

2nd Interim Report on Grant Agreement for an Action SA/CEN/ENTR/503/2012-11 Ambient Air Quality

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CEN/TC 264/WG 34 "Anions/cations in PM_{2,5}"

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1. Introduction

Air Quality Directive 2008/50/EC, annex IV, requires the measurement of cations, anions, elemental and organic carbon (EC/OC) in PM_{2,5}. To meet these requirements, the European Commission has issued Mandate M/503 "Ambient air quality" for the development of standards regarding automated measurements of particulate matter in ambient air and the measurement of its chemical composition (organic and elemental carbon, inorganic components).

Working group CEN/TC 264/WG 34 "Anions/cations in PM_{2,5}" will be responsible for the development of a standard method for the measurement of anions/cations in PM_{2,5}. NEN, the Netherlands Standardization Institute, will provide the secretariat of WG 34 and will perform the administrative management of the standardization work.

The European Standard will describe a validated method for the determination of the mass of water soluble anions and cations in the PM_{2,5} fraction of particulate air pollutants.

In 2011, WG 34 published CEN/TR 16269 *Ambient air - Guide for the measurement of anions and cations in PM_{2,5}*. This document will be the basis for the development of the European Standard.

This final report describes the progress of CEN/TC 264/WG 34 "Anions/cations in PM_{2,5}" in providing validation work for WI 0264163 "Ambient air – Standard method for measurement of anions/cations in PM_{2,5}".

This validation work has been split into 4 work packages as outlined below:

- WP1: Literature review
- WP2: Lab tests, EMEP equivalence test
- WP3: Field tests
- WP4: Statistical evaluation

WP1 is completed and the Literature review has been published..

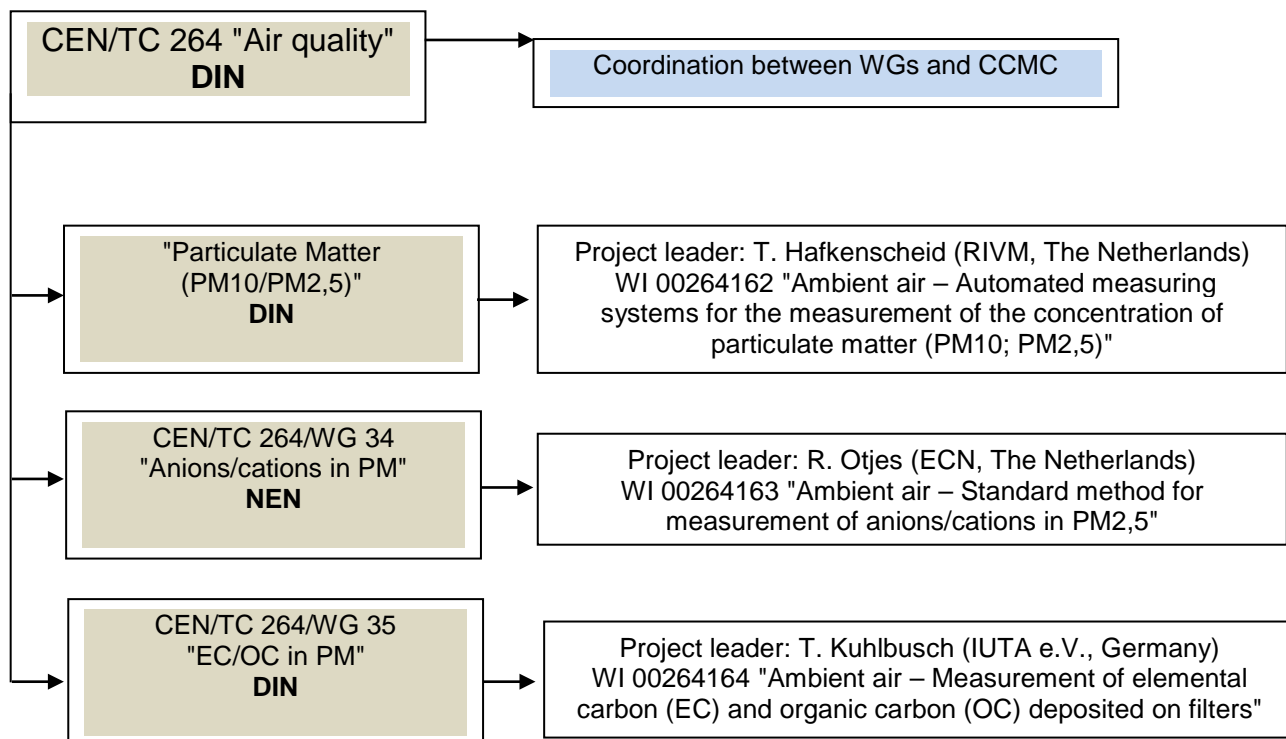
WP2 is completed with the laboratory tests comprising the ruggedness test and the EMEP equivalence test. The ruggedness tests were focused on the artefact induced by volatile inorganic substances and performance of the various filter analysis methods.

WP3 is completed with field validation tests being performed in Ispra (Rural Background, Italy), Barcelona (Urban Background, Spain), Duisburg (Urban Background, Germany), Amsterdam (Roadside, the Netherlands), Waldhof (Rural Background, Germany) and Cabauw (Rural Background, the Netherlands). Samples from the field sites were distributed to the following laboratories for analysis: CNR (Italy), ECN (the Netherlands), FMI (Finland), ISCII (Spain), TNO (the Netherlands) and UMB (Austria).

WP4 is completed with statistical analysis performed on the field validation results to calculate the measurement uncertainty of a single measured result.

2. Structure of the work in CEN/TC 264 – Air Quality

In order to perform the work, the following structure was established. Only the working groups covered by Mandate M/503 are shown:



It was decided that WG 34 & WG 35 would share resources for the field sampling. WG 35 undertook all of the field sampling and provided sampled filters to WG 34 for analysis. A common sampling media for all sampling was agreed between the two working groups. Joint meetings between the two groups took place throughout the work packages to ensure efficient and complaint working practices.

3. Status of the work programme

Work Package 1

The literature review on measurement of ions in PM_{2,5} has been published (CEN/TC 264 WG34 N81) and is included in Annex A of this report.

Work Package 2

Results from the literature study were used to define the direction of the laboratory tests.

A laboratory inter-comparison was held for the 6 laboratories taking part in WP3 and the findings are reported in Annex B.

Laboratory tests characterizing the sampling artefacts were also conducted. Pre-loaded quartz filters with mixtures of NH₄NO₃ and (NH₄)₂SO₄ were prepared. Subsequently the filters were exposed to sampling conditions that were expected to lead to evaporation. By measuring on line the extra NH₃ and HNO₃ behind the filter, evaporation velocity characteristics of NH₄NO₃ was observed. It seems that two different phases of evaporation exist: a high rate phase followed by a low rate phase. The high velocity rate is in the order of 20 µg/h and the low rate in the order of 2 µg/h. It is assumed that the latter represents evaporating NH₄NO₃ with affinity to the quartz filter material. The transition between both phases is dependent on the quantity of NH₄NO₃ on the filter and the relative humidity

(approximately 80 µg at 40% rH and 230 µg at 75% rH). The velocity at the high rate phase correlates with the calculated deficit of NH₃ and HNO₃ when compared to the atmospheric equilibrium concentrations. This relationship could not be found for the low velocity phase. The average amount of NH₄NO₃ seen at the WP3 field trial would have been 27% higher when losses were taken into account, assuming that 50% of the time the sampled NH₄NO₃ was exposed to low velocity phase evaporating conditions. Changing atmospheric conditions during sampling can easily lead to this magnitude of losses. Cl⁻ also endures evaporation losses, though induced by HNO₃.

Concern was raised with respect to the homogeneous filter loading during the field trials. This was of importance because filter punches were analysed by the participating laboratories. The homogeneity was tested by having one lab analysing the total set of punches coming from two different field trial filters. For all components the relative standard deviation was less or equal to the analytical uncertainty. It was therefore concluded that inhomogeneity of filter loadings as applied at the field validation tests was not detectable.

The European standard for PM accepts the variability of the evaporation losses by convention. This rules out the sampling effects and as a consequence lets the working range of the method be dominated by the analysis uncertainties. According to the definition of PM_{2,5} for the purpose of the European Standard, working range for the ions follows the working range of EN12341 and be restricted by the analytical results presented in statistical analysis report of WP4. Taking the conclusion of this laboratory tests into account, the method will not be suited for the objectives (to support air quality assessment and management) of the standard. Results for NH₄⁺, NO₃⁻ and Cl⁻ should be considered as indicative. In order to determine the PM ions quantitatively and meet the objectives of the standard, denuder filter pack methods or on line analysers as MARGA should be applied.

The full report on the laboratory tests has been published (CEN/TC 264/WG 34 N95) and is included in Annex C of this report.

Work Package 3

The six field validation tests were performed in Ispra (Rural Background, Italy), Barcelona (Urban Background, Spain), Duisburg (Urban Background, Germany), Amsterdam (Roadside, the Netherlands), Waldhof (Rural Background, Germany) and Cabauw (Rural Background, the Netherlands). Samples from the field sites were distributed to the following laboratories for analysis: CNR Italy, ECN the Netherlands, FMI Finland, ISCII Spain, TNO the Netherlands and UMB Austria.

The results for this field site have been completed and sent to the National Physical Laboratory (WP4 - Statistical evaluation of data and reporting). Reports on each validation site are included in Annex D, part 1 to 6.

Consistent site working procedures were implemented by the working group writing Standard Operating procedures (SOPs) for:

1. Operation of the Digital high volume sampler;
2. Filter handling, treatment and marking.

These SOPs are included in Annex E, parts 1 and 2.

The table below reports the analytical methods used by each lab for the analysis of the field samples:

Lab	Analytical method
CNR	IC ⁽¹⁾ for all ions
ECN	IC for anions, Flow injection for NH ₄ ⁺ , ICP-OES ⁽²⁾ for Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺
FMI	IC for all ions
ISCI	IC for anions, Photometry for NH ₄ ⁺ , AAS ⁽³⁾ for Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺
TNO	IC for anions, Continuous flow NH ₄ ⁺ , HR-ICP-MS ⁽⁴⁾ for Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺
UMB	IC for all ions

⁽¹⁾ IC: Ion Chromatography

⁽²⁾ ICP-OES: Inductively coupled plasma atomic emission spectroscopy

⁽³⁾ AAS: Atomic absorption spectroscopy

⁽⁴⁾ HR-ICP-MS: High resolution inductively coupled plasma atomic emission spectroscopy

Work Package 4

The results from each sample analysed by the 6 laboratories were statistically analysed to calculate the uncertainty in a single measured result. The uncertainty analysis was performed on the whole dataset as well as by site and concentration range. The overall uncertainty includes inter-laboratory variability, between laboratory variability and between sampler variability.

In addition to the statistical analysis, method detection limits from laboratory blank filters were calculated along with field blank levels to assess the contamination of filters due to handling and storage.

The results from the statistical analysis, detection limits, field blanks are included in Annex F of this report.

Comparisons between the field samples and the data from collocated EMEP denuder pack samplers were carried out at 3 of the 6 sites: Ispra, Duisburg and Cabauw. The analysis of the EMEP samples was carried out by the FMI laboratory.

The field sample data from the Waldhof site were also compared with the data from a Marga analyser.

