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Convention on Long-Range Transboundary Air Pollution

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Long-range Transboundary Air Pollution

Norwegian Institute for Water Research

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Summary

Twenty-one laboratories from 13 countries accepted the invitation to join the ICP Waters chemical intercomparison and successfully reported results. The lower number of participants this year likely resulted from the global covid-19 pandemic, leading to the lockdown of several nations during the spring of 2020. Two sets of samples were prepared and successfully distributed to the participants: one for the determination of ions and one for the metals. In general, the results were good with an overall acceptance of 81% (± 20% of the "true value", and for pH and conductivity ± 0.2 pH units and ± 10%, respectively). The highest acceptances (> 90%) were obtained for some of the ions and metals, with a maximum of 100% for sodium. This year, the acceptance for pH was also very good (75%). The lowest acceptance rate was for total phosphorus 41% of the results being accepted. This number was originally reported as 18% due to an error with the units. A relatively low acceptance was also achieved for alkalinity which likely resulted from the large number of different titration methods used by the participating laboratories. General trends in the choice of techniques continue to shift towards plasma from atomic absorption, and to mass detection from ionic emission. This is especially promising for the determination of metals at low levels.

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CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR
POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING EFFECTS OF AIR POLLUTION
ON RIVERS AND LAKES

Intercomparison 2034:
pH, Conductivity, Alkalinity, NO$_3$-N, Cl, SO$_4$, Ca, Mg, Na, K, TOC, Total-P, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Preface

The Chemical Intercomparison Test is a tool to ensure consistency in the measurements conducted by the laboratories reporting data to the International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters).

The objective of the Programme is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the aims is to detect long-term trends in effects of acidic deposition on surface water chemistry and aquatic biota, and to reveal the dose/response relationship between water chemistry and aquatic biota.

The ICP Waters was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then, ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports, and publications covering the effects of long-range transported air pollution have been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Environment Agency leads the programme. The Programme Centre's work is supported financially by the Norwegian Environment Agency.

We hereby report the results from the 34th intercomparison of chemical analysis.

Cathrine Brecke Gundersen

ICP Waters Programme Centre
Oslo, November 2020

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Summary

The chemical inter-laboratory comparison is an important tool for the ICP Waters to ensure consistency and comparability of the surface water monitoring results among the programme participants. The test is conducted yearly and is based on the "round robin" principle. In short, the same water sample is distributed to all the participating laboratories which analyse the sample for a set repertoire of parameters with their method of choice. Then, the results are compiled and analysed using the Youden test statistic. The "true value" for each parameter is calculated as the median of the reported results after excluding extreme observations. Two different sets of samples are prepared and distributed, one for the determination of ions and the other for metals.

The 2034 edition of the test was conducted in the period from May to November 2020. A total of 21 laboratories representing 13 different countries signed up and successfully reported results to the database. This is a decline compared to the 32-38 participants participating in the preceding three editions. A likely explanation for the decline is the global covid-19 pandemic situation, causing lockdown of several nations during spring 2020. The lower number of participants can influence the results of the intercomparison test, both with regards to the statistical analysis and to the distribution of different of analytical techniques used for the determination of the various parameters. The participants were invited to determine pH, conductivity, alkalinity, nitrate+nitrite nitrogen, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorus, aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. The acceptance limit was typically at $\pm$ 20% of the "true value", except for pH and conductivity ($\pm$ 0.2 pH units and $\pm$ 10%, respectively).

Overall, the acceptance rates for the 2034 edition were good and comparable to the results from recent years. 81% of the results were within the target threshold (the median of all the parameter acceptance rates). Several different factors can influence the acceptance rate, such as the concentration of the analyte in the sample and the choice of analytical techniques among the laboratories. The highest acceptances (> 90%) were obtained for some of the ions and metals, with a maximum of 100% for sodium. These parameters are typically of higher concentrations in surface waters and are determined using well-established analytical methods. In contrast to previous years, the acceptance rate for pH was very good (75%).

The poorest acceptance rate was obtained for total phosphorous, at 41%. This number was originally reported as 18%, due to an error with the unit. Relatively low acceptance was also observed for alkalinity (44%) and nitrate-nitrite nitrogen (47%). For the former, the low acceptance rate likely resulted from the use of 9 different methods among the 16 laboratories reporting results for alkalinity. This was supported by the distribution of the results in the Youden chart, clearly indicating strong systematic effects. For nitrate-nitrite nitrogen, the poorer acceptance rate was likely caused by the low sample concentration, producing a higher variability in the results.

For several of the parameters, different analytical techniques had been used by the various laboratories. The use of different techniques can challenge the unity of the results, with the effect typically being more severe for low analyte concentrations. For several of the ions, five and six different techniques had been used, while for the metals the number of different techniques was at three to five. Some overall patterns in the preferred technique could be found: Ion chromatography was preferred for the determination of the negatively charged ions, and ion chromatography or some form of plasma technique (ICP-OES/ICP-MS) were most frequently employed for the positively charge ions. For all the metals, the sensitive ICP-MS was the preferred technique of choice. This confirms the trends

observed in the last years, that plasma techniques are taking over for the more traditional atomic absorption techniques, and that the much more sensitive mass detector is replacing the optical emission spectroscopy detector.

For certain of the parameters with re-occurring low acceptance ratios and/or clear systematic effects from the use of different analytical techniques, measures should be considered to improve the precision of the results. This is especially important for comparison of monitoring results across borders. In this edition of the intercomparison test, alkalinity appeared to be the parameter most severely affected by the use of different measurement techniques.

1   Introduction

The international cooperative programme for assessment and monitoring of the effects of air pollution on rivers and lakes (ICP Waters) works to assess the degree to which atmospheric pollution has affected surface waters. The programme was established in 1985 under the Executive Body of the United Nations Economic Commission for Europe (UNECE). The Focal Centres in each country contributes with data from their national monitoring programmes.

To ensure that the results across the entire ICP Waters are consistent and comparable, inter-laboratory quality controls are necessary, as stated in the "ICP Waters Programme Manual" (1). In a multi laboratory programme, typical causes of inconsistency include the use of different types of analytical techniques, errors in the calibration procedure, etc. The between-laboratory control carried out by the Programme Centre of ICP Waters is based on the "round robin" concept meaning that the same sample is analysed by the different participating laboratories using their analytical principle and method of choice. The analytical results are analysed using the Youden test statistics (2, 3) that assesses the consistency of the results between the laboratories, and can also indicate whether the results are affected by a systematic effect (e.g. different analytical techniques give slightly different results) or only by random errors (typically at levels close to the limit of quantification). The Youden test is briefly described in Annex C. The levels of the variables should be set to be as close to the expected natural levels as possible, and that the range from year-to-year shall cover the variation among countries of the participating laboratories.

Several factors can contribute to the acceptance ratio and these should be considered when evaluating the results, and when considering measures to improve the results from individual laboratories. For example, different methods used by different laboratories may give systematically different results (higher or lower). Based on the method used by most of the participating laboratories, the "true value" may be biased. Such systematic effect will be evident in the distribution of the results in the Youden chart, by the points residing *along* the 45° angled line. One other cause of poor acceptance ratio is when the concentration in the sample is low, and close to the limit of quantification of the method used. This will most often appear in the Youden chart as a distribution of the results *perpendicular to* the 45° angled line.

This thirty-fourth chemical intercomparison test, called 2034, covered the determination of the following constituents of natural surface waters: pH, conductivity, alkalinity, nitrate+nitrite nitrogen, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, total phosphorus, aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. While most of these variables have been part of the test since it started, total organic carbon and aluminium was included in 2009, and total phosphorus in 2017.

2   Procedures of the intercomparison

Two different sets of samples were prepared by the Programme Centre and distributed to the participating laboratories: one pair for the determination of major ions and one pair for the determination of metals (as agreed upon at the Task Force meeting in Burlington, Canada, 2009). The procedure for the preparation of the two sample sets is presented in Annex B. The samples were shipped from the Programme Centre during week 26, and there were no reported delays or other issues with the shipment. To ensure the integrity and minimal degradation of the samples, the participants were encouraged to conduct the analyses as soon as possible after reception.

The analytical results were treated by the Youden method (2, 3) to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme, and to assess potential systematic and/or random error in the distribution of the results. For each variable, the "true value" was calculated as the median of the reported results, after excluding extreme observations. This way of setting the "true value" is considered acceptable if the participants mainly use the same analytical techniques. However, this is not always the case, and for parameters such as pH and alkalinity different techniques/methods are frequently used and producing strong systematic bias in the results. Since not one method can be argued to be better than another, this issue has persisted in the inter-laboratory harmonisation.

The criteria for acceptable results were for most variables ± 20% of the "true value", as outlined in the Manual for Chemical and Biological Monitoring (1). Exceptions from this were pH and conductivity, for which the acceptance limits were set to ± 0.2 pH units and ± 10%, respectively. For pH the acceptance limit was extended due to overall poor acceptance ratios, while for conductivity the limit was reduced due to the overall good results for this parameter.

3   Results and Discussion

In the 2034 edition of the chemical intercomparison test, a total of 21 laboratories (representing 13 different countries) registered to participate, and successfully registered their results. This is a decline compared to the 32-38 laboratories participating in the preceding three editions. A likely explanation for the decline is the global covid-19 pandemic situation, causing lockdown of several nations during spring 2020. Information about the participating laboratories is provided in Appendix A, both by the identity of the laboratories (Table 3) and by a summary of the different countries represented (Table 4). There was no report of delayed delivery of samples or other issues with the customs, which has previously been encountered.

In Table 1, the results from the 2034 chemical intercomparison test is summarised, constituting for each parameter: the number of participants, the acceptance ratio, and for comparison the acceptance ratio from the three previous years. Overall, the results were good with the median of the acceptance ratio indicating that 81% of the results were within the general target accuracy of $\pm$ 20%, or the special accuracy limit for pH and conductivity ($\pm$ 0.2 pH units and $\pm$ 10% respectively).

Throughout this chapter the results for each variable will be presented and discussed based on acceptance ratio (Table 1) and the visual distribution of the results in the Youden chart (Figures 1-19). In the Youden chart, each laboratory is presented by one point, and the distribution of points can indicate the occurrence of random and/or systematic errors among the laboratories. The acceptance limit (typically $\pm$ 20 % of the mean true values for the sample pair) is illustrated in the charts as a circle. Note that laboratories with results that strongly deviated from the others has been excluded from the charts. Information on the different analytical techniques used by the laboratories is shown in Table 2. Factors that are typically found to influence the compliance among the results are low parameter values, the use of several different analytical methods for the determination of the same parameter, both leading to increased variability in the results.

For more detailed information on the uncertainty of the "true values" see Table 5 (Appendix C). The calculation has been performed according to ISO 13528 (2005), "Statistical methods for use in proficiency testing by interlaboratory comparisons". The individual results reported by the laboratories are listed in Table 6 (Appendix D), and more detailed statistics for each parameter is presented in Tables 7.1 to 7.20 (Appendix D).

Table 1. Summary of the results including the true values, number of participating laboratories, and acceptance rate in the 2034 edition and the three previous years (1933, 1832, and 1731) for each parameter.

Parameter (unit)	Sample-pair	True value		limit, %	Number of pairs		Acceptable results for intercalibration (%)			
		Sample 1	Sample 2		Tot.	Accept.	2034	1933	1832	1731
pH	AB	6.72	6.68	2.9	20	15	75	60	81	53
Conductivity (mS/m)	AB	6.06	9.68	10	20	16	80	79	85	77
Alkalinity (mmol/L)	AB	0.141	0.143	10	16	7	44	62	0	17
Nitrate+nitrite-nitrogen (µg/L)	AB	44.0	55.5	20	17	8	47	69	85	35
Chloride (mg/L)	AB	9.5	18.9	20	20	18	90	93	81	82
Sulphate (mg/L)	AB	3.49	4.71	20	21	16	76	75	96	90
Calcium (mg/L)	AB	3.38	3.54	20	19	17	89	90	93	83
Magnesium (mg/L)	AB	0.67	1.28	20	19	18	95	93	82	93
Sodium (mg/L)	AB	6.39	11.6	20	20	20	100	96	86	86
Potassium (mg/L)	AB	0.9	1.11	20	20	19	95	85	82	69
Total organic carbon (mg/L)	AB	5.41	5.57	20	15	11	73	80	74	81
Total phosphorous (µg/L)	AB	26.6	28.5	20	17	7	41	35	33	21
Aluminium (µg/L)	CD	18.85	122.65	20	15	12	80	55	57	82
Iron (µg/L)	CD	23.14	80.42	20	16	15	94	76	95	74
Manganese (µg/L)	CD	4.56	44.62	20	15	14	93	71	91	100
Cadmium (µg/L)	CD	1.8	1.8	20	16	15	94	77	88	92
Lead (µg/L)	CD	3.79	6.60	20	16	14	88	73	65	88
Copper (µg/L)	CD	10.9	30.29	20	16	15	94	75	84	95
Nickel (µg/L)	CD	7.68	7.64	20	16	15	94	77	87	100
Zinc (µg/L)	CD	12.69	17.8	20	15	12	80	61	91	96
Total					349	280	81	(75)	(79)	(76)

3.1 pH

Values of pH were reported by 20 laboratories, among which 75% were within the acceptable limit (± 0.2 pH units of the "true value", Table 1). This was a very good accomplishment. During previous years, pH has typically been associated with poor acceptance ratio and this has been attributed to the use of different measuring methods. An example is the different practices of stirring or not stirring the sample during determination can give a systematic error, and this is especially the case for samples with lower total ionic strength (4, 5). This year, the number of laboratories using each of the different was relatively evenly distributed and this may have contributed to unity in the reported results, e.g. no heavy bias towards one measurement technique (Table 2). Seven laboratories had used electrometric determination with equilibration, seven laboratories had used electrometric determination with stirring, five laboratories had used electrometric determination without stirring, and one laboratory reported to have used another unidentified method. The Youden chart showed some indication of both systematic and random error in the distribution of results for pH (Figure 1).

It is important to remember that pH is a difficult parameter to determine accurately, and that it will be influenced by different practices of sampling storage and handling, as well as the use of different analytical techniques. It must be stressed that this parameter should be determined as soon as possible after the samples have arrived at the laboratory.

3.2 Conductivity

Measured conductivity has typically been consistently of good acceptance rate during the previous years, and this was also the case for this 2034 edition. Conductivity was reported by 20 laboratories which provided an acceptance rate of 80% (± 10% of the "true value", Table 1).

All the 20 laboratories reported to have used electrometry for the determination of conductivity (Table 2). The high consistency in the results among the laboratories was confirmed by the Youden chart (Figure 2) in which most of the points were evenly distributed around origo. Two laboratories reported results consistently lower than the consensus of the remaining participants. Conductivity is highly temperature dependent, and improper temperature correction may lead to deviating results. Conductivity will vary by 2% for each degree at the temperatures round room temperature.

3.3 Alkalinity

Alkalinity was reported by 16 of the laboratories, producing an acceptance rate of 44% (± 20% of the "true value", Table 1). This was a poor acceptance rate compared to the results from the previous years, also when considering the level of alkalinity in the sample. One explanation to this may be the large number of different analytical techniques employed for the determination of alkalinity.

A total of seven different techniques were used by the 16 participating laboratories and constituted: gran plot titration (4 laboratories), one end point (pH 4.5) titration (3 laboratories), one end point (other pH) titration (3 laboratories), two end point titration (3 laboratories), colorimetry (1 laboratory), one end point (pH 5.6) titration (1 laboratory), and another unidentified method (1 laboratory).

The Youden chart for alkalinity (Figure 3) show systematic effects in the distribution of the results, likely due to the use of different analytical techniques and methods.

3.4 Nitrate + nitrite-nitrogen

A total of 17 laboratories reported results for nitrate+nitrite nitrogen of which 47% of the results were within the acceptance limit (± 20% of the "true value", Table 1). This was a relatively low acceptance rate compared to the previous recent years. The concentration in the samples this year was relatively low (44.0 and 55.5 µg L^{-1}), but still comparable to previous years.

Regarding the choice of analytical techniques and methods (Table 2), most laboratories had used ion chromatography (10 laboratories), followed by automatized photometry with Cd reduction (5 laboratories), manual photometry with Cd reduction (1 laboratory), and another unidentified form of photometry (1 laboratory).

The Youden chart for nitrate+nitrite-nitrogen indicated both some random and systematic effects (Figure 3), likely resulting from a combination of low concentration in the samples and the use of different analytical techniques and methods for its determination.

3.5 Chloride

For chloride, a high acceptance rate at 90% (± 20% of the "true value") was produced by the 20 participating laboratories (Table 1). According to Table 2, ion chromatography was the technique of choice by most of the participants (14 laboratories). Other methods included photometry with autoanalyzer (2 laboratories), argentometry (1 laboratory), capillary electrophoresis (1 laboratory), electrometry (1 laboratory), and manual titration using Hg (1 laboratory).

The distribution of the results in the Youden diagram (Figure 4) was very uniform and with little sign of systematic or random effects. Only a few laboratories reported results that were lower than the consensus of the other participating laboratories.

3.6 Sulphate

Sulphate concentrations were reported by all the 21 participating laboratories, producing an acceptance rate at 76% (± 20% of the "true value", Table 1). This was in agreement with the results from previous years having samples of comparable sulphate concentrations (~4 mg L^{-1}).

Ion chromatography was the technique of choice for most of the participating laboratories (14 laboratories), followed by photometry (3 laboratories), ICP-OES (2 laboratories), capillary electrophoresis (1 laboratory), and nephelometry (1 laboratory).

The Youden chart in Figure 6 demonstrated good precision of the results, and with only a few values being a little higher or lower than to the rest.

3.7 Calcium

The acceptance rate for calcium was high, at 93% (± 20% of the "true value", Table 1), for the 19 reporting laboratories. This was in accordance with the results from the previous recent years.

The different techniques that had been used for the determination of calcium (Table 2) constituted ICP-OES (7 laboratories), ion chromatography (6 laboratories), ICP-MS (3 laboratories), FAAS (2 laboratories), and capillary electrophoresis (1 laboratory). Despite the use of several different

analytical techniques, the unity of the results was very good, with only a weak systematic effect evident in the Youden diagram in Figure 7.

3.8 Magnesium

Levels of magnesium was reported by 19 laboratories. The acceptance ratio was high, at 95% (± 20% of the "true value"), which was good considering the relatively low concentrations in the samples (~ 1 mg L^{-1}). The different techniques and methods that had been used for the determination of magnesium are listed in Table 2, and constituted ICP-OES (7 laboratories), ion chromatography (6 laboratories), ICP-MS (3 laboratories), FAAS (2 laboratories), and capillary electrophoresis (1 laboratory).

Only a very weak systematic effect was evident in the distribution of the results in the Youden chart in Figure 8.

3.9 Sodium

Sodium achieved the highest acceptance rate this year, at 100% (± 20% of the "true value", Table 1) Results were provided by 20 laboratories. Sodium has typically achieved high acceptance rates during the previous years. This year, the sodium concentration in the sample was relatively high (6 - 12 mg L^{-1}). Six different techniques had been used by the laboratories for the determination of sodium: ICP-OES (7 laboratories), ion chromatography (6 laboratories), ICP-MS (3 laboratories), FAAS (2 laboratories), capillary electrophoresis (1 laboratory), and flame photometry (1 laboratory).

The good agreement of the sodium concentrations between the laboratories was confirmed by the distribution in the Youden chart showing very little sign of spread in the data (Figure 9).

3.10 Potassium

For potassium, 20 laboratories reported results from which 95% were within the acceptable threshold (± 20% of the "true value", Table 1). The high acceptance was in accordance with the results from the previous years.

Regarding the choice of analytical techniques (Table 2), the distribution was as follows: 7 laboratories had used ICP-OES, 6 had used ion chromatography, 3 had used ICP-MS, 2 used FAAS, and 1 laboratory each had used capillary electrophoresis or flame photometry. Looking at the Youden chart for potassium in Figure 10, the precision among the laboratories was very good. Only one laboratory reported results that were lower than the consensus of the remaining laboratories.

3.11 Total organic carbon

Concentrations of total organic carbon was reported by 15 laboratories, among which 73% were within the target threshold (± 20% of the "true value", Table 1). This was comparable to the results from the previous years.

