Field parameters comparability and uncertainty estimation through collaborative field trial

B.LEPOT, M.P.STRUB, A.MORIN – National Institute for Industrial Environment and Risks (INERIS), Chronic Risks Dept, avenue de bergoide, BP 2, Verneuil en Halatte, 60550, France.

AQUAREF

On-site exercice : a french first attempt

With the support of the French River Basin Agencies (RBAs), the French Ministry of Ecology and its local offices, the French National Institute for Industrial Environment and Risks (INERIS) organised in June 2007 a collaborative field trial on a minor tributary of the River Seine near Paris. This trial was the first national attempt at improving knowledge of the effect, in natural river water, of sampling activity undertaken as part of regulatory monitoring. The sampling spot was selected for its central location, because its rural characteristics are representative of the majority of the RBAs' sampling stations, and because it enabled more than 40 people to be brought together in a secure environment. 14 sampling teams that took part in the trial, all of which were selected by the RBAs.

Fig1 : location of sampling interlabory study site

River Mauldre in Epône
Main characteristics of sampling site location

Catchment: 400 km²; flow: 0.98m3/s ; full board width: 8 m ; Hydro ecoregion : limestone table ; no flow modifying equipment, e.g. dam; 6 WWTP (total EC: 500 000)

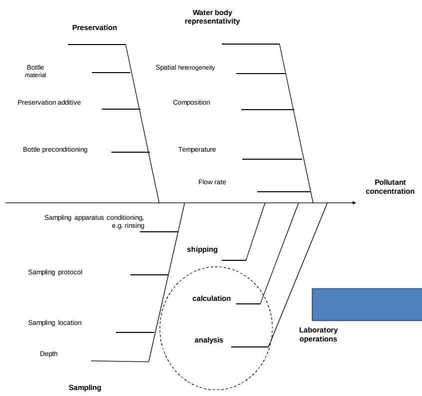

Fig 2 : Ishikawa's diagram of potentiel sources of variability in pollutants concentation determination

•The aim of this study was to :

- make the list of the sampling procedures used by public authorities contractors,
- evaluate several sampling procedures, including standardised ones, to approach the variability induced by sampling operations vs. subsequent analytical processes. *"Sampling operations" are defined here as sampling performance plus external non controlled inputs, e.g. weather.*
- evaluate the accuracy of the measured field parameters.

Preliminary step :

- *Establishing the "Sampling activities" working group*
- *Elaboration of objectives and methodology*
- *Sampling spot selection*
- *Sampling teams selection*
- *Advisory group constitution*

1st national sampling collaborative trial June 26th , 2007

Field parameters evaluation

- **Overview of individual procedures**
- **QA/QC questionnaire**

Protocol comparison

Sampling according :

- In-house protocol
- Prescribed (standardised) protocol

INERIS :

- Collection and shipping of samples
- Analysis of all samples

June – July, 2007

Processing of analytical results and QA/QC questionnaires

- Estimation of field parameters uncertainty
- Evaluation of individual parameters uncertainty
- Estimation of sampling part in overall uncertainty

Fig 3 : Field sampling collaborative trial : overview

Field parameters evaluation

Methodology

This evaluation proceeded in two steps (Fig. 4):

- Step 1: each participant was to measure field parameters in a specified order with his own apparatus & procedures. The measurement was carried out in a common volume of natural water and within a given time. Each measurement was duplicated with the same apparatus.
- Step 2: *a posteriori* metrological control of the measurement apparatus was realised, with the purpose to highlight variations related to the calibration or the metrological survey of the measuring device. The standard solutions used on site were provided by INERIS.

Field parameters measurement

Parameters are measured in a specified order :

1. **Dissolved oxygen (in % and mg/l)**
2. **Temperature (in °C)**
3. **Conductivity (in µS/cm)**
4. **pH (in pH unit)**

Each measurement is duplicated by each sampling team with the same apparatus. The two measurements are carried out sequentially , measurement 2 being the replicate of measurement 1.

All data are collected on a standardised form provided by the organizer, in order to ensure homogeneity of information.

Step 1: *Parameters measurement in a common volume*

Optional adjustment of apparatus before measurement, to sampling team's choice.

*The sampling teams immerse their probes simultaneously in the common volume and read the result on request of the organizer, **result** expressed **in** a **prescribed unit** with **prescribed significant digits number.***

Step 2 : *Metrological control of equipments using common standards*

For equipments checking , the organizer provides the metrological means:

***Oxygen**: Comparison with INERIS oxymeter (successfully controlled and calibrated before and after the comparison)*

***Temperature** : Comparison with an INERIS temperature probe traceable to international standards.*

***pH meter** : Metrological control on site vs. a standard solution provided by INERIS (certified value: 6.867 ± 0.012 pH units).*

***Conductimeter** : Metrological control on site vs. a standard solution provided by INERIS (certified value 495.8 µS/cm ± 1%).*

Fig 4 : Methodology for field parameters evaluation

Apparatus

- Each participant was required to provide some information on his own equipment (commercial brand, identification / quality procedures, measurement range). The aim was to estimate the distribution of the measurement instruments used on field and to evaluate the influence of equipment on the results.
- Several participants use multi parameters probes. The most cited instrument brand is WTW (Fig 5): it is used by 57% of the sampling teams for the measurement of pH, Oxygen and Conductivity. HACH and YSI representation is alike (14%).

