ACQUISITION OF STABILITY DATA FOR PESTICIDES IN WATER SAMPLE THROUGH PROFICIENCY TESTS

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INTRODUCTION

In the fields of quality control, the stability of molecules is of paramount importance. This assertion is especially true for the analysis of organic micropollutants in water.

The pieces of information related to the stability of the analytes are fragmented and incomplete, and the concerned parties (laboratories [1], public authorities, ordering parties, proficiency test provider [2],…) are interested in getting truthful data on this topic to ensure the robustness of the methods and the reliability of the analyses.

In order to avoid that each laboratory spend time and money to validate some data stability of its own, it was decided to carry out a collaborative study in the framework of a proficiency test, to collect a big amount of data from many laboratories in a short period of time. The aim of this study is therefore to evaluate the stability in water of a huge number of molecules of pesticides, in the real conditions of a proficiency test, collecting data from many laboratories to obtain some results that take into account all the components intervening in the analytical variability.

DESIGN OF THE STUDY

In the framework of the round of February 2017 of a proficiency testing scheme dedicated to the determination of pesticide in water, it was offered the participants to analyze three surface water samples spiked in pesticides and all coming from the same batch, respectively at D+2, D+4 and D+9 after the day of the production. It was also asked independently to a single laboratory to analyze a sample at D0, the day of the production; about half of the molecules were thus analyzed at D0.

SAMPLES PRODUCTION

The samples were prepared by spiking, bottle by bottle, one liter of water by 1 ml of a solution of 109 molecules in methanol. The target concentrations in the water range from 120 ng/l to 220 ng/l. The one liter samples were packed in brown glass bottles. They were shipped in refrigerated parcels and the laboratories were asked to store the samples in a refrigerated room until the date of analysis.

ANALYSIS

The participants were asked to analyze one sample at D+2, one at D+4 and the last one at D+9. The laboratories analyzed the samples with the analytical technique(s) they wanted, but were asked to proceed the same way for each of the sample. LC-MS/MS and GC-MS/MS, according to the molecules, were the techniques the most used.

STATISTICAL TREATMENT

A standard report [3] to assess the proficiency of the participants was provided soon after the test and then a detailed report about the stability study, including the graphs showed in figure 1 and 2 for all the molecules, was sent to the laboratories of the test. In the this additional report, only the data of the laboratories that fully follow the dates defined for the study were used.

RESULTS and DISCUSSION

RATE OF RECOVERY

For most of the molecules, concentrations quantified in the test meet quite well with the theoretical spiking values; for 81% of the molecules, the obtained assigned values are within 20% of the theoretical spiking value.

Seven molecules (carbofuran, chlordecone, clethodim, cypermethrin, nicosulfuron, rimsulfuron and thiabendazole) show some relative differences that are between 20% and 40%, showing some losses, except for nicosulfuron and thiabendazole for which the relative biais is positive. Five molecules (anthraquinone, cyhalothrine lamba, cymoxanil, deltamethrin, iprodione) show some losses bigger than 40% of the theoretical value at the first analysis on D+2. Three molecules are not recovered at the first analysis on D+2 : dimethylamine (searched by only one participant), flumioxazine (limits of quantification and a few very low values) and folpet (considering the prevalence of the five limits of quantification compared to one higher result).

Finally for four molecules (dicofol, fosetyl, N-butylbenzenesulfonamide and N,N-dimethyl-N'-p-tolylsulphamide), the dispersion of the results do not allow to estimate the adequacy with the theoretical spiking.

It should also be considered that for several quoted molecules, a difference between the assigned value and the theoretical spiking value is noticed at D+2 but without evolution afterwards, as for example for anthraquinone (-68% at D+2 and quite constant after) and deltamethrin (-41% at D+2 and quite constant after). It could be a quickly reached equilibrium with the evolution of a part of the product or hypothetically a lower spiking than expected.

STABILITY

For most of the molecules, no significant evolution can be highlighted between the three dates of analyses. Indeed, for 90% of the molecules, the robust means obtained at D+4 and D+9 are not further than 10% of the robust mean obtained at D+2 (see the example of Boscalid in figure 1).