Most of the laboratories (11 laboratories) had used the technique of combustion for the determination of total organic carbon, while 3 laboratories had used the UV/peroxodisulphate technique, and 1 laboratory had used another unidentified method. The Youden chart for total organic carbon showed some systematic error in the distribution of the results (Figure 11).

3.12 Total Phosphorus

17 laboratories reported results for total phosphorus (Table 1). The acceptance rate was 41%, which is higher than the previous years. The acceptance rate was previously reported as 18% as there had been an error in the concentration units, resulting in numbers being erroneously seen as zero values. After recalculating, the results look much better.

According to table 2, most laboratories had used photometry for the determination of total phosphorus (13 laboratories), followed by ICP-OES (4 laboratories), ICP-MS (1 laboratory), and another unidentified method (1 laboratory). Total phosphorus was only recently included in the chemical intercomparison (in 2017).

The revised Youden plot (Figure 12) is dominated by random errors, and several results are outside the 20% error boundaries. This is likely due to the total phosphorous concentrations being relatively low, and the acceptance rate of total phosphorous has been relatively low the previous years as well. The results also indicate that laboratories using ICP-OES have reported slightly lower concentrations than laboratories using photometry for the determination.

3.13 Aluminium

Concentrations of aluminium were reported by 15 laboratories, producing an acceptance rate at 80% (± 20% of the "true value", Table 1). This was a good accomplishment compared to the previous years. The concentration of aluminium in the two samples of sample set CD differed more than usual, representing low (19 µg L^{-1}) and intermediate (123 µg L^{-1}) aluminium levels compared to the concentrations from recent previous years.

Only three different techniques had been used for the determination of aluminium (Table 2): ICP-MS (8 laboratories), ICP-OES by (5 laboratories), and GFAAS (2 laboratories).

The large difference between the two samples made it challenging to display both acceptance rates in the Youden chart (Figure 13). However, since all samples were within the acceptance rate for the high-concentration sample, D, only the acceptance rate for the low-concentration sample C was illustrated in the chart by two vertical blue lines. The Youden chart indicated both some systematic and some random error in the distribution of the results for aluminium.

3.14 Iron

Results reported for iron showed a relatively high acceptance ratio at 94% for the 16 reporting laboratories (± 20% of the "true value", Table 1). This was comparable to the acceptance rates from previous years, even though the iron concentration in the samples this year was a little lower.

Atomic techniques had been most frequently used for the determination of iron, detecting either mass, light emission or absorption: ICP-MS by 8 laboratories, ICP-OES by 5 laboratories, and 1 laboratory each used either FFAAS, GAAS, or photometry (Table 2).

The Youden chart for iron showed mainly some random error in the distribution of the results, while a few laboratories reported results that were either higher or lower than the consensus of the other laboratories (Figure 14).

3.15 Manganese

The acceptance rate for manganese was at 93% for the 15 laboratories providing results (± 20% of the "true value", Table 1). There was a relatively large difference in the concentration between the two samples in the sample set (CD). One of the samples represented low (5 µg L^{-1}) manganese concentration while the other was high (45 µg L^{-1}), compared to the samples from the previous years.

For the determination of manganese 9 laboratories had used ICP-MS, 4 had used ICP-OES, 1 had used FAAS, and 1 had used GFAAS (Table 2).

The Youden chart in Figure 15 showed some random error in the distribution of the results. While most laboratories agreed on the concentration of the lowest sample, there was some discrepancies for the sample with the high concentration (still within the (± 20% of the "true value"). Due to the large difference in concentration between the two samples, the acceptance limit was only illustrated for the low-concentration sample C (two blue vertical lines).

3.16 Cadmium

Cadmium was determined by 16 of the laboratories providing results with 94% acceptance (± 20% of the "true value", Table 1). This was a good result, and comparable to the results from the previous years.

Plasma techniques were most frequently employed for the determination of cadmium (Table 2). 9 laboratories had used ICP-MS and four ICP-OES. The atomic absorption technique, GFAAS had been used by 3 laboratories. Looking at the Youden chart for cadmium in Figure 16, there was little spread in the data for cadmium.

3.17 Lead

For lead, results were reported by 16 laboratories, producing an acceptance rate at 88% (± 20% of the "true value", Table 1). This agreed with the results from the previous years.

According to Table 2 all laboratories had used atomic techniques for the determination of lead, with detection of either mass, emission or absorption. ICP-MS had been used by 9 laboratories, GFAAS by 4 laboratories, and ICP-OES by 3 laboratories. Looking at the Youden distribution of the results in Figure 17, there was only some very weak systematic effect and one reported value being lower than the rest.

3.18 Copper

The acceptance rate for copper was at 94% for the results provided by 16 laboratories (± 20% of the "true value", Table 1). This was good and comparable to the results from the previous years. Atomic techniques were preferred for copper determination (Table 2): ICP-MS by 9 laboratories, ICP-OES by 4 laboratories, and GFAAS by 3 laboratories. The distribution of the results in the Youden chart in Figure 18 looks good, and with only a small random effect in the distribution of the results.

3.19 Nickel

Results for nickel was reported by 16 laboratories for which 94% of were classified as acceptable according to the target limit (± 20% of the "true value", Table 1). The analytical techniques employed for the determination of nickel constituted ICP-MS by 9 laboratories, ICP-OES by 4 laboratories, and

GFAAS by 3 laboratories (Table 2). The Youden chart of the nickel results (Figure 19) confirms good precision of the results, with only one value being high for one of the samples analysed.

3.20 Zinc

Concentration of zinc in the samples were determined by 15 laboratories from which 80% fulfilled the acceptance criteria (± 20% of the "true value", Table 1). This was considered as good compared to the results reported in the three last editions of the test.

A few different techniques had been used for the determination of zinc (Table 2). ICP-MS was the most frequently employed, used by 9 laboratories. ICP-OES was used by 4 laboratories, and GFAAS and FAAS was used by 1 laboratory each. The distribution of the results in the Youden plot looked good (Figure 20), with only a weak systematic error and two values reported to be lower than the rest.

Table 2. Statistical summary of the results from the 2034 edition, including information of the different analytical techniques used by the laboratories.

Parameter and method	Sample pair	True value S1	S2	No. lab. Total	Om	Median S1	S2	Sample 1 Ave.	Stdev	Sample 2 Ave.	Stdev	Rel.stdev.av.% S1	S2	Rel. error % S1	S2
pH	AB	6.72	6.68	20	0	6.72	6.68	6.72	0.13	6.69	0.12	1.9	1.8	0.0	0.2
Elec., equilibration				7	0	6.75	6.68	6.73	0.15	6.72	0.14	2.2	2.1	0.3	0.6
Elec., stirring				7	0	6.77	6.74	6.75	0.11	6.71	0.11	1.7	1.7	0.5	0.5
Elec., non-stirring				5	0	6.64	6.66	6.67	0.13	6.67	0.11	2.0	1.6	-0.6	-0.1
Other method				1	0			6.60		6.51				-1.7	-2.5
Conductivity	AB	6.06	9.68	20	2	6.06	9.68	6.02	0.17	9.60	0.35	2.9	3.7	-0.7	-0.8
Electrometry				20	2	6.06	9.68	6.02	0.17	9.60	0.35	2.9	3.7	-0.7	-0.8
Alkalinity	AB	0.141	0.143	16	3	0.140	0.142	0.144	0.020	0.145	0.020	13.9	13.5	2.2	1.2
Gran plot titration				4	1	0.142	0.144	0.155	0.027	0.154	0.019	17.7	12.0	9.7	7.5
One end point(other)titr.				3	1			0.152		0.151				7.8	5.6
One end point(pH5.4)titr.				3	0	0.121	0.131	0.133	0.031	0.133	0.035	23.5	25.9	-5.4	-6.8
Two end points titration				3	0	0.143	0.144	0.143	0.010	0.145	0.009	7.0	6.2	1.4	1.6
Colorimetry				1	0			0.138		0.141				-2.1	-1.4
One end point(pH5.6)titr.				1	0			0.138		0.142				-2.1	-0.7
Other method				1	1			0.265		0.275				87.9	92.3
Nitrate + nitrite-nitrogen	AB	44.0	55.5	17	5	44.5	55.2	45.6	8.0	53.6	7.9	17.5	14.7	3.5	-3.5
Ion chromatography				10	3	44.0	55.5	45.0	2.3	55.1	7.9	5.2	14.2	2.3	-0.7
Auto.,photometry, Cd red				5	2	45.6	55.6	42.2	10.8	52.5	10.5	25.7	19.9	-4.0	-5.5
Man.,photometry Cd red				1	0			40.2		45.0				-8.6	-19.0
Photometry, other method				1	0			64.7		54.8				47.1	-1.3
Chloride	AB	9.5	18.9	20	2	9.5	18.9	9.4	0.6	18.7	0.7	6.3	3.5	-1.1	-1.0
Ion chromatography				14	1	9.5	18.9	9.3	0.5	18.7	0.7	5.5	4.0	-1.7	-1.2
Photometry, autoanalyzer				2	1			8.2		18.3				-13.9	-2.9
Argentometry				1	0			9.4		19.1				-0.9	1.1
Cap. electrophoresis				1	0			10.2		18.5				7.4	-2.0
Electrometry				1	0			9.9		19.0				3.9	0.6
Manual titration, Hg				1	0			10.0		19.3				5.4	1.9
Sulphate	AB	3.49	4.71	21	1	3.49	4.71	3.40	0.38	4.72	0.41	11.3	8.7	-2.4	0.3
Ion chromatography				14	1	3.50	4.71	3.46	0.12	4.80	0.29	3.5	5.9	-0.8	1.9
Photometry				3	0	3.47	4.76	3.19	0.67	4.41	0.78	21.1	17.7	-8.4	-6.2
ICP-OES				2	0			3.69		4.88				5.8	3.6
Cap. electrophoresis				1	0			3.70		4.70				6.2	-0.1
Nephelometry				1	0			2.40		4.30				-31.1	-8.6
Calcium	AB	3.38	3.55	19	1	3.38	3.55	3.37	0.20	3.62	0.34	6.0	9.4	-0.3	2.1
ICP-OES				7	0	3.27	3.46	3.30	0.07	3.49	0.09	2.0	2.5	-2.4	-1.5
Ion chromatography				6	1	3.38	3.64	3.38	0.34	3.66	0.28	10.1	7.5	-0.1	3.1
ICP-MS				3	0	3.39	3.48	3.40	0.07	3.52	0.08	2.1	2.2	0.5	-0.8
FAAS				2	0			3.40		3.54				0.6	-0.2
Cap. Electrophoresis				1	0			3.70		4.80				9.5	35.3
Magnesium	AB	0.67	1.28	19	1	0.67	1.28	0.66	0.04	1.29	0.06	6.2	4.6	-0.4	1.1
ICP-OES				7	0	0.66	1.28	0.66	0.02	1.29	0.03	3.2	2.6	-0.3	0.8
Ion chromatography				6	1	0.63	1.24	0.65	0.07	1.29	0.11	10.6	8.4	-3.0	1.1
ICP-MS				3	0	0.69	1.34	0.69	0.03	1.31	0.05	4.1	3.6	3.5	2.6
FAAS				2	0			0.65		1.28				-2.6	0.0
Cap. Electrophoresis				1	0			0.69		1.29				3.8	0.8

*Om.: Sample pair omitted from the calculations

Variable and method	Sample pair	True value		No. labs		Median		Sample 1		Sample 2		Rel. stdev. Av %		Rel. error %	
		S1	S2	Tot.	Om	S1	S2	Ave.	Stdev	Ave.	Stdev.	S1	S2	S1	S2
Sodium	AB	6.39	11.60	20	0	6.39	11.60	6.36	0.20	11.66	0.31	3.1	2.7	-0.3	0.5
ICP-OES				7	0	6.42	11.86	6.43	0.23	11.85	0.25	3.6	2.1	0.7	2.1
Ion chromatography				6	0	6.38	11.60	6.30	0.22	11.66	0.19	3.5	1.6	-1.3	0.5
ICP-MS				3	0	6.51	11.60	6.43	0.15	11.70	0.29	2.3	2.5	0.7	0.8
FAAS				2	0			6.22		11.40				-2.7	-1.8
Cap. Electrophoresis				1	0			6.40		11.40				0.2	-1.7
Flame photometry				1	0			6.30		11.00				-1.3	-5.2
Potassium	AB	0.90	1.11	20	1	0.90	1.11	0.91	0.05	1.11	0.05	5.5	4.9	0.9	0.0
ICP-OES				7	0	0.92	1.13	0.93	0.03	1.14	0.05	2.7	4.3	3.2	3.1
Ion chromatography				6	0	0.86	1.10	0.89	0.06	1.09	0.06	7.2	5.3	-1.4	-1.5
ICP-MS				3	0	0.88	1.07	0.88	0.01	1.07	0.01	0.8	1.1	-2.0	-3.6
FAAS				2	1			0.89		1.05				-1.1	-5.4
Cap. Electrophoresis				1	0			1.02		1.16				13.3	4.5
Flame photometry				1	0			0.88		1.10				-2.2	-0.9
Total organic carbon	AB	5.41	5.57	15	1	5.46	5.58	5.48	0.65	5.64	0.72	11.9	12.7	1.4	1.3
Combustion				11	1	5.37	5.47	5.36	0.66	5.44	0.66	12.3	12.2	-0.9	-2.3
UV/peroxodisulphate				3	0	6.21	6.12	5.91	0.69	6.36	0.62	11.7	9.8	9.2	14.2
Other method				1	0			5.41		5.53				0.0	-0.7
Total phosphorous	AB	26.6	28.5	17	1	26.6	28.5	25.7	5.2	27.9	4.5	20.4	16.1	-3.6	-2.0
Photometry				11	1	27.3	28.5	26.6	4.5	27.7	4.0	17.1	14.5	-0.1	-2.6
ICP-OES				4	0	20.5	24.4	20.4	2.2	25.9	4.3	10.7	16.7	-23.3	-9.2
ICP-MS				1	0			35.0		37.0				31.6	29.8
Other method				1	0			28.0		29.0				5.3	1.8
Aluminium	CD	18.9	122.7	15	1	18.9	122.7	20.0	2.9	125.1	11.8	14.7	9.4	6.0	2.0
ICP-MS				8	0	18.7	122.7	19.0	1.5	124.0	7.6	7.8	6.1	0.8	1.1
ICP-OES				5	1	21.1	122.6	21.3	4.8	123.0	7.8	22.5	6.3	13.0	0.3
GFAAS				2	0			21.2		133.4				12.4	8.8
Iron	CD	23.1	80.4	16	1	23.1	80.4	23.1	3.7	80.5	4.0	15.9	5.0	-0.1	0.2
ICP-MS				8	0	23.3	81.4	24.0	2.9	81.6	3.6	12.2	4.4	3.9	1.4
ICP-OES				5	0	22.1	77.0	20.7	3.6	77.4	2.2	17.3	2.8	-10.6	-3.7
FAAS				1	0			21.6		80.7				-6.7	0.3
GFAAS				1	0			29.5		88.0				27.3	9.4
Photometry				1	1			41.8		93.8				80.6	16.6
Manganese	CD	4.56	44.62	15	1	4.56	44.62	4.56	0.21	44.97	2.14	4.6	4.8	-0.1	0.8
ICP-MS				9	0	4.57	44.53	4.52	0.17	44.97	2.15	3.7	4.8	-0.9	0.8
ICP-OES				4	0	4.49	44.05	4.50	0.10	44.03	1.18	2.2	2.7	-1.2	-1.3
FAAS				1	0			5.10		48.80				11.8	9.4
GFAAS				1	1			5.61		60.29				23.0	35.1
Cadmium	CD	1.80	1.77	16	1	1.80	1.77	1.82	0.10	1.76	0.09	5.4	5.1	1.2	-0.4
ICP-MS				9	0	1.80	1.79	1.83	0.06	1.80	0.05	3.4	2.7	1.7	1.6
ICP-OES				4	0	1.85	1.75	1.84	0.17	1.73	0.14	9.4	7.9	2.0	-2.5
GFAAS				3	1			1.75		1.68				-2.8	-5.5
Lead	CD	3.79	6.60	16	1	3.79	6.60	3.76	0.28	6.54	0.43	7.4	6.5	-0.7	-1.0
ICP-MS				9	0	3.71	6.60	3.74	0.15	6.61	0.22	4.0	3.4	-1.4	0.2
GFAAS				4	0	3.80	6.44	3.67	0.49	6.32	0.77	13.2	12.3	-3.0	-4.3
ICP-OES				3	1			4.05		6.63				6.9	0.4

*Om.: Sample pair omitted from the calculations

Variable and method	Sample pair	True value		No. lab.		Median		Sample 1		Sample 2		Rel.std.av. %		Rel. error %	
		S1	S2	Total	Om	S1	S2	Ave.	Stdev	Ave.	Stdev	S1	S2	S1	S2
Copper	CD	10.9	30.3	16	1	10.9	30.3	10.9	0.4	30.5	1.2	3.3	4.0	0.0	0.8
ICP-MS				9	0	10.9	30.3	10.8	0.3	30.3	0.9	2.6	3.0	-0.7	0.2
ICP-OES				4	1	10.8	29.5	10.8	0.5	29.6	0.4	4.8	1.4	-1.4	-2.4
GFAAS				3	0	11.3	31.8	11.3	0.3	32.1	1.4	2.2	4.4	3.3	5.8
Nickel	CD	7.68	7.64	16	1	7.68	7.64	7.71	0.32	7.74	0.26	4.2	3.3	0.4	1.3
ICP-MS				9	0	7.69	7.64	7.76	0.22	7.73	0.20	2.8	2.6	1.0	1.1
ICP-OES				4	0	7.63	7.70	7.82	0.46	7.82	0.42	5.9	5.4	1.8	2.3
GFAAS				3	1			7.28		7.61				-5.3	-0.4
Zinc	CD	12.69	17.80	15	1	12.69	17.80	12.42	1.21	17.41	1.77	9.7	10.2	-2.1	-2.2
ICP-MS				9	0	12.60	17.80	12.45	1.39	17.63	1.57	11.2	8.9	-1.8	-1.0
ICP-OES				4	0	12.79	18.08	12.79	0.16	18.01	0.44	1.2	2.4	0.8	1.2
FAAS				1	0			10.70		13.10				-15.6	-26.4
GFAAS				1	1			17.55		30.90				38.4	73.6

*Om.: Sample pair omitted from the calculations

pH
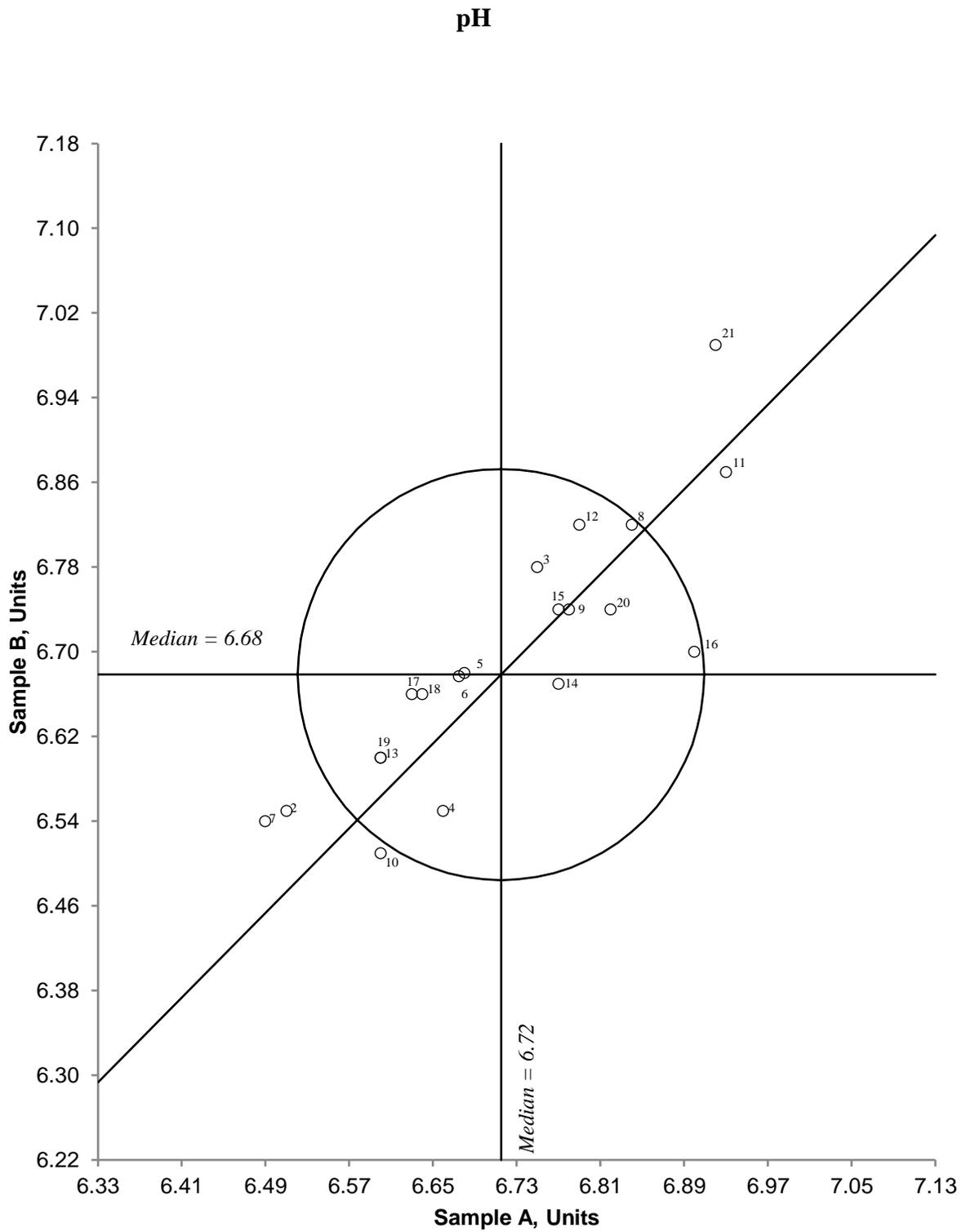
Figure 1. Youden diagram for pH. Sample pair AB. Acceptable limit, given by circle, is 2.9%.

