REPORTS OF THE FINNISH ENVIRONMENT INSTITUTE 5| 2015

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Jari Nuutinen, Riitta Koivikko, Mirja Leivuori and Markku Ilmakunnas

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PREFACE

Finnish Environment Institute (SYKE) is appointed National Reference Laboratory in the environmental sector in Finland. The duties of the reference laboratory include providing interlaboratory proficiency tests and other comparisons for analytical laboratories and other producers of environmental information. The testing and the calibration laboratories as well as the proficiency testing provider (Proftest SYKE) of the SYKE laboratory center have been accredited by the Finnish Accreditation Services (EN ISO/IEC 17025, EN ISO/IEC 17043, www.finas.fi).

This proficiency test has been carried out under the scope of the SYKE reference laboratory and it provides an external quality evaluation between laboratory results, and mutual comparability of analytical reliability.
The success of the proficiency test requires confidential co-operation between the provider and participants.

Thank you for your participation!

ALKUSANAT

Suomen ympäristökeskus (SYKE) toimii ympäristönsuojelulain nojalla määrättynä ympäristöalan vertailulaboratoriona Suomessa. Yksi tärkeimmistä vertailulaboratorion tarjoamista palveluista on pätevyyskokeiden ja muiden vertailumittausten järjestäminen. SYKEn laboratoriotoiminnan testaus-, kalibrointi- ja tutkimustoiminta sekä vertailumittausten järjestäminen (Proftest SYKE) ovat FINAS – akkreditoituja (SFS-EN ISO/IEC 17025, SFS-EN ISO/IEC 17043, www.finas.fi).

Tämä pätevyyskoe on toteutettu SYKEn vertailulaboratorion toiminta-alueella ja se antaa ulkopuolisen laadunarvion laboratoriotulosten keskinäisestä vertailtavuudesta sekä laboratorioiden määritysten luotettavuudesta.
Pätevyyskokeen onnistumisen edellytys on järjestäjän ja osallistujien välinen luottamuksellinen yhteistyö.

Lämmin kiitos yhteistyöstä kaikille osallistujille!

Helsinki 19 February 2015 / Helsingissä 19. helmikuuta 2015

Marja Luotola

Director of Laboratory / Laboratorionjohtaja

CONTENTS

1 Introduction

Proftest SYKE carried out the proficiency test (PT) for analysis of oil hydrocarbons in water and soil in November-December 2014 (OIL 09/14). A total of 15 laboratories participated in the PT. In the PT the results of Finnish laboratories providing environmental data for Finnish environmental authorities were evaluated. Additionally, other water and environmental laboratories were welcomed in the proficiency test.

The proficiency test was carried out in accordance with the international guidelines ISO/IEC 17043 [1], ISO 13528 [2] and IUPAC Technical report [3]. The Proftest SYKE has been accredited by the Finnish Accreditation Service as a proficiency testing provider (PT01, ISO/IEC 17043, www.finas.fi/scope/PT01/uk). The organizing of this proficiency test is included in the accreditation scope, with the exception of C5-C10 hydrocarbons.

2 Organizing the proficiency test

2.1 Responsibilities

Proftest SYKE, Finnish Environment Institute (SYKE), Laboratory Centre
Hakuninmaantie 6, FI-00430 Helsinki, Finland
Phone: +358 295 251 000, Fax. +358 9 448 320

The responsibilities in organizing the proficiency test were as follows:

Jari Nuutinen	coordinator and analytical expert
Mirja Leivuori	substitute of coordinator
Riitta Koivikko	proficiency test trainee
Anne Markkanen	technical assistance
Helena Tanttu	technical assistance
Keijo Tervonen	technical assistance
Ritva Väisänen	technical assistance
Markku Ilmakunnas	technical assistance
Sari Lanteri	technical assistance

Subcontracting:
Ramboll Finland Oy / Ramboll Analytics (T039, www.finas.fi/scope/T039/uk) for the analysis of homogeneity and stability of samples N3O and M5B.

2.2 Participants

In total 15 laboratories participated in this proficiency test (Appendix 1), 13 from Finland and 2 from other EU countries. Altogether 60 % (n = 9) of the participating laboratories used accredited analytical methods at least for a part of the measurements. 14 participants analysed oil hydrocarbons in water, 10 participants analysed oil hydrocarbons in soil, and 8 participants

analysed volatile hydrocarbons (C5-C10). For this proficiency test, the organizing laboratory (T003, www.finas.fi/scope/T003/uk) has code 16 (SYKE, Helsinki).

2.3 Samples and delivery

Three types of samples were delivered to the participants; synthetic sample, surface water and soil samples. The synthetic samples A1O and A2B were prepared from commercial reference materials (BAM, AccuStandard, UltraScientific and Chiron). The surface water sample N3O was collected from the lake Kattilajärvi, South Finland. The soil sample M4O was used previously PT SYKE 4/2004 as the sample H2 [4]. The oil contaminated soil was originally taken from old gasoline station in Härmälä area in Tampere, Finland. In the current proficiency test (OIL 09/14), the sample was remixed, divided into new vessels and the homogeneity of the samples was tested. The soil sample M5B was prepared from VOC free soil material which was spiked with C5-C10 compounds and preserved with methanol. The sample preparation is described in details in the Appendix 2.

When preparing the samples, the purity of the used sample vessels was secured by using new sample vessels as well as checking blank samples in each sample patch. According to the test results all used vessels fulfilled the purity requirements.

The samples were delivered on 17 December 2014 to the international participants and 18 November 2014 to the national participants. The samples arrived to the participants mainly on 19 November, one participant received the samples on 20 November 2014. The parallel sample for the N3O was missing from the sample package of some participants. The missing sample was sent on 19 November and participants received it within one or two days.

The samples were requested to be measured latest on 8 December 2014.

The results were requested to be reported latest on 8 December 2014, all participants delivered the results on time. The preliminary results were delivered to the participants via email on 12 December 2014.

2.4 Homogeneity and stability studies

Based on the earlier similar proficiency tests, the synthetic samples as well as water and soil samples are known to be homogenous and stable. Here, the soil sample M4O (>C10-C40) was previously used in the SYKE Proficiency Test 4/2004 and demonstrated then to be homogenous [4]. As the sample was remixed and divided to new vessels, the homogeneity of the sample M4O was tested by analyzing >C10-C40 as duplicate determination from the six sub samples (Appendix 3). According to the homogeneity test results the sample M4O was considered homogenous.

The homogeneity of the soil sample M5B was tested from the six sub samples (Appendix 3). The criterion for homogeneity was not fulfilled, which was taken into consideration in the performance evaluation. The concentration analysed by the subcontracting laboratory for the homogeneity test was lower compared to the theoretical and assigned values. However, it was

similar to the value the participant reported as their result in the PT. No proper cause for the low value was found, thus the homogeneity test values were used as such.

The stability of the samples A1O, N3O and M4O was checked by analyzing the samples before they were distributed to the participants as well as during or in the end of the requested time of analysis (Appendix 4). The stability criterion was fulfilled and the samples were considered stable.

Further, the synthetic samples (A1O, A2B and the addition solution L3O) as well as sample M5B were weighed at SYKE before the delivery and reweighed by the participants after the sample receiving. The difference of these two measurements was allowed to be < 1 %. If the difference was higher, the sample was replaced, which was the case for only one participant.

2.5 Feedback from the proficiency test

The feedback from the proficiency test is shown in Appendix 5. Due to the error from provider's side, the duplicate sample bottle for N3O was sent to the participants in two-day delay. Proftest SYKE is currently updating the results processing program and simultaneously the electronic interface will be improved. All the feedback is valuable and is exploited when improving the activities.

2.6 Processing the data

2.6.1 Pretesting the data

The normality of the data was tested by the Kolmogorov-Smirnov test. The outliers were rejected according to the Grubbs or Hampel test before calculating the mean. The results which differed more than 50 % or 5 times from the robust mean were rejected before the statistical robust results handling. The replicate results were tested using the Cochran-test. If the result has been reported as below detection limit, it has not been included in the statistical calculations.

More information about the statistical handling of the data is available in the Guide for participant [5].

2.6.2 Assigned values

The assigned values and their uncertainties are presented in Appendix 6. The PTB traceable calculated concentration was used as the assigned value for the synthetic sample A1O (>C10-C40). For the sample A2B (C5-C10), the calculated concentration used as the assigned value is based on the NIST traceable naphtha and BETX mixture as well as gravimetrically certified C5-C9 mixture. For the calculated assigned values the expanded measurement uncertainty (k=2) was estimated using standard uncertainties associated with individual operations involved in the preparation of the sample. The main individual source of the uncertainty was the uncertainty of the purity and/or concentration in the stock solutions.

For the sample N3O the robust mean was used as the assigned value (n≥12), for the sample M5B the median (n<12, resembling the theoretical value, Appendix 2) and for the other samples the mean (n<12) of the results reported by the participants was used as the assigned value. The uncertainty of the assigned value was calculated using the robust standard deviation or standard deviation of the reported results [2, 5]. After reporting the preliminary results no changes have been done for the assigned values.

The expanded uncertainty of the calculated assigned values were 1.9 % (A1O, >C10-C40) and 3.5 % (A2B, C5-C10). When using the robust mean, mean or median of the participant results as the assigned value, the uncertainties of the assigned values varied from 3.3 % to 22.3 % (Appendix 6).

2.6.3 Standard deviation for proficiency assessment and z score

The target value for the standard deviation for proficiency assessment was estimated on the basis of the analyte concentration, the results of homogeneity and stability tests, the uncertainty of the assigned value, and the long-term variation in the former proficiency tests. The standard deviation for proficiency assessment at 95 % confidence level was set to 20–40 % depending on the measurements. After reporting the preliminary results no changes have been done for the standard deviations of the proficiency assessment values.

When using the robust mean, mean or median as the assigned value, the reliability was tested according to the criterion $u / s_p \leq 0.3$, where u is the standard uncertainty of the assigned value (the expanded uncertainty of the assigned value (U) divided by 2) and s_p is the standard deviation for proficiency assessment [3]. The criterion was fulfilled here only partly.

The reliability of the target value of the standard deviation and the corresponding z score was estimated by comparing the robust standard deviation (s_{rob}) or the standard deviation (sd) of the reported results with the deviation for proficiency assessment (s_p). The criterion value for this correlation is < 1.2, which was here only partly fulfilled.

Due to low number of the results, the criterion for the reliability of the assigned value[1] and for the reliability of the target value for the deviation[2] was not met in the following cases, and, therefore, the evaluation of the performance is weakened in this proficiency test:

Sample	Measurement
N3O	>C10-C40 [1,2]
M4O	>C10-C21 [1,2]; >C10-C40 [1]; >C21-C40 [1]
M5B	C5-C10 [1,2]

3 Results and conclusions

3.1 Results

The results and the performance of each laboratory are presented in Appendix 8 and the summary of the results in Table 1. The terms in the results tables are explained in Appendix 7. The reported results with their expanded uncertainties (k=2) are presented in Appendix 9. The summary of the z scores is shown in Appendix 10 and z scores in the ascending order in Appendix 11. The participants were requested to report the replicate measurement results for all measurements. The results of the replicate determinations are presented in Table 2 (ANOVA statistics).

Table 1. The summary of the results in the proficiency test OIL 09/2014.

Analyte	Sample	Unit	Assigned value	Mean	Rob. mean	Median	SD rob	SD rob %	2*s_p %	n (all)	Acc z %
>C10-C21	A1O	mg/ml	0.482	0.48		0.48			30	7	71
	M4O	mg/kg	78.1	78.1	77.7	74.0	23.5	30.2	40	9	67
>C10-C40	A1O	mg/ml	0.976	0.99	0.99	1.00	0.06	6.1	20	11	91
	M4O	mg/kg	251.9	251.8	253.6	260.3	53.4	21.0	35	10	90
	N3O	mg/l	0.576	0.58	0.58	0.56	0.13	23.2	30	14	79
>C21-C40	A1O	mg/ml	0.481	0.48		0.50			30	7	71
	M4O	mg/kg	178.4	178.4	178.4	175.4	43.1	24.1	40	9	89
C5-C10	A2B	µg/ml	144.9	133.2	133.2	135.2	45.6	34.2	30	8	63
	M5B	mg/kg	8.6	7.65	7.65	8.60	2.74	35.8	30	8	63

Rob. mean: the robust mean, SD rob: the robust standard deviation, SD rob %: the robust standard deviation as percent, 2*s_p %: the total standard deviation for proficiency assessment at the 95 % confidence interval, Acc z %: the results (%), where $|z| \leq 2$, n(all): the total number of the participants.

The robust standard deviation of oil hydrocarbons (>C10-C40) was for the synthetic sample A1O 6 %, for the water sample N3O 23 %, and for the soil sample M4O 21 % (Table 1). The robust standard deviations were slightly lower when compared to the previous similar proficiency test Proftest SYKE 9/2012 [6], where the deviations were 8 %, 23 %, and 29 %, respectively. The robust standard deviation was not calculated when the number of results within the statistical evaluation was low (n ≤ 7, A1O: >C10-C21 and >C21-C40).

For volatile oil hydrocarbons (C5-C10) the robust standard deviation was 34 % for the synthetic sample A2B and 36 % for the soil sample M5B. In the previous similar proficiency test Proftest SYKE 8b/2010 [7], the robust standard deviation for the synthetic sample was 23 %.

The estimation of the robustness of the methods could be done by the ratio s_b/s_w, which should not exceed 3 for robust methods. For oil hydrocarbons (>C10-C40) the ratio varied in this test from 1.7 to 2.6, which was much lower than in the previous similar proficiency test Proftest SYKE 9/2012 [6], where the ratio for oil hydrocarbons (>C10-C40) varied from 5.2 to 15.

Table 2. The summary of repeatability on the basis of replicate determinations (ANOVA statistics).

Analyte	Sample	Unit	Ass.val.	Mean	s_w	s_b	s_t	s_w%	s_b%	s_t%	s_b/s_w
>C10-C21	A1O	mg/ml	0.482	0.48	0.0195	0.0111	0.0225	4.0	2.3	4.7	0.57
	M4O	mg/kg	78.1	78.1	5.13	21.3	21.9	6.6	27	28	4.1
>C10-C40	A1O	mg/ml	0.976	0.99	0.0271	0.0493	0.0563	2.7	5.0	5.7	1.8
	M4O	mg/kg	251.9	251.8	16.9	44.7	47.8	6.6	17	19	2.6
	N3O	mg/l	0.576	0.58	0.104	0.176	0.205	18	30	35	1.7
>C21-C40	A1O	mg/ml	0.481	0.48	0.0355	0.115	0.120	7.4	24	25	3.2
	M4O	mg/kg	178.4	178.4	14.9	36.9	39.8	8.3	20	22	2.5
C5-C10	A2B	µg/ml	144.9	133.2	6.63	39.1	39.6	4.9	29	29	5.9
	M5B	mg/kg	8.6	7.65	0.563	2.42	2.48	7.3	31	32	4.3

Ass.val.: assigned value; s_w: repeatability standard error; s_b: standard error between laboratories; s_t: reproducibility standard error.

