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STUDY REPORT

Report on uncertainties and zeta-scores

This document is for informational purposes only and is based on results and observations of interlaboratory schemes of A.G.L.A.E.

December 2016

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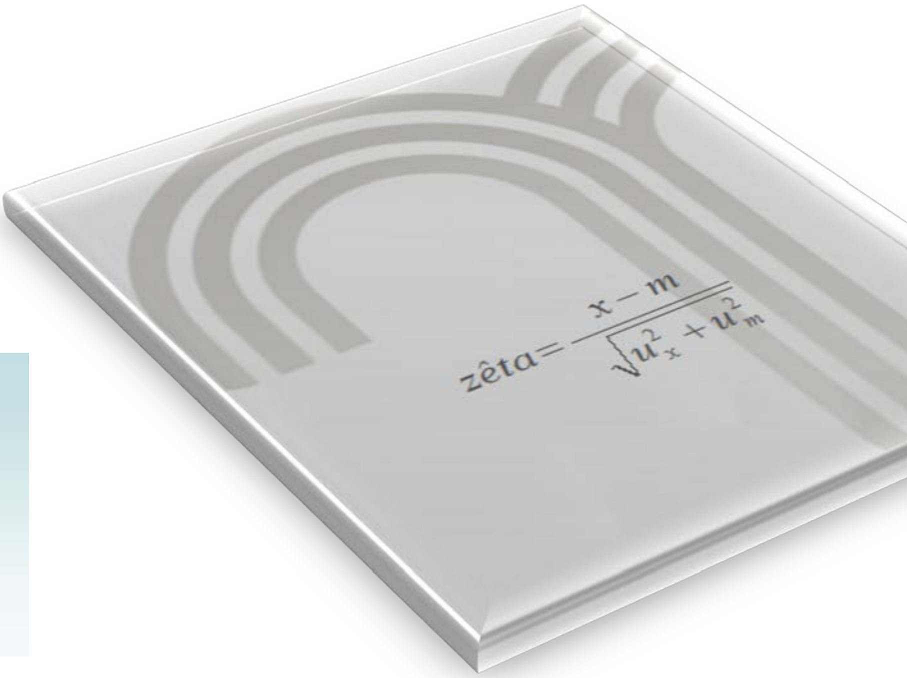

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ABSTRACT

During our proficiency testing in physical-chemistry, participants have the possibility to assess their uncertainties. We studied the percentage of laboratories which provided uncertainties, the uncertainties given and the percentage of underestimated uncertainties.
This study has been carried out according to the type of parameter and the nature of samples analysed. We also examined the evolution of data between 2013 and 2015.
Uncertainties could be linked to families of parameters.

Family	Median expanded relative uncertainty (k=2)
Chemical analysis	10%
Metals	14%
Organics	30%
Indexes	20%
Physical measurements	5%

We also observed that the nature of the sample can have an effect on uncertainty, especially for metals. For these parameters, laboratory uncertainties and the percentage of underestimated uncertainties are lower on clean waters than on wastewater and solid matrices.
There was little change between 2013 and 2015. The percentage of laboratories accompanying their results was already high in 2013 and increased slightly in 2014 and 2015. The uncertainties given by the laboratories have slightly enlarged and thus a slight reduction in the number of underestimated uncertainties was observed.

CONTENTS

PRESENTATION AND COMMENTS

TABLE OF FIGURES

1. INTRODUCTION

Since 2012, laboratories which participating in our "physico-chemical" proficiency testings have had the possibility to report their results with an uncertainty, which is assessed with a zeta-score calculation (for more information on the zeta-score please see annex A1).
This document draws up a first report on uncertainties given and their assessment. This study has been carried out according to the type of parameter and the type of matrix. We also studied the evolution of data between 2013 and mid-2015.

2. STUDY IMPLEMENTATION

2.1. Presentation of data

Studied data are the statistics gathered from 2013 to mid-2015 during our "physico-chemical" proficiency testings:
- the percentage of results given with an uncertainty;
- median uncertainty given by laboratories;
- the percentage of underestimated uncertainties (zeta-scores >|2,00|).

This represents a total of 2 965 sets of data collected from 273 proficiency testings with in average 40 participating laboratories. Note that we have not taken into account the data of 2012, the first year where the participants could give measurement uncertainties.

2.2. Presentation of parameters and matrix families

Parameters studied have been grouped together in parameter families like described below:

Parameter family	Parameters grouped together
Base parameters	Anion, Cation, free and total chlorine, Colour, total alkalinity, composite alkalinity, degree of hardness, total organic carbon, dissolved organic carbon, TNK, COD, BOD_5
Indexes	$KMnO_4$ indexes, anionic surfactants index, phenol index, total cyanide index, free cyanides, total hydrocarbons index
Metals	Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cr^{+6}, Cu, Fe, Gd, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sn, Sr, Te, Ti, Tl, U, V, W, Zn, Sum (Cr+Cu+Ni+Zn)
Organics	Alkylphenols, chloroacetic acid, AOX, biphenyl, bisphenol A, C_{10}-C_{13} chloroalkanes (SCCPs), Chloroanilines, Chlorobenzenes, Chlorobenzenes-light, Chlorophenols, Chlorophyll a, Chlorotoluenes, VOHs, Perfluorinated compounds, DEHP, BTX, Brominated diphenylethers, epichlorhydrin, Alkylphenols ethoxylates, PAHs, Microcystins, Nitro-aromatics, Organotin compounds, Pesticides (organochlorinated, organophosphates, triazines, etc.), PCBs, Pharmaceuticals (diclofenac, ibuprofen, etc.)
Physical measurements	pH, salinity, turbidity, TSS, conductivity, dissolved O2, redox potential, loss on ignition at 550°C, soluble fraction, dry matter, dry residue at 105°C, dry residue at 180°C, dry residue of the eluate

The following types of matrices were used in the interlaboratory tests:

Matrix	Type of matrix	Parameter families
Solid matrices	Sludges, soils, sediments, wastes	Base parameters, metals, organics, physical measurements
Natural waters	Surface waters possibly settled, filtered or diluted	Base parameters, indexes, organics
Clean waters	Public drinking water, bottled waters, surface waters settled and/or filtered	Base parameters, metals, organics, physical measurements
Waste waters	Industrial or urban waste waters possibly settled or diluted	Base parameters, metals, organics, indexes, physical measurements
Saline and bracketing waters	Natural saline waters	Base parameters, physical measurements

3. STUDY OF PERCENTAGES OF RESULTATS GIVEN WITH AN UNCERTAINTY

For each test, we calculate the percentage of results returned with a measurement uncertainty. This percentage can illustrate the progress of laboratories in the estimate of measurement uncertainties. We studied this percentage according to the type of parameter implemented and the type of matrix analysed. We have also paid a particular attention to its evolution since 2013.
On average, about 80% of the results are returned with a measurement uncertainty. This percentage varies according to the type of parameter implemented.

3.1. Percentage of results given with an uncertainty according to the type of parameter

The table bellow gathers median percentages of laboratories giving results with an uncertainty as a function of the type of parameter carried out.

Parameter's families	% of laboratories which have given results with an uncertainty
	Median
Base parameters	70%
Indexes	77%
Metals	75%
Organics	82%
Physical measurements	64%

The graph below shows the percentages of results given with an uncertainty for each family of parameters with box plots (for more information on the interpretation of this type of graph, see Appendix A3 "Statistical tools").

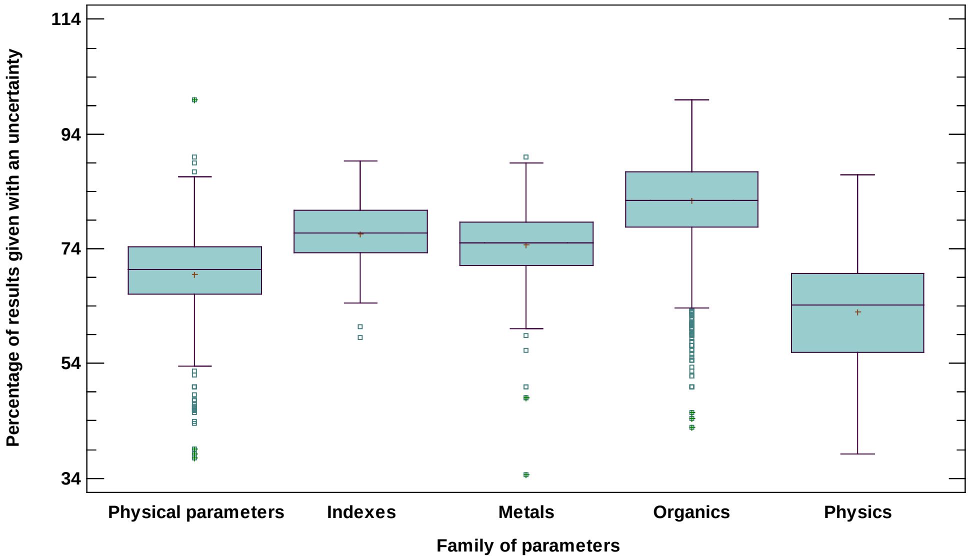


Figure 1: box plot of results given with an uncertainty according to parameters family

There are significant differences between each family of parameters. The simplest parameters to analyse (and the simplest ones for measurement uncertainty estimate) are paradoxically those for which laboratories give the least of results with uncertainty (64% for physical measurements and 70% for base parameters whereas for organic pollutants this percentage rises to 82%).

It also appears that there are large variations within each family of parameters as shown with the family-detailed box plots.

For metals (see graph below), there is one parameter in particular for which the percentage of results given with an uncertainty is clearly lower; it is the sum Cr + Cu + Ni + Zn. We remind you that the uncertainty on the sum of parameters can be easily calculated from the law of propagation of the uncertainty.

$$u(Cr + Cu + Ni + Zn) = \sqrt{u^2(Cr) + u^2(Cu) + u^2(Ni) + u^2(Zn)}$$

where u(X) is the standard uncertainty associated to the X measurement (Cr, Cu, Ni and Zn measurement are considered as independent).

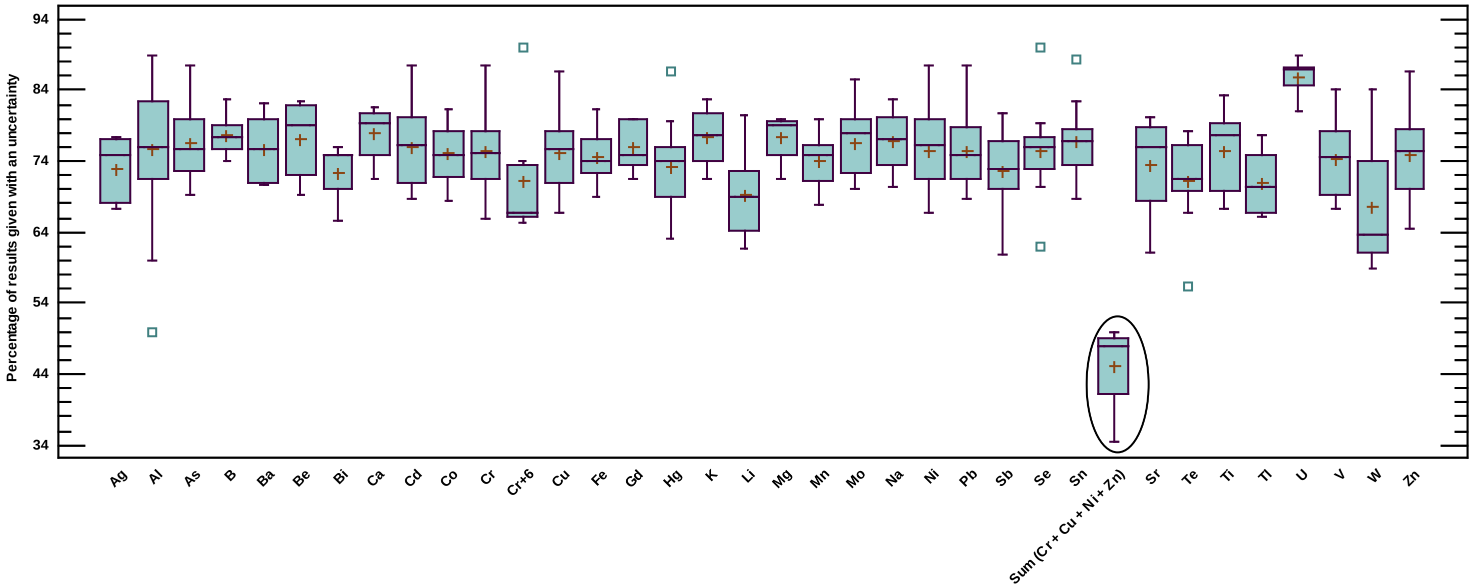


Figure 2: box plot of percentages of results given with an uncertainty for metals

For the "Base parameters" family, lower percentages can be noted for colour and isocyanuric acid. On the contrary, for ClO_4^- the percentage of results given with an uncertainty is higher.

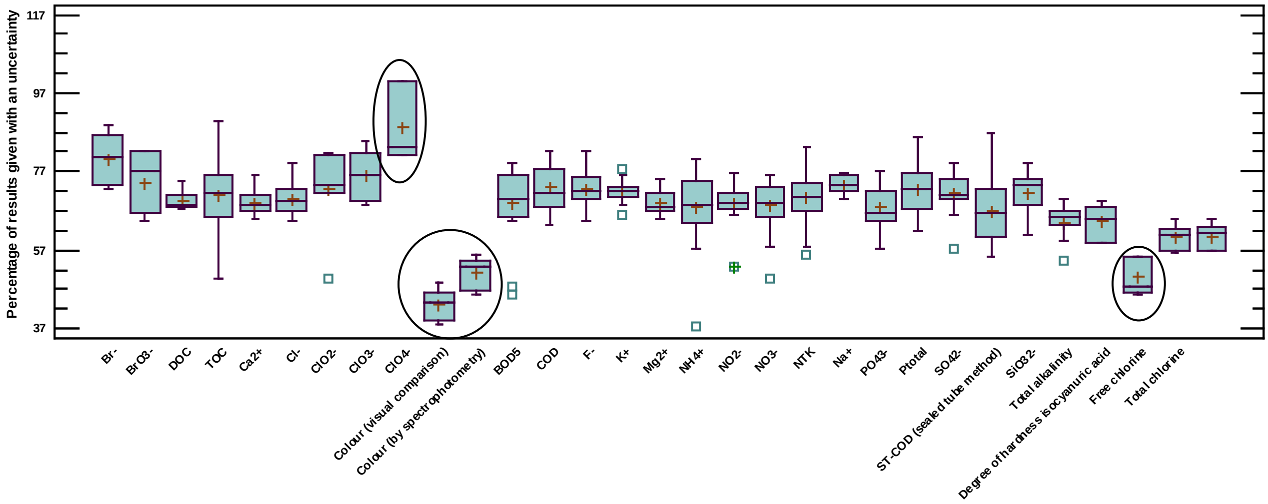


Figure 3: box plot of percentages of results given with an uncertainty for base parameters

For organics also the percentage of results given with an uncertainty varies according to the parameters analysed. It is lower for AOX and chlorophyll a.

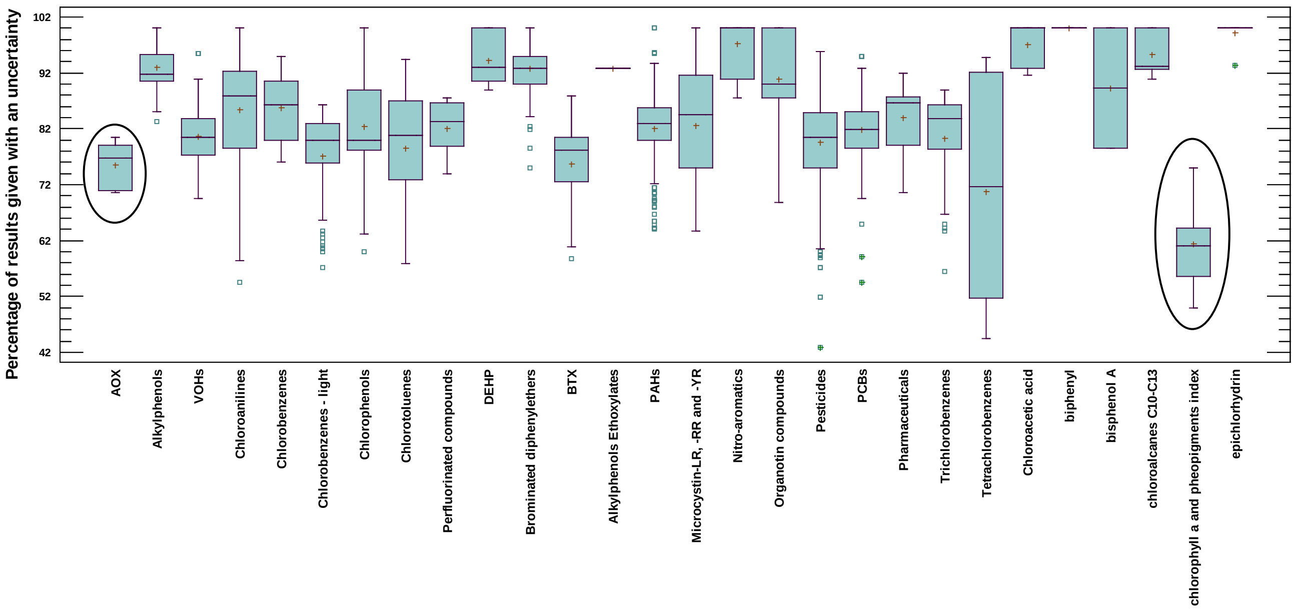


Figure 4: box plot of percentages of results given with an uncertainty for the organics

For indexes, the percentage of results given with an uncertainty is relatively homogeneous and varies from 70% to 80% depending on the parameter.