Conductivity
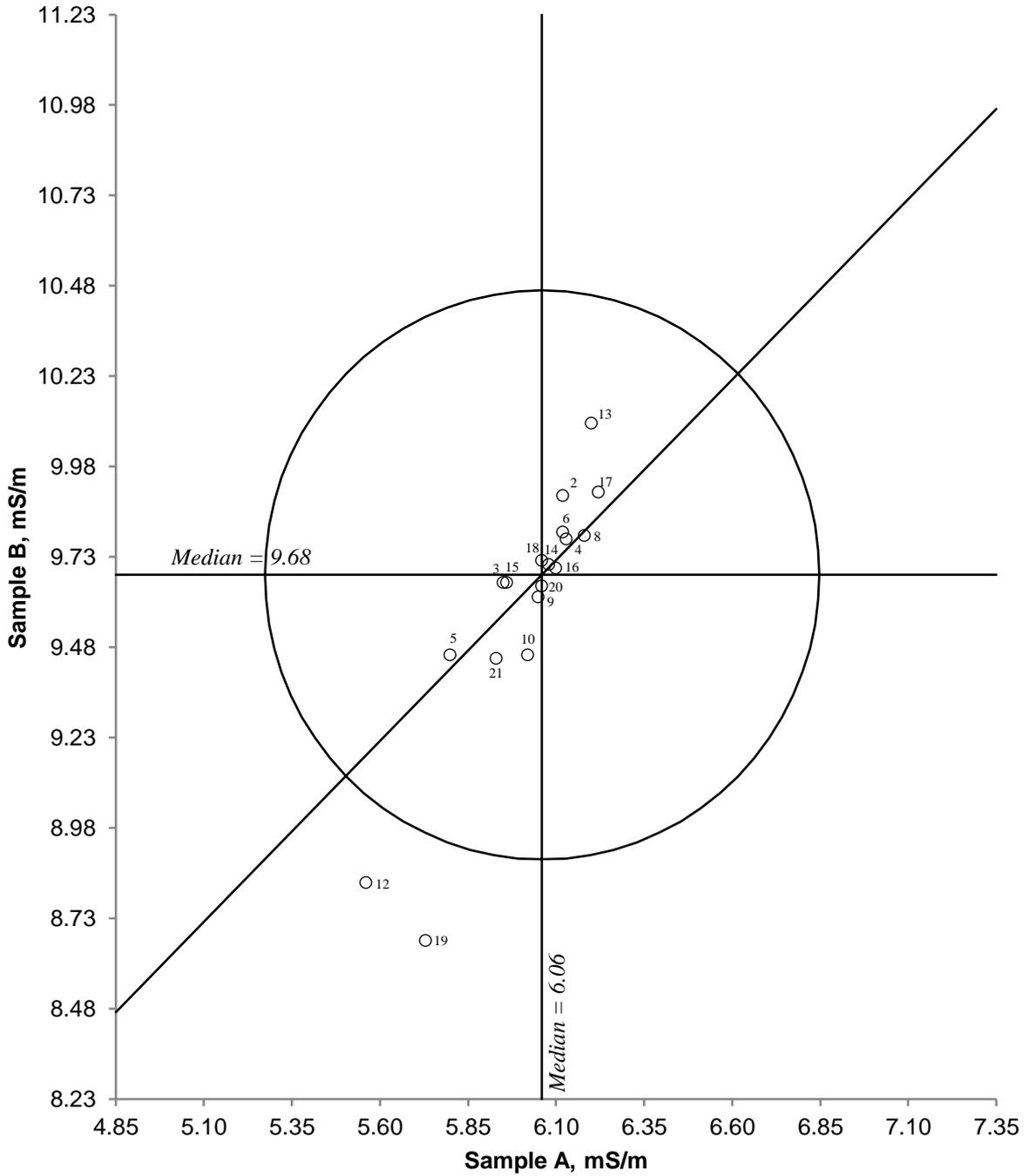
Figure 2. Youden diagram for conductivity. Sample pair AB. Acceptable limit, given by circle, is 10%.

Alkalinity

Figure 3. Youden diagram for alkalinity. Sample pair AB. Acceptable limit, given by circle, is 10%.

Nitrate + nitrite-nitrogen
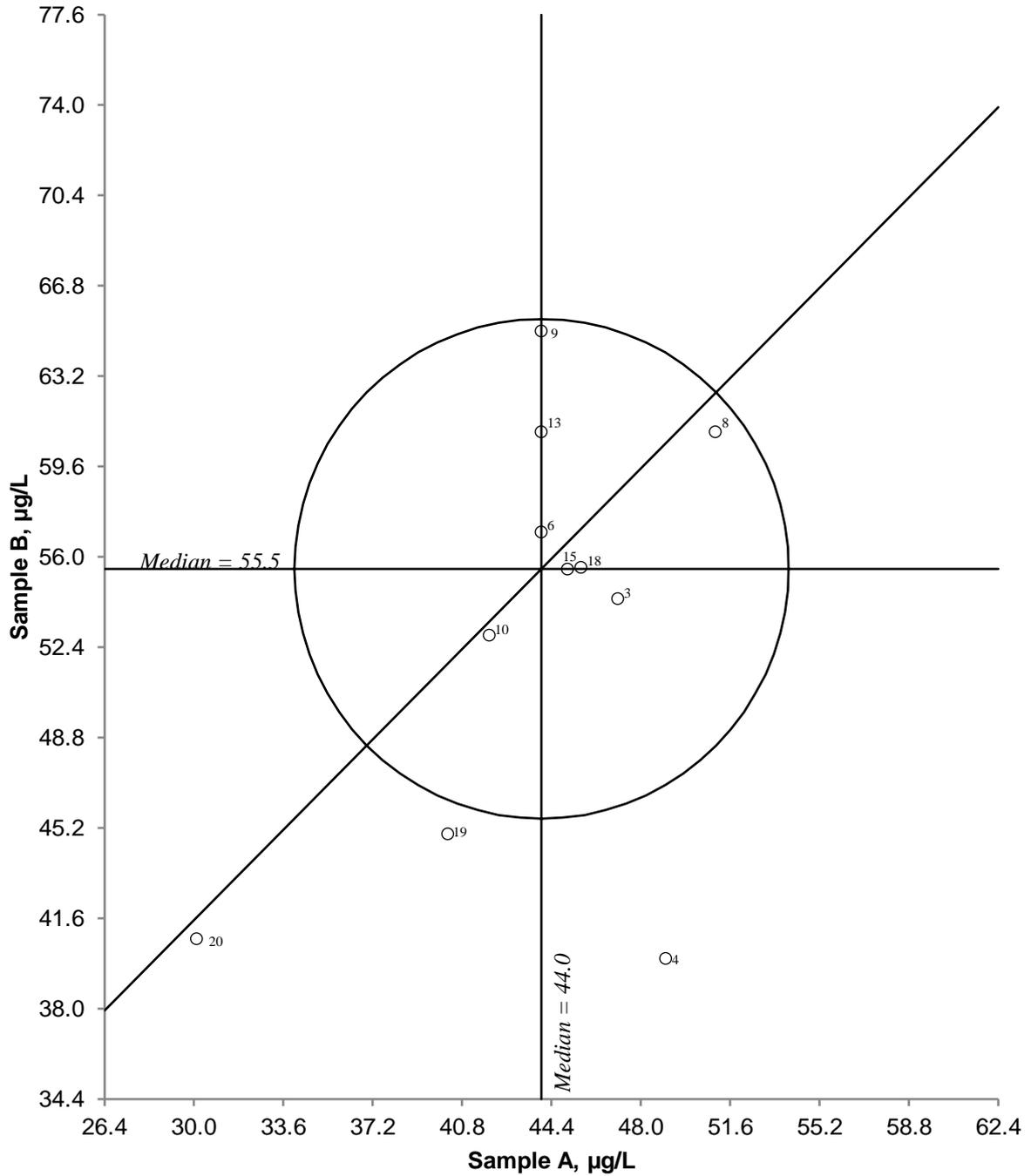
Figure 4. Youden diagram for nitrate+nitrite-nitrogen. Sample pair AB. Acceptable limit, given by circle, is 20%.

Chloride
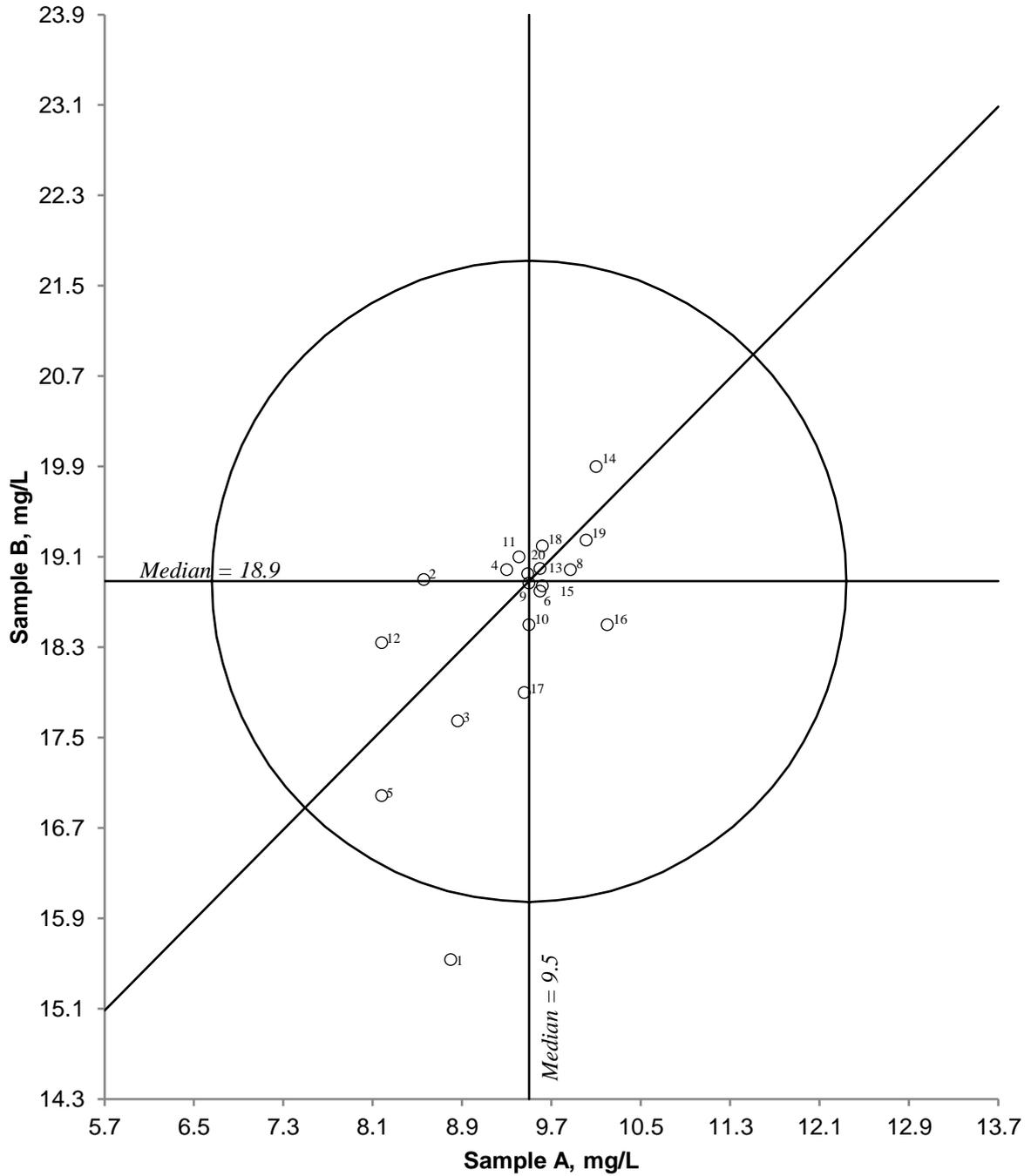
Figure 5. Youden diagram for chloride. Sample pair AB. Acceptable limit, given by circle, is 20%.

Sulphate
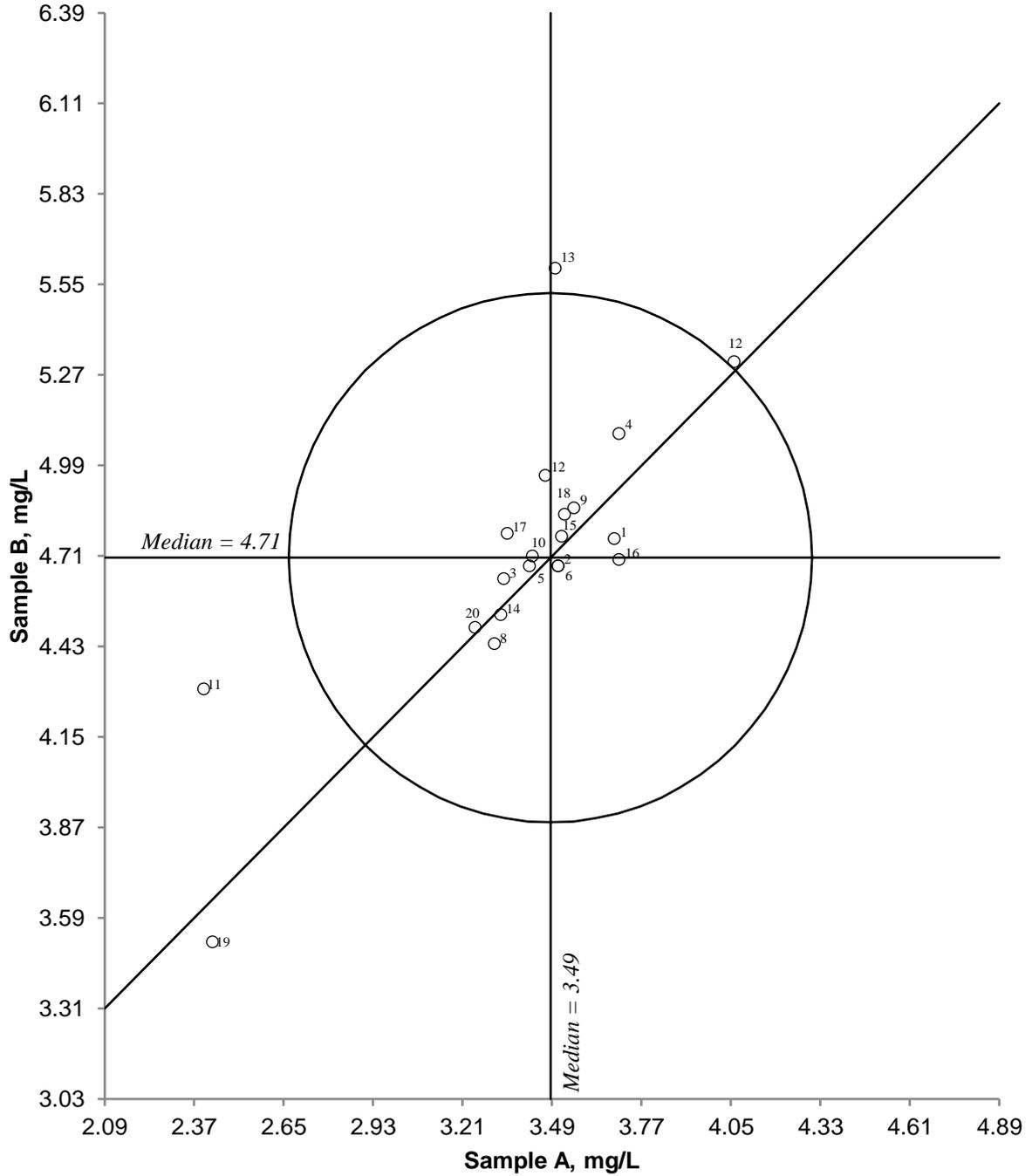
Figure 6. Youden diagram for sulphate. Sample pair AB. Acceptable limit, given by circle, is 20%.
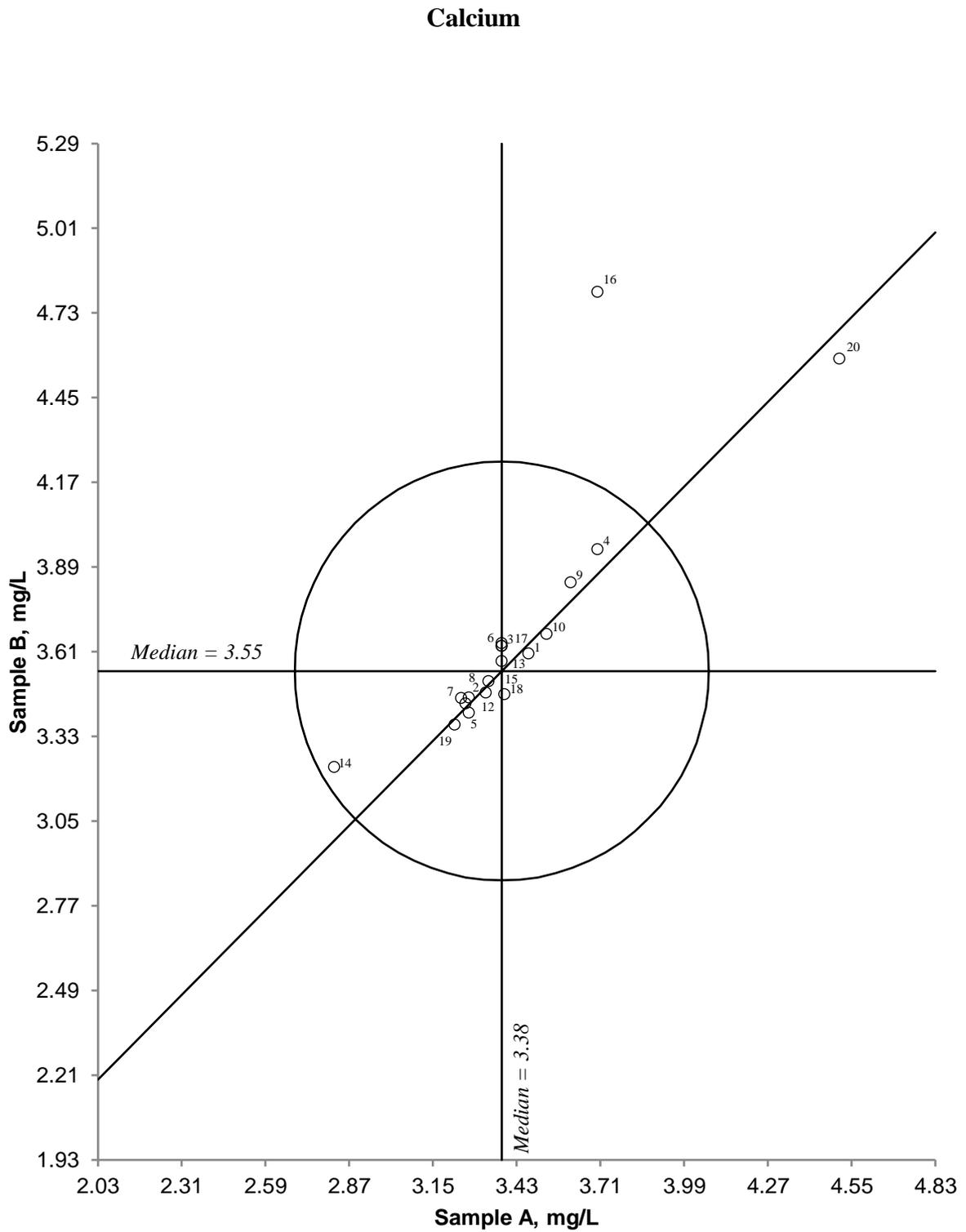
Calcium

Figure 7. Youden diagram for calcium. Sample pair AB. Acceptable limit, given by circle, is 20%.