Only a few molecules show a distinctive profile of evolution through time:

- cymoxanil, for which it is found 0.025 µg/l at D+2 (-84% compared to the spiking value), 0.015 µg/l at D+4 and then mostly limits of quantification at D+9.
- fenoxycarb for which it is found 0.185 µg/l at D+2, 0.171 µg/l at D+4 and finally 0.140 µg/l at D+9.
- procymidone, for which it is found 0.106 µg/l at D+2, 0.096 µg/l at D+4 and finally 0.078 µg/l at D+9.
- cypermethrin, for which the theoretical spiking value is 0.200 µg/l, the analysis at D0 by only one laboratory gives 0.150 µg/l, the analysis by the participants at D+2 0.138 µg/l, at D+4 0.132 µg/l and finally 0.100 µg/l at D+9 (see figure 2).

However, even in the four cases mentioned above, the intervals of uncertainties around the assigned value (fine dotted lines on the graphs) are overlapping each other and cannot therefore be considered as significantly different from a statistical point of view. The width of these intervals depends on the number of results and on their dispersion. As these populations are sometimes reduced, one or two further results can significantly increase the standard deviation of the results and the uncertainty of the assigned value.

Finally, for some other molecules, a little lower concentration at D+9 or a slightly decrease between the second and the ninth day, could show a possible slow evolution but the data are not enough to conclude (bifenox, difenoconazole, fenpropidine, kresoxym-methyl, mercaptodimethur, metconazole).

