste. It further explains the underlying statistical concept for the calculation of reproducibility and repeatability from intercomparisons data. In addition all single values, results of the statistical evaluation as well as background information on the validation materials used are described and explained.

Abbreviations

Throughout this report the following abbreviations are used:

ANOVA	Analysis of variances
CAS	Chemical Abstracts System
CEN	Comitteé Européen de Normalisation
DG	Directorate General
ECN	Energy Research Centre for the Netherlands
EU	European Union
IES	Institute for Environment and Sustainability
IT	Information Technology
ISO	International Organization for Standardisation
JRC	Joint Research Centre
MILC	Measure Interlaboratory Comparison
p	Number of labs
r	Repeatability limit
R	Reproducibility limit
s_r	Repeatability standard deviation
s_R	Reproducibility standard deviation
TC	Technical Committee

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Introduction to the validation project

Project HORIZONTAL is interdisciplinary aiming at a harmonisation and horizontal standardisation of test procedures, in particular for sludge, soils and biowastes. It was created as in response to the European Commission Mandate M 330 given to CEN, asking for the development and validation of those standards in support of forthcoming EU Directives, such as:

- The revision of the Sewage Sludge Directive 86/278/EEC.
- The Directive on the biological treatment of biodegradable waste.
- The initiative on a legal framework for soil monitoring in Europe.

This mandate explicitly considers standards for the entire analytical procedure (i.e., sampling, pre-treatment and analytical measurement methods for inorganic, organic, hygiene and biological parameters). These are grouped into classes according to their physical/chemical properties, which in turn determine the methods needed to quantify the potential impact on human and animal health, plant uptake, soil function and groundwater quality. As the materials generally feature a mixture of different types of contaminants, it is important to provide an integrated answer covering evaluation of all relevant pollutants.

In order to fulfil the requirements of the aforementioned mandate, the European Commissions Joint Research Centre (JRC) and its Directorate-General for Environment (DG ENV) together with the Technical Committees of the European Standardisation Committee (CEN TCs) concerned designed a pre-normative research initiative called Project HORIZONTAL and presented it to the Commission and the Environmental Authorities in the Member States.

After an extensive literature research and careful evaluation of the feasibility of a given horizontal standard, the standards were drafted and finally validated in a European laboratory intercomparison.

The underlying statistical concept, information about the materials used, details about the participants, measurement results obtained as well as the derived performance characteristics obtained for the determination of Kjeldahl nitrogen are described hereafter.

1.1 Statistical concept underlying the validation

According to the requirements of the work package concerning data handling & interpretation of the project HORIZONTAL-ORG the respective validation intercomparisons have to be evaluated according to the principles laid down in ISO standard 5725-2:1994. In particular repeatability and reproducibility of the draft standard methods have to be determined. The determination of trueness would require the availability of independent reference values for the materials investigated. This, however, is not possible and was not requested in the frame of this work. In the following, the approach chosen is explained.

1.1.1 Introduction to the statistical model

The statistical model used in ISO 5725 for estimation of accuracy of a measurement method assumes that every test result is the sum of three components:

$$y = m + B + e$$

y: test result

m: general mean

B: laboratory component of bias under repeatability conditions

e: random error occurring in every measurement under repeatability conditions

In the workprogram the quantification of term *e* is explicitly asked for (i.e. repeatability and reproducibility). The repeatability variance is measured directly as the variance of the error term *e*, but the reproducibility depends on the sum of the repeatability variance and the between-laboratory variance:

$$\sigma_r = \sqrt{\mathrm{var}(e)}$$

$$\sigma_R = \sqrt{\sigma_L^2 + \sigma_r^2} \qquad \text{with} \qquad \sigma_L = \sqrt{\mathrm{var}(B)}$$

However, soil, biowaste and sludge are multi-phase materials, i.e. they contain two or more distinct types of particles which are fundamentally different in their properties and composition. As a consequence, this introduces an important source of variation for the intercomparison exercise which needs to be considered, i.e. the inherent heterogeneity of the materials.

Thus, a contribution of variation between samples *H* is introduced to the general statistical model:

$$y = m + B + e + H$$

Using ANOVA techniques the different variances are calculated and separated for the evaluation.

1.1.2 Requirements for precision experiment

Layout of the experiment

A suite of 10 to 12 different materials (soil, sludge and biowaste) has been made available for the intercomparison exercise. For each parameter investigated, at least 10 to laboratories should be nominated to participate. The same laboratories should be used for different parameters as far as possible. Due to the complexity of analysis and the respective workload to the laboratories, it was decided to propose three materials for the validation of the Kjeldahl nitrogen draft standard.

Each laboratory received two bottles of each material and was be requested to perform 6 independent analyses per material[1] (3 per bottle) using the respective draft standard methods. The 6 analysis per material should be carried out under repeatability conditions (i.e. same operator[2], same equipment, within a short period of time). As far as possible, also the different materials should be measured under repeatability conditions; however, changes of e.g. operator or equipment are permitted, but must be reported. Likewise, different materials can be analysed on different days if necessary.

Equipment used in the experiment needed to be checked prior to the experiment according to the requirements of the draft standard. The results of these checks have to be documented. Similarly, date and time of each measurement had to be recorded for verification of repeatability conditions.

An appropriate timeframe for the entire exercise has been set and was to be respected.

Recruitment of the laboratories

Each sub-workpackage leader of HORIZONTAL was asked to select the laboratories using the information from section 5.2 of ISO 5725-2:1994 and provide the signed questionnaires (see also Annex 1). The workpackage leaders were responsible for providing the laboratories with the draft standard method and explaining the context of this exercise.

Preparation and use of the materials

Materials used for the exercise were prepared according to the general requirements for reference materials as laid down in ISO Guide 34. Materials were accompanied by instructions for use.

Reporting of results

Online submissions of results using an internet-based IT platform as well as XLS-Spreadsheets were used. In case of online data submission, the participating laboratories received a unique and confidential login and password in due time, enabling them to

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[1] Independent analysis means analysis of independent test portions, applying the entire analytical scheme to this test portion, from e.g. extraction to quantification. For instance it does not mean replicate injections of aliquots into a GC-MS instrument.

[2] Operator in this context may also consist of a fixed team of persons, e.g. one person performing extraction, one clean-up, one quantification.

enter their data in a structured form. For authentication purposes a signed printout had to be submitted by mail.

The online data submission included a detailed questionnaire for additional information on the measurements.

1.1.3 Statistical analysis

Statistical analysis of data followed the requirements of ISO 5725-2:1994 and ISO 5725-5:1998. Appropriate tests for the homogeneity of variance, detection of outliers and normal distribution were applied. Statistical evaluation was done using an Excel Macro, developed, tested and successfully applied in other occasion by ECN. Evaluation was executed jointly by JRC and ECN.

1.2 Validation exercise for Kjeldahl nitrogen

1.2.1 Samples dispatched for the validation of Kjeldahl nitrogen

After a preliminary rough screening, the following materials were used for the validation round of Kjeldahl nitrogen:

- Compost 1 — A pollutant loaded compost material from Vienna
- Compost 2 — A pollutant loaded compost materia from Germany
- Sewage Sludge 1 — A mixed sewage sludge from Essen, Germany
- Sewage Sludge 2 — A mixed municipal WWTP sludge from North Rhine Westphalia, Germany
- Soil 4 — A sludge amended soil from Hohenheim, Germany
- Soil 5 — An agricultural soil from Reading, UK

A more detailed description of background concentrations can be found in Annex 2 to this report. The samples were dispatched simultaneously to all participants using a private courier service.

1.2.2 Draft standards to be followed

The draft standards to be followed could be downloaded following this link, which is situated on the website of the Project HORIZONTAL:

http://www.ecn.nl/docs/society/horizontal/Kjeldahl_N_Standard_for_validation.pdf

1.2.3 Analytical program

Of each of the six materials 2 bottles had to be analyzed and each bottle had to analyze independently three times. As mentioned above analyses were to be done under repeatability conditions. Results were to be reported referring to DRY MATTER content. The choice, how to apply d.m. correction was free for each participant.

1.2.4 Timing and Submission of data

Dispatch of samples was done on the 18th of October 2006. For users of the Online data submission system (MILC), User Registration was possible from 14th of November 2006 with opening of the MILC Data Submission on 1st of December 2006. The deadline for submission of results has been set for Kjeldahl nitrogen to the 31st of January 2007. After that no further submission was possible.

Alternatively the participants were allowed to submit data electronically as Excel sheet using simply Email.

All data were treated in a confidential way. Any presentation hereafter will refer only to numerical data and it will not be possible to identify the originating laboratory. Lab Codes displayed are NOT related to the order of laboratories hereafter.

