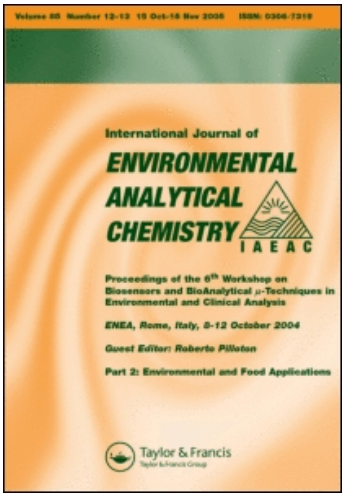

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Bias highlighting in the acquisition of pesticide concentration in soil solution

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Bias highlighting in the acquisition of pesticide concentration in soil solution

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A variety of sources can specifically create uncertainty and/or bias in scientific process and stage of acquisition measurement data when *in situ* data acquisition is considered. From the sequence of data acquisition in an experimental site and a bibliographic review of possible biases, a set of experiments is proposed to quantify the global bias in the measurement of pesticide concentration. The analysis begins with the data which wants to be initially measured by instrumentation use and ends with the data finally presented. The data acquisition is then chronologically analysed in steps, describing the data states between which bias may exist. The study specifically focuses on the data with regard to the pesticide concentration in soil solution. Large biases, have been found, depending on the compound's passage through ceramic cups or during storage. These losses can be respectively attributed to the adsorption and screening processes, and the adsorption and transformation reaction, the intensity of which varies according to the sensitivity of compounds for these processes. Advice and solutions to minimize the bias that occurred in the studies are then provided (change in device or strategy, pesticide rejection, data correction). The general study and acceptance of the notion of bias are finally advocated.

Keywords: Data quality; Bias; Pesticide concentration; Sampling; Suction cups

1. Introduction

Environmental exposure to pesticides is traditionally assessed using a range of tools including laboratory and field experiments, and use of computer-simulation models. Although the estimation of predicted environmental concentrations is based increasingly on the use of predictive environmental fate models to save time, money, and human resources, experimental studies are still needed. Notably, models always use field data that have to be calibrated and validated.

Logically, according to the purposes and conditions of the field study, a particular type of measuring instrument will be used to gain direct access to a part

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of the necessary data. However, whatever the type of instrument used, these devices always introduce several types of errors and uncertainties in data measurement and acquisition.

Thus, good bases to enable analysis of field data, develop theories about pesticide transfers, and validate pesticide transfer models [1] are logically quality field data, i.e. in our context, data for which errors are controlled (known and limited or corrected). Even if probabilistic simulation is the probable future basis of modelling [2], knowledge of the sources and magnitude of uncertainty and bias remains essential for the decision-maker to be able to assess to what extent decisions can be made in all confidence from modelling results [3].

An error on data is defined as 'the result of a measurement minus the true value of the measurand (particular quantity subject to measurement)' [4] and contains a random and systematic component. Concerning the measurement method, the uncertainty of measurement has been formally defined as 'a parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the measurand' [5] or informally defined as 'the interval around the result of a measurement that contains the true value with high probability' [6]. The bias is then specifically 'the difference between the expectation of the test result and an accepted reference value' [7]. In practice, this expectation is estimated as the mean of a large number of measurements and is essentially systematic [8]. This bias affects all the observations identically (e.g. data on particular pesticide concentration will always undergo the same process of adsorption on glass container walls), but not always equally (in our example, the adsorption intensity will notably depend on the pesticide characteristics), coherently producing higher results (e.g. concentration of products) or more commonly, when using devices, values lower than true values (e.g. adsorption on sampling tubes, degradation in sampling bottles, losses through the ceramic cup wall, etc.). The bias is given as a fixed value (generally a percentage of the true data). We can resume these three notions in figure 1, which represents a theoretical probability distribution of a method measurement where a cross represents a single measurement.

A variety of sources can create uncertainty and/or bias in scientific process and stage of acquisition measurement data. Specifically, if *in situ* data acquisition is considered, typical sources of errors may include the intrinsic variability in the field (spatially and temporally), the performance and adequacy of the sampling strategy and measuring equipment, and the uncertainty associated with analytical determinations (limits of detection, definitive identification of analytes) [1].