The results from these comparisons are included in Annex G of this report.

3.1 Contract item 2012-11.2.1 – Anions/cations in PM_{2,5}

1/ Identification	<ul style="list-style-type: none"> • WI number 00264163, prEN 16913 • Contract item 2012-11.2.1 • Covers item 2 of mandate M/503 Ambient Air Quality
2/ Title	Ambient Air – Standard method for measurement of NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , NH ₄ ⁺ , Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ in PM _{2,5} as deposited on filters
3/ Progress of work	<p>present stage: Stage code 30.99 Dispatch Enquiry draft to CCMC</p> <p>next stage: Stage code 45.99 Dispatch FV draft to CCMC</p>
4/ Milestones so far	<p>Validation work:</p> <ul style="list-style-type: none"> • WP1: Literature review: Published (CEN/TC 264/WG 34 N81), see Annex A. • WP2: Lab inter-comparison and tests: Completed and results published (CEN/TC 264/WG 34 N95), see Annex B & C. • WP3: Field tests: Completed, see Annex D and E • WP4: Statistical evaluation: Completed, see Annex F. <p>Development of standard:</p> <ul style="list-style-type: none"> • Preparation of a first working document • Discussion and modification of the working document in meetings • Submission of prEN 16913 to CEN enquiry, see Annex H
5/ Next steps and remaining work	<p>Listing of the milestones still be to achieved:</p> <p>Development of standard:</p> <ul style="list-style-type: none"> • Pre-evaluation of the technical comments given during CEN enquiry and preparation of a modified text of prEN 16913 accordingly • Discussion and approval of the proposed answers to the CEN enquiry comments and modified text by WG • Submission of modified of prEN 16913 to CEN Formal Vote • Preparation of final draft of prEN 16913 <p>This project is in line with the original timeframe. In case of any unforeseen events that might influence these steps and the timeframe of the project, the Commission will be informed.</p>

6/ Documents	<p>Annex A: Report Work Package 1: Summary of literature review on measurement of ions in PM_{2,5}</p> <p>Annex B: Laboratory inter-comparison</p> <p>Annex C: Laboratory Tests</p> <p>Annex D: Field Validation Site Reports</p> <p>Annex E: Standard Operating Procedures (SOPs)</p> <p>Annex F: Statistical analysis of Field Validation Measurements</p> <p>Annex G: Comparison between field samples and EMEP denuder pack samples and Marga</p> <p>Annex H: prEN 16913 to CEN enquiry</p>
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Annex A: Report Work Package 1: Summary of literature review on measurement of ions in PM_{2,5}

This has been supplied as a separate document:

ANNEX A_N 81 Report WP1_Summary of literature review.pdf



EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

SA/CEN/ENTR/503/2012-11 "Ambient Air Quality"

CEN/TC 264/WG 34 "Anions and cations in PM_{2.5}"

REPORT

SUMMARY OF LITERATURE REVIEW ON MEASUREMENT OF IONS IN PM_{2.5}

Work Package 1

Contract item 2012-11.2.1

CEN/TC 264 work item number 00264163

Annex B: Laboratory Intercomparison

Introduction

The 6 analysis laboratories from work package 3 took part in the 31st round of the EMEP laboratory inter-comparison. Each laboratory received 4 synthetic precipitation samples. The samples consisted of de-ionized water, containing different amounts of sulphate, nitrate, ammonium, magnesium, sodium, chloride, calcium and potassium. The EMEP assigned values for each test sample is given in Table 1. NH_4^+ and NO_3^- are expressed as equivalent amounts of oxidised nitrogen ($\text{NH}_4\text{-N}$ & $\text{NO}_3\text{-N}$ respectively) and SO_4^{2-} as an equivalent amount of oxidised sulphur ($\text{SO}_4\text{-S}$).

	Na µg/ml	$\text{NH}_4\text{-N}$ µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Cl µg/ml	$\text{NO}_3\text{-N}$ µg/ml	$\text{SO}_4\text{-S}$ µg/ml
G1	0.208	0.160	0.136	0.124	0.102	0.154	0.274	0.673
G2	0.329	0.214	0.204	0.114	0.115	0.232	0.396	0.776
G3	0.476	0.267	0.306	0.155	0.192	0.347	0.529	1.319
G4	0.465	0.348	0.374	0.175	0.217	0.386	0.612	2.436

Table 1 EMEP assign values for laboratory inter-comparison exercise

The uncertainty in these assigned values, expressed with a level of confidence of 95%, was $\leq 0.18\%$ of value, for all components. This uncertainty is considered negligible and is not included in any subsequent data analysis.

The EMEP data quality objectives for laboratory analysis of acidifying and eutrophying compounds are:

- 10% accuracy or better for oxidised sulphur and oxidised nitrogen in single analysis in the laboratory
- 15 % accuracy or better for other components in the laboratory

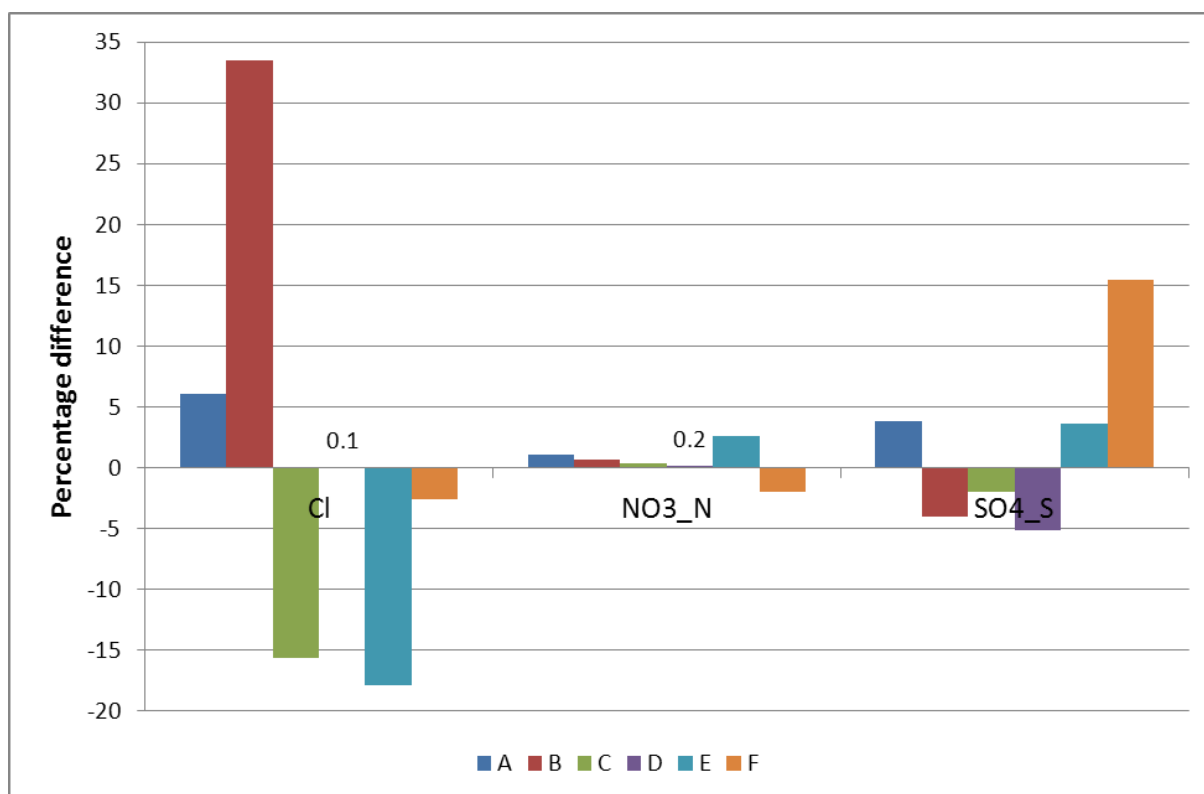
The combined sampling and analysis uncertainty should be between 15 - 25%.

The EMEP minimum required detection limits for laboratory analysis are:

SO_4^{2-} as S	0.032 mg /l	or	1 µmol/l
NO_3^- as N	0.014 mg /l	or	1 µmol/l
NH_4^+ as N	0.028 mg /l	or	2 µmol/l
Cl^-	0.107 mg /l	or	3 µmol/l
Ca^{2+}	0.012 mg /l	or	0.3 µmol/l
K^+	0.012 mg /l	or	0.3 µmol/l
Mg^{2+}	0.007 mg /l	or	0.3 µmol/l
Na^+	0.007 mg /l	or	0.3 µmol/l

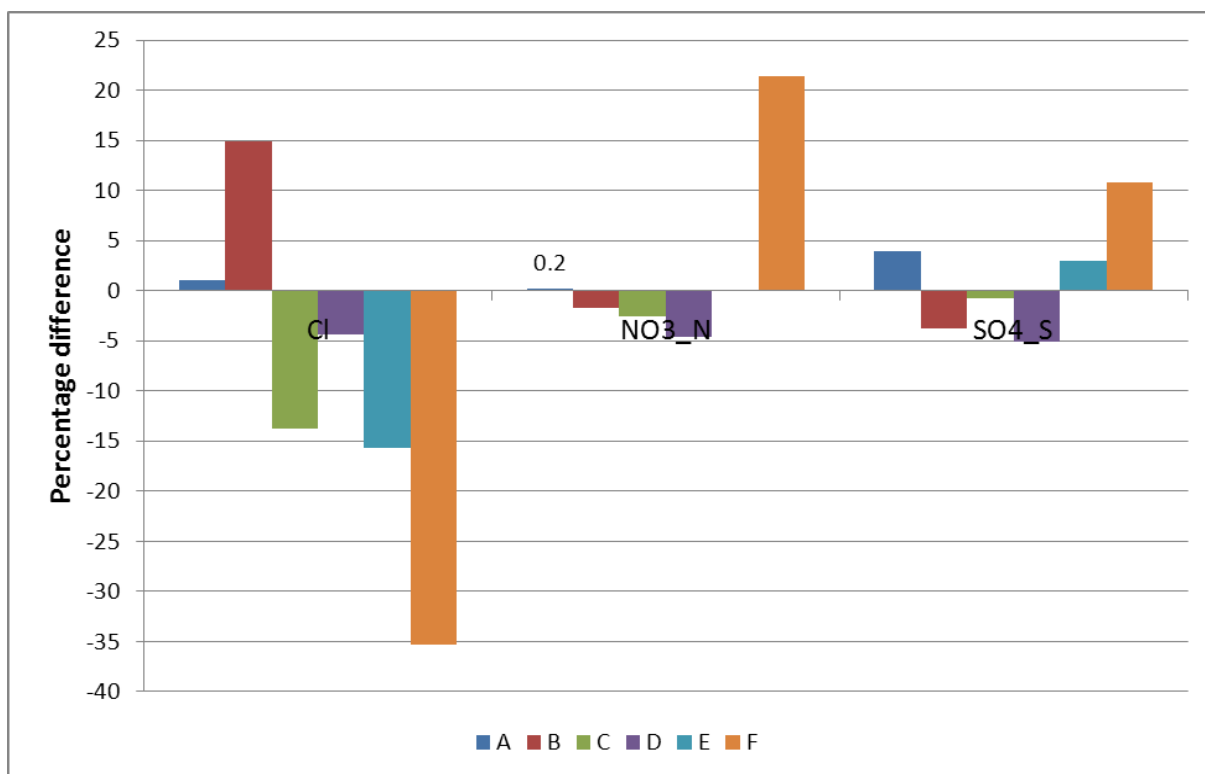
Results

Figures 1 to 8 show the percentage difference for each test sample between participant results and the assigned value. The interval on the y-axis has been set at 5% to allow easy comparison with the EMEP data quality objectives for laboratory analysis of 10% and 15%. Participant identities of labs a-f have been anonymised.