Magnesium
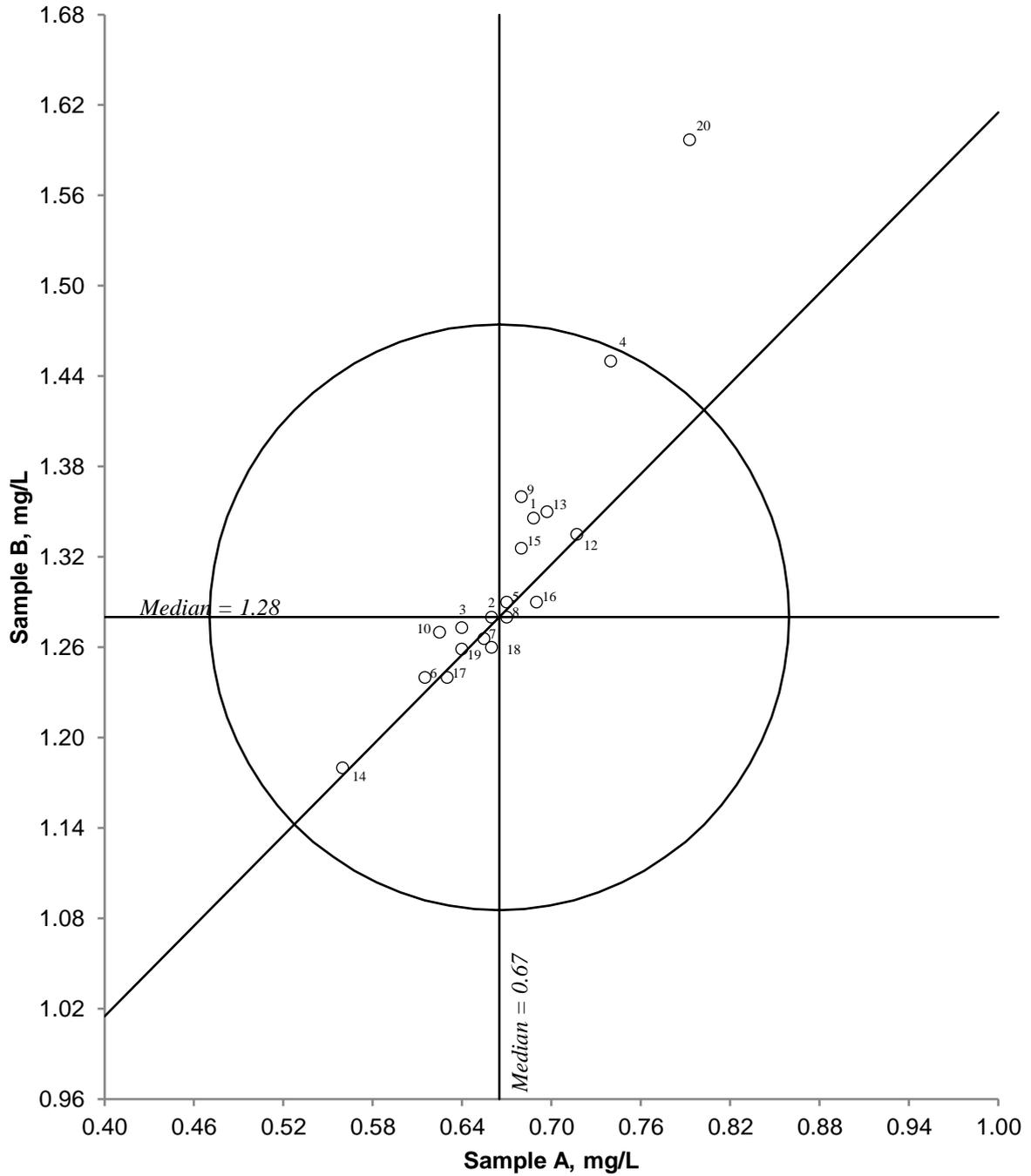
Figure 8. Youden diagram for magnesium. Sample pair AB. Acceptable limit, given by circle, is 20%.

Sodium
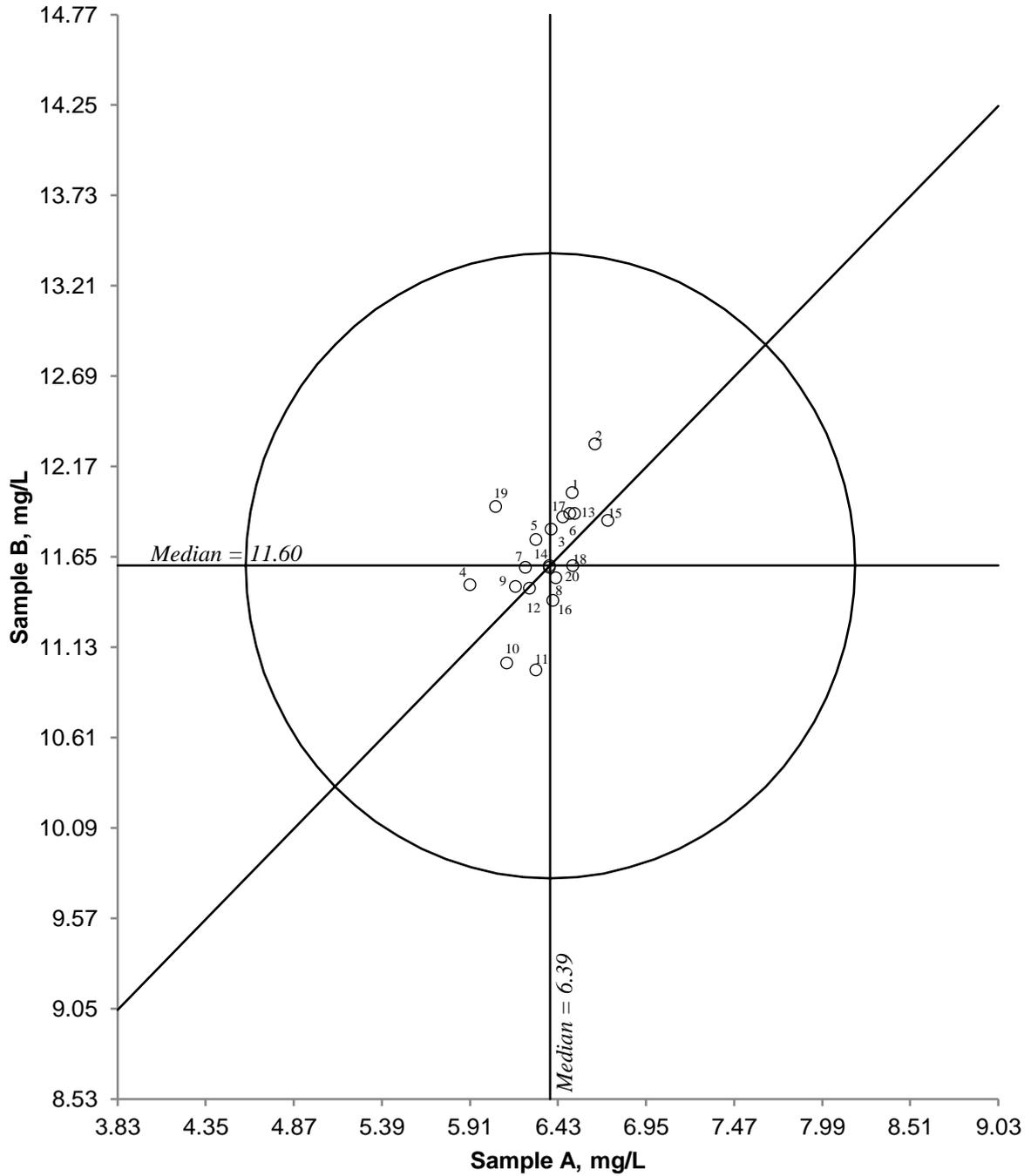
Figure 9. Youden diagram for sodium. Sample pair AB. Acceptable limit, given by circle, is 20%.

Potassium
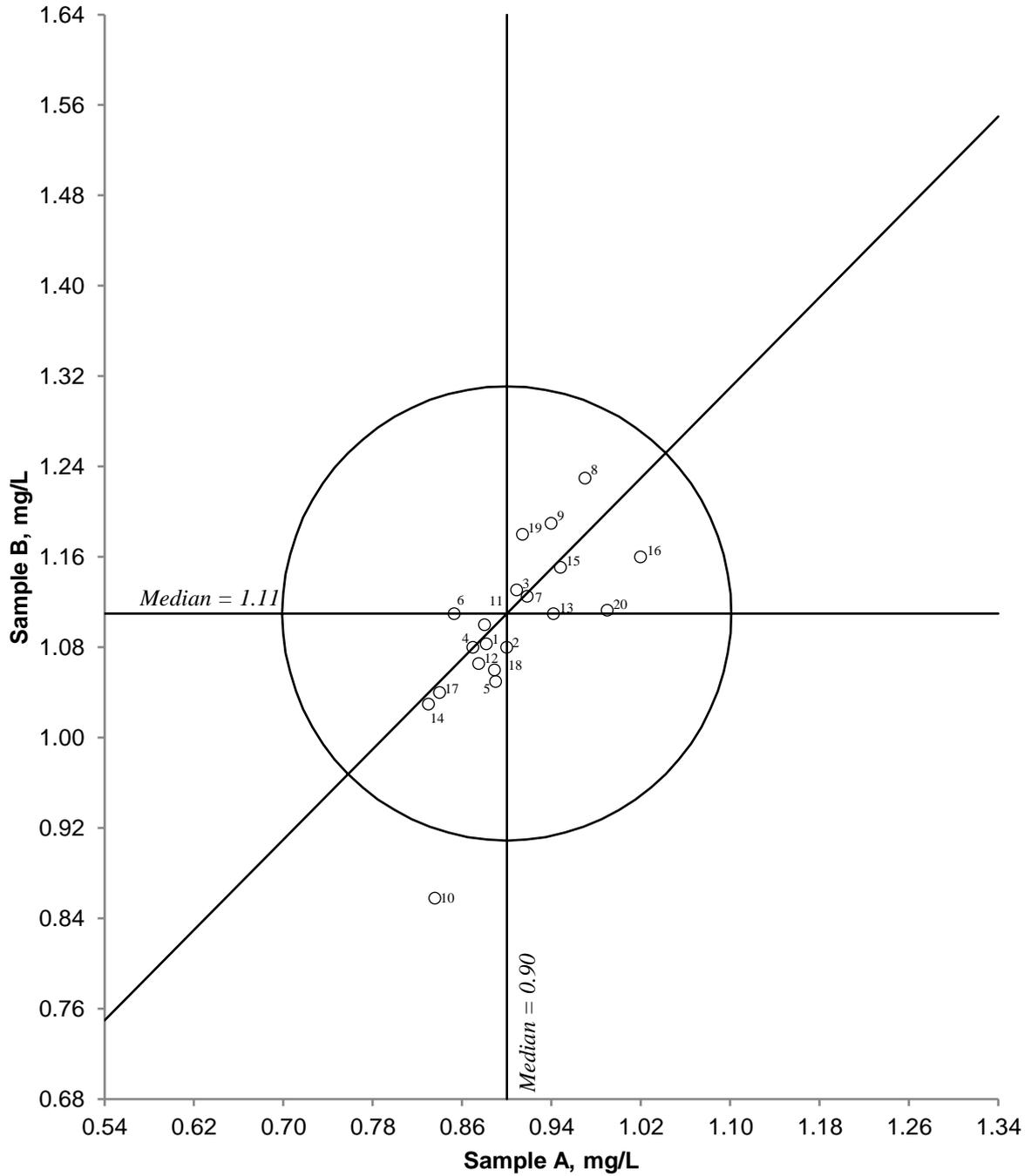
Figure 10. Youden diagram for potassium. Sample pair AB. Acceptable limit, given by circle, is 20%.

Total organic carbon
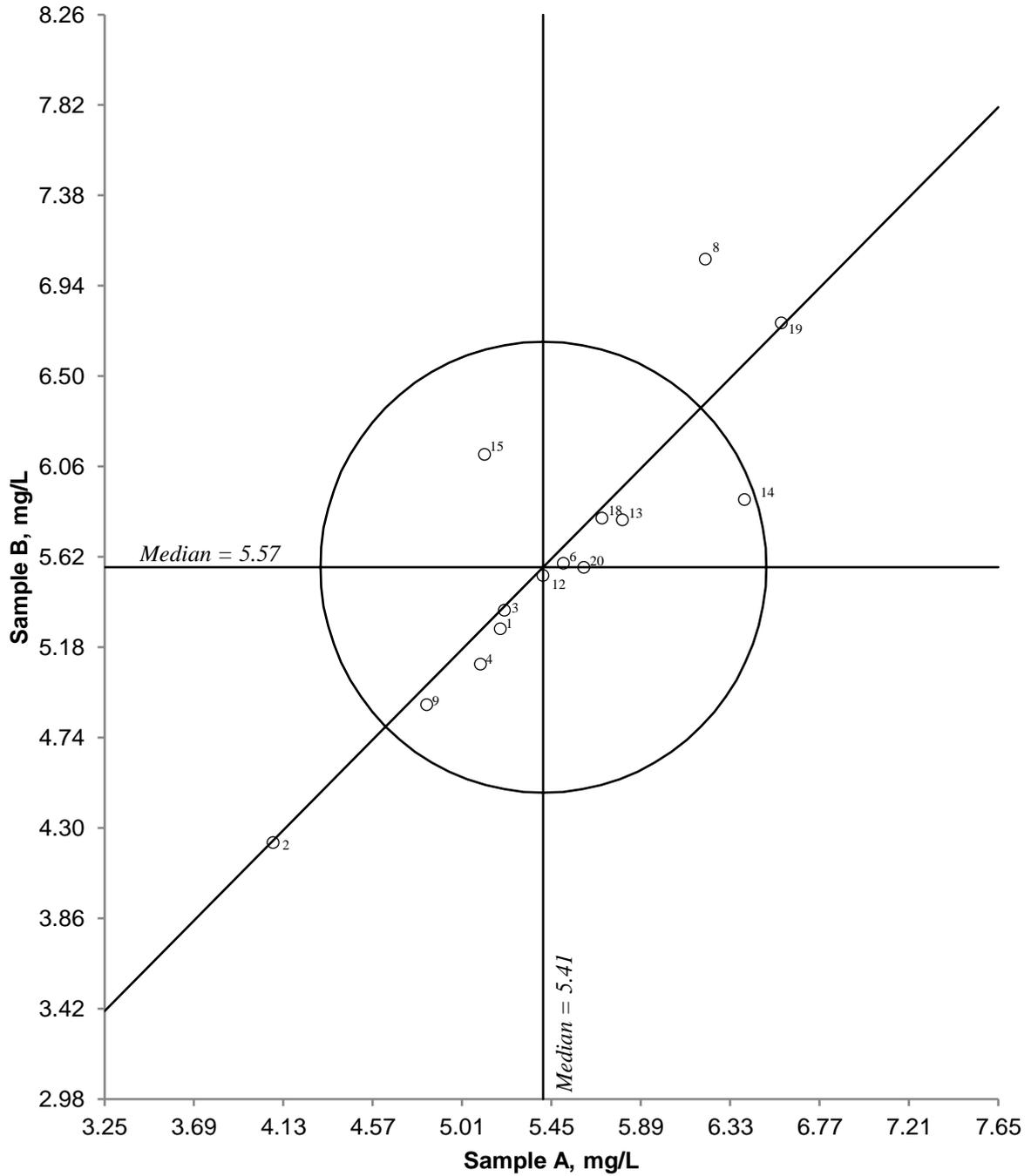
Figure 11. Youden diagram for total organic carbon. Sample pair AB. Acceptable limit, given by circle, is 20%.

Total phosphorous
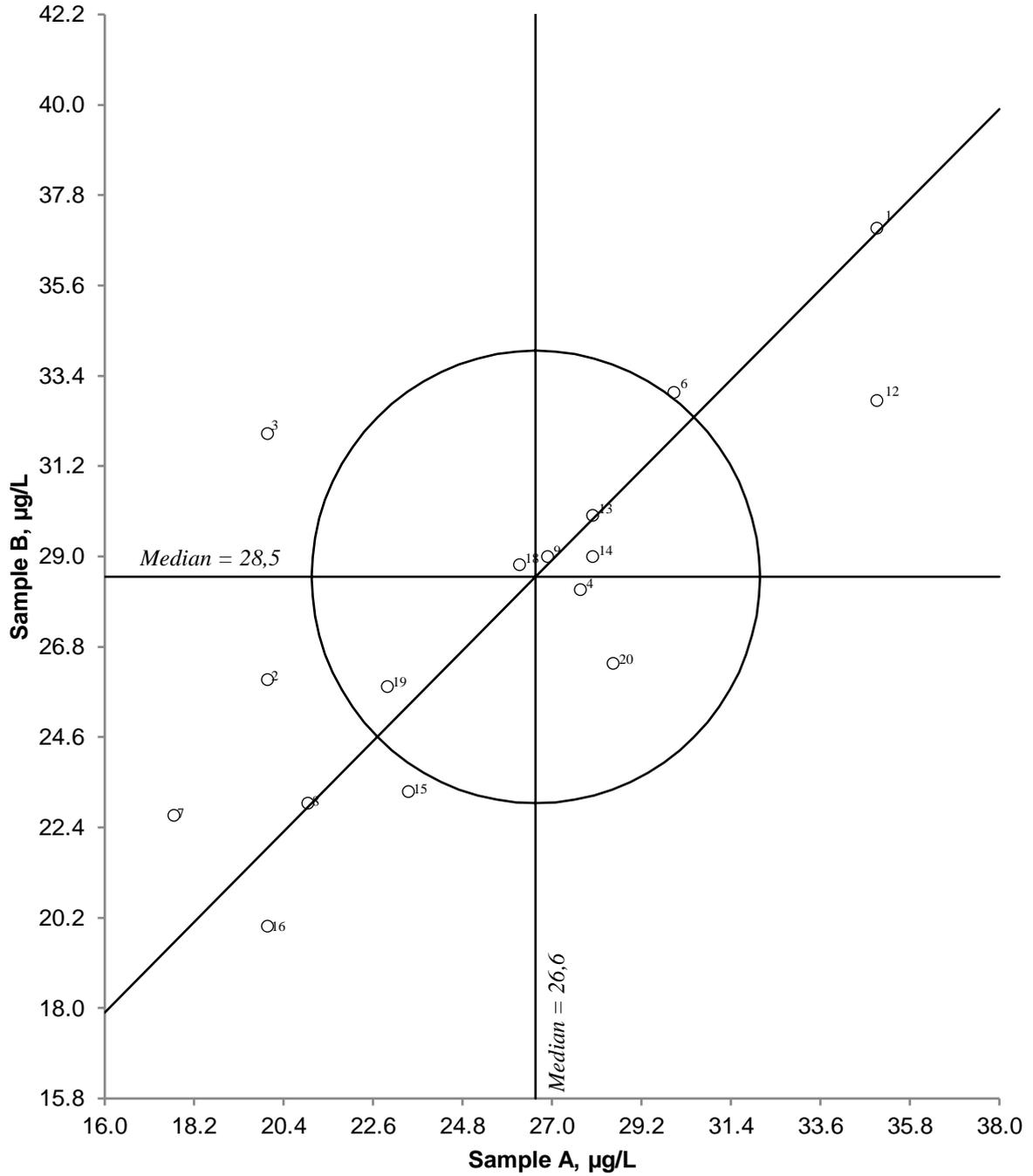
Figure 12. Youden diagram for total phosphorus. Sample pair AB. Acceptable limit, given by circle, is 20%.

