WRC WATER RESEARCH CENTRE

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CO-ORDINATION OF ANALYTICAL QUALITY CONTROL FOR DOE HARMONISED MONITORING SCHEME

Final Contract Report to the Department of the Environment, covering the period 1974-1984

Project Leader: D T E Hunt

Authors : S Blake
M J Gardner
D T E Hunt

August 1984

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External: DOE Nominated Officer - 16 copies

Internal: Director, appropriate Assistant Director, plus 3 copies to Divisional Scientific Staff

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SUMMARY

This report summarises the progress made on the contract over the period 1974-1984.

The objective of the work has been to ensure that the analytical results obtained by different laboratories in the Harmonised Monitoring Scheme for River Water Quality are adequately comparable for their intended use. The report describes briefly the approach adopted for collaborative Analytical Quality Control to achieve this objective, and illustrates the results obtained for all the determinands examined in tests of inter-laboratory bias.

The AQC scheme has been successful in allowing the achievement of the required comparability of analytical results for the following determinands; chloride, ammoniacal nitrogen, total oxidised nitrogen (TON) nitrite-nitrogen, suspended solids, BOD (ATU), pH and electrical conductivity. In the case of the trace metals cadmium, copper, lead, mercury, nickel and zinc, the required degree of comparability has, however, not been achieved.

Reasons for the failure to attain the required comparability of analytical results for these determinands are considered, as are also reasons for the poorer progress than was originally expected. It is concluded that detailed re-assessment of the trace metals methods used by participating laboratories, and of their application, is necessary to determine the sources of bias and to rectify them. It is also concluded that progress has been impeded by the lack of well-tested methods for trace metals at the start of the work, and by the limited effort for the work available in participating laboratories. The technical approach to AQC adopted is, however, adjudged to have been successful.

Recommendations are made concerning the conduct of any future Analytical Quality Control work for national river water monitoring.

CONTENTS

1. INTRODUCTION

The Scheme for the Harmonised Monitoring of the Quality of Inland Fresh Water (hereafter the 'Harmonised Monitoring' or 'HM' Scheme) has been described in detail elsewhere[1,2]. After a review of its objectives, these have been restated[2] as:-

1. To provide the DOE with consistent, detailed information on concentrations of substances in water at representative points on the country's river system, sufficient to permit the identification of national trends in water quality.

2. To meet the requirements for data on loads of materials entering estuaries from rivers.

3. To meet the requirements of the EC Decision on the Exchange of Monitoring Information, and the WHO Global Monitoring scheme.

4. To remain sufficiently flexible to permit some adaption to supply information which might be required both to meet future EC directives, and to support the UK position in negotiations on directives.

The analytical data required to fulfil these objectives is provided, under the Harmonised Monitoring Scheme, by Regional Water Authorities in England and Wales and by River Purification Boards in Scotland. Recognising that such data would be provided by many different laboratories and that, unless special steps were taken, the results might well suffer a serious lack of comparability because of analytical errors, the Department of the Environment let a contract to the Water Research Centre (WRC) to coordinate Analytical Quality Control (AQC) work. This work has aimed to ensure that the results obtained from the participating laboratories are of adequate accuracy and comparability.

The contract began in 1974 and, with renewals, has run until 1984. This report summarises the work undertaken during that period, discusses the results which have been obtained and the problems and successes of the AQC programme and makes general recommendations concerning the conduct of AQC work of the kind described, based on experiences with the Harmonised Monitoring Scheme.

In order to illustrate the results obtained during the work, examples are given here of the comparability attained by participating laboratories in both the main and follow-up tests of inter-laboratory bias. The detailed results obtained for each determinand are not reproduced, because these have already been published, by arrangement with DOE, in a series of WRC Technical Reports and papers in the 'The Analyst'; a list of such publications is given in Table 7.

2. THE APPROACH ADOPTED FOR ANALYTICAL QUALITY CONTROL

The approach to AQC adopted for the Harmonised Monitoring Scheme has been described in detail elsewhere[3], and is summarised in Figure 1. It aims to ensure that the analytical requirements are clearly and unambiguously specified, that laboratories select methods capable of meeting such requirements, that the selected methods are applied in such a manner that the requirements are achieved and that adequate accuracy and comparability, once attained, are maintained during the monitoring programme.

The activities shown in Figure 1 are sequential in nature - that is, no stage should be entered until the preceding stage has been satisfactorily completed. The aim is to do everything possible to eliminate sources of error before making tests of inter-laboratory bias, because it is difficult to obtain a direct, experimental estimate of bias for all the different types

of water likely to be encountered and because such bias, if present, may be very difficult to eradicate when laboratories are widely separated geographically[3].

Another important aspect of the sequential character of the approach is the fact that the precision of analytical results is assessed, and improved if necessary to meet the target, before the final assessment of inter-laboratory bias is attempted. In this way, the bias test can be designed in such a manner (e.g. in terms of the number of replicate determinations) that its results are (so far as possible) unambiguously interpretable[3].

The detailed designs of the precision and bias tests are governed by the particular determinand and the required accuracy. In Harmonised Monitoring AQC work, it has been usual to conduct the precision test over a period of 10 days, duplicate determinations being made on each day on each of the following solutions:-

(i) A blank
(ii) A low concentration standard solution
(iii) A high concentration standard solution
(iv) A real sample
(v) The same sample, spiked with the determinand.

By this means, data on the precision of analytical results is obtained for both standards and samples, at concentrations covering the entire range of the method. Additionally, the recovery of the added spike provides a check on certain sources of bias prior to the inter-laboratory bias test itself.

The accuracy of stock standard solutions has been checked by direct comparison, by laboratories, of their solutions with portions of a concentrated standard distributed by WRC.

The control charts established by laboratories are an important factor in the maintenance of the required accuracy. Shewhart-type control charts have been recommended by WRC, though an investigation has also been made - in part, under the present contract - of the potential value of cumulative sum ('Cusum') techniques(4). The latter have certain advantages over Shewhart systems, but the Shewhart type is simpler to construct, maintain and interpret and is recommended if only one type of chart is to be kept, unless prior experience has been gained of both approaches(4).

The main inter-laboratory bias test has typically involved the analysis of two real samples and a dilute standard on each of four or five days. The follow-up tests have also involved four or five replicate determinations, but on only one real sample (usually) in a single day for economy of participants' effort.

To avoid the difficulties of coordinating AQC work in approximately 30 laboratories simultaneously, a tiered system was used. At First Tier level, one laboratory in each RWA and the Forth RPB in Scotland participated. After successful completion of First Tier Work, the laboratories concerned then acted as coordinators for Second Tier Laboratories (if any) in their own authority or region. On successful completion of Second Tier work, the laboratories joined the First Tier participants in follow-up tests of inter-laboratory bias.

Coordination of the AQC work has been accomplished by the Analytical Quality Control (Harmonised Monitoring) Committee, which consisted of representatives of all Regional Water Authorities, Forth River Purification Board (representing the RPB's) DOE, the Scotttish Development Department and the Welsh Office. The Chairman was provided by WRC, and the Secretary by DOE. Technical secretaryship, and the production of Committee papers, were undertaken by WRC. The Committee, which reported to the Freshwater Monitoring Management Group, met 49 times during the contract period - i.e. an average of five times a year.

Under the terms of the contract, WRC provided technical coordination of the AQC work; this involved particularly the design and conduct of the tests, including distribution of samples and standards, and data interpretation and reporting. In the earlier part of the contract period, WRC provided about 1 man-year of effort per annum for the task, but as the scope of the work grew this was increased to about 2 man-years per annum in the later stages.

3. DETERMINANDS DEALT WITH AND TARGET ACCURACIES

Table 1 lists the determinands on which the AQC(HM) Committee has undertaken work, in approximately chronological order, together with the latest agreed requirements for the accuracy of analytical results.

For most determinands, the precision and bias targets have been established in terms of alternative absolute (i.e. concentration) or percentage figures, the larger to apply at any given concentration. (This approach, now widely accepted in the UK Water Industry, allows for the fact that the relative standard deviation of analytical results increases markedly at low concentrations in the range of a method, reaching about 30% at the limit of detection. This fact makes it impossible to set a percentage error target (say a maximum relative total standard of 5%, which may be appropriate and necessary at high concentations) to apply over the entire range of concentations).

The target limit of detection (defined as in reference 3) may, for practical purposes, be taken as equal to the absolute total error target. The latter is the sum of the bias target and twice the total standard deviation target (the total standard deviation multiplied by 2 gives the random error, at the 95% confidence level, on an individual analytical result).

Thus, for example, the target detection limit for mercury can be simply calculated from Table 1 as approximately (0.05 + (0.025 x 2)) = 0.1 µg/l. Similarly, for chloride the target limit of detection is approximately 1 mg/l.

For most of the trace metals listed in Table 1, the total metal content of unfiltered samples has been taken as the determinand of interest. Only in the case of cadmium, considered in more detail below, has the work been directed at filterable metal.

In certain cases, the determinand and/or the accuracy targets have been amended during the course of the work. In the case of Biochemical Oxygen Demand (BOD), laboratories were originally permitted to measure either BOD (Total) or inhibited Biochemical Oxygen Demand, BOD (ATU). A change to BOD (ATU) only was necessitated both by European Community (EC) and UK national requirements. The original bias and total standard deviation targets for BOD were 1.0 mg O_2/l and 0.5 mg O_2/l respectively (giving a total error target of 2.0 mg O_2/l). Because of the increased risk of misclassification of river qualities as the permitted error on BOD results increases, the AQC (HM) Committee and its 'parent', the Freshwater Monitoring Management Group, decided to tighten the targets to 0.5 mg O_2/l (bias) and 0.25 mg O_2/l (total standard deviation), giving a total error target of 1.0 mg O_2/l.

In the case of cadmium, the original determinand was total cadmium and the absolute error targets in early 1982 were 0.5 µg/l (bias) and 0.25 µg/l (total standard deviation), giving an (absolute) total error target and (approximate) detection limit target of 1 µg/l*. At the request of Freshwater Monitoring Management Group these targets were revised downwards by a factor of ten in 1982, to a total error target (absolute) of 0.1 µg/l.

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* Originally, they had been half those values - see discussions on copper, lead, nickel and zinc below.

The reasons for the change were problems in the calculations of loads to sea and the (then) proposed EC Directive on cadmium discharges, which included a Freshwater Environmental Quality Standard of 1.0 µg/l. (Although the final version of the Directive includes an EQS for freshwater of 5.0 µg/l, rather than 1.0 µg/l, there is also a requirement within the Directive to monitor, nationally, against a value of 1 µg/l. The latter would imply, on the basis of UK practice, a target limit of detection of 0.1 µg/l. The final version of Directive, however, includes an implied limit of detection target of 0.25 µg/l).

In the cases of copper, lead, nickel and zinc, the original absolute precision and bias targets were one-half of those quoted in Table 1. Early in the work on these determinands, however, the targets were doubled to their current values in an attempt to achieve more rapid progress. At the time of discussions on cadmium (see above), WRC asked the Freshwater Monitoring Management Group to reconsider the targets for the other trace metals, on the grounds that it was thought likely that they could give rise to similar problems in load calculations, and because national EQS values were then being derived for copper, lead, nickel and zinc. Because the EQS values were not then firmly established, the Freshwater Monitoring Management Group declined to amend the requirements, but advised that they should be kept under review. The apparent cessation of Freshwater Monitoring Management Group activities, and the ending of the AQC contract, have precluded any further changes.

With regard to mercury the EC Directive on discharges to the aquatic environment by the chlor-alkali electrolysis industry implies a limit of detection requirement of 0.05 µg/l for EQS monitoring. This Directive was published in 1982, by which time work on mercury to an implied target of 0.1 µg/l was in train. No change in target was considered at that time, and the work on mercury has since revealed difficulties in meeting the existing requirement.

4. RESULTS AND PROGRESS

The success of the AQC approach adopted in attaining the required degree of comparability of analytical results from different laboratories is illustrated in Figures 2-10. These show typical results for First Tier laboratories in the main inter-laboratory bias tests for chloride, ammoniacal nitrogen, total oxidised nitrogen, nitrite-nitrogen, suspended solids and ash*, BOD (ATU), pH+ and conductivity. For those determinands, all - or virtually all - the First Tier laboratories successfully completed the precision tests and, as the diagrams show, attained the requisite degree of comparability in the inter-laboratory bias test.

In considering these results, it should be noted that the criterion applied to the individual laboratories' results in these inter-laboratory tests (and in the subsequent follow-up tests, discussed below) was that the 'maximum possible bias' (95% confidence level) should not exceed the relevant target value. This is, of course, a more stringent criterion than that the mean bias should lie inside the target, but it is considered important that bias should be closely controlled because its effects - unlike those of random analytical error - are not ameliorated by the fact that, in routine monitoring, summary statistics are derived from many measurements at a given sampling location.

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* Determination of ash was discontinued soon after the AQC bias test was completed.

+ The work on pH determination did not address the problems of pH measurement in waters of low ionic strength and buffer capacity, a subject of increasing interest because of concerns about possible progressive acidification of upland waters, and the inter-laboratory bias test used buffer solutions only, because samples were not sufficiently stable for distribution. The WRC is currently coordinating AQC work on pH measurement in upland waters, in collaboration with the Freshwater Biological Association.

There would clearly be little or no merit in attaining the required degree of comparability at one time, but failing to sustain it over the period of monitoring. The AQC scheme shown in Figure 1 is so designed that there should be, after completion of the first inter-laboratory bias test, a sound basis for the maintenance thereafter of the degree of comparability attained. This is checked by means of the follow-up inter-laboratory bias tests; these have normally been conducted at six-monthly intervals after the main inter-laboratory test, and have included those Second Tier laboratories which have successfully completed earlier stages of the sequential scheme (Figure 1) within their own organisations (see Section 2). The results of follow-up tests for chloride, ammoniacal nitrogen, total oxidised nitrogen, nitrite-nitrogen, suspended solids (using both Kaolin and microcrystalline cellulose suspensions), electrical conductivity and pH are summarised in Figures 11-18. For each test, the number of laboratories involved is given in the figure and the excess of that number over 11 can usually+ be taken as the number of Second Tier laboratories which participated.

In almost all the follow-up tests, over 70% of the participating laboratories achieved the required target; in many cases the percentage was much higher. Although there were instances of failure to meet the targets, the extent to which the latter were exceeded was usually fairly small. For these determinands, therefore, the results obtained - often over a period of many years - can be regarded as broadly satisfactory; the failures which do occur, however, illustrate the value of the continuing check on comparability provided by the follow-up tests. Some determinands - notably ammoniacal nitrogen and suspended solids - have obviously given more difficulty than others.

+ In a few cases, not all the First Tier laboratories may have participated in a follow-up test.

Turning next to the trace metal determinands, the position has here been far less satisfactory. Tables 2-5 contain the results of the last* inter-laboratory bias test for copper, lead, nickel and zinc. It can be seen from these tables (which are taken from the full report of the work on these metals, reference 5) that, despite the considerable time devoted to them, a serious lack of comparability remains. The possible reasons for this have been discussed in detail in the full report of the work(5); they are thought to include a lack of proven, well-tested analytical methods for these determinands at the start of the AQC for them, inadequate control of calibration bias and the protracted nature of the work itself. The latter has, in many of the participant's organisations, spanned a period in which one or more laboratory reorganisations has been conducted. It is felt that, unless the analytical system is established, tested and, if necessary, improved over a period which is short in relation to major cycles of laboratory change, useful progress will be difficult, or impossible, to attain.

