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Final Report on Standards, Measurement and Testing Programme

Project SMT4-CT96-2094

HARMONISATION OF AIR QUALITY MEASUREMENTS IN EUROPE (‘HAMAQ’)

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February 2000

RESTRICTED COMMERCIAL

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SUMMARY

Aims and Objectives

The overall aim of the HAMAQ project has been to improve the consistency of air quality measurements made by EU member states, particularly the key measurements associated with the EC's Air Quality Directives. The project aimed to achieve this by assessing, and subsequently improving, the comparability of a range of 'primary' methods used throughout Europe, generally at a national level, to certify gas calibration mixtures. These standards, normally in the form of compressed gases in high pressure cylinders, are then used as transfer standards for the calibration of instruments deployed at air-quality monitoring sites. The specific objectives of this project are therefore:

- to develop the methodology whereby internationally-acceptable gas mixtures can be produced for use as calibration standards and certified in concentration so as to promote widespread uniformity and accuracy of air quality measurements throughout Europe;

- to demonstrate the equivalence of different 'primary' methods available at a national level in different member states for providing nationally traceable calibrations of air quality measurements of atmospheric pollutants (CO, NO, NO_2, SO_2 and C_6H_6) in order that these methods can be employed to certify the stable gas calibration mixtures produced commercially;

- to develop improved gas cylinder passivation treatments through collaborative work with the industrial partners, and to evaluate their effectiveness in order to provide more accurate and stable long lifetime calibration gas mixtures of CO, NO, NO_2, SO_2 and C_6H_6;

- to provide knowledge transfer, in order to promote improved measurements, especially in Member States where the air quality measurement infrastructure is not yet fully mature or is not yet of demonstrated accuracy.

Partnership

The partnership assembled to address these aims and objectives comprised seven leading European metrology laboratories, and European and national reference laboratories.

The partners involved were:

1. The National Physical Laboratory, UK (co-ordinator)
2. The Nederlands Meetinstitut, The Netherlands
3. The European Reference Laboratory for Air Pollution at the EU Joint Research Centre, Ispra, Italy
4. The Laboratoire National d'Essais, France
5. Umweltbundesamt Offenbach Pilotstation, Germany
6. VTT Chemical Technology together with the Finnish Meteorological Institute, Finland
7. Institute de Salud Carlos III, Spain

Workprogramme

The workprogramme of the HAMAQ project was organised in four workpackages (WP's):

- WP1 - Involved the production and stability testing of a batch of fifteen cylinders of each of CO, NO, SO_2, NO_2 and benzene at concentrations appropriate for the calibration of air quality analysers. Stability tests were carried out at designated pilot laboratories.
- WP2 - Involved a first intercomparison of different selected national primary facilities using the cylinder gases produced in WP1 as transfer standards. WP2 was aimed at **establishing** the comparability of different national primary facilities.
- WP3 - Involved a second intercomparison of the national primary facilities with the aim of demonstrating **improved** comparability, to a target level of ±1%. In addition to being a repeat of the first intercomparison, all partners were given the opportunity to measure all of the gases.
- WP4 - The findings of the project were to be disseminated to all relevant European groups through a technical workshop organised by the coordinator.

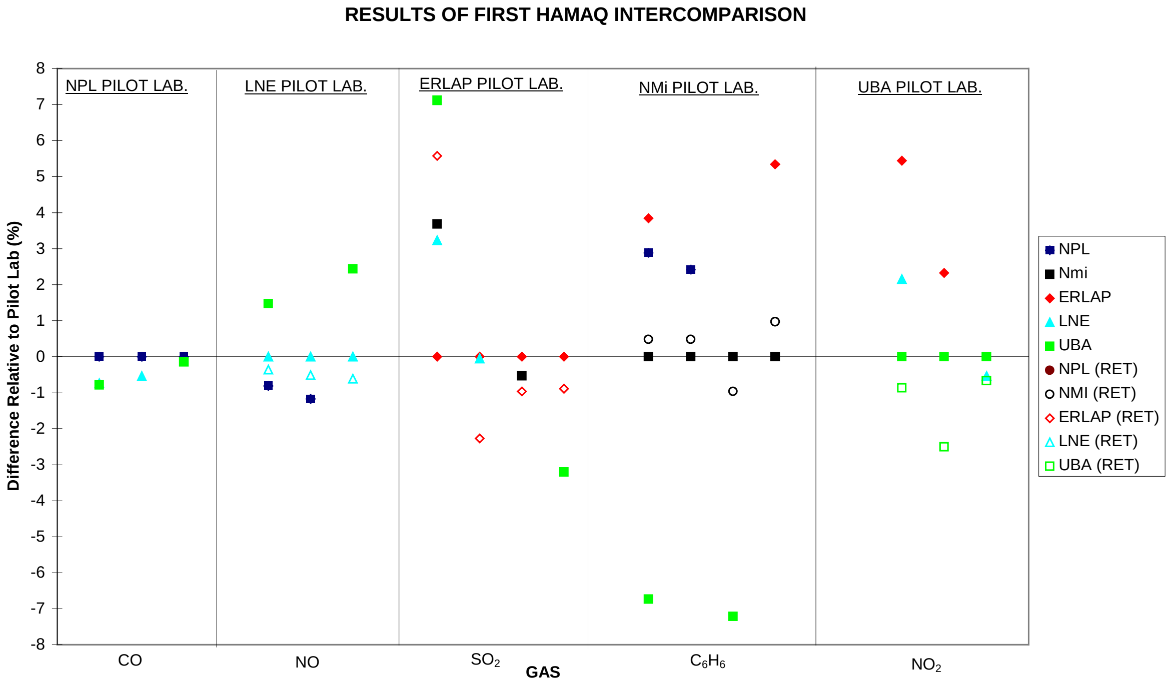
Results

Following production of the batches of gas mixtures by the commercial gas companies stability tests were carried out as planned (WP1).

There was no decay evident in any of the cylinders of CO or NO. For the benzene gas mixtures fourteen of the batch of fifteen remained stable throughout the eighteen months of stability measurements although two of these had evidently decayed by 20% immediately after production. The remaining cylinder also showed evidence of immediate post production decay and this continued throughout the eighteen months of stability tests. Over this time decay of 28% was observed.

For measurements of the SO_2 cylinders, a batch of six cylinders showed good stability over six months. Over the following twelve months two of these cylinders showed signs of decay (of 5% and 10%). For the NO_2 cylinders, three of a batch of fifteen cylinders showed signs of decay of approximately 5% over a period of two years.

The first intercomparison (WP2) commenced in March 1997 and was completed by December 1997. The maximum discrepancies observed in the first intercomparison for CO, NO, SO_2, NO_2 and C_6H_6 were 0.8%, 2.8%, 3.7%, 5.4% and 7.2% respectively. The results are shown in the figure below. The results were discussed at a series of technical meetings aimed at identifying measures which would improve the level of agreement to the target level of ±1% in the second intercomparison.



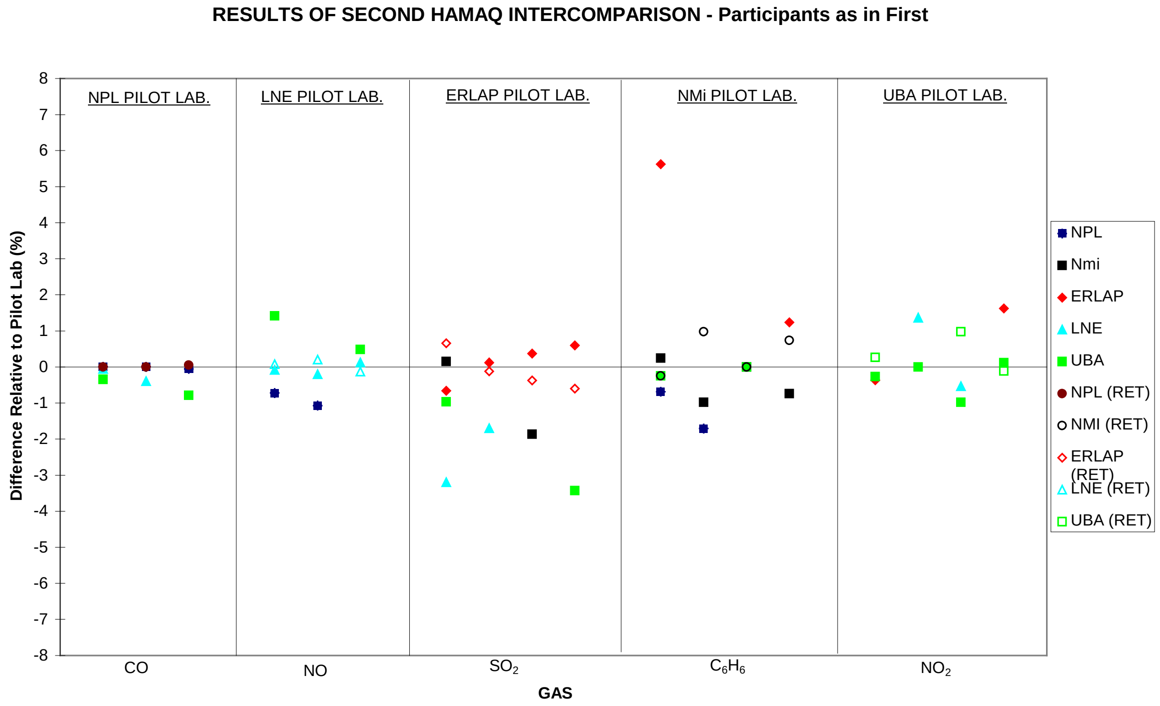
The second intercomparison (WP3) commenced in January 1998 and was completed in January 1999.

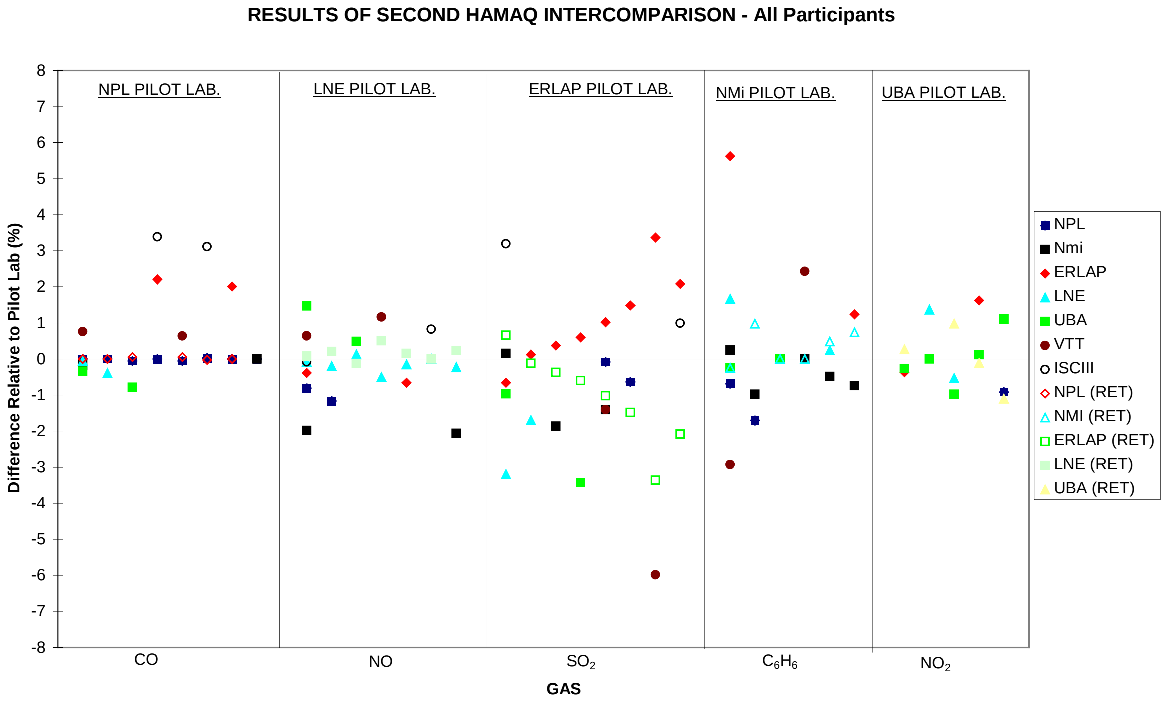
Considering first those partners involved in the first intercomparison, the results obtained in the second intercomparison are shown in the figure overleaf. As can be seen from the figure the maximum observed discrepancies for CO, NO, SO_2, NO_2 and C_6H_6 are 0.8%, 2.2%, 3.4%, 1.6% and 5.6% respectively. The (2σ) scatter for these compounds are ± 0.5%, ± 1.3%, ± 2.6%, ±1.6% and ± 3.4% respectively - close to, but not achieving, the target level of agreement of ±1%. In almost all cases the observed discrepancies are not statistically significant and simply reflect the range of measurement uncertainties obtainable at the highest metrological level. Overall, the level of consistency has been improved over that obtained in the first intercomparison with the scatter (ie the 1σ standard deviation) in the first being 2.5% and in the second being 1.2%, representing an improvement by a factor of two.

In the second intercomparison, all partners were given the opportunity to measure all components by whichever technique was normally employed in the partner laboratory. The results for all participants are shown in the second figure overleaf. The observed scatter for this exercise, including all participants, is 2.4%.

The results of WP2 and WP3 have established, for the first time, the realisable level of consistency between primary methods employed for the above compounds at the (very low) concentration values relevant to air quality monitoring.

The findings of the project, the links to the standardisation activities of CEN and some examples of how traceability is achieved in a number of European member states were the subject of a HAMAQ European Workshop. The Workshop, which formed the focus of WP4, was hosted at NPL on 28th and 29th September 1999 and was attended by over sixty delegates, including representatives from all EU member states.





Conclusions

The following conclusions can be drawn from the HAMAQ project:

- The comparability of a range of metrology level primary facilities in leading European metrology institutes and national reference laboratories has been established and improved upon significantly within HAMAQ. Broadly speaking, comparabilities in the range 1-3%

have been achieved for the compounds CO, NO, SO_2, NO_2 and benzene at concentration levels appropriate for the calibration of field analysers.

- Compressed gases in cylinders can be used as transfer standards to determine the comparability of metrology level primary facilities although stability can be an issue for low concentration SO_2 and NO_2 gas mixtures. The impact of stability problems can be minimised by careful planning of the intercomparison: by reducing the timescale for the measurements to less than four months; by introducing redundancy; and by requiring initial (‘out’) and final (‘in’) pilot laboratory measurements. In only one case (VTT/FMI - ERLAP individual SO_2) was the maximum discrepancy between laboratories participating in the second intercomparison caused by cylinder instability.

- Compressed gases in cylinders can be used as accurate field calibration gases for the compounds covered in HAMAQ. For SO_2 and NO_2 compressed gases in cylinders can be used with some confidence if certification periods of 6-9 months are applied and frequent audit checks are implemented. If the traceability chain between field calibration gases and primary facilities is kept short then it should be possible to realise accuracies of ±3% for field calibration gases - small in comparison with the overall uncertainty of ± 15% sought by the Air Quality Directives for sites where concentrations approach limit values.

- The collaborative work and technical interactions throughout the HAMAQ project have contributed in a significant way to the development of a harmonised European metrological infrastructure which will continue to improve the quality of a very large and important European air quality dataset. Furthermore the HAMAQ International Workshop, attended by over sixty delegates from all European member states and beyond, ensured that the findings of the project were disseminated widely.

- The HAMAQ Intercomparison will serve as a model for future intercomparisons and collaborative work in this area of metrology. Certain features of the intercomparisons contributed significantly to the success of the project: firstly the inclusion of redundancy (through individual bilateral intercomparisons and a circulation cylinder intercomparison - minimising the risk associated with cylinder instability or cylinders being lost during shipment); and secondly the use of a two phase approach which allows laboratories to demonstrate improvements in their measurement capabilities in a second intercomparison.

1. INTRODUCTION

Air quality measurements are made at over one thousand measurement stations at sites across Europe. Many of these stations form part of nationally coordinated monitoring networks. The accuracy of measurements of gaseous pollutants made by continuous monitors at these stations is determined by a number of factors including the type of instrumentation used, the effects of sampling and the calibration of the instrumentation. Calibration of these analysers in the field is most often accomplished using compressed calibration gases in cylinders. These gases are currently produced by a number of commercial gas companies throughout Europe and the concentration of the target gas in the cylinder is certified, directly or indirectly, with respect to reference gases. Included in the European Air Quality Daughter Directives is the requirement that assigned national reference laboratories become responsible for the quality assurance and quality control of these reference gases and ensuring the traceability of field measurements to these reference gases.

The overall aim of the HAMAQ project, which was conducted during the period 1st December 1996 - 30th November 1999, was to enable improvements in the consistency of air quality measurements made within the member states of the EU in support of these new Directives. Specifically, the aim of HAMAQ has been to improve the comparability of the primary reference methods, at the highest metrological level, used for the certification of low concentration gas calibration mixtures of CO, NO, NO_2, SO_2 and C_6H_6. These primary facilities are maintained in a number of metrological institutes and reference laboratories within Europe.

The HAMAQ project is the first project to establish the current level of agreement between the various primary methods employed throughout Europe for these gases, using compressed gases in cylinders as transfer standards. Given the requirements of the new Directives for overall measurement uncertainties of ± 15%, for sites where measurements frequently exceed specified limit values, a target level of agreement of ± 1% was set by the partners within the project. This target, if achieved, would ensure that this contribution to the overall measurement uncertainty would not be significant.

The partners involved in the project are:

1. The National Physical Laboratory (NPL), United Kingdom, which develops and maintains a large range of primary gas standards, and is responsible for underpinning air quality measurements made as part of the UK national rural and urban monitoring networks, as well as local measurements made under the auspices of local and regional authorities.

2. The Nederlands Meetinstituut (NMi), the Netherlands, which is responsible for providing primary reference mixtures to the national institute responsible for the management of national air quality monitoring networks (RIVM, Ministry of Public Health and the Environment). In addition, NMi provide primary reference mixtures and certified reference materials to local environmental authorities.

3. The European Reference Laboratory for Air Pollution (ERLAP) at the EC Joint Research Centre, Ispra, which has responsibility for the harmonisation of air pollution

measurements within European air-quality monitoring networks. This is achieved through a number of activities including: preparatory work for future regulations; harmonisation of current directives; development and validation of new monitoring techniques; organisation of pilot studies; development of measurement strategies; participation in international air monitoring programmes and standardisation activities (CEN/ISO). ERLAP currently organises intercomparison exercises on a regular basis with the objective of ensuring the quality and comparability of European air pollution measurements.

4. The Laboratoire National d'Essais (LNE, France) is part of a group of institutes, including INERIS and Ecole de Mines de Douai, which are known collectively as the French Central Laboratory for Quality Assurance (LCSQA). These institutes are responsible for the validation of measurements made as part of national and local air quality monitoring networks.

5. Umweltbundesamt Langen (UBA), formerly located at Offenbach, is one of two German institutes responsible for the harmonisation of air quality monitoring throughout the country. Each German Bundesland has a central laboratory in which transfer standards for CO, SO_2, and NO_2 are certified with respect to reference methods. Once or twice each year comparison measurements are organised by either UBA or LUA (North Rhine - Westfalia) to ensure the consistency of measurements between these networks.

6. VTT Chemical Technology (Finland) together with The Finnish Meteorological Institute (FMI) have been involved with air quality monitoring since 1970. At present, FMI manages seven national and international networks which include a total of nineteen monitoring stations in Finland.

7. Instituto de Salud Carlos (ISC III) is the reference laboratory of the Spanish Atmospheric Pollution Network, and organises intercomparison exercises throughout the country. As part of its international quality assurance activities ISC III have worked in conjunction with ERLAP, NILU and the US EPA.

2. OBJECTIVES

The specific objectives of the project are:

a) to develop the methodology whereby internationally-accepted calibration gas standards can be produced and certified in concentration so as to promote widespread uniformity and accuracy of air quality measurements throughout Europe;

b) to demonstrate the equivalence of different 'primary' methods available in different member states for providing nationally traceable calibrations of air quality measurements of atmospheric pollutants (CO, NO, NO_2, SO_2 and C_6H_6) in order that these methods can be employed to certify stable gas calibration mixtures produced commercially;

c) to help develop improved gas cylinder surface passivation treatments by means of the industrial partners, and to evaluate their effectiveness in order to provide more accurate, stable long-lifetime calibration gas mixtures for CO, NO, NO_2, SO_2 and C_6H_6;

d) to provide knowledge transfer, in order to promote improved measurements across Europe - particularly in Member States where the air quality measurement infrastructure is not yet fully mature or is not yet of demonstrated accuracy.