Aluminium
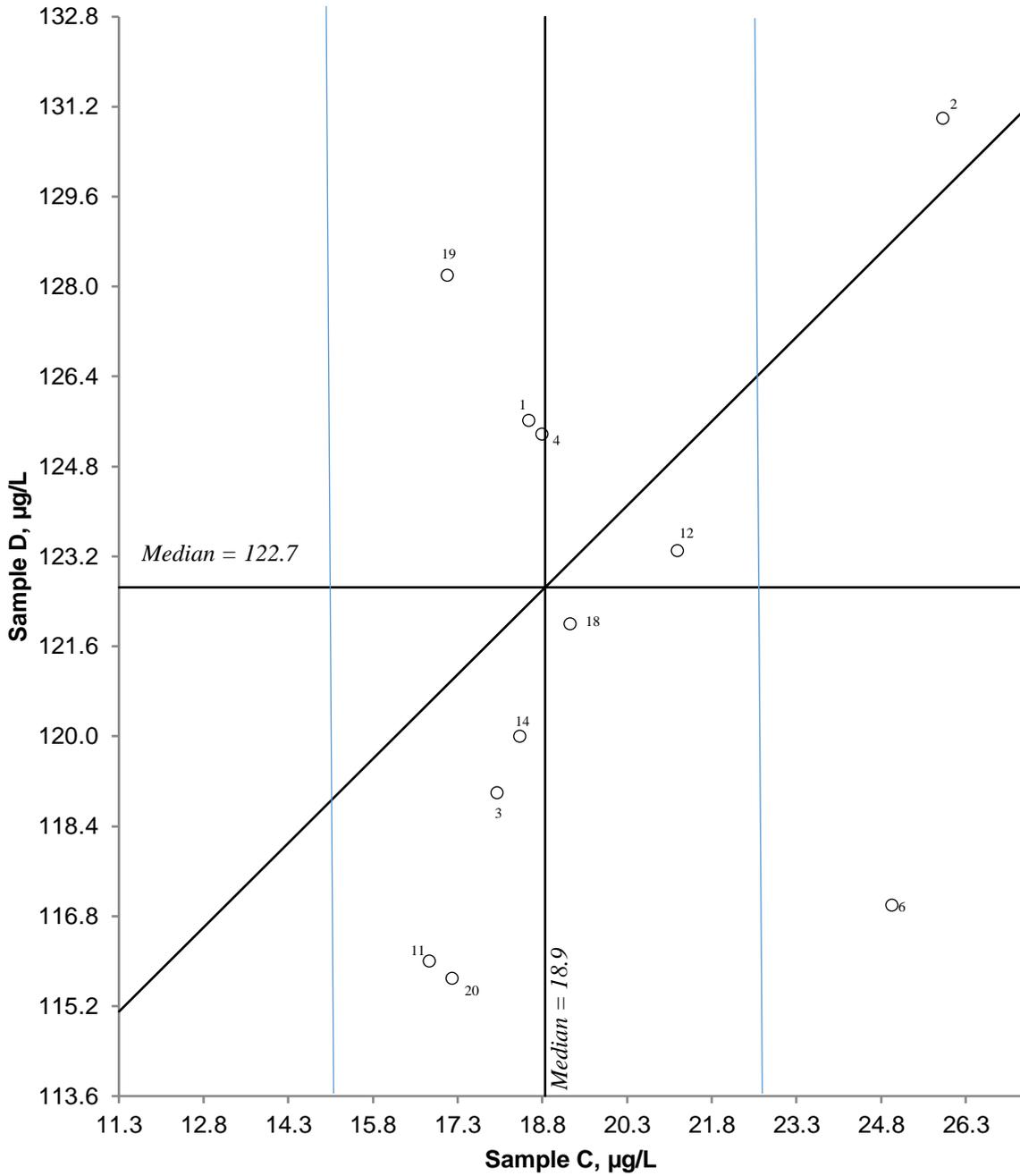
Figure 13. Youden diagram for aluminium. Sample pair CD. Acceptable limit for sample C is illustrated by the two blue vertical lines, at 20%. For sample D, the acceptance rate at 20% is outside the plot area and therefore not visible.

Iron
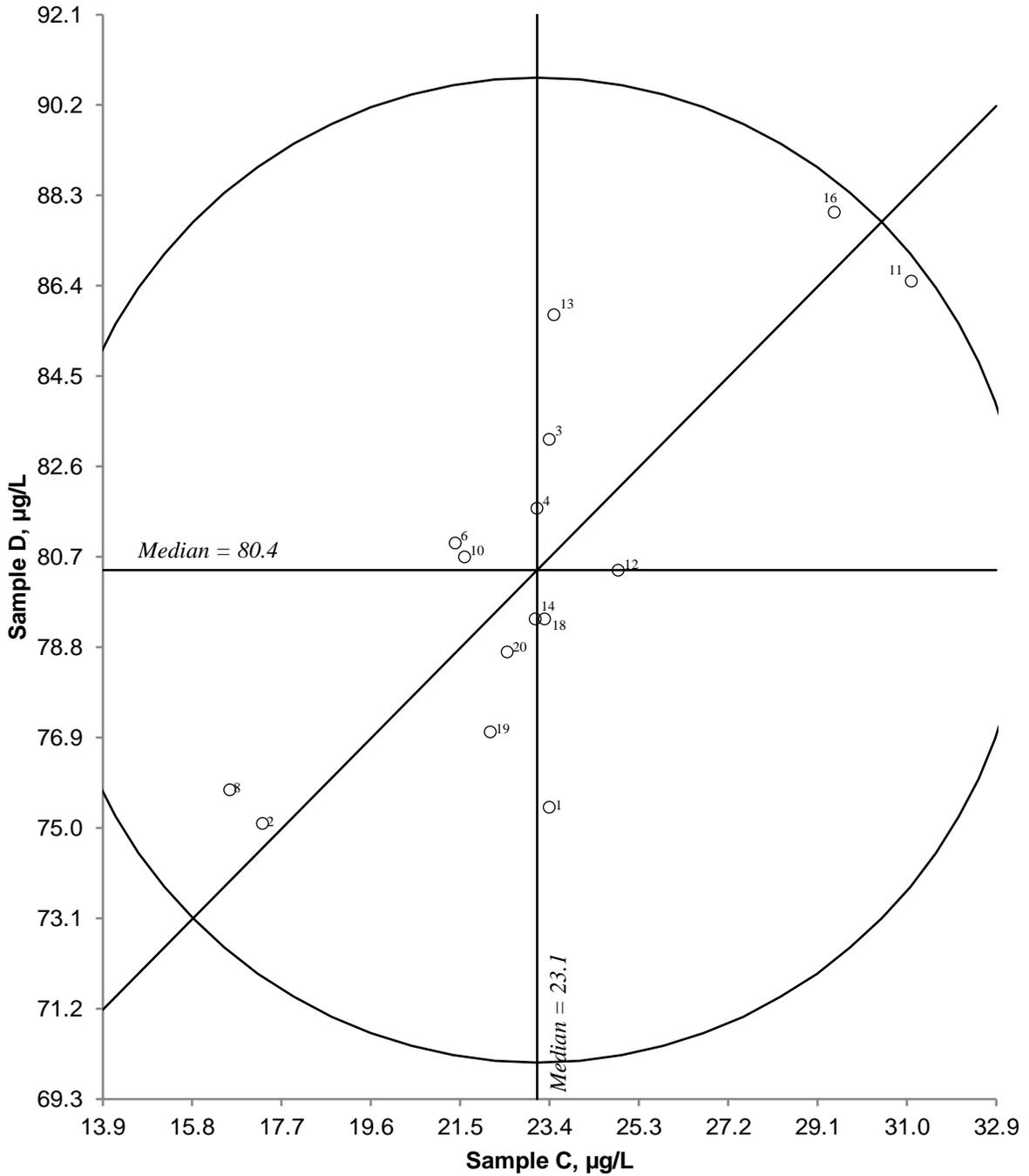
Figure 14. Youden diagram for iron. Sample pair CD. Acceptable limit, given by circle, is 20%.

Manganese
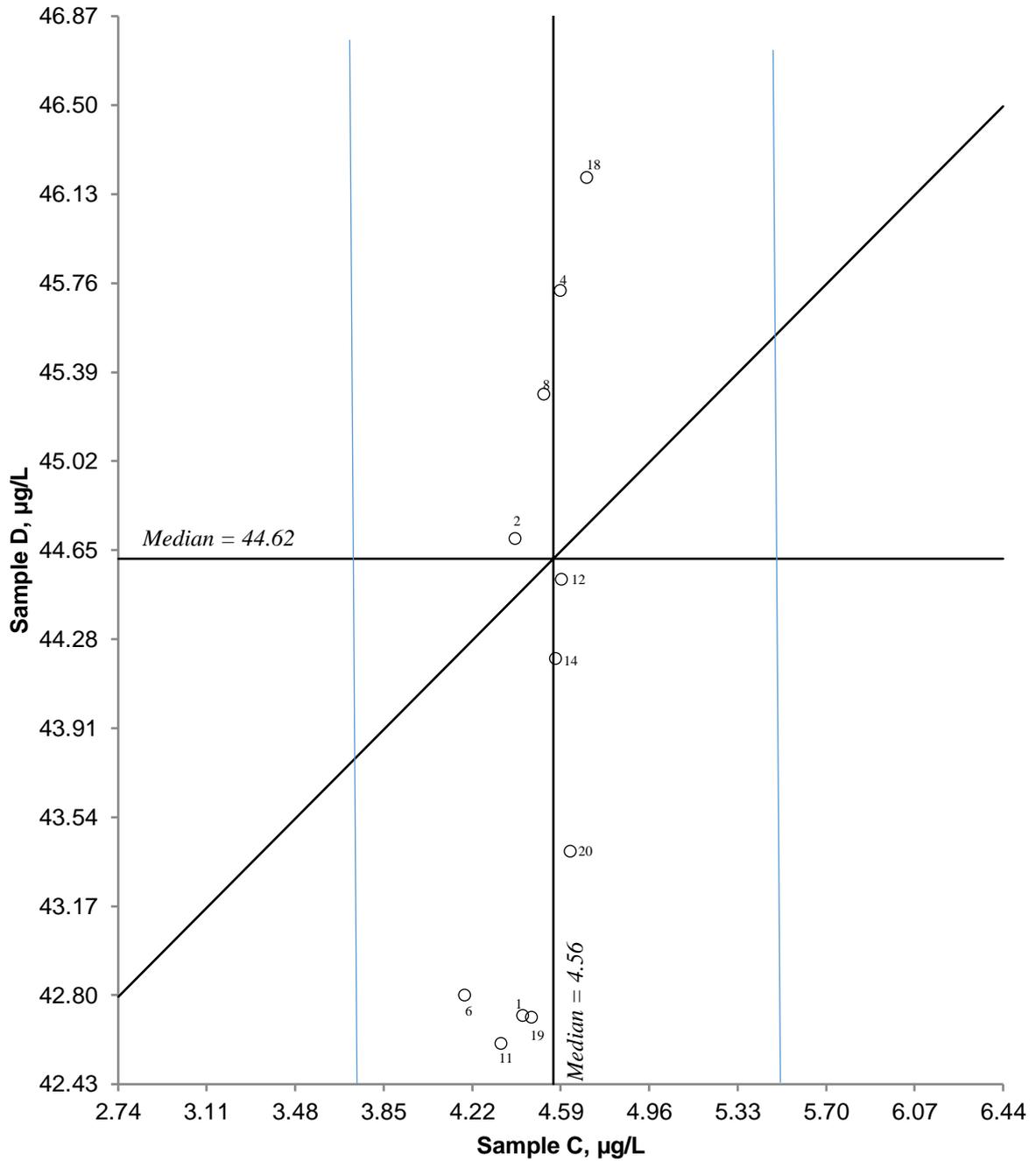
Figure 15. Youden diagram for manganese. Sample pair CD. Acceptable limit for sample C is illustrated by the two blue vertical lines, at 20%. For sample D, the acceptance rate at 20% is outside the plot area and therefore not visible.

Cadmium
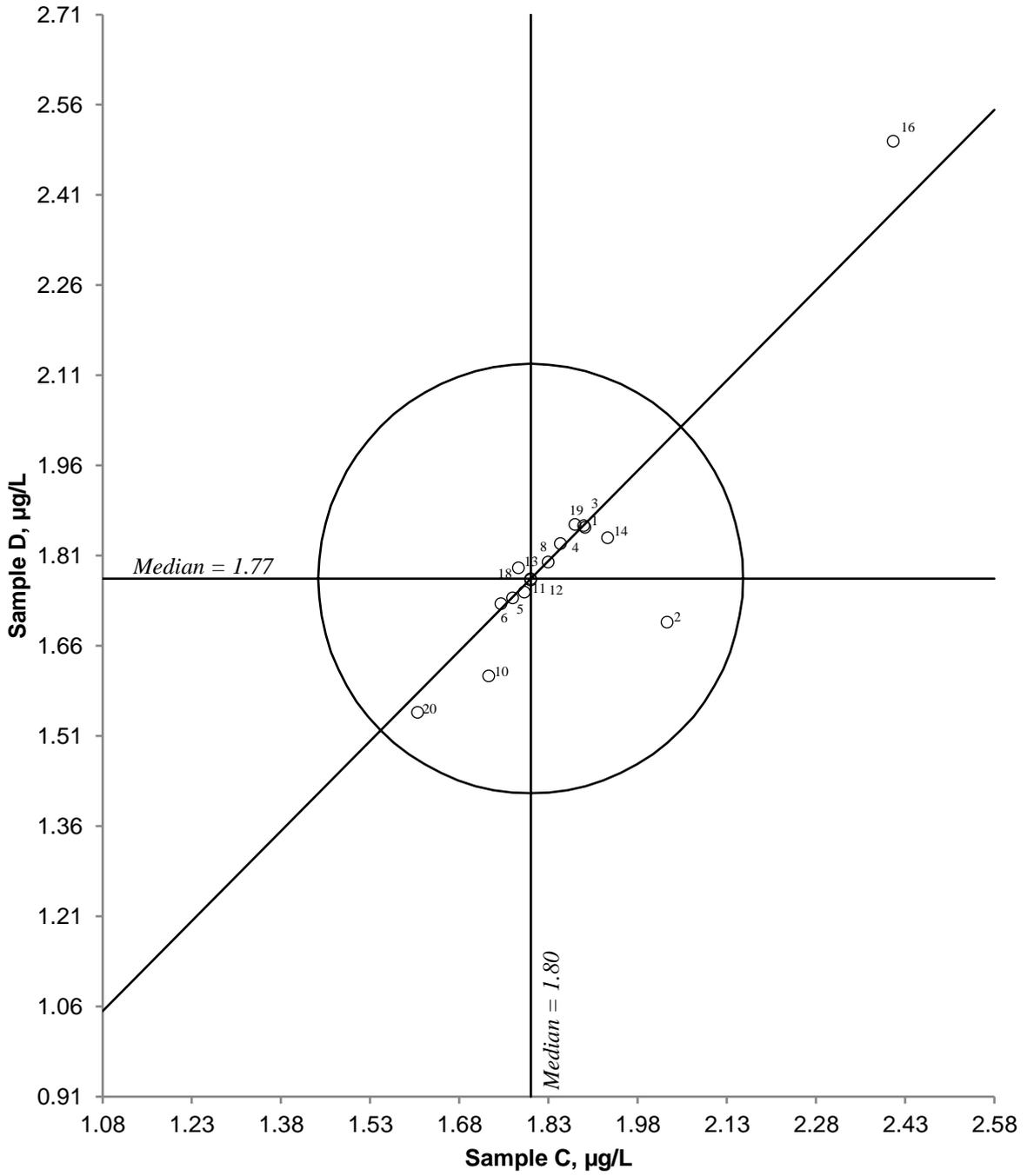
Figure 16. Youden diagram for cadmium. Sample pair CD. Acceptable limit, given by circle, is 20%.

Lead
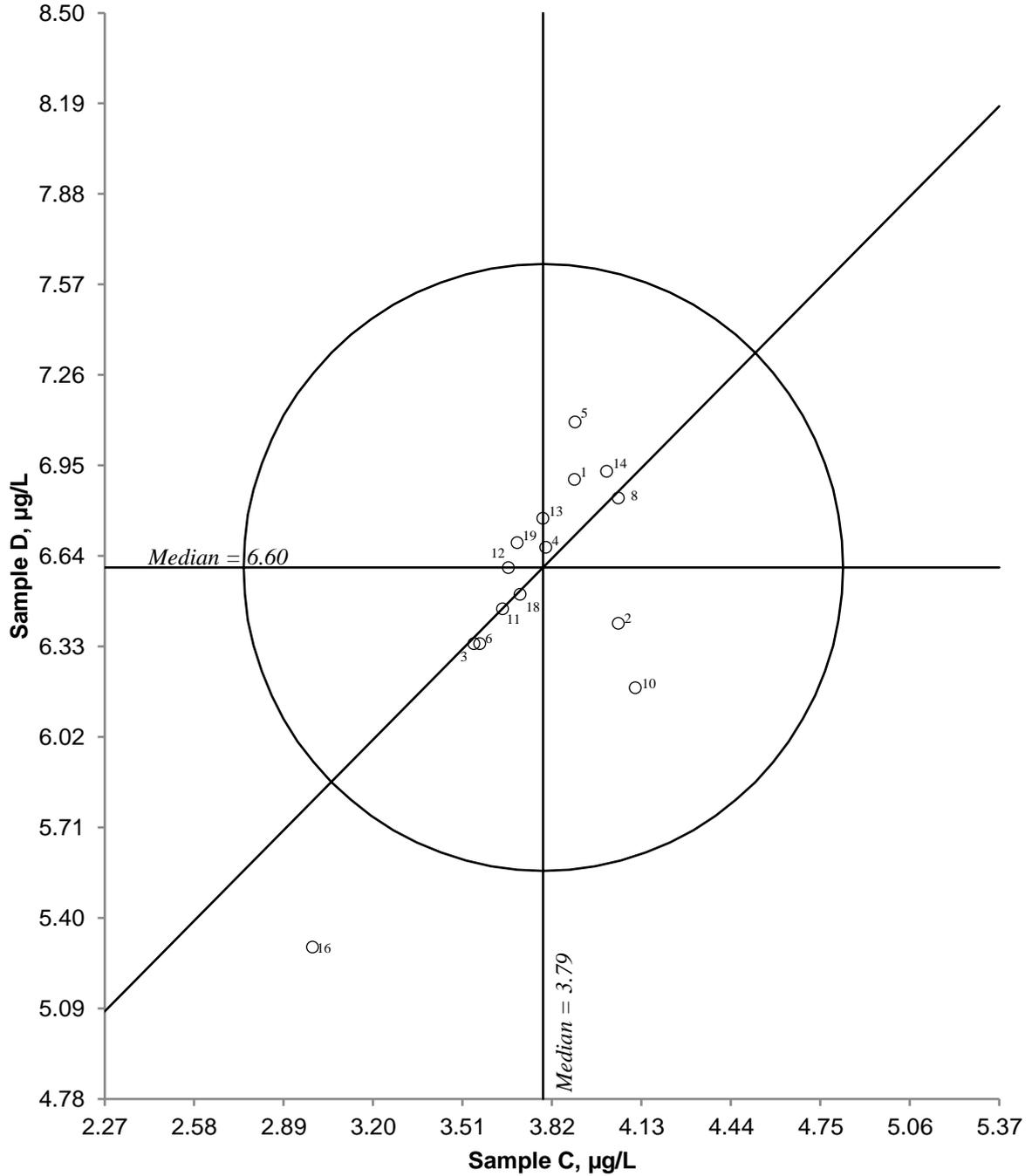
Figure 17. Youden diagram for lead. Sample pair CD. Acceptable limit, given by circle, is 20%.