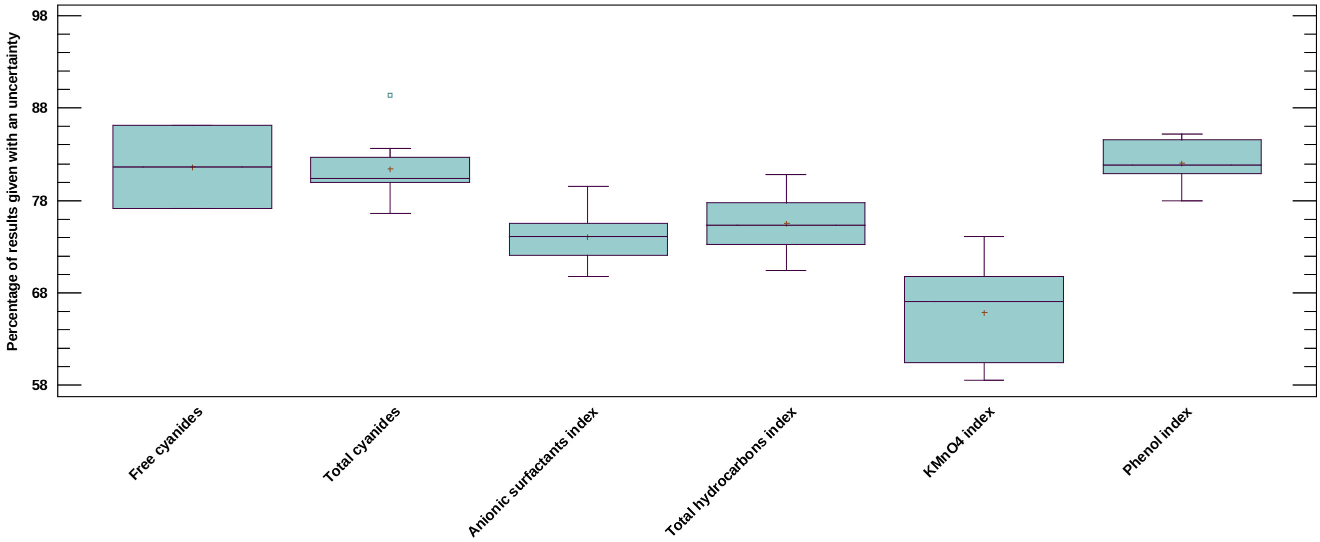


Figure 5: box plot of percentages of results given with an uncertainty for the indexes

For physical measurements, the percentage of results given with an uncertainty varies from 45% for the loss on ignition to 70% for the TSS.

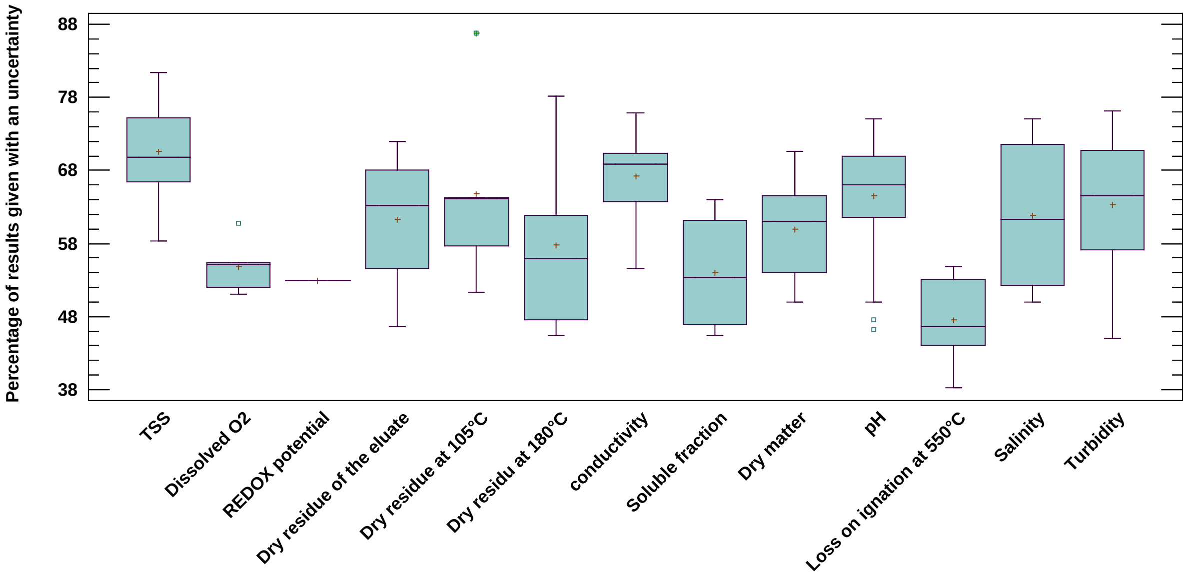


Figure 6: box plot of percentages of results given with an uncertainty for the physical measurements

3.2. Percentage of results given with an uncertainty according to parameters family and type of matrixes

We have seen that the percentage of results given with an uncertainty could vary depending on the type of parameter analysed. We also wanted to see if this percentage could vary according to the type of matrix. For each family of parameters, we have therefore calculated the median of the percentage of results given with an uncertainty as a function of the different matrixes analysed.

However, it is necessary to remain cautious on these observations because the type of parameter implemented can be correlated with the matrix, in particular for indexes and "Physical measurements", and to a lesser extent for base parameters. For example, the 'physical' parameters provided in water are not the same as the ones provided in solid matrices. The deviations of the percentages of results given with an uncertainty that we observe between each matrix are thus indirectly related to the type of parameter analysed.

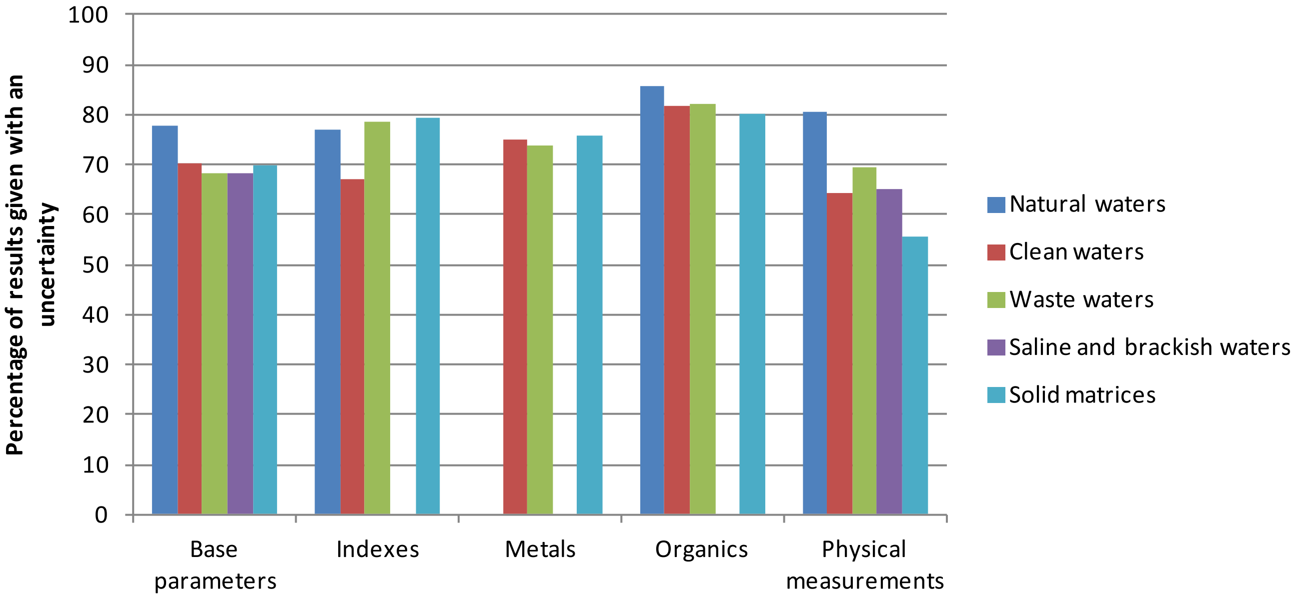


Figure 7: Median percentages of results given with an uncertainty for each family of parameters and for each matrix

Therefore, we have studied the percentages of results given with an uncertainty according to the type of matrix for families of parameters well distributed over each matrix, namely metals and organics.

For metals, there is no significant difference between the percentages of results reported with uncertainty on the different matrices.

Matrix	% of laboratories which have given uncertainties for metals
	Median
Clean waters	75%
Waste waters	74%
Solid matrices	76%

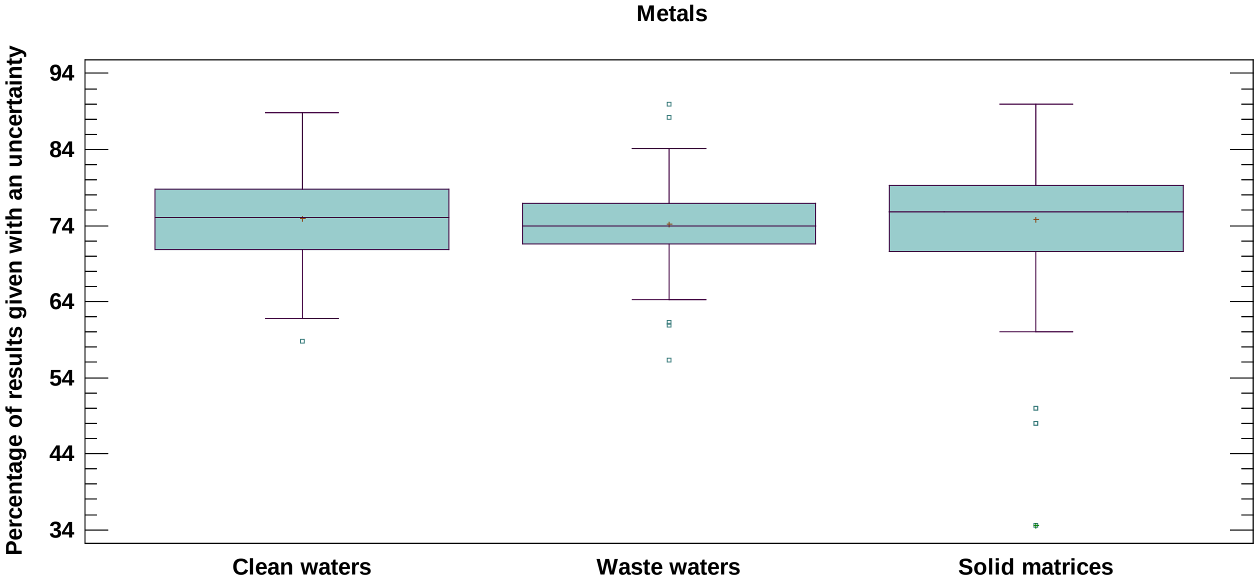


Figure 8: box plot of percentages of results given with an uncertainty according to the matrix for metals

For organics, the differences from one matrix to another are slight (even if statistically significant). The percentage of results given with an uncertainty is higher on natural waters and lower on solid matrices. There is no significant difference between clean waters and waste waters.

Matrix	% of laboratories which have given uncertainties for organics
	Median
Natural waters	86%
Clean waters	82%
Waste waters	82%
Solid matrices	80%

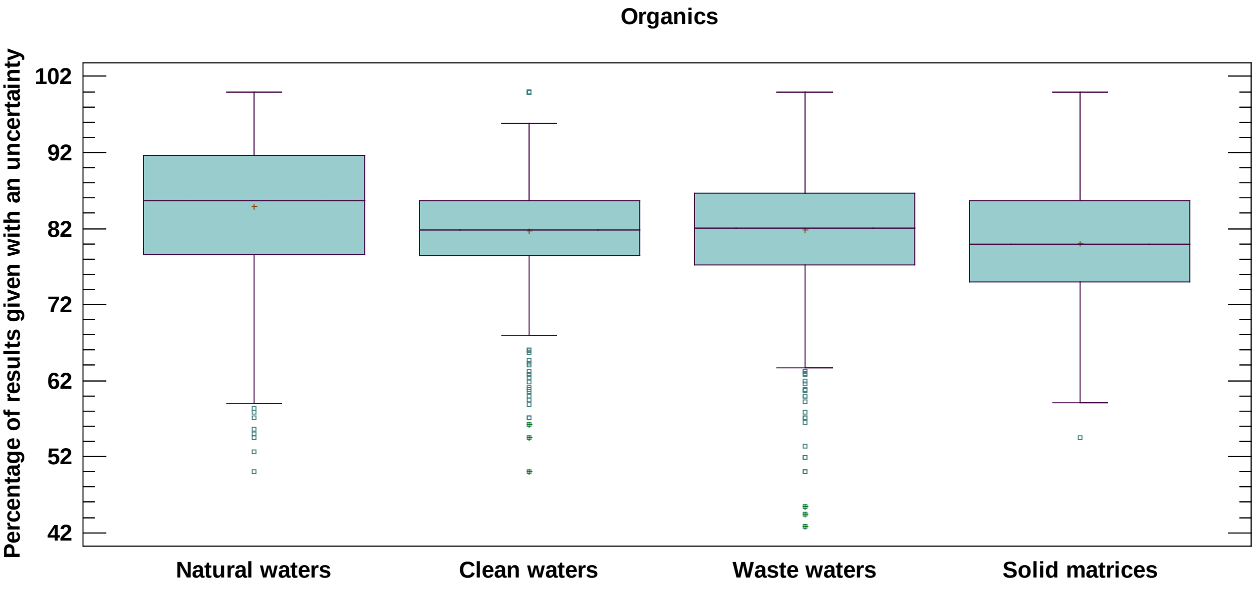


Figure 9: box plot of the percentage of results given with an uncertainty according to the matrix for organics

3.3. Evolution of the percentage of results given with uncertainty since 2013

Although the percentage of results given with uncertainty was already very high in 2013, we could note a slight increase every year. In 2013, this percentage (median per year) was 77%. It rose to 79% in 2014 and then to 81% in 2015.