In addition to the information provide a Helpdesk was implemented in order to give quick and individual response to the participants during and immediately after the validation study. In case of doubt and suspected transcription errors, further enquires were conducted by JRC.

1.2.5 Participants

The following table lists the participating organizations and entities in the validation exercise for the horizontal Kjeldahl nitrogen standard;

- Austria
  - Amt der Steirmärkischen Landesregierung
  - barbara - Engineering, Consulting, Research & Service GmbH
  - Magistrat der Stadt Wien
  - NUA Umweltanalytik GmbH
  - Universität für Bodenkultur Wien
  - Umweltbundesamt
  - Österreichische Agentur für Gesundheit und Ernährungssicherheit
- Belgium
  - VITO
- Czech Republic
  - Central Institute for Supervising and Testing in Agriculture (UKZUZ)
- France
  - CEMAGREF - UR QELY
  - Institut Pasteur de Lille - Dep. Eaux et Environnement
  - SAS Laboratoire
- Germany
  - Hessisches Landeslabor
- Hungary
  - Central Laboratory of National Institute for Agricultural Quality Control
  - Chemical Laboratory Mertcontrol Ltd,

1.3 Summary results and derived performance characteristics

The result of the various statistical evaluation including outlier tests, calculation of repeatability and reproducibility standard deviation for the congeners of interest can be found in Annex 3 of this report. In addition, all data submitted by the participants as well as those considered for the calculation of the performance characteristics are listed in Annex 3 to this report.

Based on these calculations the following results were obtained in the validation round upon statistical evaluation according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table1).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures. The repeatability limit was calculated using the relationship: $r_{test} = f \cdot \sqrt{2} \cdot s_{r,test}$ with the critical range factor f = 2.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures. The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor f = 2.

Table 1 - Results of the interlaboratory comparison studies of Kjeldahl nitrogen in treated biowaste, sludge and soil. All concentrations are expressed in g/kg dm.

Matrix	Parameter	Mean	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	Total no of data reported
Sludge 1	Kjeldahl	38.02	1.41%	4.36%	1.499	4.638	8	1	42	0	48
Sludge 2	Kjeldahl	35.27	1.24%	6.18%	1.221	6.100	9	1	48	0	54
Compost 1	Kjeldahl	16.22	2.15%	15.5%	0.978	7.043	9	2	42	0	54
Compost 2	Kjeldahl	12.68	4.50%	16.4%	1.597	5.839	10	1	54	0	58
Soil 4	Kjeldahl	1.62	7.19%	24.3%	0.327	1.107	11	0	44	0	44
Soil 5	Kjeldahl	1.83	4.42%	16.6%	0.226	0.852	9	1	46	0	52

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit (comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs.

1.4 Annexes

Annex 1: Model questionnaire to be filled by the participating laboratories

Annex 3: Report on the validation materials used

Annex 2: Statistical calculations

Annex 3: Data submitted

Annex 1:

Model questionnaire to be filled by the participating laboratories

Model questionnaire to be filled by the participating laboratories

Name of laboratory:
Contact person:
Contact details: email:
Phone:
Fax:
Mail address of lab:

Dispatch address of lab for shipment of samples (no PO boxes!):

Title of measurement method (copy attached):

Our laboratory is willing to participate in the precision experiment for this draft standard method.

Yes ☐ No ☐

As participant we understand that:

- All essential apparatus, chemicals and other requirements specified in the method must be available in our laboratory when the programme begins
- Specified timing requirements such as starting and finishing date of the programme must be rigidly met
- The method must be strictly adhered to
- Samples must be handled in accordance with instructions
- A qualified operator must perform the measurements

Having studied the method and having made a fair appraisal of our capabilities and facilities, we feel that we will be adequately prepared for cooperative testing of this method.

Comments:

…………………………………………………………………………………….
Signature Date

Annex 2:

Report on the validation materials used

Abstract

This report gives an overview on the available analytical information on the following raw materials to be used for the production of validation materials of the so-called Project HORIZONTAL:

- Four sludge materials from Düsseldorf, Germany,
- An agricultural soil material from Reading, United Kingdom;
- A compost material from Vienna, Austria;
- A compost material from Korschenbroich, Germany;
- A sludge-amended, agricultural soil from Pavia Province, Italy;
- A sludge-amended soil from Barcelona, Spain
- A sludge-amended soil from Essen, Germany
- A long-term sludge exposed soil from Hohenheim, Germany

List of Abbreviations

Throughout this report the following abbreviations are used.

AOX	absorbable organic halogens
C_{org}	organic carbon content
C_{total}	total carbon content
CAT	cation exchangeable
CDD	chlorinated dibenzodioxin
CDF	chlorinated dibenzofuran
DEHP	di(2-ethylhexyl)phthalate
DM	dry matter
EPA	Environment Protection Agency
EU	European Union
FM	fresh matter
Hp	hepta
Hx	hexa
IES	Institute for Environment and Sustainability
IRMM	Institute for Reference Materials and Measurements
JRC	Joint Research Centre
LAS	linear alkylsulfonates
LoD	limit of detection
LUA	Landesumweltamt
N_{total}	total nitrogen content
NH_4-N	Ammonium nitrogen
NO_3-N	Nitrate nitrogen
NP	nonylphenol
NRW	North Rhine Westphalia
O	octa
P	poly
PAH	polycyclic aromatic hydrocarbon
PCB	polychlorinated biphenyl
Pe	penta
T	tetra
TEQ	toxicity equivalent
UBA	Umweltbundesamt
WHO	World Health Organization
WWTP	waste water treatment plant

1 Introduction

This report gives an overview on the available analytical information on the following raw materials to be used for the production of validation materials of the so-called Project HORIZONTAL:

- Four sludge materials from Düsseldorf, Germany,
- An agricultural soil material from Reading, United Kingdom;
- A compost material from Vienna, Austria;
- A compost material from Korschenbroich, Germany;
- A sludge-amended, agricultural soil from Pavia Province, Italy;
- A sludge-amended soil from Barcelona, Spain
- A sludge-amended soil from Essen, Germany
- A long-term sludge exposed soil from Hohenheim, Germany

The following analytical information was gathered partly before and during the sampling of the raw materials, to be used for the production of the HORIZONTAL validation materials. The material were sampled by IES and shipped to IRMM in the course of the year 2005. The information gathered was then completed by various analytical screenings for PAHs and PCBs done by the Institute for Reference Materials and Measurements, Geel, Belgium, for phthalates done by UBA, Berlin, Germany, for PBDE done by IIQAB-CSIC, Barcelona, Spain, for trace elements and some selected major and minor elements by the Institute for Environment and Sustainability, Ispra, Italy.

The work compiled hereafter is based on the numerous additional efforts of the scientists working at various members of the consortium Project HORIZONTAL-Org and contributing organisations.

This work is gratefully acknowledged.

2 Overview on property values

2.1 Sludge materials from Düsseldorf, Germany

The various sewage sludge materials originate from various installations in the North Rhine Westphalia and were produced and sampled by staff from the Landesumweltamt (LUA) NRW under the responsibility from Dr. K. Furtmann.

In total, four sludge materials (Sludge A and D from a major municipal WWTP, Sludge B from a municipal WWTP with industrial input, and Sludge C from a municipal WWTP with high PCB-Content,) were obtained and will be blended to two final materials. Before sampling the following analytical data for a typical sample were received.

Table 1 – Analytical data obtained on an average sludge sample in LUA NRW (with courtesy of K. Furtmann, LUA, Düsseldorf)

Parameter	*Concentration*
PCB	120 ug/kg
DEHP	110 mg/kg
PAH	5 mg/kg (EPA)
PCDD/F	15 ng TE/kg
PBDE	400 ug/kg
NP	40 mg/kg
LAS	3 g/kg
AOX	300 mg/kg

Subsequent screening led to the information displayed hereafter. It should be stressed that the data were obtained as SCREENING information on the UNTREATED or partially treated raw materials. Therefore, the final target values, which are relevant for the validation intercomparison can be different.

