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Acquisition of stability data for pesticides in water sample through proficiency tests

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Abstract
In the framework of a proficiency test for multiresidue determination, three water samples, coming from the same batch, were sent to each of the 25 participants. They were asked to analyze the first one 2 days after the production ($D + 2$), the second one at $D + 4$ and the last one at $D + 9$. $D + 2$ was selected as the first date of analysis in order to allow all the participants to receive their samples. Prior to the analysis, the samples were stored at 4 °C. The samples were distributed in 1-l bottle from a batch spiked with more than 100 pesticides. The spiking concentrations ranged from 120 ng/l to 227 ng/l. Apart from the usual proficiency evaluation with assigned values and *z*-scores, comparisons between the results at the different dates of analysis were made. Most of the substances were found to be stable during the considered period in the conditions of the test, but some profiles of evolution were highlighted for some others.

Keywords Stability · Pesticides · Water · Proficiency testing schemes

Introduction

In the fields of quality control, the stability of substances 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, 3], etc.) are interested in getting truthful data on this topic in order to ensure the reliability of the methods and therefore the analyses' results.

This study aims to evaluate the stability in water of a huge number of pesticides, analyzed in the conditions of routine samples.

Experimental

In the framework of the round of February 2017 of proficiency test 37 m (fresh water: multipesticides), it was offered the participants to analyze three surface water samples all coming from the same batch, at $D + 2$, $D + 4$ and $D + 9$ after the day of the production D. Some characteristics of this water are given in Table 1; the corresponding analysis was performed by a laboratory accredited to the ISO/IEC 17025 [1] standard. Samples were spiked with more than 100 pesticides. The samples were shipped in refrigerated parcels, and the laboratories were asked to store the samples in a refrigerated room until the date of analysis.

In addition, one laboratory carried out an analysis at $D0$, the day of production of the samples, for about one half of the introduced pesticides. These data were provided in complement in the graphs dedicated to each substance. The first analysis at $D + 2$ remained, however, the reference in this study.

One hundred and nine substances were tested in this study. In order to follow the possible changes between the three analyses as precisely as possible, only the results of the participants who strictly followed the entire protocol were used in the statistical treatment. Therefore, for a given substance, the population of laboratories at two dates was

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Table 1 Characteristics of the surface water used in the test

Parameter	Result	Unit
Temperature of determination of the pH	20.1	°C
pH	8.2	pH unit
Conductivity at 25 °C	780	µS/cm
Suspended solids	16	mg/l
Nitrates	19	mg NO_3^-/l
Chlorides	27	mg Cl^-/l
Sulfates	81	mg SO_4^{2-}/l
Calcium	130	mg Ca/l
Magnesium	26	mg Mg/l
Sodium	13	mg Na/l
Turbidity	12	FNU
Total organic carbon	3.1	mg/l

the same. Nevertheless, each laboratory being free to participate or not to each of the analytical parameter, the population of laboratories was not the same from one pesticide to another.

Results and discussion

Coefficient of variation

The coefficients of variation [4] in the study showed the reliability that could be attributed to the assigned values which were compared to assess the stability of the substances. From an analytical point of view, the coefficients of variation allowed sorting out those whose analysis was under control and those which raised difficulties.

The substances that set more difficulties were: (1) on the one hand folpet, *N*-butylbenzenesulfonamide, *N*,*N*-dimethyl-*N*'-*p*-tolylsulfamide, galaxolide, dicofol (values between 100 and 900 ng/l) and fosetyl for which no assigned value was attributed due to this dispersion, as well as a low population for some of them, and (2) on the other hand chlordecone, cymoxanil (low concentration), cyhalothrin lambda, iprodione, isoxaflutole, mesotrione, nicosulfuron and triclocarban for which an assigned value was attributed but with a high coefficients of variation that reached 50 %.