Similar considerations may apply to mercury. The results of the last* test of inter-laboratory bias for this determinand, given in Figure 19, again reveal problems(6). However, there are differences between mercury and the other trace metals discussed above:

(i) An SCA method for mercury, capable of meeting the requirements of the scheme, was available at the start of the work. This method, or variants of it, were used by many of the participants.

(ii) A greater measure of improvement during the course of repeated bias tests was observed than in the case of the other metals.

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* Normally, only one mn inter-laboratory bias test was conducted (see Figure 1). In the cases of copper, lead, mercury, nickel and zinc several such tests were undertaken because of the problems which arose.

(iii) The biggest problems remaining appear to lie with the determination of mercury at low concentrations (see Figure 19). Contamination - not thought to be a major factor in the poor results for the other metals - may, therefore, be a major cause of the difficulties.

In the case of cadmium at low concentrations (to a target limit of detection of about 0.1 µg/l), it must be noted that time pressure in the closing year of the contract has prevented the full, sequential AQC Scheme being applied, in that no remedial action between the precision and bias test could be undertaken if the results of the former were unsatisfactory(7). The inter-laboratory bias test - some data from which are given in Figure 20 is valuable, however, in showing to what extent compatability exists at present. Although the results shown in Figure 20 (and others in the full report of the work) clearly indicate that the required degree of comparability has not been attained, the laboratories' performances were better than might have been feared on the basis of the problems encountered with the other trace metals and the low concentrations of cadmium involved.

In addition to the work on analysis per se, discussed above, the problems of sample collection handling and preservation have also been considered in relation to the same determinands. Sample collection and handling procedures in the HM Scheme were investigated by questionnaire and appeared, with some exceptions, to be satisfactory in principle. Many laboratories have examined, by means of detailed experimental tests, the stability of samples taken for the determination of ammoniacal nitrogen, total oxidised nitrogen, and nitrite-nitrogen - again, with broadly satisfactory results. Unfortunately, pressures of effort and time have precluded similar work on suspended solids (except in a couple of cases), BOD (ATU), mercury and pH. (Work on trace metal sample stability, with the exception of mercury, was considered unnecessary because of existing knowledge). The work of the AQC (HM) Committee on sampling and sample preservation is being reported(8).

To summarise the technical aspects, it is apparent that the sequential AQC scheme of Figure 1 has proved effective in achieving the required accuracy and comparability for many determinands. The required comparability has not been achieved, however, in the case of the trace metals cadmium, copper, lead, mercury, nickel and zinc. The previous success of the sequential AQC Scheme in achieving comparability of results for lead in drinking water shows that the flaw does not lie the technical approach to AQC used, but rather in the analytical methods themselves and/or in their application.

Whilst it is important that the failures to achieve adequate comparability of results be clearly identified, it is equally important that the results obtained be placed in a correct perspective. Even in the case of the trace metals, where the required comparability was not achieved, the shortfall is relatively small (inter-laboratory bias up to about ± 20%, rather than ± 10% (5)) in relation to the very poor comparability of results for such determinands obtained by water analysis laboratories 10 years ago, as revealed by the WRC's distribution of 'Standard Analytical Samples'(9). However, it is disappointing that the level of performance attained for the DOE lead survey(10) could not be achieved in this work, for any of the trace metals examined.

Turning next to the time taken to reach the standard of comparability described above, it must first be noted that there is a consensus opinion that it has been far longer than was envisaged at the start of the work in 1974. The average number of determinands dealt with per annum, over the ten-year period, is less than two, which may be regarded as disappointing. Examination of Table 6 - a summary of progress over the period - reveals that the time taken to deal with the trace metals, without full success in the end, has been considerable.

The reasons for this slow progress have been discussed on a number of occasions by the AQC(HM) Committee. It was concluded that major factors have been the lack of established, proven analytical methods for the trace metals at the commencement of AQC work on them, the limited effort available in participating laboratories for AQC work for the Harmonised Monitoring Scheme and, over the last few years of the contract, the effects of laboratory reorganisations.

In the case of BOD, the changes with respect to the required determinand and accuracy caused considerable work, including repetition of tests by some laboratories. The technical difficulties of attaining the more stringent requirements were large, however, and a decision had ultimately to be made to repeat the tests again after all laboratories had adopted the new (draft) SCA method. Though essentially successful, this approach inevitably took considerable time and effort.

Although it has been suggested that the sequential AQC approach of Figure 1 may have contributed to the slow progress, the great majority of AQC(HM) Committee members considered that the time savings which might have arisen had a different approach been used would be very small in relation to the other sources of delay described above. Moreover, the use of alternative approaches or a scaled-down version of the sequential scheme would, they believed, have introduced reductions in the quality of the work disproportionate to any small increase in speed achieved. The authors subscribe to this view, and consider that any attempt to improve the rate of progress of work of the kind described must address the two major difficulties : method availability and the limited available effort for nationally-coordinated AQC. The work of the SCA has helped deal with the former, and it is felt that a wider appreciation of the uses of Harmonised Monitoring data itself might assist the latter. With regard to the technical approach to AQC, it would expedite nationally-coordinated work if all within - authority AQC work were done in the same way and to similar standards, but this seems unlikely to occur in the near future.

With respect to reporting the AQC work, both WRC Technical Reports and papers for 'The Analyst' have been produced on various subjects by arrangement with DOE. Most such publications have appeared in the name of the Analytical Quality Control (Harmonised Monitoring) Committee. A full list is given in Table 7. Appendix A lists meetings at which the work of the AQC (HM) Committee has been presented.

5. CONCLUSIONS AND RECOMMENDATIONS

Inter-laboratory Analytical Quality Control is an essential component of any programme of work, such as the Harmonised Monitoring Scheme, which involves the comparison of analytical results obtained by different laboratories. Numerous studies (see, for example, reference 9) have shown that unless such AQC is undertaken, results are likely often to be of poorer comparability than is adequate for the use to be made of them.

By means of a sequential AQC Scheme, the AQC work undertaken by the Analytical Quality Control (Harmonised Monitoring) Committee since 1974, coordinated by the Water Research Centre under DOE contract, has been able to achieve the degree of comparability required in First, or First and Second, Tier Harmonised Monitoring laboratories for many determinands. These are: chloride, ammoniacal nitrogen, total oxidised nitrogen (TON), nirite-nitrogen, suspended solids, BOD (ATU), pH and electrical conductivity. For the trace metals lead, copper, cadmium, nickel, zinc and mercury, however, the required degree of comparability has not been achieved. In the cases of copper, lead, nickel and zinc, doubling the current bias targets would result in a 'pass' by most laboratories but the results for cadmium and mercury are even less satisfactory in relation to the current targets. It is not, however, suggested that the targets for copper, lead, nickel and zinc be relaxed. On the contrary, it is likely that they should now be made more stringent because of load calculations and EQS monitoring.

The two principal problems which have arisen in the AQC work in general are the slower than expected progress and the failure to achieve the required comparability of results for the trace metals, noted above.

In early stages of the work, the basic approach to the AQC work had to be introduced to laboratories and staff unfamiliar, in many cases, with the procedures involved. This may have slowed progress to some extent, but if so the long-term benefit of introducing the procedures to laboratories is thought to have more than outweighed any short-term cost. The changes of determinand and targets for BOD, and the effort required to achieve the revised, more stringent target for this determinand (with its non-chemical aspects) have also impeded progress over a substantial period of the contract. In the later stages of the work, progress has been impeded by the problems encountered in dealing with the trace metals, particularly. Thus, a common set of causes underlies both the principal problems in these later years of the contract.

It is clear that either the analytical methods selected by laboratories, or their application (or both) are not adequate to allow the bias targets for the trace metals to be met. When the methods for lead, copper, nickel and zinc were being selected in 1977, no SCA or similarly well-tested methods were available, and this fact has undoubtedly made the work more difficult. However, the fact that a well-tested method was available for mercury, and that the performance of individual laboratories has fluctuated during the course of bias tests for the metals, indicates that application of the methods in laboratories is also a factor. A lack of available effort for the work in participating laboratories has often been cited in the Analytical Quality Control (Harmonised Monitoring) Committee as a reason for slow progress in conducting tests, and seems likely also to be at least partly responsible for the evident lack of effective remedial measures between repeated tests of inter-laboratory

bias. Reorganisation of laboratory facilities, and conflict of the AQC work for Harmonised Monitoring with internal Authority AQC work have also been raised as problems affecting the progress of the work. Most members of the AQC (HM) Committee have agreed that the technical approach to AQC adopted is well-founded and not a major contributor to the delays.

In summary, the AQC work conducted has allowed adequate comparability of results from different laboratories to be achieved for the majority of the determinands dealt with, but not for the trace metals. Principal reasons for the slower than expected progress are believed to have been a lack of well-tested methods for many of the trace metals at the time when AQC work on them started, coupled with a lack of available effort for the work in participating laboratories.

The problems encountered with the determination of trace metals, in particular, emphasise the need for continued inter-laboratory Analytical Quality Control if comparability of results to the level required by the Harmonised Monitoring Scheme is to be achieved - indeed, without such AQC, the current position, though not satisfactory, may well deteriorate and the same may be true for the satisfactory position attained, and subsequently maintained over many years, for the other determinands. If reliance is placed in future upon within-Authority AQC work to attain comparability, it is recommended that the effectiveness (or otherwise) of such an approach be assessed by distributions of samples and/or standards to participating laboratories from time to time.

It is further recommended that all participating laboratories undertake a detailed examination of the analytical systems they employ for the determination of the trace metals listed above, so that factors preventing the achievement of adequate accuracy and comparability can be identified and rectified. However, given the introduction of Environmental Quality Standards for EC

List II determinands, it would be prudent for DOE and the water undertakings to review the requirements for national trace metals monitoring and revise the accuracy targets if necessary. (At the same time, any remaining deficiencies in limits of detection in relation to load calculations could be identified and rectified). In this way, if water undertakings need to introduce new methods to meet changed requirements, they may do so without needless expenditure of effort improving current methods which may soon require complete replacement.

Finally, it is recommended that consideration be given to the possibility of increasing the effort available for Harmonised Monitoring AQC work in participating laboratories, however such work is to be conducted and coordinated in future. If national collation of analytical data on river water quality from different laboratories is to continue and is to have value, such data must be adequately comparable, and achieving such comparability - by whatever means - will continue to require substantial effort. A clear exposition of the uses made of such data, and the value of it to Central Government, might be a good starting point for a consideration by DOE and the water undertakings of the best approach to, and effort required for, future Analytical Quality Control for national river water monitoring.

REFERENCES

1. SIMPSON, E.A., 'The Harmonization of the Monitoring of the Quality of Inland Fresh Water', Journal of the Institution of Water Engineers and Scientists, 1978, 32, 45

2. Department of the Environment and National Water Council, Standing Technical Committee Reports, No. 33, 'Standing Technical Advisory Committee on Water Quality, Third Biennial Report, February 1979 - January 1981', HMSO, London, 1983

3. WILSON, A.L., 'Approach for Achieving Comparable Analytical Results from a Number of Laboratories', Analyst, 1979, 104, 273

4. DEWEY, D.J., and HUNT, D.T.E., 'The Use of Cumulative Sum Charts (CUSUM Charts) in Analytical Quality Control', Water Research Centre Technical Report TR 174, 1982

5. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Lead, Copper, Cadmium, Nickel and Zinc in River Waters' Water Research Centre Technical Report TR 213, In press.

6. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Total Mercury in River Waters' Water Research Centre Technical Report, In press.

7. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Trace Concentrations of Dissolved Cadmium in River Waters' Water Research Centre Technical Report, In press.

8. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Sample Collection, Preservation and Storage' Water Research Centre Technical Report, In press.

9. AUSTIN, P.W., CRANE, L., DEWEY, D.J., NIELD, A.H. and SPENCE, I.H., 'Standard Analytical Samples : Results of Distributions 5,6,7,8 and 9' Water Research Centre Technical Report TR 65, 1977

10. RANSON, L. and WILSON, A.L., 'Determination of Lead in Tap Water : Inter-Laboratory Harmonization' Water Research Centre Technical Report TR 28, 1976

11. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Chloride in River Waters' Water Research Centre Technical Report TR 27, 1976

12. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Chloride in River Waters' Analyst, 1979, 104, 290-298

13. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Ammoniacal Nitrogen in River Waters' Water Research Centre Technical Report TR 58, 1976

14. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Ammoniacal Nitrogen in River Waters' Analyst, 1982, 107, 680-688

15. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Total Oxidised Nitrogen and Nitrite in River Waters' Water Research Centre Technical Report TR 63, 1977

16. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Total Oxidised Nitrogen and Nitrite in River Waters' Analyst, 1982, 107, 1407-1416

17. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Total Suspended Solids and Ash (Non-volatile suspended solids) in River Waters' Water Research Centre Technical Report TR 163, 1981

18. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Total Suspended Solids in River Waters' Analyst 1983, 108, 1365-1373

19. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Biochemical Oxygen Demand (ATU) in River Waters' Water Research Centre Technical Report, In press.

20. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Biochemical Oxygen Demand (ATU) in River Waters' Analyst, Submitted for publication.

21. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Total Mercury in River Waters' Analyst, Submitted for publication.

22. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Trace Concentrations of Dissolved Cadmium in River Waters' Analyst, Submitted for publication.

23. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of Lead, Copper, Cadmium, Nickel and Zinc in River Waters' Analyst, Submitted for publication.

24. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of the pH in River Waters' Water Research Centre Technical Report TR 196, 1984

25. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of the Electrical Conductivity in River Waters' Water Research Centre Technical Report TR190, 1983

26. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) COMMITTEE. 'Accuracy of Determination of the Electrical Conductivity and the pH Value of River Waters' Analyst, 1984, 109, 431-437

27. DEWEY, D.J. and CRANE, L., 'The Determination of Suspended Solids and Ash in Waters by Filtration and Ignition' Water Research Centre Technical Report TR 127, 1980

APPENDIX A

MEETINGS AT WHICH THE WORK OF THE AQC(HM) COMMITTEE HAS BEEN PRESENTED

1.	Joint meeting of RSC and IWPC Queens University, Belfast	20 January 1982
2.	Meeting of the Southern Region of RSC, Microchemical Methods Group Portsmouth Polytechnic	5 April 1982
3.	Seminar at the University of Technology Loughborough	16 January 1984
4.	Meeting of the North-West Region of RSC University of Lancaster	14 March 1984

Table 1. Current Accuracy Requirements

Notes: (1) The maximum tolerable total error is given by twice the total standard deviation target plus the bias target.

(2) The target Limit of Detection is essentially equal to the maximum tolerable total error (absolute, not percentage). For example, for chloride it is 1 mg/l and for cadmium it is 0.1 µg/l.

The larger of the two alternatives applies for any result.