For the synthetic sample A2B, volatile oil hydrocarbons (C5-C10) the ratio was in this test 5.9 (Table 2), which was higher than in the previous similar proficiency test Proftest SYKE 8b/2010 [7], where the ratio for volatile oil hydrocarbons (C5-C10, only synthetic sample) was 2.7. In this PT, the ratio was slightly lower for the soil sample M5B, being 4.3.

3.2 Analytical methods

The participants were allowed to use different analytical methods for the measurements in the PT. The details of the used methods were collected from the participants with an electronic questionnaire delivered together with the samples. Altogether 14 participants (93%) replied to the questionnaire. The used analytical methods and results of the participants grouped by methods are shown in more detail in Appendix 12. The statistical comparison of the analytical methods was possible for the data where the number of the results was ≥ 5. However, in this PT there were not enough results for statistical comparison. Thus, the comparison is based on the graphical result evaluation.

Oil hydrocarbons (>C10-C40) in water

All participants determined oil hydrocarbons in water using the method based on the standard EN ISO 9377-2 [8], one participant used the modified standard EN ISO 9377-2. The water sample was mainly extracted with hexane; also pentane and heptane were used for extraction. Most of the participants (77 %) removed the polar substances by clean up on Florisil/Na_2SO_4, also Florisil and Al_2O_3 were used for clean up. The purified aliquot was analysed by GC-FID (11 participants) or by GS-MS (2 participants). Several different injectors were used (split/splitless, on-column, PTV, and MMI). In the graphical evaluation no significant differences were observed between different methods. However, 92 % of the GC-FID results were satisfactory whereas both results achieved with GC-MS were unsatisfactory (Appendix 12, 13).

Oil hydrocarbons (>C10-C40) in soil

Most participants used the method based on ISO 16703 (8 participants) to determine oil hydrocarbons in soil [9]. Two participants used the method based on the standard EN 14039 [10]. The soil sample M4O was mainly extracted with acetone/hexane followed by shaking or sonication, also acetone/heptane, acetone/hexane/water/methanol, and acetone/pentane

mixtures were used for the extraction. Most of the participants (70 %) purified the extract on Florisil/Na_2SO_4, also Florisil, and Na_2SO_4 were used. The aliquot was analysed using GC-FID (8 participants) or GC-MS (2 participants). Statistical comparison between the applied methods could not be done due to low number of the results, but according to the graphical evaluation systematic differences between the used methods were not observed (Appendix 12, 13).

Volatile oil hydrocarbons (C5-C10) in soil

Seven participants determined C5-C10 in soil using headspace GC-MS and one participant used headspace GC-FID. Four participants used the method based on ISO 22155 [11], one participant used outdated version of ISO 15009:2012 [12], and one participant used internal method based on draft standard ISO/FDIS 16558-1:2013 [13]. Identification and calculation of the C5-C10 compounds were done with various methods; library search, scanning ions *m/z* 40-300 or 35-350 and selected ion monitoring (SIM) for selected compounds. Statistical comparison between the applied methods could not be done due to low number of the results. Despite several different measurement methods five participants (63%) had satisfactory results for both synthetic A2B and soil M5B samples. Only two participants have accredited the C5-C10 determination for the soil samples.

The Environmental Administration in Finland has recently published *Risk assessment and sustainable risk management of contaminated land* –report [14, in Finnish] where recommendation has been given how the volatile oil hydrocarbons (C5-C10) should be determined. The recommendation is based on the consensus by the workgroup of Finnish laboratory representatives conducting analyses on oil hydrocarbons. In summary, the volatile oil hydrocarbons (C5-C10) are recommended to be determined from total ion chromatogram (TIC) with headspace-GC-MS instrument (HS-GC-MS). The C5-C10 result is calculated as the sum of all the compound signals from n-pentane to n-decane (including these signals). The calibration should be done with a mixture of several hydrocarbons (including both linear, iso- and cycloalkanes, and aromatic hydrocarbons). The draft standard ISO/FDIS 16558 lists the compounds which can be used for the calibration [13].

3.3 Uncertainties of the results

All the participants but one reported the expanded uncertainties (k=2) for at least some of their results (Table 3, Appendix 9). The range of the reported expanded uncertainties varied between the measurements and the sample types. The uncertainties were reported for all the results where accredited methods were used.

Several approaches were used for estimating of measurement uncertainty (Appendix 14). The most used approach was based on data from method validation (Method 8). Two participants used MUkit measurement uncertainty software for the estimation of their uncertainties. Generally, the used approach for estimating measurement uncertainty did not make definite impact on the uncertainty estimates.

Table 3. The ranges of the expanded measurement uncertainties (k=2, U%) reported by the participants.

Analyte	A1O %	M4O %	N3O %	A2B %	M5B %
>C10-C21	15-30	20-40	-	-	-
>C10-C40	9.3-35	20-40	9.3-42	-	-
>C21-C40	15-30	20-40	-	-	-
C5-C10	-	-	-	25-40	25-40

4 Evaluation of the results

The evaluation of the participants was based on the z scores, which were calculated using the assigned and the estimated target values for the total deviation (Appendix 8). The z scores were interpreted as follows:

Criteria	Performance
$\lvert z \rvert \leq 2$	Satisfactory
$2 < \lvert z \rvert < 3$	Questionable
$\lvert z \rvert \geq 3$	Unsatisfactory

In total, 77 % of the results were satisfactory when total deviation of 20–40 % from the assigned values were accepted. Altogether 60 % of the participating laboratories used accredited analytical methods at least for a part of the measurements and 88 % of their results were satisfactory. The summary of the performance evaluation and comparison to the previous performance is presented in Table 4. Proftest SYKE carried out the similar proficiency test (without C5-C10) in 2012 where 81 % of the results were satisfactory [6].

Oil hydrocarbons (>C10-C40)

For the analysis of oil hydrocarbons (>C10-C40), 87 % of the all results (A1O, M4O, and N3O) were satisfactory when total deviation of 20–35 % from the assigned values were accepted. The performance was better than in the previous similar PT, Proftest SYKE 9/2012 [6], where 74 % of the results were satisfactory.

Oil hydrocarbons (>C10-C21 and >C21-C40)

71 % of the results for both the sample A1O; >C10-C21 and A1O; >C21-C40 were satisfactory when total deviation of 30 % was accepted. For the sample M4O; >C10-C21, 67 % of the results were satisfactory when total deviation of 40 % was accepted. For the sample M4O; >C21-C40, 89 % of the results were satisfactory when total deviation of 40 % was accepted. The amount of satisfactory results were similar compared to the previous similar PT, where 70, 80, 67, 78 % of the results were satisfactory, respectively [7]. In this PT the performance was enhanced for >C21-C40.

Volatile oil hydrocarbons (C5-C10)

For the analysis of volatile oil hydrocarbons (C5-C10), 63 % of the results for both A2B and M5B were satisfactory when total deviation of 30 % from the assigned values was accepted. This was well in line with the previous similar PT Proftest SYKE 8b/2010 [7], where 62 % of the results were satisfactory for the synthetic sample. The current PT is the first time when

volatile oil hydrocarbons were measured from soil sample. The performance of the soil sample was as good as with the synthetic sample, thus no matrix effect was observed.

Table 4. Summary of the performance evaluation in the proficiency test 09/2014.

Analyte	Sample	2 · s_p, %	Satisfactory results, %	Assessment
>C10-C21	A1O	30	71	Five satisfactory and two unsatisfactory results. In the PT SYKE 9/2012 the performance was satisfactory for 92 % of the results [6].
	M4O	40	67	High uncertainty of the assigned value. Six satisfactory, one questionable, and two unsatisfactory results. In the PT SYKE 9/2012 the performance was satisfactory for 91 % of the results [6].
>C10-C40	A1O	20	91	Good performance. In the PT SYKE 9/2012 the performance was satisfactory for 88 % of the results [6].
	M4O	35	90	Good performance. In the PT SYKE 9/2012 the performance was satisfactory for 62 % of the results [6].
	N3O	30	79	High uncertainty of the assigned value. Eleven satisfactory, one questionable, and two unsatisfactory results. In the PT SYKE 9/2012 the performance was satisfactory for 71 % of the results [6].
>C21-C40	A1O	30	71	High uncertainty of the assigned value. Five satisfactory and two unsatisfactory results. In the PT SYKE 9/2012 the performance was satisfactory for 100 % of the results [6].
	M4O	40	89	High uncertainty of the assigned value. Mainly good performance. In the PT SYKE 9/2012 the performance was satisfactory for 64 % of the results [6].
C5-C10	A2B	30	63	Five satisfactory, two questionable, and one unsatisfactory results. In the PT SYKE 8b/2010 the performance was satisfactory for 62 % of the results [7].
	M5B	30	63	High uncertainty of the assigned value. Only informative assessment. The performance evaluation is weakened due to the low number of participants and homogeneity test which did not fulfil the criterion.

5 Summary

Proftest SYKE carried out the proficiency test (PT) for analysis of oil hydrocarbons in water and soil in November-December 2014. Three types of samples were delivered to the participants; synthetic sample, surface water and soil samples. In total, 15 laboratories participated in the PT.

Either the calculated concentration, robust mean, mean or median of the results reported by the participants was chosen to be the assigned value depending on the analyte. The uncertainty for the assigned value was estimated at the 95 % confidence interval and for calculated assigned values it was 1.9–3.5 %, for assigned values based on the robust mean it was 15.5 %, for assigned values based on the mean it varied from 3.3 to 20.9 %, and for median based assigned value the uncertainty for the assigned value was estimated to 22.3 %.

The evaluation of the performance was based on the z scores. In this proficiency test 77 % of the data was regarded to be satisfactory when the deviation of 20 to 40 % from the assigned value was accepted.

6 Summary in Finnish

Proftest SYKE järjesti marras-joulukuussa 2014 pätevyyskokeen öljyhiilivetyjä vedestä ja maasta analysoiville laboratorioille. Pätevyyskokeen osallistujille toimitettiin synteettinen-, pintavesi- ja maanäyte. Pätevyyskokeeseen osallistui yhteensä 15 laboratoriota.

Mittaussuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa, keskiarvoa tai tulosten mediaania. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 1.9–3.5 % laskennallista pitoisuutta vertailuarvona käytettäessä ja kun vertailuarvo määritettiin muilla keinoin, sen laajennettu epävarmuus vaihteli välillä 3.3–22.3 %.

Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 20–40 %. Koko aineistossa hyväksyttäviä tuloksia oli 77 %.

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APPENDIX 1: Participants in the proficiency test

Country	Participants
Czech Republic	ALS Czech Republic s.r.o. Prague 9, Na Harfe 9, 190 00, Czech Rep.
Finland	Ahma Ympäristö Oy, Rovaniemi Borealis Polymers Oy, laboratoriopalvelut, Kulloo Ekokem Oy Ab, Riihimäki Kokemäenjoen vesistön vesiensuojeluyhdistys ry, Tampere Metropolilab Oy, Helsinki Nab Labs Oy / Ambiotica Jyväskylä Neste Oil Oyj / Laadunvarmistus, Naantali Neste Oil Oyj, Tutkimus ja kehitys/Vesilaboratorio, Kulloo Novalab Oy, Karkkila Ramboll Finland Oy, Ramboll Analytics, Lahti SGS Inspection Services Oy, Kotka SSAB Europe Raahe, Raahe SYKE, Ympäristökemia Helsinki
Sweden	SSAB 95 SEDAC Laboratoriet, Borlänge, Sweden

APPENDIX 2: Preparation of the samples

Oil hydrocarbons (middle and heavy fractions, >C10-C40) - the samples A1O and N3O
All the dilutions were made by weighting.

Sample A1O:

Solutions	Preparation
Diesel oil + Lubricating oil (BAM-K010)	101.20 mg/ml in 100.2 ml hexane → c = 1.01 mg/ml

The vial A1O (3ml) was sent to the participants.

Sample N3O:

Solutions	Preparation
A: Diesel oil (BAM-K008)	2999.83 mg oil in 49.7 ml hexane → c = 60.83 mg/ml
B: Lubricating oil (BAM-K009)	3000.00 mg oil in 49.8 ml hexane → c = 60.24 mg/ml
L3O	5.0 ml A + 5.0 ml B into 99.6 ml of isopropanol → c = 6.055 mg/ml
N3O	100 µl L3O into 1 litre of water → c = 0.606 mg/l

The vial L3O (3ml) was sent to the participants.

Oil hydrocarbons (C5-C10) - the samples A2B and M5B
All the dilutions were made by weighting.

A2B and addition solution for M5B were made by mixing BETX mixture (Ultra Scientific BETX Mixture, Product Number: BTX-2000N), C5-C9 mixture (Petrochemical Qualitative Standard C5-C9, Product no: S-4145), and Naphtha (20.010 mg/ml) (AccuStandard, Catalog No.HS-003S-40X).

BETX mixture:

Compound	mg/ml
Benzene	2.010
Ethylbenzene	2.005
Toluene	2.008
o-Xylene	2.009
m-Xylene	2.009
p-Xylene	2.009
BETX mixture	12.050

C5-C9 mixture:

Compound	Wt. % (w/w)	Purity
n-Pentane	20 %	99.5 %
n-Hexane	20 %	97 %
n-Heptane	20 %	99 %
n-Octane	20 %	99 %
n-Nonane	20 %	99 %

Dilution solution A was made as follows: 0.107 ml of the C5-C9 mixture was diluted with 4.015 ml methanol (JT Baker, Burge&Trap quality).

A2B was made by mixing 0.235 ml BTEX mixture, 0.504 ml Naphtha and 0.096 ml dilution solution A of C5-C19 mixture. **Final theoretical concentration for the A2B is 144.7 mg/ml.**

A portion of 3 ml of the A2B was sent to the participants in 4 ml vial.

Addition solution B for the M5B was made by mixing 0.491 ml BETX mixture, 0.495 ml Naphtha and 0.243 ml dilution solution A of C5-C9 mixture.

M5B was made by adding 20 g soil, 2 ml water, 1 ml addition solution B and 20 ml methanol (JT Baker, Purge&Trap quality).

Final theoretical concentration for the sample M5B (C5-C10) is 9.836 mg/kg.

APPENDIX 3: Homogeneity of the samples

The soil sample M4O was previously used in the SYKE Proficiency Test 4/2004 and demonstrated then to be homogenous [4]. However, as the sample was divide to new vessels, the homogeneity of the samples M4O was tested by analyzing >C10–C40 as duplicate determination from the six sub samples. Homogeneity testing was carried out in September 2014.