Note: Participant F's result for Cl was reported as below their detection limit, so a value of half their detection limit has been used.

Figure 1 **Results for sample G1** **Anions**



Note: Participant F's result for Cl was reported as below their detection limit, so a value of half their detection limit has been used.

Figure 2 Results for sample G2 Anions

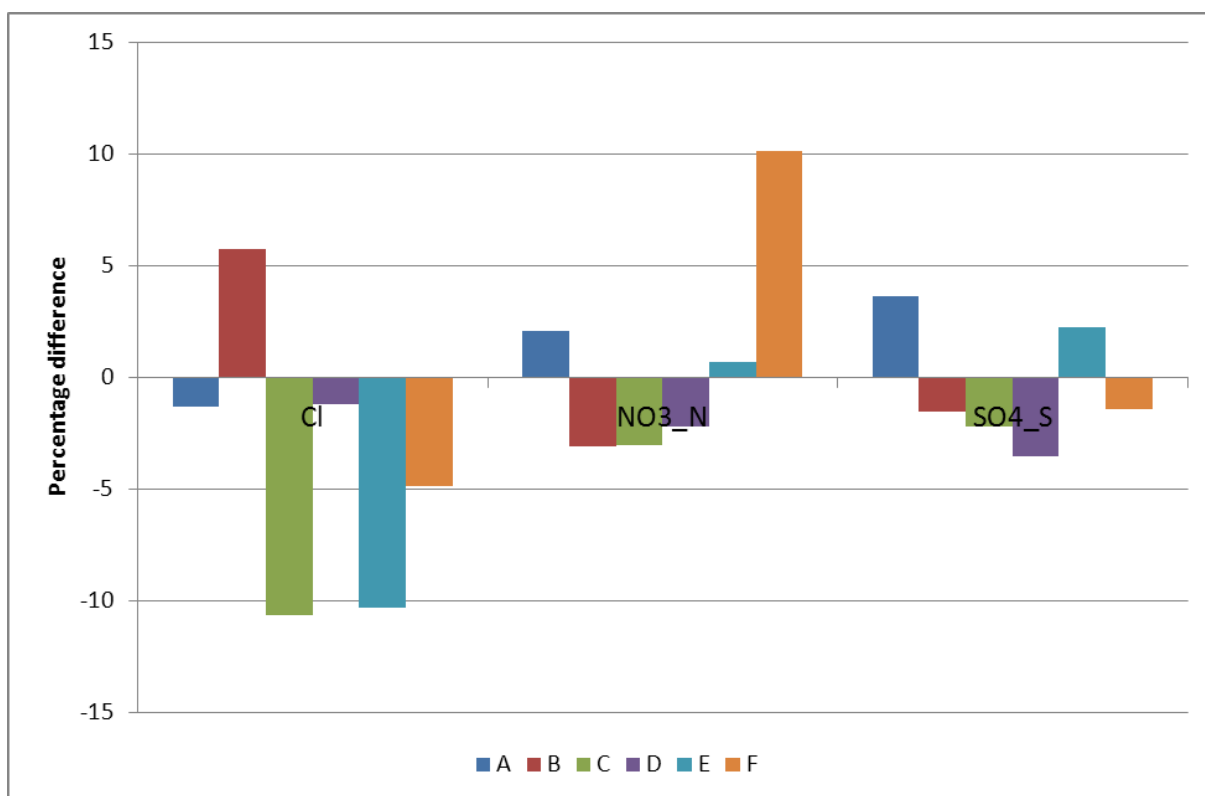


Figure 3 Results for sample G3 Anions

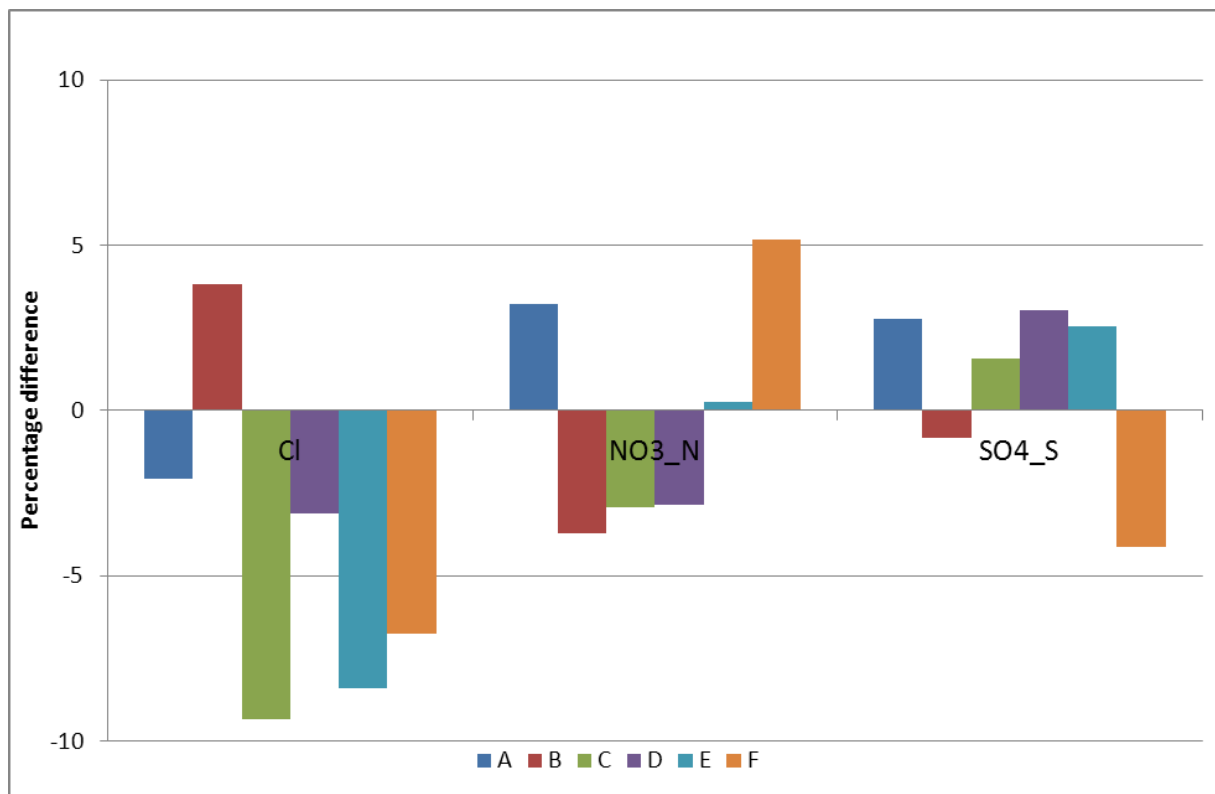


Figure 4 Results for sample G4 Anions

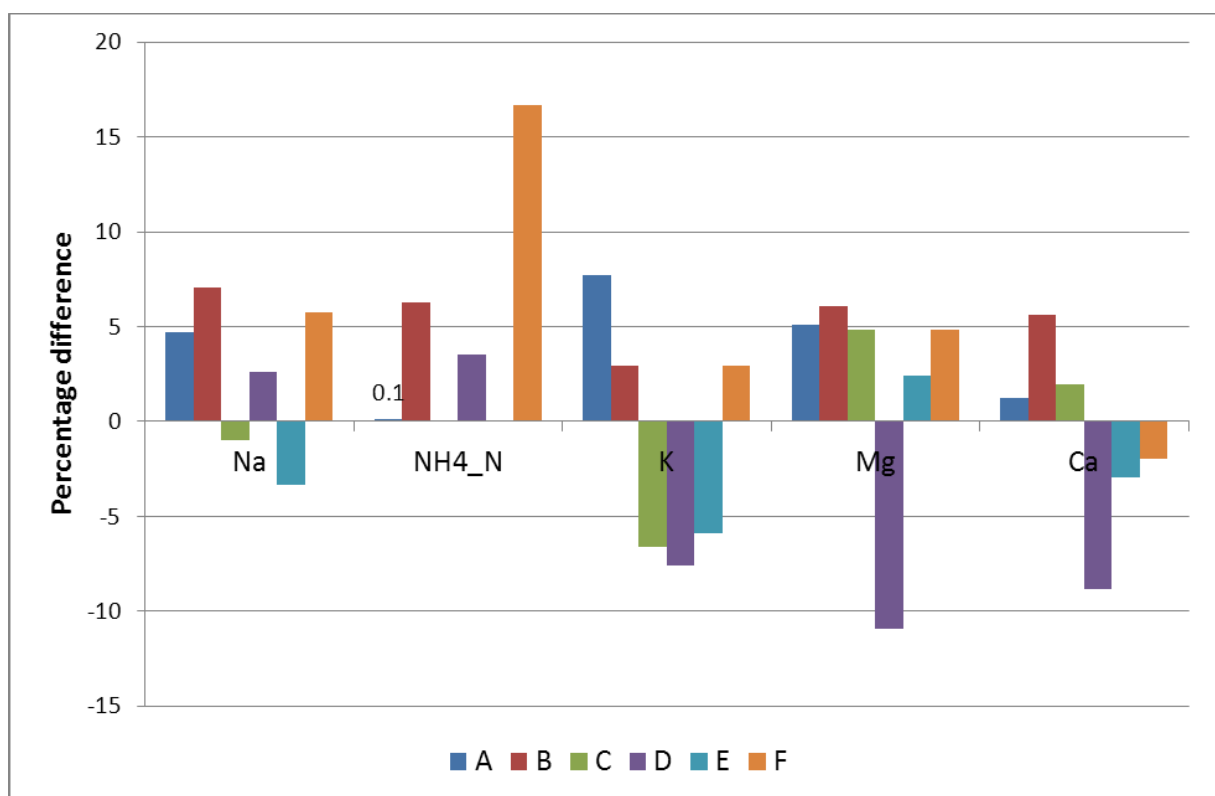


Figure 5 Results for sample G1 Cations

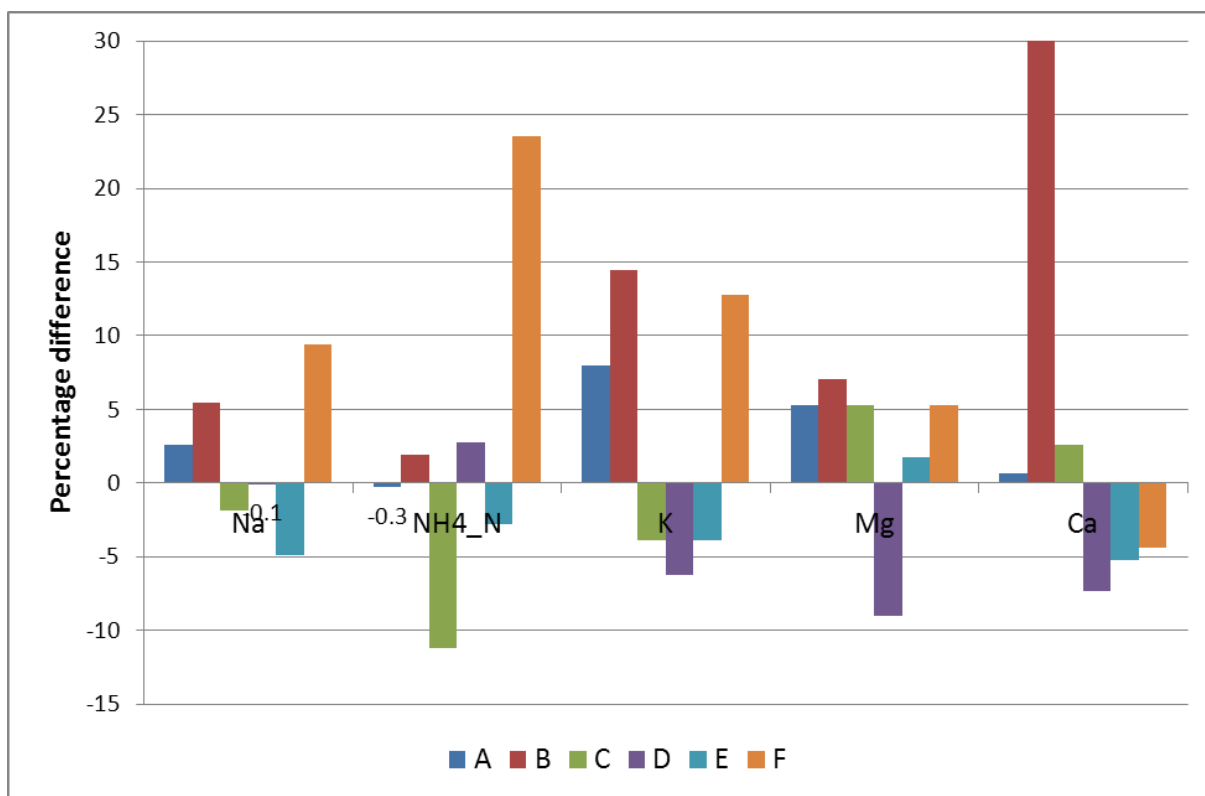


Figure 6 Results for sample G2 Cations

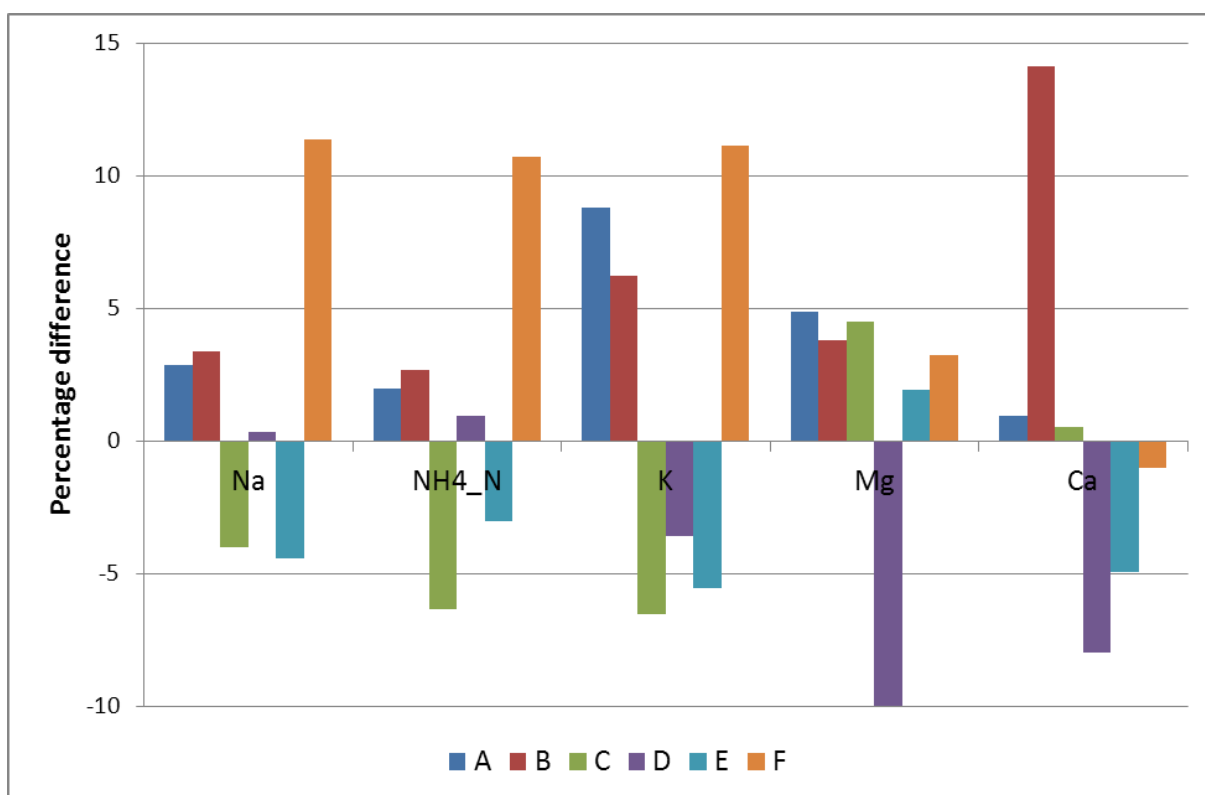


Figure 7 Results for sample G3 Cations

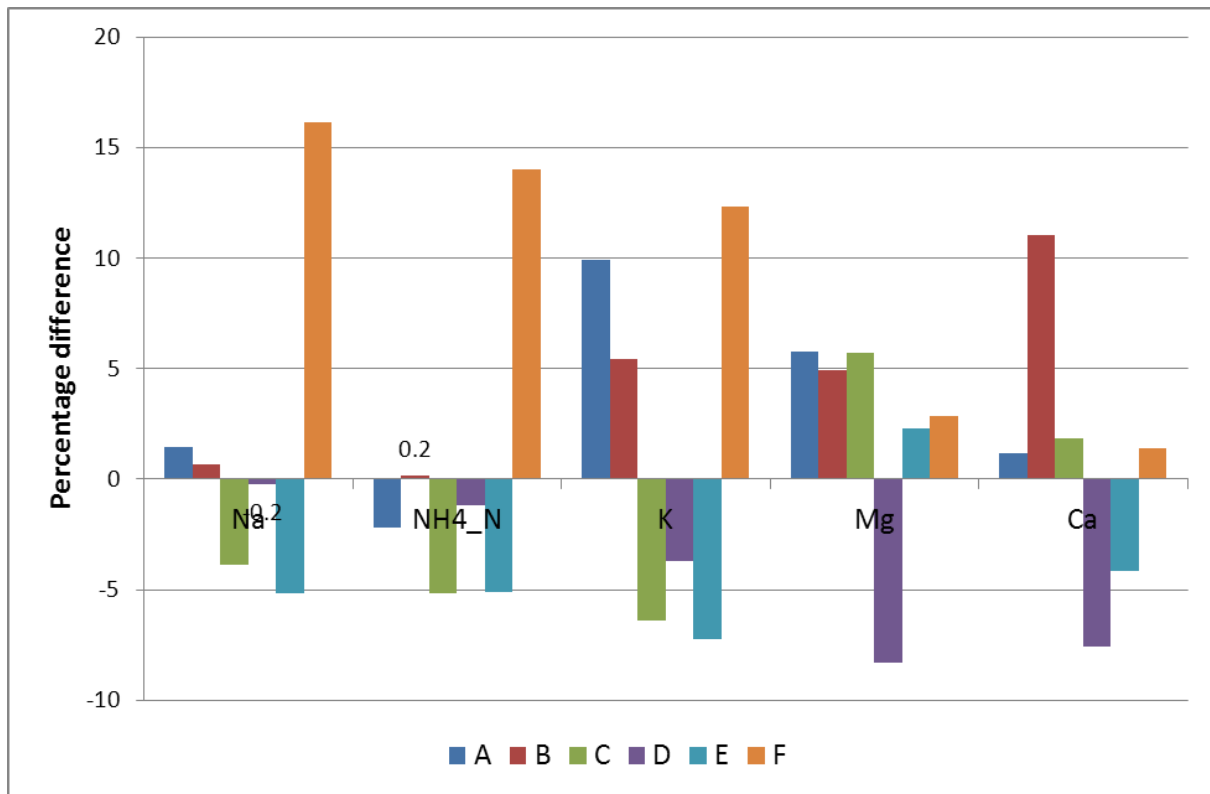


Figure 8 Results for sample G4 Cations

Performance summary

Anions

Laboratory F reported that the detected Cl concentration was below their detection limit for test samples G1 and G2, therefore a value of half their detection limit was used for these two results.

Table 2 gives the number of measurements outside the EMEP data quality objectives for laboratory analysis for each test sample.

Test Sample	Anions	Cations
G1	4	1
G2	4	3
G3	1	1
G4	0	2

Table 2 Number of measurements outside the EMEP data quality objectives for laboratory analysis