This error may represent a large portion of the results and therefore limits the conclusions that may be drawn in the low ppb range. A large sampling bias coupled with analytical errors of similar severity could result in the collection of grossly erroneous data [9]. For example, the potential sampling bias due to both sampling mechanisms and flexible tubing materials is of the same order of magnitude (i.e. ±5–20%) as analytical errors for volatile organic compounds [10]. Systematic differences in concentrations, ranging from a factor of 2 to 5, have also been observed between samples taken after purging from wells cased with different materials [9].

This study specifically concentrates on bias. The aim is not specifically to find and individually characterizes all possible bias-creating processes (e.g. sorption, volatilization, etc.). Thus, this work is based on an experimental sequence that must *globally*

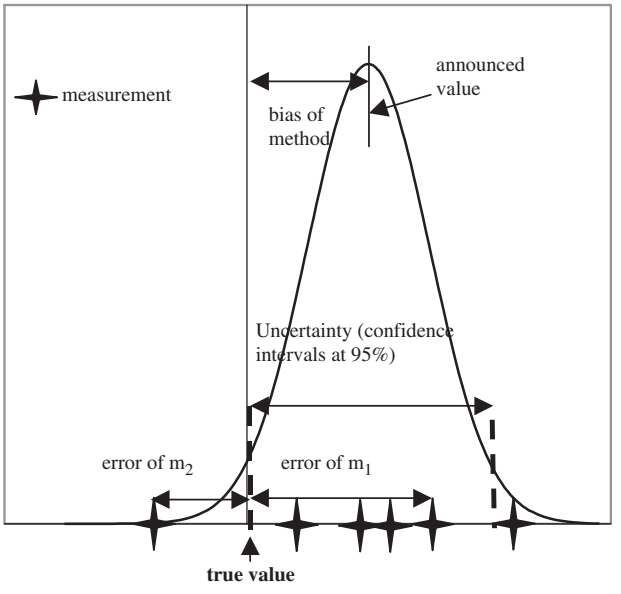

Figure 1. Theoretical definition of notions of error of a measurement, uncertainty and bias of a method measurement (m_1 is the first measurement, m_2 is the second measurement).

quantify a bias coming from data acquisition in order to correct it when possible (by changing the instrumentation, sample strategy, or data correction), or at least to be aware of it.

Knowing that bias is theoretically assessed from a large number of measurements [8], in our case, the use of only three measurements will merely make it possible to express its existence or not. The data aimed at in this study are pesticide concentrations in soil solution. An evaluation of the quality of the chosen data acquisition sequence is made.

In the first instance, the data-acquisition context is described. From the sequence of acquisition practised at our experimental site and a bibliography of possible biases, a set of experiments is then proposed to quantify the global bias in measuring pesticide concentration. Finally, the results of these experiments are presented and discussed, and advice and solutions are then given to minimize the bias that occurred.

2. Principles and method

As is usual in field studies, the installed devices must achieve certain scientific aims while, notably, not being destructive for the media and limiting expenditure related to time, money, and human resources. Following these criteria, certain types of devices and strategies appeared inevitable to us (e.g. suction cups for monitoring the pesticide concentration in a soil solution), but it is possible to adapt those with respect to others (e.g. storage time, etc.).

2.1. *General context*

The project here deals with the *in situ* monitoring of pesticide transfers in the soil of a wine-growing catchment area (France, Haut-Rhin, Rouffach).

Soil-solution sampling was carried out using ceramic suction samplers (or 'ceramic porous cups'). These comprise a hollow PVC tube with a porous ceramic cup at the lower end and an arrangement of valves at the upper end. The porous cups used are referred to by SDEC as SPS 200 (France).