Table 2 – Analytical data obtained on a first screening on the sludge samples from LUA NRW

	Sewage sludge A Dusseldorf	*sewage sludge D Dusseldorf*
PCB (ng/g)		
28	62	35
52	101	65
101	31	38
118	49	40
153	30	33
105	24	11
138	46	38
156	<1	<1
180	34	23
170	23	19
PAH (ng/g)		
Naphtalene	34	381
Acenaphtylene	15	43
Acenaphthene	81	108
Fluorene	94	1167
Phenantrene		3440
Anthracene	22	344
Flouranthene	316	4817
Pyrene	235	3011
Benz(a)anthracene	473	791
Chrysene	691	1078
Benz(b)fluoranthene	538	1688
Benz(k)fluoranthene	228	635
Benz(a)pyrene	383	1114
Indeno(1,2,3-c,d)pyrene	92	229
Dibenzo(a,h)anthracene	71	70
Benzo(g,h,i)perylene	80	185

Table 3 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Sludge D (1)		0.135		41.474	3.85
Sludge B (2)	0.538	0.034		30.634	5.47
Sludge A (3)	0.184	0.037		31.399	1.46
Sludge C (4)		0.354	1.528	6.678	2.29

Table 4 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Sludge 2 (B)
Tetra-BDE-47	55.4
Penta-BDE-100	9.59
Penta-BDE-99	69.4
Hexa-BDE-154	5.91
Hexa-BDE-153	7.72
Hepta-BDE-183	5.09
Octa-BDE-196	nq
Octa-BDE-197	nq
Octa-BDE-203	9.70
Deca-BDE-209	2216
TOTAL	2379

Table 5 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena, IES, Ispra, Spain). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Sludge 1 (D)	2.65	29.0	53.3	359	1231	33.8	78.4	4.38	< 0.05	23.2	786
Sludge 2 (B)	1.19	31.1	62.6	202	278	29.9	72.2	2.51	< 0.05	11.8	625
Sludge 3 (A)	1.68	36.0	62.1	332	847	41.6	119	4.51	< 0.05	11.6	1237
Sludge 4 (C)	5.63	19.8	116	273	726	51.1	473	6.18	< 0.05	44.4	2015

Table 6 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Sludge 1 (D)	21.54	5.8	8.44	0.99	10.3	1.01	4367	<15	50448
Sludge 2 (B)	10.67	3.66	6.92	0.46	14.91	0.77	5217	<15	57633
Sludge 3 (A)	7.31	6.63	6.84	0.35	12.87	0.68	3733	<15	60369
Sludge 4 (C)	43.79	9.65	5.27	1.63	5.22	1.07	5628	<15	23945

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Sludge 1 (D)	0.3	2403	101	1002	350	15	1944	132
Sludge 2 (B)	0.31	315	97	879	172	12	514	180
Sludge 3 (A)	0.31	1281	153	1567	265	16	1440	168
Sludge 4 (C)	0.55	231	628	2625	371	81	1101	244

2.2 Agricultural soil material from Reading, United Kingdom

The material was proposed by the University of Reading (S. Nortcliff) and was sampled from a site called "*Frogmore Farm*" which was featured in the "*Metals*" Report for HORIZONTAL. This site is close to Reading with soils developed on flintyloamy periglacial materials over Chalk, has a long and well documented history of sludge application. The focus of the work of Nortcliff *et al.* undertook at this site and the monitoring and control at the site (by Thames Water and the subsequent subsidiary bodies dealing with sludge application to soil) was on metals (and metal loads), with no analysis or indeed any form of investigation in to organics in the broadest sense.

The analytical information produced in the context of the screening of the raw material is displayed below.

Table 7 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Soil 3 (Reading)		0.032		0.119	6.69

Table 8 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 3 (Reading)	0.15	7.06	27.9	13.8	152	9.01	26.7	3.00	< 0.05	25.8	93.1

Table 9 – Analytical data obtained on a first screening on the sludge-amended soil from Reading (courtesy of IRMM)

Parameter	*Concentration*
PCB	**ng/g**
28	<1
52	<1
101	<1
118	<1
153	<1
105	<1
138	<1
156	<1
180	<1
170	<1
PAH	**ng/g**
Naphtalene	<10
Acenaphtylene	21
Acenaphthene	<10
Fluorene	<10
Phenantrene	<10
Anthracene	<10
Flouranthene	818
Pyrene	776
Benz(a)anthracene	565

Parameter	*Concentration*
Chrysene	608
Benz(b)fluoranthene	824
Benz(k)fluoranthene	329
Benz(a)pyrene	799
Indeno(1,2,3-c,d)pyrene	779
Dibenzo(a,h)anthracene	118
Benzo(g,h,i)perylene	394

Table 10 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 3 (Reading)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	1.03
Hexa-BDE-154	0.03
Hexa-BDE-153	nq
Hepta-BDE-183	nq
Octa-BDE-196	nq
Octa-BDE-197	nd
Octa-BDE-203	nd
Deca-BDE-209	272
TOTAL	273

Table 11 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 3 (Reading)	0.15	7.06	27.9	13.8	152	9.01	26.7	3.00	< 0.05	25.8	93.1

Table 12 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 3 (Reading)	79.36	4.77	1.12	0.96	1.94	0.17	4107	443	2102

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 3 (Reading)	0.42	13	45	69	69	69	216	92

Table 13 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg*** *µg/g*
Soil 3 (Reading)	0.12

2.3 Compost from Vienna, Austria

The fresh compost material was obtained from the Austrian Federal Environment Agency (UBA, Vienna), which had used a sub-batch of the raw material for national intercomparson. The remainder of the material was stored at 4°C until shipment to IRMM for further processing. The following analytical information was provided by UBA Austria and completed with various screenings.

Table 14 – Analytical data on compost material received from UBA Austria Inorganic and sum parameters

Parameter	*Unit*	*Sample fraction used*	*Observed mean*
B CAT	mg/l F.M.	Fresh sample, <10mm	6.1
K CAT	mg/l F.M.	Fresh sample, <10mm	2624
Mg CAT	mg/l F.M.	Fresh sample, <10mm	242
P CAT	mg/l F.M.	Fresh sample, <10mm	49
B CAT	% D.M.	Fresh sample, <10mm	0.0017
K CAT	% D.M.	Fresh sample, <10mm	0.72
Mg CAT	% D.M.	Fresh sample, <10mm	0.07
P CAT	% D.M.	Fresh sample, <10mm	0.01
NO3-N	mg/kg F.M.	Fresh sample, <10mm	3.5
NH4-N	mg/kg F.M.	Fresh sample, <10mm	230
Ctotal	% D.M.	<45°dry, milled	29
Corg	% D.M.	<45°dry, milled	27
Ntotal	% D.M.	<45°dry, milled	1.7
P	mg/kg D.M.	<45°dry, milled	2596
K	mg/kg D.M.	<45°dry, milled	11019
K	% D.M.	<45°dry, milled	1.10
B	mg/kg D.M.	<45°dry, milled	60
Cd	mg/kg D.M.	<45°dry, milled	0.46
Cr	mg/kg D.M.	<45°dry, milled	25
Cu	mg/kg D.M.	<45°dry, milled	46
Hg	mg/kg D.M.	<45°dry, milled	0.20
Ni	mg/kg D.M.	<45°dry, milled	18
Pb	mg/kg D.M.	<45°dry, milled	45
Zn	mg/kg D.M.	<45°dry, milled	198
Ca	mg/kg D.M.	<45°dry, milled	68776
Ca	% D.M.	<45°dry, milled	6.9
Mo	mg/kg D.M.	<45°dry, milled	0.8
S	mg/kg D.M.	<45°dry, milled	2137
Fe	mg/kg D.M.	<45°dry, milled	9959
Mn	mg/kg D.M.	<45°dry, milled	418
Na	mg/kg D.M.	<45°dry, milled	742
Co	mg/kg D.M.	<45°dry, milled	4.1
AOX	mg/kg D.M.	<30° dry, milled	62

Table 15 – Analytical data on compost material received from UBA Austria Polycyclic aromatic hydrocarbons

PAH	*Unit*	*Result*
Naphthaline	µg/kg DM	9.3
Acenaphthylene	µg/kg DM	8.6
Acenaphthene	µg/kg DM	5
Fluorene	µg/kg DM	8.0
Phenanthrene	µg/kg DM	89
Anthracene	µg/kg DM	27
Fluoranthene	µg/kg DM	487
Pyrene	µg/kg DM	380

PAH	*Unit*	*Result*
Benzo(a)anthracene	µg/kg DM	278
Chrysene	µg/kg DM	317
Benzo(b)fluoranthene	µg/kg DM	365
Benzo(k)fluoranthene	µg/kg DM	193
Benz(a)pyrene	µg/kg DM	320
Indeno(1,2,3-c,d)pyrene	µg/kg DM	233
Dibenz(a,h)anthracene	µg/kg DM	67
Benzo(g,h,i)perylene	µg/kg DM	225
Sum EPA	µg/kg DM	3013
Sum EPA	mg/kg DM	3.0

Table 16 – Analytical data on compost material received from UBA Austria Sum PCDDs and PCBs

Parameter			
Dioxine	TEQ (ITEF)	ng/kg DM	7.3
PCB	TEQ (WHO)	ng/kg DM	3.5
	Σ Ballschmiter	mg/kg DM	0.05