Determinand	Precision target*	Bias target**
Chloride	5% of determinand concentration or 0.25 mg l^{-1}	10% of determinand concentration or 0.5 mg l^{-1}
Ammoniacal Nitrogen Total Oxidised Nitrogen Nitrite	5% of determinand concentration or 0.025 mg N l^{-1}	10% of determinand concentration or 0.05 mg N l^{-1}
Suspended Solids and Ash	5% of determinand concentration or 0.5 mg l^{-1}	10% of determinand concentration or 1 mg l^{-1}
BOD (ATU)	0.25 mg O_2 l^{-1} standard deviation on sample measured in test (whether diluted or not). BOD of diluted samples to be >4.0 mg O_2 l^{-1} on sample measured in test	0.5 mg O_2 l^{-1} in sample measured in test
Pb, Cu, Ni, Zn	5% of determinand concentration or 2.5 ug l^{-1}	10% of determinand concentration or 5 ug l^{-1}
Cd	5% of determinand concentration or 0.025 ug l^{-1}	10% of determinand concentration or 0.05 ug l^{-1}
Hg	5% of determinand concentration or 0.025 ug l^{-1}	10% of determinand concentration or 0.05 ug l^{-1}
pH	0.05 pH unit	0.1 pH unit
Conductivity	5% of determinand concentration or 1.25 uS cm^{-1}	10% of determinand concentration or 2.5 uS cm^{-1}

* target refers to total standard deviation of analytical results
**target refers to maximum tolerable bias

Table 2. Results of the most recent test of inter-laboratory bias (January 1983) — Copper
(All results in μ/1 unless otherwise indicated)

Laboratory Number	Low concentration river water				Standard solution				High concentration river water			
	Mean result	Standard deviation	Difference from mean of all results (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean value (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean of all results (%)	Maximum possible bias (%)
1	25.11	0.86	0.36	1.37	39.33	0.71	−0.67	−1.50	55.65	1.48	2.44	5.65
2	24.25	0.65	0.49	−1.25	38.88	0.85	−1.13	−2.13	54.63	0.85	0.55	2.40
3	23.63	1.60	−1.12	−3.00	36.75	3.12	−3.25	−6.92*	49.75	4.37	−8.42	−17.88*
4	20.85	0.45	−3.89	−4.42	31.60	0.82	−8.40*	−9.37*	48.48	0.86	−10.77*	−12.63*
5	26.63	1.50	1.88	3.65	38.48	0.64	−1.52	−2.28	56.45	0.53	3.91	5.06
6(1)	27.17	0.46	2.43	2.97	36.37	0.79	−3.62	−4.55	55.37	1.45	1.92	5.07
7(2)												
8	26.30	1.61	1.56	3.45	38.40	0.88	−1.60	−2.64	58.70	1.15	8.05	10.54*
9	24.45	0.58	0.71	1.38	41.20	1.26	1.20	2.68	56.45	1.73	3.91	7.66
10(1)												
11	25.75	0.50	1.01	1.59	36.75	0.96	−3.25	−4.38	54.50	3.00	0.32	6.82
Mean of all laboratories	24.74				Mean of all laboratories	37.67			Mean of all laboratories	54.33		
WRC (analysed) value	24.6				WRC value (prepared concn)	40			WRC (analysed value	58.0		

Notes

(1) Although Laboratories 6 and 10 did analyse the solutions distributed in this test, their original results are not presented because no evidence was available that the precision of the method used was adequate. Laboratory 6 subsequently performed analysis using the method for which precision tests had been performed. These results are shown but have not been used in the calculation of the mean result of laboratories owing to their late receipt.

(2) Laboratory 7 did not report results for this test.

Table 3. Results of the most recent test of inter-laboratory bias (January 1983) — Lead
(All results in μg/1 unless otherwise indicated)

Laboratory Number	Low concentration river water				Standard solution				High concentration river water			
	Mean result	Standard deviation	Difference from mean of all results (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean value (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean of all results (%)	Maximum possible bias (%)
1	26.52	0.58	2.30	2.98	39.31	1.11	−0.69	−2.00	55.62	0.75	8.46	10.19*
2	24.50	0.71	0.28	1.11	36.88	1.03	−3.13	−4.34	51.63	0.25	0.68	1.26
3	21.63	1.89	−2.59	−4.81	36.25	2.20	−3.75	−6.34*	46.13	4.01	−10.04*	−19.30
4	23.63	0.95	−0.59	−1.70	34.63	3.35	−5.38*	−9.32*	52.88	0.85	3.12	5.09
5	23.55	0.24	−0.67	−0.95	37.23	0.13	−2.77	−2.92	50.53	0.47	−1.46	−2.55
6(1)	27.90	1.53	3.68	5.47*	42.42	0.89	2.42	3.47	52.47	0.61	2.32	3.72
7(2)												
8(1)												
9	26.20	0.96 1.98	3.10		42.70	0.50	2.70	3.29	56.20	1.50	9.59	13.06*
10(1)												
11	23.50	4.43	−0.72	−5.94*	33.75	2.75	−6.25*	−9.49*	46.00	4.08	−10.30*	−19.74*

Mean of all laboratories 24.22
WRC (analysed) value 25.5

Mean of all laboratories 37.89
WRC value (prepared concn) 40

Mean of all laboratories 51.28
WRC (analysed) value 55.1

The target for maximum possible bias is 10% of the concentration of the sample of 5 μg/1 (whichever is the larger).
*Exceeds target
The values given for maximum possible bias are quoted at a confidence level of 95%

Notes

(1) Although Laboratories 6, 8 and 10 did analyse the solutions distributed in this test, their original results are not presented because no evidence was available that the precision of the method used was adequate. Laboratory 6 subsequently performed analysis using the method for which precision tests had been performed. These results are shown but have not been used in the calculation of the mean result of laboratories owing to their late receipt.

(2) Laboratory 7 did not return results for this test.

Table 4. Results of the most recent test of inter-laboratory bias (January 1983) — Nickel (All results in μg/1 unless otherwise indicated)

Laboratory Number	Low concentration river water				Standard solution				High concentration river water			
	Mean result	Standard deviation	Difference from mean of all results (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean value (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean of all results (%)	Maximum possible bias (%)
1	24.62	1.33	1.86	3.42	39.92	0.85	−0.08	−.08	63.49	0.73	7.23	8.95
2	26.13	1.80	3.37	5.48*	38.25	2.25	−1.75	−4.40	66.88	3.92	12.95*	20.63*
3	20.63	1.18	−2.13	−3.52	34.13	1.80	−5.88*	−7.99*	51.50	3.66	−13.02*	−20.18*
4	21.00	0.96	−1.76	−2.89	31.75	2.65	−8.25*	−11.36*	57.00	1.50	−3.73	−6.66
5	22.48	0.30	−0.28	−0.63	37.30	1.49	−2.70	−4.45	59.18	0.72	−0.05	−1.46
6(1)	25.07	1.17	2.31	3.70	38.47	2.63	−1.52	−4.61	70.00	2.59	18.22 *	23.29*
7(2)												
8(1)												
9	21.95	0.82	−0.81	−1.79	37.95	0.82	−2.05	−3.01	60.20	0.96	1.67	3.55
10(1)												
11	22.50	1.29	−0.26	−1.78	35.75	1.26	−4.25	−5.73*	56.25	1.71	−5.03	−8.37

Mean of all laboratories 22.76
WRC (analysed) value 25.6

Mean of all laboratories 37.26
WRC value (prepared concn) 40

Mean of all laboratories 59.21
WRC (analysed) value 66.0

The target for maximum possible bias is 10% of the concentration of the sample of 5 μg/1 (whichever is the larger).
*Exceeds target
The values given for maximum possible bias are quoted at a confidence level of 95%

Notes

(1) Although Laboratories 6 8 and 10 did analyse the solutions distributed in this test, their original results are not presented because no evidence was available that the precision of the method used was adequate. Laboratory 6 subsequently performed analysis using the method for which precision tests had been performed. These results are shown but have not been used in the calculation of the mean result of laboratories owing to their late receipt.

(2) Laboratory 7 did not report results for this test.

Table 5. Results of the most recent test of inter-laboratory bias (Janaury 1983) — Zinc
(All results in μg/1 unless otherwise indicated)

Laboratory Number	Low concentration river water				Standard solution				High concentration river water			
	Mean result	Standard deviation	Difference from mean of all results (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean value (μg/1)	Maximum possible bias (μg/1)	Mean result	Standard deviation	Difference from mean of all results (%)	Maximum possible bias (%)
1	20.51	0.09	0.36	0.46	38.92	0.94	−1.08	−2.19	52.59	0.88	4.54	6.58
2	20.25	1.32	0.10	1.66	34.75	0.65	−5.25*	−6.01*	50.00	0.41	−0.61	−1.57
3	18.25	1.00	−1.90	−3.07	36.00	1.76	−4.00	−6.07*	45.88	1.60	−8.81	−12.55*
4	19.13	2.66	−1.02	−4.15	33.88	0.63	−6.13*	−6.87*	46.88	3.42	−6.82	−14.83*
5	18.98	0.33	−1.17	−1.56	39.90	0.54	−0.10	−0.73	50.23	0.17	−0.16	−0.56
6(1)	25.55	0.99	5.40*	6.57*	41.20	0.68	1.20	2.00	54.57	0.40	8.48	9.42
7(2)												
8	23.08	0.90	2.93	3.99	38.85	0.95	−1.15	−2.27	54.65	0.39	8.63	9.54
9	19.75	0.00	−0.40	−0.40	39.50	0.96	−0.50	−1.63	51.25	0.58	1.87	3.22
10(1)												
11	21.25	2.63	1.10	4.20	36.50	1.73	−3.50	−5.54*	51.00	3.27	1.38	9.01
Mean of all laboratories	20.15				Mean of all laboratories	37.29			Mean of all laboratories	50.31		
WRC (analysed) value	20.9				WRC value (prepared concn)	40			WRC (analysed) value	55.2		

The target for maximum possible bias is 10% of the concentration of the sample of 5 μg/1 (whichever is the larger).
*Exceeds target
The values given for maximum possible bias are quoted at a confidence level of 95%

Notes

(1) Although Laboratories 6 and 10 did analyse the solutions distributed in this test, their original results are not presented because no evidence was available that the precision of the method used was adequate. Laboratory 6 subsequently performed analysis using the method for which precision tests had been performed. These results are shown but have not been used in the calculation of the mean result of laboratories owing to their late receipt.

(2) Laboratory 7 did not return results for this

Table 6. Summary of Progress to End of Contract - July 1984

Key to activities in the sequential programme of Analytical Quality Control (AQC) used in the Harmonised Monitoring Scheme.

For each determinand the following stages form the sequence of AQC work at each laboratory.

A Commencement of within laboratory precision and recovery tests

B Completion of A above and, where relevant, comparison of calibration standards. Establishment of within laboratory control charts.

C Tests of inter-laboratory bias

D On satisfactory completion of stage C, routine 6-monthly follow-up checks are commenced.

E Reporting of First Tier work : (i) as a WRC Technical Report
(ii) as a WRC TR and a paper in the "Analyst"

F Examination of sample stability

Table 6 continued

The following table summarises progress under these headings:

Determinand	Year Work Begun	Progress in First tier - 11 labs A	B	C	D	E	F	Number of Second labs at stage D *
chloride	1974	✓	✓	✓1975	✓	✓ii	NA	18
ammonia	1975	✓	✓	✓1975	✓	✓ii	✓	18
nitrite	1975	✓	✓	✓1975	✓	✓ii	✓	18
TON	1975	✓	✓	✓1975	/	✓ii	✓	18
suspended solids	1976	✓	✓	✓1976	✓	✓ii	✓	9
BOD (N1)	1976	✓	✓	✓1977	✓N1	NA	NA	9
BOD(ATU) (N2)	1982	✓	✓	✓1983	-	✓ii	-	0
lead	1977	✓	✓	✓1979	-N3	✓ii	N5	- N7
copper	1977	✓	✓	✓1979	-N3	✓ii	N5	- N7
nickel	1977	✓	✓	✓1979	-N3	✓ii	N5	- N7
zinc	1977	✓	✓	✓1979	-N3	✓ii	N5	- N7
cadmium (high level)	1977	✓	✓	✓1979	N4	✓ii	N5	- N7
conductivity	1980	✓	✓	✓1982	✓	✓ii	-	0 N6
pH	1980	✓	✓	✓1982	✓	✓ii	-	0 N6
mercury	1980	✓	✓	✓1982	-N3	✓ii	N5	- N7
cadmium (low level)	1983	✓	✓	✓1983	-N4	✓ii	N5	- N7

Notes

Year work begun : Year shown is year of start of Stage A
✓ : Indicates that stage has been reached, though not necessarily completed successfully in all laboratories in the case of stages C, D and F
NA : Not applicable
- : Stage not reached

Laboratory 11 did not participate in the initial tests of precision, but successfully joined the scheme at a later date

Table 6 continuted

* The number of laboratories participating at Second Tier level has fluctuated with successful completion of precision tests and entry into the follow-up test series and with laboratory reorganisations.

N1 : Early BOD work had covered BOD(Total). After the NWC Classification of River Water Quality specified only BOD(ATU), FMMG decided that the latter was required for the Scheme. A change in targets was also agreed (to one half the original value) and laboratories were asked to submit precision data for BOD(ATU) if they had previously reported only BOD(Total). The majority of laboratories were unable to meet these new targets with their existing methods and after several bias tests the decision was taken to restart BOD - see note N2.

N2 : Work on BOD(ATU) was restarted in 1982 and successfully completed in 1983. Laboratories used the draft SCA method for BOD with several minor amendments/recommendations made by the Committee.

N3 : (i) METALS : Several inter-laboratory bias tests have been conducted, without full comparability being attained, since 1979. The final test of inter-laboratory bias was conducted in February 1983. Without a complete re-examination of methods and repeat of precision testing it was felt that no further progress could be made. Laboratories were unable to devote the extra effort required to achieve this before the end of the contract and so it was decided to report the work to this stage.

(ii) MERCURY : Although precision tests were completed satisfactorily the subsequent bias tests were unsuccessful. After a repeat of the comparison of standards test, the results from a third inter-laboratory bias test (in December 1983) showed a significant improvement, although several laboratories still failed to meet the specified targets. No time was available to continue tests for this determinand.

N4 : CADMIUM : Work on this determinand to a target limit of detection of 0.1ug/l began in 1982. The ending of the contract precluded normal application of the sequential AQC Scheme, though precision and bias tests were conducted. The bias test revealed a number of failures to meet the target.

N5 : (i) METALS - PRESERVATION : The availability of suitable method of preservation precluded the need to test for sample stability for the metals Cd,Cu,Pb,Ni and Zn.

(ii) MERCURY - PRESERVATION : The use of an acid/dichromate preservative has been recommended by many workers and was agreed by the Committee for use by the participating laboratories.

Table 6 continued

Several laboratories, however, with current methods incorporating other preservatives did not change to that agreed by the Committee. Tests of the ability of the various preservatives employed by the laboratories were not undertaken because the bias test was not successfully completed by all laboratories and because of lack of time before the contract ended.

N6 : No Second Tier laboratories had reached this stage by the end of the contract.

N7 : Failure of First Tier laboratories to complete bias tests prevents Second Tier work proceeding.