The measurements were carried out between May and October after the application of pesticide. Two passages per week (usually Mondays and Wednesdays) were organized to collect data and samples. Samples collected by the devices therefore remained *in situ* for a maximum of 5 days. For soil solutions, because of the analytical and financial requirements, the sample volume in a ceramic cup had to be more than 30 mL for analysis, otherwise the sample would be rejected. A 0.7 bar depression was applied using a portable pump. The samples (with a volume of 30–50 mL) were collected in 50 mL glass bottles via PTFE tubes (diameter: 2 mm; length: 1.5 m). Samples were transported between the sampling site and our laboratory (storage site) in an icebox (at about 10°C) by car (1 h journey time) and stored before analysis in our laboratory, in the dark inside a freezer (−20°C). The analysis was performed outside the laboratory. The duration of storage, which may be variable, must be determined by the study but must not exceed 6 months. Samples were transported between the storage site and the analysis laboratory by freezer van (with a constant temperature of −20°C).

The useful pesticide characteristics are described in table 1. As the fate of the compound after sampling is studied, this useful information concerns rather the aquatic fate of the monitored pesticides [11]. These data come from various databases [12–15]. Although certain values in this table and their accuracy are debatable, this compilation will serve as an illustration of results by giving size orders.

The chosen pH and temperature values (pH 7 and temperature 20°C and 25°C) correspond approximately to the general sampling conditions (the pH of the water sampled is about 7).

2.2. *Principles of bias analysis in data acquisition*

The study specifically focuses on the 'concentration of pesticide X in the soil solution'. The various phases in its acquisition were analysed to investigate all possible sources of bias. This analysis begins with a bibliographic review of possible biases (the analytical biases during pesticide analysis are examined here).

2.2.1. Method of bias analysis. The bias analyses of data acquisition 'concentration of pesticide X in the soil solution' are described in figure 2. The analysis begins with the data actually aimed by instrumentation use ('concentration of pesticide X in a soil solution') and ends with the data finally presented (in underlined italics in figure 2). The data acquisition is then examined chronologically in steps describing the data state (in italics in figure 2) between which bias may exist (in bold in figure 2; the numbers in parentheses fit with the experiments). When feasible, the possibilities of information loss are evaluated quantitatively by experiments (with our pesticides monitored and instrumentation) even if they are

Table 1. Pesticide characteristics.

Common name	Chemical classification	pK_a	Molecular mass (g/mol)	Solubility (mg/l) (T(°C)/pH) (averaged value)	Log H (atm.m^3/mol)	Log K_{oc} (averaged value)	Log K_{ow} (averaged value)	Hydrolysis half-life (day) (T ambient; pH = 7)	Photolysis half-life (day) (pH = 7)	(Bio)degradation half-life
Carbendazim	Benzimidazol carbamate	4.48	191.19	8 (20/7)	−10.8	2.25	1.64	>35	Stable	Long half–life
Cymoxanil	Aliphatic nitrogen	9.7	198.18	780 (20/7)	<−9.4	2.62	0.67	stable <2 5600 (−20°C)[a]	**0.2**	**4–5**
Diuron	Phenylurea	/	233.1	36.4 (25/−)	−9.3	2.63	2.74	>500	43	70 (DT90)
Glufosinate-ammonium	Organophosphorus amino acid	$pK_1 < 2$ $pK_2 = 2.9$ $pK_3 = 9.8$	198.1	1 370 000 (22/5)	<−13.4	2.13	<0.1	>300	>300	
Glyphosate	Organophosphorus amino acid	$pK_1 = 1.6$ $pK_2 = 2.3$ $pK_3 = 5.7$ $pK_4 = 10.2$	169.08	10 833 (20/2)	−11.7	**3.87**	−2.4	>30 stable	<69 stable	**Short half-life**
Kresoxym-methyl	Strobilurine	None	313.3	2 (20/−)	−8.4	2.45	3.4	34	<30	Contradictory
Pyrimethanil	Pyrimidine	3.52	199.26	121 (25/6.1)	−7.4	2.6	2.8	>1000	**2**	Possible
Simazine	Triazine	1.62 $pK_b = 12.3$	201.66	6.2 (20/−)	–	2.3	2.1	>200 stable	Long half-life	Possible
Terbuthylazine	Triazine	2 $pK_b = 12$	229.72	8.5 (20/−)	−7.4	2.71	3.2	>200	–	–

[a]Extrapolated value from data in [15].