Table 17 – Analytical data on compost material obtained by screening in IRMM

Parameter	*Result in ng/g*
PCB	
28	2
52	2
101	4
118	3
153	10
105	1
138	8
156	1
180	5
170	<1
PAH	
Naphtalene	<10
Acenaphtylene	<10
Acenaphthene	<10
Fluorene	<10
Phenantrene	<10
Anthracene	26
Fluoranthene	611
Pyrene	510
Benz(a)anthracene	888
Chrysene	957
Benz(b)fluoranthene	1531
Benz(k)fluoranthene	547
Benz(a)pyrene	1101
Indeno(1,2,3-c,d)pyrene	416
Dibenzo(a,h)anthracene	81
Benzo(g,h,i)perylene	295

Table 18 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Compost 1 (Vienna)
Tetra-BDE-47	4.02
Penta-BDE-100	0.19
Penta-BDE-99	2.59
Hexa-BDE-154	nq
Hexa-BDE-153	0.23
Hepta-BDE-183	0.04
Octa-BDE-196	nq
Octa-BDE-197	nq
Octa-BDE-203	1.44
Deca-BDE-209	17.4
TOTAL	25.9

Table 19 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Compost 1 (Vienna)		0.058		1.426	5.57

Table 20 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Compost 1 (Vienna)	0.39	7.36	31.9	41.0	365	12.7	49.5	0.04	0.79	0.13	208

Table 21 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Compost 1 (Vienna)	20.63	4.31	6.17	4.26	1.99	2.49	1602	<15	10521

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Compost 1 (Vienna)	0.35	3496	81	375	79	55	653	60

Table 22 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg** µg/g*
Compost 1 (Vienna)	0.17

2.4 Agricultural soil, sludge amended soil from Pavia, Italy

This sludge-amended soil material was obtained during a monitoring campaign, which aimed at a generic description of the over-all soil quality in Pavia Province, Italy. The material, which was collected from the upper horizon, originates from a small farm called "*Cascina Novello*". During the characterisation of the site, the following analytical information was obtained on a pooled sample of a sub-area of the farm of 20 X 20 m^2.

Table 23 – Analytical data on Pavia soil

Parameter	*Result*
Al	7.13 Wgt%
As	22.4 mg/kg
Cd	0.79 mg/kg
Cr	59 mg/kg
Cu	30.8 mg/kg
Hg	0.08 mg/kg
Ni	34.4 mg/kg
Pb	24.6 mg/kg
Zn	95 mg/kg
C	0.91 Wgt %
2,3,7,8-TCDD	0.047 pg/g
1,2,3,7,8-PeCDD	0.15 pg/g
1,2,3,4,7,8-HxCDD	0.19 pg/g
1,2,3,6,7,8-HxCDD	1.5 pg/g
1,2,3,7,8,9-HxCDD	0.74 pg/g
1,2,3,4,6,7,8-HpCDD	26 pg/g
OCDD	382 pg/g
2,3,7,8-TCDF	0.68 pg/g
1,2,3,7,8-PeCDF	0.53 pg/g
2,3,4,7,8-PeCDF	0.71 pg/g
1,2,3,4,7,8-HxDF	1.00 pg/g
1,2,3,6,7,8-HxDF	0.66 pg/g
2,3,4,6,7,8-HxDF	1.6 pg/g
1,2,3,7,8,9-HxDF	0.27 pg/g
1,2,3,4,6,7,8-HpDF	12 pg/g
1,2,3,4,7,8,9-HpDF	0.68 pg/g
OCDF	33 pg/g
I-TEQ	2.0 pg/g
WHO-TEQ	1.7 pg/g

In addition, the screening performed at IRMM did not reveal significant quantities of PCBs and PAHs, which were all below the LoDs (1 ng/g for PCBs and 10 ng/g for PAHs, respectively).

Table 24 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g TM	µg/g TM	µg/g TM	µg/g TM	Wgt. %
Soil 5 (Pavia)		0.005		0.011	1.54

Table 25 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 5 (Pavia)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	0.39
Hexa-BDE-154	nq
Hexa-BDE-153	nq
Hepta-BDE-183	0.08
Octa-BDE-196	nq
Octa-BDE-197	nd
Octa-BDE-203	nd
Deca-BDE-209	670
TOTAL	671

Table 26 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 5 (Pavia)	0.33	18.4	57.3	22.5	426	30.5	20.6	2.00	< 0.05	38.1	87.8

Table 27 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 5 (Pavia)	69.39	12.9	1.45	2.24	4.25	1.16	6118	255	1789

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 5 (Pavia)	1.84	62	38	108	55	66	597	110

Table 28 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg*** *µg/g*
Soil 5 (Pavia)	0.06

2.5 Sludge-amended-soil from Barcelona, Spain

The sludge-amended soil material from Barcelona sampled upon indication from the Barcelo'- Group in Barcelona.

Table 29 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Soil 2 (Lleida T.)		0.015		0.183	11.38

Table 30 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 2 (Lleida T.)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	1.59
Hexa-BDE-154	0.45
Hexa-BDE-153	nq
Hepta-BDE-183	0.48
Octa-BDE-196	1.60
Octa-BDE-197	nq
Octa-BDE-203	nq
Deca-BDE-209	1000
TOTAL	1004

Table 31 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 2 (Lleida T.)	0.59	14.1	32.7	53.6	405	18.6	18.4	2.24	< 0.05	31.8	111

Table 32 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 2 (Lleida T.)	44.43	10.67	14.29	2.53	3.44	2.04	4116	780	3396

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 2 (Lleida T.)	0.64	65	26	125	59	17	547	65

Table 33 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	***Hg*** *µg/g*
Soil 2 (Lleida T.)	0.10

2.6 Sludge amended soil from Essen, Germany

The German sludge-amended soil from Essen, which was provided as the three sludge materials by LUA NRW, did not feature significant concentrations of the PCB congeners 28, 52, 101, 118, 153, 105, 138, 156, 180, 170, but had detectable amounts of some PAHs.

Table 34 – Analytical screening data on the German sludge-amended soil.

Parameter	*Concentration (ng/g)*
Naphtalene	<10
Acenaphtylene	<10
Acenaphthene	<10
Fluorene	<10
Phenantrene	<10
Anthracene	<10
Fluoranthene	28
Pyrene	20
Benz(a)anthracene	24
Chrysene	47
Benz(b)fluoranthene	76
Benz(k)fluoranthene	20
Benz(a)pyrene	35
Indeno(1,2,3-c,d)pyrene	35
Dibenzo(a,h)anthracene	10
Benzo(g,h,i)perylene	26

Table 35 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	*DBP*	*DCHP*	*DEHP*	*Water*
	µg/g dm	µg/g dm	µg/g dm	µg/g dm	Wgt. %
Soil 4 (Essen)		0.011		0.302	0.55

Table 36 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 4 (Essen)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	nq
Hexa-BDE-154	nq
Hexa-BDE-153	nq
Hepta-BDE-183	nq
Octa-BDE-196	nq
Octa-BDE-197	nq
Octa-BDE-203	1.28
Deca-BDE-209	19.1
TOTAL	20.3

Table 37 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	Co	Cr	Cu	Mn	Ni	Pb	Sb	Tl	V	Zn
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 4 (Essen)	0.52	5.45	26.1	8.05	320	4.03	27.3	2.73	< 0.05	29.5	78.1

Table 38 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	SiO2 (%)	Al2O3 (%)	CaO (%)	K2O (%)	Fe2O3 (%)	MgO (%)	TiO2 (PPM)	S (PPM)	P2O5 (PPM)
Soil 4 (Essen)	79.47	4.42	0.85	0.6	0.86	0.07	2163	189	2019

Sample	Na2O (%)	Cl (PPM)	Pb (PPM)	Zn (PPM)	Cu (PPM)	Ni (PPM)	Mn (PPM)	Cr (PPM)
Soil 4 (Essen)	0.45	19	42	87	683	60	462	61

Table 39 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

Sample	Hg µg/g
Soil 4 (Essen)	0.04

2.7 Long-term sludge exposed soil from Hohenheim-Stuttgart, Germany

Similarly, an additional sludge exposed soil was sampled at the University of Hohenheim, Stuttgart, were a test soil was long-term exposed to elevated concentrations of sewage sludge.