Table 7. ANALYTICAL QUALITY CONTROL (HARMONISED MONITORING) PUBLICATIONS

Subject	Type of Publication	Reference
Chloride	WRC Technical Report	11
	Analyst Paper	12
Ammonia	WRC Technical Report	13
	Analyst Paper	14
Nitrite & TON	WRC Technical Report	15
	Analyst Paper	16
Suspended Solids	WRC Technical Report	17
	Analyst Paper	18
	Preparative Work, WRC TR	27
BOD (ATU)	WRC Technical Report	19
	Analyst Paper	20
Mercury	WRC Technical Report	6
	Analyst Paper	21
Cadmium	WRC Technical Report	7
	Analyst Paper	22
Metals (Pb,Cu,Ni,Zn)	WRC Technical Report	5
	Analyst Paper	23
pH	WRC Technical Report	24
Conductivity	WRC Technical Report	25
pH & Conductivity	Analyst Paper	26
Sample Stability	WRC Technical Report	8
CUSUMS	WRC Technical Report	4

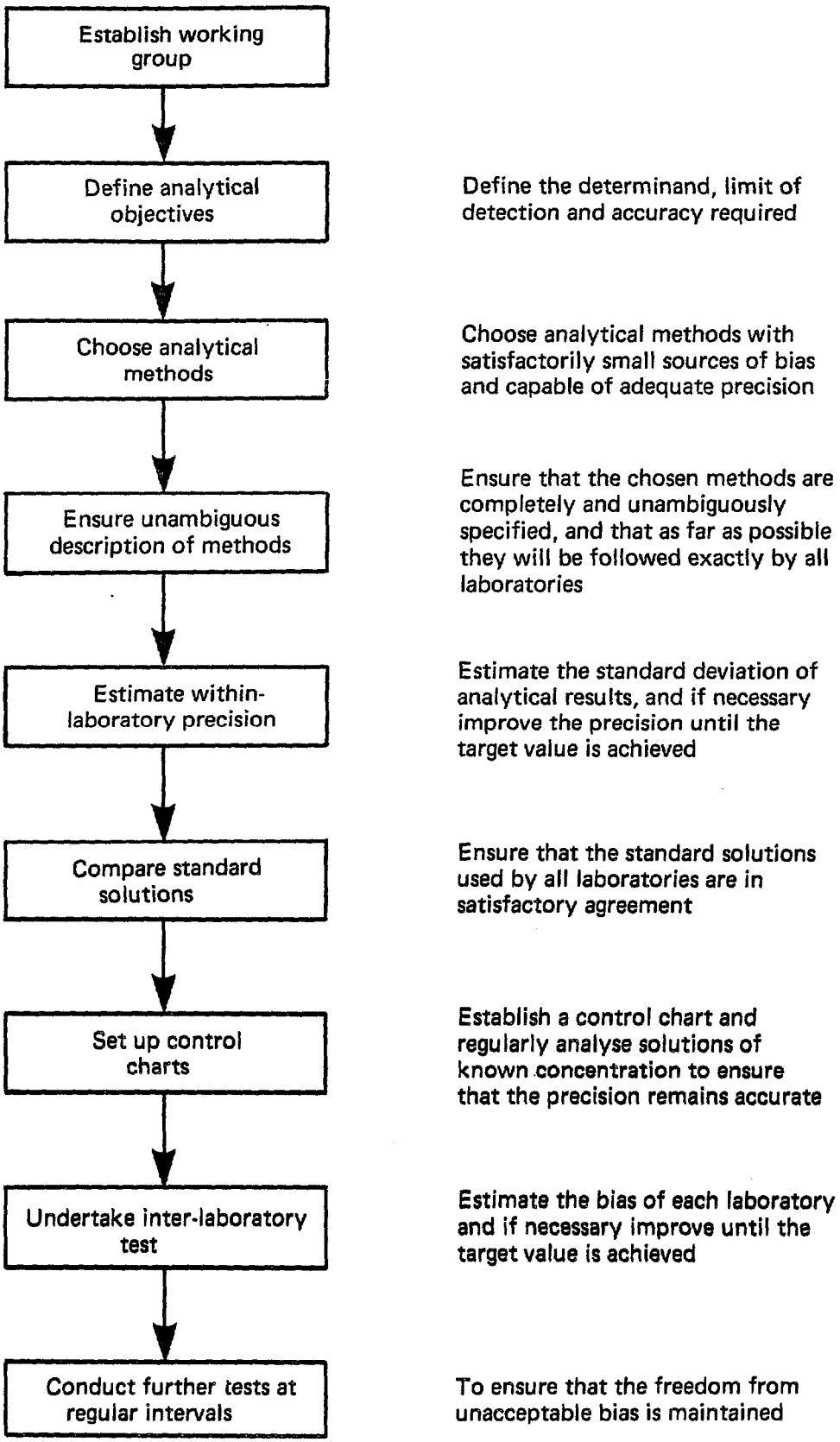


Fig. 1 Approach adopted for analytical quality control

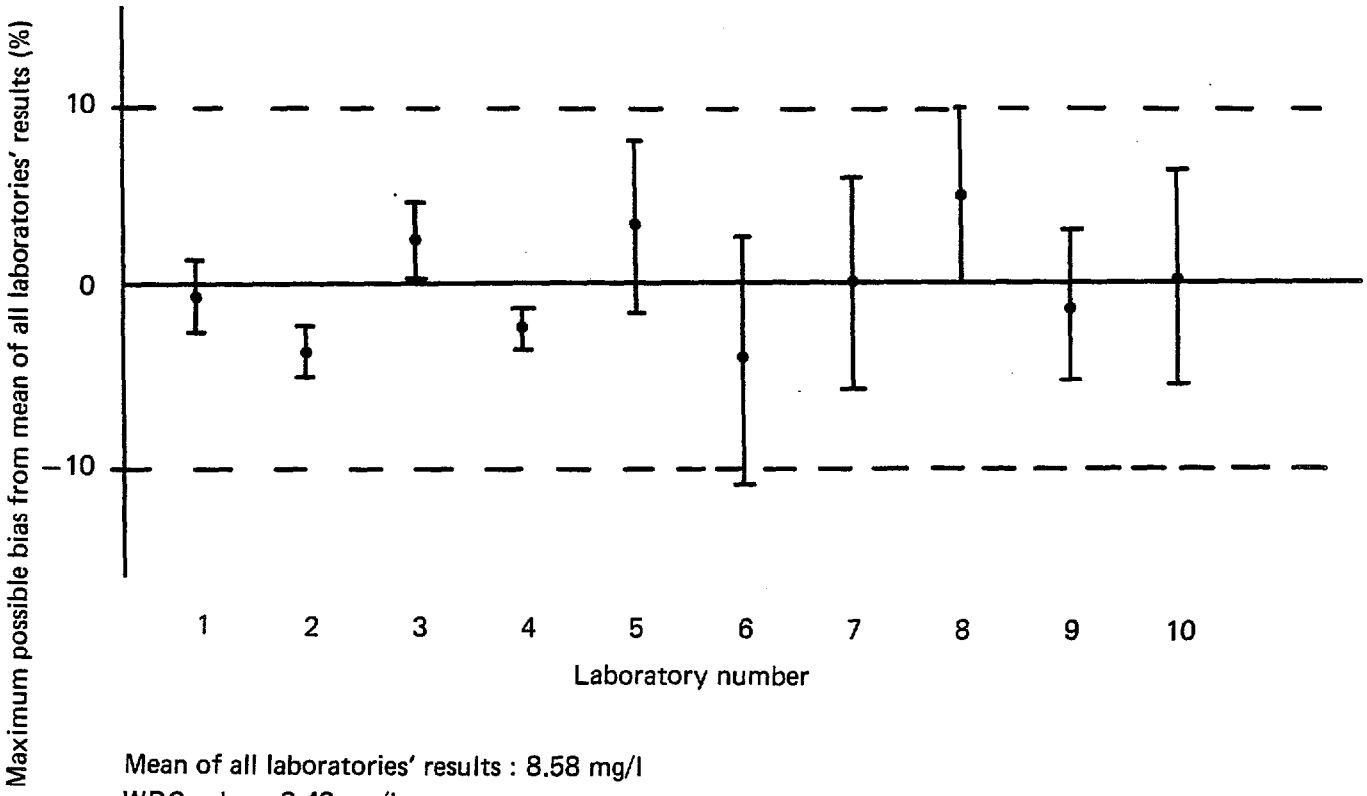
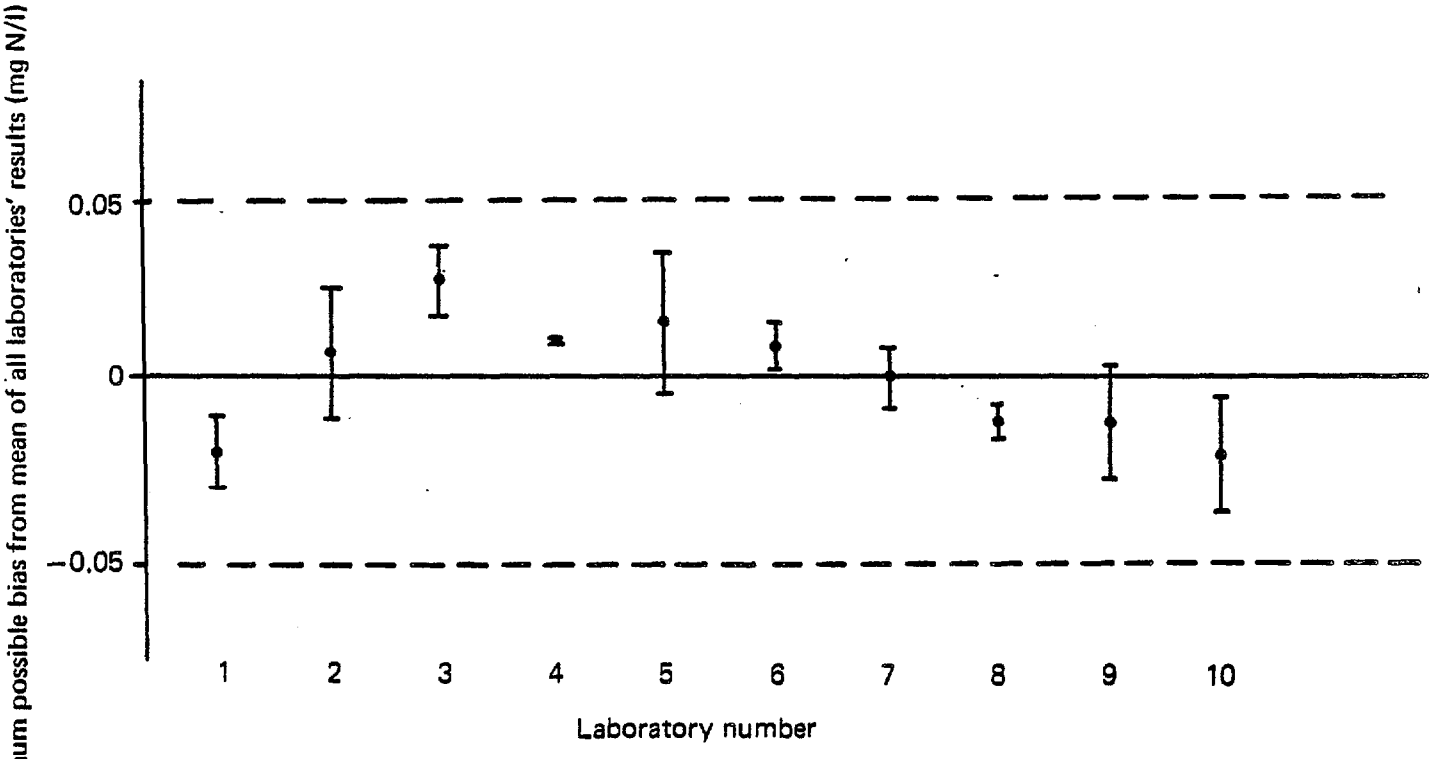


Fig. 2 Results from the inter-laboratory bias test for chloride, for a distributed river water sample

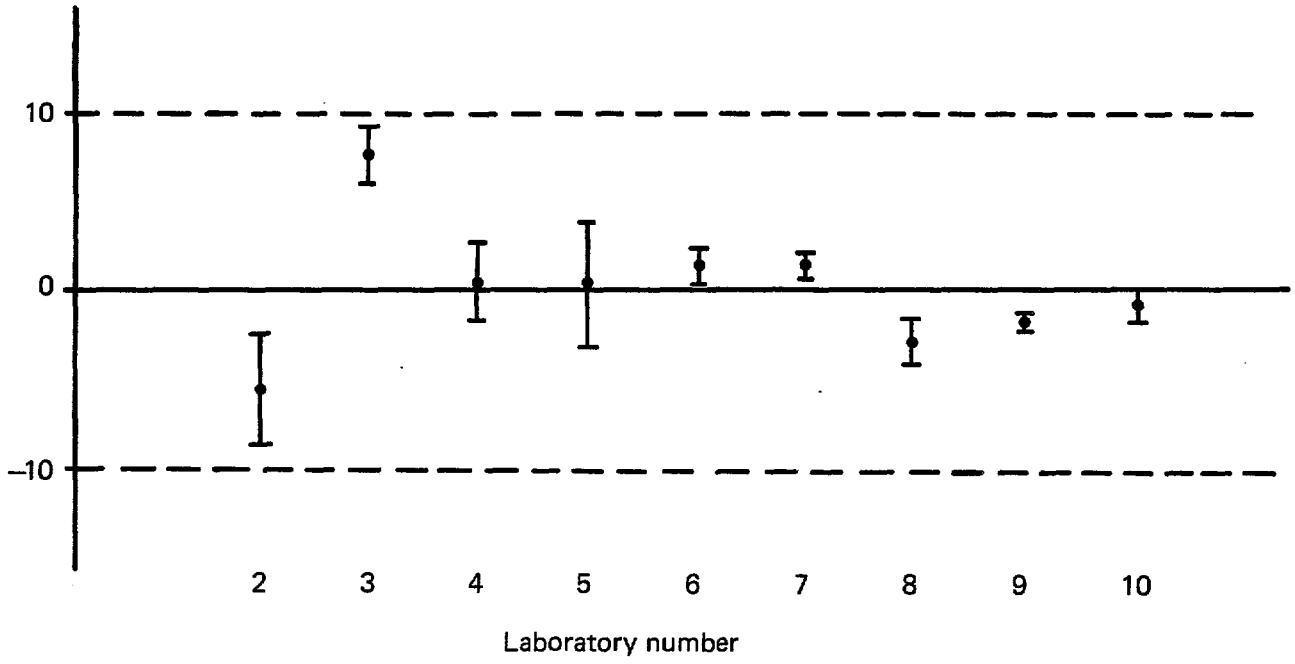


Mean of all laboratories' results : 0.242 mg N/l

Expected value : 0.240 mg N/l

– – – – 0.05 mg N/l bias target

Fig. 3 Results from the inter-laboratory bias test for ammoniacal nitrogen, for a distributed spiked river water sample