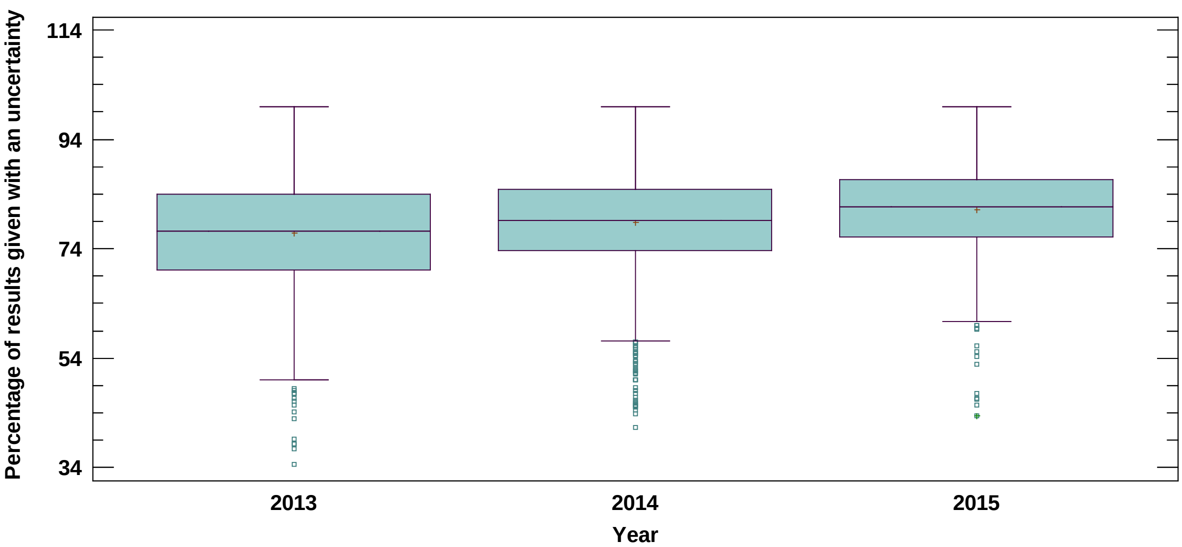


Figure 10: box plot of the percentage of results given with an uncertainty year per year

This tendency is more or less strong and regular according to the type of parameter. For metals, the percentage raised from 71.5% in 2013 to 79.5% in 2015. For organics, there was a + 1.5% increase of results given with an uncertainty in 2015 compared to 2013 and 2014 to reach at a rate of 83.5%. For base parameters, the rate of results given with an uncertainty rose from 68% in 2013 to 73% in 2015. For physical measurements, the rate rose from 62% in 2013 to 66% in 2015. The rate of results given with an uncertainty did not change significantly for the indexes (statistically insignificant).

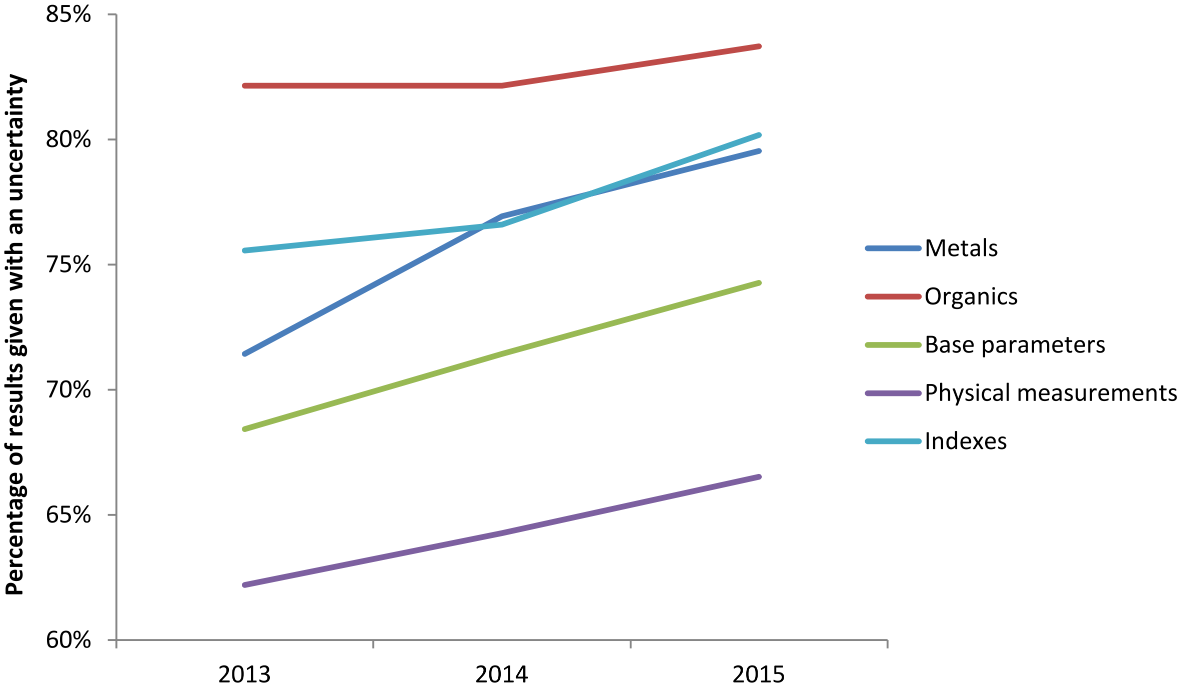


Figure 11: evolution of percentages of uncertainties between 2013 and 2015 according to parameters family

4. STUDY OF THE MEDIAN UNCERTAINTY OF LABORATORIES

For each test, we calculate the median of uncertainties given by the laboratories. These uncertainties are expressed in the relative form (in %) with a coverage factor of 2 (k=2).
By studying the distribution of median uncertainties in the following chart, we can see that the median laboratory uncertainty varies from 5% to 40%, the most observed median uncertainty being 30%. Six uncertainties are particularly observed: 5%, 10%, 15%, 20%, 25%, 30% and to a lesser extent 40%.

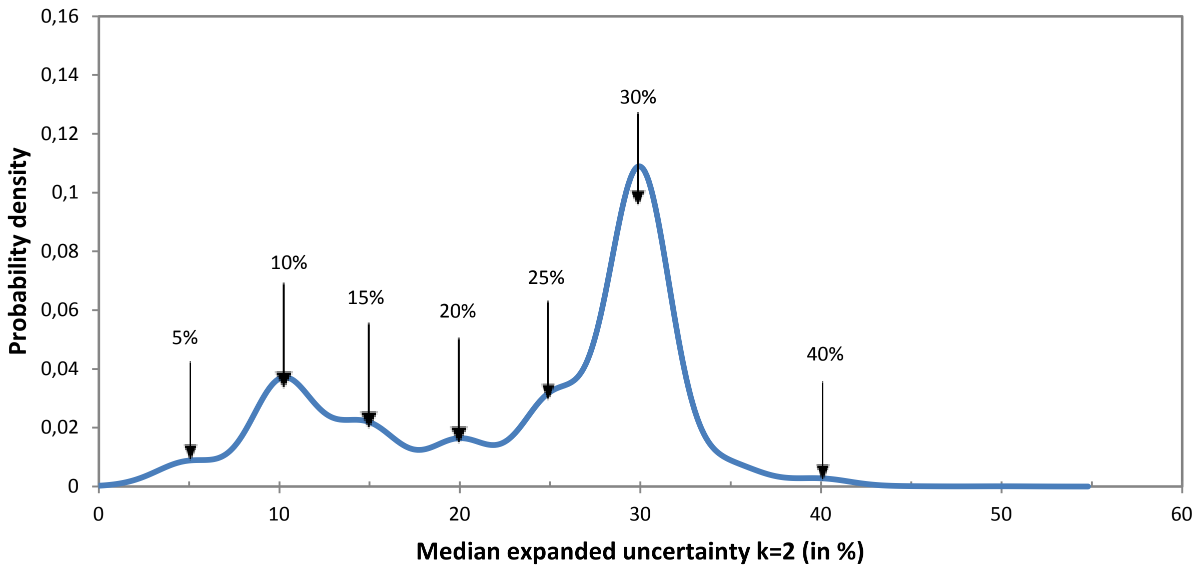


Figure 12: Kernel plot of median uncertainties (k=2)

Note: See Appendix 3 for more information about this type of graph

We have linked these uncertainties to the type of parameter and also to the type of matrices analysed, as presented in Sections 4.1 and 4.2 below. We have also studied the uncertainty values as a function of time (evolution since 2013) in section 4.3.

4.1. Uncertainty according to parameters family

The most commonly observed uncertainties highlighted earlier can be related to the type of parameter analysed, except for 25% and 40% uncertainties.

Parameters family	Median expanded relative uncertainty (k=2)
Base parameters	10%
Indexes	20%
Metals	14%
Organics	30%
Physical measurements	5%

The graph below shows the median expanded relative uncertainty (k = 2) for each family of parameters with box-plots. The differences between each parameters family are statistically significant at the 5% error risk.

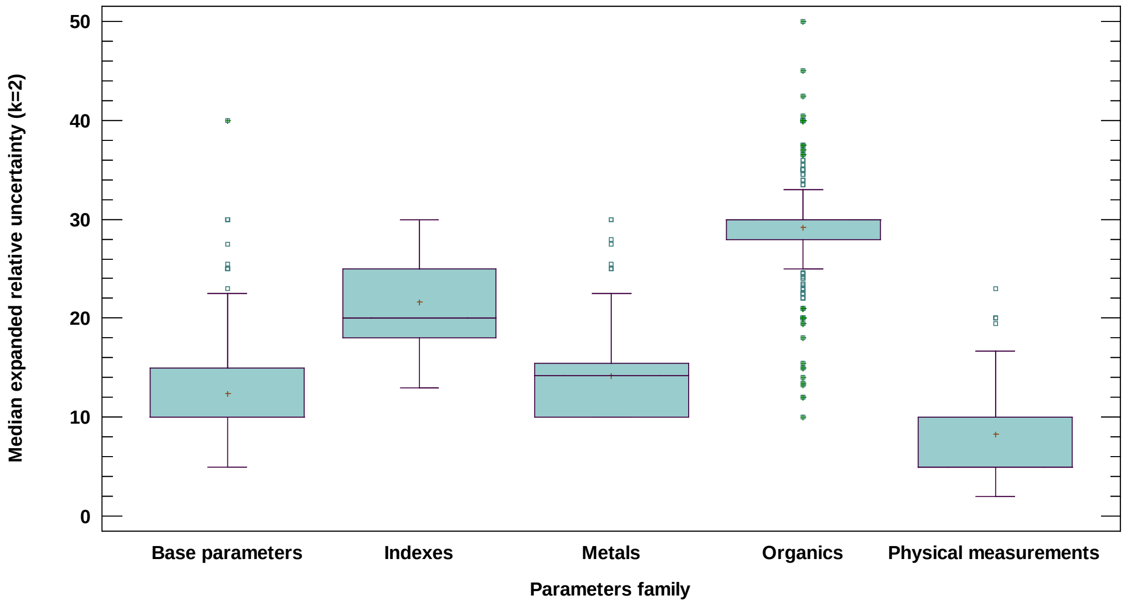


Figure 13: box plot of expanded relative uncertainty according to parameters family

The most observed median uncertainty (30%) is clearly related to organic micropollutants. This is logical given the large number of parameters of this family (245 parameters).
The uncertainties of this family of parameters are relatively comparable.

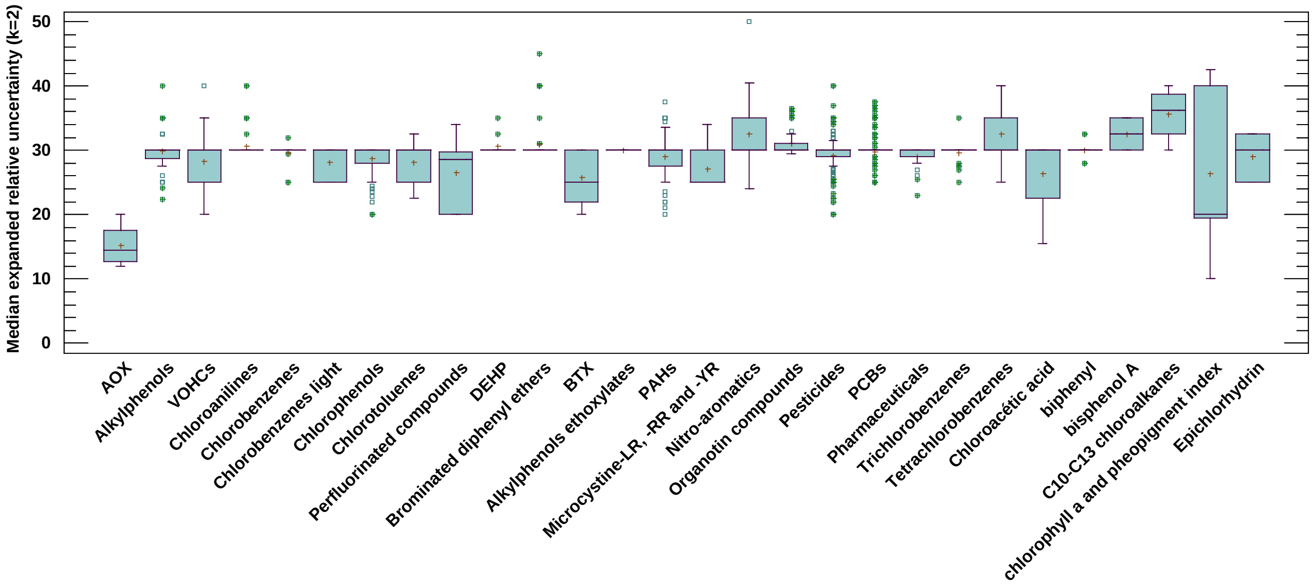


Figure 14: box plot of expanded relative uncertainties for organics

In the graph below, we have classified the median uncertainties of each organic family in ascending order from left to right. It can be seen that the majority of the parameters have a median uncertainty of 30%, except for particular cases such as AOX or C_{10}-C_{13} chloroalkanes.

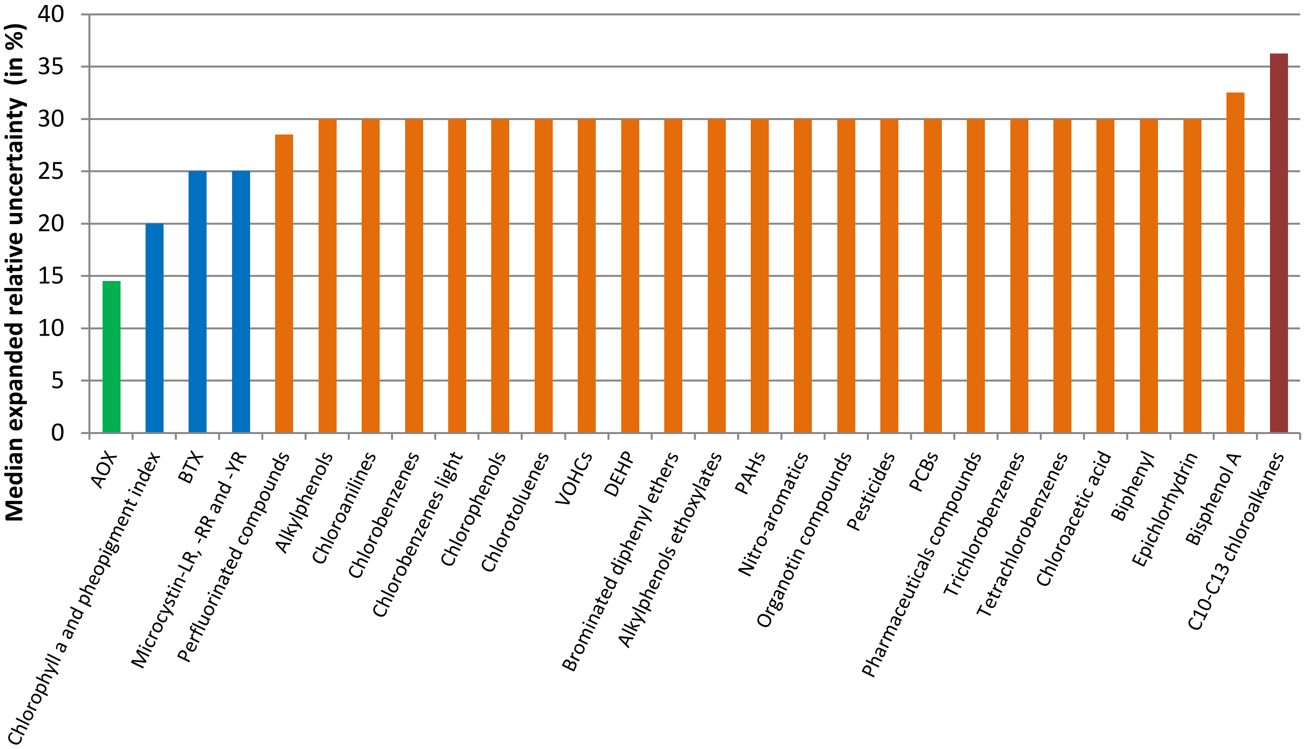


Figure 15: Bar chart of median expanded relative uncertainty relative uncertainties ranked in ascending order for organics

For the indexes family, cyanides, permanganate index and phenol index have a median uncertainty inferior to 20%. The anionic surfactants index has a median uncertainty a little higher that 22.5%, but comparable. Only the total hydrocarbon index stands out with a median uncertainty of almost 30%.