Criteria for homogeneity:

$$s_a/s_p < 0.5 \text{ and } s_{bb}^2 < c, \text{ where}$$

s_p % = standard deviation for proficiency assessment
s_a = analytical deviation, standard deviation of the results within sub samples
s_{bb} = between-sample deviation, standard deviation of the results between sub samples

$c = F1 \cdot s_{all}^2 + F2 \cdot s_a^2$, where
$s_{all}^2 = (0.3 \cdot s_p)^2$
F1 = 2.21, when the number of sub samples is 6
F2 = 1.69, when the number of sub samples is 6

Sample / Analyte	Concentration mg/kg	n	s_p%	s_p	s_a	s_a / s_p	$s_a/s_p < 0.5$?	s_{bb}	s_{bb}^2	c	$s_{bb}^2 < c$?
M4O / >C10-C40	271,5	6	17,5	47,5	15,9	0,3	yes	13,8	189,9	875,6	Yes

Conclusion: The sample M4O was considered to be homogenous.

Homogeneity of the sample M5B was tested by six replicated measurements.

Criteria for homogeneity:

$$s_{bb} < 0.5 \cdot s_p$$

Sample / Analyte	Concentration mg/kg	n	s_p%	s_p	0.5 · s_p	Standard deviation (s_{bb})	$s_{bb} < 0.5 \cdot s_p$?
M5B / C5-C10	3,3	6	15	0,5	0,25	0,403	No

Conclusion: The criterion for homogeneity was not fulfilled for the sample M5B. This was taken into consideration in the performance evaluation. The concentration analysed by the subcontracting laboratory was lower compared to the theoretical and assigned values. The subcontracting laboratory used hexane as reference for the calculations, which might have, for its part, caused the lower concentration values as the sample was a mixture of BETX mixture, C5-C9 mixture and naphtha. Despite thorough investigations, no other possible sources of error were discovered.

APPENDIX 4: Stability of the samples

The samples were delivered to the participants on 18 November 2014 and they were requested to be analysed latest on 8 December 2014.

The stability of samples was tested by analysing the samples prior delivery (A_0) and during or in the end of the requested time of analysis (A_1).

Criterion for stability: $D < 0.3 \cdot s_p$, where

D = |the difference of the sample results measured prior delivery (A_0) and during or in the end of the requested time of analysis (A_1)|

s_p = standard deviation for proficiency assessment

Sample Analyte [unit]	Date	Result	Difference	$0.3 \cdot s_p$	$D < 0.3 \cdot s_p$	Remarks
A1O >C10-C40 [mg/ml]	4 Nov 2014 (A_0)	0.993	|D| = 0.054 D = 5.5 %	0.03	**No**	The criterion for stability was not fulfilled but the difference was within the expanded measurement uncertainty (10 %), thus the sample is considered stable.
	16 Dec 2014 (A_1)	0.939				
M4O >C10-C40 [mg/kg]	19 Sep 2014 (A_0)	271.48	|D| = 40.63 D = 15 %	13.2	**No**	The criterion for stability was not fulfilled but the difference was within the expanded measurement uncertainty (18 %), thus the sample is considered stable.
	16 Dec 2014 (A_1)	230.85				
N3O >C10-C40 [mg/l]	5 Nov 2014 (A_0)	0.60	|D| = 0.012 D = 2.0 %	0.026	**Yes**	The criterion for stability was fulfilled and there was no inconsistency between the stability test and the data of the PT.
	20 Nov 2014 (A_1)	0.612				

Conclusion: The stability could be regarded sufficient for all samples.

APPENDIX 5: Feedback from the proficiency test

FEEDBACK FROM THE PARTICIPANTS

Participant	Comments on technical execution	Action / Proftest
4	The participant reported that the vessels for A2B and M5B were leaking during the transport.	New samples were sent to the participant.
Nearly all	The second bottle for the sample N3O was missing.	The provider delivered the second bottle within two days.

Participant	Comments to the results	Action / Proftest
14	The participant requested for the missing zeta scores.	The uncertainties of results were missing. The zeta scores could be calculated only when the uncertainty is reported for the results.

FEEDBACK TO THE PARTICIPANTS

Participant	Comments
7	The method codes were reported erroneously, the code was corrected by the provider.
4	Despite satisfactory result for A1O; >C10-C40, the results of >C10-C21 and >C21-C40 were both unsatisfactory. Also with the soil sample (M4O), the situation was similar. The PT provider recommends participant to verify their extraction and integration procedures.
All	The recently published *Risk assessment and sustainable risk management of contaminated land* –report [14, in Finnish] gives recommendation how the volatile oil hydrocarbons (C5-C10) should be determined. The organizer suggests the participants to consider integrating this recommendation to their analytical procedures.

APPENDIX 6: Evaluation of the assigned values and their uncertainties

Analyte	Sample	Unit	Assigned value	Expanded uncertainty	Expanded uncertainty, %	Evaluation method of assigned value	u/s_p
>C10-C21	A1O	mg/ml	0.482	0.02	3.3	Mean	0.11
	M4O	mg/kg	78.1	16.3	20.9	Mean	0.52
>C10-C40	A1O	mg/ml	0.976	0.02	1.9	Calculated value	0.10
	M4O	mg/kg	251.9	32.2	12.8	Mean	0.37
	N3O	mg/l	0.576	0.09	15.5	Robust mean	0.52
>C21-C40	A1O	mg/ml	0.481	0.10	19.9	Mean	0.66
	M4O	mg/kg	178.4	26.9	15.1	Mean	0.38
C5-C10	A2B	µg/ml	144.9	5.1	3.5	Calculated value	0.12
	M5B	mg/kg	8.6	1.92	22.3	Median	0.74

Criterion for reliability of the assigned value $u/s_p \leq 0.3$,
where

s_p= target value of the standard deviation for proficiency assessment
u = standard uncertainty of the assigned value

If $u/s_p \leq 0.3$ the assigned value is reliable and the z scores are qualified.

APPENDIX 7: Terms in the results tables

Results of each participant

Analyte	The tested parameter
Sample	The code of the sample
z score	Calculated as follows: $z = (x_i - X)/s_p$, where x_i = the result of the individual laboratory X = the reference value (*the assigned value*) s_p = the target value of the standard deviation for proficiency assessment
Assigned value	The reference value
2× s_p %	The target value of total standard deviation for proficiency assessment (s_p) at the 95 % confidence level
Lab's result	The result reported by the participant (the mean value of the replicates)
Md	Median
Mean	Mean
SD	Standard deviation
SD%	Standard deviation, %
n (stat)	Number of results in statistical processing

Summary on the z scores

S – satisfactory ($-2 \le z \le 2$)
Q – questionable ($2 < z < 3$), positive error, the result deviates more than $2 \cdot s_p$ from the assigned value
q – questionable ($-3 < z < -2$), negative error, the result deviates more than $2 \cdot s_p$ from the assigned value
U – unsatisfactory ($z \ge 3$), positive error, the result deviates more than $3 \cdot s_p$ from the assigned value
u – unsatisfactory ($z \le -3$), negative error, the result deviates more than $3 \cdot s_p$ from the assigned value

Robust analysis

The items of data are sorted into increasing order, $x_1, x_2, x_i, \ldots, x_p$.
Initial values for x^* and s^* are calculated as:
x^* = median of x_i ($i = 1, 2, \ldots, p$)
s^* = 1.483 · median of $|x_i - x^*|$ ($i = 1, 2, \ldots, p$)

The mean x^* and s^* are updated as follows:
Calculate $\varphi = 1.5 \cdot s^*$. A new value is then calculated for each result x_i ($i = 1, 2 \ldots p$):

$$x_i^* = \begin{cases} x^* - \varphi, & \text{if } x_i < x^* - \varphi \\ x^* + \varphi, & \text{if } x_i > x^* + \varphi, \\ x_i & \text{otherwise} \end{cases}$$

The new values of x^* and s^* are calculated from:

$$x^* = \sum x_i^* / p$$

$$s^* = 1.134 \sqrt{\sum (x_i^* - x^*)^2 / (p-1)}$$

The robust estimates x^* and s^* can be derived by an iterative calculation, i.e. by updating the values of x^* and s^* several times, until the process convergences [2].

APPENDIX 8: Results of each participant

Participant 1												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C21	mg/ml	A1O		-0.021	0.482	30	0.48	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		0.592	78.1	40	87.4	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		0.553	0.976	20	1.03	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		1.705	251.9	35	327.1	260.3	251.8	50.8	20.2	10
	mg/l	N3O		-0.683	0.576	30	0.52	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		1.157	0.481	30	0.56	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		1.752	178.4	40	240.9	175.4	178.4	38.0	21.3	8
C5-C10	µg/ml	A2B		-1.031	144.9	30	122.5	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		1.194	8.6	30	10.14	8.60	7.65	2.4	31.5	8

Participant 2												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C40	mg/ml	A1O		-0.579	0.976	20	0.92	1.00	0.99	0.1	5.4	10
	mg/l	N3O		-1.256	0.576	30	0.47	0.56	0.58	0.1	17.8	14

Participant 3												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C21	mg/kg	M4O		10.109	78.1	40	236.0	74.0	78.1	21.6	27.6	7
>C10-C40	mg/kg	M4O		0.751	251.9	35	285.0	260.3	251.8	50.8	20.2	10
	mg/l	N3O		-4.329	0.576	30	0.20	0.56	0.58	0.1	17.8	14
>C21-C40	mg/kg	M4O		9.602	178.4	40	521.0	175.4	178.4	38.0	21.3	8
C5-C10	µg/ml	A2B		-3.009	144.9	30	79.5	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		1.008	8.6	30	9.90	8.60	7.65	2.4	31.5	8

Participant 4												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C21	mg/ml	A1O		3.541	0.482	30	0.74	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		-4.680	78.1	40	5.0	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		0.241	0.976	20	1.00	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		-2.198	251.9	35	155.0	260.3	251.8	50.8	20.2	10
	mg/l	N3O		0.278	0.576	30	0.60	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		-3.042	0.481	30	0.26	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		-0.796	178.4	40	150.0	175.4	178.4	38.0	21.3	8
C5-C10	µg/ml	A2B		-2.710	144.9	30	86.0	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		-2.016	8.6	30	6.00	8.60	7.65	2.4	31.5	8

Participant 5												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C21	mg/ml	A1O		7.856	0.482	30	1.05	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		2.426	78.1	40	116.0	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		11.004	0.976	20	2.05	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		0.513	251.9	35	274.5	260.3	251.8	50.8	20.2	10
	mg/l	N3O		2.755	0.576	30	0.81	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		7.263	0.481	30	1.01	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		-0.572	178.4	40	158.0	175.4	178.4	38.0	21.3	8

Participant 5												
Analyte	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2*s_p, %**	**Lab's result**	**Md**	**Mean**	**SD**	**SD%**	**n (stat)**
C5-C10	µg/ml	A2B		2.236	144.9	30	193.5	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		-0.019	8.6	30	8.58	8.60	7.65	2.4	31.5	8

Participant 6												
Analyte	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2*s_p, %**	**Lab's result**	**Md**	**Mean**	**SD**	**SD%**	**n (stat)**
>C10-C21	mg/ml	A1O		-0.332	0.482	30	0.46	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		0.538	78.1	40	86.5	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		-0.507	0.976	20	0.93	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		1.057	251.9	35	298.5	260.3	251.8	50.8	20.2	10
	mg/l	N3O		-0.810	0.576	30	0.51	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		-0.173	0.481	30	0.47	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		0.942	178.4	40	212.0	175.4	178.4	38.0	21.3	8
C5-C10	µg/ml	A2B		1.293	144.9	30	173.0	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		0.023	8.6	30	8.63	8.60	7.65	2.4	31.5	8

Participant 7												
Analyte	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2*s_p, %**	**Lab's result**	**Md**	**Mean**	**SD**	**SD%**	**n (stat)**
>C10-C21	mg/ml	A1O		-0.060	0.482	30	0.48	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		-0.937	78.1	40	63.5	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		0.930	0.976	20	1.07	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		-0.650	251.9	35	223.3	260.3	251.8	50.8	20.2	10
	mg/l	N3O		-1.042	0.576	30	0.49	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		1.498	0.481	30	0.59	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		-0.521	178.4	40	159.8	175.4	178.4	38.0	21.3	8

Participant 8												
Analyte	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2*s_p, %**	**Lab's result**	**Md**	**Mean**	**SD**	**SD%**	**n (stat)**
>C10-C21	mg/ml	A1O		0.048	0.482	30	0.49	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		-0.391	78.1	40	72.0	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		-0.143	0.976	20	0.96	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		-1.279	251.9	35	195.5	260.3	251.8	50.8	20.2	10
	mg/l	N3O		0.417	0.576	30	0.61	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		-0.062	0.481	30	0.48	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		-1.567	178.4	40	122.5	175.4	178.4	38.0	21.3	8
C5-C10	µg/ml	A2B		-1.433	144.9	30	113.8	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		-3.419	8.6	30	4.19	8.60	7.65	2.4	31.5	8

Participant 9												
Analyte	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2*s_p, %**	**Lab's result**	**Md**	**Mean**	**SD**	**SD%**	**n (stat)**
>C10-C21	mg/kg	M4O		-1.959	78.1	40	47.5	74.0	78.1	21.6	27.6	7
>C10-C40	mg/kg	M4O		-0.304	251.9	35	238.5	260.3	251.8	50.8	20.2	10
	mg/l	N3O		0.509	0.576	30	0.62	0.56	0.58	0.1	17.8	14
>C21-C40	mg/kg	M4O		0.353	178.4	40	191.0	175.4	178.4	38.0	21.3	8

Participant 10												
Analyte	**Unit**	**Sample**	-3 0 3	**z score**	**Assigned value**	**2*s_p, %**	**Lab's result**	**Md**	**Mean**	**SD**	**SD%**	**n (stat)**
>C10-C40	mg/ml	A1O		-0.574	0.976	20	0.92	1.00	0.99	0.1	5.4	10
	mg/l	N3O		-0.608	0.576	30	0.52	0.56	0.58	0.1	17.8	14

Participant 12												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C40	mg/l	N3O		0.162	0.576	30	0.59	0.56	0.58	0.1	17.8	14

Participant 13												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C21	mg/ml	A1O		0.353	0.482	30	0.51	0.48	0.48	0.0	3.7	5
	mg/kg	M4O		-0.262	78.1	40	74.0	74.0	78.1	21.6	27.6	7
>C10-C40	mg/ml	A1O		0.574	0.976	20	1.03	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		0.343	251.9	35	267.0	260.3	251.8	50.8	20.2	10
	mg/l	N3O		1.609	0.576	30	0.72	0.56	0.58	0.1	17.8	14
>C21-C40	mg/ml	A1O		0.603	0.481	30	0.52	0.50	0.48	0.1	24.4	6
	mg/kg	M4O		0.409	178.4	40	193.0	175.4	178.4	38.0	21.3	8
C5-C10	µg/ml	A2B		0.212	144.9	30	149.5	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		-3.217	8.6	30	4.45	8.60	7.65	2.4	31.5	8