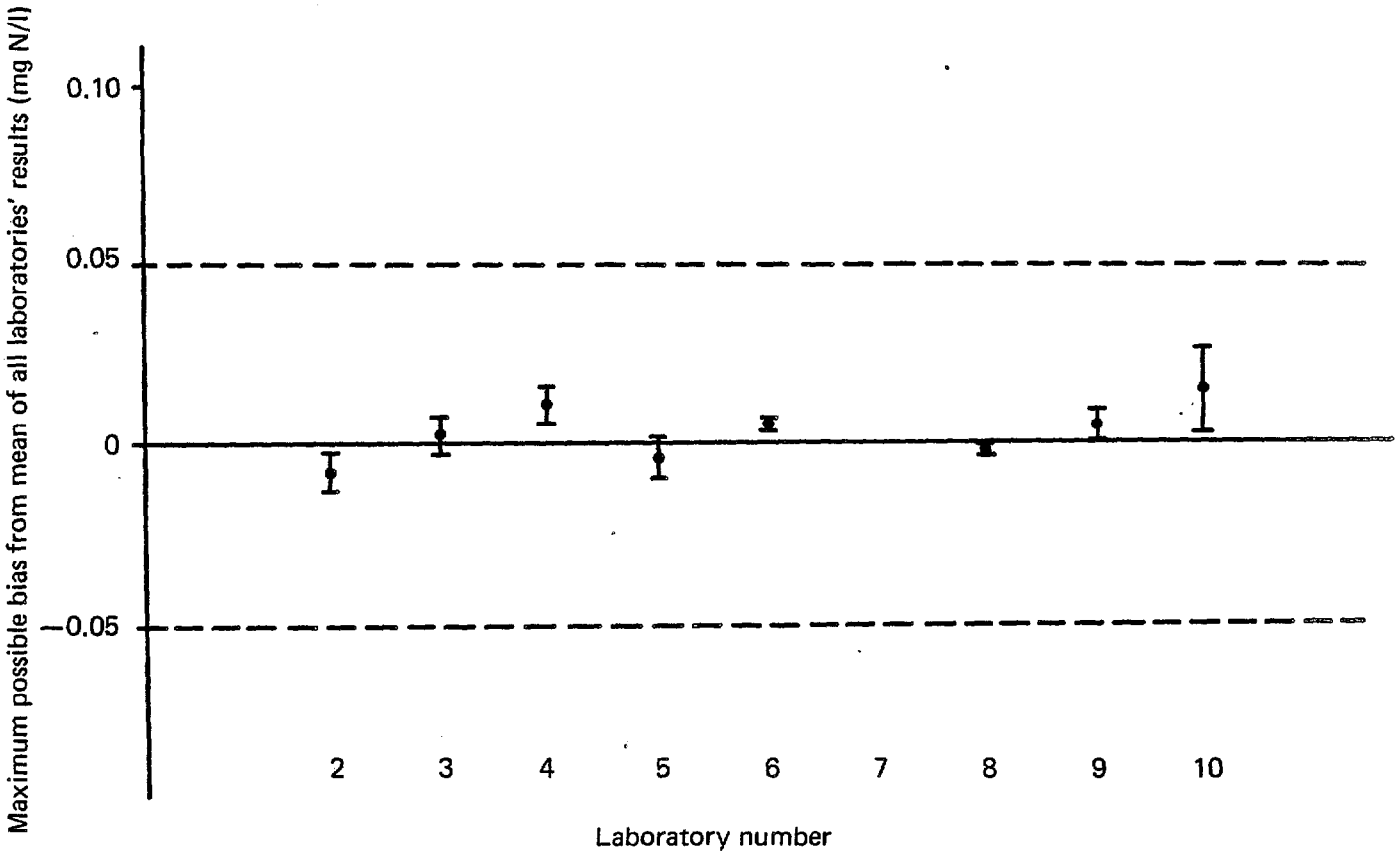


Mean of all laboratories' results : 5.29 mg N/l

Expected value : 5.22 mg N/l

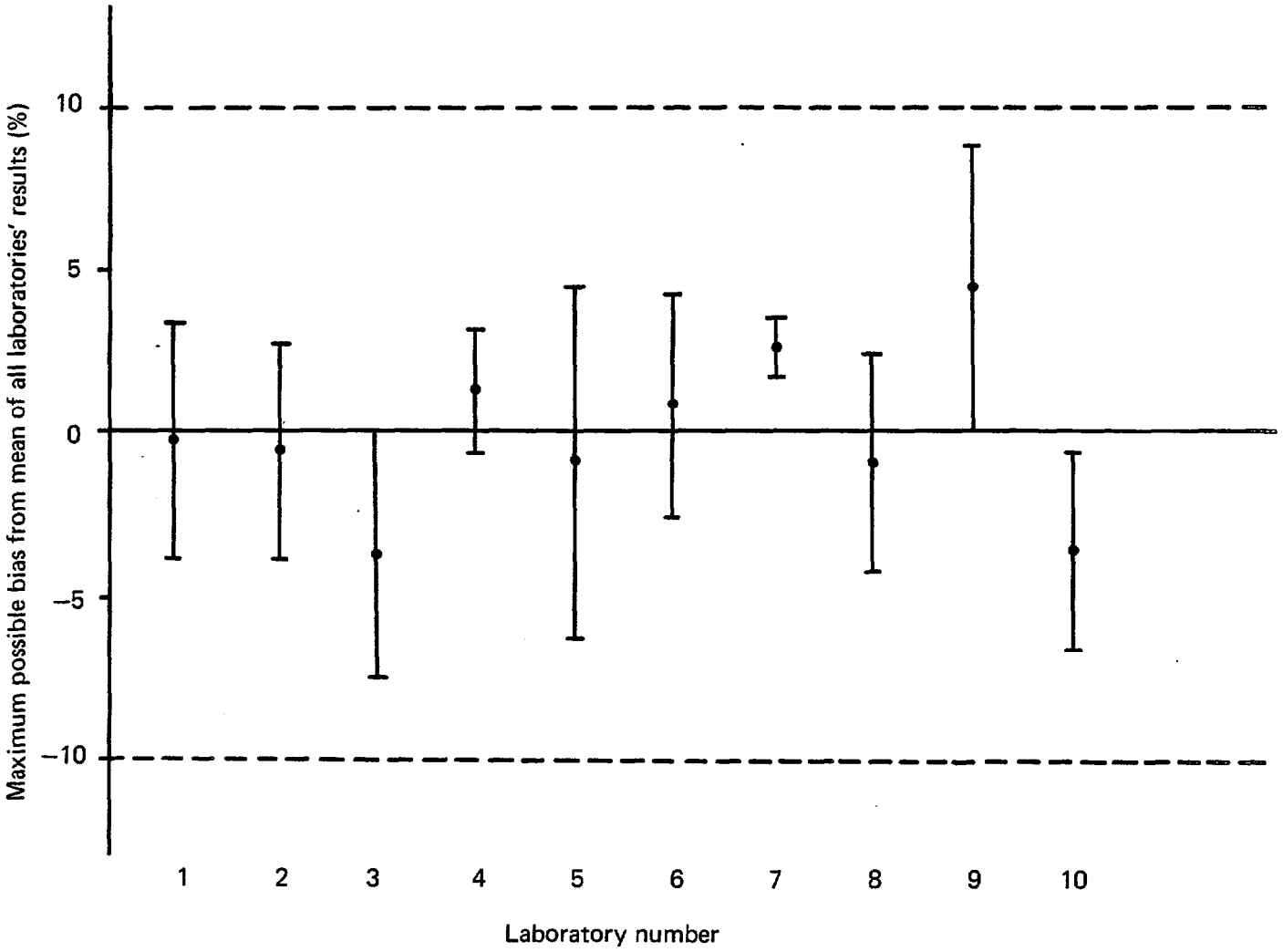
– – – – –10% bias target

Fig. 4 Results from the inter-laboratory bias test for total oxidised nitrogen (TON), for a distributed spiked river water sample



(Laboratory 7 does not routinely determine nitrite – nitrogen for the HM scheme)
Mean of all laboratories' results : 0.107 mg N/l
Expected value : 0.103 mg N/l
– – – – 0.05 mg N/l bias target

Fig. 5 Results from the inter-laboratory bias test for nitrite-nitrogen, for a distributed spiked river water sample

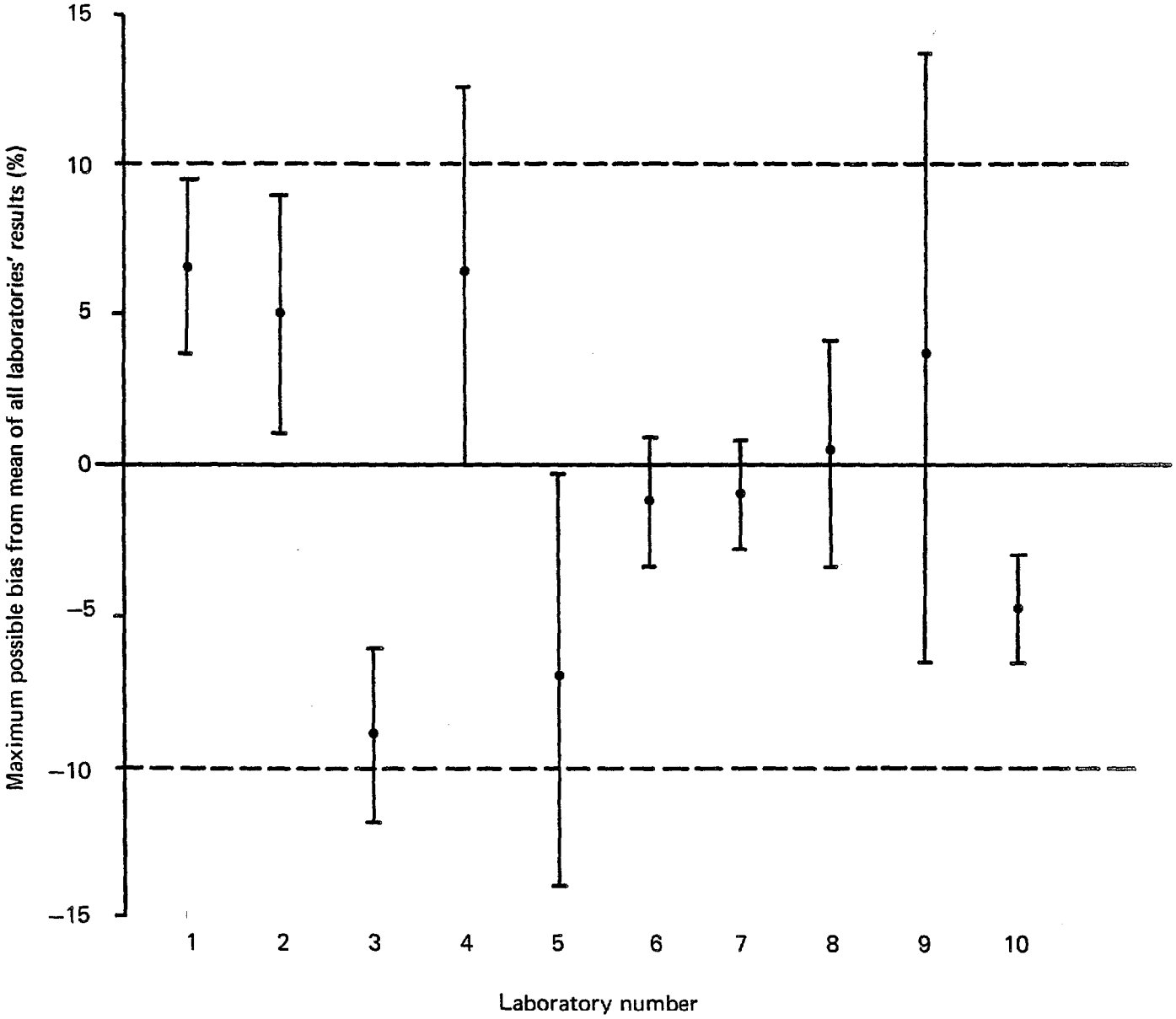


Mean of all laboratories' results : 48.8 mg/l

Expected value : 50.2 mg/l

– – – – –10% bias target

Fig. 6 Results from the inter-laboratory bias test for total suspended solids, for a distributed kaolin suspension

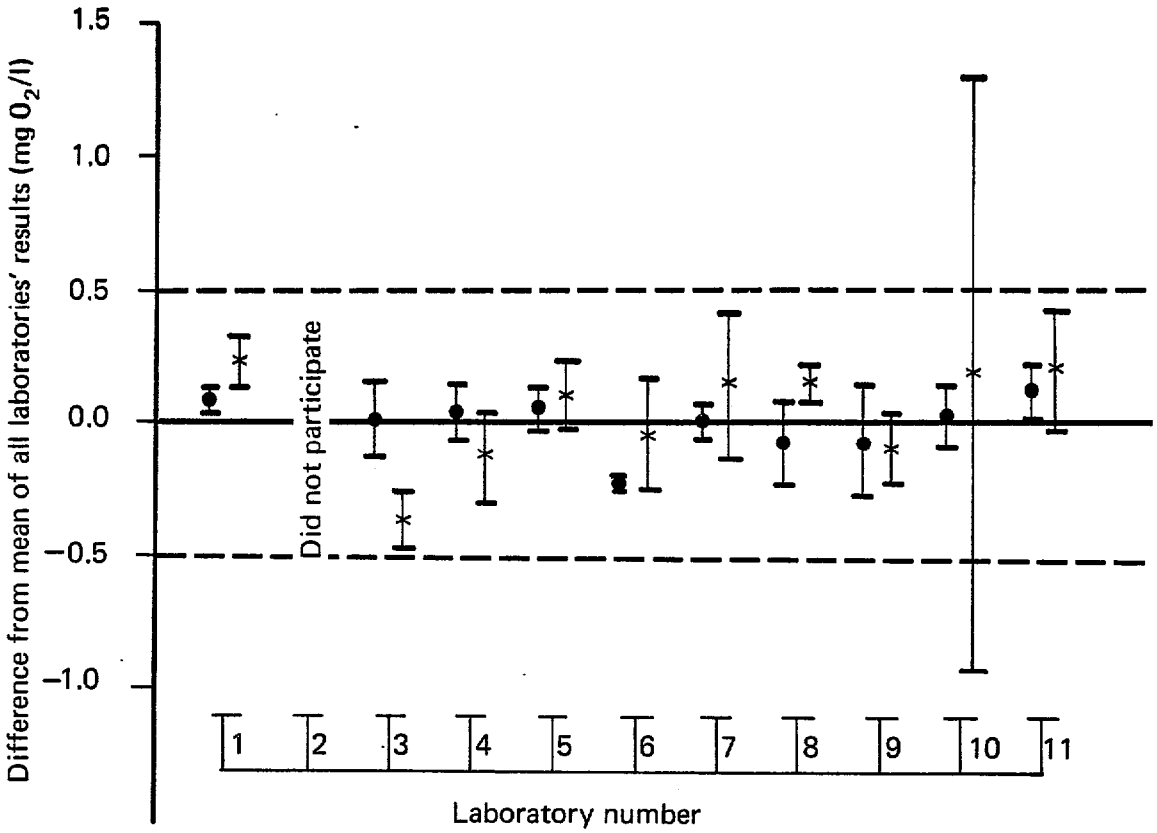


Mean of all laboratories' results : 44.6 mg/l

Expected value : 45.8 mg/l

– – – – – 10% bias target

Fig. 7 Results from the inter-laboratory bias test for ash, for a distributed kaolin suspension



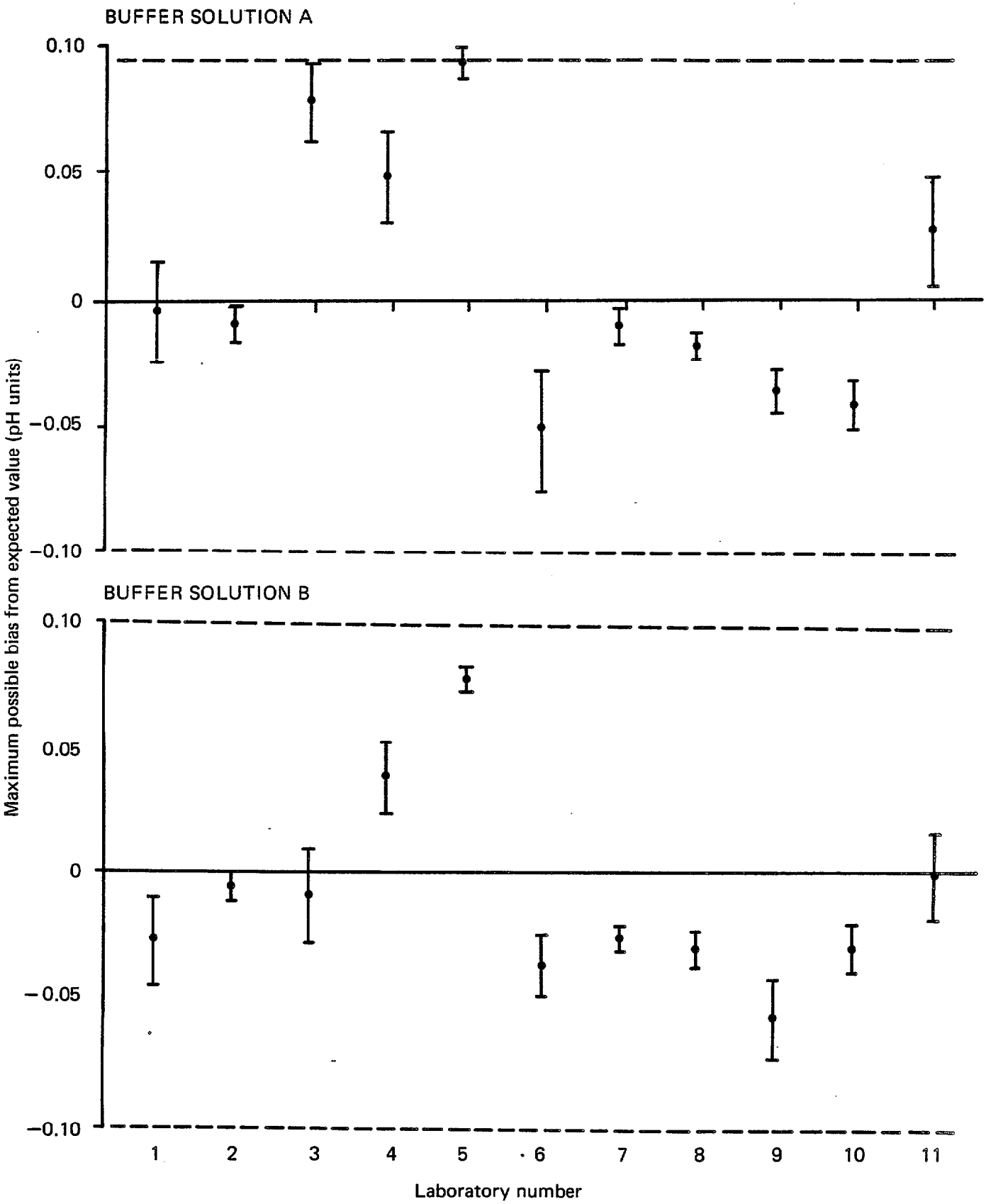
● Low standard. Mean of all laboratories = 1.11mg O_2/l.
Expected value (SCA) = 1.15mg O_2/l.