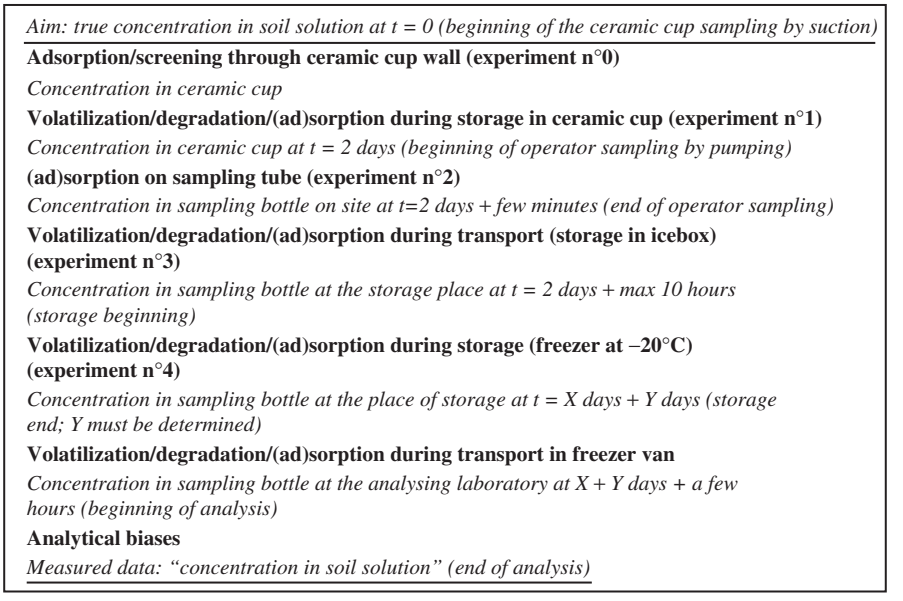

Figure 2. Analysis of the data acquisition 'concentration of pesticide X in soil solution' (t = the time).

qualitatively described in the literature. Each is numbered and explained in detail in Section 3.

2.2.2. Possible losses during data acquisition. Without knowing the importance of the four major processes playing a role in global bias (adsorption, screening, volatilization and degradation), the main problematic acquisition steps presented in the bibliography are described.

2.2.3. Possibilities of adsorption/screening through the ceramic cup wall during solution passage. The concentrations of pesticides sampled by ceramic cups can be biased by the material and in particular by the passage through the ceramic matrix [16–19]. A deterioration of the solution after passage through ceramic porous cups was observed for sample volumes lower than 50 mL [20–21]. Thus, for a 10 mL sample, this information loss can vary from 40 to 70% for atrazine and diuron, and is positively correlated with the rate of organic carbon in solution (0 and 5 mg L^{-1}, respectively, for the previous percentages). This possibility of bias has been studied at length for the monitored pesticides, and elements of explanation have been given [22]. Beltran *et al.* have also developed a similar experiment [23].

During the storage time, organic chemicals can be lost from a water sample through volatilization, sorption, and transformation reactions. However, the portion of each one is not quantified in each case. Another study presents an approach estimating the most probable loss processes during the holding time for an organic chemical, based on its chemodynamic properties [11]. This method is used and is discussed in the last part of this presentation.