Participant 14												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C40	mg/ml	A1O		0.246	0.976	20	1.00	1.00	0.99	0.1	5.4	10
	mg/kg	M4O		0.036	251.9	35	253.5	260.3	251.8	50.8	20.2	10
	mg/l	N3O		-0.880	0.576	30	0.50	0.56	0.58	0.1	17.8	14

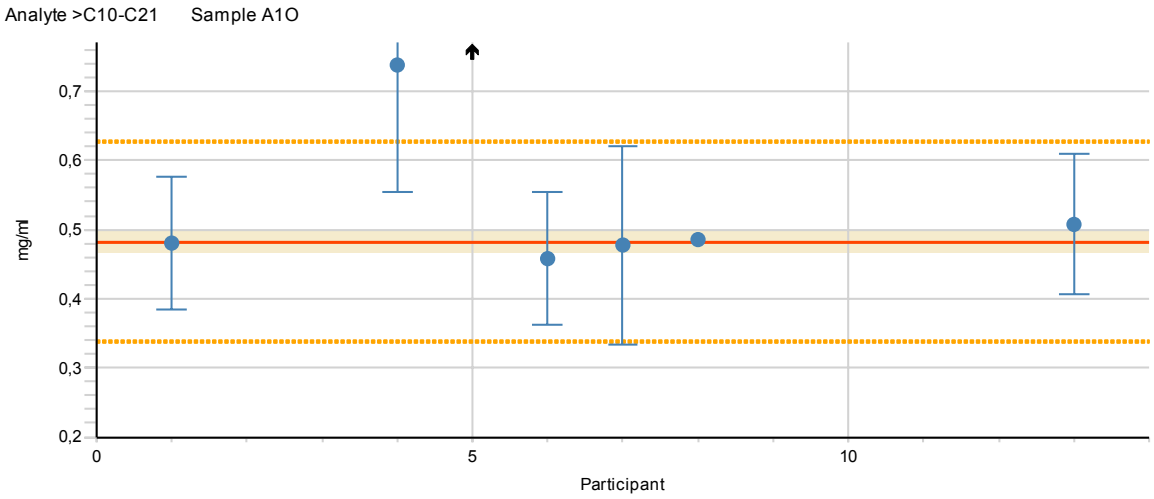
Participant 15												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
>C10-C40	mg/ml	A1O		0.482	0.976	20	1.02	1.00	0.99	0.1	5.4	10
	mg/l	N3O		5.214	0.576	30	1.03	0.56	0.58	0.1	17.8	14

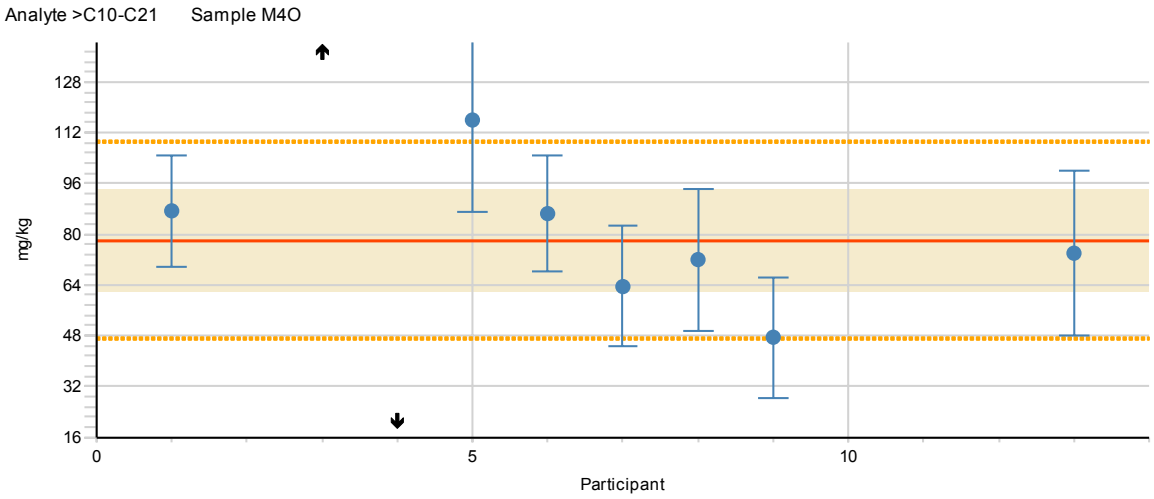
Participant 16												
Analyte	Unit	Sample	-3 0 3	z score	Assigned value	2*s_p, %	Lab's result	Md	Mean	SD	SD%	n (stat)
C5-C10	µg/ml	A2B		0.133	144.9	30	147.8	135.2	133.2	40.2	30.2	8
	mg/kg	M5B		0.543	8.6	30	9.30	8.60	7.65	2.4	31.5	8

APPENDIX 9: Results of participants and their uncertainties

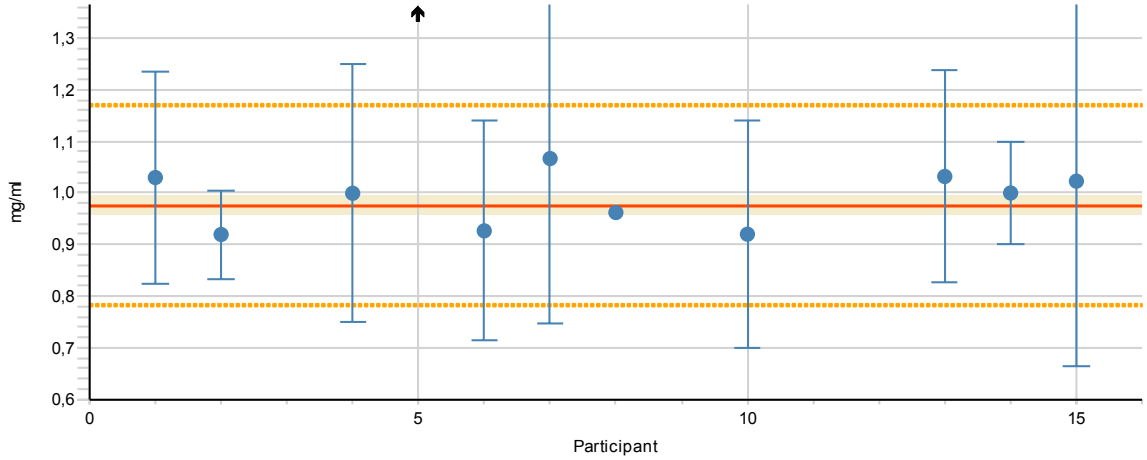
In figures:

- The dashed lines describe the standard deviation for the proficiency assessment, the red solid line shows the assigned value, the shaded area describes the expanded measurement uncertainty of the assigned value, and the arrow describes the value outside the scale.