3. WORKPROGRAMME

The technical work programme of the HAMAQ project was organised in four workpackages. These are described in outline below:

(i) Workpackage 1 (WP1): Production and stability test of calibration gas mixtures

The main elements of this workpackage involved:

- One specialist gas company (Messer) preparing, testing and supplying fifteen cylinders of each of NO, NO_2 and SO_2, at the low concentrations required for the calibration of air quality analysers, to the partners responsible for the relevant intercomparison (piloted by LNE, UBA and JRC respectively). The concentrations are given in Table 1 below.
- Another specialist gas company (Scott Gases) preparing, testing and supplying fifteen cylinders of each of CO and C_6H_6 at appropriate concentrations to the partners responsible for the relevant intercomparison (piloted by NPL and NMi respectively).
- Measurements of the stability of the prepared mixtures by the selected pilot laboratories.

TABLE 1: GASES, CONCENTRATIONS AND PILOT LABORATORIES IN THE HAMAQ PROJECT

Gas	Concentration (nominal)	Pilot Laboratory	'Core' Participants involved in First Intercomparison
CO	20 ppm	NPL	LNE, UBA
NO	200 ppb	LNE	NPL, UBA
SO_2	200 ppb	JRC	LNE, NMi, UBA
NO_2	200 ppb	UBA	LNE, JRC
C_6H_6	20 ppb	NMi	NPL, UBA

(ii) Workpackage 2 (WP2): First Intercomparison

This workpackage required NPL, ERLAP-JRC, NMi, UBA and LNE to coordinate a first intercomparison and act as pilot laboratories for the gases CO, SO_2, C_6H_6, NO_2 and NO respectively. The aim of this intercomparison was to assess the current level of agreement between established primary facilities at the selected laboratories. These measurements would establish the absolute accuracies achievable for the certification of gas cylinders at the highest metrological level. The intercomparison was conducted during the period March-December 1997, in accordance with a measurement protocol agreed by the partners (see Annex 1).

Following this exercise a number of technical meetings were held with the aim of improving measurement procedures where necessary, in order to achieve the target level of agreement of ± 1% in the second intercomparison to follow.

(iii) Workpackage 3 (WP3): Second Intercomparison

The second intercomparison was conducted during the period January-December 1998. The intercomparison comprised a repeat of the first intercomparison, involving the 'core' laboratories involved in the first intercomparison each measuring only a subset of the gases using *different* primary methods where feasible. New gas mixtures were used for this intercomparison. In addition, all partner institutes (including ISCIII and VTT/FMI) were given the opportunity to measure all of the gases.

(iv) Workpackage 4 (WP4): Dissemination and Knowledge Transfer

The findings of the project were to be disseminated to European national network co-ordinators and other parties involved in the preparation and certification of calibration gas mixtures for air quality measurements through an international workshop.

The workprogramme for the project is shown schematically taking the CO intercomparison as an example, in Figure 1.

4 RESULTS OBTAINED

4.1 WP1: PRODUCTION AND STABILITY TESTING OF CALIBRATION GAS MIXTURES

The calibration gas mixtures required for the intercomparison were produced by the commercial gas companies on schedule. Fifteen cylinders of each of CO, NO, SO_2, NO_2 and C_6H_6 were distributed to the pilot laboratories (NPL, LNE, ERLAP-JRC, UBA and NMi) during the period January-March 1997.

Stability tests on a subset of the batches (typically at least six cylinders) were conducted initially during the period January-May 1997 and subsequently during the lifetime of the project. The results of the stability tests for each of the gases are given below:

4.1.1 CO stability tests

It was not anticipated that stability would be a significant problem for low concentration calibration mixtures of CO in air. Stability tests were therefore conducted on a subset comprising gas mixtures in six cylinders at the pilot laboratory (NPL) at intervals over a period of twelve months. The results are given in Table 2 overleaf.

The data in Table 2 show no evidence of decay, given the measurement uncertainties of ± 0.6%.

TABLE 2: STABILITY TEST OF GAS MIXTURES OF CO IN AIR

Cylinder (N°.)	**Date**	**Concentration (ppm)**	**% Difference**
	1998-1	20.39	
57012-01	1998-2	20.33	- 0.1
	1998-12	20.36	
	1998-1	20.39	
57012-38	1998-1	20.37	- 0.1
	1998-12	20.36	
	1998-1	20.39	
57012-39	1998-2	20.40	+ 0.4
	1998-12	20.37	
	1998-1	20.34	
57012-37	1998-2	20.34	+ 0.2
	1998-12	20.38	
		20.39	
	1998-1		
57012-31	1998-2	20.35	-0.1
	1998-12	20.37	
		20.38	
	1998-1		
57012-27	1998-1	20.34	- 0.1
	1998-12	20.76	

4.1.2 NO stability tests

It was not anticipated that stability would be a significant problem for low concentration calibration mixtures of NO. Stability tests were therefore conducted on a subset comprising seven cylinders at the pilot laboratory (LNE) at intervals over a period of twenty months. The results are given in Table 3 below.

The data in Table 3 show no evidence of decay, given the measurement uncertainties of ± 1%.

TABLE 3: STABILITY TEST ON GAS MIXTURES OF NO IN NITROGEN

Cylinder (N°.)	Date	Concentration (ppb)	% Difference
	1997-3	197.0	
A9192	1997-11	196.3	+ 0.7
	1998-9	198.3	
	1997-3	195.3	
A9035	1997-12	195.8	+ 0.7
	1998-11	196.7	
	1997-4	196.0	
A9601	1997-12	196.1	- 0.2
	1998-9	195.6	
	1997-4	196.8	
A9600	1997-12	196.8	+ 0.3
	1998-9	197.4	
	1997-3	196.2	
A9594	1997-12	196.2	+0.4
	1998-10	197.0	
	1997-3	192.9	
A9595	1997-12	193.4	+ 0.3
	1998-9	193.4	
	1997-4	191.6	
A9642	1997-8	192.0	+ 1.5
	1997-12	194.1	
	1998-11	194.4	

4.1.3 SO_2 stability tests

Stability tests in the SO_2 mixtures were conducted on a set of six cylinders at the pilot laboratory (JRC-ERLAP). The results are shown in Figure 2. Initially, an intensive series of weekly measurements were carried out for the first month, followed by measurements at intervals of typically 5-10 weeks over a period of twenty months.

Given the measurement uncertainty of ± 3% (at 95% confidence level) there is no evidence of decay in any of the six cylinders over the first 24 weeks (5.5 months) of measurements. Measurement following this show no indication of decay in three of the cylinders for the remaining 64 weeks, some indication of decay (5% over 64 weeks) in another and a decay of 10% over 64 weeks in a fifth cylinder. A sixth cylinder was used and exhausted as part of the second intercomparison.

This data therefore suggests that low concentration gas mixtures of SO_2 in air can be used successfully as transfer standards for the comparison of primary facilities. It also suggests that these cylinder gases can be used as field calibration mixtures if a sensible certification period is ascribed to the calibration gases. On the basis of the measurements reported here a certification period of six months is justified.

Alternatively, cylinder gases could be used for longer periods in the field if these field calibration mixtures were checked periodically as part of regular audits. Audit intervals of three months would identify any significant decay in cylinder gases.

4.1.4 C_6H_6 Stability tests

The benzene gas mixtures were produced at a nominal concentration of 20 ppb. At such low concentrations it was anticipated that stability may have been a problem and therefore careful stability checks were viewed as an important part of this project.

A series of five measurements were carried out at all fifteen benzene cylinders during the first three months after arrival at the pilot laboratory. The results are shown in Figure 3. These measurements gave stable concentrations in the range 20-22 ppb for twelve of the fifteen cylinders. The remaining three cylinders gave concentrations in the range 14-18 ppb with two of these showing some indication of decay. The concentrations in the range 14-18 ppb may be an indication of early post production decay, of 16-27%, from the batch nominal concentration of 20 ppb.

Measurements were repeated at intervals of 15-20 weeks for the following 60 weeks. None of the twelve cylinders measured at 20-22 ppb showed any evidence of decay. Of the remaining three cylinders two appeared stable at concentrations of 16 and 17 ppb and the third showed evidence of further decay to a concentration of 13 ppb.

On the basis of this data it can be deduced that stable benzene gas mixtures of concentrations of 20 ppb can be produced and used successfully in intercomparisons of metrology level primary facilities. Furthermore if some quality checks are made in the period following production theses gases can be used with confidence as field calibration gases over periods of one year.

4.1.5 NO_2 stability tests

The stability of the NO_2 calibration mixtures was evaluated from a comparison of measurements made on fourteen cylinders at the beginning of the project with measurements made after 65, 118 and 126 weeks. The results are shown in Figure 4. Initial measurements on a fifteenth cylinder revealed significant decay below the nominal value and this was not included in further stability tests.

After sixty five weeks decay was evident in three cylinders from the batch of fourteen. The concentration of NO_2 in these cylinders had decreased by 8%, 6% and 4%.

The measurements at weeks 118 and 126 show that of these three cylinders two appeared to increase in concentration, resulting in net concentration changes over the two year period of -5% and -2%. However two different cylinders show decay of 5% and 6% relative to the measurements at week sixty five.

On the basis of the data presented here it can be concluded that cylinder gases can be used for the metrology level comparison of primary facilities but that the significant risk (21%) of decay of magnitude 4%-8% in the first year requires that the intercomparisons are conducted over as short a timescale as possible, that some redundancy should be built into the intercomparison, and that final measurements are made at the pilot laboratory. In the case of HAMAQ this redundancy was achieved by carrying out both individual bilateral intercomparisons and circulation cylinder intercomparisons.

In addition, the probability of decay should be taken account of in using the cylinders as field calibration gases. Certification periods of six months and regular (3 monthly) audit checks would build confidence in the use of cylinder gases for field calibration of NO_2 analysers.

4.2 WP2: FIRST INTERCOMPARISON

The first intercomparison was conducted during the March-December 1997, in accordance with a measurement protocol agreed by the partners (see Annex 1). The results for each of the target gases are discussed below.

4.2.1 First Intercomparison for CO

NPL acted as pilot laboratory for the CO intercomparison, LNE and UBA were the other participants. The results of the first CO intercomparison, for both the circulation cylinders and the individual bilateral intercomparisons are shown in Figure 5.

[Note: A common format is adopted for all of the intercomparison results presented in Figures 5-14. Part (i) gives the circulation cylinder results plotted relative to the mean of the initial and final pilot laboratory measurements - for the CO intercomparison the initial pilot laboratory (NPL) measurement is not available. The dotted line in the circulation cylinder plots gives a ‘consensus’ value derived by taking a weighted mean of all measurements. The weighting factor is calculated as the inverse variance of the measurement.]

Part (ii) of each plot gives the individual cylinder measurements of each participating laboratory (labelled) relative to the mean of the initial and final pilot laboratory measurements which are shown but not labelled.

The largest discrepancy in the derived concentrations of CO in the three cylinders that were intercompared initially in the first intercomparison was 2.1% (NPL-UBA, for both circulation and individual cylinders). The UBA and LNE results were however, in good agreement, with differences of 0.1% - this difference was not significant given the reported measurement uncertainties. Following a series of investigations it was discovered that the cause of this uncertainty was related to the NPL measurements which were made relative to primary standards of CO in nitrogen. For the particular analyser used the response of the analyser was found to be sensitive to the nature of the balance gas used (synthetic air or nitrogen). A revised set of NPL measurements (shown in Figure 5) gave a maximum discrepancy of 0.8% for the circulation cylinder (NPL-UBA) and discrepancies for the individual cylinders of 0.5% (NPL-LNE) and 0.2% (NPL-UBA). These discrepancies are not significant given the reported measurement uncertainties. The CO results obtained in the first intercomparison were therefore already within the target level of agreement aimed at in the second intercomparison.

4.2.2 First Intercomparison for NO

LNE acted as pilot laboratory for the NO intercomparison, NPL and UBA were the other participants. The results of the NO intercomparisons, for both the circulation and the individual bilateral intercomparisons are shown in Figure 6.

Within the reported measurement uncertainties (1.3% relative for LNE, 2.4% for NPL and 2.0% for UBA) there were no significant differences in the measurements reported and the results were close to the target level of agreement aimed at in the second intercomparison.

In order to meet the target level of agreement of ±1% there was therefore a requirement for NPL and UBA to modify their measurement procedures in order to achieve uncertainties lower than ± 1%.

4.2.3 First Intercomparison for SO_2

ERLAP-JRC acted as pilot laboratory for the SO_2 intercomparison, NMi, UBA and LNE were the other participants. The results of the SO_2 intercomparison for both circulation cylinder and the individual bilateral intercomparisons are shown in Figure 7.

The individual cylinder intercomparison results for LNE and NMi show good agreement (+1.0% and 0.0% differences relative to the mean ERLAP-JRC value). However the UBA individual measurements are 3% lower than the ERLAP-JRC value.

The results obtained for the circulation cylinder appeared initially to show worse agreement. The initial measurements at ERLAP-JRC during February/March 1997 yielded consistant values, with no evidence of decay, giving a mean of 201.0 ± 3.1 ppb. Subsequently measurements at NMi (July/August 1997) gave a value of 208.4 ± 0.8 ppb, and at UBA (October 1997) gave a value of 215.3 ± 0.6 ppb. Further measurements at LNE (December 1997) gave a value of 207.5 ± 2.6 ppb.

A final measurement of the cylinder upon return to ERLAP during March 1998, gave a value of 212.2 ± 3.1 ppb. The most likely explanation of these measurements is that the concentration of the gas in the cylinder increased shortly after leaving ERLAP during March 1997, due to environmental conditions encountered during transport. It can be hypothesised that the apparent increase in concentration is a consequence of the soaking process employed by the commercial gas company. In this process, prior to filling the gas cylinder with SO_2/Air at a nominal concentration of 200 ppb, the cylinder are soaked with SO_2/Air mixtures at much higher concentrations, around 100 ppm, in order to deactivate any potentially active sites on the inside surface of the cylinder. It is possible therefore that this process had created reservoirs of SO_2 which could subsequently desorb due to changes in temperature and/or due to rough handling to cause the observed increase in concentration.

If the results of this intercomparison are expressed relative to the final ERLAP measurement the maximum deviation in the measurements is reduced to 3.7%.

It was noted by all groups that it is essential to pre-condition the regulator used for the SO_2/Air cylinder to allow a sufficiently long time for the analyser readings to stabilise (typically 45 minutes).

Given the good level of agreement between JRC-ERLAP, NMi and LNE the requirement was for UBA to improve their measurement procedure and re-evaluate their uncertainty estimate in order to achieve the target level of agreement of ±1% in this second intercomparison.

4.2.4 First Intercomparison for Benzene

NMi acted as pilot laboratory for the C_6H_6 intercomparison. NPL, UBA and ERLAP-JRC were the other participants in the first intercomparison. The results of the C_6H_6 intercomparison, for both circulation cylinder and the individual bilateral intercomparisons are shown in Figure 8.

The results obtained by NMi, NPL and ERLAP-JRC for the circulation cylinder are consistent within the reported measurement uncertainties. The individual cylinder intercomparison measurements by these laboratories are also consistent within their combined measurement uncertainties. The NMi-UBA differences of 7%, obtained for both circulation and individual cylinders, are larger than the combined measurement uncertainties. The discrepancy was subsequently found to be due to absorption effects in the regulator used by UBA to make the measurements. Using a regulator supplied by NMi the measurements were repeated at UBA and the level of agreement was improved to better than 1%.

In order to meet the target level of agreement of ± 1% there was a requirement for NPL and ERLAP-JRC to improve their measurement procedures in order to reduce their reported measurement uncertainties, from values of ± 4% and ± 7%, to values closer to ± 1%.

4.2.5 First Intercomparison for NO_2

UBA acted as pilot laboratory for the NO_2 intercomparison. ERLAP-JRC and LNE were the other participants in the NO_2 intercomparison. The results of the NO_2 intercomparison, for both circulation cylinder and the individual bilateral intercomparisons are shown in Figure 9.

For both circulation and individual cylinder measurements UBA and LNE are in agreement within the reported measurement uncertainties. However for both circulation and individual cylinders the ERLAP-JRC measurements are higher than those made by UBA, by 5.4% and 3.3% respectively. In order to meet the target level of agreement of ±1% there was therefore a requirement for ERLAP-JRC and UBA to improve their measurement procedure to produce reduced measurement uncertainties.

4.3 WP3: SECOND INTERCOMPARISON

Following completion of the first intercomparison in December 1997 a progress meeting was held at ISCIII, Madrid, with the aim of reviewing status at the end of the first intercomparison. This was followed by further technical discussions at NPL during April 1998 and UBA, Offenbach during June 1998. The aim of the technical discussions was to identify causes of discrepancy and to define improved measurement strategies to enable the partners involved in the first intercomparison to achieve agreement to the target level of agreement of ± 1% in the second intercomparison.

The second intercomparison was carried out during the period January-December 1998. The results were discussed at a progress meeting at ERLAP-JRC during January 1999. The results for each of the target gases are discussed below:

4.3.1 Second Intercomparison for CO

All project partners participated in the second CO intercomparison. The results of this intercomparison are shown in Figure 10.

Considering firstly the results obtained by the ‘core’ participants involved in the first intercomparison (NPL, UBA and LNE) the maximum discrepancy observed for both circulation and individual cylinder intercomparison was 0.8% (NPL-UBA, individual intercomparison). This was not significant given the reported measurement uncertainties. Target level of agreement of ± 1% was therefore achieved in the second intercomparison.

Of the other partners involved in the second CO intercomparison: the measurements by both VTT/FMI and NMi, for the circulation and individual cylinders, are within ± 1% of the measurements by the pilot lab. However, ERLAP-JRC and ISCIII measurements show discrepancies of + 2% and + 3% respectively, relative to the pilot lab measurements.

In the case of ISCIII this discrepancy is not significant however the JRC measurement is at the limits of significance given the reported measurement uncertainties. The difference was later found to be due to an error in the estimated volume of a syringe used in the static dilution rig used.

From the results reported here it appears that the lowest measurement uncertainties (less than 0.5%) are obtained by calibrating an analyser, in an appropriate concentration range, using gravimetrically prepared calibration mixtures. Measurements using calibration mixtures prepared by alternative techniques yield measurement uncertainties in the range 1%-3%.

4.3.2 Second Intercomparison for NO

All project partners participated in the second NO intercomparison. The results of this intercomparison are shown in Figure 11.

Considering firstly the results obtained by the ‘core’ participants involved in the first intercomparison (LNE, NPL and UBA) the maximum discrepancy observed is 2.2% (NPL-UBA, circulation cylinder). This discrepancy is statistically significant given that the error bars of NPL and UBA, when combined, are 2.0%. The NPL and UBA individual cylinder measurements show discrepancies of -1.1% and +0.5% respectively relative to LNE. These differences are not significant.

For all of the partners involved in the second NO intercomparison the individual cylinder measurements show that there are no significant differences relative to LNE and all of the measurements fall within an envelope of + 1.2% to -2.1% relative to the pilot laboratory measurements.

4.3.3 Second Intercomparison for SO_2

All project partners participated in the second SO_2 intercomparison. The results of this intercomparison are shown in Figure 12.

Considering first the results obtained by the ‘core’ participants involved in the first intercomparison (JRC, NMi, LNE and UBA) the maximum discrepancy is 3.4% (JRC-UBA, individual cylinder), close to limits of statistical significance. However, for the circulation cylinder the JRC-UBA difference is 1.0% which is not significant. The JRC-LNE circulation cylinder measurements differ by 3.2% but this difference is not significant.

For the other participants (NPL, ISCIII and VTT/FMI) none of the observed differences were significant. The largest discrepancy observed was 6.0% (JRC-VTT/FMI individual cylinder measurements).

Given that the measurement uncertainties for ISCIII and VTT/FMI, at ±6%, are significantly larger than those of the other participants which are in the range ±0.7% to ±2.0% it was agreed that another intercomparison with a new cylinder, involving JRC, VTT/FMI and ISCIII would be carried out. Initial measurements were carried out by JRC during January 1999 followed by measurements at VTT/FMI (April 1999), followed by ISCIII (November 1999) before returning to JRC for a final measurement during December 1999. These new results show discrepancies, relative to the mean pilot laboratory value, of -1.4% for VTT/FMI and 3.5% for ISCIII. Given the measurement uncertainties for the JRC, VTT/FMI and ISCIII of ±2.2%, ±2.3% and ±2.8% respectively. These discrepancies are not significant and represent an improvement by a factor of two over the uncertainties achieved in the second intercomparison.

Taking these new measurements - all measurements are now enclosed within an envelope of -3.2% to +1.0% relative to the pilot laboratory.

4.3.4 Second Intercomparison for Benzene

With the exception of ISCIII all project partners participated in the second benzene intercomparison. The results of this intercomparison are shown in Figure 13.