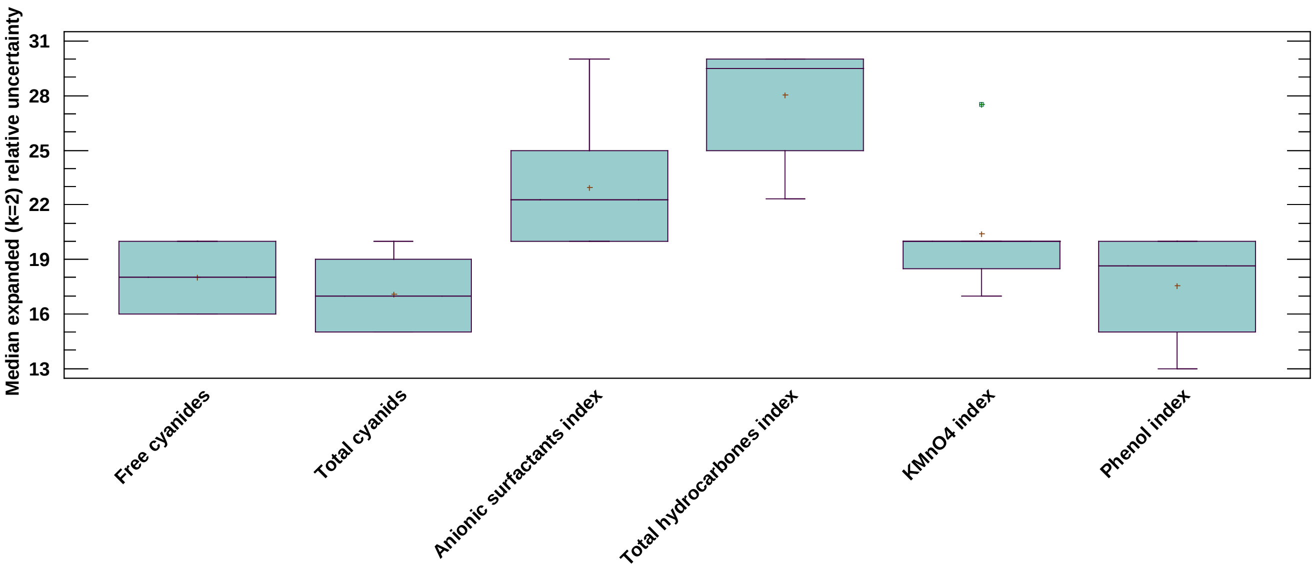


Figure 16: box plot of expanded relative uncertainties for indexes

Below are the median uncertainties observed for indexes in ascending order from left to right.

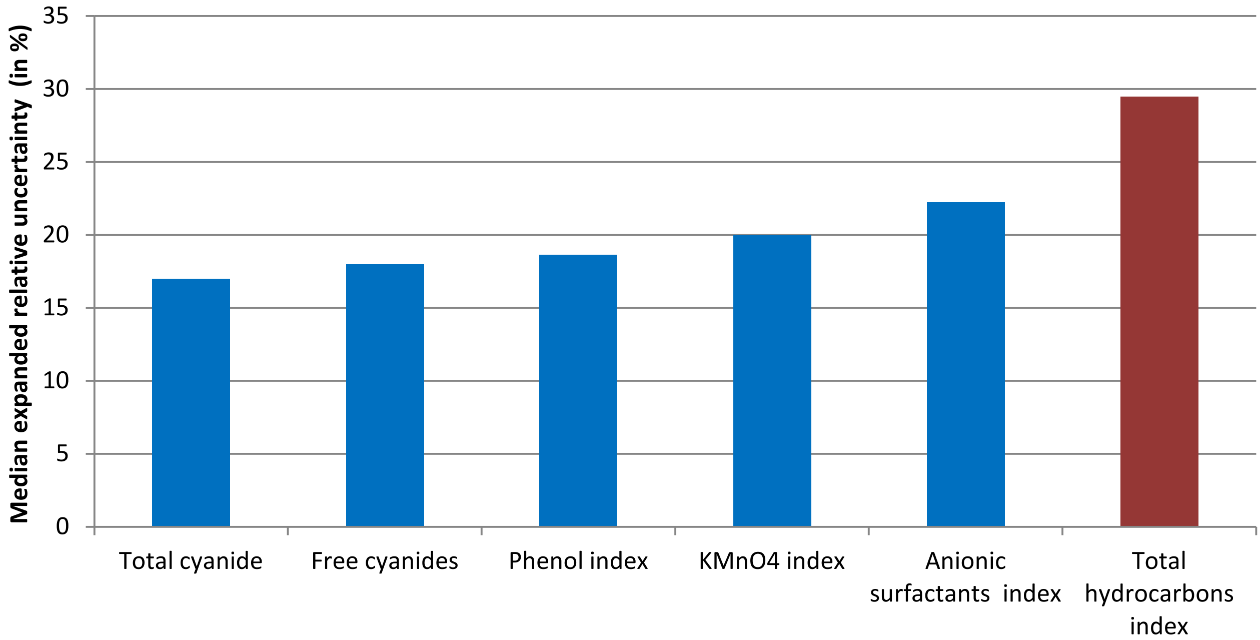


Figure 17: Bar chart of median expanded relative uncertainties ranked in ascending order for indexes

For base parameters, there are significant variations within this family of parameters.

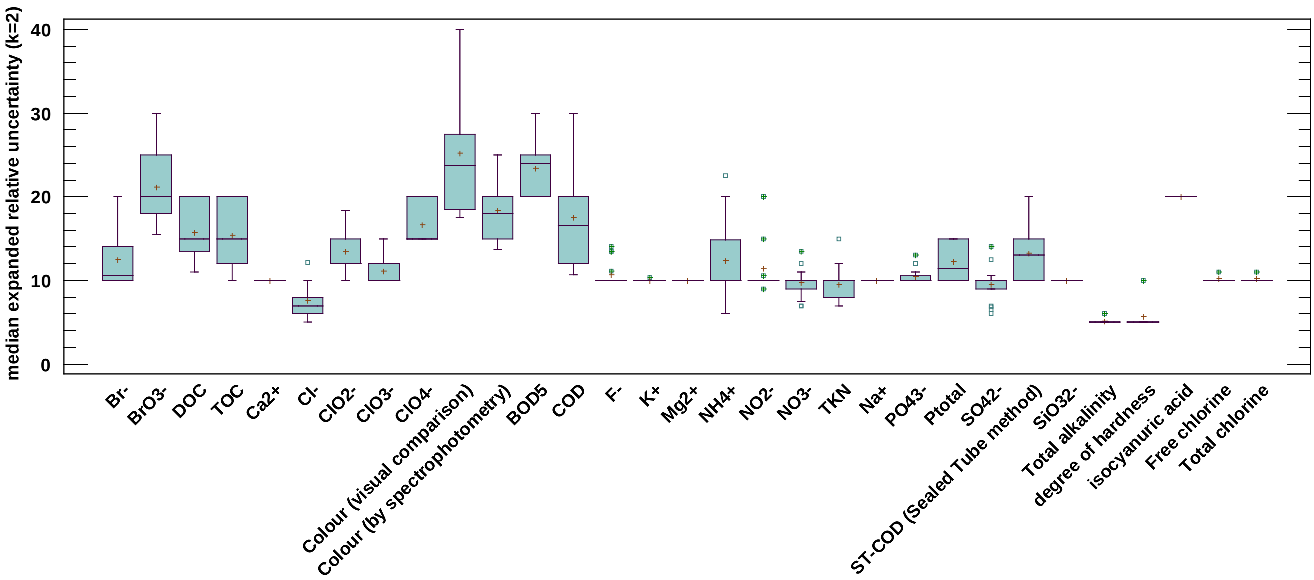


Figure 18: box plot of median expanded relative uncertainties for base parameters

These parameters can be classified into 4 groups (see graphic below). A first group of 3 parameters can be highlighted with uncertainties close to 5% (Total alkalinity, degree of hardness, and Cl-). Then there is a majority group with uncertainties between 10% and 15% which essentially gathers ions. The third group is made up of parameters with uncertainties between 15% and 20%, including DOC, TOC, perchlorates, bromates, COD (conventional method), colour by spectrophotometry and isocyanuric acid. The last group includes colour by visual comparison and BOD_5, both of which have uncertainties near 25%.

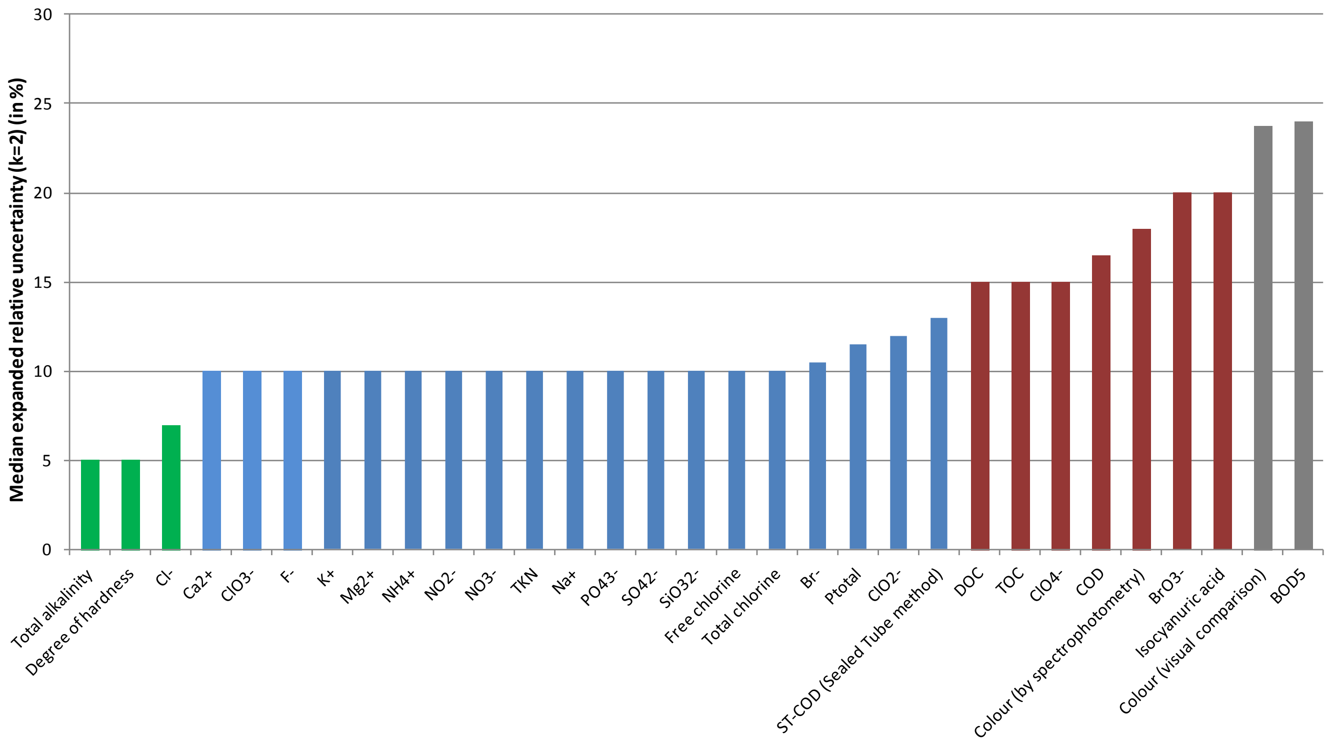


Figure 19: Bar chart of median expanded relative uncertainties ranked in ascending order for base parameters

For metals there are also important variations within this family of parameters.

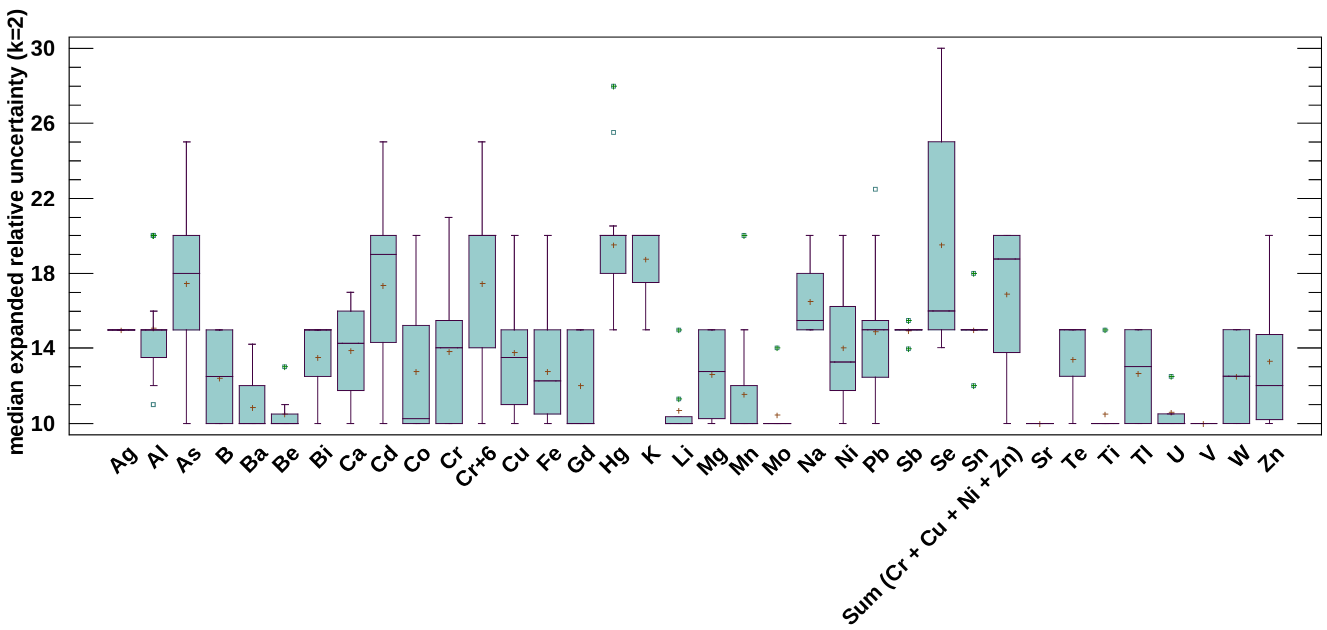


Figure 20: box plot of median expanded relative uncertainties for metals

These parameters can be classified into three groups (see graphic below). A first group of metals with an uncertainty of 10%, a second group with an uncertainty between 12% and 16%. And finally a third group with an uncertainty close to 20%.

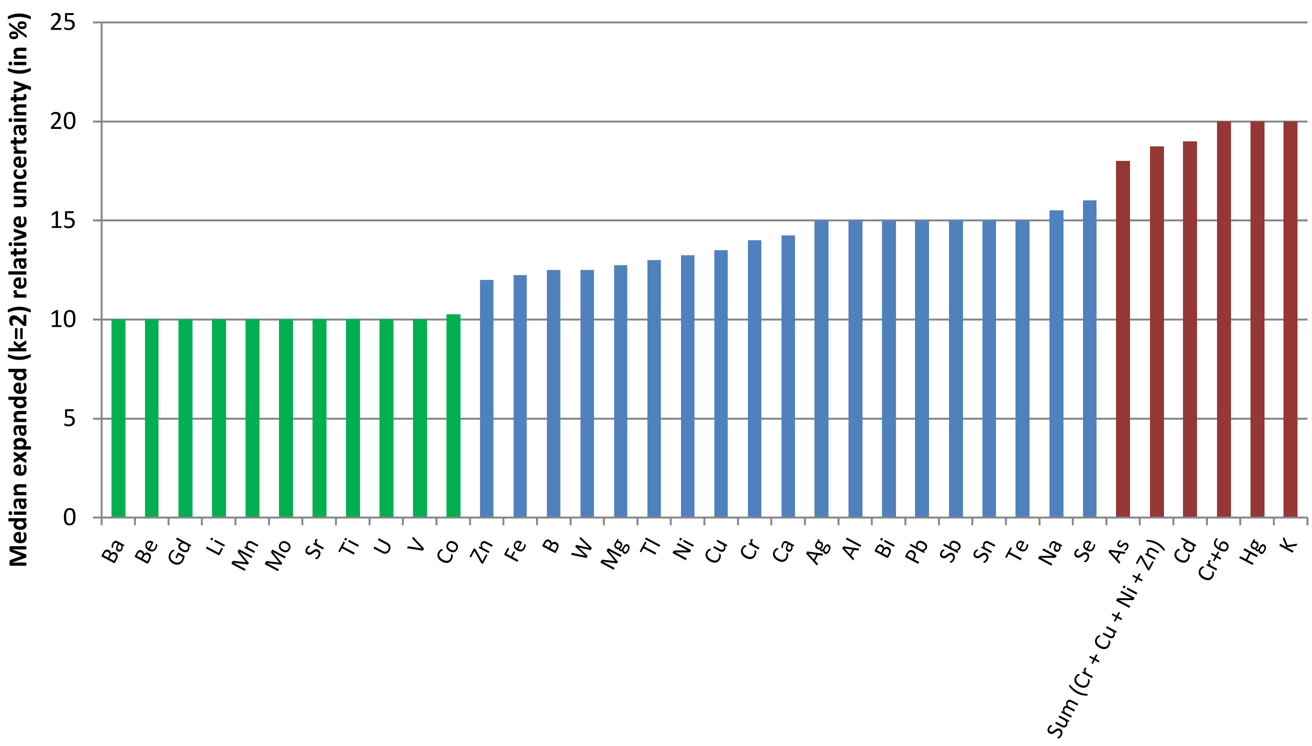


Figure 21: Bar chart of expanded relative uncertainties ranked in ascending order for metals

For physical measurements, median uncertainties also vary significantly, even if they do not exceed 15%.