2.2.4. Possibilities of (ad)sorption during storage (suction cup body, sampling tube, icebox and freezer). Organic compounds are generally distributed between dissolved and sorbed phases on the basis of the chemical structure (often synthesized in an octanol–water partition coefficient). Even if adsorption on natural organic carbon is more classical, a sizeable adsorption on inorganic surfaces may exist. Thus, adsorption problems on certain types of equipment used in sampling are reported. The data particularly concern insecticide and volatile organic compounds (VOCs). Thus, practically irreversible permethrin adsorptions on PVC are mentioned [24]. Many plastic materials widely used in well casing and sample transfer tubing have a considerable affinity for low-molecular-weight organic contaminants [1]. In particular, flexible polymeric materials have been shown to sorb or leach a number of important pollutant organic compounds. They also show a strong adsorption of chloroform, trichloromethane, trichloroethylene and tetrachloroethylene in decreasing order on PVC, silicone (the strongest adsorption because of a larger contact area), polyethylene, polypropylene, and Teflon® (generally the lowest adsorption). Vuik *et al*. did not underline the adsorption of two fungicides (etridiazole and oxamyl) with PVC [25]. In fact, significant permeation through PVC does not take place with chlorinated hydrocarbons and ketones [26], and the high molecular weight of most pesticides may therefore prevent adsorption on PVC surfaces. However, a critical evaluation of field monitoring techniques underlined the importance of the choice of materials and advocated the use of inert materials such as stainless steel or Teflon® [27]. The adsorption of some organochlorine and organophosphorus pesticides on low-density polyethylene films is confirmed but particularly the influences of temperature and contact time [28]. On the other hand, Koskinen *et al*. showed significant isofenphos adsorption on PVC body after 3 h of contact time and recommended testing pesticide adsorption on cup bodies [29]. Moreover, a previous study showed strong atrazine and metolachlor adsorption on different types of sampling tubes [30]. Leboeuf and Weber also demonstrated adsorption of phenanthrene on poly(isobutyl) methacrylate [31]. Teflon® is renowned as being an inert material [27]. Indeed, tubing made of Teflon® showed the least adsorption and leaching problems concerning VOCs [10]. For suction cups, the report is the same for various nutrients [32]. However, this opinion is still not demonstrated for several pesticides. For example, Teflon® showed the least adsorption with the permethrin insecticide, but this one nevertheless exists.

2.2.5. Possibilities of volatilization/degradation during storage (suction cup, sampling bottle in icebox and freezer). Organic chemicals such as pesticides are divided into their aqueous and gaseous phases on the basis of the Henry's law constant. In a closed container (sampling bottle and suction cup), equilibrium between water and gas in a headspace may be reached during the storage period. Logically, the compound in gaseous phase is lost when the container is opened. Pesticides can undergo multiple biotic or abiotic reactions in sampled water depending on the chemical structures and environmental conditions such as temperature, pH, biological activity, etc. However, storage of samples at low temperature may inhibit growth and biological activity of micro-organisms, and so may limit the biological degradation of compounds [33]. Puchalski *et al*. studied the stability of soil samples with pesticide during frozen storage [34]. They showed that losses during storage (up to 450 days) could be significant for certain pesticide-contaminated samples (particularly trifluralin with a reduction of

40–66% after 450 days with different types of soils, and atrazine/alachlor to a lesser degree). They also put great emphasis on the necessity of preliminary storage tests. More recently, a decrease of 20–40% when a solid-free solution with little soluble pyrethroids (bifenthrin, cis and trans-permethrin and deltamethrin) was stored at 4°C for one day was underlined [35]. This study also gives the total losses during 18 days' storage of permethrin at 20°C. No differences were found in losses between the storage times of 3 and 18 days and the temperatures of 4 and 20°C, except for trans-permethrin losses, which were higher at 4°C than at 20°C. They also described adsorption on suspended solids during storage. To avoid any biases, they thus recommended the insertion of particle analysis after storage.

3. Experimental

Experiments have been conducted to make it possible to quantitatively evaluate the bias inherent in our instrument use and strategy choice for our monitored pesticides without studying the influence of certain parameters reported in the literature (e.g. concentration, type of material, contact time, etc.). The parameter values are generally fixed by the choice in instrumentation type and field-strategy use (e.g. in our case, the type of suction cup, length of sampling tube for the studied depth, storage time in suction cups, etc.), but some, such as the worst values, could be chosen (according to the bibliography) rather than average or common values (e.g. outside temperature, concentration of solution, transport time, etc.).

3.1. *Experimental device (numbering refers to figure 2)*

3.1.1. Experiment 0. This experiment [22] was carried out with ceramic cups used *in situ* for 4 years in a clay-loam vineyard soil without preliminary cleaning. The suction samplers were held vertically with the ceramic cup completely plunged into the tank. A 0.7 bar depression was applied for the time necessary to collect 30 mL of solution contained in a 50 L tank (different titrant from the other experiments). The pesticide concentrations were measured before and after passing through the ceramic matrix. The experiment was repeated three times.