Table 40 – Data on phthalate contents (with courtesy of S. Heise, UBA, Germany)

	DiBP	DBP	DCHP	DEHP	Water
	µg/g TM	µg/g TM	µg/g TM	µg/g TM	Wgt. %
Soil 1 (Stuttgart)		0.045		0.263	17.65

Table 41 – Data on PDBE contents (with courtesy of D. Barceló and co-workers, IIQAB-CSIC, Barcelona, Spain)

	Soil 1 (Stuttgart)
Tetra-BDE-47	nq
Penta-BDE-100	nq
Penta-BDE-99	2.30
Hexa-BDE-154	0.06
Hexa-BDE-153	0.04
Hepta-BDE-183	0.04
Octa-BDE-196	nq
Octa-BDE-197	nd
Octa-BDE-203	nd
Deca-BDE-209	498
TOTAL	500

Table 42 – Screening data on some selected trace elements by ICP-AES after micro-wave assisted digestion using aqua regia (with courtesy of F. Sena). Note that these data are based on single measurements!

	Cd	***Co***	***Cr***	***Cu***	***Mn***	***Ni***	***Pb***	***Sb***	***Tl***	***V***	***Zn***
	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g	µg/g
Soil 1 (Stuttgart)	0.69	12.7	36.1	26.2	504	18.3	25.2	2.62	< 0.05	26.6	142

Table 43 – Screening data on some selected matrix constituents and elements by WDXRF (with courtesy of S. Vaccaro).

Sample	***SiO2 (%)***	***Al2O3 (%)***	***CaO (%)***	***K2O (%)***	***Fe2O3 (%)***	***MgO (%)***	***TiO2 (PPM)***	***S (PPM)***	***P2O5 (PPM)***
Soil 1 (Stuttgart)	71.94	10.06	1.33	1.86	3.66	0.88	7874	275	3571

Sample	***Na2O (%)***	***Cl (PPM)***	***Pb (PPM)***	***Zn (PPM)***	***Cu (PPM)***	***Ni (PPM)***	***Mn (PPM)***	***Cr (PPM)***
Soil 1 (Stuttgart)	1.23	50	47	212	85	69	991	129

Table 44 – Screening data on mercury by solid-sampling cold-vapour AAS using amalgamation enrichment (with courtesy of G. Locoro).

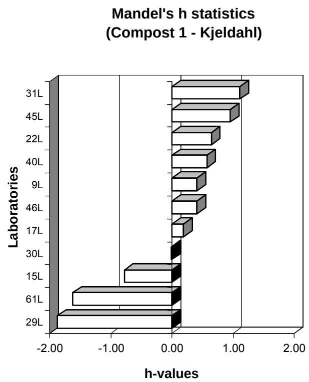
Sample	***Hg*** *µg/g*
Soil 1 (Stuttgart)	1.77

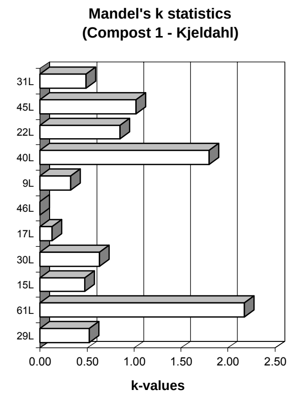
Annex 3:

Statistical calculations

Sample: **Compost 1**

Element: **Kjeldahl**





Unit: mg/g

Mandel's k statistics (Compost 1 - Kjeldahl)
Mandel's h statistics (Compost 1 - Kjeldahl)

Compost 1 - Kjeldahl -- Mean PARM = 16.22 [mg/g]

	General calc.parm.
T1=	6.87787E+02
T2=	1.14931E+04
T3=	42
T4=	214
T5=	4.0239E+00
n=	variabel
p=	9
N-table=	*5*

Mandel's statistics | End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
29L	10.9050	0.290	4	!	-1.87	0.52			Fail	10.9050	0.2901		4	3	-5.31
61L	11.5665	1.206	6		-1.62	2.18	!!		Fail	-	-	,61L	-	-	-4.65
15L	13.8195	0.264	6		-0.78	0.48			Fail	13.8195	0.2640		6	5	-2.40
30L	15.8667	0.351	3		-0.01	0.63				15.8667	0.3512		3	2	-0.35
17L	16.4100	0.071	2		0.19	0.13				16.4100	0.0707		2	1	0.19
46L	17.0000		4		0.41			Fail		17.0000			4	3	0.78
9L	17.0000	0.179	6		0.41	0.32		Fail		17.0000	0.1789		6	5	0.78
40L	17.4217	0.998	6		0.57	1.80	!!	Fail		-	-	,40L	-	-	1.20
22L	17.6267	0.473	6		0.64	0.85		Fail		17.6267	0.4729		6	5	1.41
45L	18.4517	0.566	6		0.95	1.02		Fail		18.4517	0.5659		6	5	2.23
31L	18.8720	0.270	5		1.11	0.49		Fail		18.8720	0.2701		5	4	2.66
Tot.gem	15.904	0.424 mg/g		*1%-level:*	2.22	(1.74)			9	*16.2168*		(40L ,61L)	9	8	
Tot.std=	2.672	0.374		*5%-level:*	1.82	(1.51)			2						

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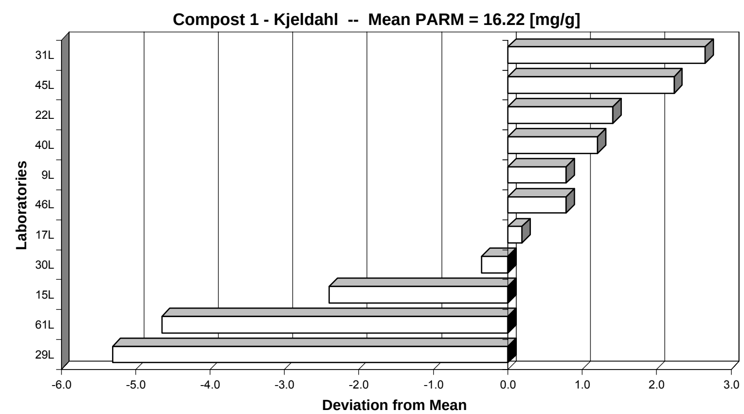
RESULTS:	**Mean =**	**16.21683**	*mg/g*				
Repeatability variance	**S2r =**	0.12194					
Repeatability std.	**Sr =**	**0.34919**	-->	2.15%		**r =**	0.9777
Between lab variance	**S2L =**	6.20586					
Reproducibility var.	**S2R =**	6.32780					
Reproducibility std.	**SR =**	**2.51551**	-->	15.51%		**R =**	7.0434
Remarks:	**2 Labs rejected! (40L ,61L)**						



Unit: mg/g

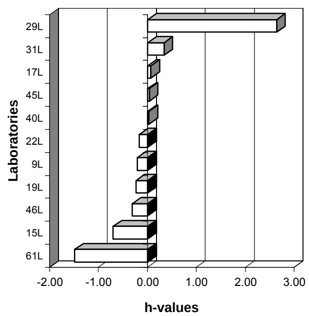
Mandel's k statistics (Compost 2 - Kjeldahl)
Mandel's h statistics (Compost 2 - Kjeldahl)

Compost 2 - Kjeldahl -- Mean PARM = 12.68 [mg/g]

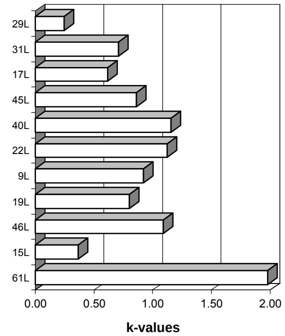
Sample: **Compost 2**

Element: **Kjeldahl**

Mandel's h statistics (Compost 2 - Kjeldahl)



Mandel's k statistics (Compost 2 - Kjeldahl)



	General calc.parm.
T1=	6.79812E+02
T2=	8.75546E+03
T3=	54
T4=	308
T5=	1.4309E+01
n=	variabel
p=	10
N-table=	*5*

Mandel's statistics | End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
61L	8.0274	1.050	6		-1.49	1.98	!!		Fail	8.0274	1.0501		6	5	-4.65
15L	11.0115	0.194	6		-0.70	0.36			Fail	11.0115	0.1936		6	5	-1.67
46L	12.5000	0.577	4		-0.31	1.09			Fail	12.5000	0.5774		4	3	-0.18
19L	12.7697	0.426	6		-0.24	0.80			Fail	12.7697	0.4257		6	5	0.09
9L	12.8833	0.488	6		-0.21	0.92			Fail	12.8833	0.4875		6	5	0.21
22L	13.0500	0.596	6		-0.17	1.12			Fail	13.0500	0.5958		6	5	0.37
40L	13.7950	0.613	6		0.03	1.16				13.7950	0.6133		6	5	1.12
45L	13.8100	0.457	6		0.03	0.86				13.8100	0.4574		6	5	1.13
17L	13.9500	0.325	2		0.07	0.61				13.9500	0.3253		2	1	1.27
31L	14.9717	0.376	6		0.34	0.71		Fail		14.9717	0.3759		6	5	2.29
29L	23.7200	0.128	4	!!	2.64	0.24		Fail	-	-	,29L	-	-		11.04
Tot.gem	13.681	0.475 mg/g		*1%-level:*	2.22	(1.74)			10	*12.6769*	(29L)		10	9	
Tot.std=	3.807	0.247		*5%-level:*	1.82	(1.51)			1						