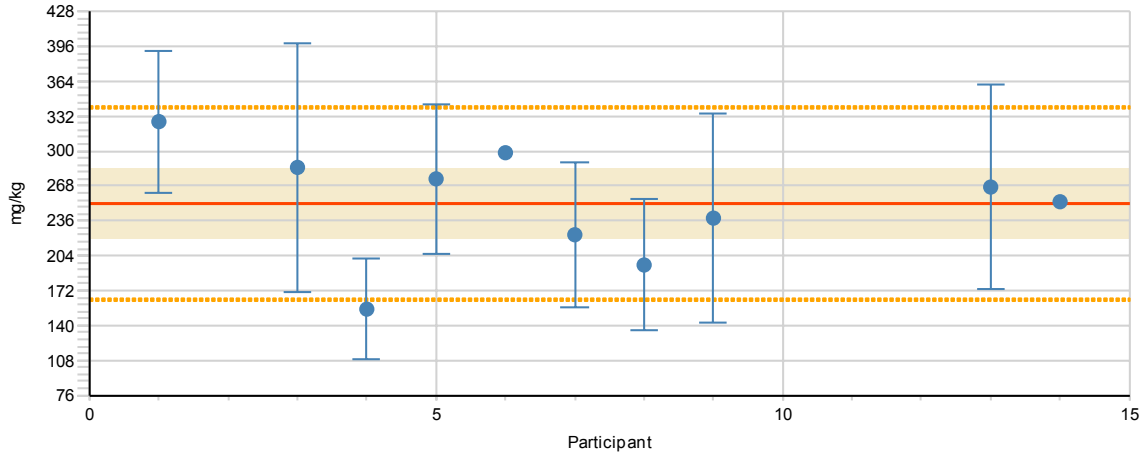




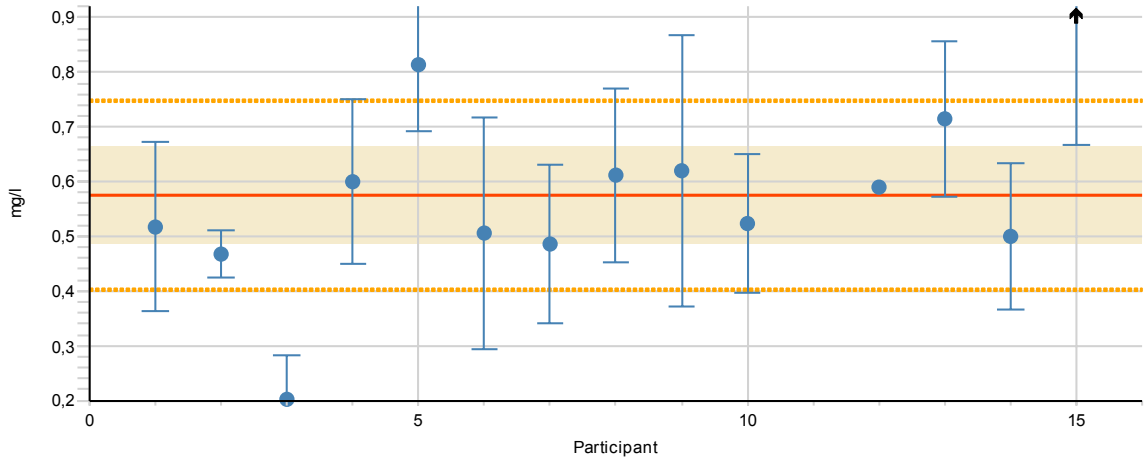
Analyte >C10-C40 Sample A1O



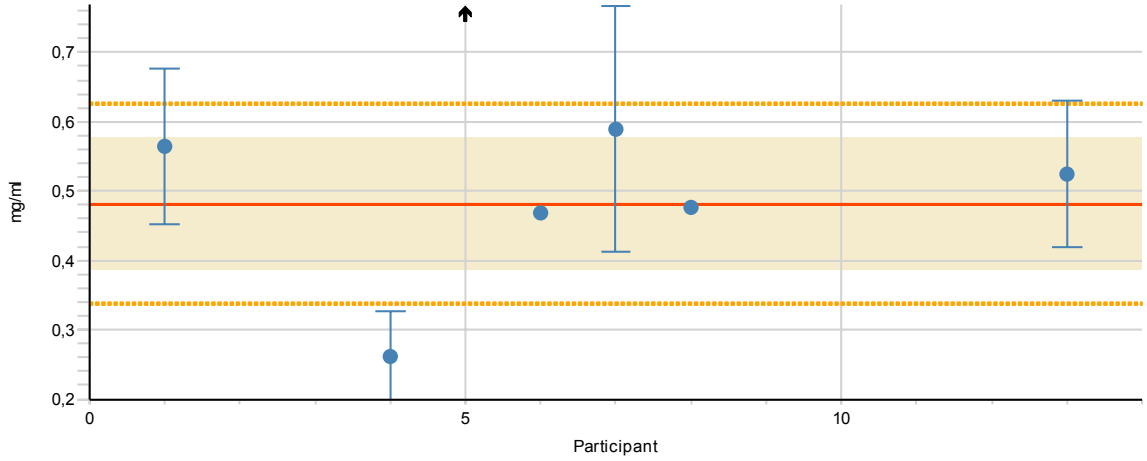
Analyte >C10-C40 Sample M4O



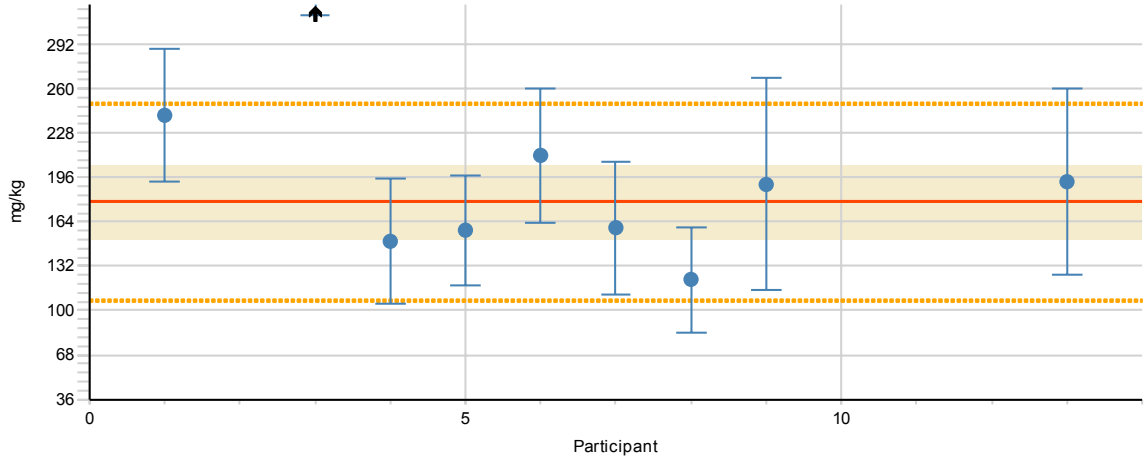
Analyte >C10-C40 Sample N3O



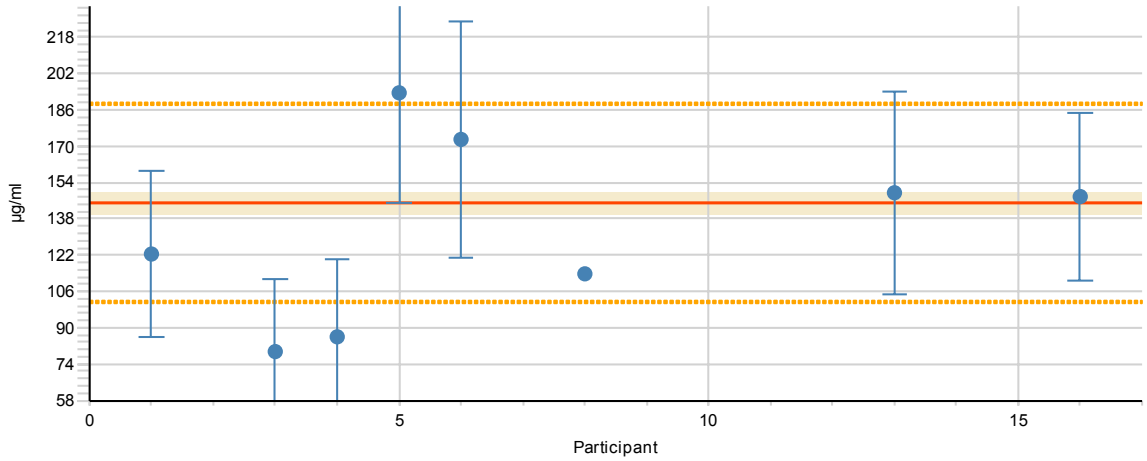
Analyte >C21-C40 Sample A1O

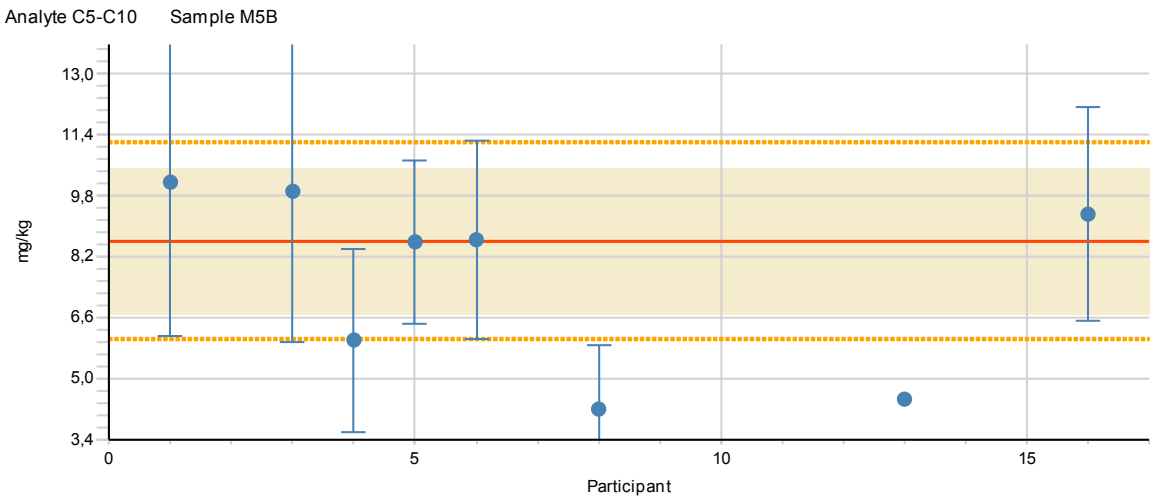


Analyte >C21-C40 Sample M4O



Analyte C5-C10 Sample A2B




Analyte C5-C10
Sample M5B
13,0
11,4
9,8
8,2
6,6
5,0
3,4
mg/kg
0
5
10
15
Participant

APPENDIX 10: Summary of the z scores

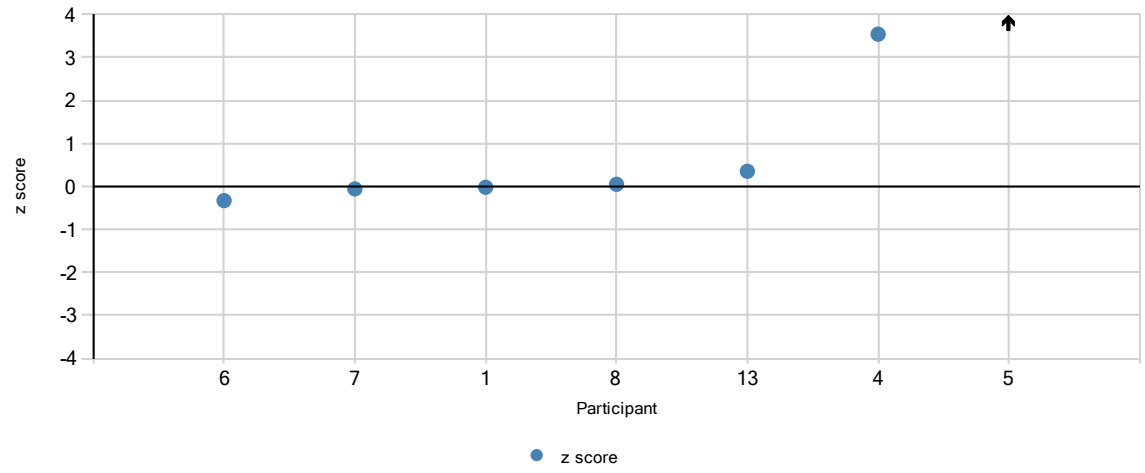
Analyte	Sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	%
>C10-C21	A1O	*S*	.	.	*U*	*U*	**S**	**S**	**S**	.	.	.	.	*S*	.	.	.	.	.	.	.	.	.	.	71,4
	M4O	*S*	.	**U**	*u*	*Q*	**S**	**S**	**S**	*S*	.	.	.	**S**	.	.	.	.	.	.	.	.	.	.	66,7
>C10-C40	A1O	*S*	*S*	.	**S**	*U*	**S**	**S**	**S**	.	*S*	.	.	*S*	**S**	*S*	.	.	.	.	.	.	.	.	90,9
	M4O	*S*	.	**S**	*q*	**S**	**S**	**S**	**S**	**S**	.	.	.	**S**	*S*	.	.	.	.	.	.	.	.	.	90,0
	N3O	*S*	*S*	**u**	**S**	**Q**	**S**	**S**	**S**	**S**	*S*	.	*S*	*S*	**S**	*U*	.	.	.	.	.	.	.	.	78,6
>C21-C40	A1O	*S*	.	.	*u*	*U*	**S**	**S**	**S**	.	.	.	.	*S*	.	.	.	.	.	.	.	.	.	.	71,4
	M4O	*S*	.	**U**	*S*	*S*	**S**	**S**	**S**	*S*	.	.	.	**S**	.	.	.	.	.	.	.	.	.	.	88,9
C5-C10	A2B	*S*	.	**u**	*q*	*Q*	**S**	.	*S*	.	.	.	.	*S*	.	.	*S*	.	.	.	.	.	.	.	62,5
	M5B	*S*	.	**S**	*q*	*S*	**S**	.	*u*	.	.	.	.	*u*	.	.	*S*	.	.	.	.	.	.	.	62,5
%		100	100	33	33	33	100	100	89	100	100		100	89	100	50	100								
accredited				6	2	2	9	7	7	2				3	2										

S - satisfactory (-2 ≤ z ≤ 2), Q - questionable (2 < z < 3), q - questionable (-3 < z < -2),
U - unsatisfactory (z ≥ 3), and u - unsatisfactory (z ≤ -3), respectively
bold - accredited, *italics - non-accredited*, normal - other
% - percentage of satisfactory results

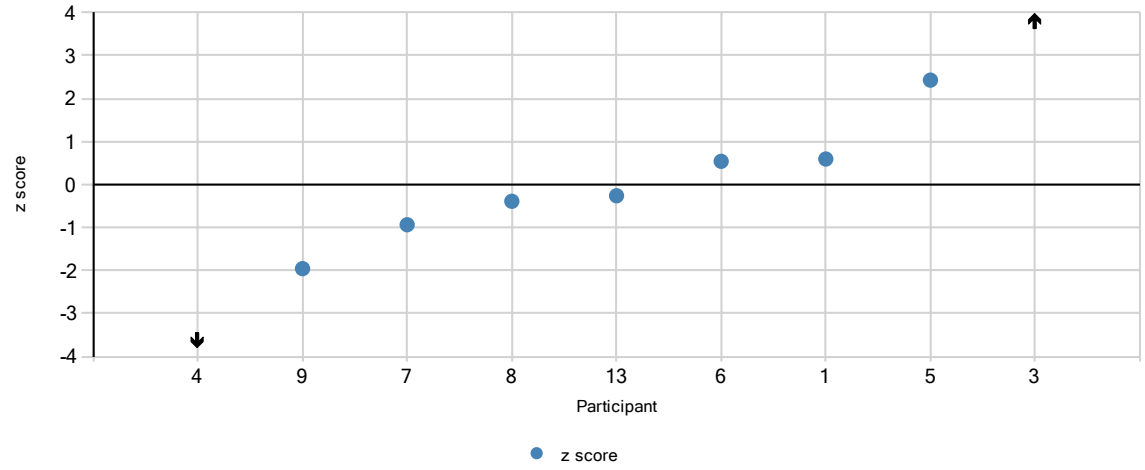
Totally satisfactory, % in all: 77 % in accredited: 88 % in non-accredited: 67