Considering first the results obtained by the 'core' participants involved in the first intercomparison (NMi, NPL, UBA and JRC) the maximum discrepancy observed in the second intercomparison is 5.6% (NMi-JRC circulation cylinder) which is not significant given the reported measurement uncertainties.

All of the measurements by the other 'core' participants, for both circulation and individual cylinders, are in agreement within their reported measurement uncertainties.

The measurements made by the other participants (LNE and VTT/FMI) are in good agreement with the pilot lab values with differences of +1.7% and -2.9% respectively for the circulation cylinder and -0.2% and 2.4% respectively for the individual cylinders. These differences are not significant given the reported measurement uncertainties.

Current measurement uncertainties for all participants are in the range ± 2% to ± 6.5%. In order to attain a level of agreement of ± 1% it would be necessary for all groups to bring about significant improvements in the primary facilities and the measurement procedures used. In maintaining accurate primary facilities for benzene at concentrations of 20 ppb problems with cylinder stability (for gravimetric techniques), purity analysis of the balance gases and sample handling during analysis are the main contributors to these uncertainties.

4.3.5 Second Intercomparison for NO_2

All project partners participated in the second NO_2 intercomparison. The results of this intercomparison are shown in Figure 14.

Considering first the results obtained by the 'core' participants involved in the first intercomparison (UBA, JRC and LNE) the JRC and LNE circulation cylinder measurements show differences of -0.4% and -0.7% respectively relative to the pilot laboratory. The individual cylinders show differences of +1.6% and +1.1% respectively relative to the pilot laboratory measurements. None of these observed differences are significant given the reported measurement uncertainties for UBA, JRC and LNE of ± 1.7%, ±1.5% and ± 1.8% respectively.

For the other participants, NMi, ISCIII, VTT/FMI and NPL show differences of 6.1%, 2.4%, 4.1% and -2.0% relative to the pilot laboratory for the circulation cylinders. Only in the case of VTT/FMI is this difference significant given the reported measurement uncertainties (2.4%, 6.0%, 2.5% and 1.5% respectively). For the individual cylinder measurements the differences for these partners are +1.3%, +1.1%, +1.0% and -0.9% respectively.

Given that the VTT/FMI measurements for the circulation cylinder (2) were significantly different from those of the pilot laboratory it was agreed that measurements would be repeated by VTT/FMI. Measurements during September 1999 gave values which gave a revised discrepancy of -3.6% relative to the pilot laboratory value. Given the measurement uncertainties reported by VTT/FMI, of ±2.2%, this discrepancy is not significant.

For all partners to achieve agreement to ±1% there is a requirement for improvements in the primary facilities and measurement problems used. In maintaining accurate primary facilities for NO_2 at concentrations of 200 ppb the purity and stability of the component gases can be a significant contribution to the overall measurement uncertainty.

4.4 WP4: DISSEMINATION

The technical findings of the HAMAQ project were disseminated at an International Workshop held at NPL on 28th and 29th September 1999. The workshop was attended by over sixty scientists representing all fifteen European member states together with representatives from Switzerland, Norway, Hungary, Poland, Slovakia, the Czech Republic and Russia. The two day workshop also included sessions on the role and activities of CEN in the implementation of the Air Quality Directives as well as case studies on how QA/QC was achieved in existing European air quality monitoring network. The meeting programme and a list of workshop participants are given in Appendix 2.

An overview of the HAMAQ project is also available on the internet (see Appendix 3 for web address). Some additional work carried out by the partners as a result of the late withdrawal of a subcontractor is reported in Appendix 4.

5. CONCLUSIONS

The following conclusions can be drawn from the HAMAQ project:

- The comparability of a range of metrology level primary facilities in leading European metrology institutes and national reference laboratories has been established and improved upon significantly within HAMAQ. Comparabilities in the range 1-3% have been achieved for the compounds CO, NO, SO_2, NO_2 and benzene at concentration levels appropriate for the calibration of field analysers.

- Compressed gases in cylinders can be used as transfer standards to determine the comparability of metrology level primary facilities although stability can be an issue for low concentration SO_2 and NO_2 gas mixtures. The impact of stability problems can be minimised by careful planning of the intercomparison: by reducing the timescale for the measurements to less than four months; by introducing redundancy; and by requiring initial (‘out’) and final (‘in’) pilot laboratory measurements. In no cases were the maximum discrepancies between laboratories participating in the second intercomparison caused by cylinder instability.

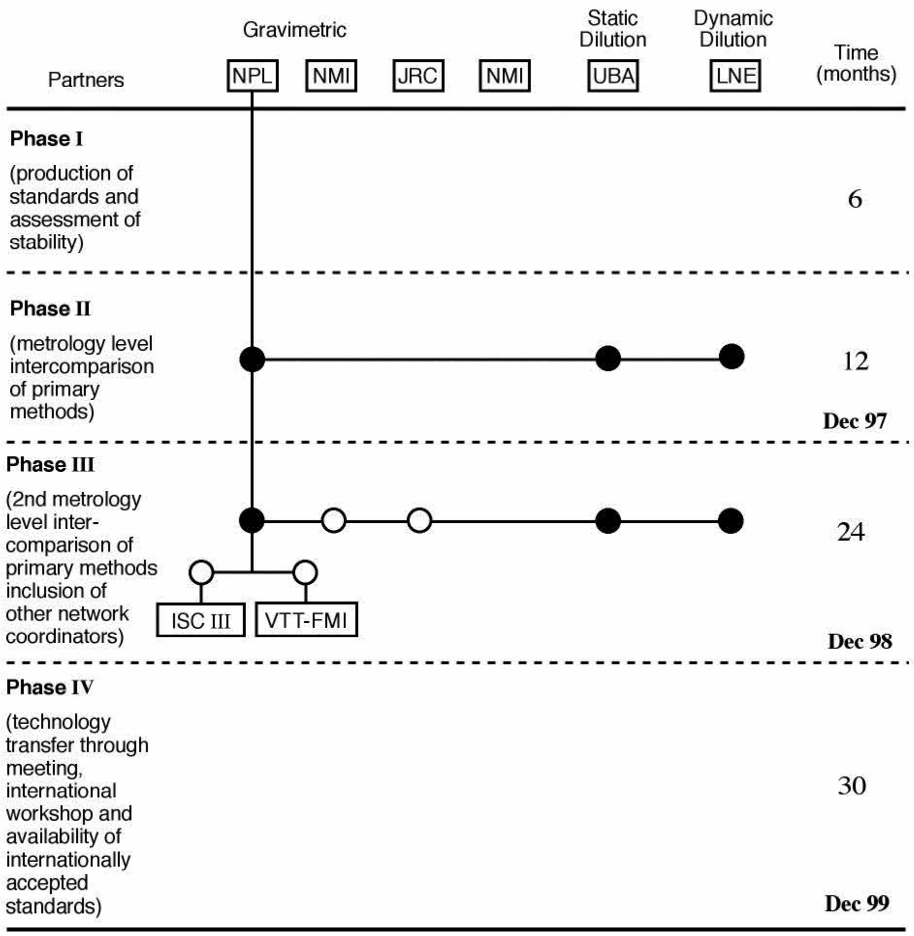
- Compressed gases in cylinders can be used as accurate field calibration gases for the compounds covered in HAMAQ. For SO_2 and NO_2 compressed gases in cylinders can be used with some confidence if certification periods of 6-9 months are applied and frequent audit checks are implemented. If the traceability chain between field calibration gases and primary facilities is kept short then it should be possible to realise accuracies of ±3% for field calibration gases - relatively small in relation to the overall uncertainty of ± 15% sought by the Air Quality Directives for sites where concentrations approach limit values.

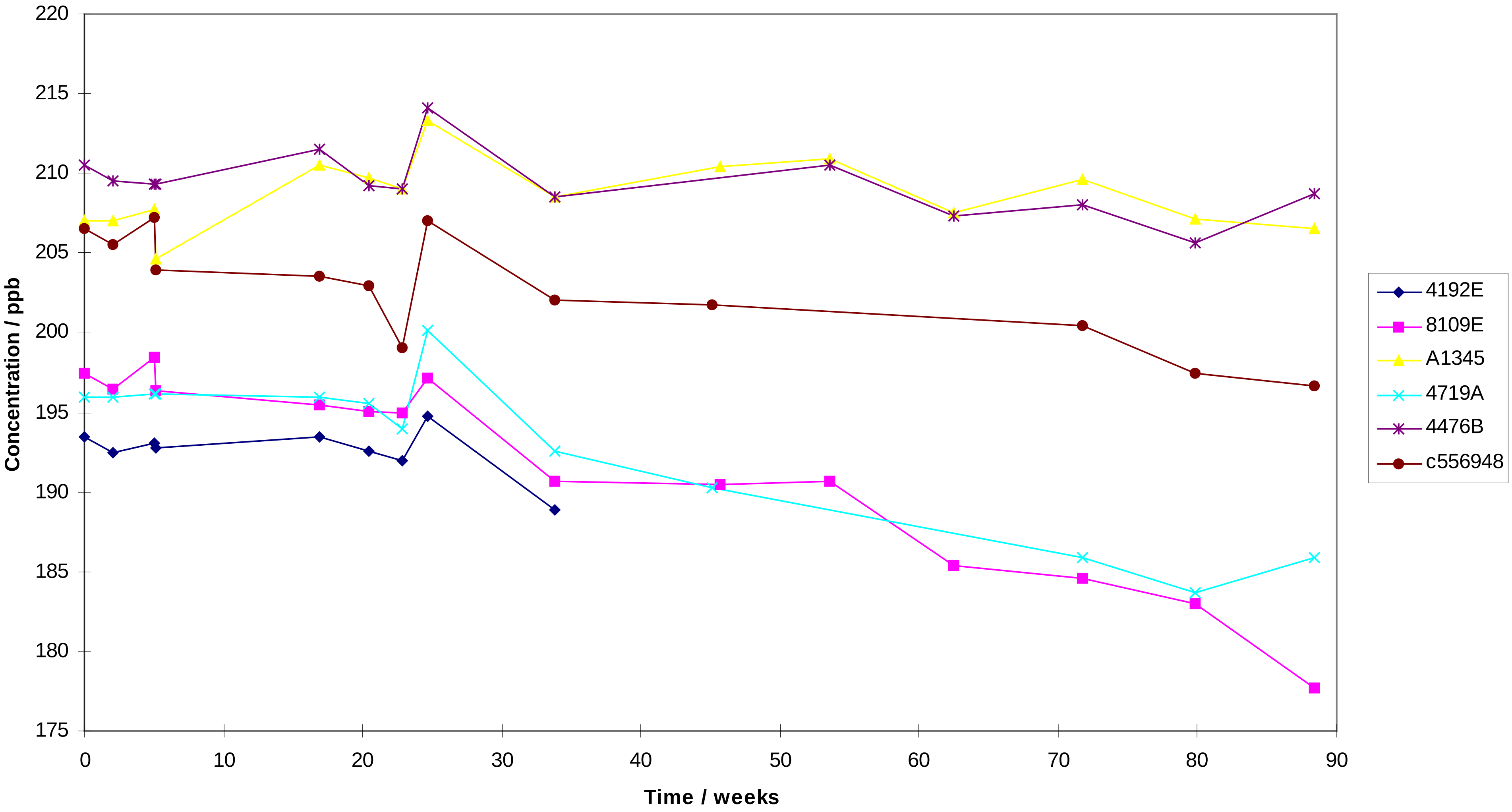
- The collaborative work and technical interactions throughout the HAMAQ project have contributed in a significant way to the development of a harmonised European metrological infrastructure which will continue to improve the quality of a very large and important European air quality dataset. Furthermore the HAMAQ International Workshop, attended by over sixty delegates from all European member states and beyond, ensured that the findings of the project were disseminated widely.

- The HAMAQ Intercomparison will serve as a model for future intercomparisons and collaborative work in this area of metrology. Certain features of the intercomparisons contributed significantly to the success of the project: firstly the inclusion of redundancy (through individual bilateral intercomparisons and a circulation cylinder intercomparison - minimising the risk associated with cylinder instability or cylinders being lost during shipment); and secondly the use of a two phase approach which allows laboratories to demonstrate improvements in their measurement capabilities in a second intercomparison.

LIST OF FIGURES

CO Primary Methods

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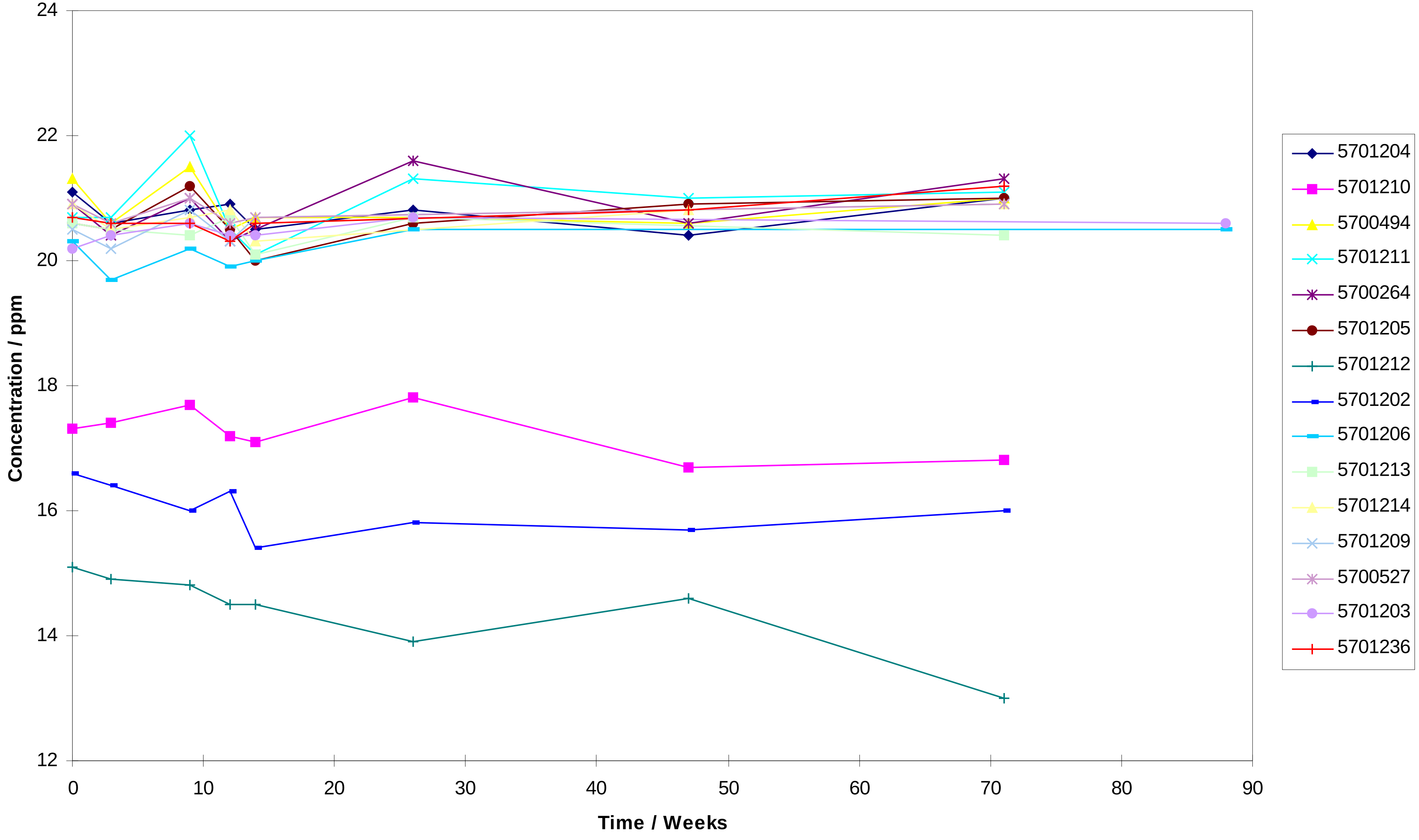
24
22
20
18
16
14
12
Concentration / ppm
0
10
20
30
40
50
60
70
80
90
Time / Weeks
5701204
5701210
5700494
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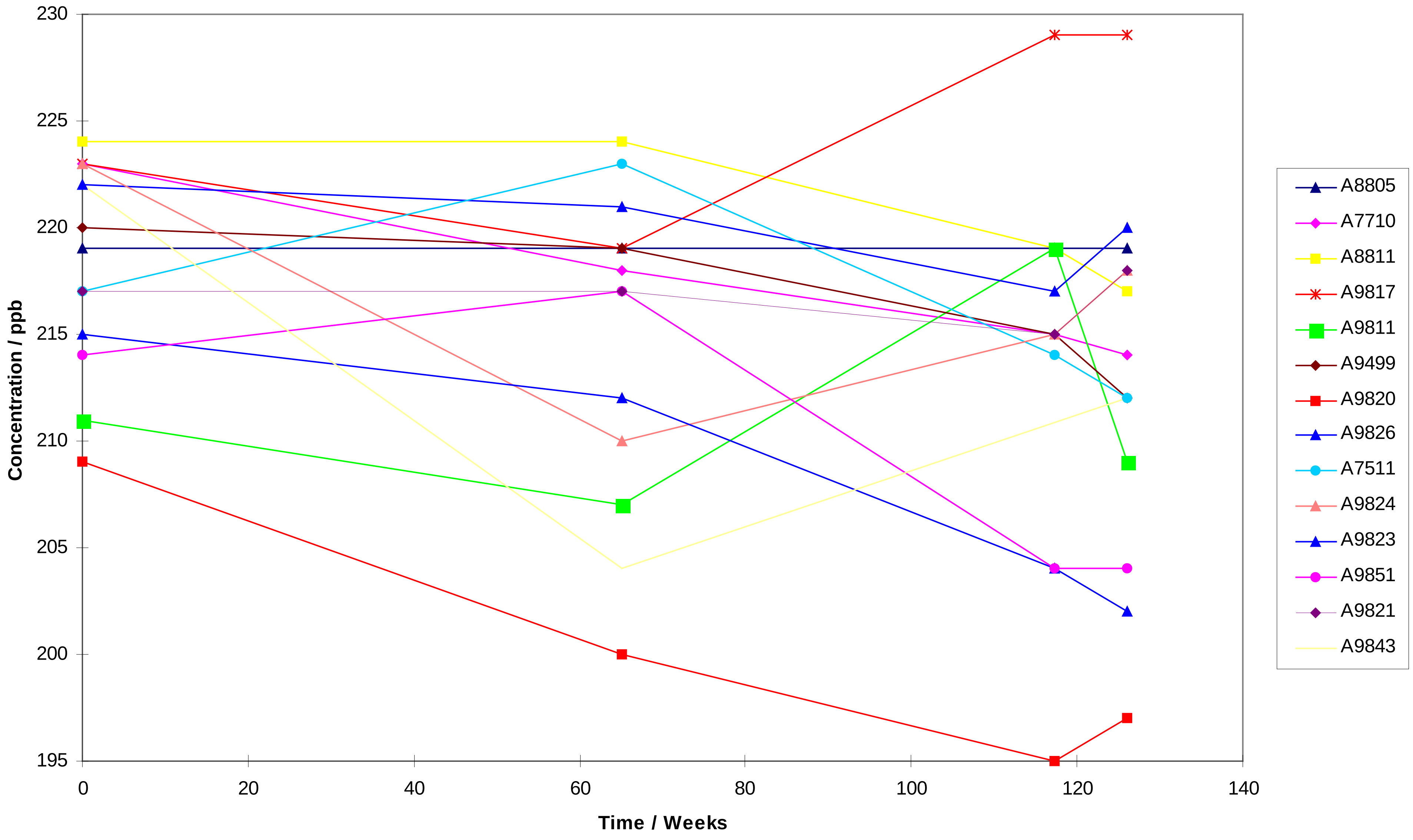
5700527
5701203
5701236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225
220
215
210
205
200
195
Concentration / ppb
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40
60
80
100
120
140
Time / Weeks
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A7710
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A9851
A9821
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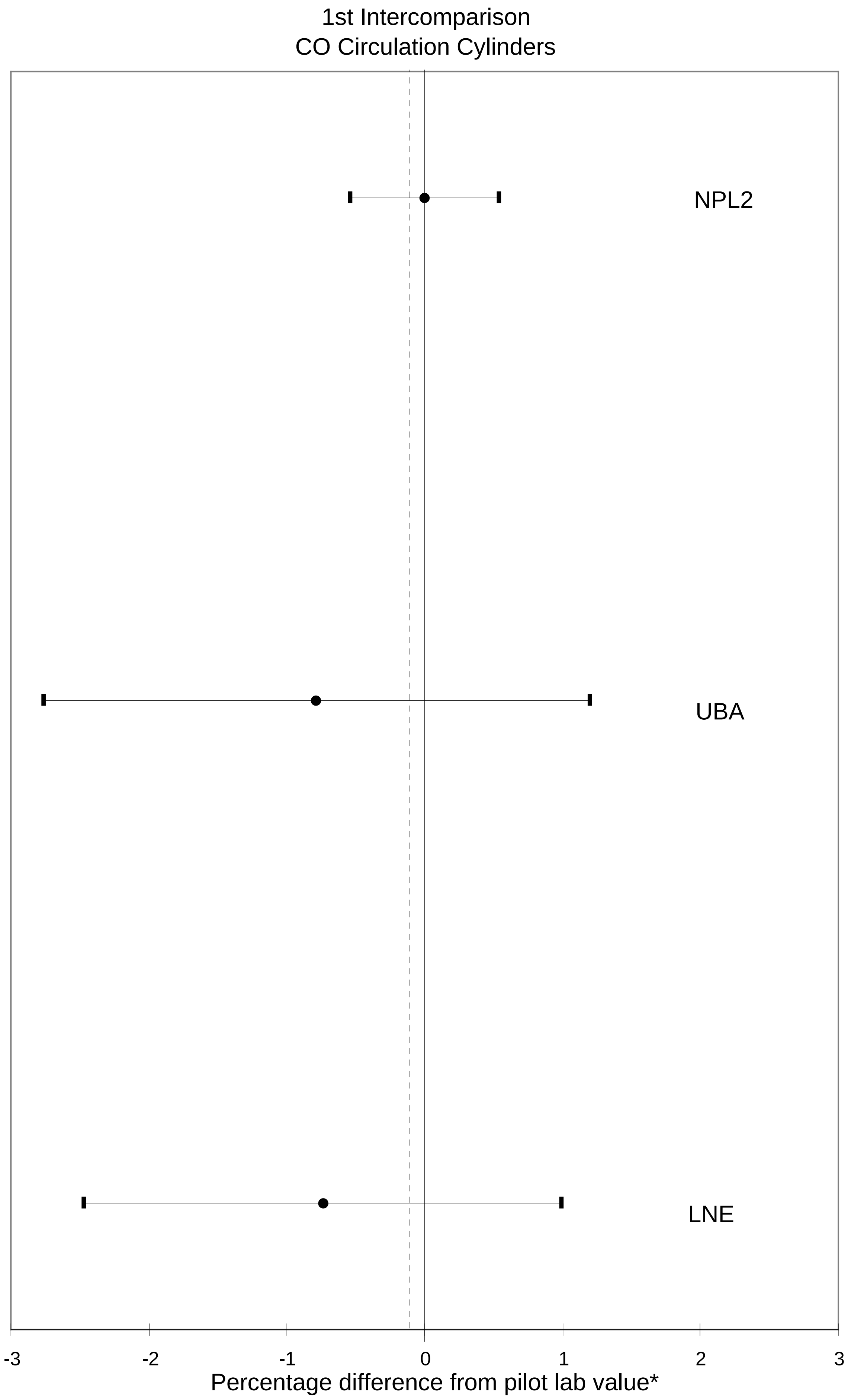
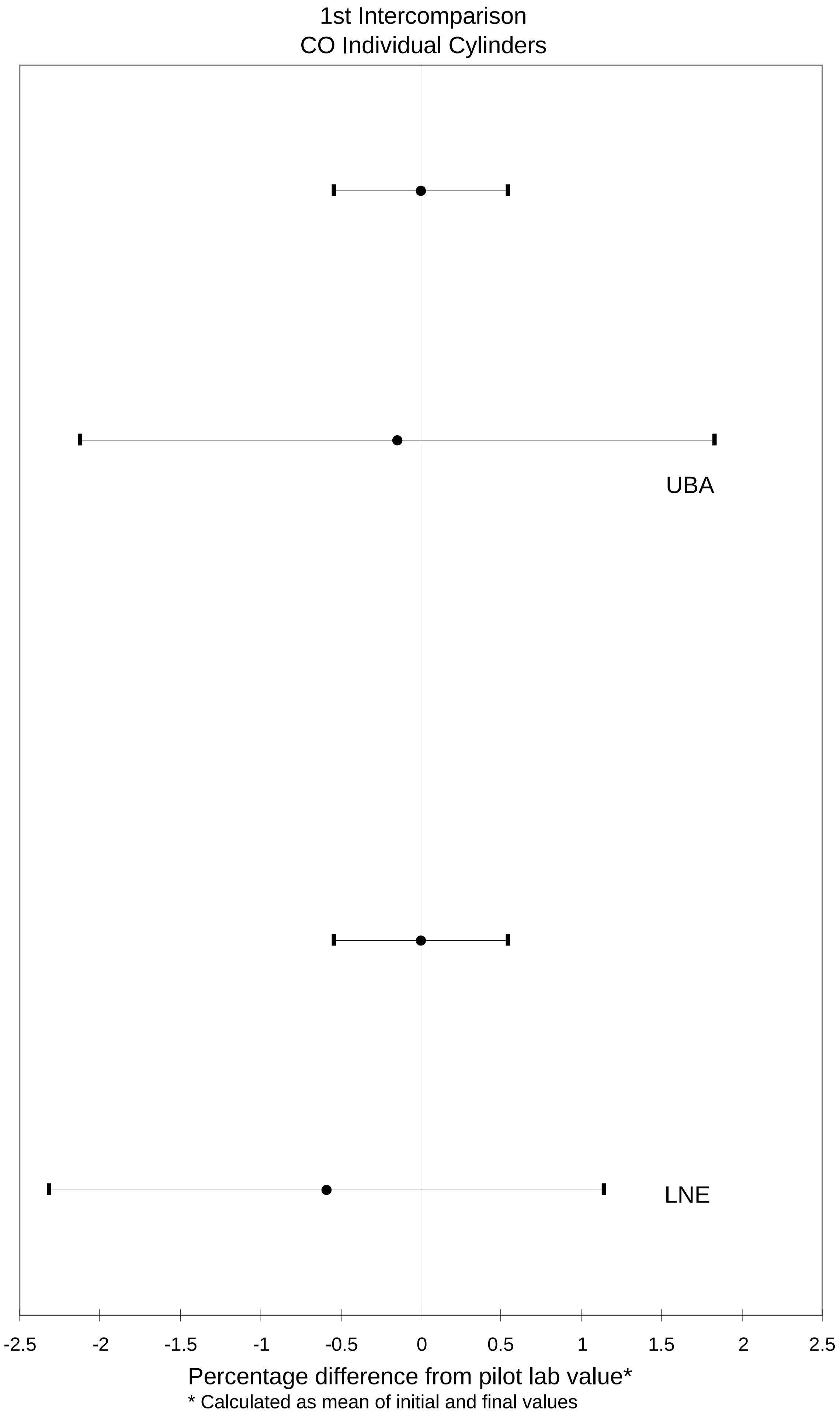