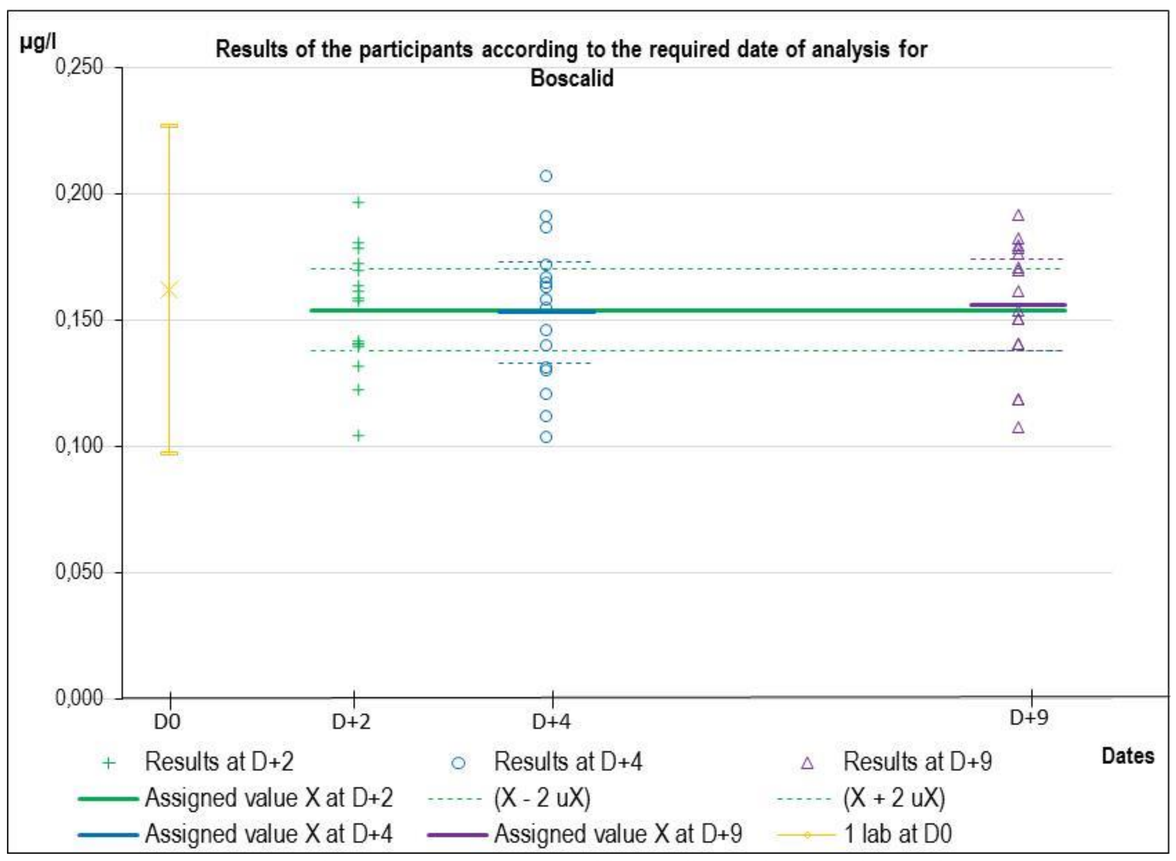

Figure 1. Results for Boscalid according to the date of analysis

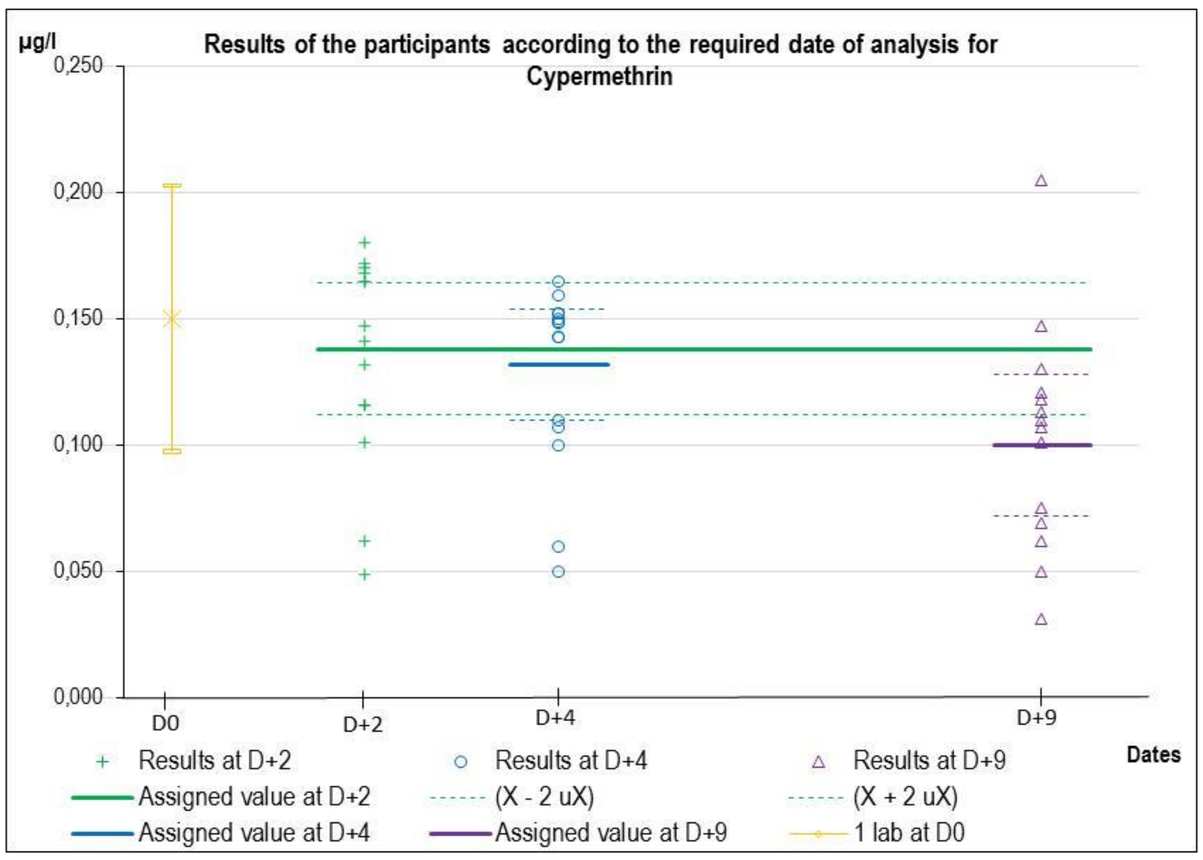

Figure 2. Results for Cypermethrin according to the date of analysis

CONCLUSION

This study, carried out in the framework of a regular proficiency testing scheme, shows that for this surface water, most of the molecules are stable over the one week studied period. However, for some of them, like cymoxanil, fenoxycarbe, procymidone and cypermethrin, the results show kinetics of degradation, which means the instability of these compounds through time in the conditions of the study. For some other molecules, the profile of evolution through time is suspicious; further investigation should be carried out to confirm it or not.

REFERENCES

[1] **ISO 17025** – General requirements for the competence of testing and calibration laboratories.
[2] **ISO 17043:2010** - Conformity assessment - General requirements for proficiency testing.
[3] **ISO 13528:2015** - Statistical methods for use in proficiency testing by interlaboratory comparisons