APPENDIX 11: z scores in ascending order

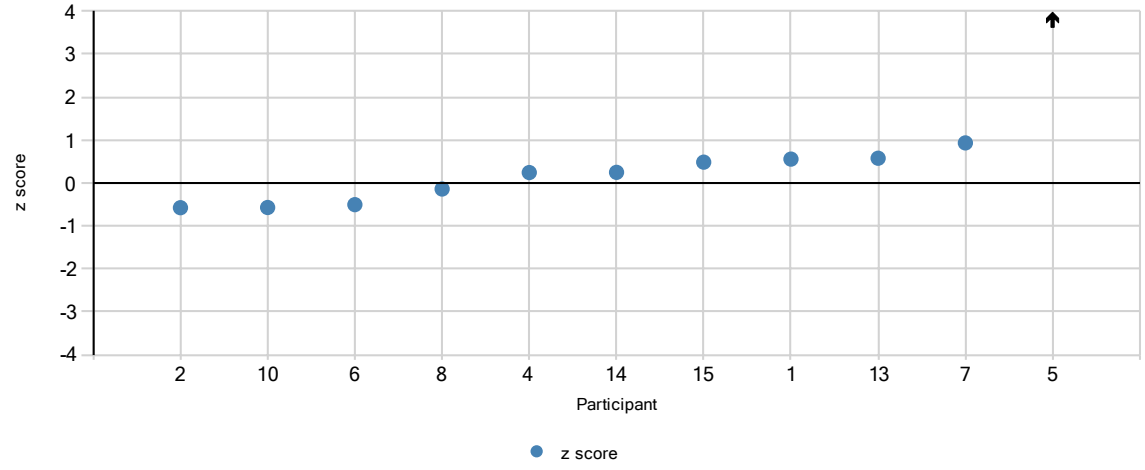
Analyte >C10-C21 Sample A1O



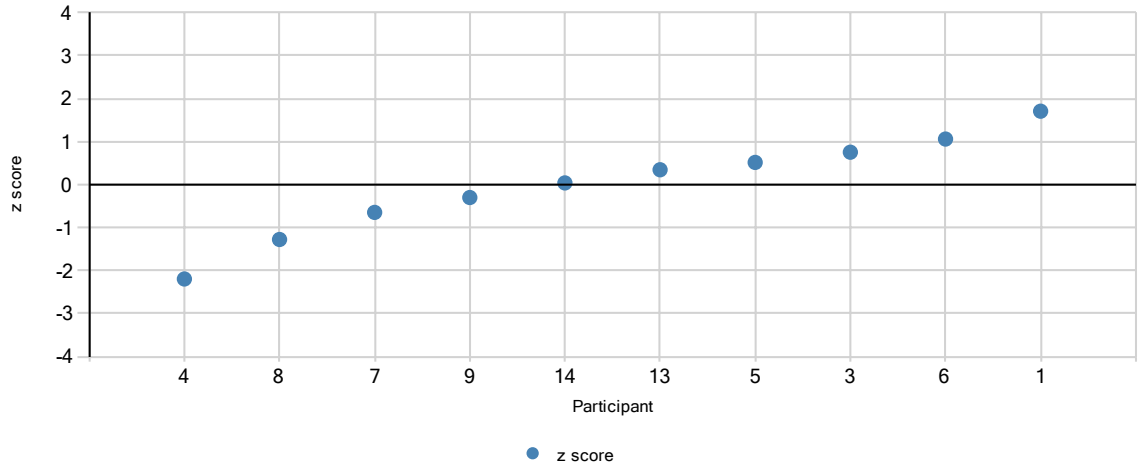
Analyte >C10-C21 Sample M4O



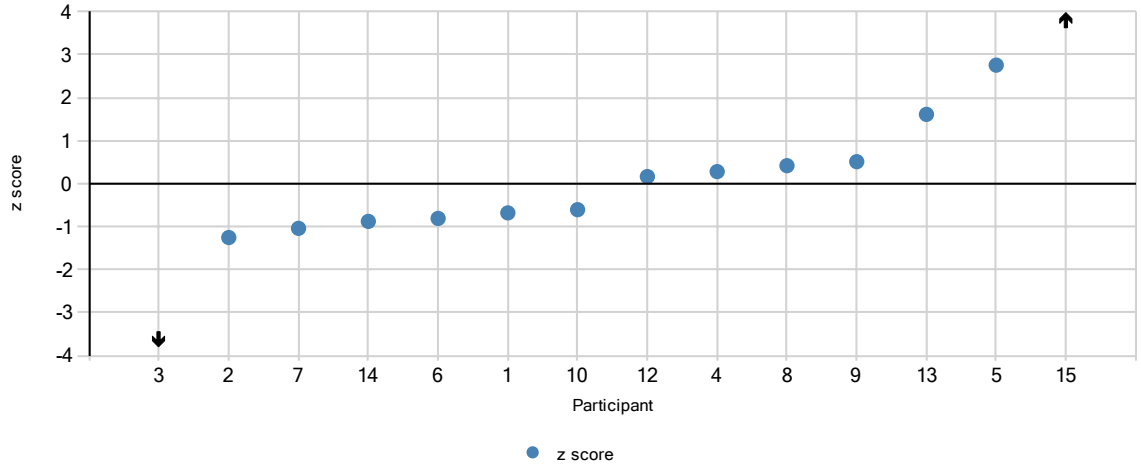
Analyte >C10-C40 Sample A1O



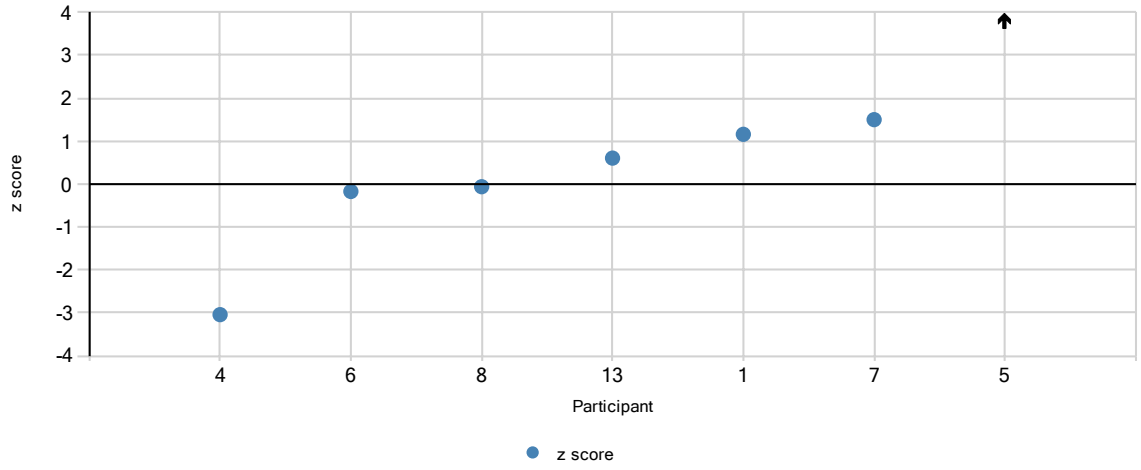
Analyte >C10-C40 Sample M4O



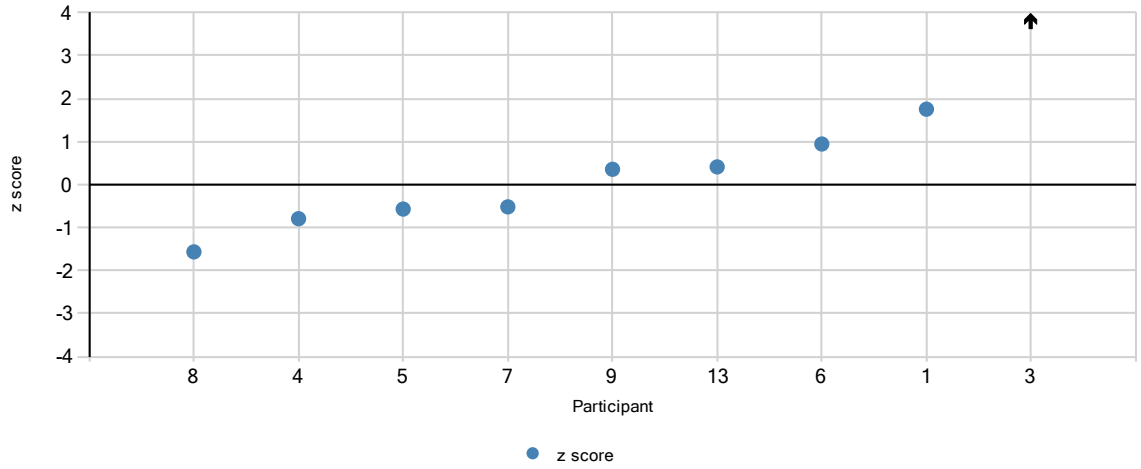
Analyte >C10-C40 Sample N3O



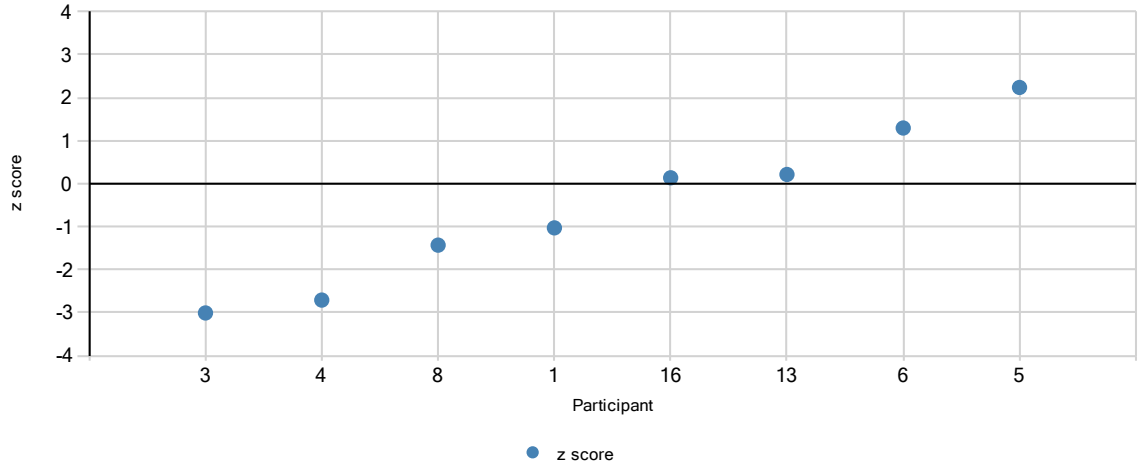
Analyte >C21-C40 Sample A1O



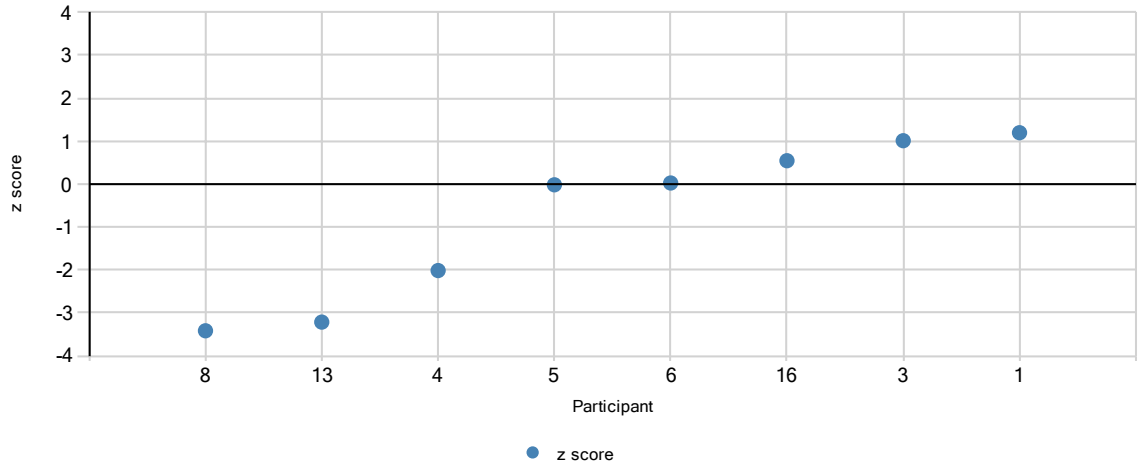
Analyte >C21-C40 Sample M4O



Analyte C5-C10 Sample A2B



Analyte C5-C10 Sample M5B



APPENDIX 12: Analytical methods

To collect the details of the used methods, an electronic questionnaire was delivered to the participants at the same time as the samples. Altogether 14 participants (93%) replied to the questionnaire. The summaries of the used methods are below.

Water – N3O, Oil hydrocarbons (>C10-C40)

Participant	Reference	Solvent	Extraction	Purification	Injection	Equipment
1	EN ISO 9377-2	Heptane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	On-column, 2 µl	GC-FID
2	EN ISO 9377-2	n-Pentane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	PTV[1], 20 µl	GC-FID
3	EN ISO 9377-2	n-Hexane	Shaking, 40 ml / 30 min	Florisil/Na_2SO_4	Splitless,1 µl	GC-MS
4	EN ISO 9377-2	n-Hexane	Stirring, 50 ml / 60 min	Florisil/Na_2SO_4	Split, 5 µl	GC-FID
5	EN ISO 9377-2	n-Hexane	Shaking, 20 ml / 10 min	Florisil/Na_2SO_4	Splitless, 0,5 µl	GC-MS
6	EN ISO 9377-2	n-Hexane	Stirring, 50 ml / 60 min	Florisil/Na_2SO_4	MMI[2] Solvent Vent, 5 µl	GC-FID
7	EN ISO 9377-2	n-Hexane	Shaking, 20 ml / 30 min	Florisil	On-column, 2 µl	GC-FID
8	EN ISO 9377-2	n-Hexane	Shaking, 50 ml / -	Florisil	Splitless, 1 µl	GC-FID
9	EN ISO 9377-2	n-Hexane	Stirring, 50 ml / 30 min	Florisil/Na_2SO_4	Splitless, 1 µl	GC-FID
10	EN ISO 9377-2	n-Hexane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	Splitless, 3,5 µl	GC-FID
13	SFS-EN ISO 9377-2, modified	Heptane	Shaking, 10 ml / 40 min	Al_2O_3	Split, 2 µl	GC-FID
14	EN ISO 9377-2	n-Pentane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	PTV[1], 1 µl	GC-FID
15	EN ISO 9377-2	n-Hexane	Shaking, 50 ml / 30 min	Florisil/Na_2SO_4	On-column, 1 µl	GC-FID

[1] PTV - Programmable temperature vaporization injector

[2] MMI - Multimode inlet (technique for large volume injection)

Soil – M4O, Oil hydrocarbons (>C10-C40)

Participant	Reference	Solvent	Extraction	Purification	Injection	Equipment
1	ISO 16703	Acetone/Heptane	Shaking, 20 g / 30 min	Florisil/Na_2SO_4	On-column, 2 µl	GC-FID
3	ISO 16703	Acetone, Hexane, MeOH, H_2O	Shaking, 20 g / 60 min	Florisil/Na_2SO_4	Splitless, 1 µL	GC-MS
4	EN 14039	Acetone/Hexane	Ultrasonic, g[1] / 60 min	Florisil/ Na_2SO_4	Split, 5 µl	GC-FID
5	ISO 16703	Acetone/Hexane	Shaking, 10 g / 60 min	Florisil/ Na_2SO_4	Splitless, 0,1 µl	GC-MS
6	ISO 16703	Acetone/Hexane	Ultrasonic, 10 g / 30 min	Florisil/ Na_2SO_4	Splitless, 2 µl	GC-FID
7	EN 14039	Acetone/Hexane	Shaking, 10 g / 60 min	Florisil	On-column, 2 µl	GC-FID
8	ISO 16703	Acetone/Hexane	Shaking, 20 g / 60 min	Florisil	Splitless, 1 µl	GC-FID
9	ISO 16703	Acetone/Hexane	Shaking, 5-10 g / 60 min	Florisil/ Na_2SO_4	Splitless, 1 µl	GC-FID
13	ISO 16703:2004 modified	Acetone/Heptane	Shaking, 15 g / 40 min	Al_2O_3	Split, 2 µl	GC-FID
14	ISO 16703	Acetone/Pentane	Ultrasonic, 10 g / 60 min	Florisil/ Na_2SO_4	PTV[2], 1 µl	GC-FID

[1] Sample amount varies

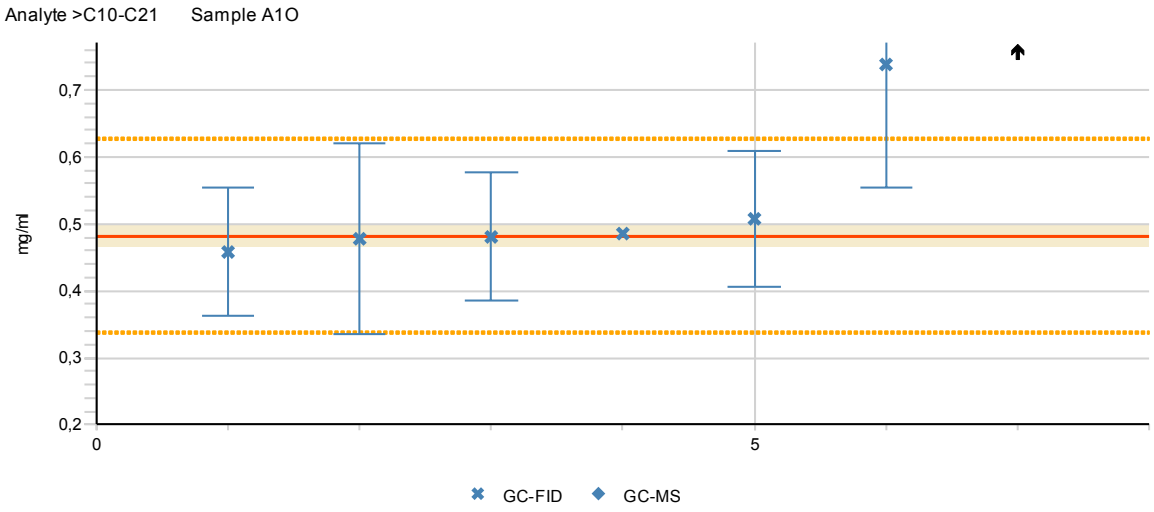
[2] PTV - Programmable temperature vaporization injector

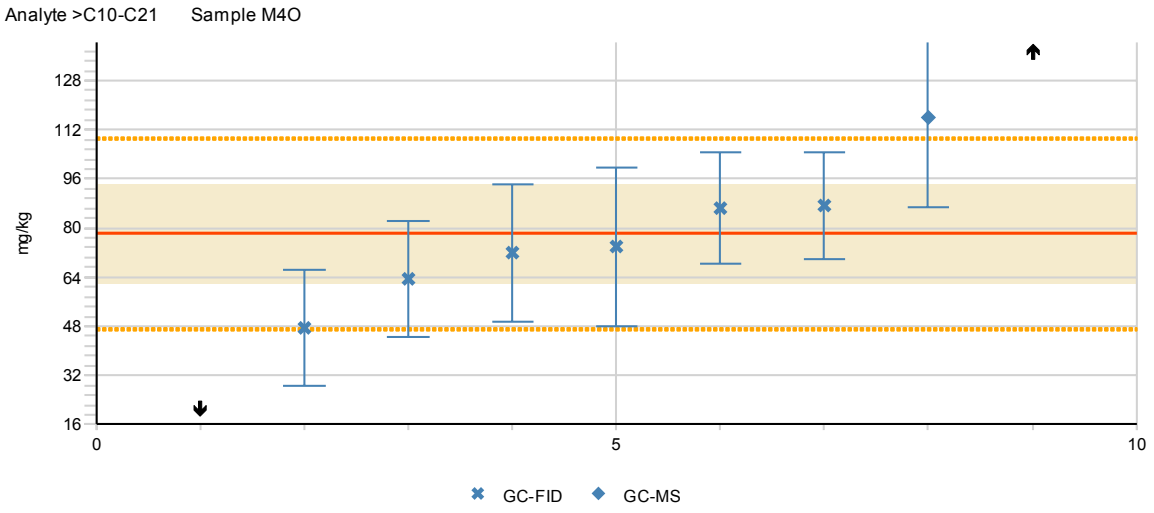
Soil – M5B, Volatile oil hydrocarbons (C5-C10)