× High standard. Mean of all laboratories = 3.82mg O_2/l.
Expected value (SCA) = 3.83mg O_2/l.

— — 0.5mg O_2/l bias target.

Note:– Laboratory 7 – Did not complete precision test.
Laboratory 10 – Bias test performed by different laboratory from that which performed precision tests; incorrect number of replicate analyses.
(Results from these laboratories not included in the mean of all laboratories).

Fig. 8 Results of the inter-laboratory bias test for BOD (ATU)

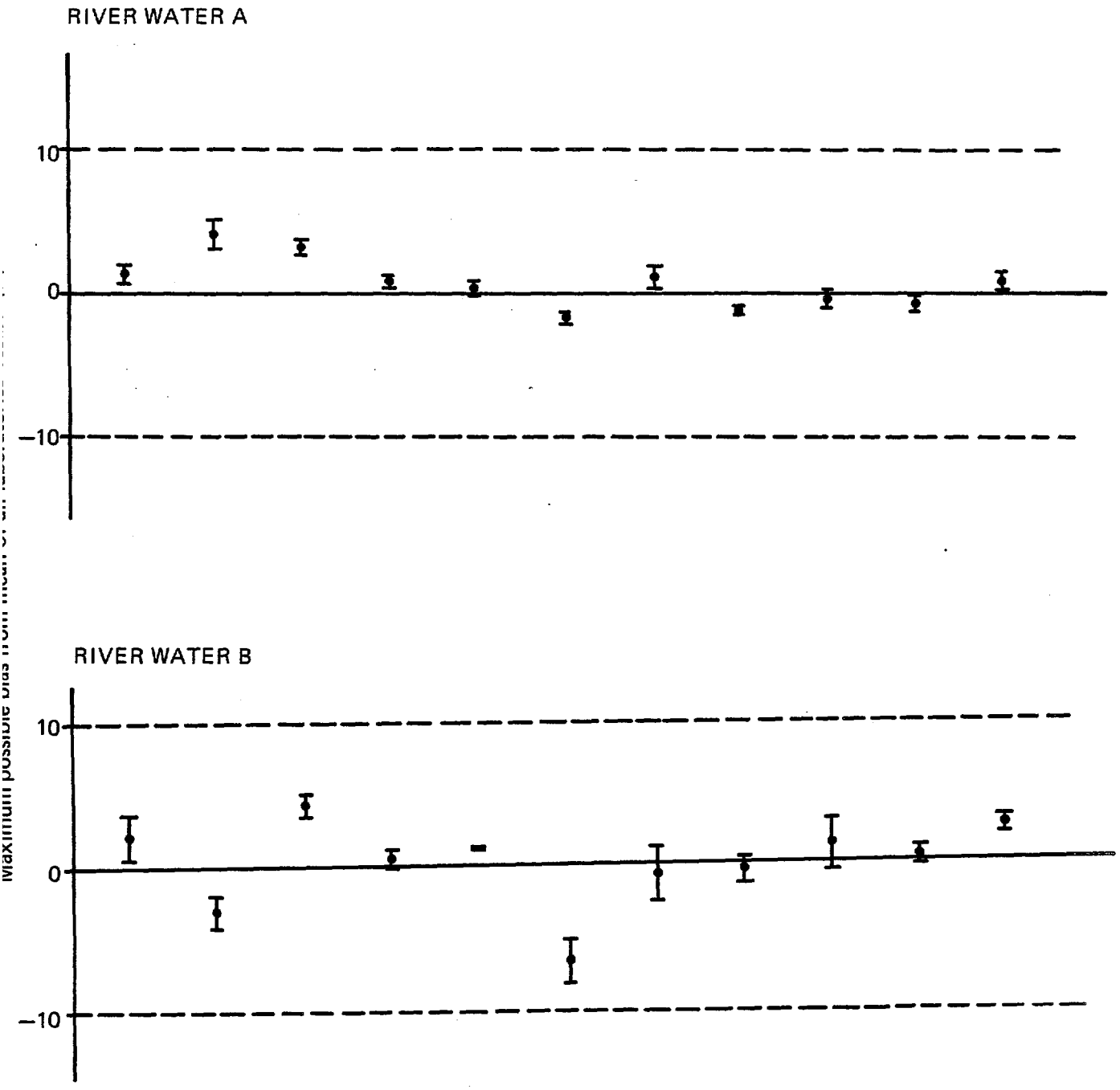


Means of all laboratories' results : 6.888 pH (A), 7.420 pH (B)

Expected values : 6.881 pH (A), 7.429 pH (B)

– – – – 0.1 pH bias target

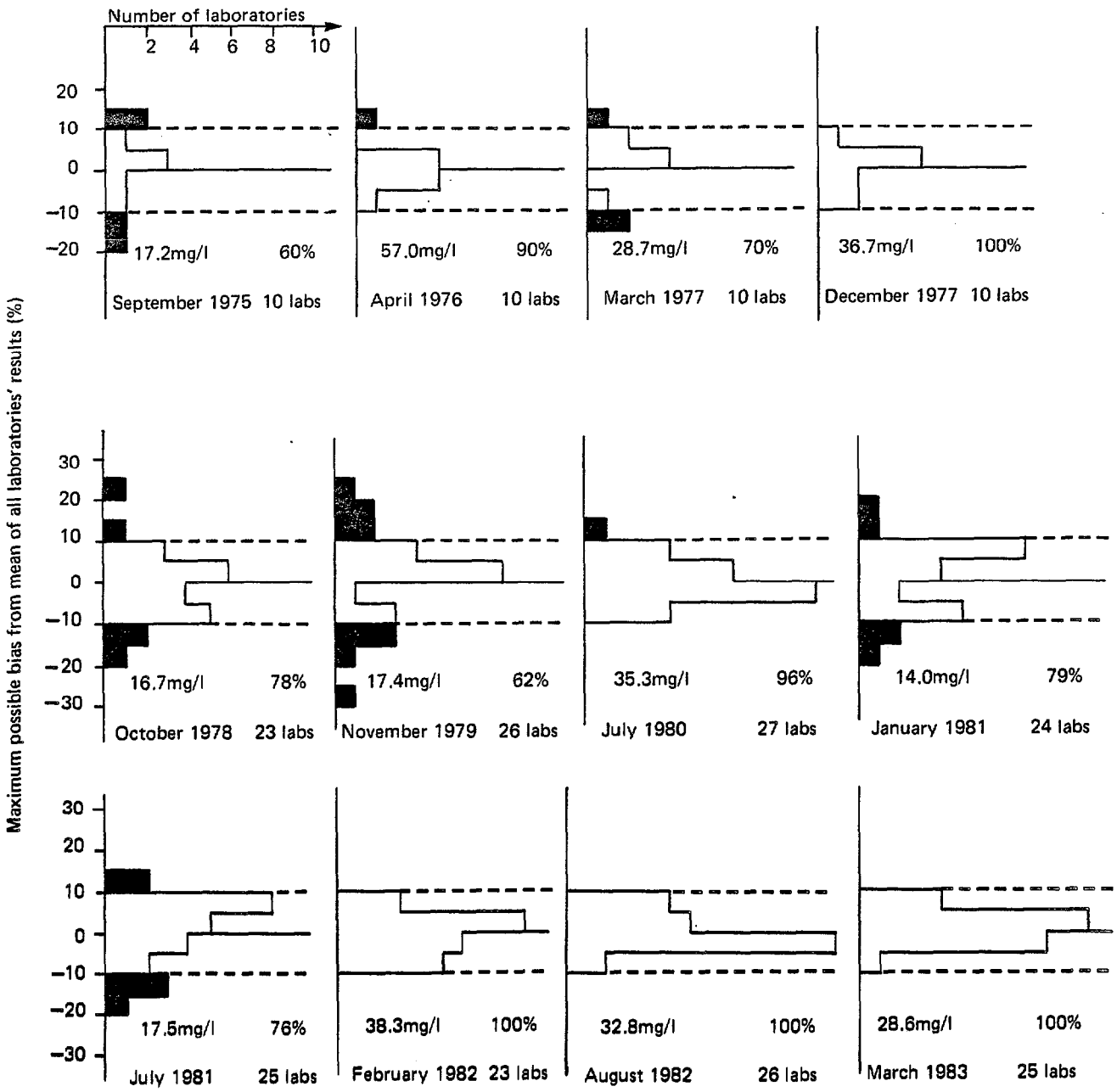
Fig. 9 Results from the inter-laboratory bias test for pH, for two distributed buffers



Means of all laboratories' results : 639.9 μS/cm (A)
208.1 μS/cm (B)

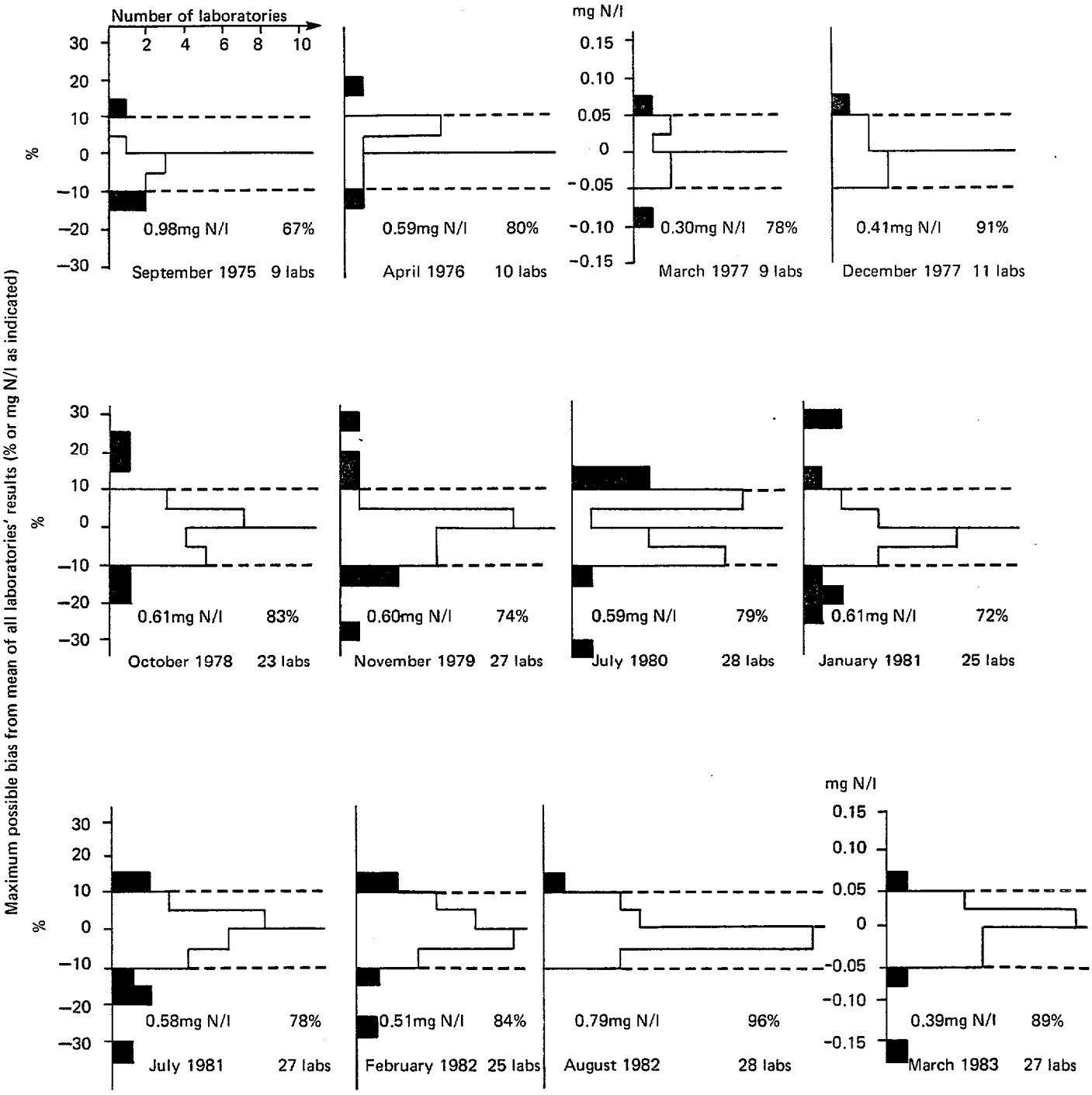
– – – – – – 10% bias target

Fig. 10 Results from the inter-laboratory bias test for conductivity, for two distributed river water samples



The mean of all laboratories' results is shown for each test, in mg/l.
The percentage of laboratories within target is also shown for each test.
– – – – – 10% bias target.