* Only final value available from NPL measurements - NPL2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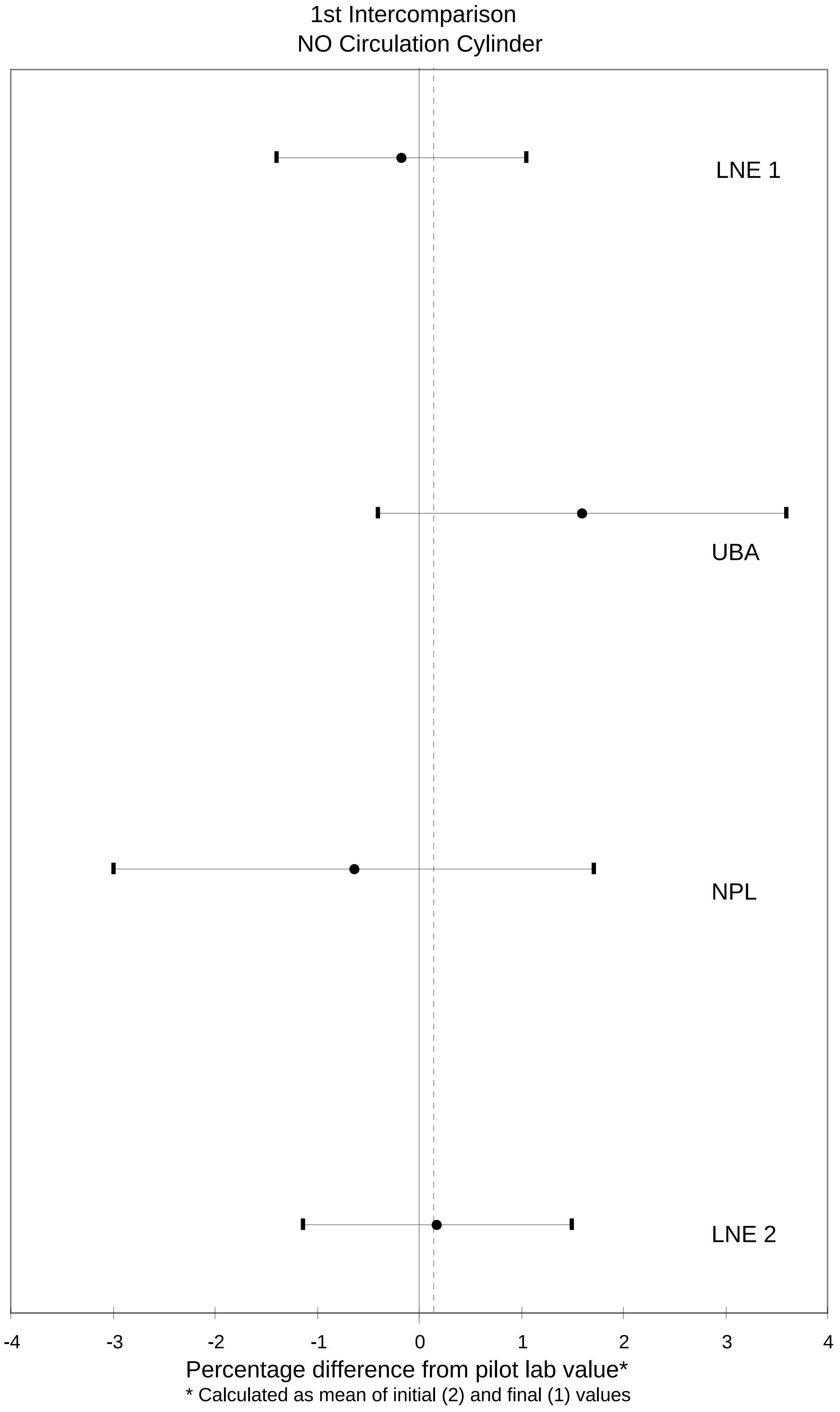
CO Individual Cylinders
UBA
LNE
-2.5
-2
-1.5
-1
-0.5
0
0.5
1
1.5
2
2.5
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values


1st Intercomparison
NO Circulation Cylinder
LNE 1
UBA
NPL
LNE 2
-4
-3
-2
-1
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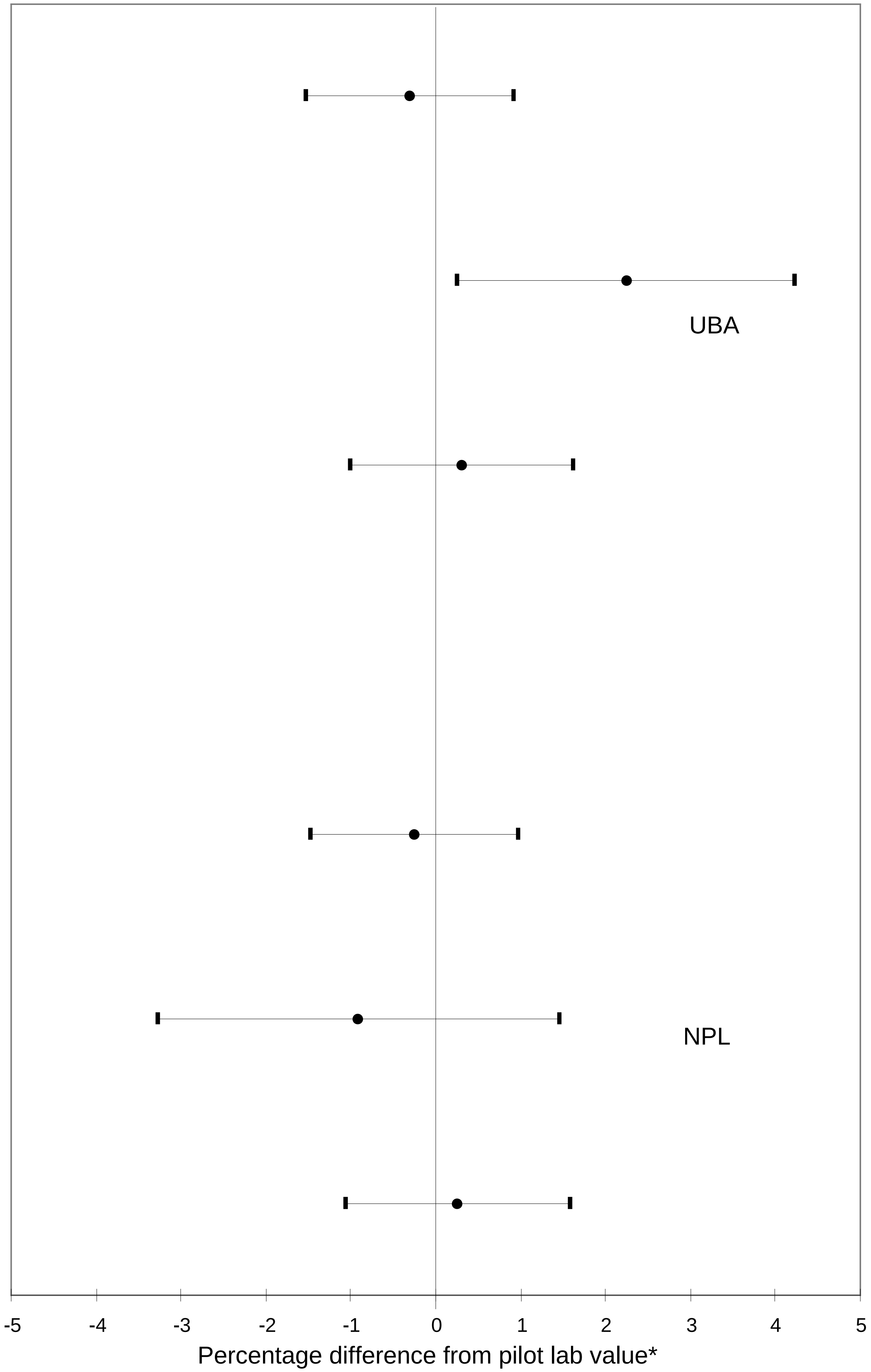
1
2
3
4
Percentage difference from pilot lab value*
* Calculated as mean of initial (2) and final (1) values

1st Intercomparison
NO Individual Cylinders



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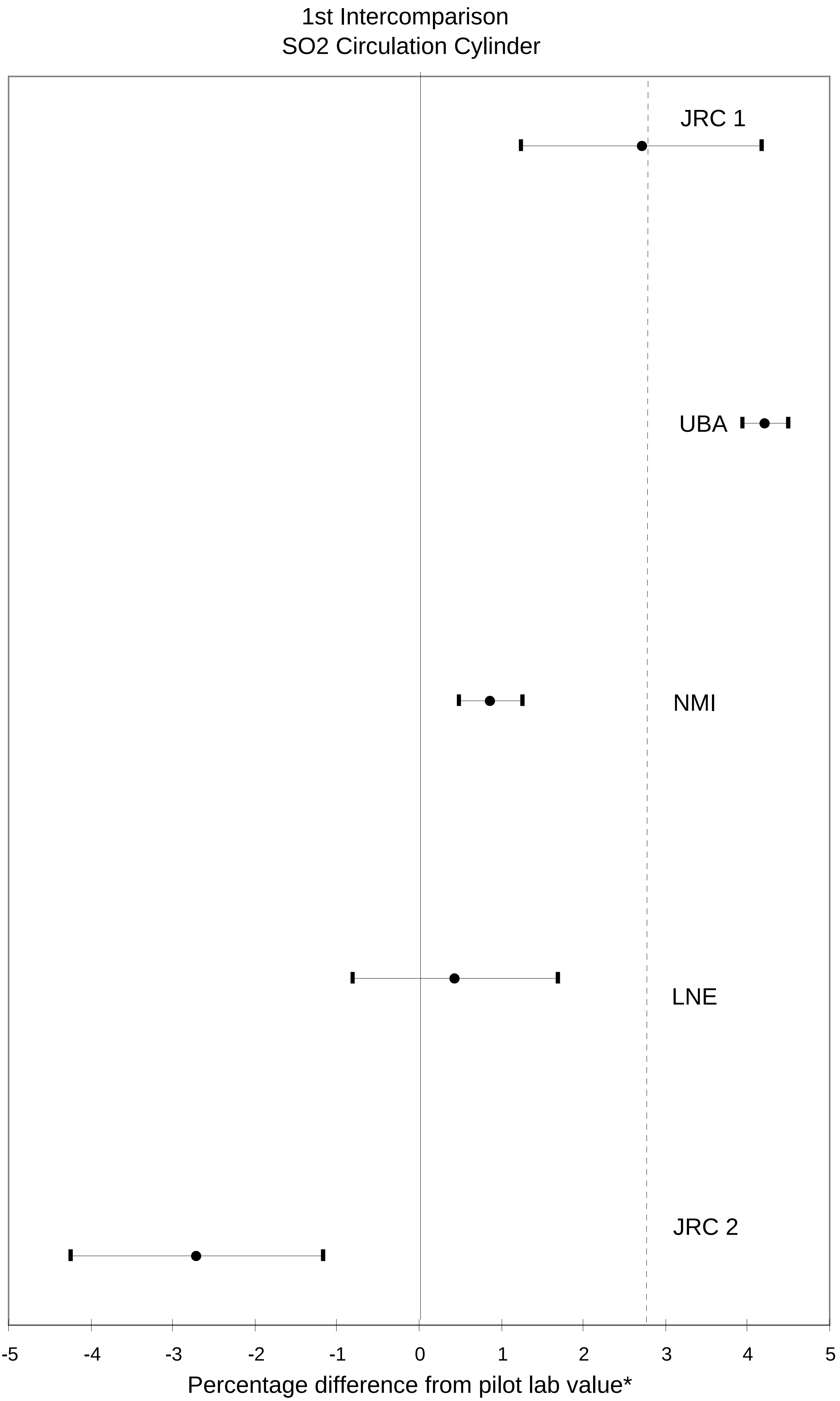