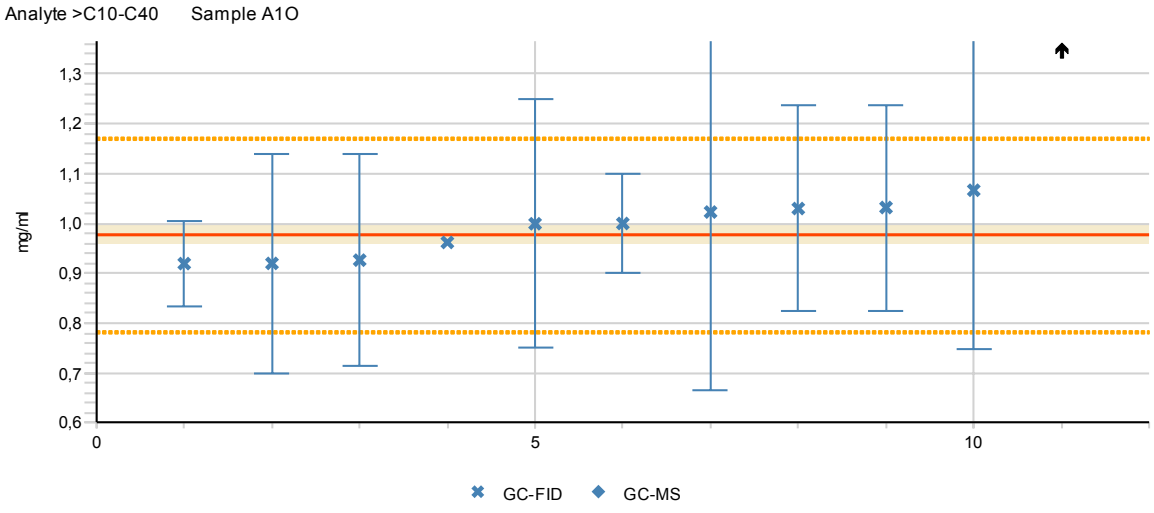
Participant	Reference	MS mode	Standards	Equipment
1				Headspace GC-FID
3	SFS-ISO 15009:2007	SCAN: Integration (TIC) from C5 to C10 library search	Internal standard	Headspace GC-MS
4	internal method / as in prEN ISO 16558-1:2013	as in prEN ISO 16558-1:2013		Headspace GC-MS
5	ISO 22155	SCAN: ions 40-300	Internal standard	Headspace GC-MS
6	ISO 22155		Internal standard	Headspace GC-MS
8	SFS-EN ISO 22155	SCAN	Internal standard	Headspace GC-MS
13		SCAN: ions 35-350	External standard	Headspace GC-MS
16	SFS-EN ISO 22155	SIM: BTEX and oxygenate ions and hexane m/z 57, methyl-cyclohexane m/z 55	Internal standard	Headspace GC-MS

APPENDIX 13: Results grouped according to the methods

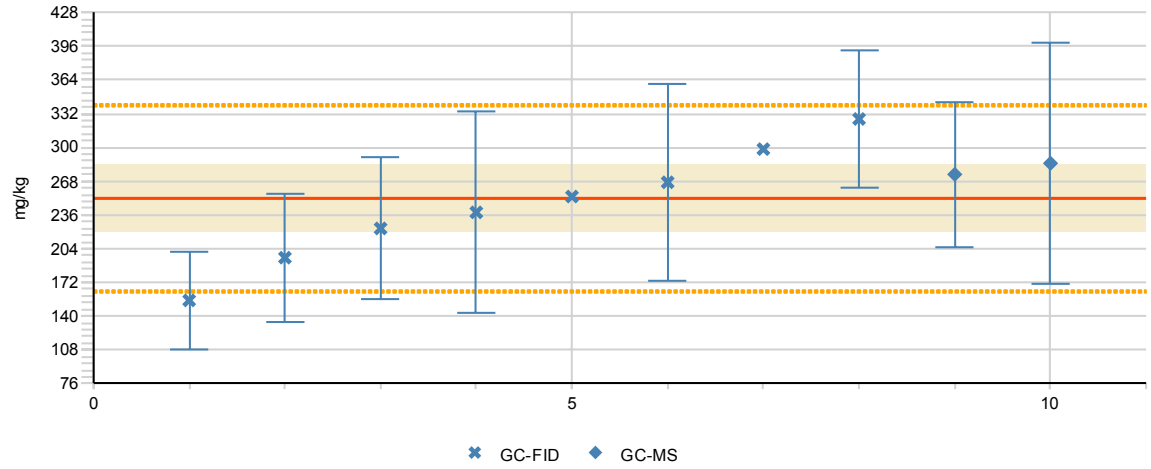
The explanations for the figures are described in the Appendix 9.



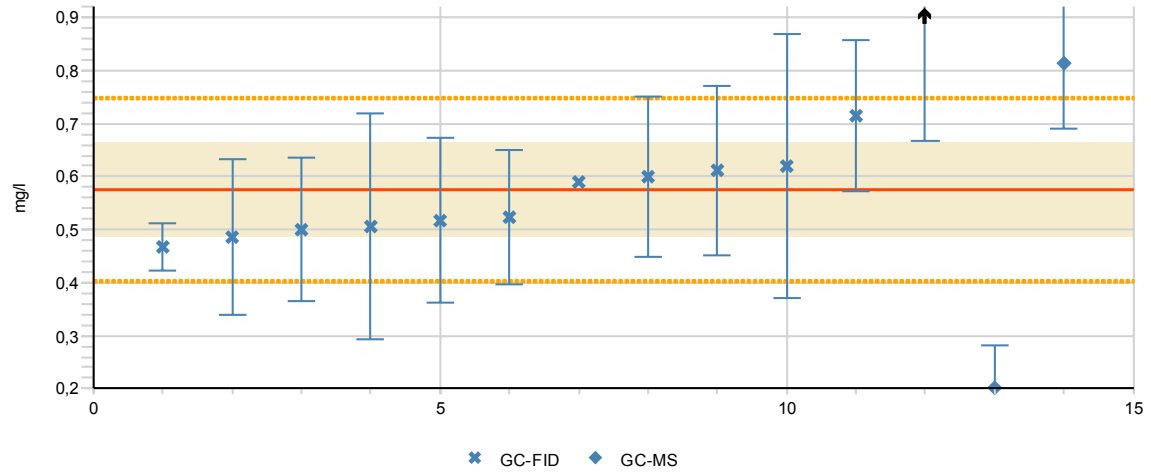




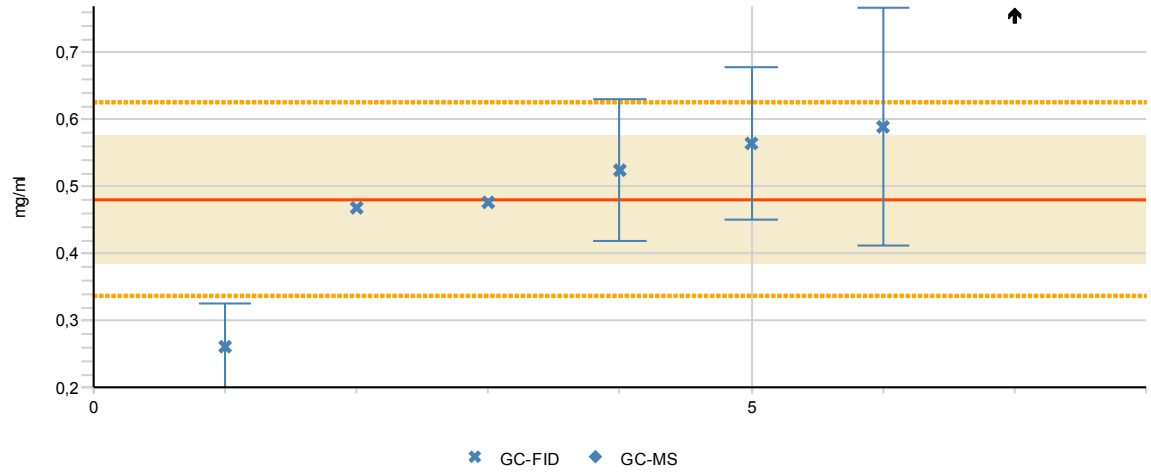
Analyte >C10-C40 Sample M4O



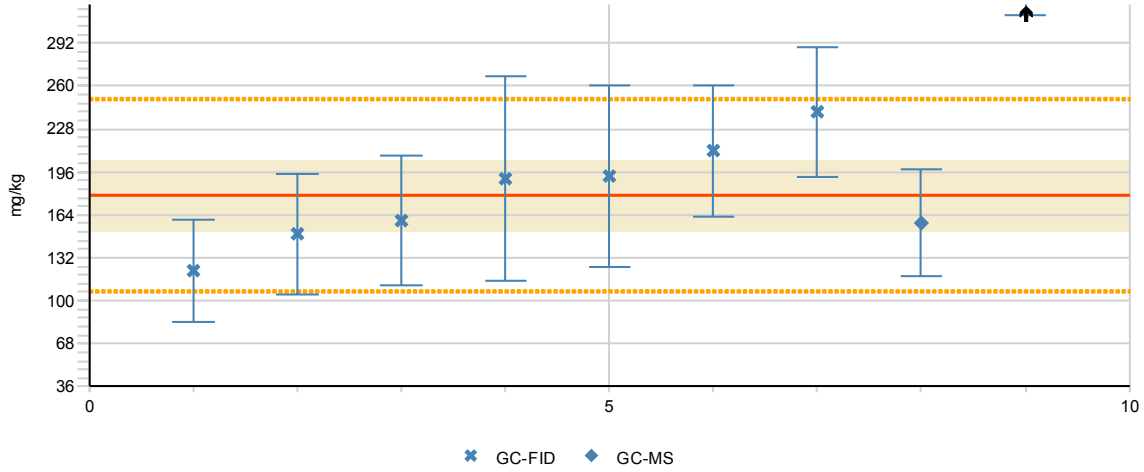
Analyte >C10-C40 Sample N3O



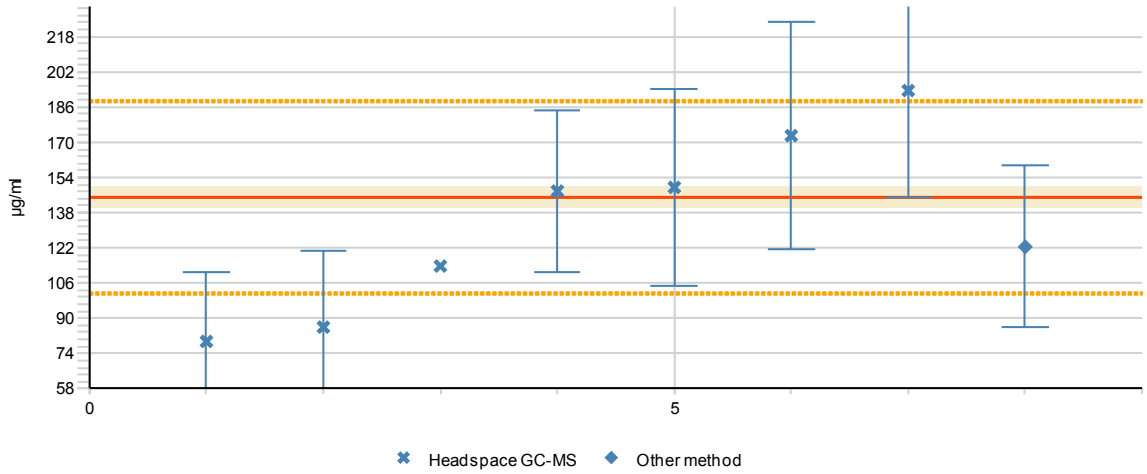
Analyte >C21-C40 Sample A1O



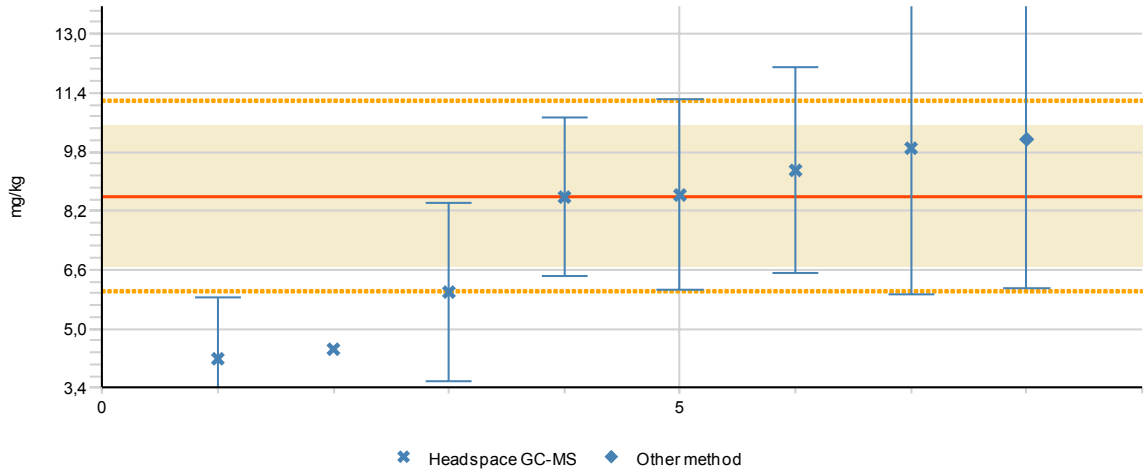
Analyte >C21-C40 Sample M4O



Analyte C5-C10 Sample A2B



Analyte C5-C10 Sample M5B



APPENDIX 14: Examples of measurement uncertainties reported by the participants

In figures, the presented measurement uncertainties are grouped according to the method of estimation. The following procedures are used for the estimation of the expanded measurement uncertainty at 95 % confidence level (k=2). In figures, the corresponding method numbers are used.

1. Using the IQC data only from synthetic control sample and/or CRM (X-chart), see e.g. NORDTEST TR 537[1)]. **Using MUkit measurement uncertainty software**[3)].