Generally, to comply with the field sampling strategy, new 1 L bottles were chosen to receive samples after the experiments, even if the final volumes were low. Sealing was ensured using polypropylene plugs with triseal joints. During experiments, the averaged measured laboratory temperature was about 22°C, −20°C in the freezer and between 10°C (first day) and 16°C (after 5 days) in the icebox. At the end of the experiment, plastic bottles were used for the analysis of glyphosate and glufosinate-ammonium, and glass bottles were used for the rest.

For the other experiments, a titrant of pesticides was contained in a 50 L glass tank and used as an initial solution (noted as 'IS') for all the experiments. After IS homogenization, six samples were taken directly in the IS (three in 1 L glass bottles and three in 1 L plastic bottles). The samples were then immediately placed in the freezer for 8 days and transferred to the freezer van at the analysis laboratory. The average initial pesticide concentrations, 'C_{IS}', calculated according to equation (1), are described in table 2. Each experiment used this initial solution.

Table 2. Average initial concentrations[a].

Concentration (μg/L)	Glyphosate	Glufosinate	Carbendazim	Diuron	Terbuthylazine	Simazine	Cymoxanil	Pyrimethanil	Kresoxym-methyl
Mean	433	97	37	293	233	35	3.2	423	44
CV (%)	26.6	3.6	10.3	7.1	10.8	14.2	144	5.9	73

[a]CV: coefficient of variation for three samples.

The coefficient of variation is large for cymoxanil and kresoxym-methyl because of possible problems in the analytical procedure or in the sampling in the initial solution. All the experiments were repeated three times in the same way (three final values) except experiment 1 with one replication (two final values).

3.1.2. Experiment 1. In the laboratory, the suction samplers were held vertically above a container (ambient temperature). A volume of 100 mL was directly sampled in the IS and directly introduced into a ceramic cup. After 5 days, 50 mL was sampled by turning the suction sampler upside down (25 mL in a 1 L glass bottle and 25 mL in a 1 L plastic bottle). After sampling, the bottles were held in the freezer for 3 days and transferred to the freezer van at the analysis laboratory. The final concentrations were analysed.

3.1.3. Experiment 2. A 50 mL volume was sampled directly in the IS by pumping at 0.7 bar via a new PTFE tube. The protocol was repeated. The first nine samples were rejected. The 50 mL samples, numbered 10, 12, and 14, were each filled into one 1 L plastic bottle (numbers 11, 13, and 15, respectively, in 1 L glass bottles). The same sampling was done for the samples numbered 100, 102, and 104 for plastic bottles and 101, 103, and 105 for glass bottles (the previous samples were also rejected). After sampling, the bottles were held in the freezer for 8 days and transferred to the freezer van at the analysis laboratory. The final concentrations were analysed.

3.1.4. Experiment 3. Two 50 mL samples were taken directly in the IS (1 in 1 L glass bottles and 1 in 1 L plastic bottles). The samples were immediately held in the icebox for 2 h. Next, they were stored in the freezer for 8 days minus 2 h. Then, they were finally transferred to the freezer van at the analysis laboratory. The final concentrations were analysed.

3.1.5. Experiment 4. Two 50 mL samples from the IS (1 in 1 L glass bottle and 1 in 1 L plastic bottle) were taken. The samples were immediately placed in the freezer for 3 months and transferred to the freezer van at the analysis laboratory. The final concentrations were analysed.

3.2. *Analysis*

All analyses were carried out by the Pasteur Institute of Lille (France) certified by the French Ministries of Health and the Environment. The compounds diuron, cymoxanil, simazine, terbuthylazine, carbendazime, pyrimethanil, and kresoxym-methyl were analysed by LC-MS-MS with on-line concentration. The limits of quantification were $0.02\,\mu g\,L^{-1}$ for diuron, simazine and terbuthylazine, $0.05\,\mu g\,L^{-1}$ for cymoxanil, carbendazim and pyrimethanil, and $0.1\,\mu g\,L^{-1}$ for kresoxym-methyl, glyphosate, and glufosinate-ammonium. For simazine, terbuthylazine, carbendazim, and diuron, the method fulfilled all the French requirements relative to quality (COFRAC) and is validated according to standard XP T 90-210 [36]. For glufosinate-ammonium and glyphosate, the method of analysis involved derivatization with FMOC and detection by LC-MS-MS. The quantification limit is $0.1\,\mu g\,L^{-1}$.