Fig. 11 Results of inter-laboratory follow-up tests for chloride using distributed river water samples

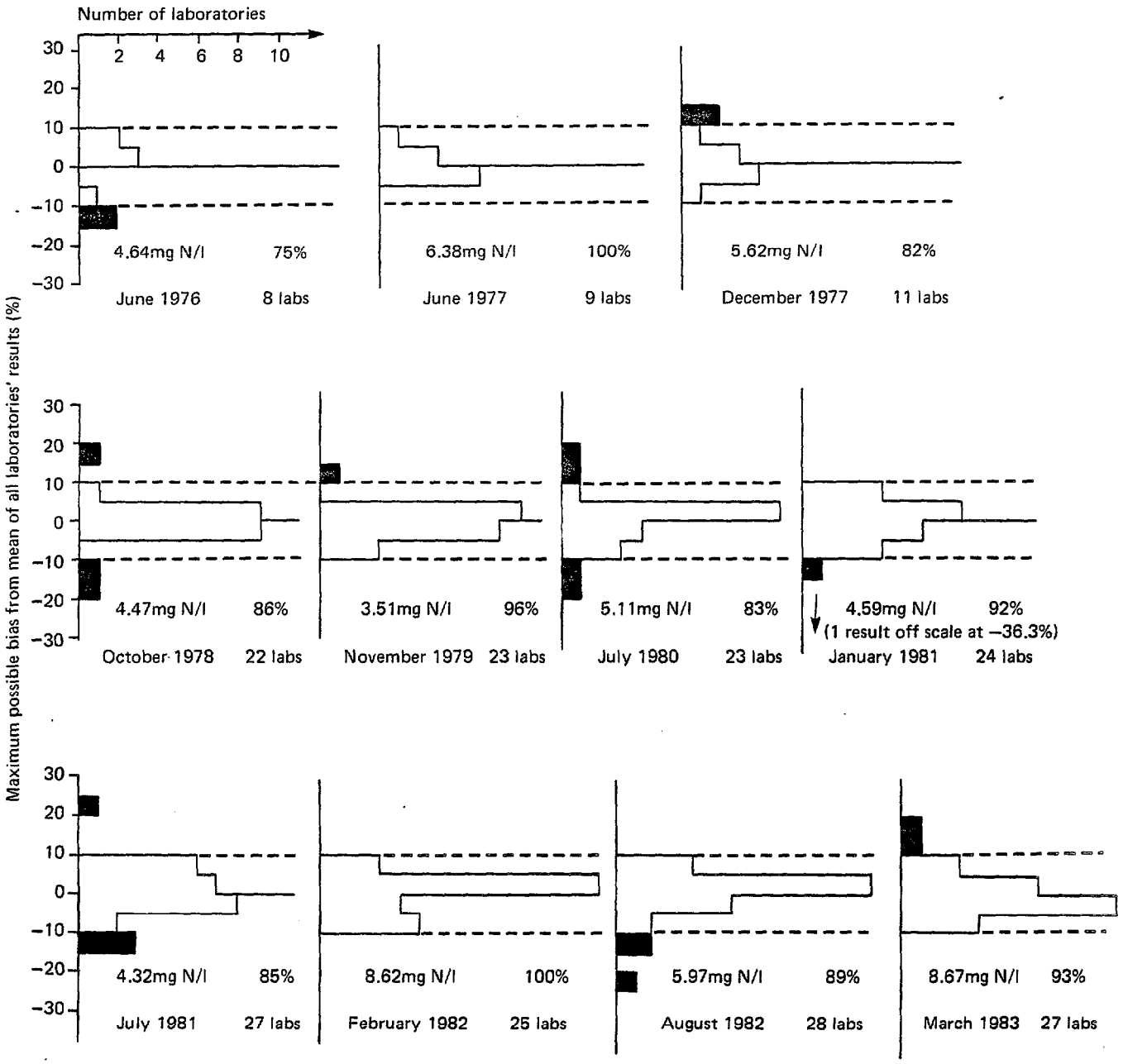


The mean of all laboratories' results is shown for each test, in mg N/l.

The percentage of laboratories within target is also shown for each test.

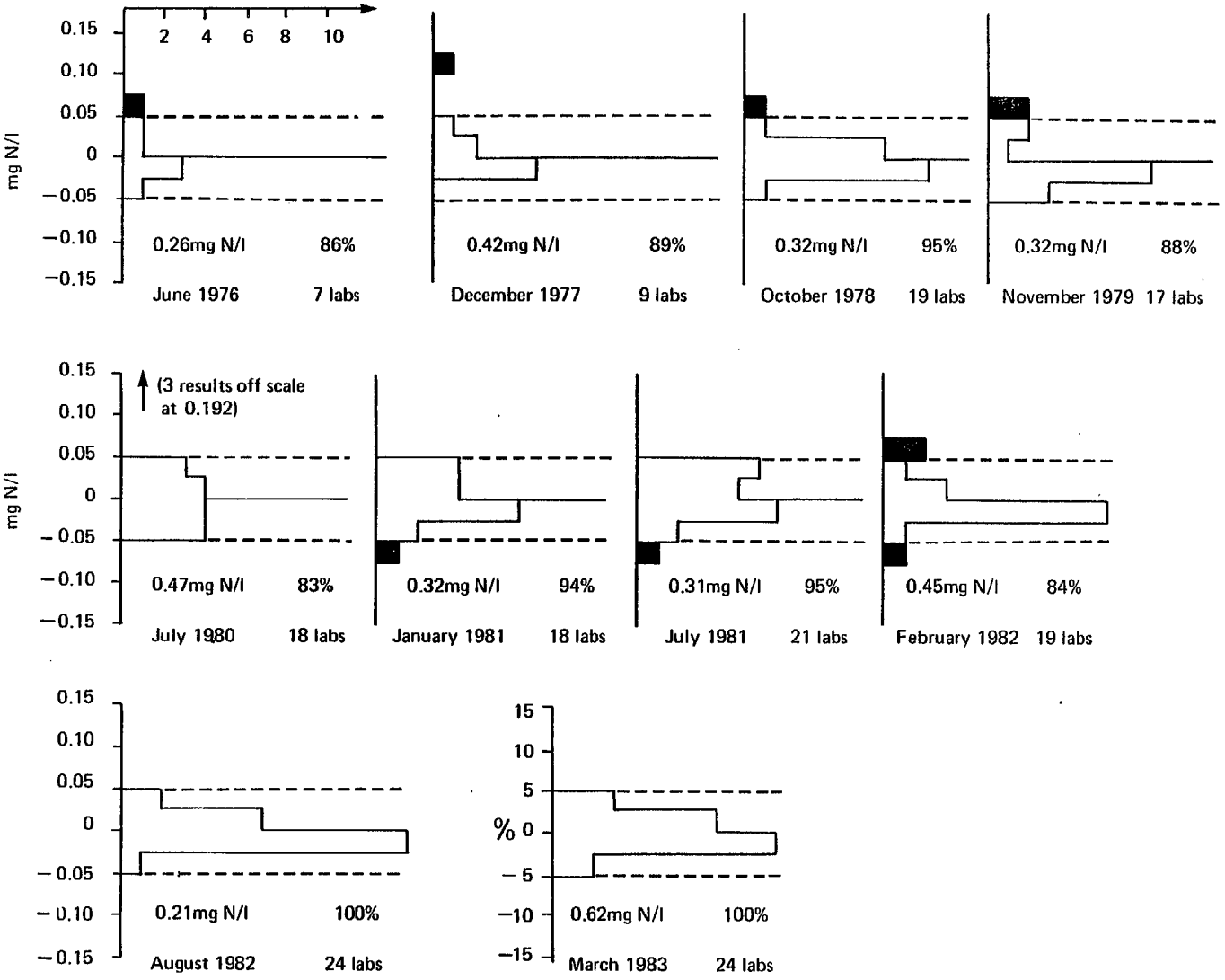
– – – – –0.05mg N/l or 10% bias target.

Fig. 12 Results of inter-laboratory follow-up tests for ammoniacal nitrogen using distributed river water samples



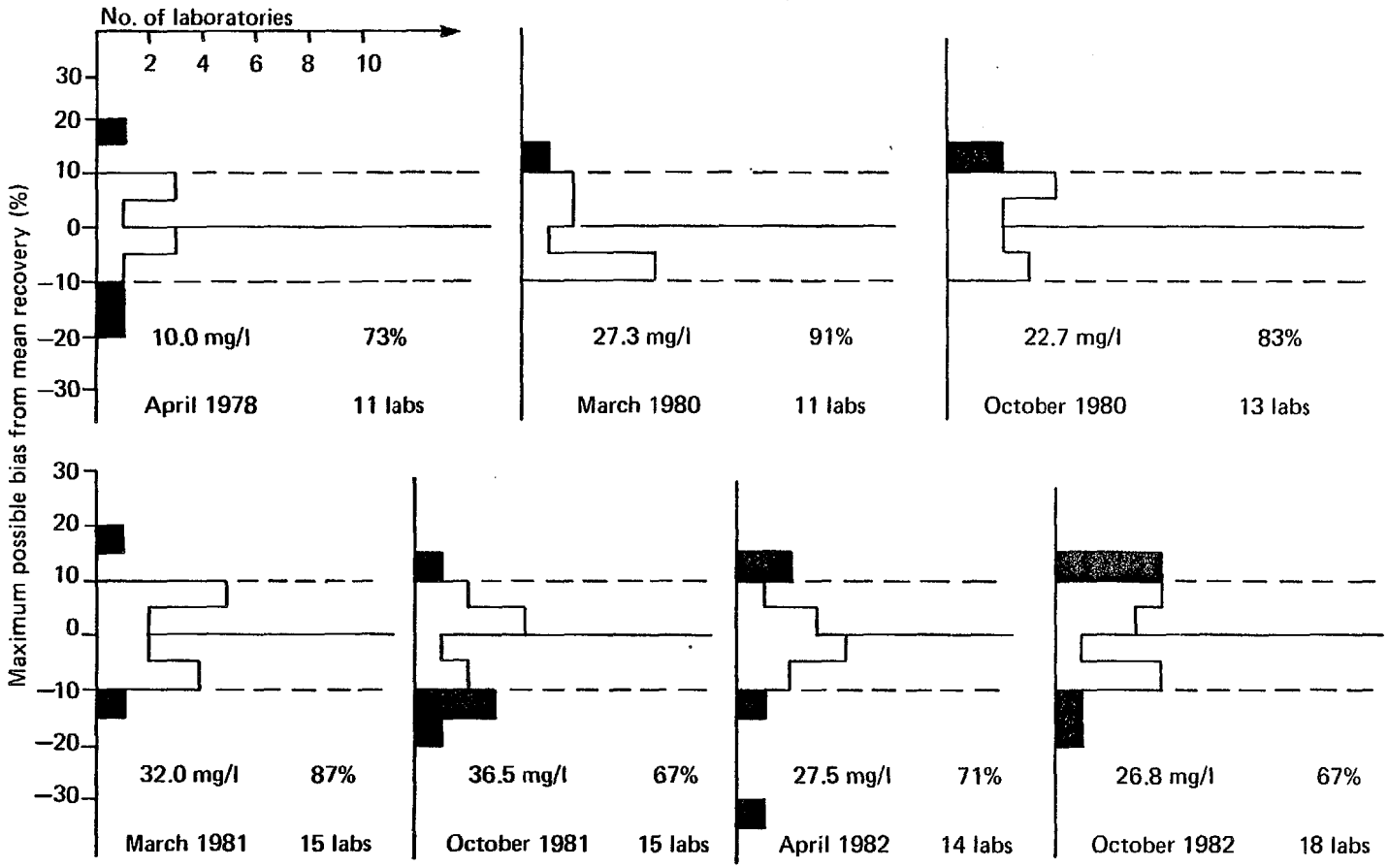
The mean of all laboratories' results is shown for each test, in mg N/l.
The percentage of laboratories within target is also shown for each test.
– – – – – 10% bias target.

Fig. 13 Results of inter-laboratory follow-up tests for total oxidised nitrogen (TON) using distributed river water samples



The mean of all laboratories' results is shown for each test, in mg N/l.
The percentage of laboratories within target is also shown for each test.
------ 0.05mg N/l or 10% bias target.

Fig. 14 Results of inter-laboratory follow-up tests for nitrite-nitrogen using distributed river water samples

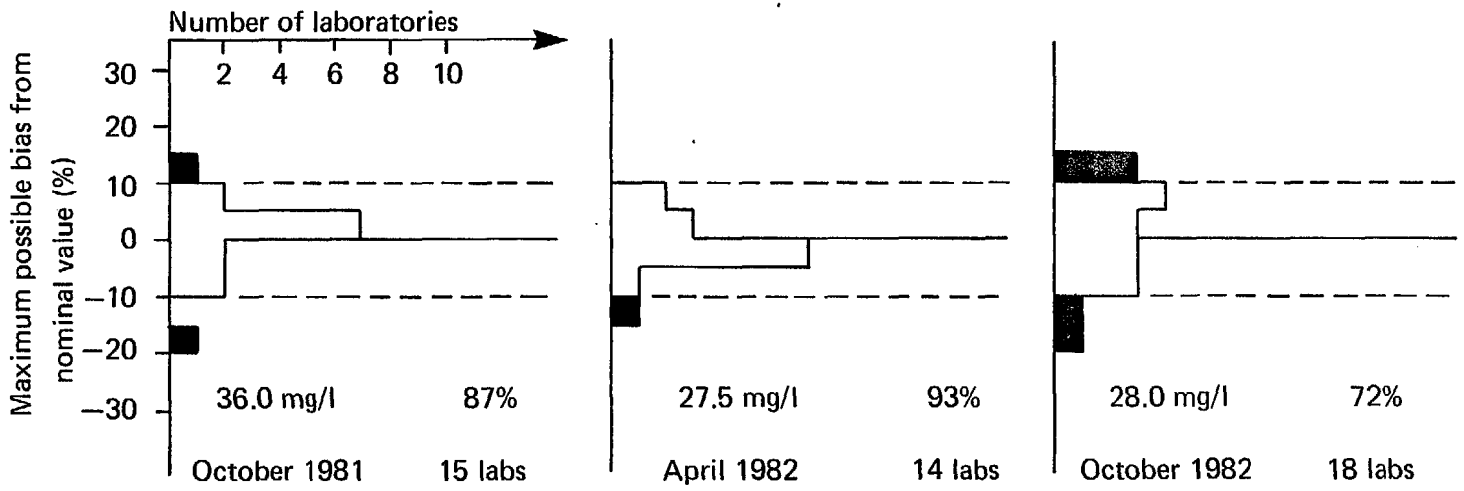


The nominal concentration is shown for each test, in mg/l.

The percentage of laboratories within target is also shown for each test.

– – – – – 10% bias target. Mean recoveries varied from 89.5% to 96.7%.

Fig. 15 Results of inter-laboratory follow-up tests for suspended solids using distributed kaolin suspensions



The nominal concentration is shown for each test, in mg/l.

The percentage of laboratories within target is also shown for each test.

– – – – – 10% bias target. Mean recoveries varied from 99.1% to 101.7%.