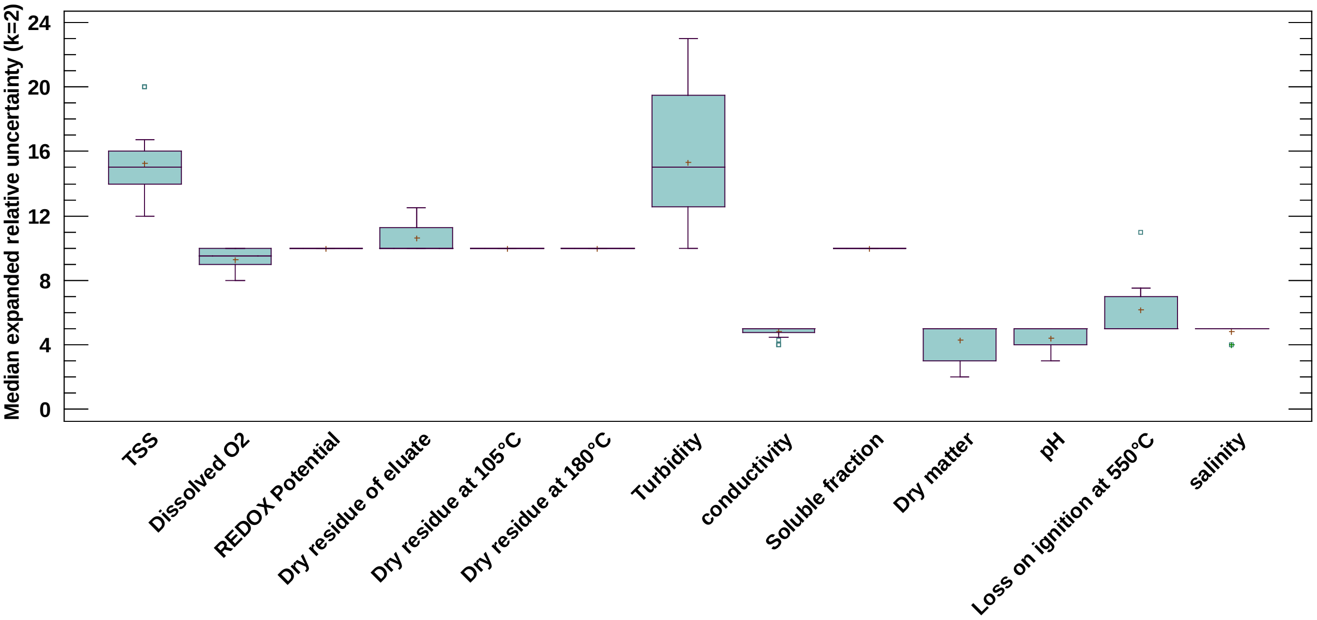


Figure 22: box plot of median expanded relative uncertainties for physical measurements

TSS and turbidity have the greatest uncertainties with a median at 15%. Then there are the dry residues, the soluble fraction, the redox potential and the dissolved oxygen. And finally, the loss on ignition at 550°C, the dry matter, the conductivity and the pH with the lowest median uncertainties at 5%.

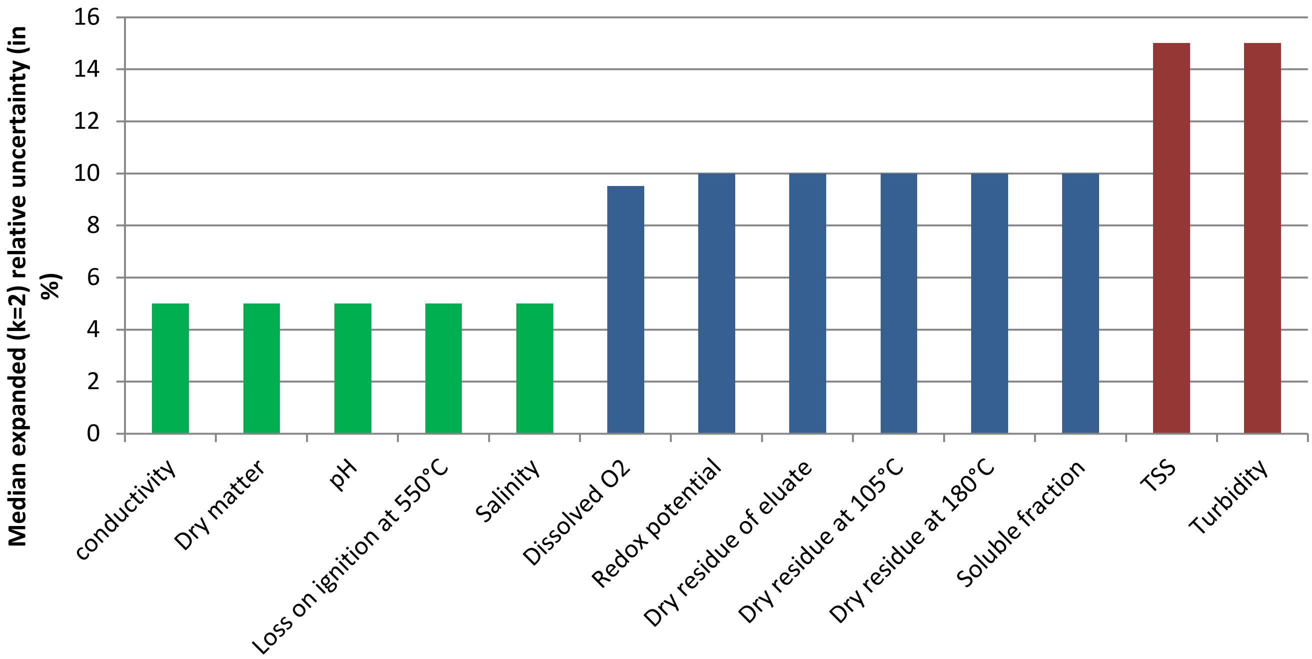


Figure 23: Bar chart of expanded relative uncertainties ranked in ascending order for metals

4.2. Uncertainty according to the parameters family and the matrix

We also examined the uncertainties according to the type of matrix analysed.

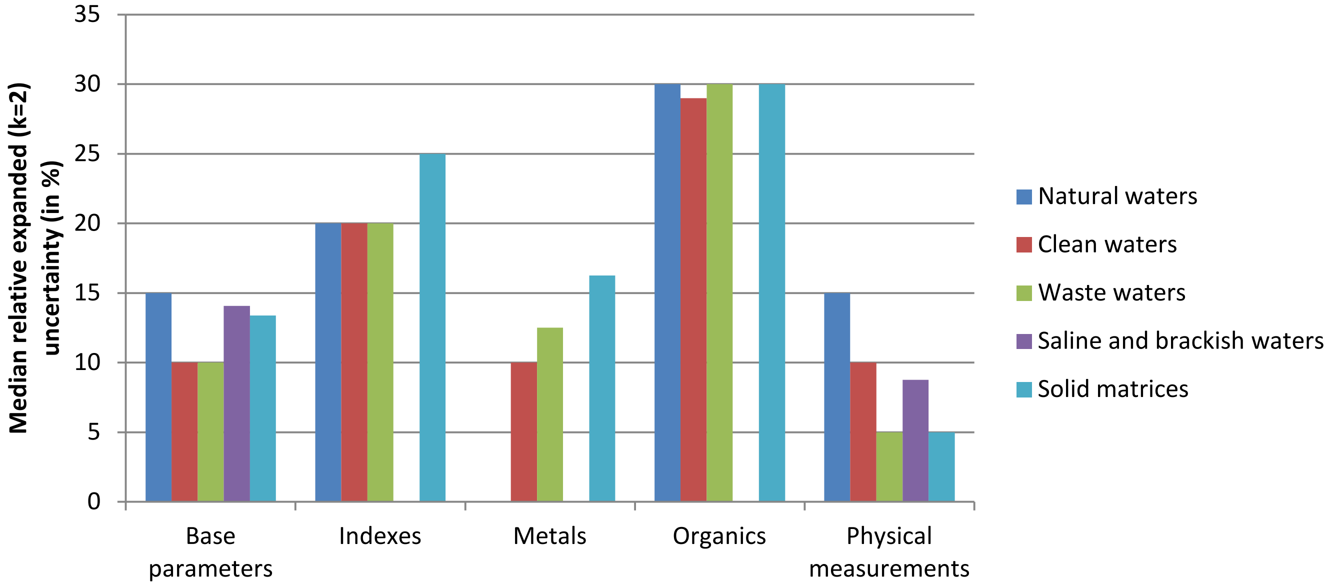


Figure 24: Bar chart of expanded relative uncertainties according to the parameters family and the matrix

It can be seen that the uncertainty announced by the laboratories varies significantly as a function of the type of matrix. However, it is not systematically the same parameters that are implemented on each matrix. These variations are therefore potentially due to the type of parameter analysed and not to a "Matrix" effect on laboratories uncertainty. This is particularly true for physical measurements and indexes.

We have therefore studied the uncertainties of the laboratories as a function of the type of matrix for the families of parameters sufficiently distributed on each matrix, that is to say metals and organics.

For metals, the matrix certainly has an effect on uncertainty. The median uncertainty of laboratories on clean water is 10%, 12.5% on waste water and finally 16.25% on solid matrices.

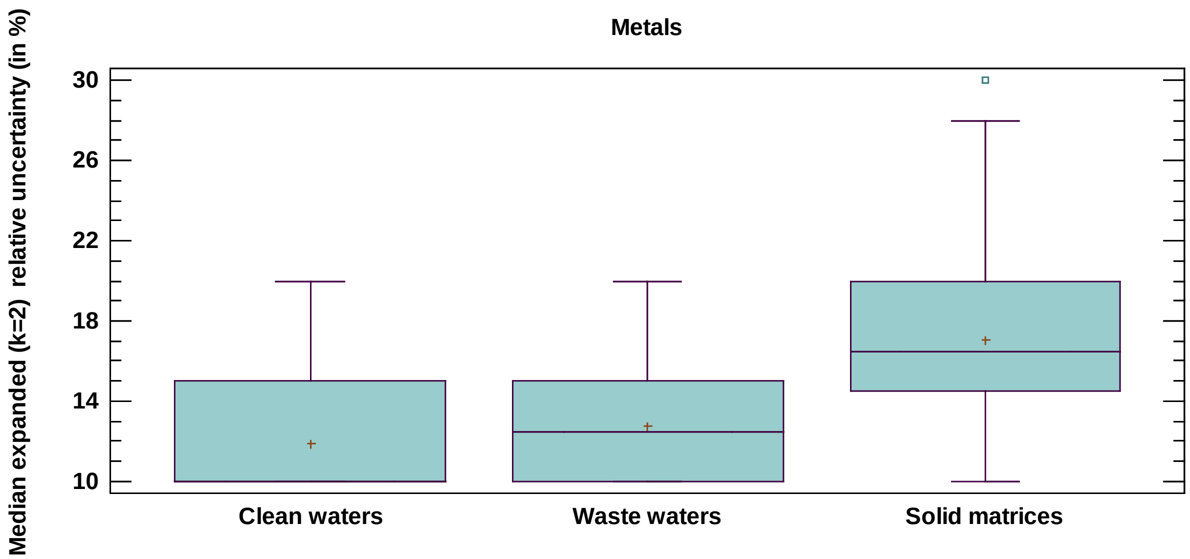


Figure 25: box plot of expanded relative uncertainties according to the matrix for metals

For organics, the deviations observed from one matrix to another are reduced. However, it was noted that uncertainties in clean water tend to be smaller. Those given on solid matrices tend to be higher. Finally, there is no significant difference between natural and waste waters.

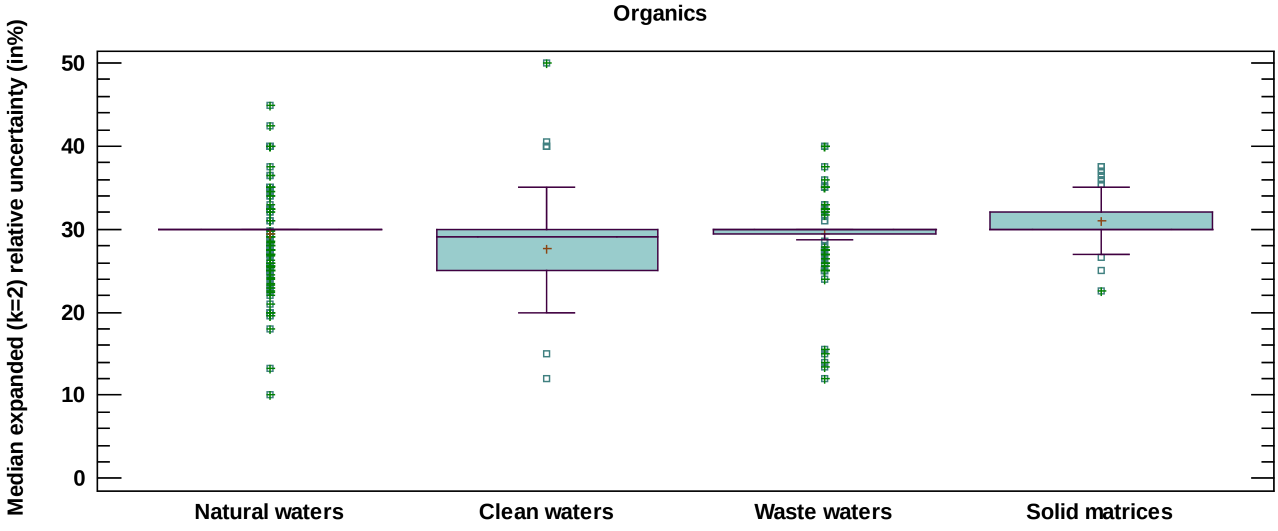


Figure 26: box plot of expanded relative uncertainties according to the matrix for organics

4.3. Evolution of given uncertainties since 2013

Overall, we observe that laboratory uncertainties have increased slightly since 2013. The median uncertainty in 2013 was 25%, rising to 28.5% in 2014 and then to 30% in 2015.

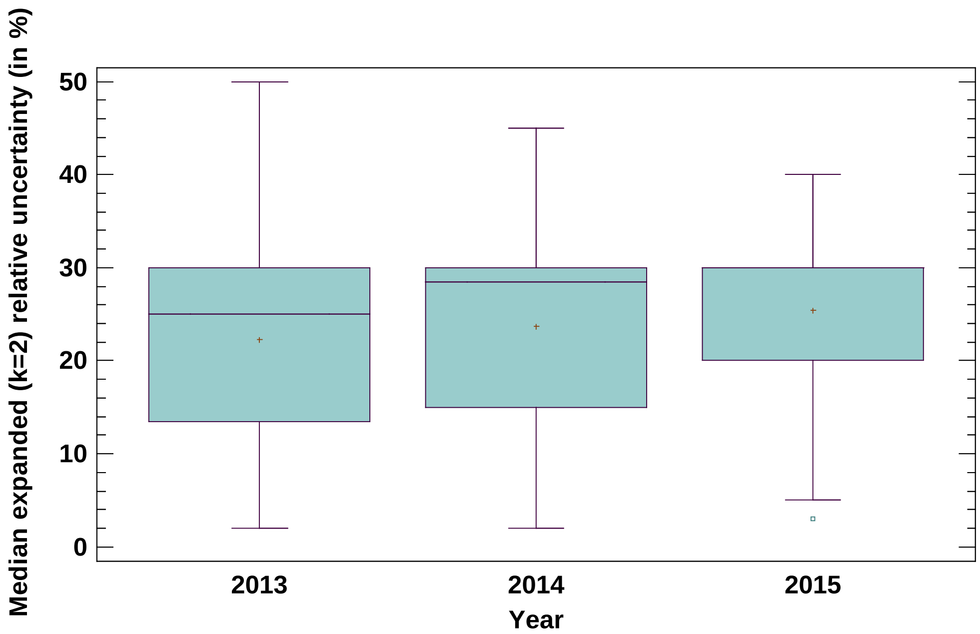


Figure 27: Box plot of expanded relative uncertainties from 2013 to 2015

Looking at this trend as a function of parameters family, we see that there has been no evolution for organics, base parameters and indexes. For metals, the median laboratory uncertainty increased from 13.4% to 15% in 2014 and then to 15% in 2015. For physical measurements, there was an increase in the median uncertainty 1.5% in 2015 compared to 2013 and 2014, but this variation is not statistically significant.