In total 16 results were reported that did not meet the EMEP data quality objectives, this represents 33% of the total number of measurements. Even though this represents a high percentage of results, only 3 of these results were greater than twice the EMEP data quality objective.

Table 3 gives the average percentage difference between the measured concentrations and the assigned values for each component of each test solution.

Solution	Na⁺ %	NH₄⁺-N %	K⁺ %	Mg²⁺ %	Ca²⁺ %	Cl⁻ %	NO₃⁻-N %	SO₄²⁻-S %
G1	2.6	4.4	-1.1	2.0	-0.8	0.6	0.5	2.0
G2	1.8	2.3	3.5	2.6	2.7	-8.8	2.2	1.4
G3	1.6	1.1	1.7	1.4	0.3	-3.8	0.8	-0.5
G4	1.5	0.1	1.7	2.2	0.6	-4.3	-0.1	0.8
Average	1.9	2.0	1.5	2.1	0.7	-4.1	0.8	0.9

Considering the results as a whole it can be concluded that laboratory performance was of good enough quality not to invalidate the conclusions of future measurements conducted on the field samples. It was decided at the January 2014 meeting that the 6 laboratories should take part in the next round of the EMEP laboratory intercomparison. The results from this future round will be assessed in a similar fashion in the final report.

Annex C: Results of Laboratory Tests

This has been supplied as a separate document.

ANNEX C_N 95 Report WP2_Lab tests on measurement of ions in PM2.5.pdf

The logo for NEN (Dutch Normalization Institute) consists of the letters "NEN" in a bold, blue, sans-serif font, set against a light blue rectangular background.

