

# Chemical Intercomparison 0822



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- 120 laboratories were invited to participate in the intercomparison
- 78 laboratories accepted to participate
- 74 laboratories from 28 countries submitted results

# Participating countries



<b>Country</b>	<b>Labs</b>	<b>Country</b>	<b>Labs</b>
Austria	4	Malaysia	1
Belgium	2	Netherlands	1
Canada	3	Norway	1
China	2	Poland	7
Czech Republic	3	Portugal	1
Estonia	6	Romania	1
Finland	5	Russia	7
France	2	Slovenia	3
Germany	5	Spain	2
Indonesia	2	Sweden	3
Ireland	1	Switzerland	1
Italy	5	Thailand	1
Japan	1	United Kingdom	2
Latvia	1	USA	2
Lithuania	1		

# Analytical variables



- The samples were prepared from one natural lake water and one natural creek:
  - filtered through 0,45  $\mu\text{m}$  membrane filter
  - spiked with small amount of stock solutions prepared from stoichiometric compounds
- Physical variables: pH and conductivity
- Major ions: Alkalinity, nitrate, chloride, sulfate, calcium, magnesium, sodium, potassium
- Metals: Fe, Mn, Cd, Pb, Cu, Ni, Zn

# Quality of the results

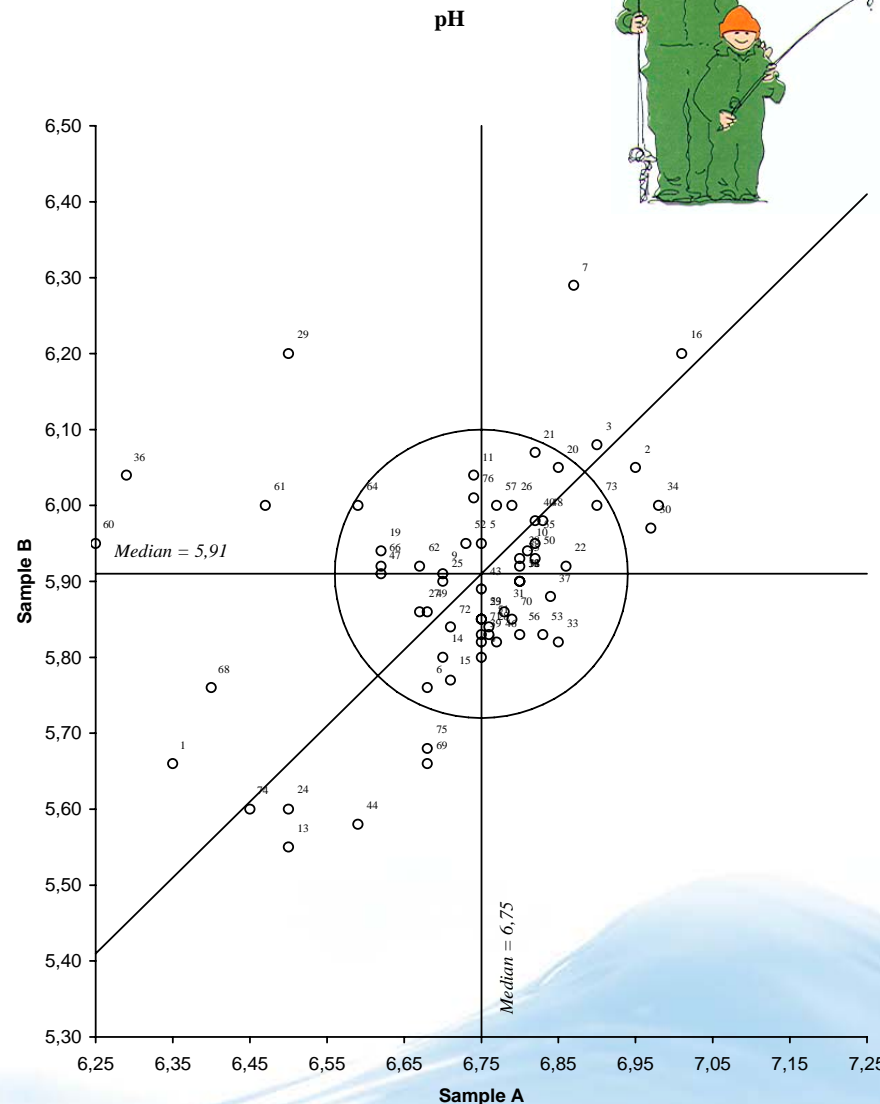


- 69 % of the results were acceptable according to the general target accuracy of  $\pm 20$  %, which is rather low
- The acceptance limit for pH was extended from 0,1 to  $\pm 0,2$  units, then 68 % of the results were acceptable
- The best results were obtained for sodium (91 %), chloride (85 %) and calcium (85 %)
- Worst results for copper (20 %), and alkalinity (35 %). The low concentrations is the major reason for the low acceptance.
- The quality of the results should be improved for several of the analytical variables

# pH



- Samples with pH around the neutrality point are more exposed to effect caused by storage and transport conditions, and might thus be more unstable
- This may be a part of the explanation for the spread of the pH results shown
- There are also systematic differences due to methods used
- It is therefore accepted to use wider acceptance limit for pH than in manual
- A low fraction of acceptable pH results have also been observed in earlier intercomparisons, and probably different explanations are involved



# "True" value



- The purpose of the intercomparison test is to evaluate the comparability of the analytical results produced by the different laboratories
- As natural samples are used the real "true" value is not known
- The median value is considered to be an acceptable estimate of the true value, when a majority are using the same analytical method

# Concentrations



- The low fraction of acceptable results for some variables, especially some of the heavy metals
- May be explained by the rather low concentrations used for these analytical variables, eg. Cu
- When concentrations are close to the detection limits for the methods used, it must be expected that the spread of the results will be greater than  $\pm 20\%$ .
- Update of manual with relevant methods
- Preferred concentrations?

# Reference method ?



- Which methods should be selected as reference methods in the future?
- Today ICP-AEs or ICP-MS are the dominating methods, more than half of the laboratories are using these methods. (Atomic absorption techniques are reference methods for metals in the Manual)
- Ion chromatography is used by about 80 % of the laboratories for anions, nearly 50 % of the laboratories for cations (Different methods given in the manual)

# Some conclusions



- Normalizing the analytical methods used is necessary to increase the comparability of the results produced
- Reference analytical methods in the Manual are outdated for the sensitive waters of this programme
- Add DOC?