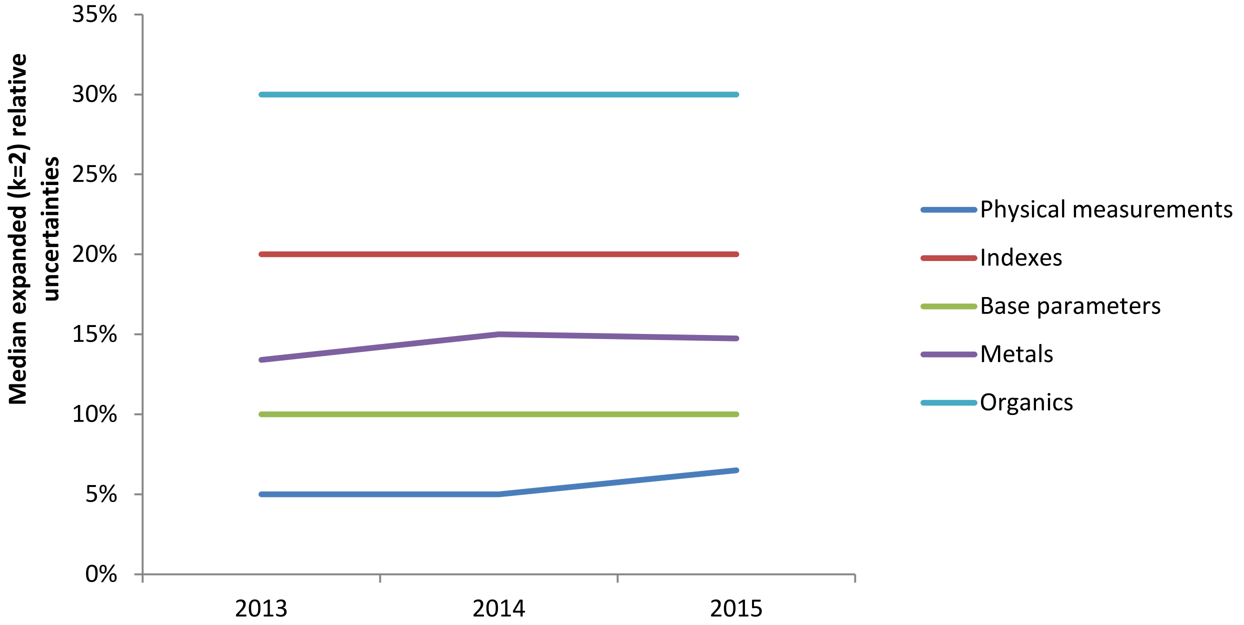


Figure 28: evolution of expanded (k=2) relative uncertainties between 2013 and 2015 according to the parameters family

5. STUDY OF UNDER-ESTIMATED UNCERTAINTIES

In paragraph 4 above, we studied the uncertainty values reported by the laboratories with their results. Now, let us see how these uncertainties are reliable.

The analytical uncertainties given by the laboratories are evaluated with a zeta-score. This indicator makes it possible to check whether the uncertainty given has not been underestimated, which is the case when a zeta-score exceeds the value of two in absolute value. For each parameter used in a test, we calculated the percentage of underestimated uncertainties, that is, zeta-scores> | 2,00 |.

The graph below shows these percentages in probability density:

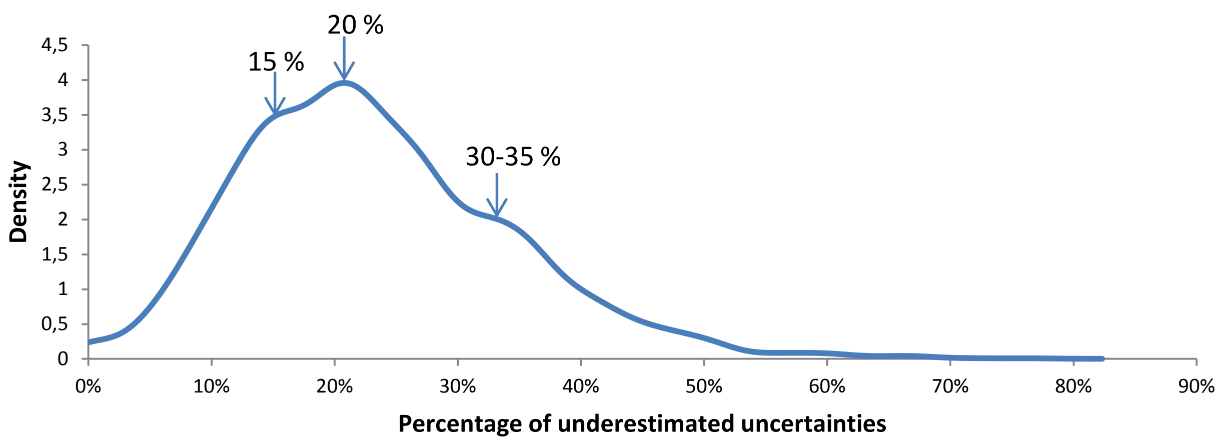


Figure 29: Kernel density plot of uncertainty percentages underestimated

It can be seen that these data do not have a unimodal, but a slightly multimodal one. We cannot therefore speak of "one average percentage of uncertainties underestimated". There are one or more factors that lead to greater or lesser percentages of underestimated uncertainties. Three percentages of underestimated uncertainties are highlighted in this graph: 15%; 20% and 30-35%.

5.1. Percentage of underestimated uncertainties as a function of the type of parameter

We first studied the distribution of the percentages of underestimated uncertainties as a function of the type of parameter implemented.

Parameters family	Percentage of underestimated uncertainty Median
Base parameters	19
Indexes	26
Metals	19
Organics	23,5
Physical measurements	15

The type of parameter used does not explain the three different percentages of underestimated uncertainties, although there are many different percentages from one family of parameters to another.

Below are the percentages of median underestimated uncertainties for each family of parameters ranked in ascending order from left to right.

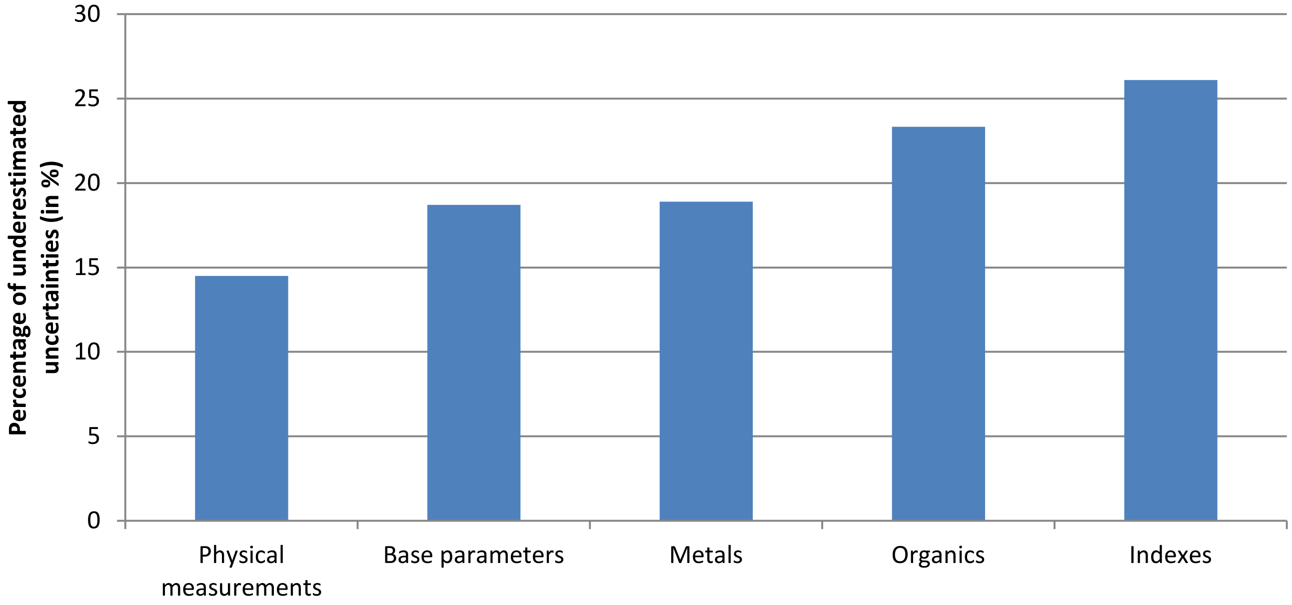


Figure 30: bar plot of the median percentage of underestimated uncertainties according to the parameters family

Please note that only percentages observed for base parameters and metals (19%) are not significantly different. The box plot also allows us to see that the distributions of the results present for some families asymmetric distributions.

We have therefore searched which factor could be the cause of this phenomenon by studying the correlation between the reproducibility of the results and the percentages of underestimated uncertainties.

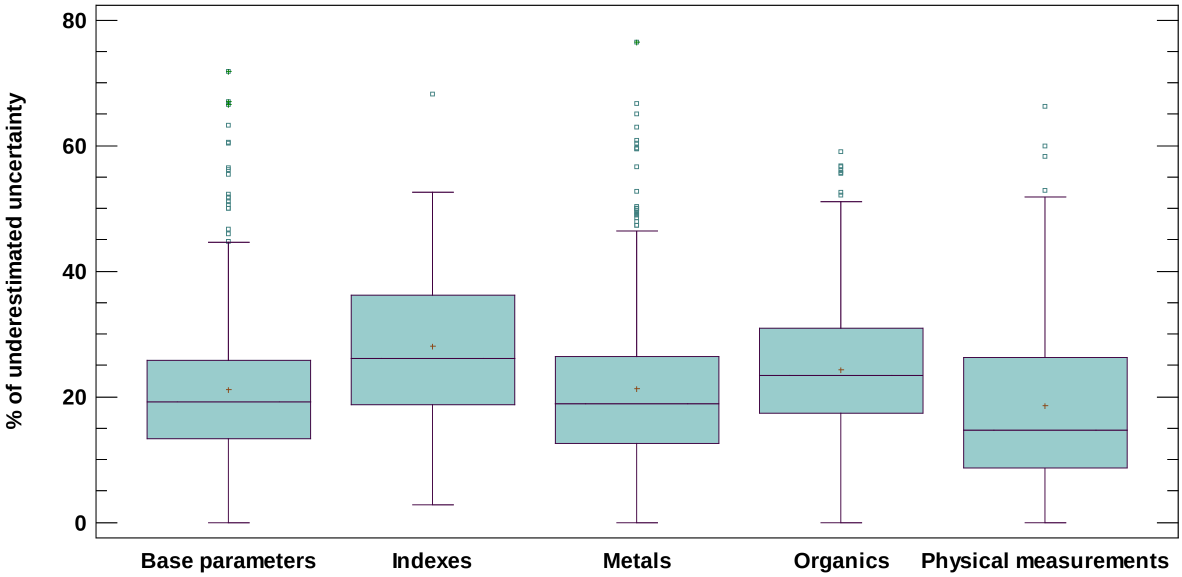


Figure 31: box plot of the percentage of underestimated uncertainties according to the parameters family

5.2. Percentage of underestimated uncertainties according to the CVR% and type of parameter

The graph below shows the percentage of uncertainties underestimated as a function of the reproducibility coefficient of variation. We can see that when the reproducibility of the results degrades, there are more uncertainties underestimated.

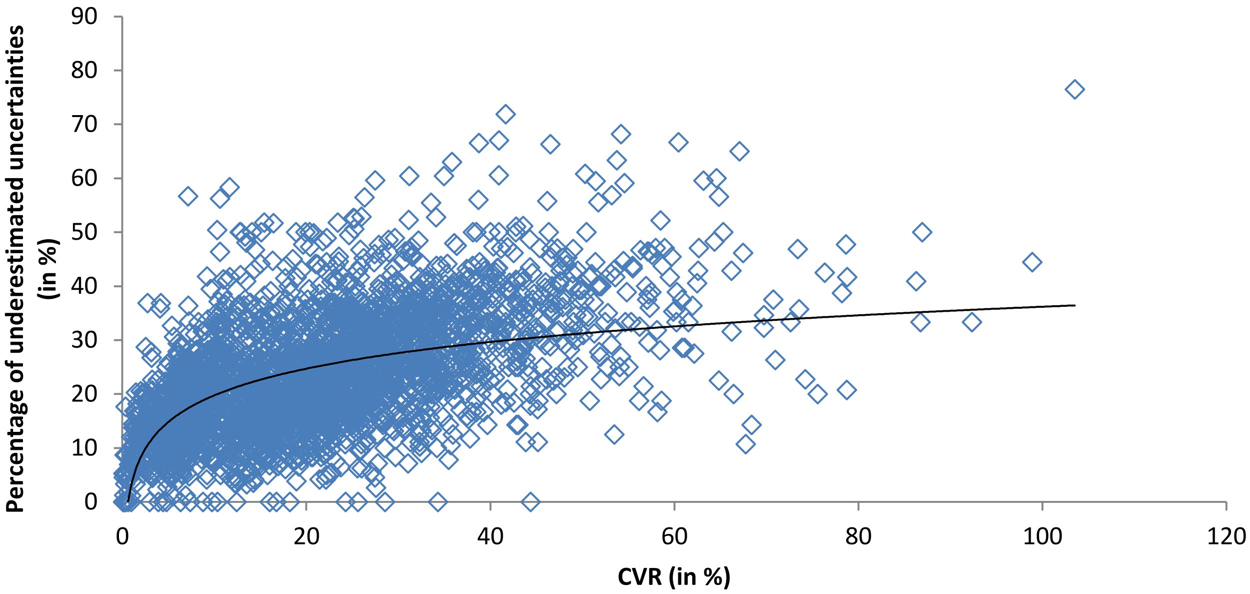


Figure 32: Graph of distribution of the percentage of uncertainties underestimated as a function of CVR

By separating the data according to the type of parameter implemented, it is also seen that the CVR% evolves according to the type of parameter implemented.

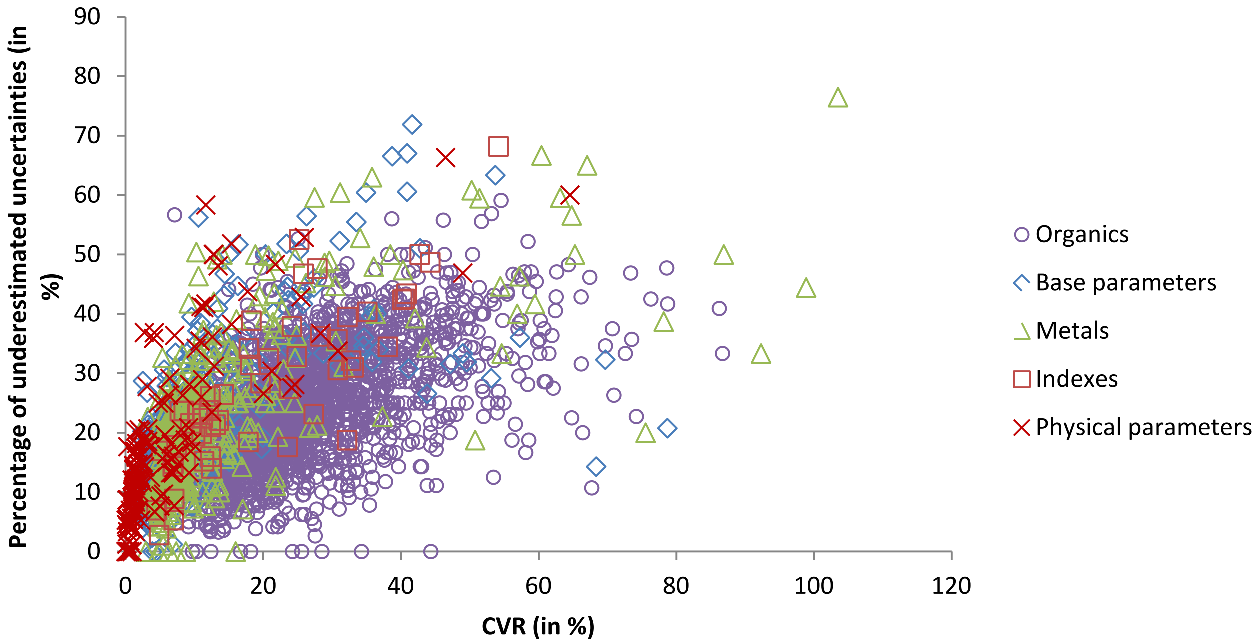


Figure 33: graph of distribution of the percentage of underestimated uncertainties as a function of CVR by parameters family

For each family of parameters, if the coefficient of variation increases, the percentage of underestimated uncertainties also increases.