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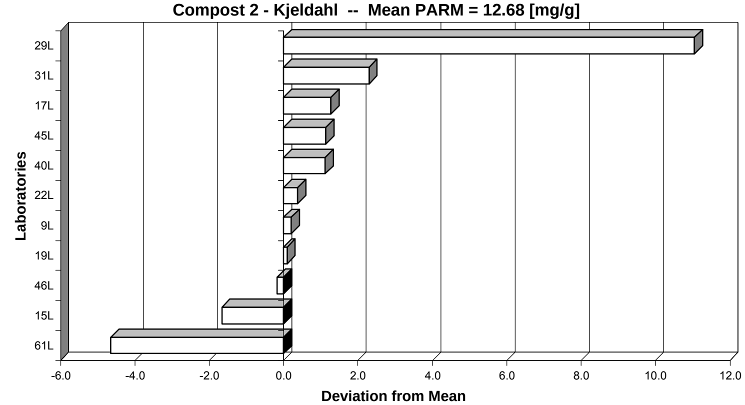
RESULTS:	**Mean =**	**12.67686**	*mg/g*			
Repeatability variance	**S2r =**	0.32521				
Repeatability std.	**Sr =**	**0.57027**	-->	4.50%	**r =**	1.5968
Between lab variance	**S2L =**	4.02333				
Reproducibility var.	**S2R =**	4.34855				
Reproducibility std.	**SR =**	**2.08532**	-->	16.45%	**R =**	5.8389
Remarks:	**1 Lab rejected! (29L)**					

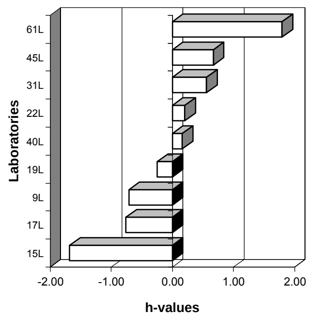
Compost 2 - Kjeldahl -- Mean PARM = 12.68 [mg/g]



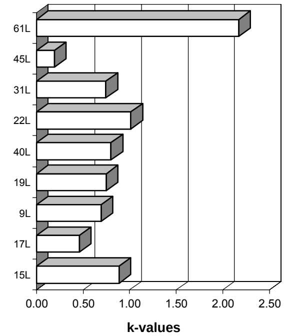
Sample: **Sludge 1**

Element: **Kjeldahl**

Mandel's h statistics (Sludge 1 - Kjeldahl)



Mandel's k statistics (Sludge 1 - Kjeldahl)



Unit: mg/g

Mandel's k statistics (Sludge 1 - Kjeldahl)
Mandel's h statistics (Sludge 1 - Kjeldahl)

Sludge 1 - Kjeldahl -- Mean PARM = 38.02 [mg/g]

General calc.parm.	
T1=	1.59799E+03
T2=	6.08905E+04
T3=	42
T4=	236
T5=	9.7418E+00
n=	variabel
p=	8
N-table=	*5*

Mandel's statistics — End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
15L	35.1812	0.626	6		-1.68	0.89			Fail	35.1812	0.6265		6	5	-2.84
17L	36.9800	0.325	2		-0.76	0.46			Fail	36.9800	0.3253		2	1	-1.04
9L	37.0667	0.489	6		-0.71	0.69			Fail	37.0667	0.4885		6	5	-0.95
19L	37.9817	0.529	6		-0.24	0.75				37.9817	0.5294		6	5	-0.04
40L	38.7717	0.565	6		0.16	0.80				38.7717	0.5650		6	5	0.75
22L	38.8650	0.716	6		0.21	1.01				38.8650	0.7156		6	5	0.84
31L	39.5500	0.526	4		0.56	0.75		Fail		39.5500	0.5260		4	3	1.53
45L	39.7717	0.136	6		0.67	0.19		Fail		39.7717	0.1356		6	5	1.75
61L	41.9730	1.530	6	!	1.80	2.17	!!	Fail	-	-	,61L	-	-		3.95
Tot.gem	38.460	0.605 mg/g		*1%-level:*	2.13	(1.73)			8	*38.0210*	(61L)		8	7	
Tot.std=	1.956	0.386		*5%-level:*	1.78	(1.5)			1						

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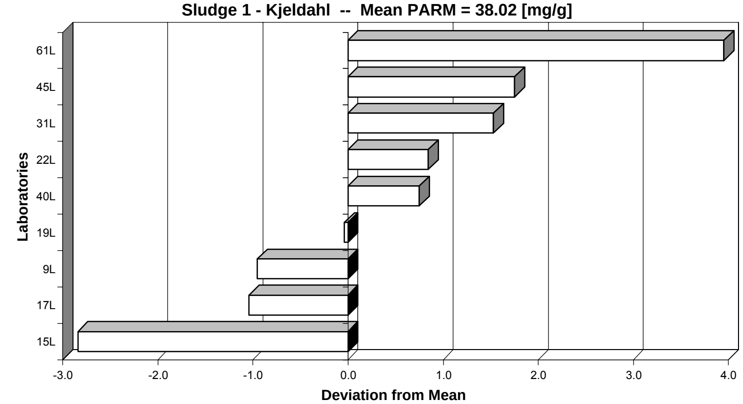
RESULTS:	**Mean =**	**38.02098**	*mg/g*			
Repeatability variance	**S2r =**	0.28652				
Repeatability std.	**Sr =**	**0.53528**	-->	1.41%	**r =**	1.4988
Between lab variance	**S2L =**	2.45705				
Reproducibility var.	**S2R =**	2.74357				
Reproducibility std.	**SR =**	**1.65637**	-->	4.36%	**R =**	4.6378
Remarks:	**1 Lab rejected! (61L)**					

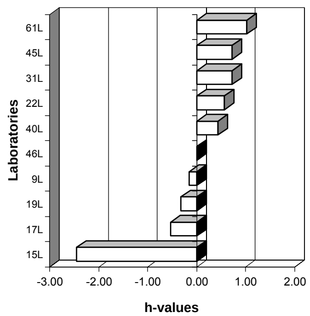
Sludge 1 - Kjeldahl -- Mean PARM = 38.02 [mg/g]



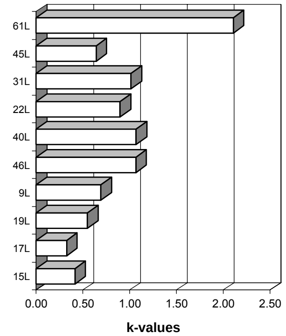
Sample: **Sludge 2**

Element: **Kjeldahl**

Mandel's h statistics (Sludge 2 - Kjeldahl)



Mandel's k statistics (Sludge 2 - Kjeldahl)



Unit: mg/g

Mandel's k statistics (Sludge 2 - Kjeldahl)
Mandel's h statistics (Sludge 2 - Kjeldahl)

Sludge 2 - Kjeldahl -- Mean PARM = 35.27 [mg/g]

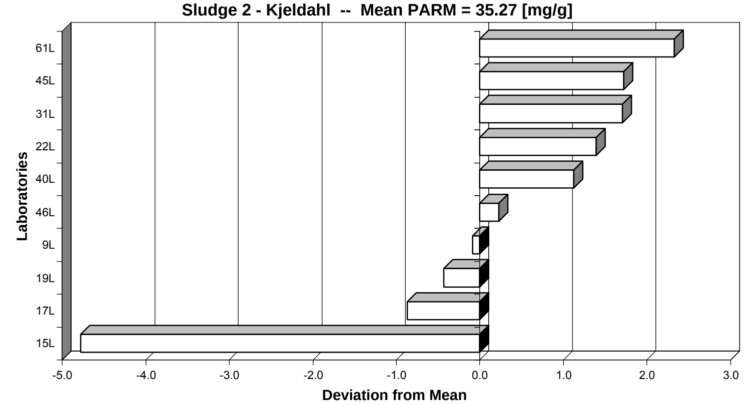
	General calc.parm.
T1=	1.69616E+03
T2=	6.01313E+04
T3=	48
T4=	272
T5=	7.4118E+00
n=	variabel
p=	9
N-table=	*5*