Copper
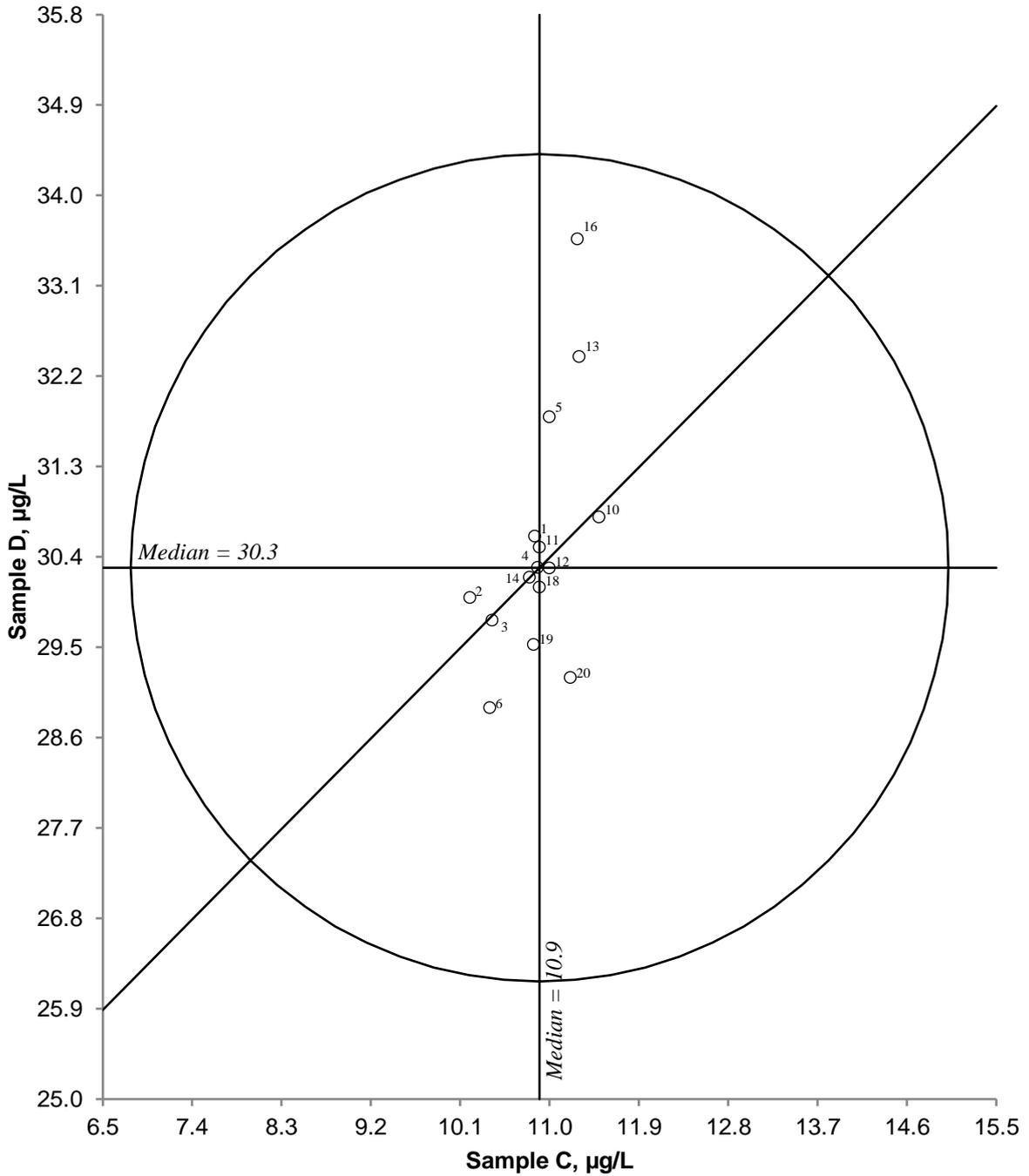
Figure 18. Youden diagram for copper. Sample pair CD. Acceptable limit, given by circle, is 20%.

Nickel
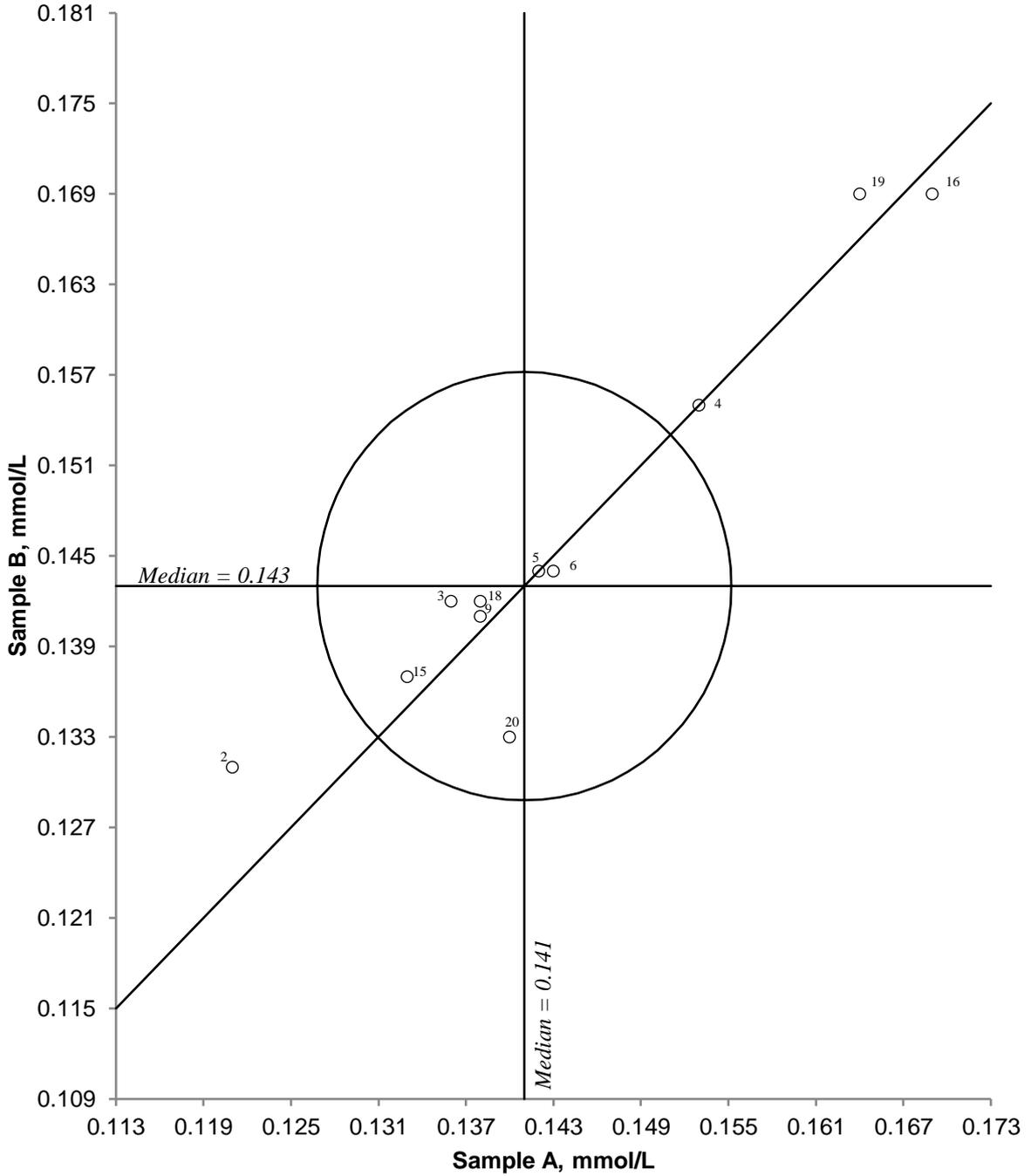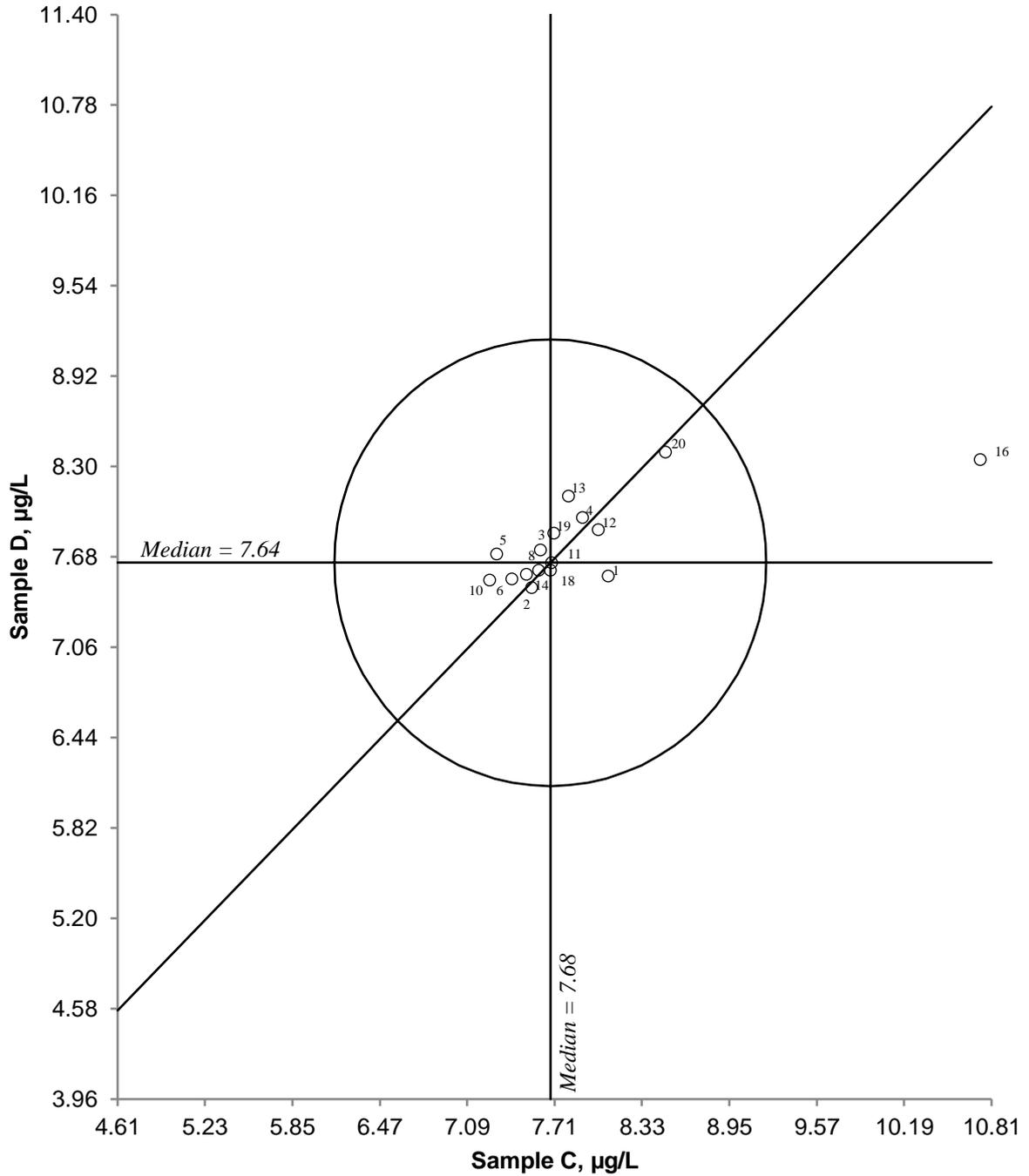

Figure 19. Youden diagram for nickel. Sample pair CD. Acceptable limit, given by circle, is 20%.

Zinc
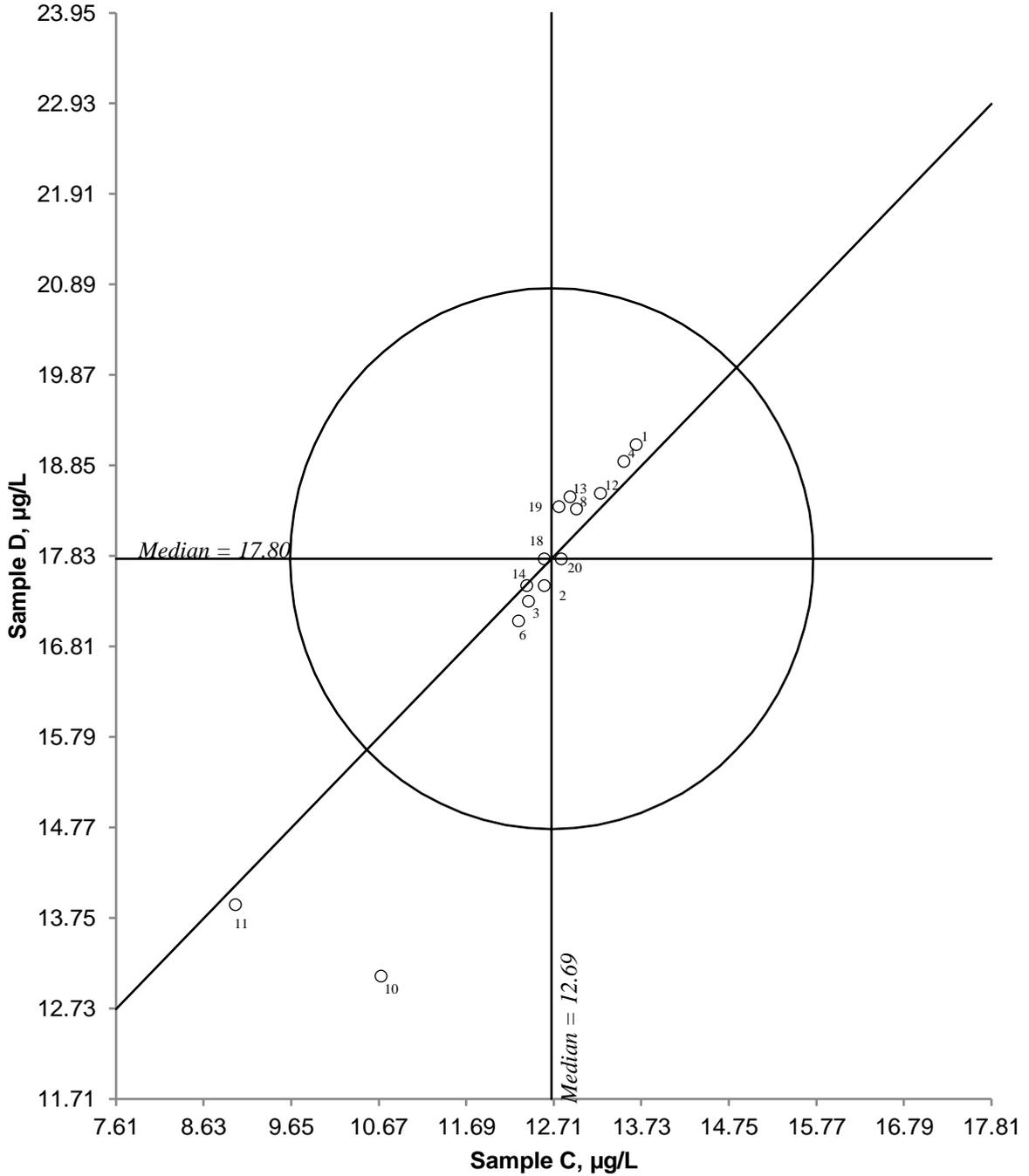
Figure 20. Youden diagram for zinc. Sample pair CD. Acceptable limit, given by circle, is 20%.

Literature

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        105/2010. NIVA SNO 6074-2010. 91p.

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        Chemists. Statistical Techniques for Collaborative Tests. Arlington, 1975.

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        Measured with Electrodes of Different Condition. Vatten 1984, 40, pp 312 -
        19 (in Norwegian).

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        Alkalinity. Limnol. Oceanogr. 1979, 24, 1161.

6.   ISO 13528 (2005): Statistical methods for use in proficiency testing by interlaboratory
        comparisons.

Appendix A. The participating laboratories

Table 3. Information of the participating laboratories including name, address, and country.

ILC_Participating laboratories			
No	**Name of Laboratory**	**Address**	**Country**
1	Vlaamse MilieuMaatschappij (VMM) Dienst Laboratorium	Raymonde de Larochelaan 1,9051 Sint-Denijs-Westrem	Belgium
2	Regional Laboratory for Analytical Control and Analysis Filial "Baltwodhoz"	199004,26,Srednii prospect, St.Petersburg	Russia
3	Bayerische Landesanstalt fuer Wald und Forstwirtschaft Abteilung 2 - Boden und Klima	Hans-Carl-von-Carlowitz-Platz 1 D-85354 Freising	Germany
4	Ufficio del Monitoraggio Ambientale - Laboratorio	Via Mirasole 22 6500 Bellinzona	Switzerland
5	Chemical Laboratory, Czech Geological Survey	Geologická 6, 152 00 Prague	Czech Republic
6	Estonian Environment Research Centre	Marja 4 D 10617 Tallinn	Estonia
7	Forest Nutrition and Water Resources Department of Ecology, Technis	H.C.v.Carlowitz-Platz 2 D-85354 Freising	Germany
8	Büsgen-Institute - Soil Science of Temperate Ecosystems	D-37077 Goettingen Buesgenweg 2	Germany
9	Institut fur Ökologie	Technikerstr. 25 6020 Innsbruck	Austria
10	Polish Academy of Sciences Institute of Botany	PAN Instytut Botaniki 31-512 Kraków ul. Lubicz 46	Poland
11	Environmental Protection Agency Environmental Research Departm	A. Gostauto str. 9, LT-01108 Vilnius	Lithuania
12	Natural Resources Wales Analytical Services (NRWAS)	NRW Analytical Services at Swansea University Faraday Building Swansea University Singleton Campus Swansea	United Kingdom
13	Bayerisches Landesamt fuer Umwelt	Ref 71 Bürgerm-Ulrich-Str. 160 D-86179 Augsburg	Germany
14	Norsk institutt for vannforskning	Gaustadalléen 21 NO-0349 OSLO	Norway
15	Marine Scotland Science Freshwater Laboratory	Faskally, Pitlochry,Perthshire,PH16 5BB, Scotland.	United Kingdom
16	Hydrochemical Laboratory by Federal State Enterprise on Water Industry	10 A Stahanovskaya str., Pskov, 180004	Russia
17	Staatliche Betriebsgesellschaft für Umwelt und Landwirtschaft (BfUL)	Haus5, FB53 Waldheimer Str. 219 D-01683 Nossen	Germany
18	Swedish University for Agricultural Sciences Aquatic Sciences and Assesment	Box 7050 750 07 Uppsala	Sweden

No	Name of Laboratory	Address	Country
ILC_Participating laboratories			
19	Institute of Biology of Komi Science Centre of the Ural Branch of the Russian Academy of Sciences IB FRC Komi SC UB RAS	Kommunisticheskaya st.,28 Syktyvkar,167982	Russia
20	Laboratoire d'écologie fonctionnelle et environnement (EcoLab)	Avenue Agrobiopole 31326 Castanet Tolosan	France
21	Institute of Environmental Protection-Puszcza Borecka station	Kolektorska 4, 01-692, Warszawa	Poland

Table 4. Overview of the different countries represented by the participating laboratories.

Country	No. of labs.	Country	No. of labs.
Austria	1	Lithuania	1
Belgium	2	Norway	1
Czech Republic	1	Poland	2
Estonia	1	Russia	3
France	1	Sweden	1
Germany	5	Switzerland	1
		United Kingdom	2

Total: 13 countries

Appendix B. Preparation of the samples

Both sample sets AB and CD were prepared using water from lake Bråtedammen, Nesodden municipality, Norway. The lake is in a partial forested and partial cultural landscape, located only a few meters from the coastline. The lake was selected for being potentially influenced by marine spray and for having relatively high levels of several of the parameters of interest in the intercomparison test.