Rate of recovery of spiked substances

In order to properly consider the possible changes between the three analyses, the targeted concentrations for spiking were rather high, between 120 ng/l and 227 ng/l for all the substances. For most of the compounds, concentrations quantified in the test met quite well with the theoretical spiking values; for 81 % of the substances, the obtained assigned values were within 20 % from the theoretical spiking value.

Seven substances (carbofuran, chlordecone, clethodim, cypermethrin, nicosulfuron, rimsulfuron and thiabendazole) showed some relative differences that were between 20 % and 40 % from the spiked value, showing some losses, except for nicosulfuron and thiabendazole for which the relative bias was positive.

Five substances (anthraquinone, cyhalothrin lambda, cymoxanil, deltamethrin and iprodione) showed some losses larger than 40 % of the theoretical value at the first analysis on $D + 2$.

Three substances were not recovered at the first analysis on $D + 2$: dimethylamine (searched by only one participant), flumioxazin (unquantified results and a few very low values) and folpet (considering the prevalence of the five unquantified results compared to one higher result).

Two substances had on the contrary much higher concentrations than the theoretical ones (more than 50 % above): piperonyl butoxide and propyzamide. As the water has not been analyzed prior to the test, it could be a natural contamination of the water. This could also be due to interference in the determination or a real spiking higher than expected.

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

It should also be considered that for several quoted substances, a difference between the assigned value and the theoretical spiking value was noticed at $D + 2$ but without change afterward, as, for example, for anthraquinone (− 68 % at D +T2 and quite constant after) and deltamethrin (− 41 % at $D + 2$ and quite constant after). It could be a quickly reached equilibrium or hypothetically a lower spiking than expected.

Stability of spiked substances

For most of the substances, no significant change between the three analyses could be highlighted between the three dates of analyses (Table 2). Indeed, for 90 % of the substances, the robust means (Algorithm A [3]) obtained at $D + 4$ and $D + 9$ were not further than 10 % of the robust mean obtained at $D + 2$ (see Fig. 1).

Moreover, among the remaining 10 %, some differences were not corresponding to a continuous evolution in the same direction through time (bromoxynil, triclocarban, diflufenicanil), but to differences which seemed more linked to analytical variations than real evolution through time.

Table 2 Relative bias to the theoretical concentration through time for the different substances