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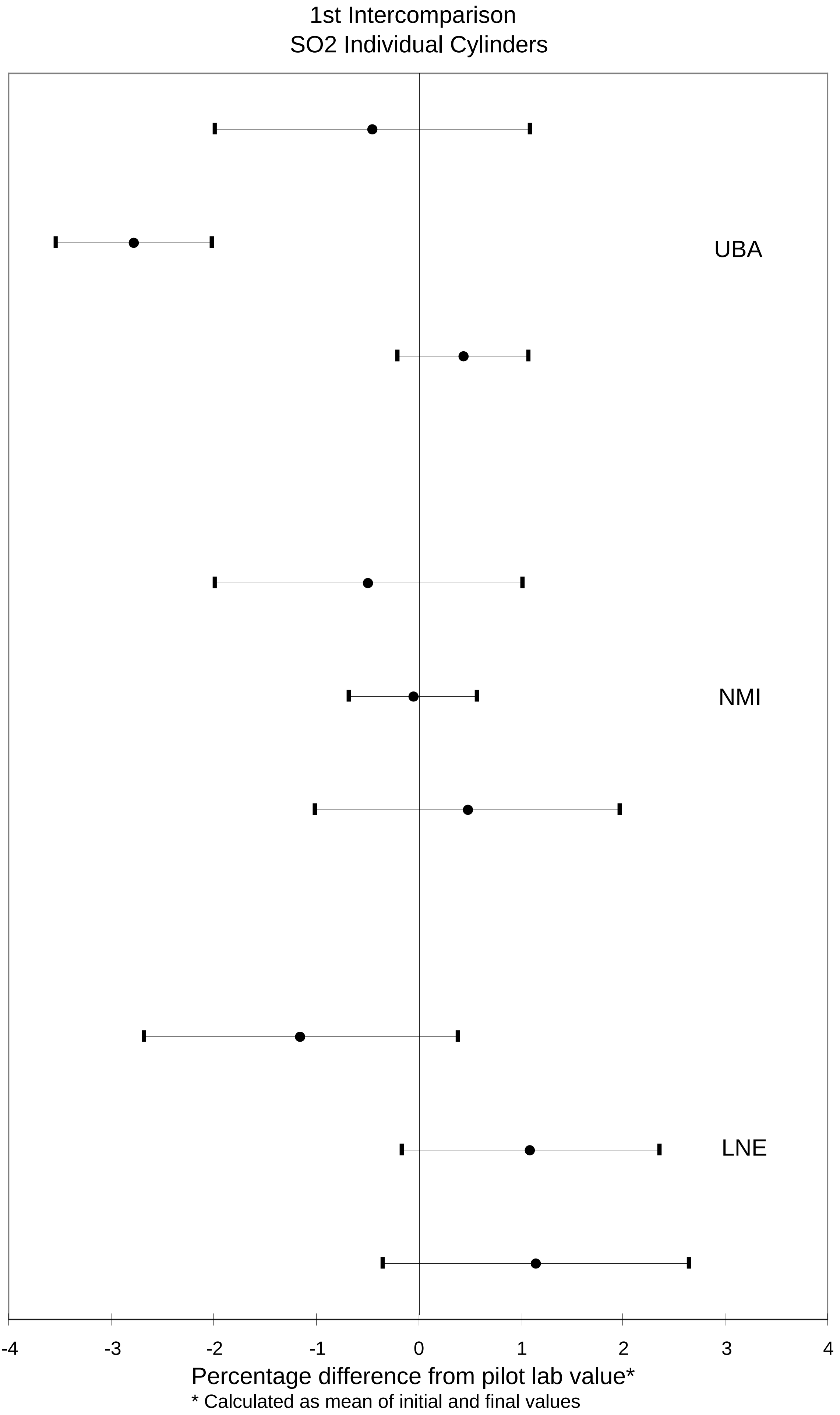
1st Intercomparison
SO2 Individual Cylinders
UBA
NMI
LNE
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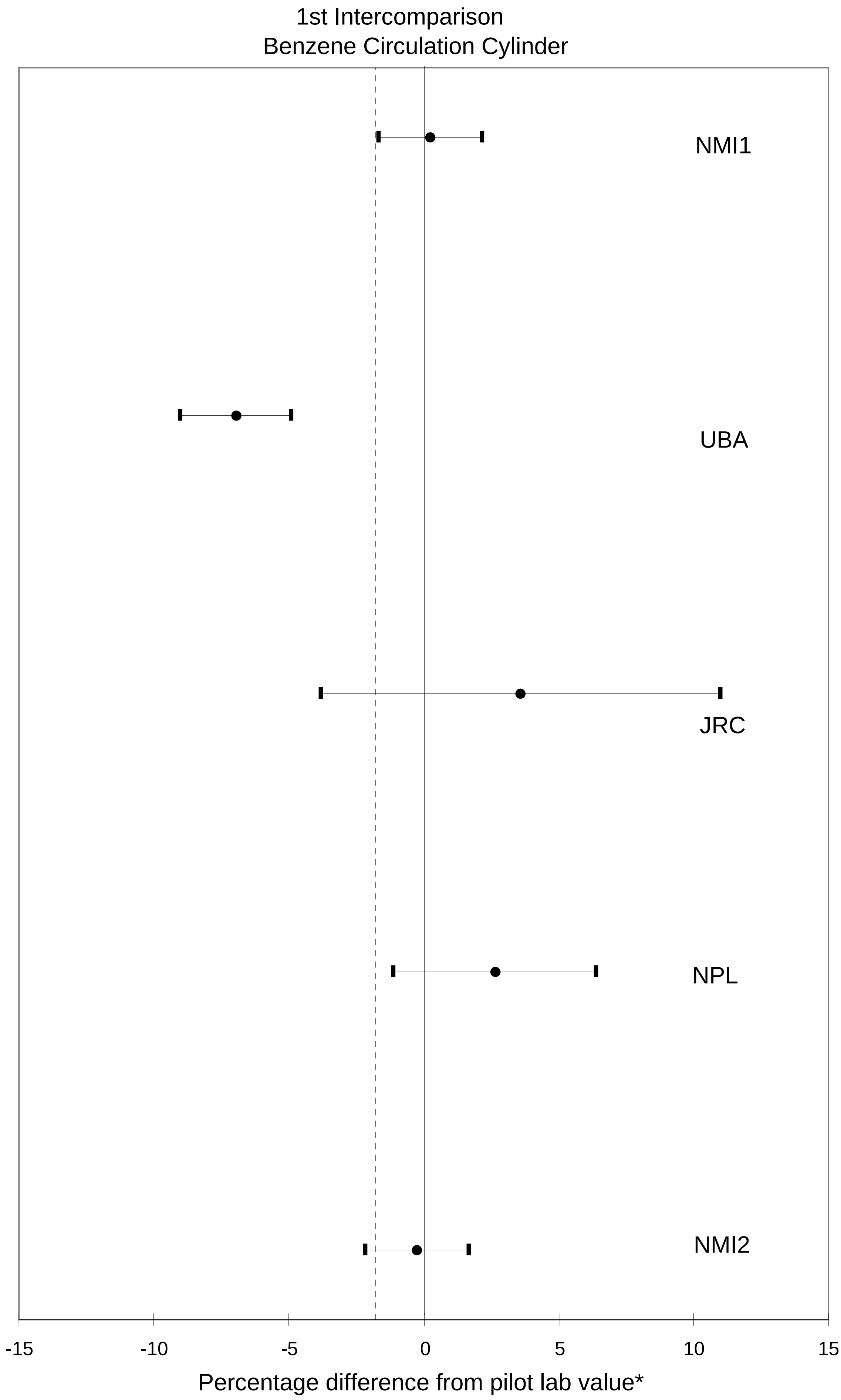
-3
-2
-1
0
1
2
3
4
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values



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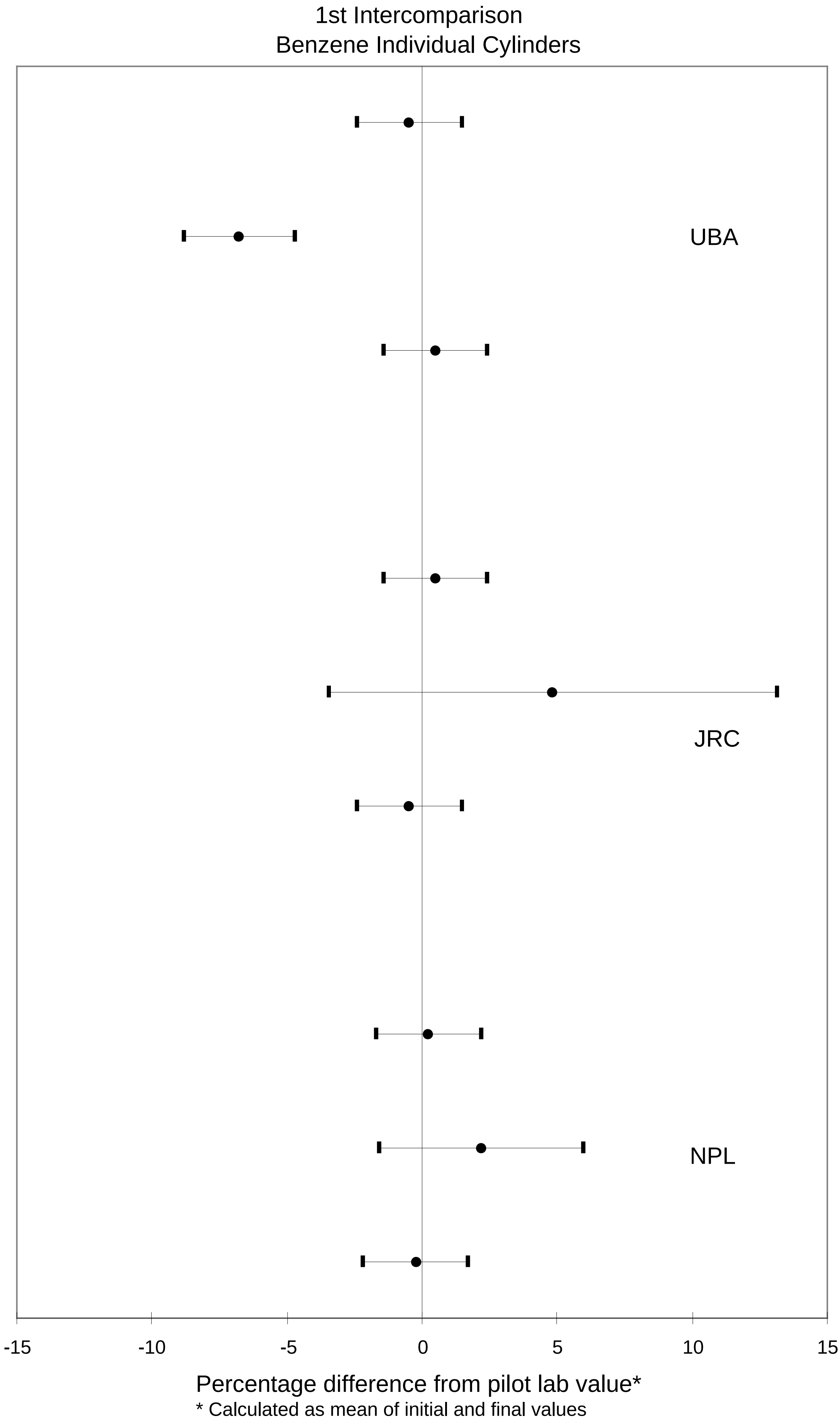
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JRC
NPL
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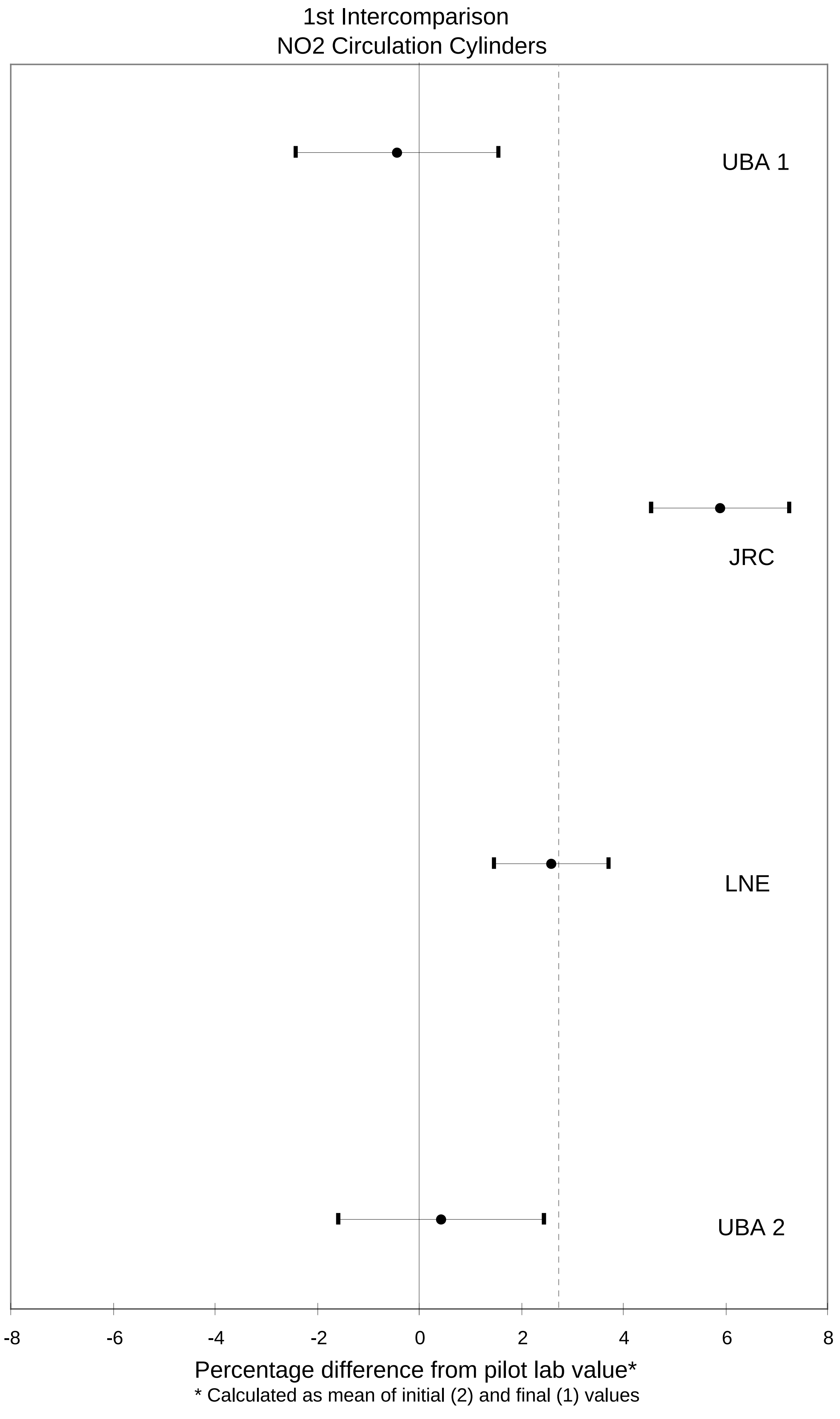
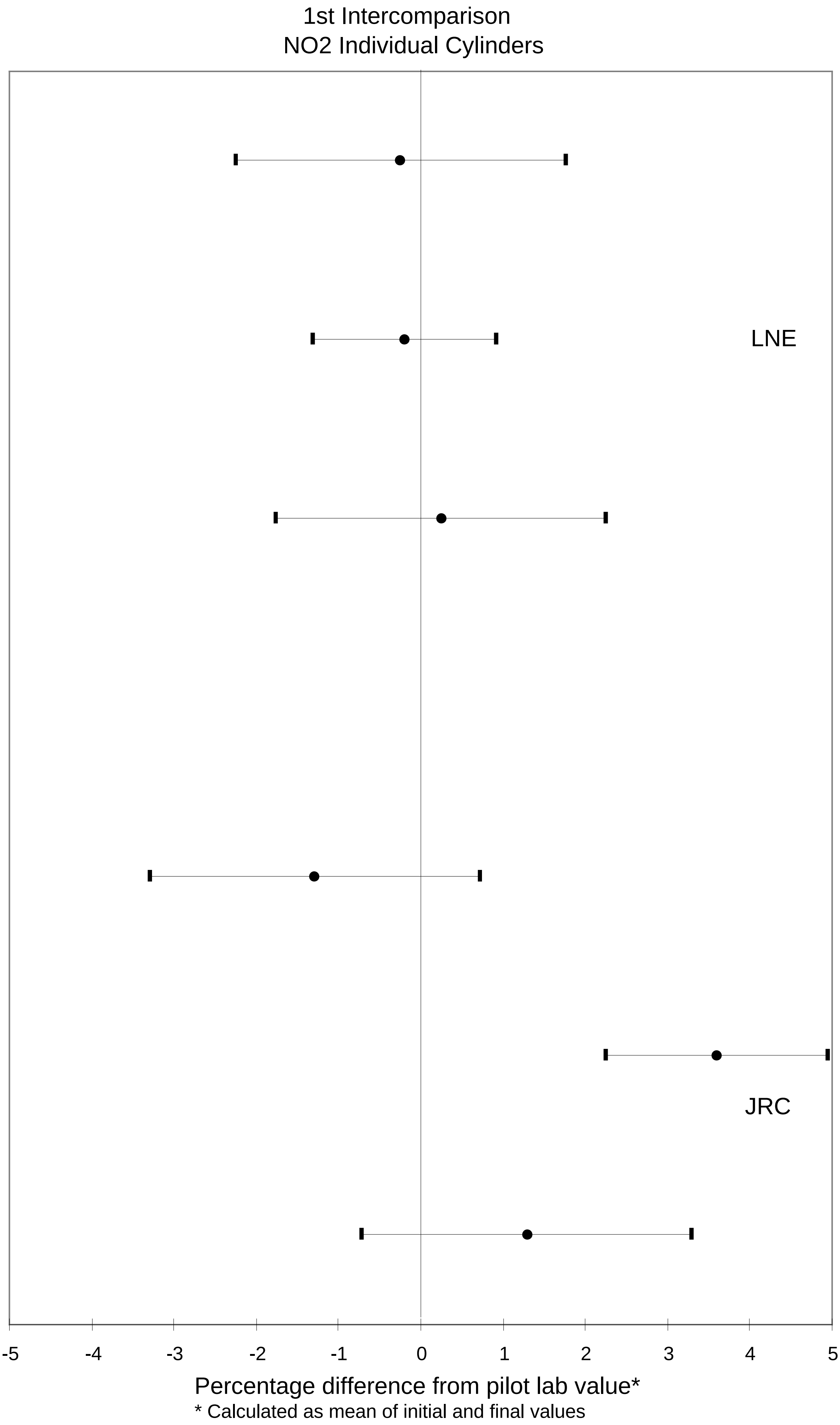
-10
-5
0
5
10
15
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values


1st Intercomparison
NO2 Circulation Cylinders
UBA 1
JRC
LNE
UBA 2
-8
-6
-4
-2
0
2
4
6
8
Percentage difference from pilot lab value*
* Calculated as mean of initial (2) and final (1) values


1st Intercomparison
NO2 Individual Cylinders
LNE
JRC
-5
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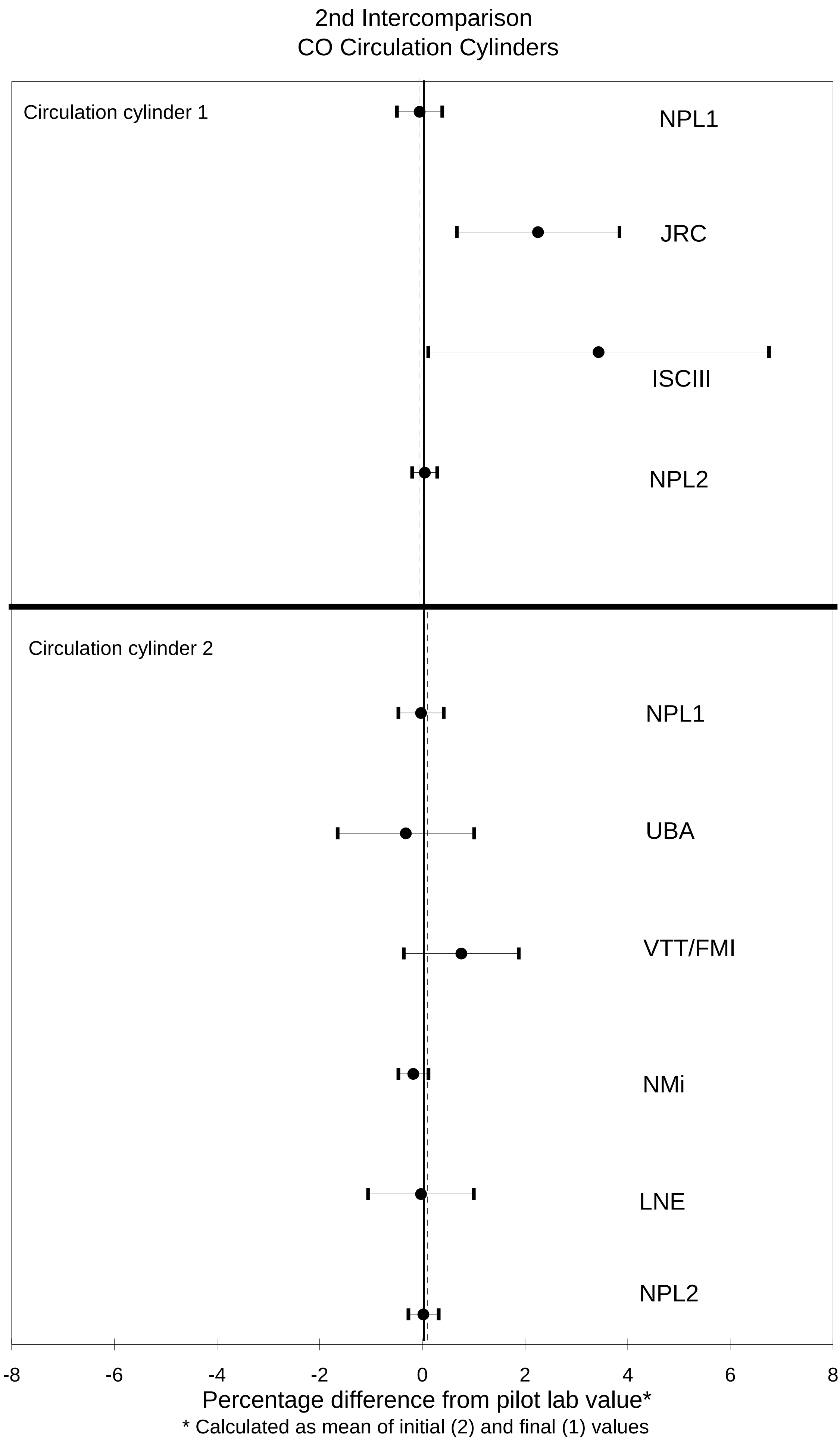
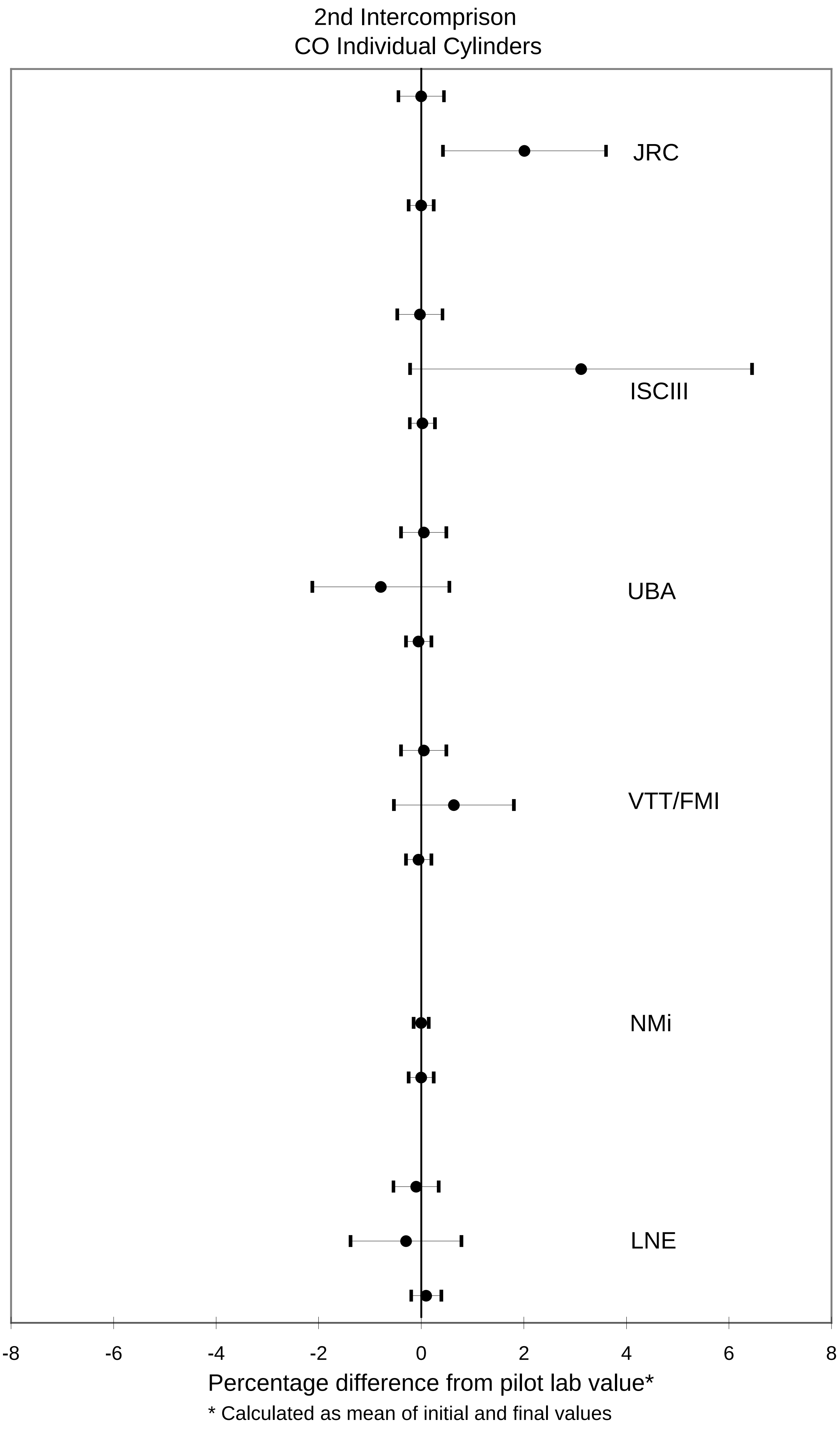
1
2
3
4
5
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values