The water was collected during the 25th of May 2019 and transported to the laboratory using two 25 L plastic containers. The water was allowed to settle for about two weeks prior to filtration through 0.45 μm cellulose acetate membrane filters. Then, the filtrate settled for one week until the below mentioned additions were made to produce sample sets AB and CD.

To produce sample set AB, some amount of nitrogen and phosphorus was added using the chemicals potassium nitrate (KNO_3) and phytic acid ($C_6H_{18}O_{24}P_6$). This addition was conducted as close as possible to the day of sample shipment to avoid biodegradation of these nutrients. Sample set CD was created by spiking with standard solution of the metals: aluminium, iron, manganese, cadmium, lead, copper, nickel, and zinc. The water was conserved by adding nitric acid to a concentration of 0.5% (v/v). A few days before shipping, the water prepared for sample set AB was distributed to 500 mL bottles and the water for sample set CD to 250 mL bottles. The samples were stored cold until they were shipped to the participating laboratories.

Appendix C. Statistical treatment of the results

Initial treatment of the analytical results

The results were assessed for the presence of potential outliers which was conducted in two subsequent steps. First, if one or both values in a sample set (AB or CD) was deviating with more than 50% from the true value, that pair of results was omitted. The remaining values were used to calculate the mean and the standard deviation of the distribution. Second, those pairs of results in which one or both values were more than three times the standard deviation higher or lower than the mean value was omitted. The remaining results were used for the final calculation for which the results are presented in Tables 7.1 - 7.20. Note that the results omitted from the second step have been marked with the letter "O".

Estimation the "true value" and uncertainty

For each variable, the "true value" is the median of the reported results after excluding strongly deviating values (i.e. outliers). Thus, the true value is the consensus value from the participants and the corresponding uncertainty is based on the method given in ISO 13528 (2005), Annex C (algorithm A).

The median value is determined and an initial value for the robust standard deviation is calculated from the absolute differences between the median value and the result of each participating laboratory according to:

S^* = 1.483 × the median of $|x_i - m|$ (i = 1, 2 …. p)

New value for the robust standard deviation is then calculated according to equations C.3-C6 in Annex C. The robust standard deviation is then derived by an iterative calculation by updating the values several times using the modified data, until the process converges.

The uncertainty u_X of the assigned value for the true value is then calculated according to chapter 5.6 in ISO 13528:

$$\mu_X = 1.25 \ x \ S^* / \sqrt{p}$$

For the estimation of expanded uncertainty U, a coverage factor of two is used:

U= 2 × u_X

It is important to note that there are some limitations to this approach for estimating the uncertainty of the true value:
- There may be no real consensus among the participants

- The consensus may be biased by the general use of faulty methodology and this bias will not be reflected in the standard uncertainty of the assigned value using this calculation.

The Youden statistical test

The measurement results reported to the intercomparison test was assessed using the method of Youden. This procedure requires that two samples are analysed for each parameter (e.g. A and B) and that each laboratory reports only one result for each sample and analytical variable. The results for sample A and B are plotted in a coordinate system in which the "true value" of sample A constitutes the x-axis and the "true value" of sample B the y-axis. Then, by plotting the individual results from each laboratory in the chart, producing one point for each laboratory (result from sample A along the x-axis and result from sample B along the y-axis), the distribution of the results among the laboratories is visualized (see Figures 1 - 20). Patterns in the distribution of the results can reveal systematic and/or random errors among the participating laboratories.

For example, if the results are affected by random errors only, the points will be spread randomly around the origo of the Youden chart. However, if systematic effects are influencing the results (e.g. from the use of different deviating analytical methods), the points in the chart will be distributed in a characteristic elliptical pattern along a $45°$ line in the chart. This is reflecting the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

The acceptance limit of the results is indicated in the Youden chart by a circle around the origo. The distance from the centre of the circle and the point of an individual laboratory is a measure of the absolute error of the result. The distance along the $45°$ line gives the magnitude of the systematic error, while the distance perpendicular to the $45°$ line indicates the magnitude of the random error. Thus, the location of the point of each laboratory in the Youden's diagram provides important information of the size and type of analytical error (random or systematic) present in the dataset, making it possible to indicate what is the source of deviation from the consensus of the participating laboratories.

Table 5. Uncertainty of the calculated "true value" for each parameter.

Variable (unit)	Sample	True value	Total no.	Robust std.dev.	Uncertainty	Expanded uncertainty
pH	A	6.72	20	0.145	0.041	0.081
	B	6.68	20	0.125	0.035	0.070
Conductivity	A	6.06	18	0.146	0.043	0.086
(mS/m)	B	9.68	19	0.239	0.069	0.137
Alkalinity	A	0.141	13	0.0198	0.0069	0.0138
(mmol/L)	B	0.143	13	0.0186	0.0065	0.0129
Nitrate + nitrite-nitrogen	A	44.0	12	4.75	1.71	3.42
(µg/L)	B	55.5	14	11.87	3.96	7.93
Chloride	A	9.5	20	0.63	0.17	0.35
(mg/L)	B	18.9	12	0.37	0.13	0.27
Sulphate	A	3.49	20	0.194	0.054	0.109
mg/L	B	4.71	20	0.266	0.074	0.149
Calcium	A	3.38	18	0.162	0.048	0.096
(mg/L)	B	3.55	19	0.222	0.064	0.127
Magnesium	A	0.67	19	0.041	0.012	0.024
(mg/L)	B	1.28	13	0.058	0.020	0.040
Sodium	A	6.39	20	0.196	0.055	0.110
(mg/L)	B	11.60	20	0.281	0.078	0.157
Potassium	A	0.90	20	0.053	0.015	0.030
(mg/L)	B	1.11	19	0.057	0.016	0.033
Total organic carbon	A	5.41	14	0.650	0.217	0.434
(mg/L)	B	5.57	14	0.646	0.216	0.431
Total phosphorous	A	26.6	16	5.70	1.78	3.56
(µg/L)	B	28.5	16	4.68	1.46	2.93
Aluminium	C	18.9	14	2.94	0.98	1.97
(µg/L)	D	122.7	14	7.76	2.59	5.19
Iron	C	23.1	15	2.11	0.68	1.36
(µg/L)	D	80.4	15	4.08	1.32	2.63
Manganese	C	4.56	15	0.190	0.061	0.123
(µg/L)	D	44.62	14	2.520	0.840	1.680
Cadmium	C	1.80	15	0.084	0.027	0.054
(µg/L)	D	1.77	15	0.079	0.025	0.051
Lead	C	3.79	15	0.231	0.075	0.149
(µg/L)	D	6.60	15	0.327	0.106	0.211
Copper	C	10.9	15	0.38	0.12	0.24
(µg/L)	D	30.3	15	0.76	0.25	0.49
Nickel	C	7.68	15	0.308	0.100	0.199
(µg/L)	D	7.64	16	0.264	0.083	0.165
Zinc	C	12.69	15	0.737	0.238	0.476
(µg/L)	D	17.80	14	0.974	0.326	0.651

Appendix D. Results reported by the participating laboratories

Table 6. Results reported by the participating laboratories.

Lab. nr.	pH, Units		Conductivity, mS/m		Alkalinity, mmol/L		Nitrate + nitrite-nitrogen, µg/L		Chloride, mg/L		Sulphate, mg/L		Calcium, mg/L		Magnesium, mg/L	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1					0.265	0.275	0.0	0.1	8.8	15.5	3.69	4.76	3.47	3.61	0.69	1.35
2	6.51	6.55	6.12	9.90	0.121	0.131	79.8	82.4	8.6	18.9	3.51	4.68	3.27	3.46	0.66	1.28
3	6.75	6.78	5.95	9.66	0.136	0.142	47.1	54.4	8.9	17.7	3.34	4.64	3.38	3.63	0.64	1.27
4	6.66	6.55	6.13	9.78	0.153	0.155	49.0	40.0	9.3	19.0	3.70	5.09	3.70	3.95	0.74	1.45
5	6.68	6.68	5.80	9.46	0.142	0.144			8.2	17.0	3.42	4.68	3.27	3.41	0.67	1.29
6	6.68	6.68	6.12	9.80	0.143	0.144	44.0	57.0	9.6	18.8	3.51	4.68	3.38	3.64	0.62	1.24
7	6.49	6.54	7.80	10.44	0.225	0.244	8.6	13.6	8.6	35.5	0.00	0.00	3.24	3.46	0.65	1.27
8	6.84	6.82	6.18	9.79			51.0	61.0	9.9	19.0	3.31	4.44	3.26	3.44	0.67	1.28
9	6.78	6.74	6.05	9.62	0.138	0.141	44.0	65.0	9.5	18.9	3.56	4.86	3.61	3.84	0.68	1.36
10	6.60	6.51	6.02	9.46			41.9	52.9	9.5	18.5	3.43	4.71	3.53	3.67	0.63	1.27
11	6.93	6.87	22.30	23.30	0.110	0.100			9.4	19.1	2.40	4.30				
12	6.79	6.82	5.56	8.83	0.270	0.278	239.0	170.0	8.2	18.3	4.06	5.31	3.33	3.48	0.72	1.34
13	6.60	6.60	6.20	10.10			44.0	61.0	9.6	19.0	3.50	5.60	3.38	3.58	0.70	1.35
14	6.77	6.67	6.08	9.71	0.186	0.175			10.1	19.9	3.33	4.53	2.82	3.23	0.56	1.18
15	6.77	6.74	5.96	9.66	0.133	0.137	45.1	55.5	9.6	18.8	3.52	4.77	3.34	3.51	0.68	1.33
16	6.90	6.70	6.10	9.70	0.169	0.169			10.2	18.5	3.70	4.70	3.70	4.80	0.69	1.29
17	6.63	6.66	6.22	9.91			79.0	86.0	9.5	17.9	3.35	4.78	3.38	3.63	0.63	1.24
18	6.64	6.66	6.06	9.72	0.138	0.142	64.7	54.8	9.6	19.2	3.53	4.84	3.39	3.47	0.66	1.26
19	6.60	6.60	5.73	8.67	0.164	0.169	40.2	45.0	10.0	19.3	2.43	3.52	3.22	3.37	0.64	1.26
20	6.82	6.74	6.06	9.65	0.140	0.133	30.1	40.8	9.5	19.0	3.25	4.49	4.51	4.58	0.79	1.60
21	6.92	6.99	5.93	9.45												

Lab. nr.	Sodium, mg/L		Potassium, mg/L		Total organic carbon, mg/L		Total phosphorous, µg/L		Aluminium, µg/L		Iron, µg/L		Manganese, µg/L		Cadmium, µg/L	
	A	B	A	B	A	B	A	B	C	D	C	D	C	D	C	D
1	6.51	12.02	0.88	1.08	5.20	5.27	35.0	37.0	18.6	125.6	23.4	75.4	4.43	42.72	1.89	1.86
2	6.65	12.30	0.90	1.08	4.08	4.23	20.0	26.0	25.9	131.0	17.3	75.1	4.40	44.70	2.03	1.70
3	6.39	11.81	0.91	1.13	5.22	5.36	20.0	32.0	18.0	119.0	23.4	83.2	4.55	47.33	1.89	1.86
4	5.91	11.49	0.87	1.08	5.10	5.10	27.7	28.2	18.8	125.4	23.1	81.7	4.59	45.73	1.85	1.83
5	6.30	11.75	0.89	1.05											1.77	1.74
6	6.50	11.90	0.85	1.11	5.51	5.59	30.0	33.0	25.0	117.0	21.4	81.0	4.19	42.80	1.75	1.73
7	6.24	11.59	0.92	1.13	2.51	3.80	17.7	22.7								
8	6.42	11.53	0.97	1.23	6.21	7.07	21.0	23.0	2.0	114.0	16.6	75.8	4.52	45.30	1.83	1.80
9	6.18	11.48	0.94	1.19	4.84	4.90	26.9	29.0			41.8	93.8				
10	6.13	11.04	0.84	0.86					18.9	110.4	21.6	80.7	5.10	48.80	1.73	1.61
11	6.30	11.00	0.88	1.10			54.0	55.0	16.8	116.0	31.1	86.5	4.34	42.60	1.79	1.75
12	6.26	11.47	0.88	1.07	5.41	5.53	35.0	32.8	21.2	123.3	24.9	80.4	4.60	44.53	1.80	1.77
13	6.53	11.90	0.94	1.11	5.80	5.80	28.0	30.0	21.0	141.0	23.5	85.8	4.70	48.60	1.78	1.79
14	6.38	11.60	0.83	1.03	6.40	5.90	28.0	29.0	18.4	120.0	23.1	79.4	4.57	44.20	1.93	1.84
15	6.72	11.86	0.95	1.15	5.12	6.12	23.5	23.3								
16	6.40	11.40	1.02	1.16			20.0	20.0	23.5	156.4	29.5	88.0	5.61	60.29	2.41	2.50
17	6.46	11.88	0.84	1.04												
18	6.52	11.60	0.89	1.06	5.70	5.81	26.2	28.8	19.3	122.0	23.3	79.4	4.70	46.20	1.80	1.77
19	6.06	11.94	0.91	1.18	6.58	6.76	23.0	25.8	17.1	128.2	22.1	77.0	4.47	42.71	1.88	1.86
20	6.38	11.59	0.99	1.11	5.61	5.57	28.5	26.4	17.2	115.7	22.5	78.7	4.63	43.40	1.61	1.55
21																

Lab.	Lead, µg/L		Copper, µg/L		Nickel, µg/L		Zinc, µg/L	
nr.	C	D	C	D	C	D	C	D
1	3.90	6.90	10.9	30.6	8.09	7.55	13.67	19.09
2	4.05	6.41	10.2	30.0	7.55	7.47	12.60	17.50
3	3.55	6.34	10.4	29.8	7.61	7.73	12.42	17.32
4	3.80	6.67	10.9	30.3	7.91	7.95	13.53	18.90
5	3.90	7.10	11.0	31.8	7.30	7.70		
6	3.57	6.34	10.4	28.9	7.41	7.53	12.30	17.10
7								
8	4.05	6.84	3.4	23.7	7.51	7.56	12.98	18.36
9								
10	4.11	6.19	11.5	30.8	7.25	7.52	10.70	13.10
11	3.65	6.46	10.9	30.5	7.69	7.64	9.00	13.90
12	3.67	6.60	11.0	30.3	8.02	7.87	13.26	18.54
13	3.79	6.77	11.3	32.4	7.81	8.10	12.90	18.50
14	4.01	6.93	10.8	30.2	7.60	7.59	12.40	17.50
15								
16	2.99	5.30	11.3	33.6	10.73	8.35	17.55	30.90
17								
18	3.71	6.51	10.9	30.1	7.68	7.59	12.60	17.80
19	3.70	6.69	10.8	29.5	7.71	7.84	12.77	18.39
20	5.40	8.00	11.2	29.2	8.50	8.40	12.80	17.80
21								

Table 5.1. Statistics - pH

Sample A

Analytical method: All
Unit: Units

Number of participants	20	Range			0.44
Number of omitted results	0	Variance			0.02
True value	6.72	Standard deviation			0.13
Mean value	6.72	Relative standard deviation			1.9%
Median value	6.72	Relative error			0.0%

Analytical results in ascending order:

7	6.49	4	6.66	12	6.79
2	6.51	6	6.68	20	6.82
13	6.60	5	6.68	8	6.84
10	6.60	3	6.75	16	6.90
19	6.60	15	6.77	21	6.92
17	6.63	14	6.77	11	6.93
18	6.64	9	6.78		

O = Omitted result

Sample B

Analytical method: All
Unit: Units

Number of participants	20	Range			0.48
Number of omitted results	0	Variance			0.01
True value	6.68	Standard deviation			0.12
Mean value	6.69	Relative standard deviation			1.8%
Median value	6.68	Relative error			0.2%

Analytical results in ascending order:

10	6.51	17	6.66	20	6.74
7	6.54	14	6.67	3	6.78
2	6.55	6	6.68	12	6.82
4	6.55	5	6.68	8	6.82
13	6.60	16	6.70	11	6.87
19	6.60	15	6.74	21	6.99
18	6.66	9	6.74		

U = Omitted result

Table 5.2. Statistics - Conductivity

Sample A

Analytical method: All
Unit: mS/m

Number of participants	20	Range		0.66	
Number of omitted results	2	Variance		0.03	
True value	6.06	Standard deviation		0.17	
Mean value	6.02	Relative standard deviation		2.9%	
Median value	6.06	Relative error		-0.7%	

Analytical results in ascending order:

12	5.56	9	6.05	4	6.13	
19	5.73	18	6.06	8	6.18	
5	5.80	20	6.06	13	6.20	
21	5.93	14	6.08	17	6.22	
3	5.95	16	6.10	7	7.80	O
15	5.96	6	6.12	11	22.30	O
10	6.02	2	6.12			

O = Omitted result

Sample B

Analytical method: All
Unit: mS/m

Number of participants	20	Range		1.43	
Number of omitted results	2	Variance		0.12	
True value	9.68	Standard deviation		0.35	
Mean value	9.60	Relative standard deviation		3.7%	
Median value	9.68	Relative error		-0.8%	

Analytical results in ascending order:

19	8.67	15	9.66	6	9.80	
12	8.83	3	9.66	2	9.90	
21	9.45	16	9.70	17	9.91	
5	9.46	14	9.71	13	10.10	
10	9.46	18	9.72	7	10.44	O
9	9.62	4	9.78	11	23.30	O
20	9.65	8	9.79			

U = Omitted result

Table 5.3. Statistics - Alkalinity

Sample A

Analytical method: All
Unit: mmol/L

Number of participants		16		Range		0.076
Number of omitted results		3		Variance		0.000
True value		0.141		Standard deviation		0.020
Mean value		0.144		Relative standard deviation		13.9%
Median value		0.140		Relative error		2.2%

Analytical results in ascending order:

11	0.110	20	0.140	14	0.186	
2	0.121	5	0.142	7	0.225	O
15	0.133	6	0.143	1	0.265	O
3	0.136	4	0.153	12	0.270	O
18	0.138	19	0.164			
9	0.138	16	0.169			

O = Omitted result

Sample B

Analytical method: All
Unit: mmol/L

Number of participants		16		Range		0.075
Number of omitted results		3		Variance		0.000
True value		0.143		Standard deviation		0.020
Mean value		0.145		Relative standard deviation		13.5%
Median value		0.142		Relative error		1.2%

Analytical results in ascending order:

11	0.100	18	0.142	14	0.175	
2	0.131	5	0.144	7	0.244	O
20	0.133	6	0.144	1	0.275	O
15	0.137	4	0.155	12	0.278	O
9	0.141	16	0.169			
3	0.142	19	0.169			

U = Omitted result

Table 5.4. Statistics - Nitrate + nitrite-nitrogen

Sample A

Analytical method: All
Unit: µg/L

Number of participants		17			Range		34.6	
Number of omitted results		5			Variance		63.6	
True value		44.0			Standard deviation		8.0	
Mean value		45.6			Relative standard deviation		17.5%	
Median value		44.5			Relative error		3.5%	

Analytical results in ascending order:

	1	0.0	O	9	44.0	8	51.0	
	7	8.6	O	13	44.0	18	64.7	
	20	30.1		15	45.1	17	79.0	O
	19	40.2		18	45.6	2	79.8	O
	10	41.9		3	47.1	12	239.0	O
	6	44.0		4	49.0			

O = Omitted result

Sample B

Analytical method: All
Unit: µg/L

Number of participants		17			Range		25.0	
Number of omitted results		5			Variance		62.2	
True value		55.5			Standard deviation		7.9	
Mean value		53.6			Relative standard deviation		14.7%	
Median value		55.2			Relative error		-3.5%	

Analytical results in ascending order:

	1	0.1	O	3	54.4	8	61.0	
	7	13.6	O	18	54.8	9	65.0	
	4	40.0		15	55.5	2	82.4	O
	20	40.8		18	55.6	17	86.0	O
	19	45.0		6	57.0	12	170.0	O
	10	52.9		13	61.0			