Substance	Mean concentration (ng/l at *D*0 and relative bias in % at *D* + 2, *D* + 4 and *D* + 9)				Substance	Mean concentration (ng/l at *D*0 and relative bias in % at *D* + 2, *D* + 4 and *D* + 9)			
	TC *D*0[a]	*D* + 2	*D* + 4	*D* + 9		TC *D*0[a]	*D* + 2	*D* + 4	*D* + 9
2,4D	0.140	− 0.4	− 3.3	7.5	Fosetyl	0.150	–	–	–
2,4-MCPA	0.150	7.3	10.0	18.0	Fosthiazate	0.190	− 10.0	− 5.3	− 3.2
Acetochlor	0.170	− 4.7	− 2.4	− 5.3	Galaxolide	0.190	–	–	–
Aclonifen	0.190	− 14.2	− 11.6	− 9.5	Hexaconazole	0.180	− 3.9	− 1.7	− 7.2
Anthraquinone	0.200	**− 68.0**	**− 67.5**	**− 68.0**	Imazalil	0.122	0.3	0.3	− 3.8
Asulam	0.190	3.2	0.5	− 8.9	Imazamox	0.150	− 2.0	6.0	− 7.3
Azoxystrobin	0.123	8.9	12.2	5.7	Imidacloprid	0.139	− 5.2	− 1.7	− 13.9
Beflubutamid	0.170	18.2	7.1	11.2	Iodosulfuron-methyl	0.140	5.7	− 0.7	5.7
Benzotriazole	0.180	− 15.6	− 10.0	3.9	Ioxynil	0.150	10.7	10.7	13.3
Bifenox	0.190	0.0	0.5	− 19.5	Iprodione	0.162	**− 48.0**	**− 43.1**	**− 57.9**
Bisphenol S	0.190	–	–	–	Isoxaflutole	0.190	− 8.4	− 14.2	− 7.4
Boscalid	0.171	− 10.0	− 10.5	− 8.8	Kresoxim-methyl	0.183	− 14.1	− 14.1	*− 23.9*
Bromacil	0.160	− 12.5	− 9.4	− 11.3	Lenacile	0.160	− 13.8	− 13.1	− 11.3
Bromoxynil	0.150	*20.7*	7.3	12.7	Mecoprop (MCPP)	0.150	14.0	6.7	14.0
Carbendazim	0.196	− 8.5	− 6.5	− 14.1	Mercaptodimethur	0.190	− 16.8	− 16.3	*− 30.5*
Carbofuran	0.203	*− 28.1*	*− 21.2*	*− 22.2*	Mesosulfuron methyl	0.140	12.9	2.9	10.0
Chlordecone	0.190	*− 30.0*	*− 31.1*	*− 27.4*	Mesotrione	0.200	4.5	− 2.0	− 1.0
Chloridazon	0.200	− 14.5	− 10.5	− 6.5	Metaldehyde	0.190	11.1	3.2	*20.5*
Chlorpropham	0.144	− 10.1	− 12.9	− 14.3	Metamitron	0.160	− 17.5	− 13.8	*− 20.0*
Clethodim	0.200	*− 21.0*	*− 27.0*	*− 29.5*	Metconazole	0.180	− 6.7	− 6.7	− 17.8
Clomazone	0.160	0.6	3.1	4.4	Methomyl	0.190	− 6.8	− 13.7	− 14.2
Cyhalothrin lambda	0.186	**− 46.9**	**− 48.5**	**− 53.9**	Metsulfuron methyl	0.140	7.9	7.9	7.9
Cymoxanil	0.170	**− 83.5**	**− 91.2**	–	N.N-Dimethyl-N'-p-tolylsulfamide	0.170	–	–	–
Cypermethrin	0.203	*− 32.0*	*− 35.0*	**− 50.7**	Napropamide	0.170	− 4.1	− 3.5	− 3.5
Cyproconazole	0.167	− 7.3	− 5.5	− 9.7	*N*-Butylbenzenesulfonamide	0.170	–	–	–
Cyprodinil	0.118	10.8	16.8	9.1	Nicosulfuron	0.140	*25.7*	16.4	*29.3*
Deltamethrin	0.182	**− 41.1**	**− 41.1**	**− 43.9**	Omethoate	0.100	− 10.0	− 11.0	− 18.0
Dicamba	0.150	− 3.3	1.3	10.0	Oxadiazon	0.167	0.8	− 2.8	− 2.8
Dichlormide	0.160	0.0	6.3	11.3	Oxadixyl	0.148	13.2	14.6	9.8
Dichlorprop	0.150	7.3	6.7	12.0	Pendimethaline	0.128	− 5.8	− 6.5	− 6.5
Dicofol	0.227	–	–	–	Piclorame	0.150	0.7	2.7	− 9.3
Didemethylisoproturon	0.160	− 6.9	− 1.9	− 9.4	Piperonyl butoxyde	0.114	**89.1**	**97.0**	**108.3**
Difenoconazole	0.143	− 4.9	− 10.5	− 18.8	Pirimicarb	0.144	− 1.3	− 3.4	− 4.8
Diflufenicanil	0.122	− 10.8	− 0.1	− 3.4	Prochloraz	0.166	0.1	− 2.9	− 5.3
Dimetachlore	0.170	5.3	8.8	7.6	Procymidone	0.143	*− 26.0*	*− 33.0*	*− 45.5*
Dimethenamide	0.170	− 0.6	1.8	3.5	Propiconazole	0.202	− 2.6	− 2.6	− 4.1
Dimethomorph	0.191	− 9.2	− 11.9	− 8.7	Propyzamide	0.170	**63.5**	**63.5**	**64.1**
Dimethylamine	0.180	–	–	–	Prosulfocarb	0.121	2.3	6.4	4.0
Dinoterbe	0.190	2.6	− 1.1	− 2.1	Prosulfuron	0.140	− 8.6	− 7.1	− 5.7
Epoxiconazole	0.180	− 2.2	− 2.8	− 3.9	Pyrimethanil	0.188	− 5.6	− 6.1	− 9.3
Ethofumesate	0.190	− 3.2	0.5	− 2.1	Quinoxyfen	0.190	− 11.6	− 10.5	− 7.9
Fenarimol	0.190	− 8.9	− 8.9	− 5.8	Rimsulfuron	0.140	− 19.3	*− 25.0*	*− 22.9*
Fenoxycarb	0.190	− 2.6	− 10.0	*− 26.3*	Sulcotrione	0.200	− 16.0	− 15.5	− 7.0
Fenpropidine	0.160	− 0.6	0.6	− 10.0	Tebuconazole	0.123	− 2.1	2.0	− 1.2
Fipronil	0.190	− 11.1	− 14.2	− 7.9	Tebutame	0.170	− 1.8	1.2	− 1.2
Fipronil sulfone	0.190	*− 22.6*	− 18.9	− 2.1	Tetraconazole	0.180	− 7.2	− 6.7	− 8.9