Fig. 16 Results of inter-laboratory follow-up tests for suspended solids using distributed microcrystalline cellulose suspensions

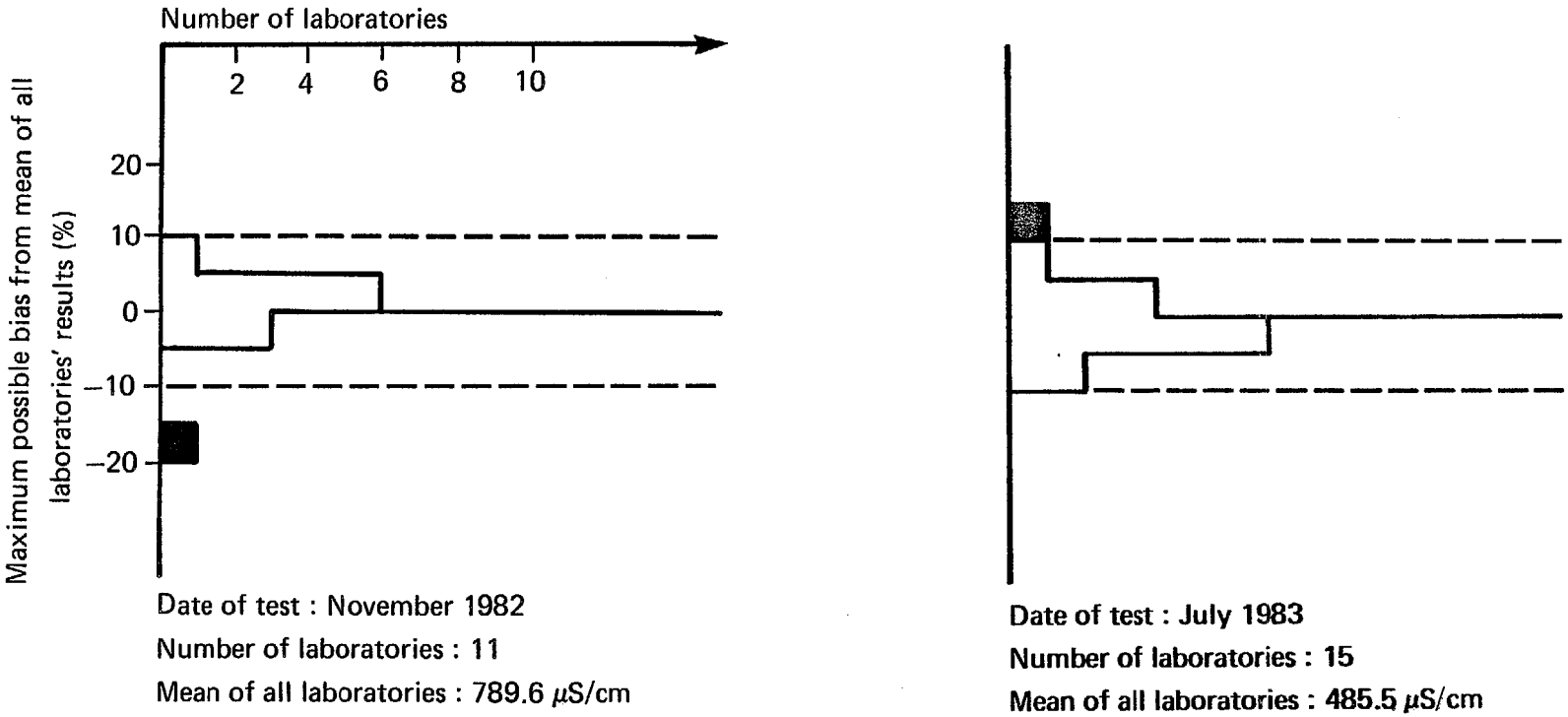


Fig. 17 Results of inter-laboratory follow-up tests for conductivity using distributed river water samples

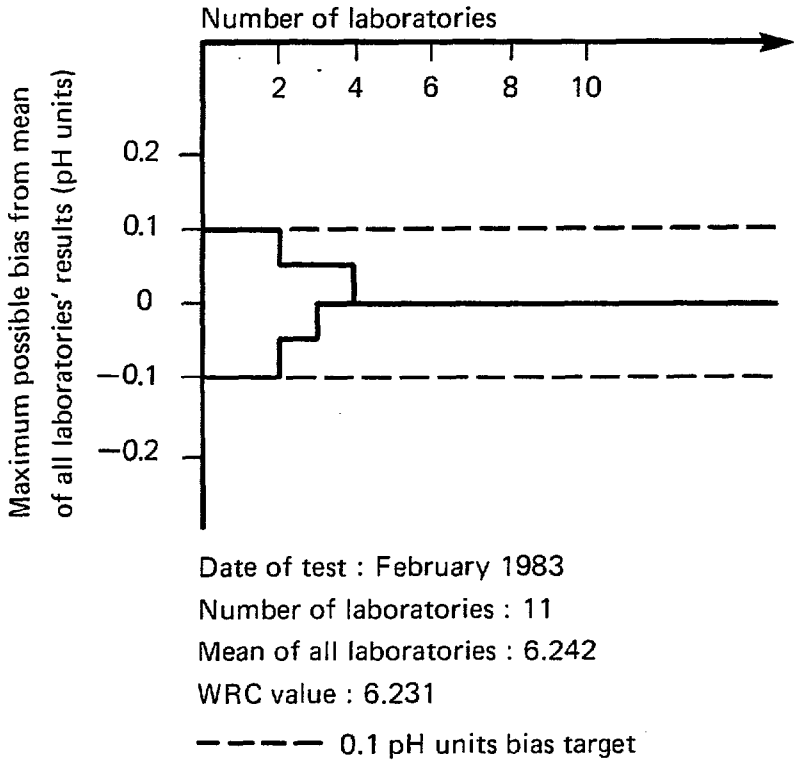
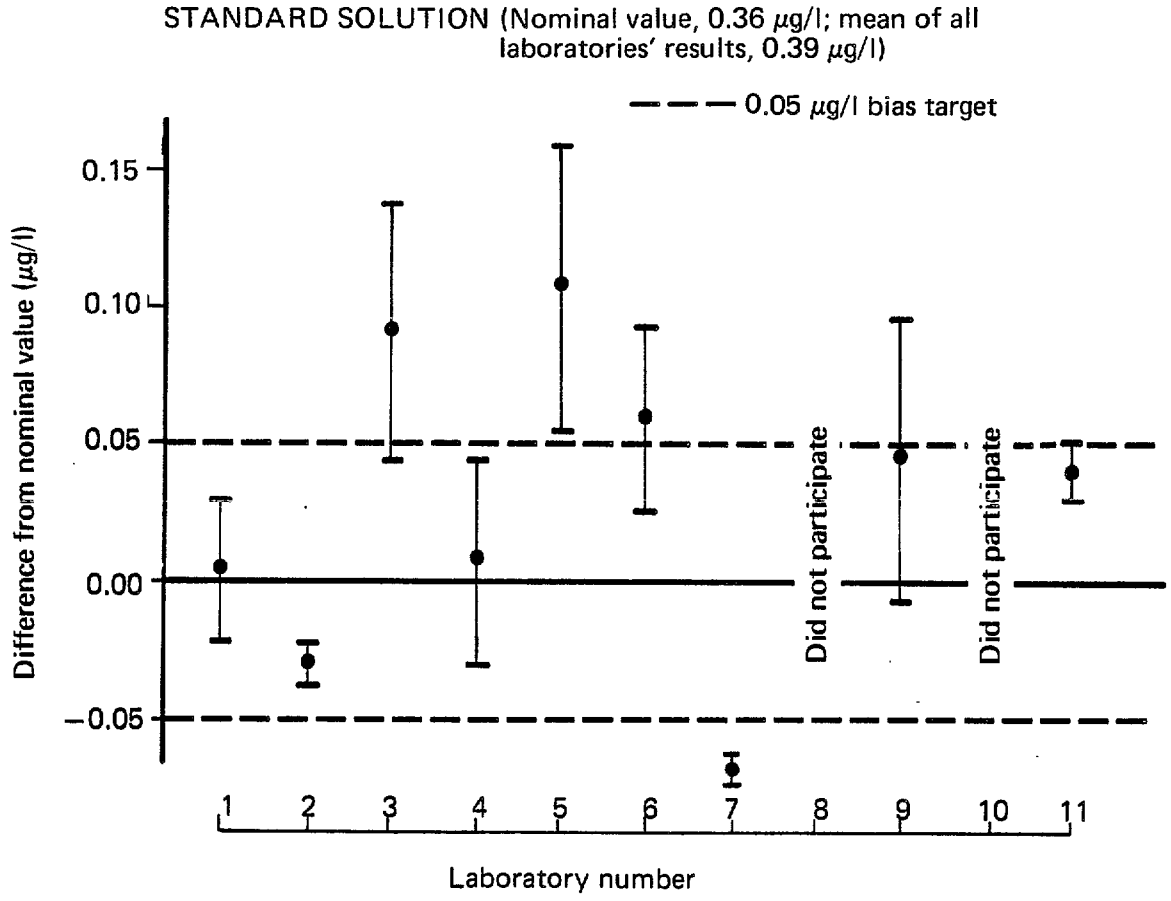


Fig. 18 Results of inter-laboratory follow-up tests for pH using distributed buffer solutions



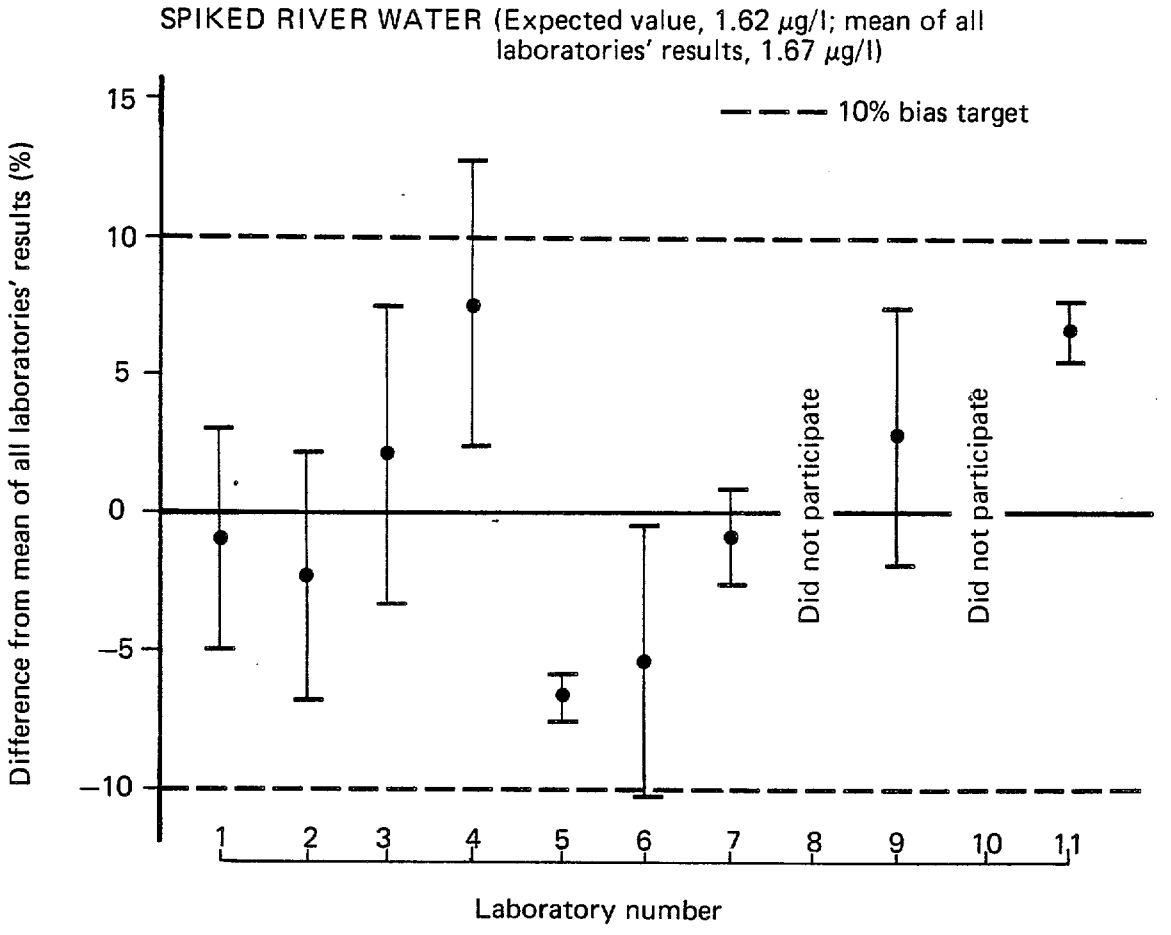
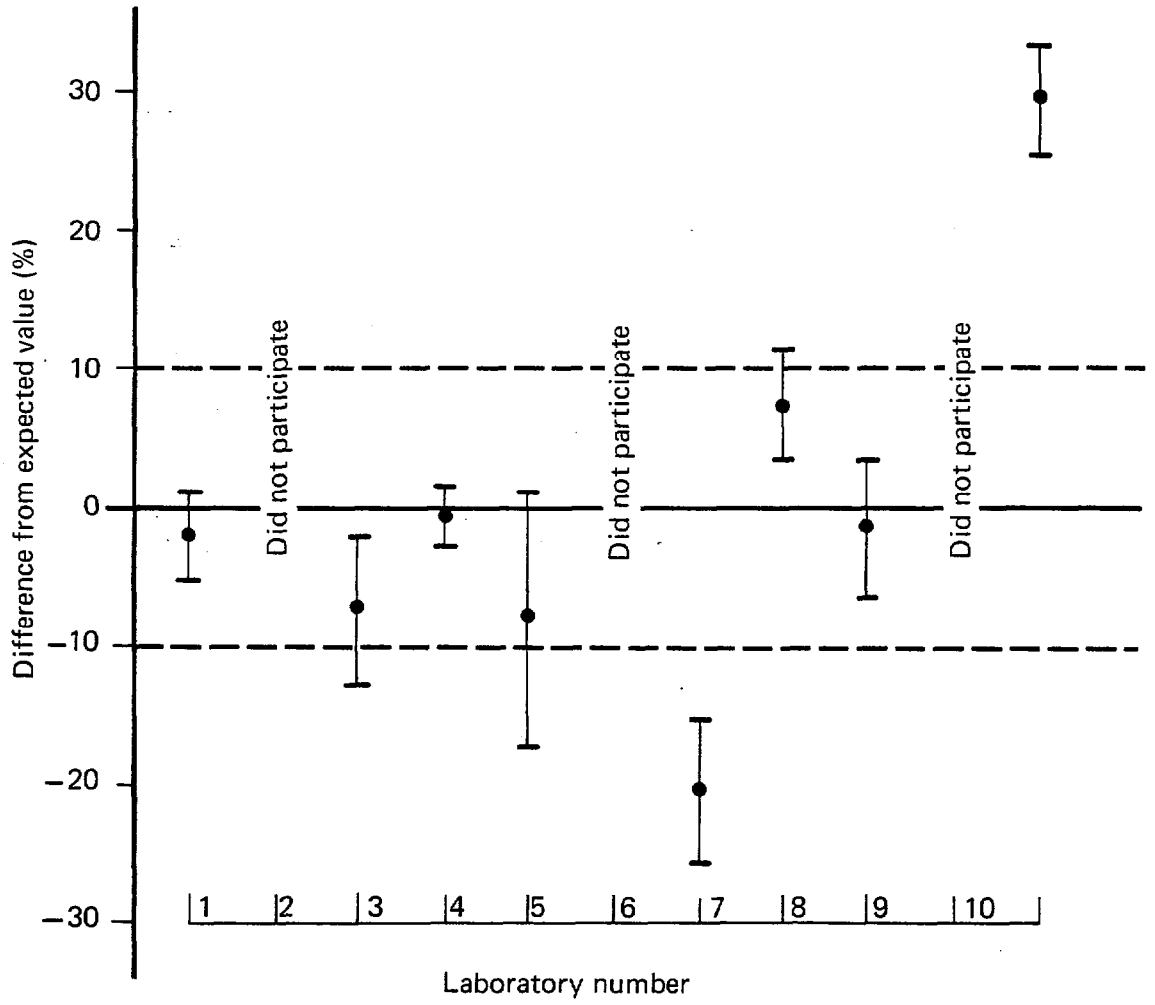


Fig. 19 Results of last inter-laboratory bias test for mercury



Mean of all laboratories' results : 1.439 μg/l

Expected value : 1.44 μg/l

– – – – –10% bias target

Fig. 20 Results from the cadmium inter-laboratory bias test, for a distributed river water sample (spiked)