2nd Intercomparison
CO Circulation Cylinders
Circulation cylinder 1
NPL1
JRC
ISCIII
NPL2
Circulation cylinder 2
NPL1
UBA
VTT/FMI
NMi
LNE
NPL2
-8
-6
-4
-2
0
2
4
6
8
Percentage difference from pilot lab value*
* Calculated as mean of initial (2) and final (1) values


2nd Intercomprison
CO Individual Cylinders
JRC
ISCIII
UBA
VTT/FMI
NMi
LNE
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-6
-4
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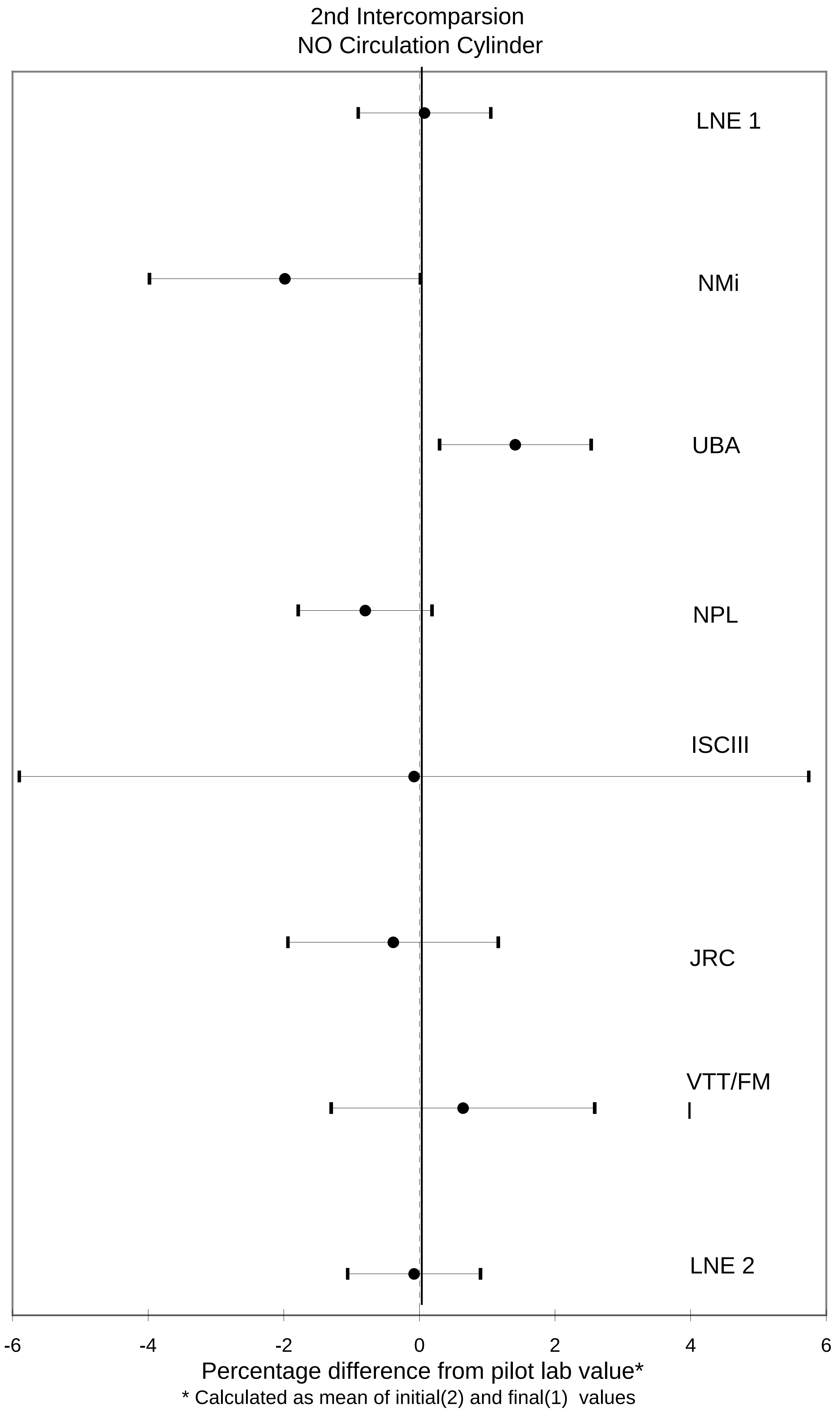
2
4
6
8
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values


2nd Intercomparsion
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LNE 1
NMi
UBA
NPL
ISCIII
JRC
VTT/FM
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LNE 2
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-4
-2
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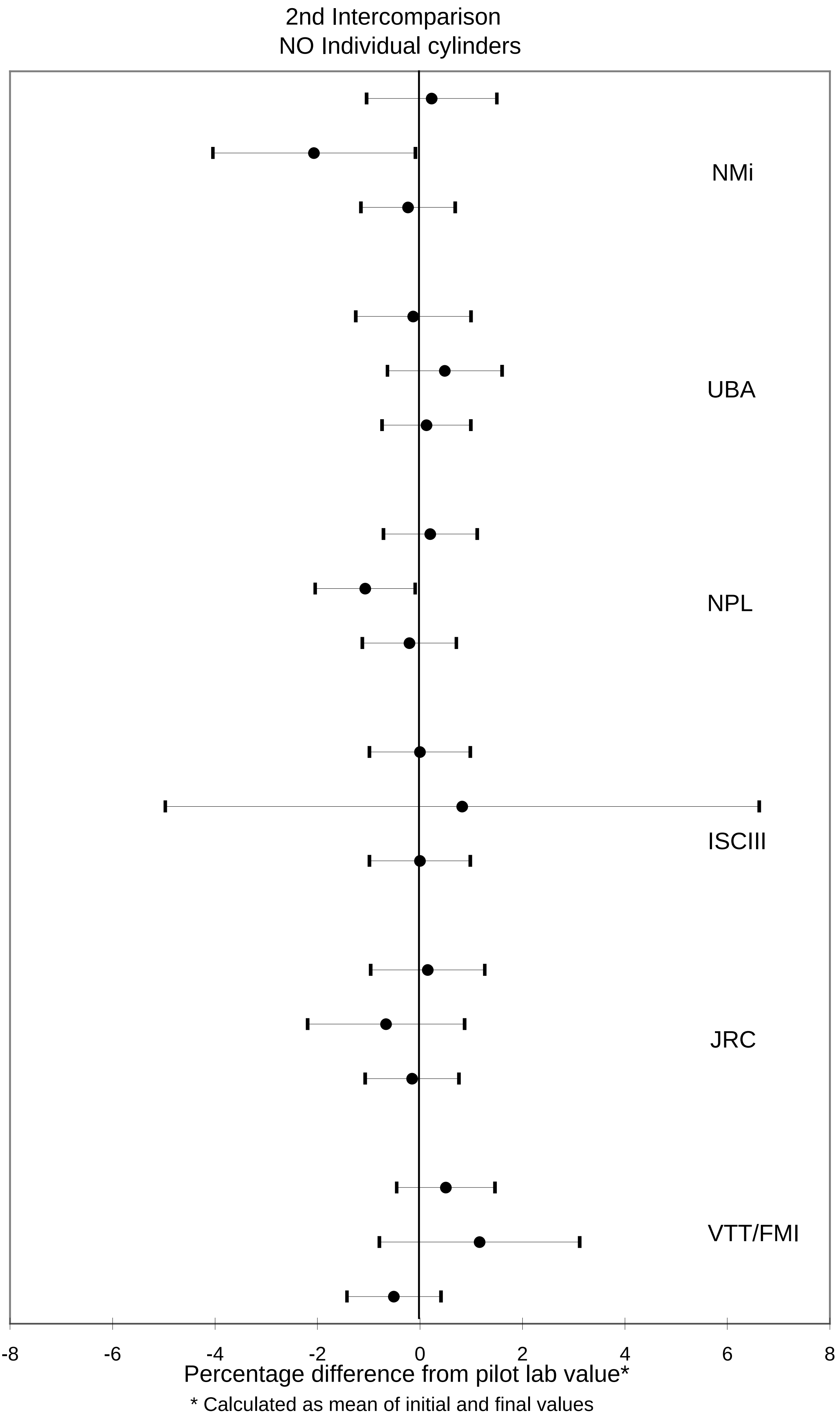
2
4
6
Percentage difference from pilot lab value*
* Calculated as mean of initial(2) and final(1) values


2nd Intercomparison
NO Individual cylinders
NMi
UBA
NPL
ISCIII
JRC
VTT/FMI
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-6
-4
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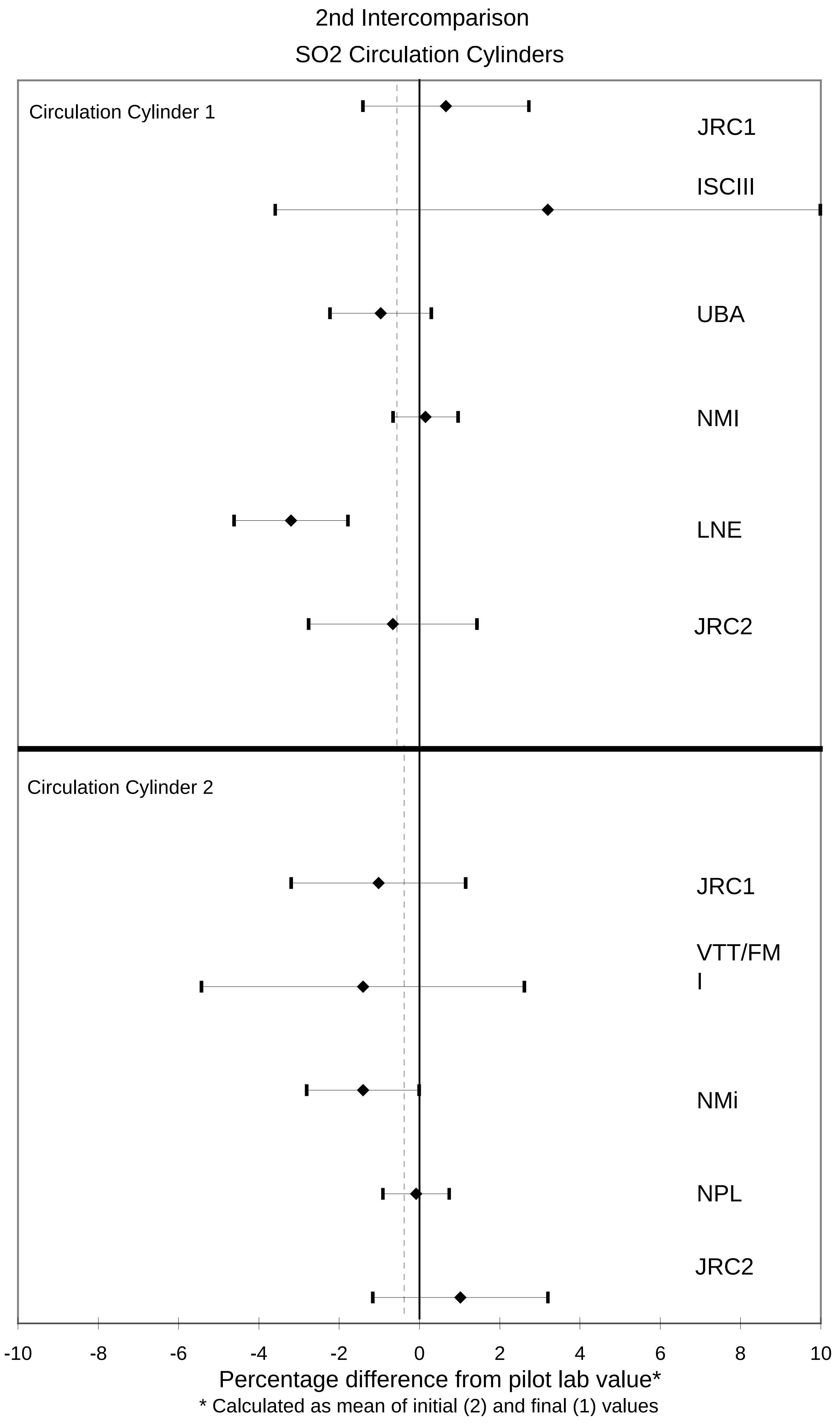
8
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values


2nd Intercomparison
SO2 Circulation Cylinders
Circulation Cylinder 1
JRC1
ISCIII
UBA
NMI
LNE
JRC2
Circulation Cylinder 2
JRC1
VTT/FMI
NMi
NPL
JRC2
-10
-8
-6
-4
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2
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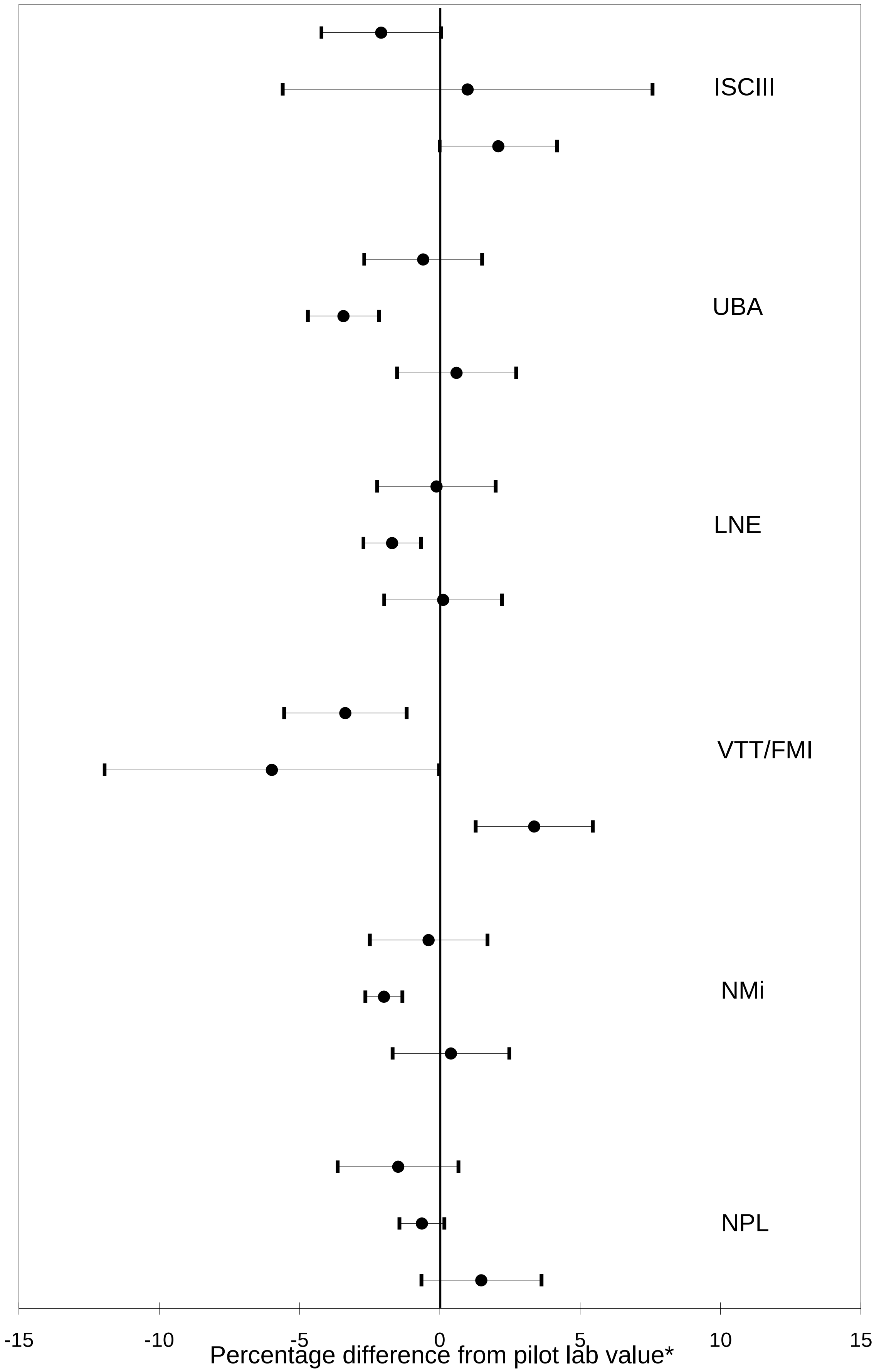
6
8
10
Percentage difference from pilot lab value*
* Calculated as mean of initial (2) and final (1) values