Table 3. Ninety-five per cent confidence intervals for the analytical procedure.

	Concentration (μg/L)	Interval at 95% (α) (%)
Simazine	0.091	16
Terbuthylazine	0.089	9
Carbendazim	0.093	17
Diuron	0.106	23
Others	All	30

The 95% confidence intervals of COFRAC analysis from spiked water are described in table 3, i.e. at concentration Y, the true value being situated between $(X - X \times \alpha)$ and $(X + X \times \alpha)$ with 95% presence probability. From a discussion with the analysis laboratory (Pasteur Institute, oral communication), the confidence intervals at 95% were taken at about ±30% of the given value for the rest of the compounds.

3.3. *Treatment method*

An average initial concentration (noted 'C_{IS}') was calculated according to equation (1):

$$C_{IS} = \left(\frac{\sum_{i=1}^{3} C_{IS_i}}{3} \right). \quad (1)$$

A concentration analysis was performed in the tank before and after the experiments. No significant degradation or adsorption (at 5% risk) existed between the beginning and the end of experiment. Thus, in what follows, the biases are calculated compared with the initial concentration in the tank. The bias (noted 'B_X') after the experiment X for each studied pesticide is defined by equation (2) with the number of replication $(n) = 3$, except for the experiment no. 1 with $n = 2$ because of a broken bottle and for experiment 2 with $n = 6$ and C_{Fsi} the final concentration of repetition i.

$$B_X = \frac{\sum_{i=1}^{n} C_{Fs}i / C_{IS}}{n}. \quad (2)$$

Specifically in the case of experiment no. 2, a paired comparison of the average concentrations of the first three measurements and the last three measurements was performed on the concentration differences using the t-statistic (test of equality between two averages based on Student's law in the case of samples associated by pair [37]). The concentrations in both cases were statistically not significantly different (with 95% confidence intervals). This is why B_X was assimilated in this case at the mean of six values.

A comparison between the population mean μ and 100% (no bias) was conducted using a conformity test with the Student test statistic t (estimated population standard deviation, one-sided test at the significance level 5% with an alternative hypothesis H_a: $\mu < 100\%$ [37]). B_X was described as 'significant bias' when the alternative hypothesis was chosen ($\mu < 100\%$) and B_X (%) $< (100 - 2\alpha)$, i.e. the analytical procedure was not involved (figure 3).

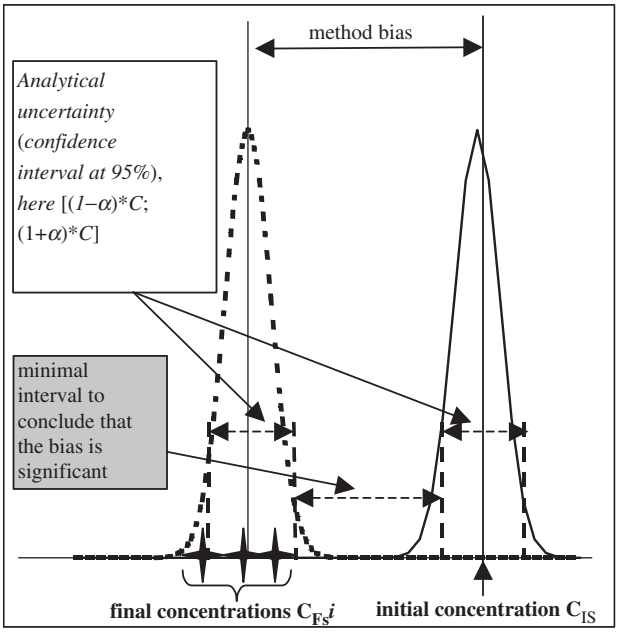

Figure 3. Principle of significant bias (distinction with analytical uncertainty).