Table 2 (continued)

Substance	Mean concentration (ng/l at *D*0 and relative bias in % at *D* + 2, *D* + 4 and *D* + 9)				Substance	Mean concentration (ng/l at *D*0 and relative bias in % at *D* + 2, *D* + 4 and *D* + 9)			
	TC *D*0[a]	*D* + 2	*D* + 4	*D* + 9		TC *D*0[a]	*D* + 2	*D* + 4	*D* + 9
Florasulam	0.190	− 11.6	− 7.9	− 11.6	Thiabendazole	0.179	*22.3*	*23.4*	*23.4*
Fludioxonil	0.199	− 1.9	− 9.5	− 2.9	Thiafluamide (flufenavet)	0.170	2.4	4.1	5.9
Flumioxazin	0.160	–	–	–	Thiamethoxam	0.126	12.6	11.8	17.3
Fluoryxypyr	0.150	0.7	− 3.3	7.3	Thifensulfuron methyl	0.140	8.6	10.0	14.3
Flurochloridone	0.200	3.0	− 2.0	− 2.5	Tolyltriazole	0.180	6.1	8.3	8.3
Flurtamone	0.200	− 5.0	− 5.5	− 7.5	Triclocarban	0.160	13.8	8.1	*25.6*
Flusilazole	0.177	− 2.0	3.7	− 7.0	Triclopyr	0.150	14.0	4.7	11.3
Foramsulfuron	0.140	12.9	*22.1*	12.1	Trinexapac-ethyl	0.200	− 7.5	− 1.0	− 3.0
Folpet	0.100	–	–	–					