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

SA/CEN/ENTR/503/2012-11 'Ambient Air Quality'

**CEN/TC 264/WG 34 'Standard method for measurement of
anions and cations in PM2.5'**

REPORT

LABORATORY TESTS ON

MEASUREMENT OF IONS IN PM2.5

Work Package 2

Contract item 2012-11.2.1

CEN/TC 264 work item number 00264163

Annex D: Field Validation site reports

D1 Ispra (Rural Background, Italy)

This has been supplied as a separate document:

ANNEX D1_WP3_Field_Report_JRC_rural_background.pdf



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SA/CEN/ENTR/503/2012-11 "Ambient Air Quality"

CEN/TC 264/WG 35 "EC/OC in PM"

REPORT: SUMMARY OF FIELD CAMPAIGN

(Joint Research Centre, Ispra)

Work Package 3

Contract item 2012-11.3.1

CEN/TC 264 work item number 00264164

D2 Barcelona (Urban Background, Spain)

This has been supplied as a separate document:

ANNEX D2_WP3_Field_Report_CSIC_urban_background.pdf



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SA/CEN/ENTR/503/2012-11 "Ambient Air Quality"

CEN/TC 264/WG 35 "EC/OC in PM"

**REPORT: SUMMARY OF FIELD CAMPAIGN
(IDAEA-CSIC, BARCELONA)**

Work Package 3

Contract item 2012-11.3.1

CEN/TC 264 work item number 00264164

D3 Duisburg (Urban Background, Germany)

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ANNEX D3_WP3_Field_Report_IUTA_urban_background.pdf



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SA/CEN/ENTR/503/2012-11 "Ambient Air Quality"

CEN/TC 264/WG 35 "EC/OC in PM"

**REPORT: SUMMARY OF FIELD CAMPAIGN
(IUTA, Duisburg)**

Work Package 3

Contract item 2012-11.3.1

CEN/TC 264 work item number 00264164

D4 Amsterdam (Roadside, The Netherlands)

This has been supplied as a separate document:

ANNEX D4_WG35_N0252_WP3_field_report_GGD_Amsterdam_PP_DJ.pdf

CEN/TC 264/WG 35 N 252

REPORT: SUMMARY OF FIELD CAMPAIGN
(GGD Amsterdam, Amsterdam, Netherlands)
Work Package 3
Contract item 2012-11.3.1
CEN/TC 264 work item number 00264164

D5 Waldhof (Rural Background, Germany)

This has been supplied as a separate document, CEN/TC 264/WG 35 N 237:

ANNEX D5_WG35_N0237_Elke_Bieber_Field_Report_Waldhof.pdf

CEN/TC 264/WG 35 N 237

CEN/TC 264/WG 34 and WG 35 Field Validation Test
Field Campaign in Waldhof (Germany), 22 May - 16 July 2014

Elke Bieber, Susanne Luck-Kopp, Maik Schütze, Andreas Schwerin,
Axel Eggert, Anke Penzlin, Markus Wallasch;
Umweltbundesamt (Federal Environment Agency), Langen and Waldhof, Germany

D6 Cabauw (Rural Background, The Netherlands)

This has been supplied as a separate document:

ANNEX D6_WP3_TNO report_ Cabauw sampling campaign.pdf

**CEN/TC 264/WG 34 and WG 35 Field Validation Test
Field Campaign in Cabauw (The Netherlands), 02 September – 13 October 2014
Aleksandra Jedynska, Marcel Moerman, Bas Henzing, Bob Ammerlaan
TNO, The Netherlands Applied Research Organization, Utrecht, The Netherlands**

Annex E: Standard Operating Procedures (SOPs)

E1 Operation of the Digitel high volume sampler

This has been supplied as a separate document:

ANNEX E1_WG35_N0210_Operation_of_Digitel_Samplers_2014-06-3.pdf

CEN/TC 264/WG 35 N 210

Standard Operating Procedure (SOP) for Digitel DHA 80 High Volume Sampler Operation

SOP version

30.06.2014

Responsible person

U. Quass, T. Kuhlbusch

Implementation of this SOP version

E2 Filter handling, treatment and marking

This has been supplied as a separate document:

ANNEX E2_WG35_N0197_SOP_Filter_handling_treatment_and_marking (1).pdf

CEN/TC 264/WG 35 N 197

Standard Operating Procedure (SOP) for High Volume Sampler Filter Handling and Treatment

SOP version

1Draft 3

Responsible person

J.P. Putaud

Implementation of this SOP version

01 October 2013

E3 Requirements for data exchange

Laboratory analysis of field samples

NPL expects only to get final collected mass results of individual anions and cations, not chromatograms. All internal quality control checks and calibrations should have been carried out internally to provide the final result. These collected masses will be turned into ambient air concentrations by NPL when they get the sample volumes from the field sites.

NPL expects to get 1 file per field site per sampler from each analysis laboratory containing the results of the analysis (there are 2 samplers run in parallel at the first and last field site). Each file should contain one result line per sample analysed from that field site. Each file will be between 40 and 60 lines long (depending on number of filters exposed at each site). Results in these files need to use the standard filter identification code used to identify the original sampled filter (SOP on filter marking).

Results files should use the following naming convention:

IPA_12345_TNO site=Ispra (IPA), sampler serial number=12345, analysis lab=TNO

Each sample will follow the SOP on filter marking as detailed below:

STATION - PM2.5 - Sampler # Holder # - Date Sampling Start (dd mm yyyy)
e.g. IPR - PM2.5 - 12345 - 07 - 11 Dec 2013

An excel template file has been produced for the IC analysis results. The first 2 data lines are for example only.

NPL also expects to get 1 file per analysis laboratory of: laboratory blanks, filter blanks and field blanks measured while analysing the field samples.

NPL also expects to get one file per laboratory containing their results from analysing inter-comparison liquid samples. This inter-comparison should have been performed before the field analysis starts.

Results from the EMEP filter packs should also be supplied in 1 file per site as final concentration data if available, if not as collected mass.

As part of the work is to try and determine detection limits, please report actual amount detected or as invalid (-999) if no peak was detected.

Field Measurements

NPL expect to get sample times, sample volumes (expressed at ambient conditions), other PM measurements, any meteorological data and relevant comments on every filter sample taken. Predominantly our analysis will be on the carbon per square cm results produced by the analysis laboratories, but we will also convert these into ambient air concentrations.

Filter sampling data should be in the standard form as defined by the SOPs. Any flow calibration data should also be supplied to allow for the correct sample volume to be calculated.

Site owned automatic and manual PM data and meteorological data should be supplied in an Excel file per instrument as daily averaged values, already corrected for calibrations. For PM data, results shall be in mass concentration units ($\mu\text{g.m}^{-3}$).

If available, automatic ion data should be supplied in an Excel file per instrument at the time base used by the instrument. Results shall be in mass concentration units ($\mu\text{g}\cdot\text{m}^{-3}$). No averaging should be done. The instrument configuration should be recorded. Any calibration data should also be supplied.

Sampling data (including sample volumes) from the EMEP filter packs should be supplied according to the SOP for this method.

Annex F: Statistical Analysis of Field Validation Data

Statistical Analysis of Anion and Cation Concentrations Collected on Filters from Field Validation Exercise

Daily PM_{2.5} samples were collected from 6 monitoring stations over 2013 & 2014 and analysed by 6 different laboratories. Sub-samples of each daily filter were analysed by each laboratory's preferred analytical technique per analyte, but following the agreed protocol defined by the draft standard. This resulted in 6 results per laboratory, per sampled filter. NPL performed a statistical analysis to determine the uncertainty of a single measured value based on between-laboratory variability, internal-laboratory variability and between sampler variability.

Laboratory blanks were analysed to determine detection limits for each ion. Field blanks were also analysed as a quality control measure for the field samples.

Analysis methodology

For the purpose of the data analysis described below, the data are divided into three data sets as follows:

Analysis methodology

For the purpose of the data analysis described below, the data are divided into three data sets as follows:

1. Data set 1 relates to those sites for which a single sampler is used by all the laboratories. The sampler used at a particular site may be the same as that used at a different site or it may be different from the samplers used at all other sites. The data set is used to investigate between- and within-laboratory effects and to quantify those effects.
2. Data set 2 relates to those sites for which at least two samplers are used by all the laboratories. As for data set 1, a sampler used at a particular site may be the same as that used at a different site, or it may be different from the samplers used at all other sites. The data set is used to investigate a between-sampler effect and to quantify that effect.
3. Data set 1 & 2 were combined and split into four concentration ranges to determine uncertainty over the range of concentrations.

The objective of the data analysis is to evaluate the standard uncertainty to be associated with an individual measured value of concentration, which combines the within-laboratory, between-laboratory and between-sampler effects. For data set 3 only the within-laboratory and between-laboratory effects were calculated.

Calculating between- and within-laboratory variability

Notation

Let there be S sites identified by the index $i, i \in \{1, \dots, S\}$, and L laboratories identified by the index: $j, j \in \{1, \dots, L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index $k, k \in K_i$. The measured values of concentration are then denoted by:

$$x_{ijk}, \quad k \in K_i, \quad j \in \{1, \dots, L\}, \quad i \in \{1, \dots, S\}.$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which measurements are made can be different from one site to another.

Data processing

The data processing comprises two stages. In a first stage, the L measured values corresponding to each site and each day are processed to remove outlying values, and normalised to remove effects associated with the factors of site, sampler and time. In a second stage, an ANalysis Of VAriance (ANOVA) is applied to the resulting data set corresponding to all sites and all days to decide whether a between-laboratory effect exists. If the effect exists, a calculation of the between- and within-laboratory standard deviations is undertaken. If the effect does not exist, a calculation of the within-laboratory standard deviation only is made. In either case, the within-laboratory standard deviation describes the repeatability standard deviation for the laboratories, which is assumed to be the same for all laboratories.

Each part of the data processing is described below.

Outlier rejection

Outlier rejection is applied to the set of measured values $x_{ijk}, j \in \{1, \dots, L\}$, provided by the L laboratories on day k at site i . Outlier rejection is applied separately for the sets of measured values provided on different days and at different sites.

Outlier rejection involves the following steps:

1. Remove any measured value that is zero, with zero interpreted as denoting a missing value;
2. For the non-zero measured values, evaluate the modified Z-score defined by

$$z_{ijk} = \frac{x_{ijk} - \text{med}(\{x_{ijk}\})}{1.483 \times \text{mad}(\{x_{ijk}\})},$$

where:

$\text{med}(\{x_{ijk}\}) = \hat{x}_{ik}$ is the median of the non-zero values $\{x_{ijk}; x_{ijk} \neq 0, j = 1, \dots, L\}$, a robust measure of location, and $\text{mad}(\{x_{ijk}\}) = \text{med}(\{|x_{ijk} - \hat{x}_{ik}|\})$ is the median-absolute deviation of those values, a robust measure of dispersion;

3. Remove any measured value for which $|z_{ijk}| > 3.5$.

The procedure for outlier rejection described in steps 2 and 3 follows the recommendation made in section 1.3.5.17 of the NIST Engineering Statistics Handbook¹. Outlier rejection can be problematic for small sample sizes, in this case when the number L of laboratories is small. The critical value (of, here, 3.5) for the absolute value of a modified Z-score, which is used to decide whether a measured value is to be considered as an outlier or not, can be adjusted to make outlier rejection easier (using a smaller value of the critical value) or harder (using a larger value). However, such an adjustment leads to a degree of “subjectivity” into the step of outlier rejection, and ought to be justified.

For the majority of the data analysis performed for this standard outlier rejection was not used in order to calculate the uncertainty of a single measured value.

Data normalisation

Following outlier rejection, the data for site i and day k is denoted by:

$$x_{ijk}, \quad k \in K_i, \quad j \in J_{ik}, \quad i \in \{1, \dots, S\},$$

where J_{ik} contains the indices of the laboratories for which measured values are retained.