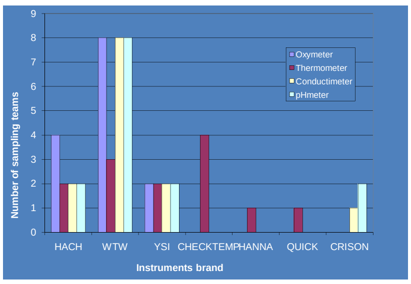

Fig 5: Apparatus used by participant for field parameters measurement

Results

- Data evaluation was carried out by the statistical tool developed for this purpose. The normality of average data was checked by Henry's curve. The statistical outliers were identified by the application of Cochran test and Grubbs test at 95% significance level. The reference values were defined by the consensus values of the selected population, after treatment (Tables1 & 2).
- After this very basic statistical approach, an approach of sampling uncertainty through a combination of the available input data was made. U_{global} in Table 1 represents the global uncertainty of the whole process: sampling, and analysis. $U_{analysis}$ in Table 2 reflects the variability of the analytical process only.
- As usual in metrological assessment, the approach used to combine the two uncertainty sources was chosen as a quadratic propagation, $U_{global} = \sqrt{U^2_{sampling} + U^2_{analysis}}$ (Eq. 1)

	Data before elimination of outliers			Statistical evaluation					
						Reproducibility		Repeatability	
Parameters	Number of values	Raw Average m	raw standard deviation σ_{repro}	Number of outliers	average m	Standard deviation σ_{repro}	Relative expanded uncertainty (k=2) U_{global},	Standard deviation σ_{rep}	CV_{rep} in %
Oxygen Natural water in mg/L	14	7.5	0.6	**2**	**7.5**	0.2	**5.3%**	0.0225	0.3%
Oxygen Natural water in %	14	77.8	6.4	**2**	**77.5**	2.0	**5.2%**	0.2	0.2%
Temperature Natural water in C	14	16.6	0.2	**1**	**16.6**	0.2	**2.4%**	0.0	0.0%
Conductivity Natural Water in µS/cm	13	764	23	**1**	**764**	24	**6.3%**	0.3	0.038%
pH Natural water	14	7.85	0.06	**0**	**7.85**	0.06	**1.5%**	0.01	0.1%

Table 1 : Results of measurements on site [before and after outliers rejection]

	Data before elimination of outliers			Statistical evaluation					
						Reproducibility		Repeatability	
Parameters	Number of values	Raw Average m	Raw standard deviation σ_{repro}	Number of outliers	Average m	Standard deviation σ_{repro}	Relative expanded uncertainty (k=2) U analysis,	Standard deviation σ_{rep}	CV_{rep} in %
Conductivity of Standard solution in µS/cm	13	498	14	**1**	**501**	7	**2.8%**	1	0.1%
pH of Standard sol.	14	6.87	0.07	**1**	**6.87**	0.07	**2%**	0.01	0.1%

Table 2 : Results of standard measurements on site [before and after outliers rejection]

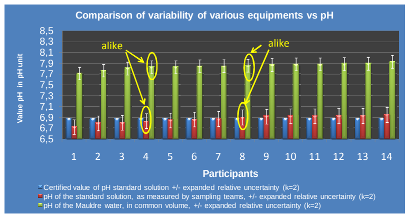

Fig 6: variability of pH vs. apparatus

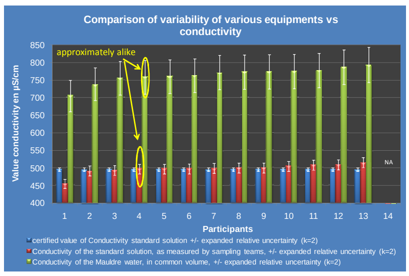

Fig 7: variability of conductivity vs. apparatus

Conclusions

- pH : $U_{sampling}$ and $U_{analysis}$ are alike (fig 6)
- Conductivity : $U_{sampling}$ is approximately 5,6% (represents 88% of U_{global}) (fig 7)

Acknowledgements

- We would like to thank the French Ministry of Ecology, the French National Agency for Water and Aquatic Environments, the River Basin Agencies, all the INERIS sampling and analytical teams, the participants and supporters of the exercise.

TRACS : "for laboratory parameters results, see M.P. Strub, B. Lepot and A. Morin, Metrological aspects of collaborative field trials, including coping with unexpected events , TrAC 28, 2, February 2009, P. 245-261"

INERIS maîtriser le risque pour un développement durable

ONEMA Office national de l'eau et des milieux aquatiques

Liberté • Égalité • Fraternité RÉPUBLIQUE FRANÇAISE Ministère de l'Écologie, de l'Énergie, du Développement durable et de la Mer

Contact : Bénédicte LEPOT- Parc Technologique Alata - BP 2 - 60550 Verneuil-en-Halatte – benedicte.lepot@ineris