Bold values: relative biases larger than 40 %

Italic values: relative biases larger than 20 %

[a]Theoretical concentration

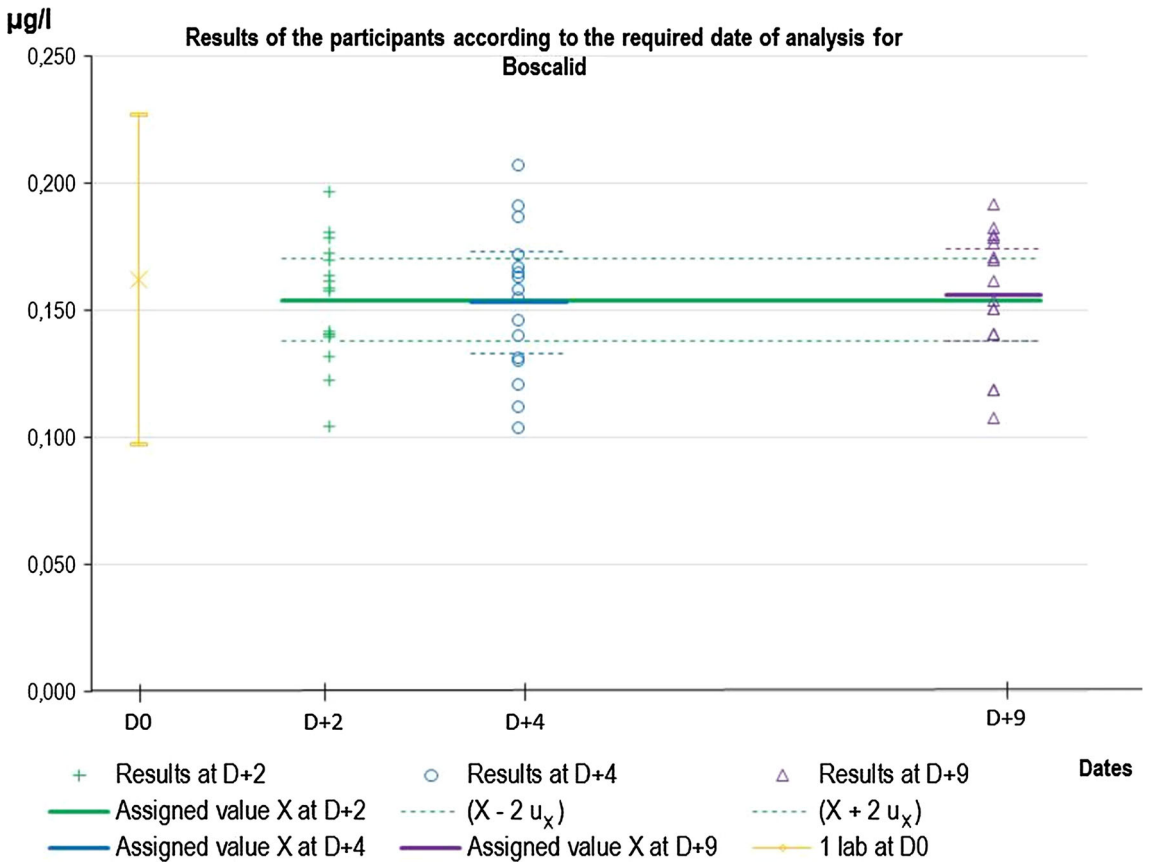

Fig. 1 Results for boscalid according to the date of analysis

Only a few substances showed a distinctive profile of evolution through time: (1) cymoxanil, for which it was found 0.025 µg/l at $D + 2$ (− 84 % compared to the spiking value), 0.015 µg/l at $D + 4$ and then mostly results below limits of quantification at $D + 9$, (2) fenoxycarb, for which it was found 0.185 µg/l at $D + 2$, 0.171 µg/l at $D + 4$ and finally 0.140 µg/l at $D + 9$, (3) procymidone, for which it was found 0.106 µg/l at $D + 2$, 0.096 µg/l at $D + 4$ and finally 0.078 µg/l at $D + 9$, and (4) cypermethrin, for which the theoretical spiking value was 0.200 µg/l, the analysis at $D0$ by only one laboratory gave 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 Fig. 2).

However, even in the four cases mentioned above, the intervals of uncertainties around the assigned value (fine dotted lines on the graphs) were overlapping each other and could not 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 were sometimes small, one or two further results could significantly increase the standard deviation of the results and the uncertainty of the assigned value [5].

Finally, for some other substances such as bifenox, difenoconazole, fenpropidine, kresoxim-methyl, mercaptodimethur and metconazole, a little lower concentration at $D + 9$ or a slightly decrease between the second and the ninth day could show a possible slow change but for which the data were not enough to conclude.

Conclusions

This study, carried out in the framework of the round of February the 37-m proficiency testing scheme (fresh water: multipesticides), showed that for this surface water most of the substances were stable over the 1-week studied period. (The robust means obtained at $D + 4$ and $D + 9$ were not further than 10 % of the robust mean obtained at $D + 2$.)