2nd Intercomparison

SO2 individual cylinders



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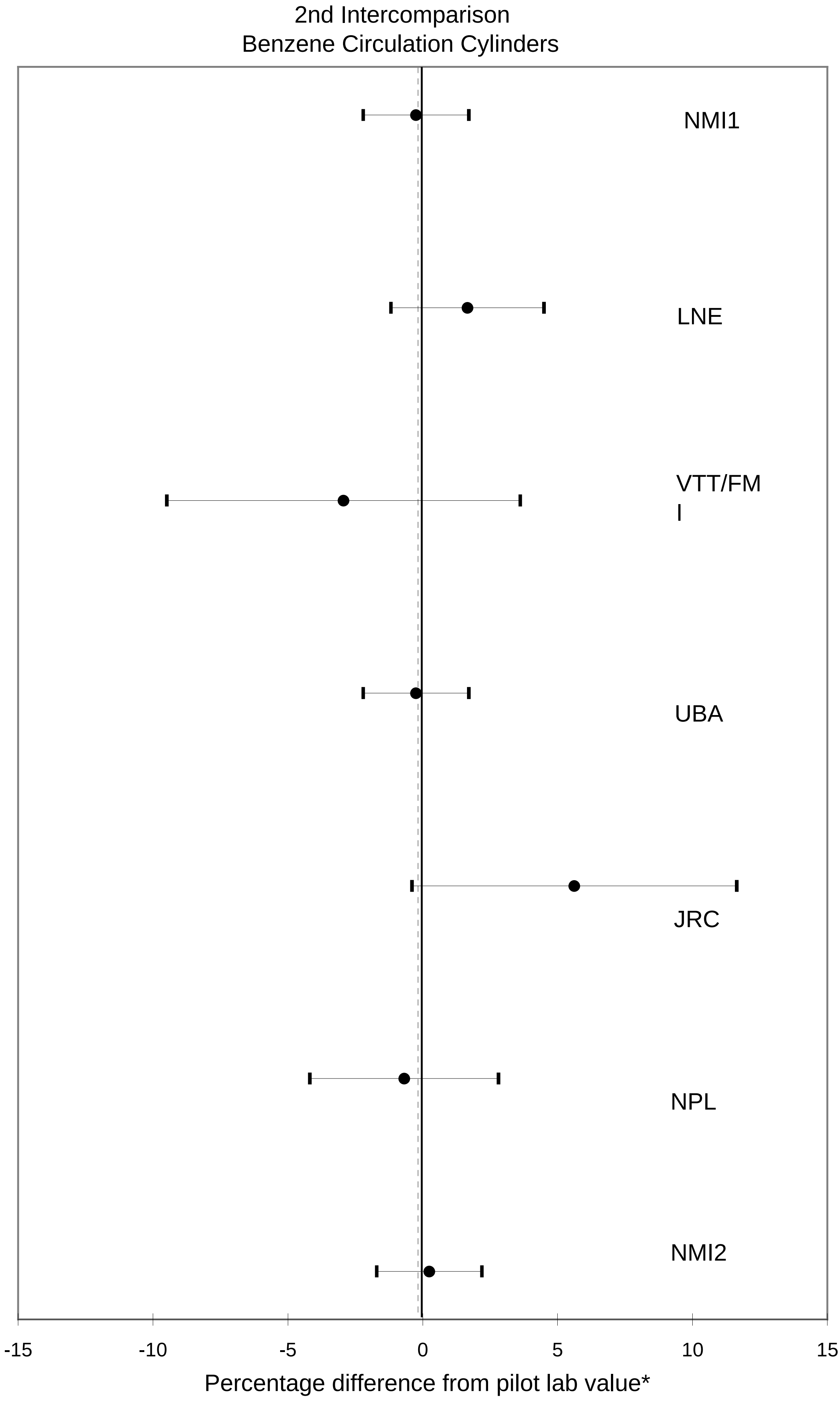

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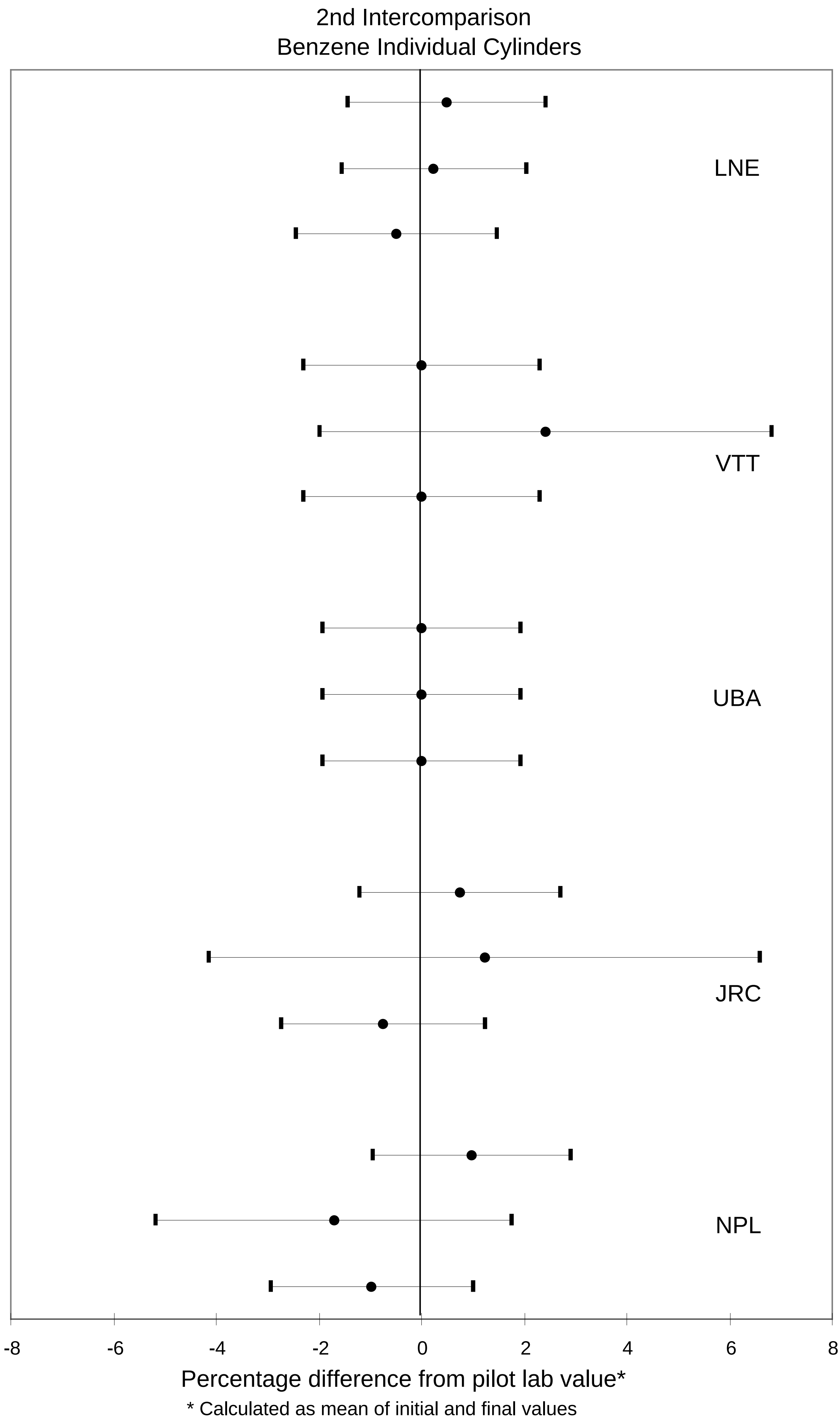
2nd Intercomparison
Benzene Individual Cylinders
LNE
VTT
UBA
JRC
NPL
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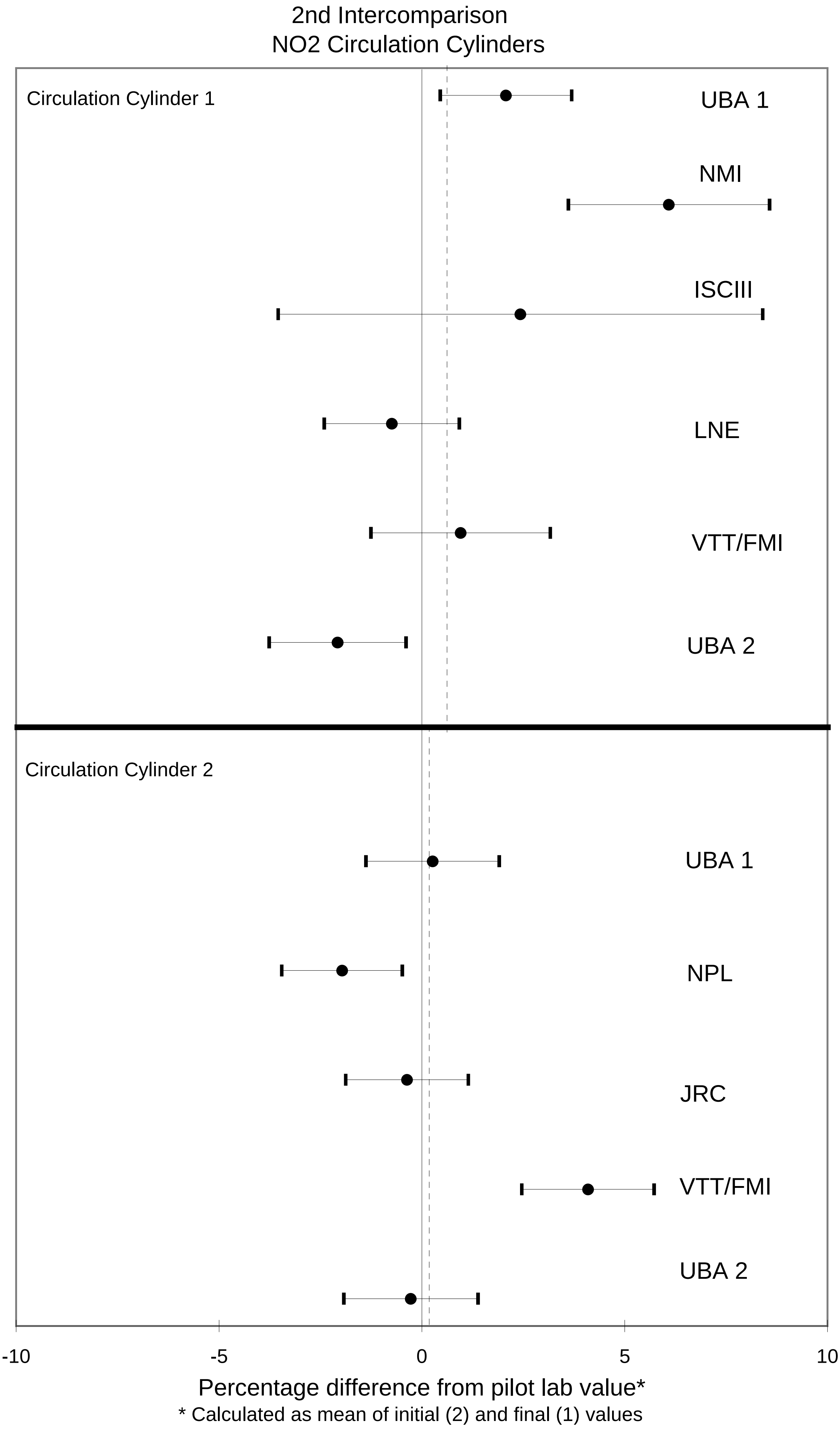
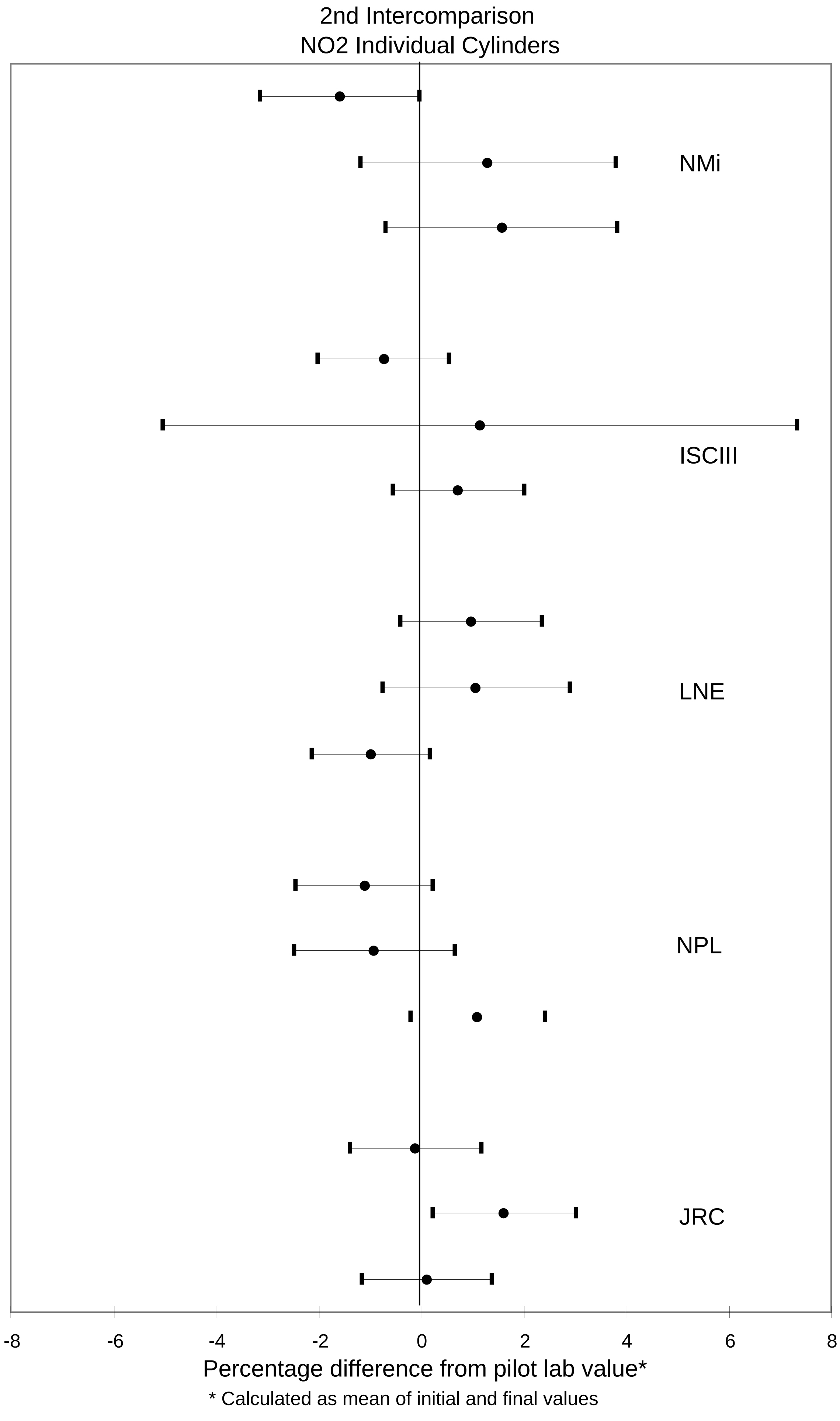
8
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values


2nd Intercomparison
NO2 Circulation Cylinders
Circulation Cylinder 1
UBA 1
NMI
ISCIII
LNE
VTT/FMI
UBA 2
Circulation Cylinder 2
UBA 1
NPL
JRC
VTT/FMI
UBA 2
-10
-5
0
5
10
Percentage difference from pilot lab value*
* Calculated as mean of initial (2) and final (1) values


2nd Intercomparison
NO2 Individual Cylinders
NMi
ISCIII
LNE
NPL
JRC
-8
-6
-4
-2
0
2
4
6
8
Percentage difference from pilot lab value*
* Calculated as mean of initial and final values

APPENDIX 1: HAMAQ: INTERCOMPARISON MEASUREMENTS PROTOCOL

A primary objective of the HAMAQ programme is to determine the level of agreement achievable between primary methods used for the preparation and measurement of gas calibration mixtures. This will be achieved by conducting two intercomparisons. In the first intercomparison the laboratories involved will assess the current level of agreement. In the second these laboratories will demonstrate a good level of agreement. The target level of consistency which we have set for ourselves is 1%. In order to achieve this target we will have to ensure that the measurements are conducted carefully and also that the results are reported in an unambiguous way.

The five gas mixtures (designated groups A …..E) together with the pilot labs responsible for conducting the intercomparisons are indicated below:

Group	Gas	Concentration	Pilot lab
A	CO	20 ppm	NPL
B	NO	200 ppb	LNE
C	SO_2	200 ppb	JRC
D	NO_2	200 ppb	UBA
E	C_6H_6	20 ppb	NMi

By now the gas mixtures prepared by Messer and Scott gases have been delivered to the pilot laboratories. An initial measurement of the 15 gas mixtures should be made by each pilot laboratory. For SO_2, NO_2 and C_6H_6 stability checks on a subset (eg 6) of the mixtures should be conducted for 3 months at the pilot laboratory. This should be done through measurements every 2-3 weeks. After this time the mixtures will be available for shipment to laboratories involved in the intercomparison. The stability data obtained will allow the pilot laboratories (JRC, UBA, NMi) to quantitatively demonstrate the stability of the mixtures in the cylinders. For example, a best fit straight line, together with uncertainties in the gradient will unambiguously quantify the stability of the mixtures within the cylinders.

An objective assessment of the statistical significance of differences between reported measurements will require:

(i) A clear and complete description of the measurement method.

Potential systematic biases in the results may be apparent from a complete description of the primary method (eg gravimetric preparation, permeation etc), the analytical method used to measure unknown gas mixtures (eg NDIR, pulsed flourescence analysers etc) as well as the sample handling procedures.

ACTION: All groups should provide a description of their measurement method to the pilot lab for each gas using the format described in enclosure 2 at the same time they report measurement results. The pilot laboratory should then forward a copy of this information to the coordinator (NPL).

(ii) A robust measurement procedure.

This measurement protocol requires that, for each gas mixture, at least three independent measurement results must be obtained under repeatability conditions and each of these measurements should be conducted using a new calibration, ie calibration > measurement; calibration > measurement; calibration > measurement. A single measurement result is usually derived from a number of sub-measurements (with no intermediate calibrations). The standard deviation of these measurements provides information on the performance of the measurement system. Repeatability conditions are defined here as conditions where mutually independent test results are obtained with the same method on identical test material in the same laboratory by the same operator using the same equipment within short intervals of time (ISO 5725). A short interval in this case could be one day.

ACTION: All groups should observe this measurement protocol and report results, including sub-measurement data, to the pilot laboratory shortly after completion of the measurement. A format for reporting results is included here as enclosure 1. The pilot laboratory should forward a copy of the results to the coordinator (NPL).

(iii) A complete description of the measurement uncertainty

A complete description of the uncertainty analysis, which should be in accordance with the procedures outlined in the ISO document “Guide to the Expression of Uncertainty in Measurement (First Edition 1993)”, should be provided to the pilot laboratories together with the measurement results. The uncertainty reported will take the form of an expanded uncertainty expressed in terms of a combined uncertainty (total standard deviation) and coverage factor.

For guidance only, some potential error sources are listed in enclosure 2, section 5.

ACTION: All groups should carry out an uncertainty analysis following the ISO guidelines and report this analysis to the pilot laboratory. The pilot laboratory should then forward a copy of the analysis to the coordinator (NPL).

<u>Reference</u>

Guide to the Expression of Uncertainty in Measurement, 1993, International Standards Organisation, ISBN 92-67-10188-9.

APPENDIX 2 : WORKSHOP PROGRAMME AND PARTICIPANTS

The Harmonisation of Air Quality Measurements in Europe

The Kaye Room, The National Physical Laboratory, 28th & 29th Sept 1999
Workshop Programme

28th SEPTEMBER

09 00 - 10 00	Registration and Coffee
10 00 - 10 15	Welcome & workshop objectives (Peter Woods/Bill Bell, NPL)
SESSION 1 -	**OVERVIEW OF MONITORING REQUIREMENTS** (chair : Emile De Saeger, ERLAP, JRC)
10 15 - 11 00	The European Air Quality Framework Directive and provisions for data quality (Emile De Saeger)
11 00 - 11 20	Overview of the role of CEN in air quality measurements (Peter Woods, NPL)
11 20 - 11 40	Progress in CEN standards for inorganics and benzene for diffusion tubes (Kevin Saunders, KERIS Ltd)
11 40 - 12 00	Trends and modeling of O_3, CO and NO_2 (Dick Derwent, UKMO)
12 00 - 12 20	The world calibration centre for surface ozone and carbon monoxide (Brigitte Buchmann, EMPA)
12 20 - 14 00	Lunch, Exhibition and Posters.
SESSION 2 -	**THE HARMONISATION OF AIR QUALITY MEASUREMENTS IN EUROPE** (chair: Anton Alink, NMi)
14 00 - 14 15	Overview of the HAMAQ project (Bill Bell, NPL)
14 15 - 14 30	Primary Methods - Gravimetry (Theo Hafkenscheid, NMi)
14 30 - 14.45	Primary Methods - Permeation (Clare Murphy, NPL)
14 45 - 15 00	Primary Methods - Static Dilution (Werner Rudolf, UBA)
15 00 - 15 15	Primary Methods - Dynamic Dilution (Tatiana Mace, LNE)
15 15 - 15 35	Review of Results (Bill Bell)
15 35 - 16 00	Coffee
16 00 - 16 20	Instability of gas calibration mixtures of ambient concentrations (Jiri Novak, CHMI)
16 20 - 16 40	EC Interlaboratory exercise: results of April 99 exercise (Annette Borowiak, JRC)
16 40 - 17 45	Round table discussion
17 45 - 20 45	Reception at Bushy House, NPL

29th SEPTEMBER

SESSION 3 -	**MONITORING IN EUROPE - CURRENT STATUS AND FUTURE PLANS** (chair : Peter Woods, NPL)
09 00 - 09 20	EUROMET Intercomparisons and CEN - the way forward (Martin Milton, NPL)
09.20 - 09.40	Air Quality Monitoring in France in the wake of the new directives (Remy Stroebel, ADEME)
09 40 - 10 00	Air Quality Monitoring in the UK (Paul Quincey, NPL)
10 00 - 10 20	Air Quality Monitoring in Greece (Mr Nikolidakis, GR MoE)
10 20 - 10 40	Harmonisation of Air Pollution Monitoring Networks in Germany (Hans-Ulrich Pfeffer, LUA-NRW)
10 40 - 11 00	Coffee
11 00 - 11 20	The role of the European Environment Agency in Air Quality Monitoring (to be confirmed)
11 20 - 11 40	Air Quality Monitoring in Finland (Jari Walden, FMI)
11 40 - 12 00	Air Quality Monitoring in Sweden (Gunnar Nyquist, ITM)
12.00 - 12.20	Air Quality Monitoring in Italy (Franco De Santis, CNR)
12 20 - 13 00	Round table discussion - the way forward
13 00	Close of Workshop.