Mandel's statistics | End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*AvX > AvST+2std*	*AvX < AvST-2std*		*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
15L	30.4925	0.225	6	!!	-2.45	0.41			Fail		30.4925	0.2245		6	5	-4.78
17L	34.4050	0.177	2		-0.54	0.33			Fail		34.4050	0.1768		2	1	-0.87
19L	34.8398	0.298	6		-0.33	0.55			Fail		34.8398	0.2981		6	5	-0.43
9L	35.1833	0.376	6		-0.16	0.69					35.1833	0.3764		6	5	-0.09
46L	35.5000	0.577	4		0.00	1.06					35.5000	0.5774		4	3	0.23
40L	36.3983	0.579	6		0.44	1.07		Fail			36.3983	0.5792		6	5	1.12
22L	36.6667	0.486	6		0.57	0.90		Fail			36.6667	0.4863		6	5	1.39
31L	36.9833	0.549	6		0.72	1.01		Fail			36.9833	0.5492		6	5	1.71
45L	36.9950	0.349	6		0.73	0.64		Fail			36.9950	0.3486		6	5	1.72
61L	37.5979	1.141	6		1.02	2.10	!!	Fail		-	-	,61L	-	-		2.32
Tot.gem	35.506	0.476 mg/g		*1%-level:*	2.18	(1.74)				9	*35.2738*	(61L)		9	8	
Tot.std=	2.050	0.275		*5%-level:*	1.80	(1.5)				1						
										54						

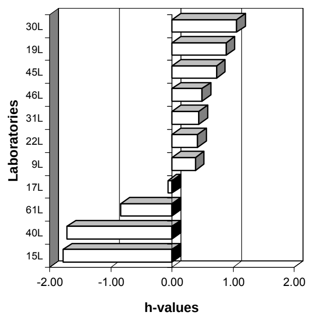
RESULTS:	**Mean =**	**35.27378**	*mg/g*			
Repeatability variance	**S2r =**	0.19005				
Repeatability std.	**Sr =**	**0.43594**	-->	1.24%	**r =**	1.2206
Between lab variance	**S2L =**	4.55636				
Reproducibility var.	**S2R =**	4.74640				
Reproducibility std.	**SR =**	**2.17862**	-->	6.18%	**R =**	6.1001
Remarks:	**1 Lab rejected! (61L)**					

Sludge 2 - Kjeldahl -- Mean PARM = 35.27 [mg/g]

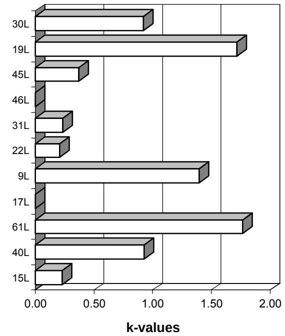


Sample:	**Soil 4**
Element:	**Kjeldahl**

Mandel's h statistics (Soil 4 - Kjeldahl)



Mandel's k statistics (Soil 4 - Kjeldahl)



Unit: mg/g

Mandel's k statistics (Soil 4 - Kjeldahl)
Mandel's h statistics (Soil 4 - Kjeldahl)

Soil 4 - Kjeldahl -- Mean PARM = 1.62 [mg/g]

	General calc.parm.
T1=	6.97604E+01
T2=	1.16386E+02
T3=	44
T4=	194
T5=	4.4967E-01
n=	variabel
p=	11
N-table=	*4*

Mandel's statistics / End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*	*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
15L	0.9896	0.025	5		-1.78	0.23			Fail	0.9896	0.0249		5	4	-0.63
40L	1.0120	0.101	5		-1.72	0.92			Fail	1.0120	0.1006		5	4	-0.61
61L	1.3245	0.192	5		-0.84	1.77	!!		Fail	1.3245	0.1922		5	4	-0.30
17L	1.6000	-	1		-0.07					1.6000 -			1		-0.02
9L	1.7600	0.152	5		0.38	1.39				1.7600	0.1517		5	4	0.14
22L	1.7725	0.022	4		0.42	0.20		Fail		1.7725	0.0222		4	3	0.15
31L	1.7800	0.025	5		0.44	0.23		Fail		1.7800	0.0255		5	4	0.16
46L	1.8000		3		0.49			Fail		1.8000			3	2	0.18
45L	1.8833	0.040	3		0.73	0.37		Fail		1.8833	0.0404		3	2	0.26
19L	1.9380	0.187	5		0.88	1.72	!	Fail		1.9380	0.1868		5	4	0.31
30L	2.0000	0.100	3		1.06	0.92		Fail		2.0000	0.1000		3	2	0.38
Tot.gem	1.624	0.084 mg/g		*1%-level:*	2.22	(1.84)			11	*1.6236*	()		11	10	
Tot.std=	0.356	0.072		*5%-level:*	1.82	(1.57)									

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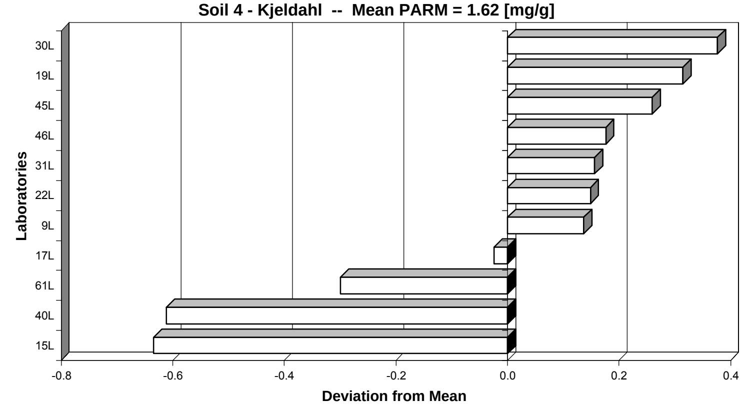
RESULTS:	**Mean =**	**1.62363**	*mg/g*				
Repeatability variance	**S2r =**	0.01363					
Repeatability std.	**Sr =**	**0.11673**	-->	7.19%		**r =**	0.3269
Between lab variance	**S2L =**	0.14263					
Reproducibility var.	**S2R =**	0.15625					
Reproducibility std.	**SR =**	**0.39529**	-->	24.35%		**R =**	1.1068
Remarks:	**none**						

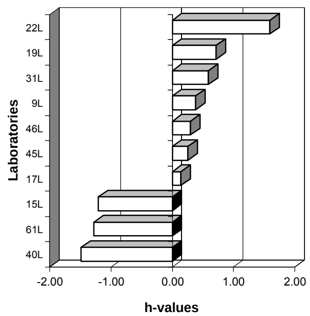
Soil 4 - Kjeldahl -- Mean PARM = 1.62 [mg/g]



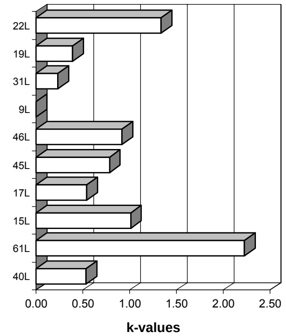
Sample: **Soil 5**

Element: **Kjeldahl**

Mandel's h statistics (Soil 5 - Kjeldahl)



Mandel's k statistics (Soil 5 - Kjeldahl)



Unit: mg/g

Mandel's k statistics (Soil 5 - Kjeldahl)
Mandel's h statistics (Soil 5 - Kjeldahl)

Soil 5 - Kjeldahl -- Mean PARM = 1.83 [mg/g]

	General calc.parm.
T1=	8.38970E+01
T2=	1.56556E+02
T3=	46
T4=	252
T5=	2.4188E-01
n=	variabel
p=	9
N-table=	*5*

Mandel's statistics — End Result:

LAB	*PARM-gem*	*Stdev*	*N*	*h-mark*	*h*	*k*	*k-mark*	*\vX > AvST+2std*	*AvX < AvST-2std*		*PARM*	*Stdev*	*Rej.labs*	*N*	*N-1*	*dev_mean*
40L	1.3617	0.056	6		-1.49	0.53			Fail		1.3617	0.0556		6	5	-0.47
61L	1.4234	0.232	6		-1.27	2.23	!!		Fail	-	-		,61L -	-		-0.41
15L	1.4437	0.105	6		-1.20	1.01			Fail		1.4437	0.1053		6	5	-0.39
17L	1.8300	0.057	2		0.14	0.54					1.8300	0.0566		2	1	0.00
45L	1.8650	0.082	6		0.26	0.78					1.8650	0.0817		6	5	0.03
46L	1.8750	0.096	4		0.29	0.92					1.8750	0.0957		4	3	0.04
9L	1.9000	0.000	6		0.38	0.00					1.9000	0.0000		6	5	0.07
31L	1.9600	0.024	4		0.59	0.24		Fail			1.9600	0.0245		4	3	0.13
19L	1.9975	0.041	6		0.72	0.39		Fail			1.9975	0.0410		6	5	0.17
22L	2.2483	0.139	6		1.59	1.33		Fail			2.2483	0.1391		6	5	0.42
Tot.gem	1.790	0.083 mg/g		*1%-level:*	2.18	(1.74)				9	*1.8312*		(61L)	9	8	
Tot.std=	0.288	0.066		*5%-level:*	1.80	(1.5)				1						