¹ www.itl.nist.gov/div898/handbook/

Data normalisation involves the following steps:

1. Evaluate the average

$$\bar{x}_{ik} = \frac{1}{L_{ik}} \sum_{j \in J_{ik}} x_{ijk},$$

where L_{ik} is the number of indices in J_{ik} ;

2. Shift the measured values by the average \bar{x}_{ik} , and scale the shifted values by \bar{x}_{ik} to obtain normalised values

$$v_{ijk} = \frac{x_{ijk} - \bar{x}_{ik}}{\bar{x}_{ik}}, \quad j \in J_{ik}.$$

The average value calculated in step 1 is taken as a reference or consensus value for the concentration of OC, EC or TC at the specific site i on the specific day k . The aim of shifting the measured values is to remove, at least approximately, any dependence of measured concentration on the time of measurement, the site at which the measurement is made, and the sampler that is used to make the measurement. The aim of scaling the shifted values is to remove, at least approximately, any dependence of the variability of measured concentration on the value of concentration. The application of scaling is based on the assumption that the repeatability standard deviation is proportional to the measured concentration, i.e., the relative repeatability standard deviation is approximately constant. The normalised data is reported as a fraction (or percentage) of the reference value.

Analysis of variance

Following outlier rejection and data normalisation, the data is denoted by:

$$v_{ijk}, \quad k \in K_i, \quad j \in J_{ik}, \quad i \in \{1, \dots, S\}.$$

Since there is no interest in the factors of site and time, an equivalent representation of the data is as

$$y_{lr}, \quad r \in \{1, \dots, R_l\}, \quad l \in \{1, \dots, L\},$$

which groups the measured values by laboratory. Here, R_l is the number of retained measured values for laboratory l over all sites and days, and each y_{lr} equates to one of the normalised values v_{ijk} .

An ANOVA is used to test the null hypothesis that the averages for the laboratories are equal, i.e., there is no laboratory effect. The ANOVA calculation must account for the fact that the data set may be unbalanced, because the numbers of measured values can be different from one laboratory to another. The function “anovan”, which is provided in Matlab’s Statistics Toolbox², can be used to perform a (multiway) ANOVA and allows for an unbalanced data set. The function returns a p value that is compared with a critical value p_c , usually 0.01 or 0.05, chosen before the analysis. If $p \geq p_c$, the null hypothesis of no laboratory effect is accepted at a $100p_c\%$ level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

Calculation of standard deviations

The within-laboratory variance (squared standard deviation) is calculated as the pooled variance s^2 of the laboratory values, and is given by

$$s^2 = \frac{1}{(\sum_{l=1}^L R_l) - L} \sum_{l=1}^L (R_l - 1) s_l^2.$$

² Matlab®, The MathWorks Inc.

where

$$\bar{y}_i = \frac{1}{R_i} \sum_{r=1}^{R_i} y_{ir}, \quad s_i^2 = \frac{1}{R_i - 1} \sum_{r=1}^{R_i} (y_{ir} - \bar{y}_i)^2.$$

If the ANOVA indicates the existence of a between-laboratory effect, then that effect is quantified by the standard deviation s_{lab} of the averages calculated for the laboratories, i.e.,

$$s_{lab}^2 = \frac{1}{L - 1} \sum_{i=1}^L (\bar{y}_i - \bar{\bar{y}})^2,$$

where

$$\bar{\bar{y}} = \frac{1}{L} \sum_{i=1}^L \bar{y}_i.$$

In the case that the null hypothesis of no laboratory effect is accepted, the between-laboratory standard deviation is taken to be zero.

Calculating between-sampler variability

Notation

Let there be S sites identified by the index $i, i \in \{1, \dots, S\}$, and L laboratories identified by the index $j, j \in \{1, \dots, L\}$. Suppose measurements are made by all L laboratories at site i on each of the days identified by the index $k, k \in K_i$, using samplers identified by index $f, f \in F_i$. The measured values of concentration are then denoted by:

$$x_{ijkf}, \quad f \in F_i, \quad k \in K_i, \quad j \in \{1, \dots, L\}, \quad i \in \{1, \dots, S\}.$$

The data set is balanced in the sense that all laboratories make measurements at all sites. However, the days K_i on which measurements are made, as well as the samplers F_i used, can be different from one site to another.

Data processing

In a similar way to that for data set 1, the data processing comprises two stages. In a first stage, considering the data for each sampler separately, the measured values corresponding to each site and each day are processed to remove outlying values. Then, considering the data for the samplers together, the values corresponding to each site and each day are normalised to remove effects associated with the factors of site and time, but preserving any sampler effect. In a second stage, an ANOVA is applied to the resulting data set corresponding to all sites, all days and all laboratories to decide whether a between-sampler effect exists. If the effect exists, a calculation of the between-sampler standard deviations is undertaken.

Following outlier rejection and data normalisation, the data is denoted by:

$$v_{ijkf}, \quad f \in F_i, \quad k \in K_i, \quad j \in J_{ikf}, \quad i \in \{1, \dots, S\},$$

where J_{ikf} contains the indices of the laboratories for which measured values are retained for site i , day k and sampler f . Since there is no interest in the factors of site, time and laboratory, an equivalent representation of the data is as:

$$y_{fr}, \quad r \in \{1, \dots, R_f\}, \quad f \in F_1 \cup \dots \cup F_S,$$

which groups the measured values by sampler. Here, R_f is the number of retained measured values for sampler f over all sites, days and laboratories, and each y_{fr} equates to one of the normalised values v_{ijkf} . As for data set 1, the data set is generally unbalanced, because the numbers of measured values can be different from one sampler to another.

If an ANOVA indicates the existence of a between-sampler effect, then that effect is quantified by the standard deviation s_{sam} of the averages calculated for the samplers, i.e.,

$$s_{sam}^2 = \frac{1}{F-1} \sum_{f=1}^F (\bar{y}_f - \bar{\bar{y}})^2,$$

where

$$\bar{y}_f = \frac{1}{R_f} \sum_{r=1}^{R_f} y_{fr}, \quad \bar{\bar{y}} = \frac{1}{F} \sum_{f=1}^F \bar{y}_f,$$

and F is the total number of samplers. In the case that the null hypothesis of no sampler effect is accepted, the between-sampler standard deviation is taken to be zero.

Combined standard uncertainty

The relative standard uncertainty u_{rel} associated with an individual measured value of concentration is given:

$$u_{rel}^2 = s^2 + s_{lab}^2 + s_{sam}^2,$$

which combines the standard deviations related to within-laboratory, between-laboratory and between-sampler effects.

The between sampler variability results showed that s_{sam}^2 was insignificant in most cases and was not included in the uncertainty calculation.

Remarks

The data analysis described, including the use of ANOVA and the calculations of the standard deviations to quantify the various effects, depends on assumptions about the homogeneity of these effects for different concentrations, sites, laboratories, samplers and time. Graphical displays of the data, in which the data is plotted against these factors, can be useful to identify obvious departures from these assumptions. In cases that the assumptions do not hold, the results of the data analysis may not be reliable expressions of the various effects considered.

Results

All results were calculated with the outlier rejection enabled.

Data set 1 – Between laboratory and internal laboratory variability

The following table gives the p values from the analysis of variance for between laboratory effects. If $p \geq p_c$, the null hypothesis of no laboratory effect is accepted at a $100p_c\%$ level of confidence. Otherwise, the null hypothesis is rejected at that level of confidence.

Ion	p
Cl ⁻	1.45×10^{-43}
NO ₃ ⁻	2.18×10^{-40}
SO ₄ ²⁻	1.15×10^{-42}
Na ⁺	2.20×10^{-63}
NH ₄ ⁺	3.30×10^{-77}
K ⁺	3.64×10^{-86}
Mg ²⁺	3.39×10^{-48}
Ca ²⁺	2.51×10^{-57}

It can be seen that all of the ions show a significant between laboratory effect at the 5% level of confidence. In all cases the between laboratory variability was calculated and included in the overall uncertainty calculations.

Between laboratory variability and internal laboratory variability were calculated for the 8 ions. These variabilities were combined by the sum of squares method to give a combined variability. The results are shown below and are equivalent to a standard uncertainty (1σ):

Ion	Between laboratory variability, %	Internal laboratory variability, %	Combined variability, %
Cl ⁻	20.6	27.2	34.1
NO ₃ ⁻	4.1	7.1	8.2
SO ₄ ²⁻	3.0	5.1	5.9
Na ⁺	11.1	11.0	15.6
NH ₄ ⁺	4.8	6.0	7.7
K ⁺	15.6	15.9	22.2
Mg ²⁺	11.4	16.5	20.0
Ca ²⁺	21.8	26.3	34.2

Data set 2 – Between Sampler Variability

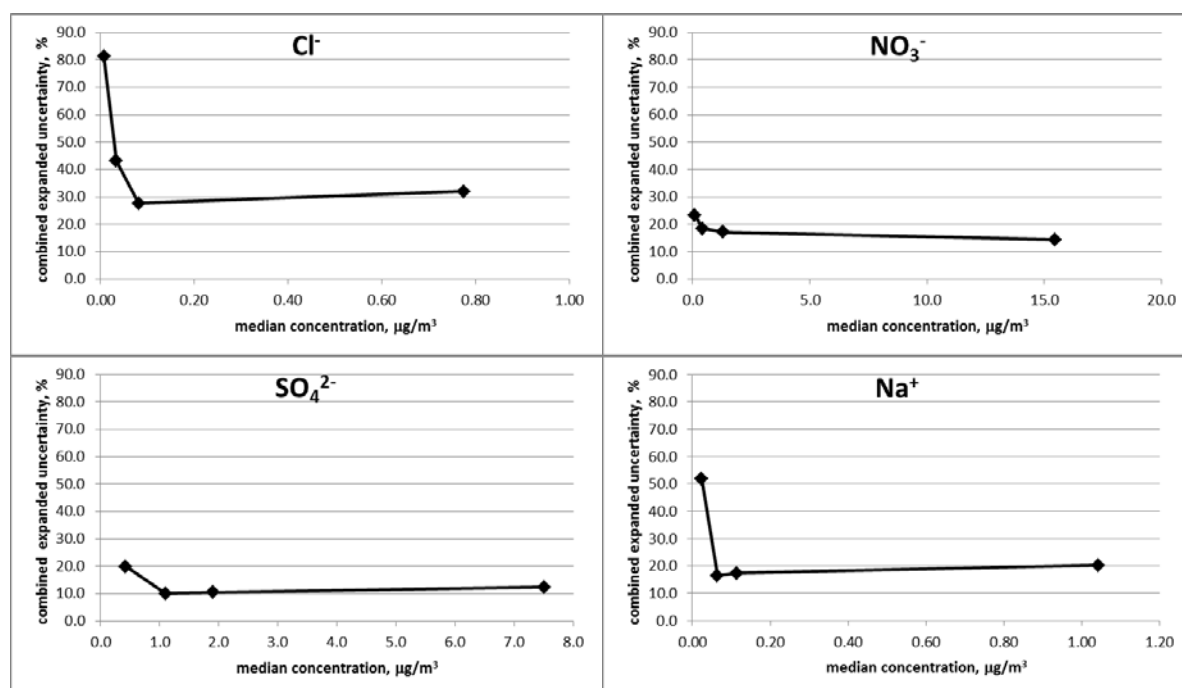
The following summarises the results of the between sampler variability. If $p \geq p_c$ the null hypothesis of no between sampler effect is accepted at a $100p_c\%$ level of confidence