2. Using the IQC data only from synthetic control sample and/or CRM (X-chart), see e.g. NORDTEST TR 537[1)]. **Without MUkit measurement uncertainty software.**

3. Using the IQC data from synthetic sample (X-chart) together with the IQC data from routine sample replicates (R-chart or r%-chart), see e.g. NORDTEST TR 537[1)]. **Using MUkit software.**

4. Using the IQC data from synthetic sample (X-chart) together with the IQC data from routine sample replicates (R-chart or r%-chart), see e.g. NORDTEST TR 537[1)]. **Without MUkit software.**

5. Using the IQC data and the results obtained in proficiency tests, see e.g. NORDTEST TR 537[1)]. **Using MUkit software.**

6. Using the IQC data and the results obtained in proficiency tests, see e.g. NORDTEST TR 537[1)]. **Without MUkit software.**

7. Using the data obtained in method validation. **Using MUkit software.**

8. Using the data obtained in method validation. **Without MUkit software.**

9. Using the "modeling approach" (GUM Guide or EURACHEM Guide Quantifying Uncertainty in Analytical Measurement)[2)]

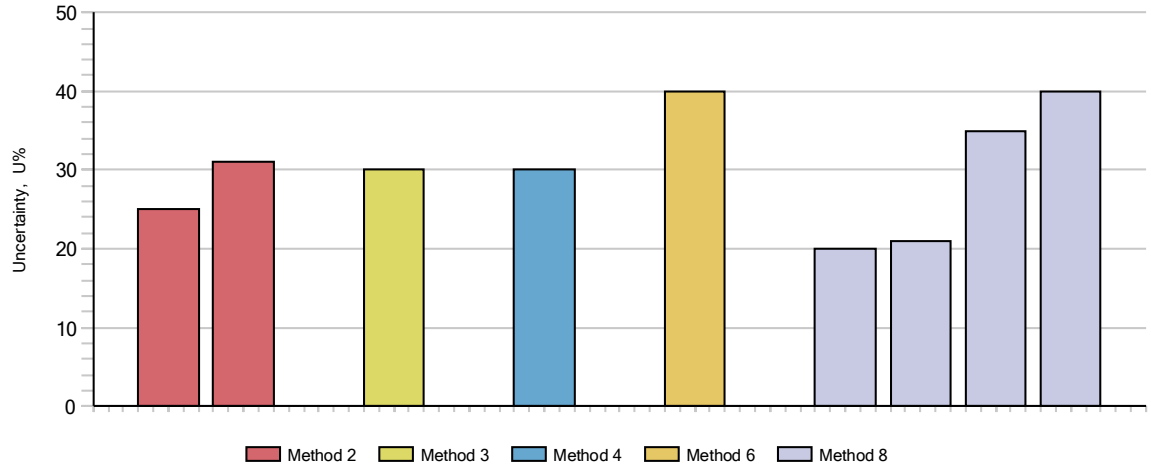
10. Other procedure, please specify

11. No uncertainty estimation

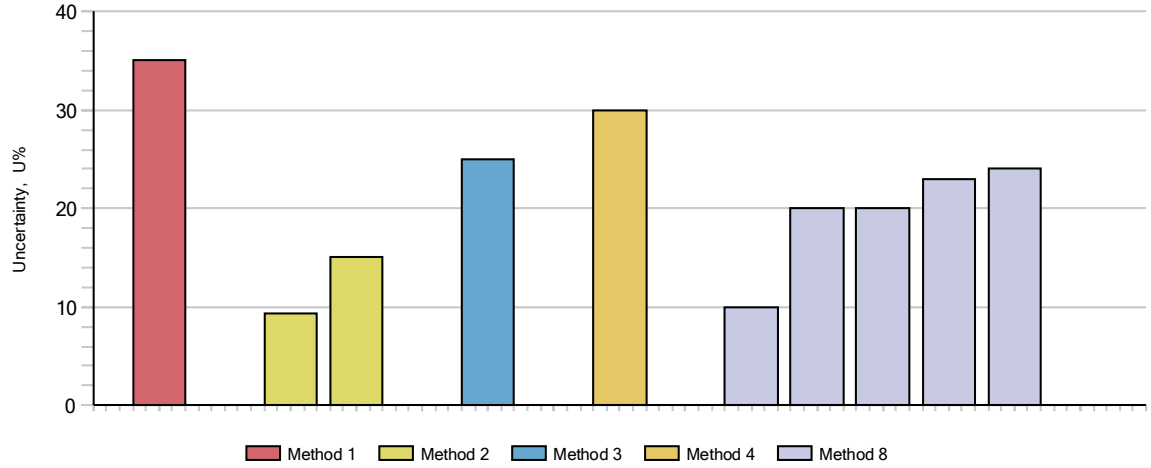
IQC = internal quality control

[1)] http://www.nordtest.info, [2)] http://www.eurachem.org, [3)] http://www.syke.fi/envical

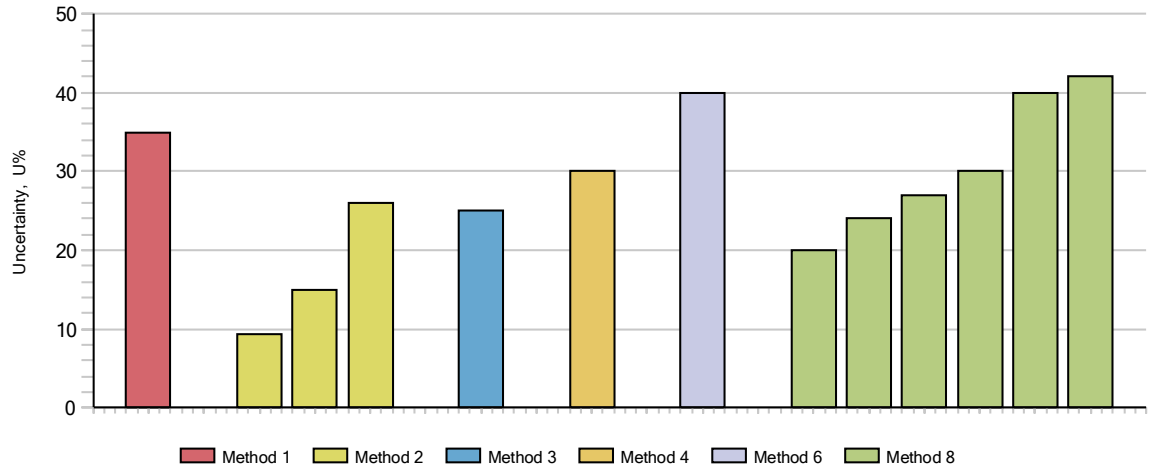
Analyte >C10-C21 Sample M4O



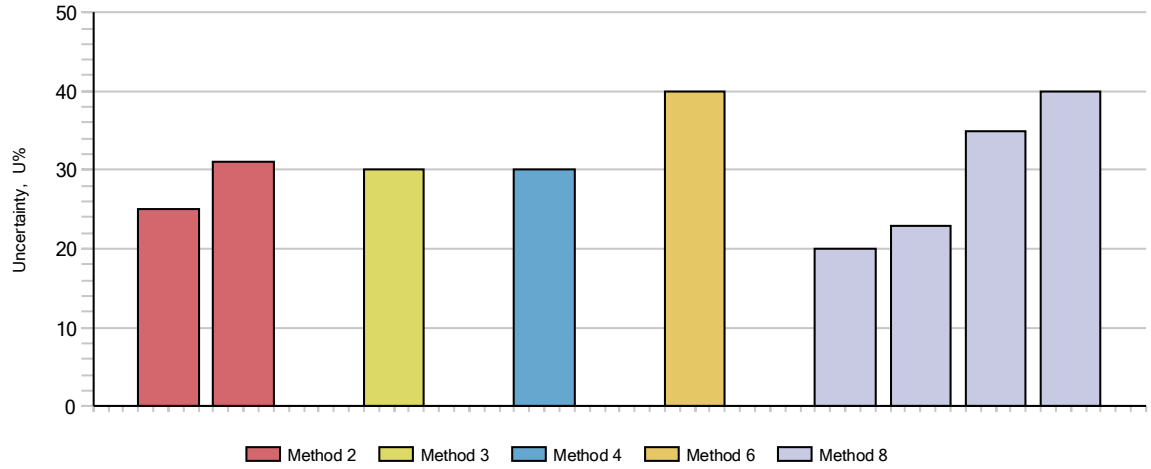
Analyte >C10-C40 Sample A1O



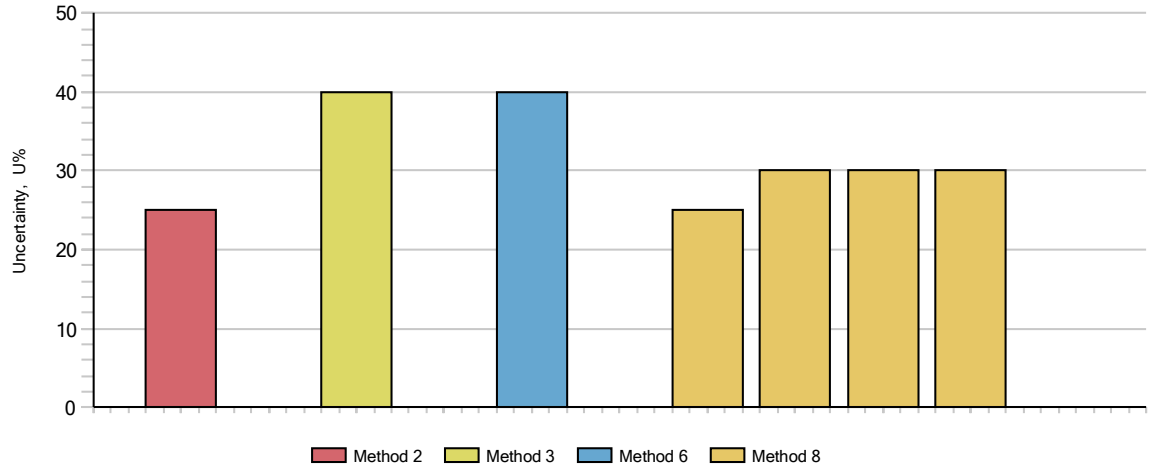
Analyte >C10-C40 Sample N3O



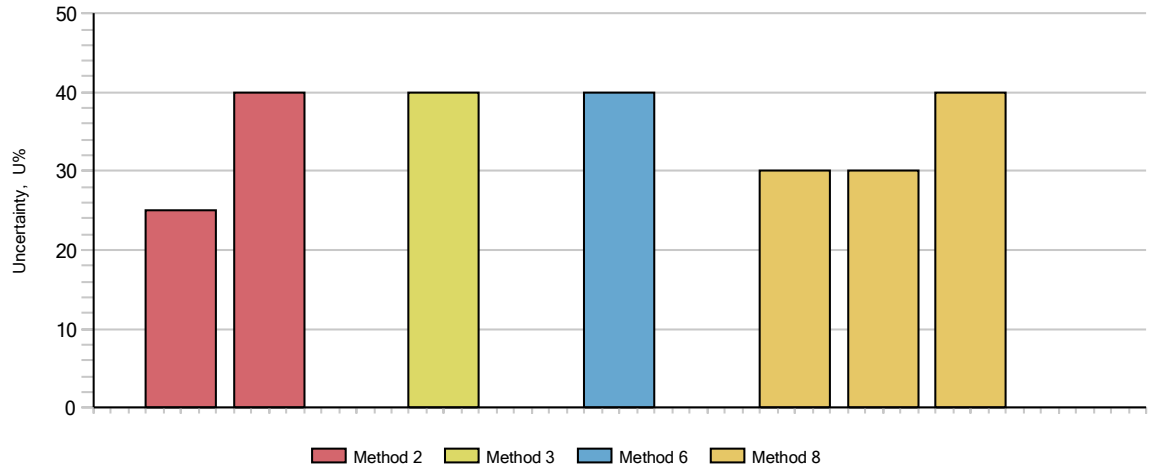
Analyte >C21-C40 Sample M4O



Analyte C5-C10 Sample A2B



Analyte C5-C10 Sample M5B



DOCUMENTATION PAGE

Publisher	Finnish Environment Institute	Date February 2015
Author(s)	Jari Nuutinen, Riitta Koivikko, Mirja Leivuori and Markku Ilmakunnas	
Title of publication	Interlaboratory Proficiency Test 09/2014 Oil hydrocarbons in water and soil	
Publication series and number	Reports of the Finnish Environment Institute 5/2015	
Theme of publication		
Parts of publication/ other project publications	The publication is available in the internet: www.syke.fi/publications | helda.helsinki.fi/syke	
Abstract	Proftest SYKE carried out the proficiency test (PT) for analysis of oil hydrocarbons in water and soil in November-December 2014. Three types of samples were delivered to the participants; synthetic sample, surface water and soil samples. In total, 15 laboratories participated in the PT. The evaluation of the performance was based on the z scores. In this proficiency test 77 % of the data was regarded to be satisfactory when the deviation of 20 to 40 % from the assigned value was accepted. Either the calculated concentration, robust mean, mean or median of the results reported by the participants was chosen to be the assigned value depending on the analyte. The uncertainty for the assigned value was estimated at the 95 % confidence interval and for calculated assigned values it was 1.9–3.5 %, for assigned values based on the robust mean it was 15.5 %, for assigned values based on the mean it varied from 3.3 to 20.9 %, and for median based assigned value the uncertainty for the assigned value was estimated to 22.3 %.	
Keywords	water analysis, soil analysis, oil hydrocarbons, proficiency test, intercomparison	
Financier/ commissioner		
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KUVAILULEHTI

Julkaisija	Suomen ympäristökeskus	Julkaisuaika Helmikuu 2015
Tekijä(t)	Jari Nuutinen, Riitta Koivikko, Mirja Leivuori ja Markku Ilmakunnas	
Julkaisun nimi	Laboratorioiden välinen pätevyyskoe 09/2014 Öljyhiilivedyt vedestä ja maasta	
Julkaisusarjan nimi ja numero	Suomen ympäristökeskuksen raportteja 5/2015	
Julkaisun teema		
Julkaisun osat/ muut saman projektin tuottamat julkaisut	Julkaisu on saatavana vain internetistä: www.syke.fi/julkaisut | helda.helsinki.fi/syke	
Tiivistelmä	Proftest SYKE järjesti marras-joulukuussa 2014 pätevyyskokeen öljyhiilivetyjä vedestä ja maasta analysoiville laboratorioille. Pätevyyskokeen osallistujille toimitettiin synteettinen-, pintavesi- ja maanäyte. Pätevyyskokeeseen osallistui yhteensä 15 laboratoriota. Pätevyyden arviointi tehtiin z-arvon avulla ja tulosten sallittiin poiketa vertailuarvosta 20–40 %. Koko aineistossa hyväksyttäviä tuloksia oli 77 %. Mittaussuureen vertailuarvona käytettiin laskennallista pitoisuutta, osallistujien tulosten robustia keskiarvoa, keskiarvoa tai tulosten mediaania. Vertailuarvolle laskettiin mittausepävarmuus 95 % luottamusvälillä. Vertailuarvon laajennettu epävarmuus oli 1.9–3.5 % laskennallista pitoisuutta vertailuarvona käytettäessä ja kun vertailuarvo määritettiin muilla keinoin, sen laajennettu epävarmuus vaihteli välillä 3.3–22.3 %.	
Asiasanat	vesianalyysi, maa-analyysi, öljyhiilivedyt, pätevyyskoe, vertailumittaus	
Rahoittaja/ toimeksiantaja		
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Painopaikka ja -aika	Helsinki 2015	

PRESENTATIONSBLAD

Utgivare	Finlands miljöcentral	Datum Februari 2015
Författare	Jari Nuutinen, Riitta Koivikko, Mirja Leivuori och Markku Ilmakunnas	
Publikationens titel	Provningsjämförelse 09/2014 Olja kolväte i ytvatten och jord	
Publikationsserie och nummer	Finlands miljöcentrals rapporter 5/2015	
Publikationens tema		
Publikationens delar/ andra publikationer inom samma projekt	Publikationen finns tillgänglig på internet: www.syke.fi/publikationer | helda.helsinki.fi/syke	
Sammandrag	Under november-december 2014 genomförde Proftest SYKE en provningsjämförelse, som omfattade bestämningen av olja kolväten i ytvatten och i förorenad jord. Totalt 15 laboratorier deltog i provningsjämförelsen. Som referensvärde för analyternas koncentration användes det teoretiska värdet eller det robusta medelvärdet av deltagarnas resultat. Resultaten värderades med hjälp av z-värden. I jämfördelsen var 77 % av alla resultaten tillfredställande, när en totalavvikelse på 20-40 % från referensvärdet accepterades.	
Nyckelord	vattenanalyser, jordanalyser, olja kolväte, provningsjämförelse, interkalibrering	
Finansiär/ uppdragsgivare		
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