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APPENDIX 3 : WEB ADDRESS

Details of the project, and links to participating laboratories can be found at the HAMAQ web page at:

www.npl.co.uk/npl/environment/news/hamaq

APPENDIX 4 : ADDITIONAL WORK

At the time the HAMAQ project was formulated it was planned that the Greek Ministry of the Environment, acting as subcontractors to NPL, would participate in the second intercomparison. Due to internal reorganisation at the Greek Ministry of the Environment this group was no longer able to participate in the intercomparison.

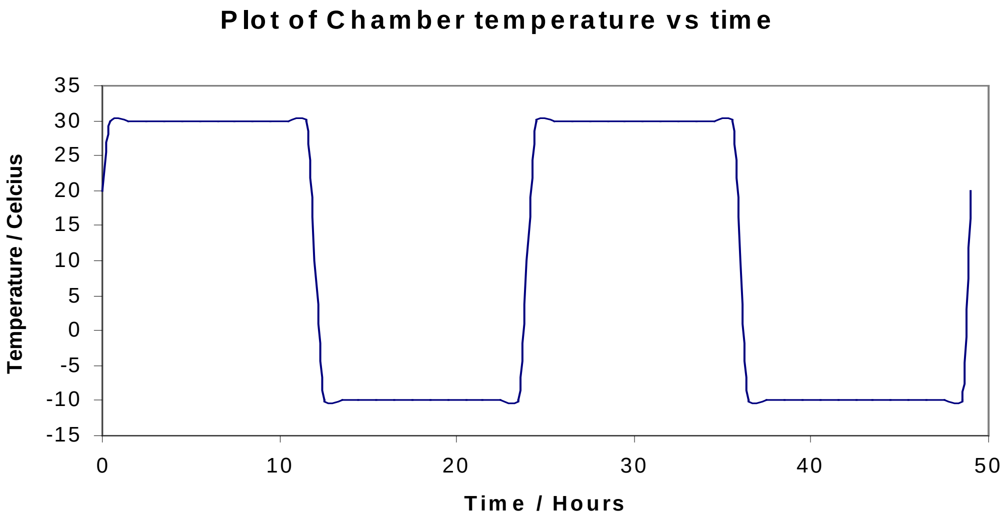
With the agreement of the Commission Officer the resources freed up as a consequence were deployed to address two outstanding issues:

- The sensitivity of low concentration SO_2 cylinders to changes in environmental temperature.
- Improving the measurement uncertainties obtained for CO analyses where analyser linearity is the dominant uncertainty - taking the CO measurements by ISCIII as a case study.

The results of these studies are described below:

1. Environmental tests on low concentration SO_2 gas mixtures in cylinders

For this study a new batch of 10 cylinders of SO_2 at nominal concentrations of 150 ppb and 200 ppb were produced by two European gas manufacturers (five cylinders were produced by each). These cylinders were measured initially relative to the primary permeation facility maintained at NPL. The cylinders were then temperature cycled between -10°C and 30°C over a period of 48 hours in an environmental chamber. The temperature profile is shown in the figure below. After temperature cycling the cylinders were allowed to equilibrate at room temperature. The concentrations were then redetermined by measurements relative to the primary permeation tube facility. The measurements before and after the environmental chamber tests are given in the table below.



RESULTS OF ENVIRONMENTAL TESTS ON SO_2 CYLINDERS

CYLINDER No.	CONCENTRATION BEFORE/PPB	CONCENTRATION AFTER/PPB	%DIFFERENCE
3290	211.03	209.51	-0.7
3292	205.98	204.92	-0.5
3289	208.92	208.10	-0.4
3288	213.06	212.41	-0.3
3291	215.24	215.62	-0.2
C162729	167.04	165.80	-0.7
C162706	163.07	163.12	0.0
C162721	160.94	160.60	-0.2
C162495	145.51	145.01	-0.3
C162728	169.76	170.84	+0.6

Given the uncertainties associated with both before and after measurements of ±1.0% (at 2σ) - none of the observed changes in concentration, ranging from -0.7% - +0.6%, are significant. It can therefore be concluded that for the cylinder types studied in this work, short term (48 hour) temperature variations of 40°C do not effect the gas concentrations within the cylinders.

Further studies on environmental tests of low concentration gases in cylinders should include a systematic study of temperature sensitivity throughout the life of a cylinder (ie as the pressure inside the cylinder is continually reduced).

2. Improved CO measurements : Case study at ISCIII

In the second HAMAQ intercomparison, measurements of CO made by ISCIII showed a discrepancy of +3.4% relative to the pilot laboratory (NPL) measurements for the circulation cylinder and +3.1% relative to the pilot laboratory measurements for the individual intercomparison. However these discrepancies were not significant given the relatively large uncertainties associated with the ISCIII measurements of ±3.3%. These uncertainties were dominated by the component associated with the non-linearity of the NDIR analyser used for the measurements.

In order to improve the measurements a set of new NPL secondary standards at concentrations of 10.02 ppm, 15.04 ppm, 24.99 ppm and 30.01 ppm were prepared and transported to ISCIII together with a new unknown HAMAQ cylinder from the original batch of fifteen. The remeasurement by ISCIII, carried out in January and February 2000 yielded a value of 20.62 ± 0.27 ppm compared with a NPL value of 20.28 ± 0.09 ppm. The discrepancy of 1.7% is not significant given the reported measurement uncertainty and the new uncertainty of ± 1.3% represents a improvement by a factor of 2.5 over the uncertainties achieved by ISCIII in the second intercomparison.

The detailed uncertainty analysis for the ISCIII measurements is given in the tables below.

Analysis 1 of the cylinder 5701208

[570120 **20.61 ppm**
8]=

Symbol	**Source & Uncertainty**	**Value**	**Distribution**	**Divisor**	**C_i**	**U_i**	ν_i
u(std)	Calibration estandar	1.0%	Normal	2	1	0.103	∞
u(z)	Zero air	0.10	Rectangular	√3	1	0.06	∞
u(a)	Analyser uncertainty	0.16	Rectangular	√3	1	0.14	∞
$u(a_1)$	Precision	0.10	Rectangular	√3		0.06	∞
$u(a_2)$	Linearity	0.12	Rectangular	1		0.12	∞
u(DAS)	Data adquisition system	0.01	Rectangular	√3		0.01	∞
u(lin)	Calibration regression line	0.01	Normal	1	1	0.01	7
u(A)	Type A uncertainty	0.06	Normal	1	1	0.06	2
Uc	combined uncertainty		Normal			**0.19**	∞
U	expanded uncertainty		Normal (k=2)			**0.38**	∞

1.9%

Analysis 2 of the cylinder 5701208

[570120 **20.61 ppm**
8]=

Symbol	**Source & Uncertainty**	**Value**	**Distribution**	**Divisor**	**C_i**	**U_i**	ν_i
u(std)	Calibration standard	1.0%	Normal	2	1	0.103	∞
u(z)	Zero air	0.10	Rectangular	√3	1	0.06	∞
u(a)	Analyser uncertainty	0.16	Rectangular	√3	1	0.14	∞
$u(a_1)$	Precision	0.10	Rectangular	√3		0.06	∞
$u(a_2)$	Linearity	0.12	Rectangular	1		0.12	∞
u(DAS)	Data adquisition system	0.01	Rectangular	√3	1	0.01	∞
u(lin)	Calibration regression line	0.25	Normal	1	1	0.25	7
u(A)	Type A uncertainty	0.05	Normal	1	1	0.05	2
Uc	combined uncertainty		Normal			**0.31**	∞
U	expanded uncertainty		Normal (k=2)			**0.62**	∞

3.0%

Analysis 3 of the cylinder 5701208

[570120 **20.63 ppm**
8]=

Symbol	**Source & Uncertainty**	**Value**	**Distribution**	**Divisor**	**C_i**	**U_i**	ν_i
u(std)	Calibration standard	1.0%	Normal	2	1	0.10	∞
u(z)	Zero air	0.10	Rectangular	√3	1	0.06	∞
u(a)	Analyser uncertainty	0.16	Rectangular	√3	1	0.14	∞
$u(a_1)$	Precision	0.10	Rectangular	√3		0.06	∞
$u(a_2)$	Linearity	0.12	Rectangular	1		0.12	2
u(DAS)	Data adquisition system	0.01	Rectangular	√3	1	0.01	∞
u(lin)	Calibration regression line	0.06	Normal	1	1	0.06	2
u(A)	Type A uncertainty	0.00	Normal	1	1	0.00	2
Uc	combined uncertainty		Normal			**0.19**	∞
U	expanded uncertainty		Normal (k=2)			**0.38**	∞

1.8%

[5701208]= 20.62 ppm ± 1.3%

APPENDIX 5: TABLES OF DATA FOR SECOND INTERCOMPARISON

TABLE A: HAMAQ 2nd INTERCOMPARISON

CO INTERCOMPARISON : PILOT LABORATORY NPL

CO Circulation Cylinder 1 (number 5701201)

Laboratory	Date Measured	Derived concentration/ppm	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory NPL = ½ (NPL_1 + NPL_2)
NPL (initial measurement: NPL_1)	13.1, 3.2, 5.2.98	20.37	0.06	0.0
LNE	2.3, 3.3, 4.3.98	20.36	0.43	0.0
NMi	25.5.98	20.33	0.06	-0.2
VTT/FMI	30.8.98	20.52	0.23	+0.8
UBA	16.9.98	20.30	0.27	-0.3
NPL (final measurement: NPL_2)	11.12.98	20.36	0.09	0.0

CO Circulation Cylinder 2 (number 5701218)

Laboratory	Date Measured	Derived concentration /ppm	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory NPL = ½ (NPL_1 + NPL_2)
NPL (initial measurement: NPL_1)	13.1, 3.2, 5.2.98	20.38	0.05	0.0
ISCIII	20.10.98	21.07	0.70	+3.4
JRC	16.11, 17.11,18.11.98	20.83	0.33	+2.3
NPL (final measurement: NPL_2)	18.12.98	20.36	0.09	0.0

CO Individual Cylinders

Laboratory	Cylinder No.	NPL initial measurement (NPL_1) ± 95% Confidence limit	Derived concentration/ppm ± 95% Confidence limit	NPL final measurement (NPL_2) ± 95% Confidence limit	% difference from pilot laboratory NPL = ½ (NPL_1 + NPL_2)
LNE	5701239	20.41 ± 0.06	20.33 ± 0.20	20.37 ± 0.09	-0.3
NMi	5701215	20.37 ± 0.05	20.37 ± 0.03		
VTT/FMI	5701237	20.36 ± 0.05	20.50 ± 0.24	20.38 ± 0.09	+0.6
UBA	5701231	20.35 ± 0.05	20.20 ± 0.27	20.37 ± 0.09	-0.8
ISCIII	5701238	20.37 ± 0.05	21.00 ± 0.70	20.36 ± 0.09	+3.1
JRC	5701227	20.36 ± 0.05	20.77 ± 0.33	20.36 ± 0.09	+2.0

TABLE B: HAMAQ 2nd INTERCOMPARISON

NO INTERCOMPARISON : PILOT LABORATORY - LNE

NO Circulation Cylinder (number 9642)

Laboratory	Date Measured	Derived Concentration/ppb	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory LNE = ½ x (LNE_1 + LNE_2)
LNE (initial measurements: LNE_1)	17.12.97	194.1	1.9	-0.1
VTT/FMI	29.1.98	195.5	3.8	+0.6
JRC	4.3.98	193.5	3.0	-0.4
ISCIII	15.6.98-21.7.98	194.1	11.3	-0.1
NPL	15.9.98	192.7	1.9	-0.8
UBA	22.10.98	197.0	2.2	+1.4
NMi	11.11.98	190.4	3.8	-2.0
LNE (final measurements: LNE_2)	24.11.98	194.4	1.9	+0.1

NO Individual Cylinders

Laboratory	Cylinder No.	LNE initial measurement (LNE_1) ± 95% confidence limits	Derived Concentration ± 95% confidence limit	LNE final measurement (LNE_2) ± 95% confidence limits	% Difference from pilot laboratory ½ x (LNE_1 + LNE_2)
VTT/FMI	A9192	196.3 ± 1.8	199.6 ± 3.9	198.3 ± 1.9	+1.2
JRC	A9600	196.8 ± 1.8	195.8 ± 3.0	197.4 ± 2.2	-0.7
ISCIII	A9595	193.4 ± 1.9	195.0 ± 11.3	193.4 ±1.9	+0.4
NPL	A9495	196.2 ± 1.8	194.5 ± 1.9	197.0 ± 1.8	-1.1
UBA	A9601	196.1 ± 1.7	196.8 ± 2.2	195.6 ± 2.2	+0.5
NMi	A9035	195.8 ± 1.8	192.2 ± 3.8	196.7 ± 2.5	-2.1

TABLE C: HAMAQ 2nd INTERCOMPARISON

SO_2 INTERCOMPARISON : PILOT LABORATORY JRC

SO_2 Circulation Cylinder 1 (number 5791F)

Laboratory	Date Measured	Derived concentration/ppb	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory JRC = ½ x (JRC_1 + JRC_2)
JRC (initial measurement: JRC_1)	10.03.	183.4	4.0	+1.0
NPL	04.06., 09.06., 15.06.	181.4	1.5	-0.1
NMi	23.07., 27.07., 28.07.	179.0	0.4	-1.4
VTT/FMI	08.09., 10.09., 11.09.	179,0	7.2	-1.4
JRC (final measurement: JRC_2)	09.11., 10.11., 01.12.	179.7	3.9	-1.0

SO_2 Circulation Cylinder 2 (number 5421C)

Laboratory	Date Measured	Derived concentration/ppb	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory JRC = ½ x (JRC_1 + JRC_2)
JRC (initial measurement: JRC_1)	14.01.	195.7	4.1	-0.7
LNE	11.03., 12.03., 13.03.	190.7	2.7	-3.2
NMi	14.04., 16.04., 16.04.	197.3	1.6	+0.2
UBA	26.06., 26.06., 26.06.	195.1	2.46	-1.0
ISCIII	30.10, 5.11, 9.11	203.3	13.8	+3.2
JRC (final measurement: JRC_2)	26.11., 27.11., 01.12.	198.3	4.1	+0.7

SO_2 Individual Cylinders

Laboratory	Cylinder No.	JRC initial measurement (JRC_1) ± 95% Confidence limit	Derived concentration ± 95% Confidence limit	JRC final measurement (JRC_2) ± 95% Confidence limit	% difference from pilot laboratory JRC = ½ x (JRC_1 + JRC_2)
NPL	4719A	191.5 ± 4.1	187.5 ± 1.5	185.9 ± 4.0	-0.6
NMi	556949	201.9 ± 4.2	197.4 ± 1.3	200.4 ± 4.2	-1.9
VTT/FMI	4452B	201.2 ± 4.2	183.0 ± 10.9	188.1 ± 4.1	-6.0
LNE	4476B	209.2 ± 4.4	205.4 ± 2.1	208.7 ± 4.4	-1.7
UBA	120 C	202.4 ± 4.3	194.3 ± 2.46	200.0 ± 4.2	-3.4
ISCIII	0715	205.7 ± 4.3	203.5 ± 13.4	197.3 ± 4.2	+1.0

TABLE D: HAMAQ 2nd INTERCOMPARISON

C_6H_6 INTERCOMPARISON : PILOT LABORATORY NMi

C_6H_6 Circulation Cylinder (number 5701213)

Laboratory	Date Measured	Derived concentration/ppb	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory NMi = 0.5 x (NMi_1 + NMi_2)
NMi (initial measurement: NMi_1)		20.5	0.4	
NPL	20.01, 21.01, 02.02	20.31	0.71	-0.7
JRC	09.03, 17.03, 25.03, 01.04	21.6	1.3	+5.6
UBA	17.05	20.4 *	0.4	-0.2
VTT/FMI	07.07	19.85	1.3	-2.9
LNE	17.08, 18.08, 19.08	20.79	0.59	+1.7
NMi (final measurement: NMi_2)		20.4	0.4	

C_6H_6 Individual Cylinders

Laboratory	Cylinder No.	NMi initial measurement (NMi_1) ± 95% Confidence limit	Derived concentration ± 95% Confidence limit	NMi final measurement (NMi_2) ± 95% Confidence limit	% difference from pilot laboratory NMi = ½ x (NMi_1 + NMi_2)
NPL	5701203	20.3 ± 0.4	20.15 ± 0.70	20.7 ± 0.4	-1.7
JRC	5701206	20.1 ± 0.4	20.5 ± 1.1	20.4 ± 0.4	+1.2
UBA	5700264	20.6 ± 0.4	20.6 ± 0.4 *	20.6 ± 0.4	0
VTT/FMI	5701210	17.3 ± 0.4	17.72 ± 0.78	17.3 ± 0.4	+2.4
LNE	5701209	20.5 ± 0.4	20.65 ± 0.25	20.7 ± 0.4	+0.2

** The UBA results are corrected for the difference using another reducer.*

TABLE E: HAMAQ 2nd INTERCOMPARISON

NO$_2$ INTERCOMPARISON : PILOT LABORATORY UBA

NO$_2$ Circulation Cylinder 1 (no. 9811)

Laboratory	Date Measured	Derived concentration/ppb	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory UBA = ½ (UBA$_1$ + UBA$_2$)
UBA (initial measurement: UBA$_1$)	7.2.98	205.6	2.8	-0.3
VTT/FMI	18.3.98	214.6	3.5	+4.1
JRC	8.4.98	205.4	3.1	-0.4
NPL	14.9.98	202.1	3.0	-2.0
UBA (final measurement: UBA$_2$)	30.11.98(?)	206.7	2.8	+0.3

NO$_2$ Circulation Cylinder 2 (no. 9817)

Laboratory	Date Measured	Derived concentration/ppb	Uncertainty (for 95% confidence limit)	% difference from pilot laboratory UBA = ½ (UBA$_1$ + UBA$_2$)
UBA (initial measurement: UBA$_1$)	7.2.98	219.3	2.8	-2.08
VTT/FMI	18.3.98	226.1	5.0	+0.96
LNE	6.4.98	222.3	3.7	-0.74
ISCIII	23-26.11.98	229.4	13.7	+2.43
NMI	24.12.98	237.6	5.9	+6.10
UBA (final measurement: UBA$_2$)	7.7.99	228.6	3.7	+2.08

NO$_2$ Individual Cylinders

Laboratory	Cylinder No.	UBA initial measurement (UBA$_1$) ± 95% confidence limits	Derived concentration ± 95% Confidence limit	UBA final measurement (UBA$_2$) ± 95% confidence limits	% difference from pilot laboratory UBA = ½(UBA$_1$ + UBA$_2$)
JRC	A7511	219.3 ± 2.8	222.6 ± 3.1	218.8 ± 2.8	+1.6
NPL	A9824	214.5 ± 2.8	210.2 ± 3.3	209.8 ± 2.8	-0.9
LNE	A9820	197.7 ± 2.3	201.8 ± 3.7	201.6 ± 2.8	+1.1
ISCIII	A9826	220.5 ± 2.8	221.4 ± 13.7	217.3 ± 2.8	+1.1
NMi	A9499	226 ± 5.1	225.4 ± 5.6	219 ± 3.4	+1.3