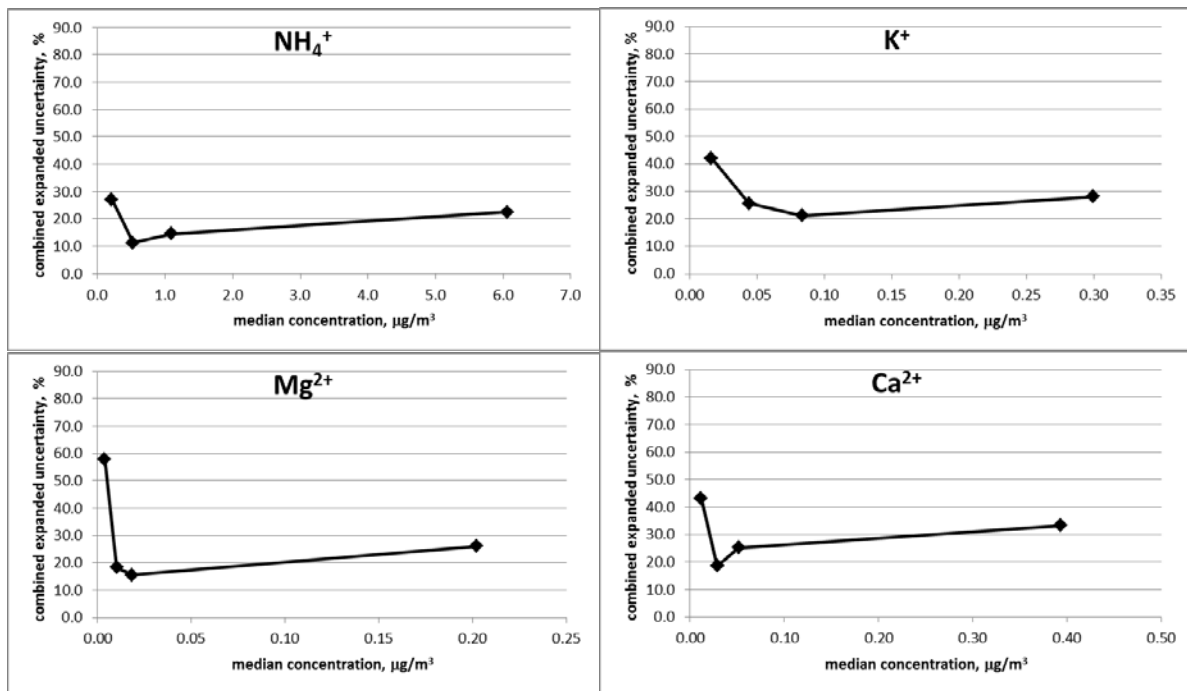
Ion	p	Significant between sampler effect	Between sampler variability, %
Cl ⁻	0.0221	Possible, 2% level	10
NO ₃ ⁻	0.5553	No	1
SO ₄ ²⁻	0.2667	No	1
Na ⁺	0.3475	No	4
NH ₄ ⁺	0.0004	Yes	4
K ⁺	0.0484	No	3
Mg ²⁺	0.0587	No	7
Ca ²⁺	0.7980	No	2

It can be seen that there is a significant between sampler effect for the NH_4^+ ion, while there is a possibly significant between sampler effect for the Cl^- ion. However, in both cases the between sampler variability is small compared to the combined between laboratory and internal laboratory variability. It is also unlikely that a sampler would sample particulate containing these ions differently compared to particulate containing other ions unless the particulate sample diameter is close to that of the size selective inlet. Therefore it can be assumed that there is not a significant between sampler effect and this uncertainty will not be included in the calculation of the uncertainty of a single measured result.

Data set 3 - Uncertainty over the measured concentration range

Results for each ion from the complete data set were ordered by concentration and then split into 4 concentration bins: 0% - 25%, 25% - 50%, 50% - 75% & 75% - 100% with equal number of measurements in each concentration bin. The combined expanded uncertainty (2σ , 95% confidence) due to between laboratory variability and internal laboratory variability were calculated for each concentration bin, the results of which are shown below. The charts have all been plotted with the same Y-axis scale to aid comparison of the uncertainty associated with the measurement of different ions.





Component	Concentration quarter	Between laboratory repeatability, %	Internal laboratory repeatability, %	Expanded combined Uncertainty, %	Minimum, $\mu\text{g.m}^{-3}$	Maximum, $\mu\text{g.m}^{-3}$	Median, $\mu\text{g.m}^{-3}$
Cl^-	Q1	56.0	58.8	81.2	0.001	0.014	0.007
Cl^-	Q2	26.8	33.8	43.1	0.014	0.052	0.033
Cl^-	Q3	12.1	24.8	27.6	0.052	0.110	0.081
Cl^-	Q4	5.9	31.5	32.0	0.110	1.440	0.775
NO_3^-	Q1	16.0	16.9	23.3	0.002	0.200	0.101
NO_3^-	Q2	6.1	17.3	18.4	0.200	0.633	0.416
NO_3^-	Q3	7.3	15.5	17.1	0.633	1.968	1.301
NO_3^-	Q4	5.0	13.4	14.3	1.968	28.913	15.441
SO_4^{2-}	Q1	7.7	18.3	19.9	0.051	0.795	0.423
SO_4^{2-}	Q2	3.8	9.2	10.0	0.795	1.406	1.100
SO_4^{2-}	Q3	6.5	8.2	10.4	1.406	2.400	1.903
SO_4^{2-}	Q4	4.2	11.7	12.4	2.400	12.592	7.496
Na^+	Q1	33.4	39.5	51.7	0.003	0.045	0.024
Na^+	Q2	6.9	14.9	8.2	0.045	0.083	0.064
Na^+	Q3	5.9	16.1	17.2	0.083	0.146	0.115
Na^+	Q4	11.2	16.7	20.1	0.146	1.936	1.041
NH_4^+	Q1	12.2	24.1	27.0	0.040	0.375	0.208
NH_4^+	Q2	5.9	9.5	11.2	0.375	0.673	0.524
NH_4^+	Q3	8.2	11.9	14.5	0.673	1.512	1.092
NH_4^+	Q4	15.8	15.9	22.4	1.512	10.616	6.064

Component	Concentration quarter	Between laboratory repeatability, %	Internal laboratory repeatability, %	Expanded combined Uncertainty, %	Minimum, $\mu\text{g}\cdot\text{m}^{-3}$	Maximum, $\mu\text{g}\cdot\text{m}^{-3}$	Median, $\mu\text{g}\cdot\text{m}^{-3}$
K ⁺	Q1	32.4	26.8	42.1	0.003	0.028	0.016
K ⁺	Q2	11.0	23.2	25.6	0.028	0.060	0.044
K ⁺	Q3	9.6	18.9	21.2	0.060	0.107	0.083
K ⁺	Q4	19.3	20.3	28.0	0.107	0.492	0.299
Mg ²⁺	Q1	27.5	51.1	58.0	0.001	0.007	0.004
Mg ²⁺	Q2	6.3	17.2	18.3	0.007	0.014	0.010
Mg ²⁺	Q3	3.8	15.0	15.5	0.014	0.023	0.018
Mg ²⁺	Q4	8.3	24.7	26.1	0.023	0.381	0.202
Ca ²⁺	Q1	24.9	35.3	43.2	0.002	0.021	0.012
Ca ²⁺	Q2	5.7	17.7	18.6	0.021	0.036	0.029
Ca ²⁺	Q3	9.8	23.2	25.2	0.036	0.067	0.052
Ca ²⁺	Q4	11.9	31.0	33.2	0.067	0.719	0.393

The uncertainty for all ions is generally consistent across the Q2 to Q4 concentration range, with a larger uncertainty for the Q1 concentration. The uncertainty for the Q1 concentrations is probably limited by the detection limit. For the Q2 to Q4 range the uncertainty of a single measurement result for all ions, except Cl^- and Ca^{2+} , is $\leq 30\%$ (2σ , 95%).

Detection Limit

Laboratory blank filters were repeatedly analysed by each laboratory and the results pooled to determine the method detection limit in μg per filter punch and $\mu\text{g.m}^{-3}$, for each ion according to the following equation:

$$\text{Detection Limit} = SD * t_{99, n-1}$$

Where:

- SD = the standard deviation of the repeated measurements
 $t_{99, n-1}$ = the student t factor with a level of confidence of 99% for $n-1$ degrees of freedom
 n = the number of repeat measurements

One laboratory appeared to have a systematic offset in their laboratory blank data and this data has been excluded from the detection limit calculations. The following table gives the calculated method detection limits for each ion and the average equivalent ambient air concentration for each ion measured on the laboratory blank filters:

		μg per filter punch	$\mu\text{g.m}^{-3}$
Ion	n	DL	DL
Cl^-	48	0.477	0.01
NO_3^-	51	1.675	0.03
SO_4^{2-}	2	45.012	0.78
Na^+	57	0.868	0.01
NH_4^+	73	1.398	0.02
K^+	63	0.243	0.001
Mg^{2+}	61	0.085	0.001
Ca^{2+}	68	0.611	0.01

It should be noted that only 2 measurements of laboratory blank detected the SO_4^{2-} ion, therefore this is an invalid detection limit. As all valid detection limits are $\leq 0.03 \mu\text{g.m}^{-3}$ it can be assumed that the real method detection limit for SO_4^{2-} can be taken as $0.03 \mu\text{g.m}^{-3}$.