However, for some of them, such as cymoxanil, fenoxycarb, procymidone and cypermethrin, the results showed fast degradation, which means the instability of these compounds through time in the conditions of the study. For some other substances, the profile of evolution through time was suspicious; further investigation should be carried out to confirm it or not.

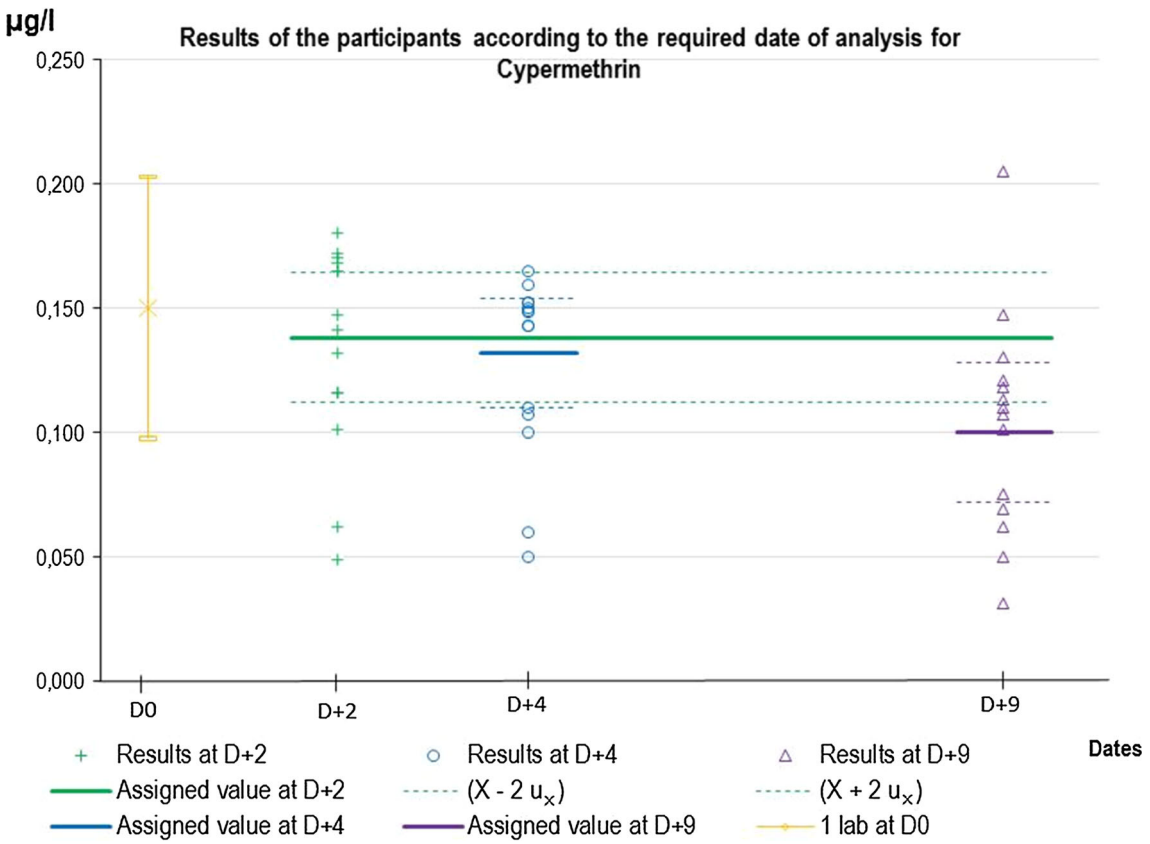

Fig. 2 Results for cypermethrin according to the date of analysis

Two substances, flumioxazin and folpet, show fast degradation not allowing them to be quantified in the test. These substances were not stable and cannot be determined in these conditions after 48 h.

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