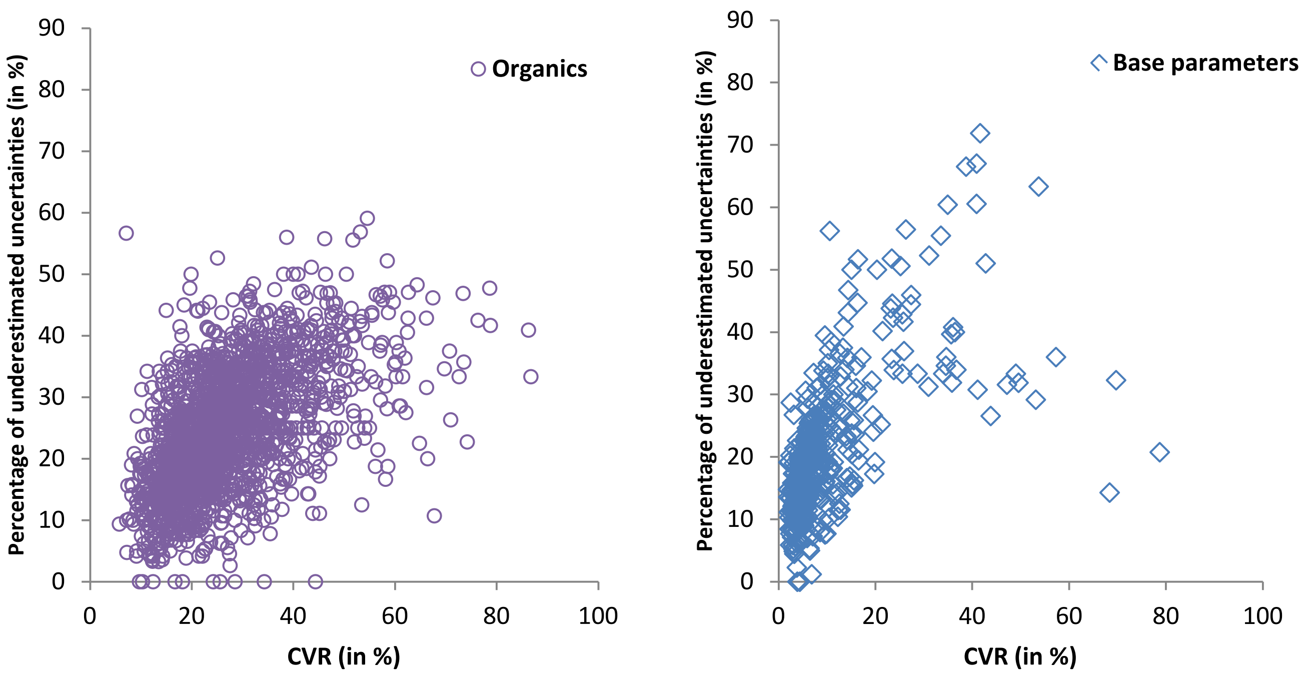


Figure 34: distribution graphs of the percentage of underestimated uncertainties as a function of CVR for organics and base parameters

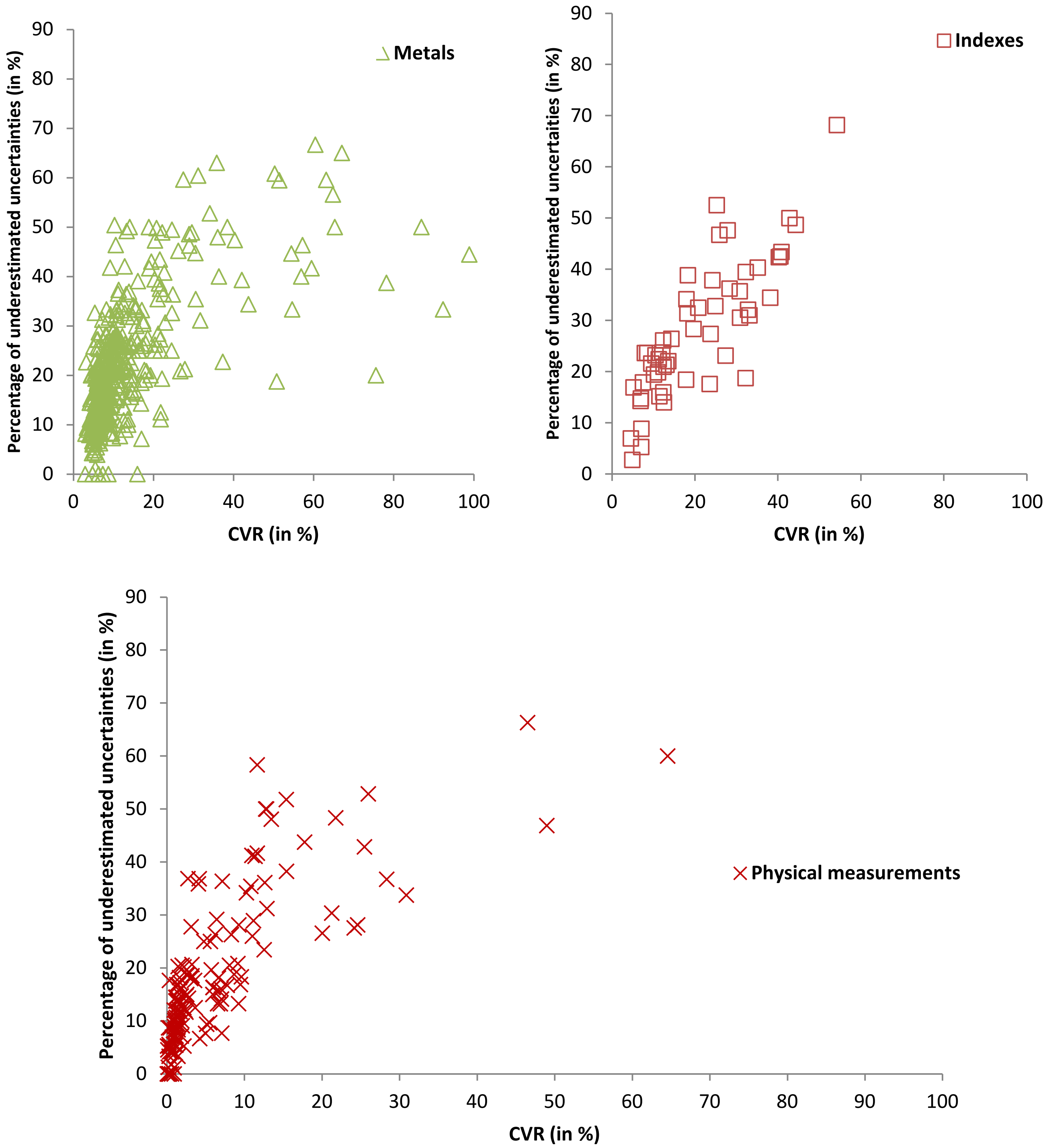


Figure 35: distribution graphs of the percentage of underestimated uncertainties as a function of CVR for metals, indexes and physical measurements

The percentage of underestimated uncertainties varies according to the type of parameter implemented but also according to the reproducibility of the results.

5.3. Percentage of underestimated uncertainties according to the matrix and parameter family

We also studied the percentage of uncertainties underestimated as a function of the type of matrix. As a reminder, it is not systematically the same parameters that are implemented on each matrix, in particular for physical measurements and indexes. The effect of the type of matrix on the percentage of underestimated uncertainties is therefore strongly correlated with the parameters implemented on each matrix.

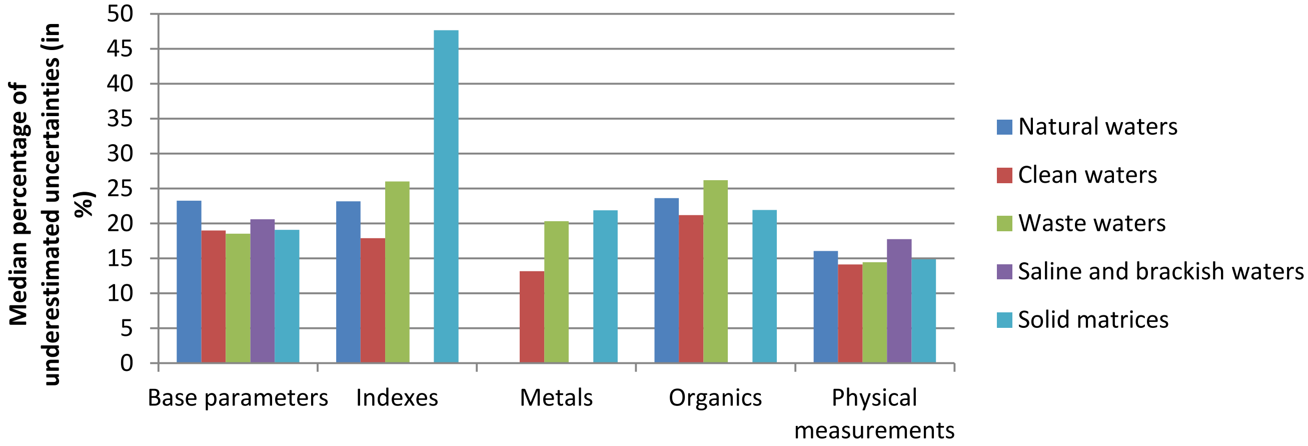


Figure 36: bar plot of median percentages of underestimated uncertainties according to the parameters family and matrices

For example, for indexes we can observe that the percentage of underestimated uncertainties is markedly higher on solid matrices. However, on solid matrices only the total hydrocarbon index is implemented. The high percentage of underestimated uncertainties can be due solely to this parameter and not to the implemented matrix. However, we observed that the matrix type certainly has an effect on this parameter (see graph below).

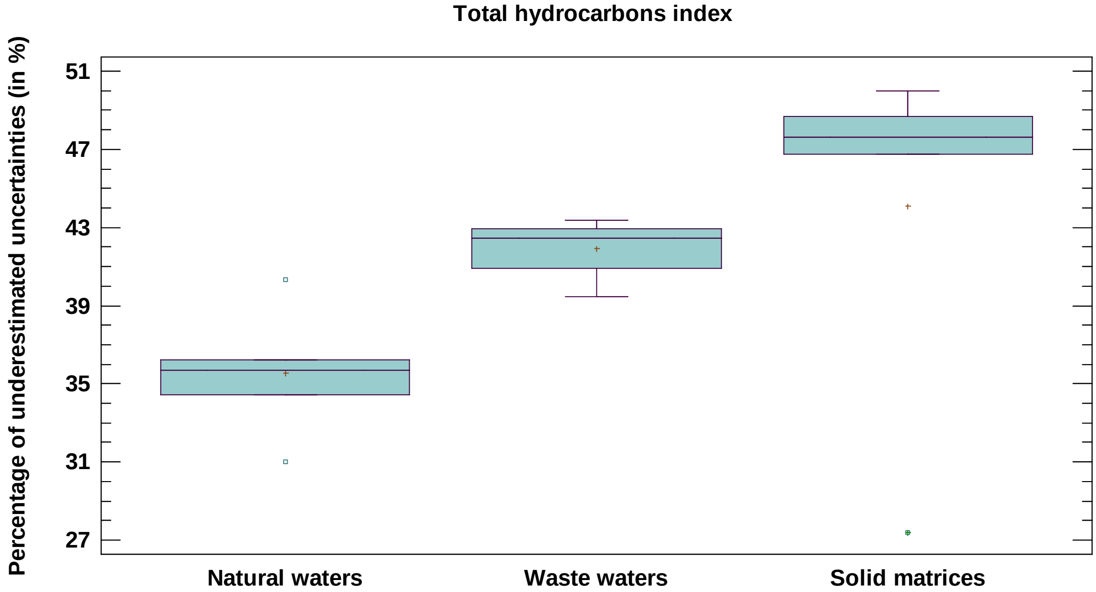


Figure 37: box plot of the percentage of underestimated uncertainties for total hydrocarbons index according to the matrix

For parameters families that are well distributed on each matrix, that is, metals and organics, we tested the significance of the deviations between the percentages of underestimated uncertainties on each matrix.
For metals, the percentage of underestimated uncertainties is lower on clean waters than on waste waters or on solid matrices.

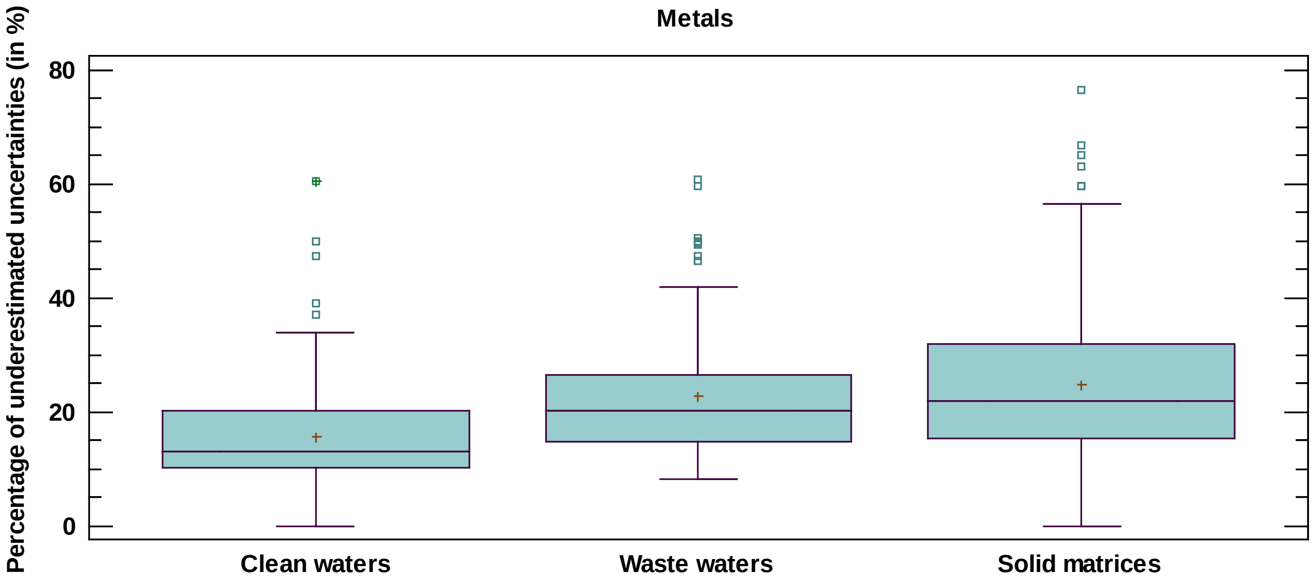


Figure 38: box plot of the percentage of underestimated uncertainties for metals

Matrices	Median percentages of underestimated uncertainties for metals
Clean waters	13%
Waste waters	20%
Solid matrices	22%

For organic micropollutants, the percentages of underestimated uncertainties are significantly different, except between clean waters and solid matrices.