Field Blanks

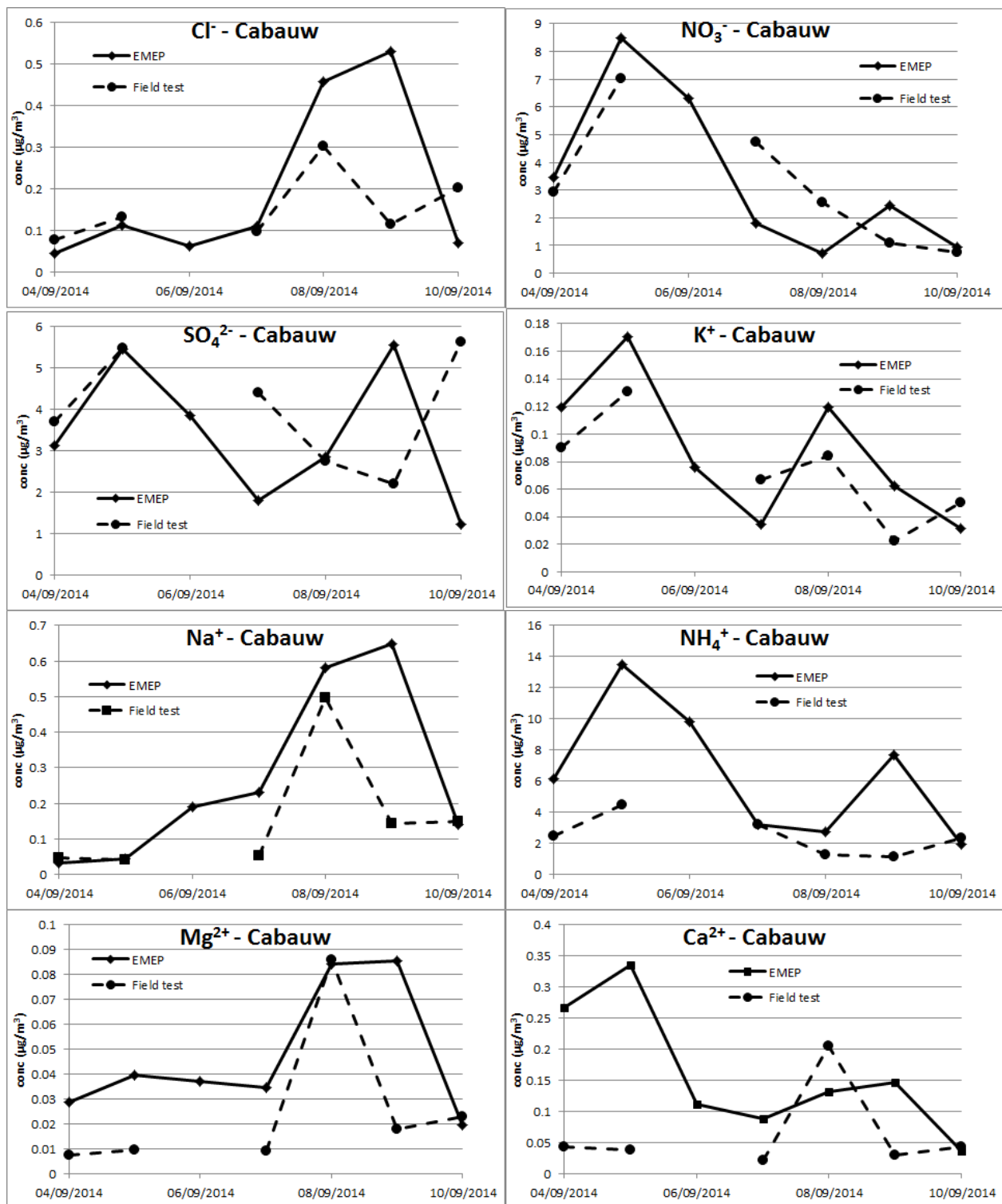
Field blanks were analysed by each laboratory and the average equivalent ambient air concentration level of each ion is shown in the table below:

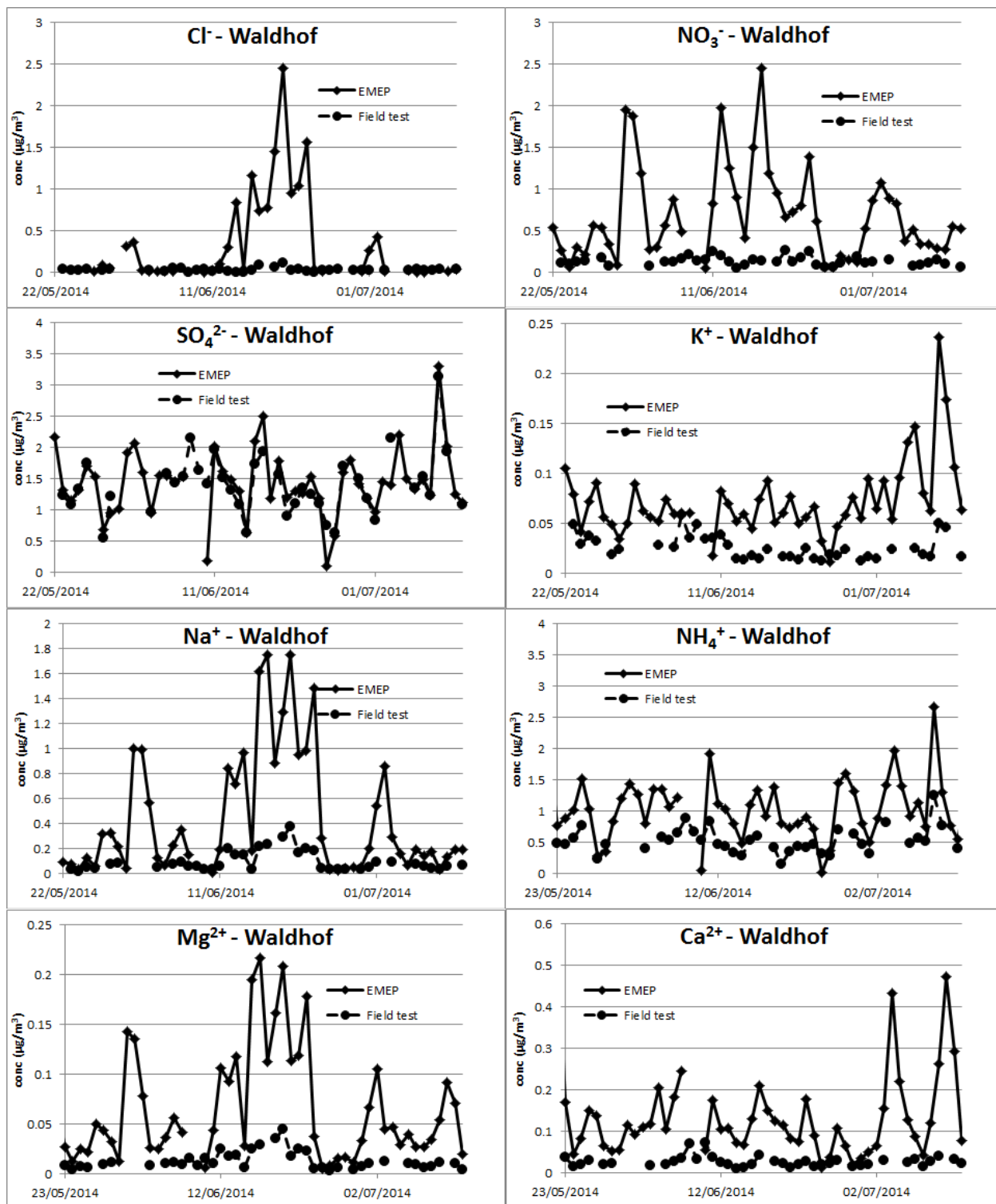
	$\mu\text{g.m}^{-3}$	
Ion	All labs	5 labs
Cl^-	0.03	0.01
NO_3^-	0.02	0.02
SO_4^{2-}	0.09	0.07
Na^+	0.02	0.01
NH_4^+	0.02	0.01
K^+	0.01	0.00
Mg^{2+}	0.00	0.00
Ca^{2+}	0.02	0.01

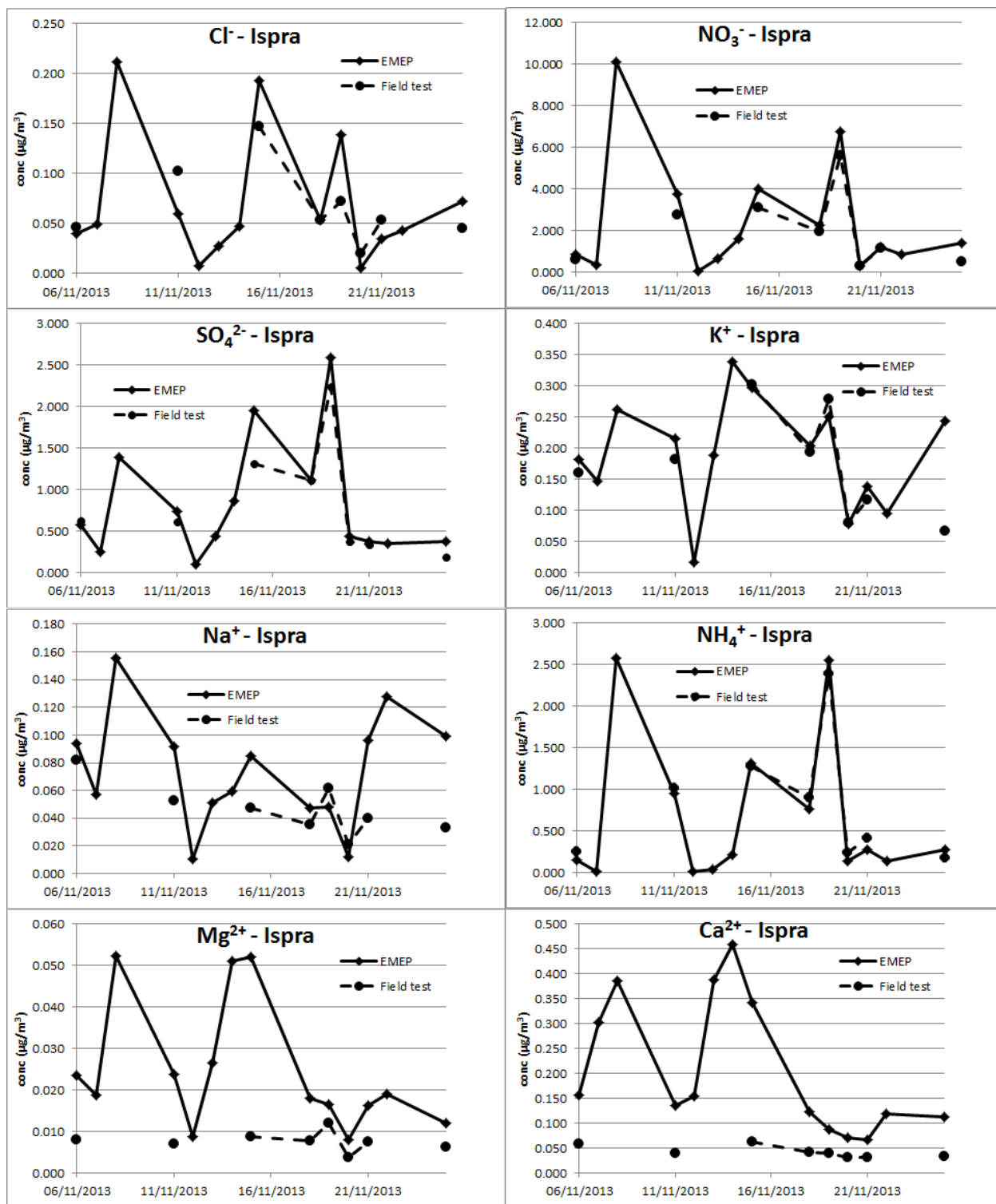
The results are very similar to the detection limits calculated from the laboratory blanks.

Annex G: Comparison between field samples with EMEP denuder pack samples and Marga

At 3 of the 6 monitoring sites (Cabauw, Waldhof and Ispra), the results from the field exercise were compared with the results obtained from EMEP denuder pack filters. The pictures below show the time trend during the measurement period. A significant difference can be observed between for most of the ions, in particular at the Waldhof site. The EMEP samplers do not have a size selective inlet, therefore it is assumed the TSP is collected by these samplers. The difference in the size collection could explain the discrepancy between the two measurement methods making them not directly comparable.







The data from the Waldhof site were also compared with the data from a collocated Marga analyser. As in the EMEP samples case, a discrepancy can be observed, although in this case it could be due to evaporation of NH_4Cl and NH_4NO_3 from the filters. The time trends for K^+ , Mg^{2+} and Ca^{2+} are not shown because of flat response (about $0.04 \mu\text{g}/\text{m}^3$) from the Marga analyser for these three species.