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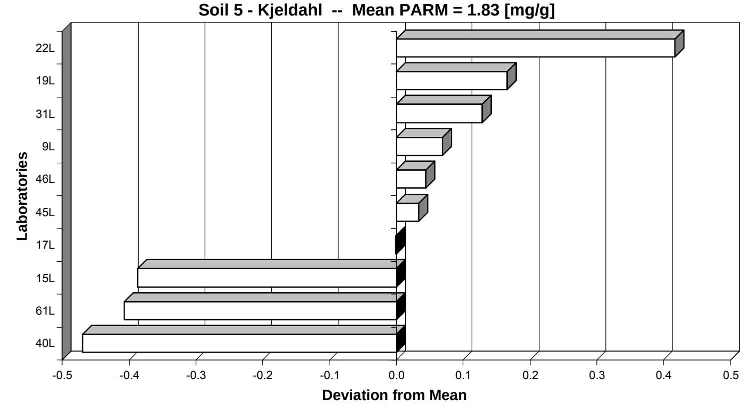
RESULTS:	**Mean =**	**1.83124**	*mg/g*			
Repeatability variance	**S2r =**	0.00654				
Repeatability std.	**Sr =**	**0.08085**	-->	4.42%	**r =**	0.2264
Between lab variance	**S2L =**	0.08608				
Reproducibility var.	**S2R =**	0.09262				
Reproducibility std.	**SR =**	**0.30434**	-->	16.62%	**R =**	0.8521
Remarks:	**1 Lab rejected! (61L)**					

Soil 5 - Kjeldahl -- Mean PARM = 1.83 [mg/g]



Annex 4:

Raw data submitted

Sample:	*Compost 1*	
Element:	*Kjeldahl*	[mg/g]
LAB	***PARM***	
15L	14.08	
15L	14.05	
15L	14.02	
15L	13.74	
15L	13.53	
15L	13.50	
17L	16.46	
17L	16.36	
22L	18.30	
22L	17.80	
22L	17.80	
22L	17.70	
22L	17.11	
22L	17.05	
29L	11.18	
29L	11.13	
29L	10.68	
29L	10.63	
30L	16.20	
30L	15.90	
30L	15.50	
31L	19.18	
31L	19.12	
31L	18.77	
31L	18.75	
31L	18.54	
40L	18.80	
40L	18.40	
40L	17.53	
40L	16.79	
40L	16.63	
40L	16.38	
45L	19.09	
45L	19.02	
45L	18.61	
45L	18.36	
45L	17.93	
45L	17.70	
46L	17.00	
46L	17.00	
46L	17.00	
46L	17.00	
61L	13.07	
61L	12.42	
61L	12.31	
61L	10.93	
61L	10.71	
61L	9.96	
9L	17.30	
9L	17.10	
9L	17.00	
9L	16.90	
9L	16.90	
9L	16.80	

Sample:	*Compost 2*	
Element:	*Kjeldahl*	[mg/g]
LAB	***PARM***	
15L	11.19	
15L	11.18	
15L	11.09	
15L	10.99	
15L	10.93	
15L	10.68	
17L	14.18	
17L	13.72	
19L	13.35	
19L	13.05	
19L	12.98	
19L	12.57	
19L	12.47	
19L	12.21	
22L	13.80	
22L	13.60	
22L	13.20	
22L	12.90	
22L	12.50	
22L	12.30	
29L	23.83	
29L	23.79	
29L	23.72	
29L	23.54	
31L	15.63	
31L	15.04	
31L	15.02	
31L	14.88	
31L	14.74	
31L	14.52	
40L	14.61	
40L	14.17	
40L	13.87	
40L	13.78	
40L	13.55	
40L	12.79	
45L	14.49	
45L	14.11	
45L	13.83	
45L	13.64	
45L	13.64	
45L	13.15	
46L	13.00	
46L	13.00	
46L	12.00	
46L	12.00	
61L	9.78	
61L	8.58	
61L	8.04	
61L	7.73	
61L	7.07	
61L	6.96	
9L	13.40	
9L	13.30	
9L	13.20	
9L	12.70	
9L	12.50	
9L	12.20	

Sample:	*Sewage Sludge 1*
Element:	*Kjeldahl*
LAB	***PARM***
15L	36.03
15L	35.70
15L	35.43
15L	34.83
15L	34.61
15L	34.50
17L	37.21
17L	36.75
19L	38.52
19L	38.43
19L	38.13
19L	38.05
19L	37.67
19L	37.09
22L	39.60
22L	39.49
22L	39.10
22L	38.90
22L	38.40
22L	37.70
31L	40.00
31L	39.80
31L	39.60
31L	38.80
40L	39.81
40L	38.96
40L	38.71
40L	38.50
40L	38.38
40L	38.27
45L	40.00
45L	39.86
45L	39.76
45L	39.69
45L	39.67
45L	39.65
61L	44.85
61L	42.44
61L	41.61
61L	41.29
61L	40.88
61L	40.77
9L	37.40
9L	37.40
9L	37.20
9L	37.20
9L	37.10
9L	36.10

[mg/g]

Sample:	***Sewage Sludge 2***
Element:	***Kjeldahl***
LAB	***PARM***
15L	30.93
15L	30.50
15L	30.43
15L	30.43
15L	30.40
15L	30.28
17L	34.53
17L	34.28
19L	35.40
19L	34.84
19L	34.82
19L	34.78
19L	34.70
19L	34.50
22L	37.21
22L	37.15
22L	36.80
22L	36.57
22L	36.31
22L	35.96
31L	37.70
31L	37.30
31L	37.20
31L	36.80
31L	36.80
31L	36.10
40L	36.93
40L	36.89
40L	36.68
40L	36.33
40L	36.17
40L	35.39
45L	37.32
45L	37.31
45L	37.24
45L	36.93
45L	36.62
45L	36.55
46L	36.00
46L	36.00
46L	35.00
46L	35.00
61L	39.36
61L	38.41
61L	37.67
61L	37.03
61L	36.93
61L	36.19
9L	35.80
9L	35.50
9L	35.00
9L	35.00
9L	34.90
9L	34.90

[mg/g]

Sample:	***Soil 4***
Element:	***Kjeldahl***
LAB	***PARM***
15L	1.02
15L	1.00
15L	1.00
15L	0.97
15L	0.96
17L	1.60
19L	2.26
19L	1.93
19L	1.85
19L	1.83
19L	1.82
22L	1.80
22L	1.78
22L	1.76
22L	1.75
30L	2.10
30L	2.00
30L	1.90
31L	1.81
31L	1.80
31L	1.78
31L	1.76
31L	1.75
40L	1.14
40L	1.04
40L	1.02
40L	1.00
40L	0.86
45L	1.93
45L	1.86
45L	1.86
46L	1.80
46L	1.80
46L	1.80
61L	1.58
61L	1.37
61L	1.36
61L	1.26
61L	1.05
9L	1.90
9L	1.90
9L	1.80
9L	1.60
9L	1.60

[mg/g]

Sample:	***Soil 5***
Element:	***Kjeldahl***
LAB	***PARM***
15L	1.63
15L	1.48
15L	1.44
15L	1.39
15L	1.37
15L	1.35
17L	1.87
17L	1.79
19L	2.06
19L	2.03
19L	2.00
19L	1.98
19L	1.97
19L	1.95
22L	2.41
22L	2.38
22L	2.31
22L	2.20
22L	2.10
22L	2.09
31L	1.98
31L	1.98
31L	1.95
31L	1.93
40L	1.46
40L	1.37
40L	1.37
40L	1.35
40L	1.32
40L	1.30
45L	1.95
45L	1.93
45L	1.90
45L	1.88
45L	1.78
45L	1.75
46L	2.00
46L	1.90
46L	1.80
46L	1.80
61L	1.63
61L	1.63
61L	1.63
61L	1.32
61L	1.22
61L	1.12
9L	1.90
9L	1.90
9L	1.90
9L	1.90
9L	1.90
9L	1.90

European Commission

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Abstract
standardisation of test procedures, in particular for sludge, soils and biowastes. In the context of this standardization project, a series of draft technical specification were designed upon an extensive desk study, fine-tuned after expert consultations and finally validated in international intercomparisons exercise.
This report summarises the work performed within the validation study of the draft standard for the determination of Kjeldahl nitrogen in soils, sludge and treated bio-waste. It further explains the underlying statistical concept for the calculation of reproducibility and repeatability from intercomparisons data. In addition all single values, results of the statistical evaluation as well as background information on the validation materials used are described and explained.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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