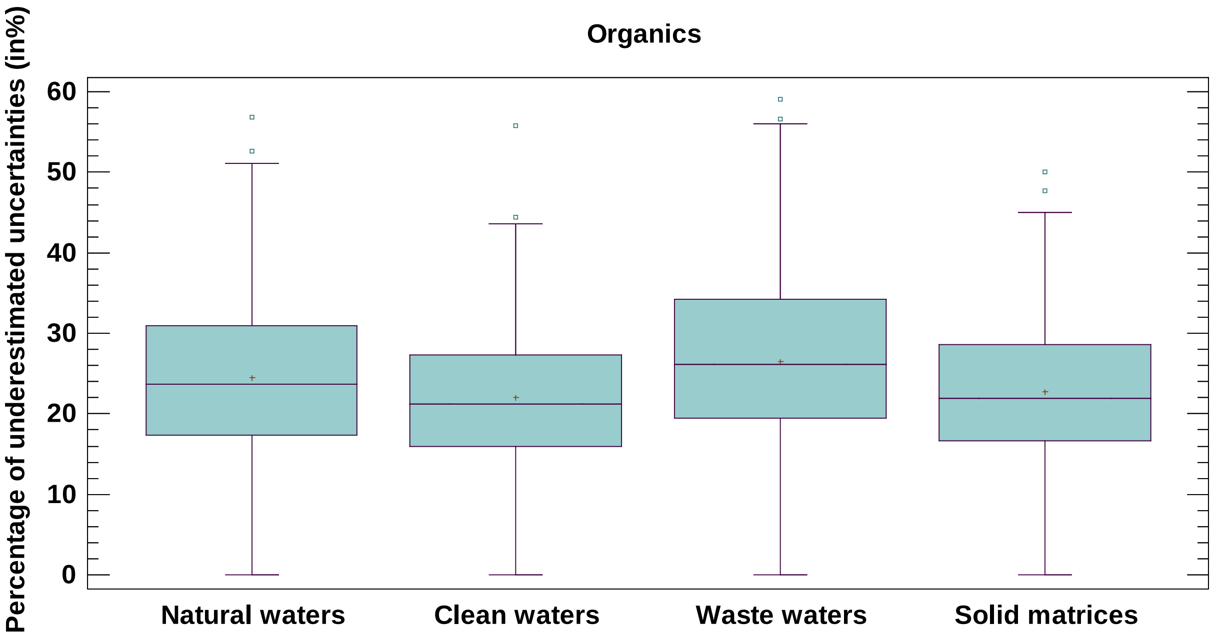


Figure 39: box plot of the percentage of underestimated uncertainties according to the matrix for organics

However, although these deviations are statistically significant, they are also quite low.

Matrices	Median percentages of underestimated uncertainties for organics
Natural waters	24%
Clean waters	21%
Waste waters	26%
Solid matrices	22%

5.4. Evolution of median percentage of underestimated uncertainties since 2013

We have studied the evolution of the percentage of underestimated uncertainties since 2013 to check if there has been an improvement in the estimate of uncertainties.

We can note a slight decrease of the underestimated uncertainties during these three years. In 2013, the median percentage of underestimated uncertainties was 23%, in 2013 it went down to 21.5% in 2014 and then to 20.5% in 2015. This decrease is small but significant.

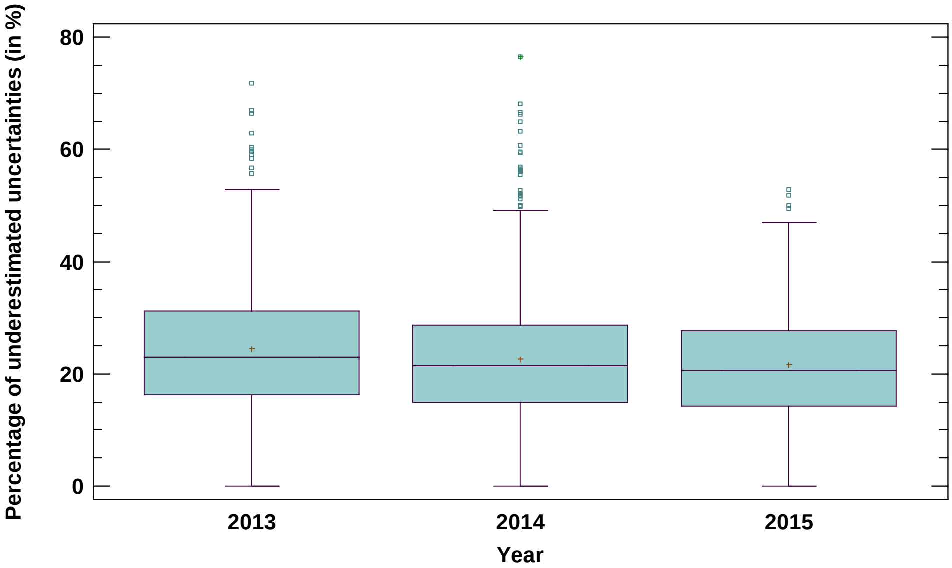


Figure 40: box plot of the percentage of underestimated uncertainties per year

This trend is different depending on the type of parameter and especially for indexes for which there was a very strong decrease in 2015 (30.5% uncertainties underestimated in 2013 and 16.5% in 2015). For the other families of parameters, the downward trends are equivalent except for the physical measurements for which there has been no significant change.

	Median percentage of underestimated uncertainties				
Year	Metals	Organics	Base parameters	Physical measurements	Indexes
2013	20,5%	25,5%	19,5%	14,5%	30,5%
2014	17,5%	22,5%	19%	15%	27,5%
2015	14%	22,5%	16%	15%	16,5%

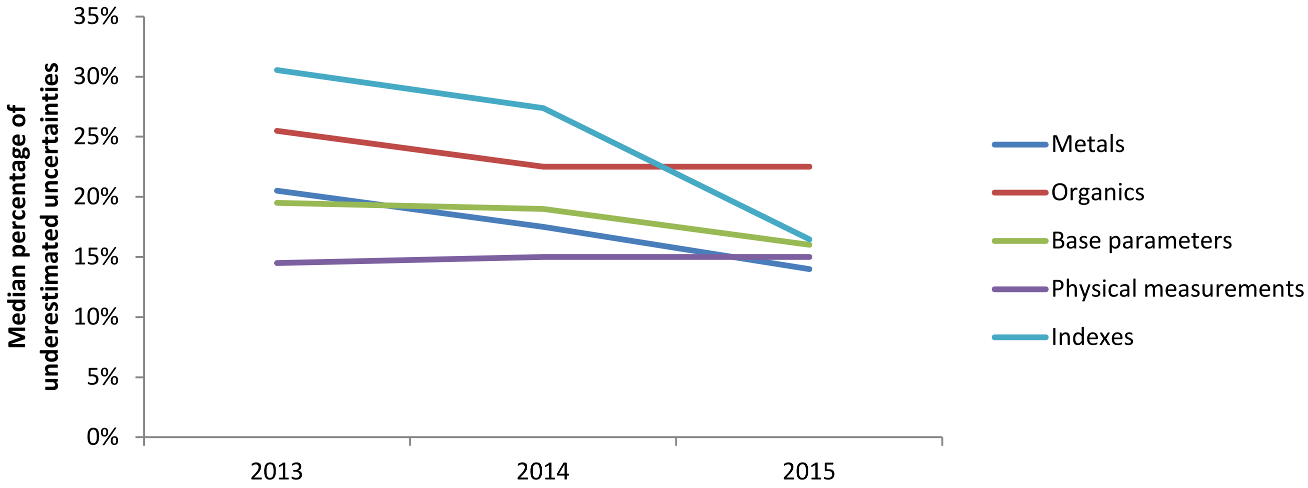


Figure 41: evolution of median percentages of underestimated uncertainties between 2013 and 2015 according to the parameters family

6. SUMMARY AND CONCLUSION

Please find in the tables below the statistics observed according to the type of parameters, nature of samples and also their evolution between 2013 and 2015 for:

- Percentages of results given with an uncertainty;
- The median expanded (k=2) relative uncertainty;
- The percentages of underestimated uncertainties (zeta-scores ≥|2.00|).

Family	% of results given with an uncertainty	Median expanded relative uncertainty (k=2)	% of underestimated uncertainty
Base parameters	70%	10%	19%
Metals	75%	14%	19%
Organics	82%	30%	24%
Indexes	77%	20%	26%
Physical measurements	64%	5%	15%

For the study of these data according to the nature of the samples analysed, we were able to study only metals and organics. For the other parameters families, there is a strong correlation between the matrix and the parameters used (the same parameters are not implemented on each matrix), which makes dangerous conclusions to draw. The table below shows statistics according to the matrix for organics and metals.

Organics

Matrix	% of results given with an uncertainty	Median expanded relative uncertainty (k=2)	% of underestimated uncertainty
Natural waters	86%	30%	24%
Clean waters	82%	29%	21%
Waste waters	82%	30%	26%
Solid matrices	80%	30%	22%

Metals

Matrix	% of results given with an uncertainty	Median expanded relative uncertainty (k=2)	% of underestimated uncertainty
Clean waters	75%	10%	13%
Waste waters	74%	12,5%	20%
Solid matrices	76%	16,25%	22%

The table below shows these data from 2013 to mid-2015 for all types of parameters and matrices.

	2013	2014	mid-2015
% of results given with an uncertainty	77%	79%	81%
Median expanded relative uncertainty (k=2)	25%	29%	30%
% of underestimated uncertainty	23%	22%	21%

The conclusion that can be drawn from this first report on uncertainties is that the laboratories participating in our tests immediately wanted to evaluate their measurement uncertainties as we can see with the high percentage of results given with a measurement uncertainty; a percentage that is still increasing over the years.

The uncertainties estimated by the laboratories fluctuate logically according to the type of analysis implemented, with lower uncertainties for the physical measurements and higher for the organic ones. The type of matrix may also have an effect on the uncertainties, especially for metals for which the uncertainties are higher on wastewater and solid matrices than on clean waters (no dissolution step, therefore less uncertainty in the analysis). We also observed that median uncertainty had increased slightly from 2013 to 2015.
Percentages of underestimated uncertainties decreased between 2013 and 2015 (reduced but significant decrease as reported in paragraph 5.4). These percentages of underestimated uncertainties are globally around 20%. This shows that the vast majority of laboratories have a good estimation of their uncertainties. It should be noted that some of this 20% of underestimated uncertainties are due to one-time analytic errors which do not have to be taken into account in uncertainty estimation (e.g. a forgotten dilution factor). This percentage of underestimated uncertainties is therefore actually lower. It varies slightly depending on the type of parameter and the matrix but also according to the reproducibility of the results (the percentage of underestimated uncertainties increases when the reproducibility of the results deteriorates).

ANNEXES

A.1. Zeta-score

Note on the use of zeta-score with consensus value as assigned value:
In the 2005 version of ISO 13528 "Statistical methods for use in proficiency testing by interlaboratory comparisons", it was mentioned that the consensus value should not be used for the zeta-score calculation because of the correlation between the consensus value and the laboratory result. Contrary to what was recommended by the standard at the time, AGLAE judged that the error made because of this correlation was negligible. The latest version of the standard, published in October 2015, has proven us correct because it is now stipulated that the zeta-scores can be calculated with the consensus value as the assigned value, especially when robust statistics are used.

The zeta-score is a statistical criterion which allows us to characterize the relevance of the measurement uncertainty evaluation associated with the result: its objective is to check the reliability of the measurement uncertainties evaluations performed by the laboratories. This indicator is interpreted in the same way as a z-score, as the critical values are the same, namely 2,00 and 3,00. If you obtain a zeta-score higher than 3,00 or several zeta-scores higher than 2,00, this indicates that you underestimated your measurement uncertainty: the uncertainty you calculated is not high enough to explain the deviation between your result and the assigned value (consensus).

Zeta-score equals to:

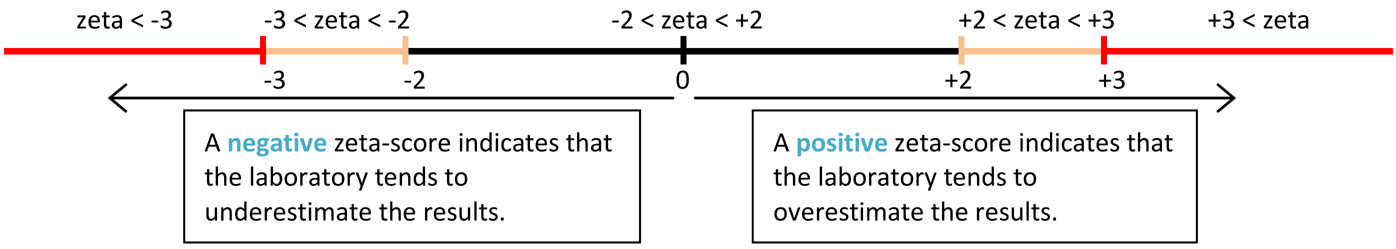
$$zeta = \frac{x - m}{\sqrt{ux^2 + um^2}}$$

with:

x: laboratory's result
m: assigned value
ux: uncertainty on the laboratory's result
um: standard uncertainty on the assigned value

Zeta-score interpretation:

$\lvert zeta \rvert < 2$	Your uncertainty allows to recover the assigned value
$2 \leq \lvert zeta \rvert < 3$	Your uncertainty does not allow to recover the assigned value with a 5% error risk
$3 \leq \lvert zeta \rvert$	Your uncertainty does not allow to recover the assigned value with a 1% error risk



Calculation example:

Interlaboratory test:
Parameter: Al
Matrix: clean water
Unit: µg/L

Consensus value (m): 195
Standard deviation (sz): 19
Standard uncertainty (um): 2,5

A laboratory analyses:
- Bottle 1, replicate 1: 200,7
- Bottle 1, replicate 2: 200,8
- Bottle 2, replicate 1: 201,2
- Bottle 2, replicate 2: 202,1
  → mean (mk): 201,2

Expanded relative uncertainty obtained for the 4 analyses: 10%

Z-score calculation: + 0,33 (ref. section 1)

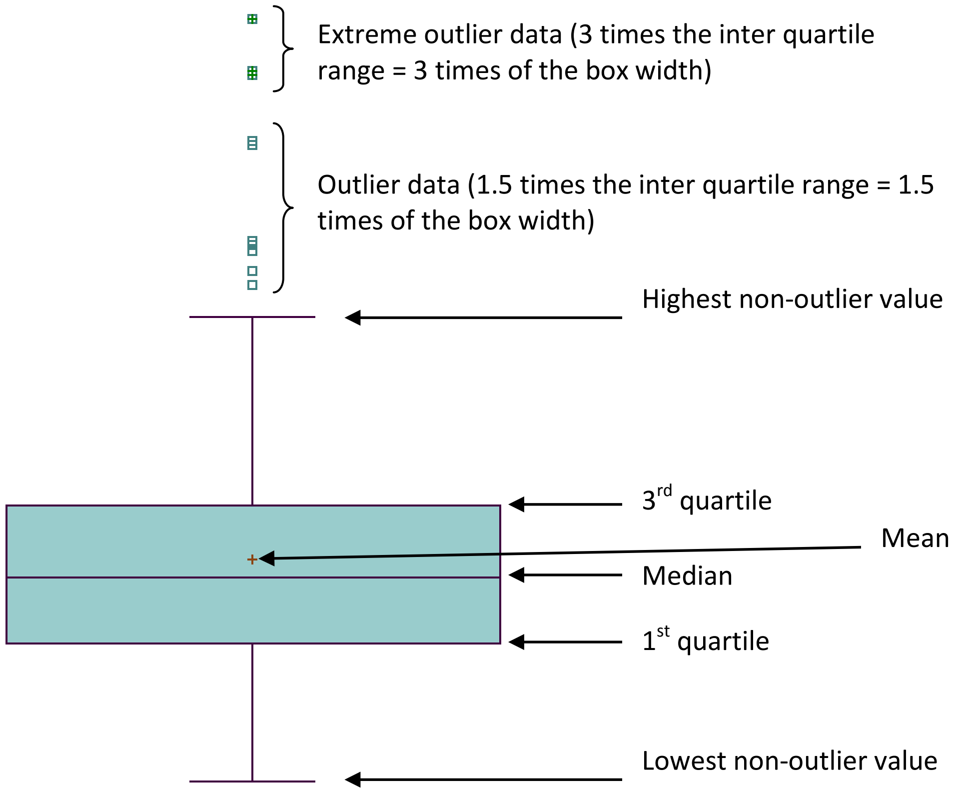
Zeta-score calculation for bottle 1, replicate 1:

$$zeta = \frac{200,7 - 195}{\sqrt{2,5^2 + \left(\frac{10\% \times \mathbf{200,7}}{\mathbf{2}}\right)^2}} = +0,55$$

Zeta-score for other results is calculated in the same way.

A.2. Box plot (Box-and-Whisker plot)

The box plot is often used to represent schematically the distribution of a variable. For a dataset, it can represent the median, quartiles (1st and 3rd), minimum and maximum values and outlier values.



A.3. Kernel density curve

In statistics, the kernel estimate (or Kernel density curve) is a non-parametric way to estimate the probability density function of a random variable. It generalizes the estimate method by histogram and allows to represent the probability density function from a data set.