U = Omitted result

Table 5.5. Statistics - Chloride

Sample A

Analytical method: All
Unit: mg/L

Number of participants	20	Range	2.0
Number of omitted results	2	Variance	0.3
		Standard	
True value	9.5	deviation	0.6
Mean value	9.4	Relative standard deviation	6.3%
		Relative	
Median value	9.5	error	-1.1%

Analytical results in ascending order:

12	8.2		11	9.4		18	9.6
5	8.2		17	9.5		15	9.6
2	8.6		20	9.5		8	9.9
7	8.6	O	10	9.5		19	10.0
1	8.8	O	9	9.5		14	10.1
3	8.9		13	9.6		16	10.2
4	9.3		6	9.6			

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	20	Range	2.9
Number of omitted results	2	Variance	0.4
		Standard	
True value	18.9	deviation	0.7
Mean value	18.7	Relative standard deviation	3.5%
		Relative	
Median value	18.9	error	-1.0%

Analytical results in ascending order:

1	15.5	O	6	18.8		13	19.0	
5	17.0		15	18.8		11	19.1	
3	17.7		9	18.9		18	19.2	
17	17.9		2	18.9		19	19.3	
12	18.3		20	19.0		14	19.9	
16	18.5		8	19.0		7	35.5	O
10	18.5		4	19.0				

U = Omitted result

Table 5.6. Statistics - Sulphate

Sample A

Analytical method: All
Unit: mg/L

Number of participants	21			Range	1.66		
Number of omitted results	1			Variance	0.15		
True value	3.49			Standard deviation	0.38		
Mean value	3.40			Relative standard deviation	11.3%		
Median value	3.49			Relative error	-2.4%		

Analytical results in ascending order:

7	0.00	O	17	3.35	15	3.52
11	2.40		5	3.42	18	3.53
19	2.43		10	3.43	9	3.56
20	3.25		12	3.47	1	3.69
8	3.31		13	3.50	16	3.70
14	3.33		2	3.51	4	3.70
3	3.34		6	3.51	12	4.06

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	21			Range	2.08		
Number of omitted results	1			Variance	0.17		
True value	4.71			Standard deviation	0.41		
Mean value	4.72			Relative standard deviation	8.7%		
Median value	4.71			Relative error	0.3%		

Analytical results in ascending order:

7	0.00	O	6	4.68	17	4.78
19	3.52		2	4.68	18	4.84
11	4.30		5	4.68	9	4.86
8	4.44		16	4.70	12	4.96
20	4.49		10	4.71	4	5.09
14	4.53		1	4.76	12	5.31
3	4.64		15	4.77	13	5.60

U = Omitted result

Table 5.7. Statistics - Calcium

Sample A

Analytical method: All
Unit: mg/L

Number of participants		19	Range		0.88
Number of omitted results		1	Variance		0.04
True value		3.38	Standard deviation		0.20
Mean value		3.37	Relative standard deviation		6.0%
Median value		3.38	Relative error		-0.3%

Analytical results in ascending order:

14	2.82	15	3.34	10	3.53	
19	3.22	3	3.38	9	3.61	
7	3.24	13	3.38	4	3.70	
8	3.26	17	3.38	16	3.70	
5	3.27	6	3.38	20	4.51	O
2	3.27	18	3.39			
12	3.33	1	3.47			

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants		19	Range		1.57
Number of omitted results		1	Variance		0.11
True value		3.55	Standard deviation		0.34
Mean value		3.62	Relative standard deviation		9.4%
Median value		3.55	Relative error		2.1%

Analytical results in ascending order:

14	3.23	12	3.48	10	3.67	
19	3.37	15	3.51	9	3.84	
5	3.41	13	3.58	4	3.95	
8	3.44	1	3.61	20	4.58	O
7	3.46	17	3.63	16	4.80	
2	3.46	3	3.63			
18	3.47	6	3.64			

U = Omitted result

Table 5.8. Statistics - Magnesium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	19	Range		0.18
Number of omitted results	1	Variance		0.00
True value	0.67	Standard deviation		0.04
Mean value	0.66	Relative standard deviation		6.2%
Median value	0.67	Relative error		-0.4%

Analytical results in ascending order:

14	0.56	18	0.66	16	0.69	
6	0.62	2	0.66	13	0.70	
10	0.63	8	0.67	12	0.72	
17	0.63	5	0.67	4	0.74	
19	0.64	9	0.68	20	0.79	O
3	0.64	15	0.68			
7	0.65	1	0.69			

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	19	Range		0.27
Number of omitted results	1	Variance		0.00
True value	1.28	Standard deviation		0.06
Mean value	1.29	Relative standard deviation		4.6%
Median value	1.28	Relative error		1.1%

Analytical results in ascending order:

14	1.18	3	1.27	1	1.35	
6	1.24	8	1.28	13	1.35	
17	1.24	2	1.28	9	1.36	
19	1.26	16	1.29	4	1.45	
18	1.26	5	1.29	20	1.60	O
7	1.27	15	1.33			
10	1.27	12	1.34			

U = Omitted result

Table 5.9. Statistics - Sodium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	20	Range	0.81
Number of omitted results	0	Variance	0.04
True value	6.39	Standard deviation	0.20
Mean value	6.36	Relative standard deviation	3.1%
Median value	6.39	Relative error	-0.3%

Analytical results in ascending order:

4	5.91	11	6.30	6	6.50
19	6.06	14	6.38	1	6.51
10	6.13	20	6.38	18	6.52
9	6.18	3	6.39	13	6.53
7	6.24	16	6.40	2	6.65
12	6.26	8	6.42	15	6.72
5	6.30	17	6.46		

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	20	Range	1.30
Number of omitted results	0	Variance	0.10
True value	11.60	Standard deviation	0.31
Mean value	11.66	Relative standard deviation	2.7%
Median value	11.60	Relative error	0.5%

Analytical results in ascending order:

11	11.00	7	11.59	17	11.88
10	11.04	20	11.59	6	11.90
16	11.40	14	11.60	13	11.90
12	11.47	18	11.60	19	11.94
9	11.48	5	11.75	1	12.02
4	11.49	3	11.81	2	12.30
8	11.53	15	11.86		

U = Omitted result

Table 5.10. Statistics - Potassium

Sample A

Analytical method: All
Unit: mg/L

Number of participants	20			Range		0.19
Number of omitted results	1			Variance		0.00
True value	0.90			Standard deviation		0.05
Mean value	0.91			Relative standard deviation		5.5%
Median value	0.90			Relative error		0.9%

Analytical results in ascending order:

14	0.83		1	0.88	9	0.94
10	0.84	O	18	0.89	13	0.94
17	0.84		5	0.89	15	0.95
6	0.85		2	0.90	8	0.97
4	0.87		3	0.91	20	0.99
12	0.88		19	0.91	16	1.02
11	0.88		7	0.92		

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	20			Range		0.20
Number of omitted results	1			Variance		0.00
True value	1.11			Standard deviation		0.05
Mean value	1.11			Relative standard deviation		4.9%
Median value	1.11			Relative error		0.0%

Analytical results in ascending order:

10	0.86	O	4	1.08	3	1.13
14	1.03		1	1.08	15	1.15
17	1.04		11	1.10	16	1.16
5	1.05		6	1.11	19	1.18
18	1.06		13	1.11	9	1.19
12	1.07		20	1.11	8	1.23
2	1.08		7	1.13		

U = Omitted result

Table 5.11. Statistics - Total organic carbon

Sample A

Analytical method: All
Unit: mg/L

Number of participants	15			Range			2.50
Number of omitted results	1			Variance			0.43
True value	5.41			Standard deviation			0.65
Mean value	5.48			Relative standard deviation			11.9%
Median value	5.46			Relative error			1.4%

Analytical results in ascending order:

7	2.51	O	1	5.20	18	5.70
2	4.08		3	5.22	13	5.80
9	4.84		12	5.41	8	6.21
4	5.10		6	5.51	14	6.40
15	5.12		20	5.61	19	6.58

O = Omitted result

Sample B

Analytical method: All
Unit: mg/L

Number of participants	15			Range			2.84
Number of omitted results	1			Variance			0.52
True value	5.57			Standard deviation			0.72
Mean value	5.64			Relative standard deviation			12.7%
Median value	5.58			Relative error			1.3%

Analytical results in ascending order:

7	3.80	O	3	5.36	18	5.81
2	4.23		12	5.53	14	5.90
9	4.90		20	5.57	15	6.12
4	5.10		6	5.59	19	6.76
1	5.27		13	5.80	8	7.07

U = Omitted result

Table 5.12. Statistics - Total phosphorous

Sample A

Analytical method: All
Unit: µg/L

Number of participants	17		Range	17.3	
Number of omitted results	1		Variance	27.4	
			Standard		
True value	26.6		deviation	5.2	
Mean value	25.7		Relative standard deviation	20.4%	
			Relative		
Median value	26.6		error	-3.6%	

Analytical results in ascending order:

7	17.7	15	23.5	20	28.5	
3	20.0	18	26.2	6	30.0	
2	20.0	9	26.9	12	35.0	
16	20.0	4	27.7	1	35.0	
8	21.0	14	28.0	11	54.0	O
19	23.0	13	28.0			

O = Omitted result

Sample B

Analytical method: All
Unit: µg/L

Number of participants	17		Range	17.0	
Number of omitted results	1		Variance	20.2	
			Standard		
True value	28.5		deviation	4.5	
Mean value	27.9		Relative standard deviation	16.1%	
			Relative		
Median value	28.5		error	-2.0%	

Analytical results in ascending order:

16	20.0	20	26.4	3	32.0	
7	22.7	4	28.2	12	32.8	
8	23.0	18	28.8	6	33.0	
15	23.3	14	29.0	1	37.0	
19	25.8	9	29.0	11	55.0	O
2	26.0	13	30.0			

O = Omitted result

Table 5.13. Statistics - Aluminium

Sample C

Analytical method: All
Unit: µg/L

Number of participants		15		Range			9.1
Number of omitted results		1		Variance			8.6
True value		18.9		Standard deviation			2.9
Mean value		20.0		Relative standard deviation			14.7%
Median value		18.9		Relative error			6.0%

Analytical results in ascending order:

8	2.0	O	14	18.4		13	21.0
11	16.8		1	18.6		12	21.2
19	17.1		4	18.8		16	23.5
20	17.2		10	18.9		6	25.0
3	18.0		18	19.3		2	25.9

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants		15		Range			46.0
Number of omitted results		1		Variance			138.9
True value		122.7		Standard deviation			11.8
Mean value		125.1		Relative standard deviation			9.4%
Median value		122.7		Relative error			2.0%

Analytical results in ascending order:

10	110.4		3	119.0		1	125.6
8	114.0	O	14	120.0		19	128.2
20	115.7		18	122.0		2	131.0
11	116.0		12	123.3		13	141.0
6	117.0		4	125.4		16	156.4

U = Omitted result

Table 5.14. Statistics - Iron

Sample C

Analytical method: All
Unit: µg/L

Number of participants	16	Range	14.5
Number of omitted results	1	Variance	13.6
		Standard	
True value	23.1	deviation	3.7
Mean value	23.1	Relative standard deviation	15.9%
		Relative	
Median value	23.1	error	-0.1%

Analytical results in ascending order:

8	16.6	14	23.1	12	24.9	
2	17.3	4	23.1	16	29.5	
6	21.4	18	23.3	11	31.1	
10	21.6	1	23.4	9	41.8	O
19	22.1	3	23.4			
20	22.5	13	23.5			

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants	16	Range	12.9
Number of omitted results	1	Variance	15.9
		Standard	
True value	80.4	deviation	4.0
Mean value	80.5	Relative standard deviation	5.0%
		Relative	
Median value	80.4	error	0.2%

Analytical results in ascending order:

2	75.1	14	79.4	13	85.8	
1	75.4	12	80.4	11	86.5	
8	75.8	10	80.7	16	88.0	
19	77.0	6	81.0	9	93.8	O
20	78.7	4	81.7			
18	79.4	3	83.2			

U = Omitted result

Table 5.15. Statistics - Manganese

Sample C

Analytical method: All
Unit: µg/L

Number of participants	15		Range	0.91		
Number of omitted results	1		Variance	0.04		
			Standard			
True value	4.56		deviation	0.21		
Mean value	4.56		Relative standard deviation	4.6%		
			Relative			
Median value	4.56		error	-0.1%		

Analytical results in ascending order:

6	4.19	8	4.52	20	4.63
11	4.34	3	4.55	13	4.70
2	4.40	14	4.57	18	4.70
1	4.43	4	4.59	10	5.10
19	4.47	12	4.60	16	5.61 O

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants	15		Range	6.20		
Number of omitted results	1		Variance	4.57		
			Standard			
True value	44.62		deviation	2.14		
Mean value	44.97		Relative standard deviation	4.8%		
			Relative			
Median value	44.62		error	0.8%		

Analytical results in ascending order:

11	42.60	14	44.20	18	46.20
19	42.71	12	44.53	3	47.33
1	42.72	2	44.70	13	48.60
6	42.80	8	45.30	10	48.80
20	43.40	4	45.73	16	60.29 O

U = Omitted result

Table 5.16. Statistics - Cadmium

Sample C

Analytical method: All
Unit: µg/L

Number of participants	16	Range	0.42
Number of omitted results	1	Variance	0.01
		Standard	
True value	1.80	deviation	0.10
Mean value	1.82	Relative standard deviation	5.4%
		Relative	
Median value	1.80	error	1.2%

Analytical results in ascending order:

20	1.61	12	1.80	1	1.89	
10	1.73	18	1.80	14	1.93	
6	1.75	8	1.83	2	2.03	
5	1.77	4	1.85	16	2.41	O
13	1.78	19	1.88			
11	1.79	3	1.89			

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants	16	Range	0.31
Number of omitted results	1	Variance	0.01
		Standard	
True value	1.77	deviation	0.09
Mean value	1.76	Relative standard deviation	5.1%
		Relative	
Median value	1.77	error	-0.4%

Analytical results in ascending order:

20	1.55	18	1.77	1	1.86	
10	1.61	12	1.77	3	1.86	
2	1.70	13	1.79	19	1.86	
6	1.73	8	1.80	16	2.50	O
5	1.74	4	1.83			
11	1.75	14	1.84			

U = Omitted result

Table 5.17. Statistics - Lead

Sample C

Analytical method: All
Unit: µg/L

			Range	1.12
Number of participants	16		Range	1.12
Number of omitted results	1		Variance	0.08
			Standard deviation	0.28
True value	3.79			
Mean value	3.76		Relative standard deviation	7.4%
			Relative error	-0.7%
Median value	3.79			

Analytical results in ascending order:

16	2.99	18	3.71	8	4.05	
3	3.55	13	3.79	2	4.05	
6	3.57	4	3.80	10	4.11	
11	3.65	1	3.90	20	5.40	O
12	3.67	5	3.90			
19	3.70	14	4.01			

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants	16		Range	1.80
Number of omitted results	1		Variance	0.18
			Standard deviation	0.43
True value	6.60			
Mean value	6.54		Relative standard deviation	6.5%
			Relative error	-1.0%
Median value	6.60			

Analytical results in ascending order:

16	5.30	18	6.51	1	6.90	
10	6.19	12	6.60	14	6.93	
3	6.34	4	6.67	5	7.10	
6	6.34	19	6.69	20	8.00	O
2	6.41	13	6.77			
11	6.46	8	6.84			

U = Omitted result

Table 5.18. Statistics - Copper

Sample C

Analytical method: All
Unit: µg/L

Number of participants	16			Range	1.3		
Number of omitted results	1			Variance	0.1		
True value	10.9			Standard deviation	0.4		
Mean value	10.9			Relative standard deviation	3.3%		
Median value	10.9			Relative error	0.0%		

Analytical results in ascending order:

8	3.4	O	1	10.9	20	11.2	
2	10.2		4	10.9	16	11.3	
6	10.4		18	10.9	13	11.3	
3	10.4		11	10.9	10	11.5	
14	10.8		5	11.0			
19	10.8		12	11.0			

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants	16			Range	4.7		
Number of omitted results	1			Variance	1.5		
True value	30.3			Standard deviation	1.2		
Mean value	30.5			Relative standard deviation	4.0%		
Median value	30.3			Relative error	0.8%		

Analytical results in ascending order:

8	23.7	O	18	30.1	10	30.8	
6	28.9		14	30.2	5	31.8	
20	29.2		12	30.3	13	32.4	
19	29.5		4	30.3	16	33.6	
3	29.8		11	30.5			
2	30.0		1	30.6			

U = Omitted result

Table 5.19. Statistics - Nickel

Sample C

Analytical method: All
Unit: μg/L

Number of participants		16		Range		1.25	
Number of omitted results		1		Variance		0.11	
True value		7.68		Standard deviation		0.32	
Mean value		7.71		Relative standard deviation		4.2%	
Median value		7.68		Relative error		0.4%	

Analytical results in ascending order:

10	7.25	3	7.61	12	8.02	
5	7.30	18	7.68	1	8.09	
6	7.41	11	7.69	20	8.50	
8	7.51	19	7.71	16	10.73	O
2	7.55	13	7.81			
14	7.60	4	7.91			

O = Omitted result

Sample D

Analytical method: All
Unit: μg/L

Number of participants		16		Range		0.93	
Number of omitted results		1		Variance		0.07	
True value		7.64		Standard deviation		0.26	
Mean value		7.74		Relative standard deviation		3.3%	
Median value		7.64		Relative error		1.3%	

Analytical results in ascending order:

2	7.47	18	7.59	4	7.95	
10	7.52	11	7.64	13	8.10	
6	7.53	5	7.70	16	8.35	O
1	7.55	3	7.73	20	8.40	
8	7.56	19	7.84			
14	7.59	12	7.87			

U = Omitted result

Table 5.20. Statistics - Zinc

Sample C

Analytical method: All
Unit: µg/L

Number of participants	15		Range		4.67	
Number of omitted results	1		Variance		1.46	
True value	12.69		Standard deviation		1.21	
Mean value	12.42		Relative standard deviation		9.7%	
Median value	12.69		Relative error		-2.1%	

Analytical results in ascending order:

11	9.00	2	12.60	8	12.98	
10	10.70	18	12.60	12	13.26	
6	12.30	19	12.77	4	13.53	
14	12.40	20	12.80	1	13.67	
3	12.42	13	12.90	16	17.55	O

O = Omitted result

Sample D

Analytical method: All
Unit: µg/L

Number of participants	15		Range		5.99	
Number of omitted results	1		Variance		3.13	
True value	17.80		Standard deviation		1.77	
Mean value	17.41		Relative standard deviation		10.2%	
Median value	17.80		Relative error		-2.2%	

Analytical results in ascending order:

10	13.10	2	17.50	13	18.50	
11	13.90	20	17.80	12	18.54	
6	17.10	18	17.80	4	18.90	
3	17.32	8	18.36	1	19.09	
14	17.50	19	18.39	16	30.90	O

U = Omitted result

Reports and publications from the ICP Waters programme

All reports from the ICP Waters programme from 2000 up to present are listed below. Reports before year 2000 can be listed on request. All reports are available from the Programme Centre. Reports and recent publications are also accessible through the ICP Waters website; http://www.icp-waters.no/

Halvorsen, G.A., Johannessen, A., Svanevik, T. Biological intercalibration: Invertebrates 2019. **ICP Waters report 133/2019**

Braaten, H.F.V., Åkerblom, S., de Wit, H.A., Skotte, G., Rask, M., Vuorenmaa, J., Kahilainen, K.K., Malinen, T., Rognerud, S., Lydersen, E., Amundsen, P.A., Kashulin, N., Kashulina, T., Terentyev, P., Christensen, G., Jackson-Blake, L., Lund, E., Rosseland, B.O. 2019. Spatial and temporal trends of mercury in freshwater fish in Fennoscandia (1965-2015). **ICP Waters report 132/2019**

De Wit, H., Garmo, Ø. (editors). 2019. Proceedings of the 33rd Task Force meeting of the ICP Waters Programme in Uppsala, May 9-11, 2019. **ICP Waters report 131/2019**

Anker Halvorsen, G., Johannessen, A., Svanevik Landås, T. 2016. Biological intercalibration: Invertebrates 2016. **ICP Waters report 130/2016**

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