Afterwards, the 'non-significant B_X' was assimilated at the value 100% (no bias). The global bias B_{SS} (during the acquisition of data: 'Concentration in Soil Solution' ('C_{SS}')) was then calculated respectively following equation (3):

$$B_{SS} = \prod_{i=0}^{4} B_i. \tag{3}$$

The influence of certain characteristics was evaluated by the statistical analysis of the linear correlation between these characteristics and B_X [37]. The linear coefficients of correlation were calculated by using all the characteristics of table 1. $B_X > 100\%$ was considered equal at 100%. All the B_X values were used, even if they were not significant. The smaller the risk, the more the correlation coefficient differed from null, and the description of the curve by the linear regression was significant.

4. Results and discussion

All the calculated B_X values are listed in table 4. Concerning simazine, B was more than 100% three times out of five, but the average variability for all the biases remained lower than 15%. An underestimation of the initial concentration could be the reason for these values. For cymoxanil, a large variability (to 193%) in B_X values existed for all the biases. Analytical problems or instability of these compounds in water (hydrolysis/photolysis) could explain this. Because of this variability, the conformity

Table 4. Bias evaluation for the experiments with significant bias (in bold, at 5% risk) and $B_X < (100 - 2\alpha)\%$ and, in parentheses, estimation of the standard population deviation for percentage bias.

Bias for step X	Glyphosate	Glufosinate	Carbendazim	Diuron	Terbuthylazine	Simazine	Cymoxanil	Pyrimethanil	Kresoxym-methyl
B_0	n.a.[a]	57% (12.5%)	**20% (7.6%)**	61% (13.3%)	**8% (5.2%)**	**60% (20.4%)**	69% (30.2%)	55% (41.5%)	**3% (0.3%)**
B_1	**19% (0.5%)**	87% (4.4%)	87% (0%)	101% (7.2%)	90% (0%)	134% (7.2%)	136% (193%)	91% (1.7%)	54% (66.8%)
B_2	113% (4.7%)	102% (5.7%)	103% (13.0%)	107% (16.5%)	104% (17.4%)	147% (24.2%)	120% (87%)	104% (16.4%)	93% (23.3%)
B_3	108% (13.3%)	98% (4.5%)	111% (3.1%)	99% (3.4%)	100% (6.5%)	118% (10.4%)	88% (98%)	103% (2.7%)	60% (34.8%)
B_4	119% (5.3%)	118% (21.4%)	**47% (1.9%)**	97% (2.7%)	**65% (1.9%)**	74% (4.1%)	**34% (25.2%)**	91% (3.0%)	**34% (4.6%)**

[a]n.a.: not analysed.

test is often true (i.e. it is impossible to reach a conclusion as to the significance of bias at the chosen significance level) despite the low calculated means (e.g. B_0).

4.1. *Discussion on possible origins of biases*

Globally, a particular bias is significant for all the compounds, but the types are different. Steps 2 (passage via a PTFE sampling tube) and 3 (transport in the icebox) appear to create no significant bias during the acquisition of data 'pesticide concentration'. In all cases, these results are coherent with the bibliography. In contrast, steps 0 and 4, in particular, and 1, to a lesser extent, show larger values of bias, but important differences exist between molecules.

According to the abacus in [11], the monitored compounds should undergo, during the storage time, no losses through volatilization (all the Henry constant logarithms are less than -7.4) and losses less than 10% through sorption to glass (because of $\log(K_{ow})$ less than 3.4). On the other hand, losses due to the transformation reaction in water may be very great, particularly when the holding time increases. In the same way, table 1 shows, in bold, the possible influencing process. Thus, the stability of cymoxanil in water is low (hydrolysis and photolysis), the biodegradation of glyphosate is facilitated, and its $\log(K_{oc})$ would indicate a strong capacity of adsorption on organic matter; pyrimethanil would be influenced by photolysis processes in water. For the others, it is more difficult to reach a decision and isolate possible processes influencing the final concentration.

A test on the conformity of the linear coefficient of correlation evaluates the influence of each characteristic on B_X and emphasizes the explanations about the biases. The characteristics used (solubility, K_{oc}, K_{ow}, half-life for hydrolysis and for photolysis) were selected by a bibliographical analysis revealing a possible influence of those on the processes. Not enough data existed to study the influence of biodegradation. Volatilization was not taken into account because of a previous article [11]. The steps considered are 1 and 4 because of the existence of several significant biases. The results of this test through a risk of 'no-conformity' are shown in table 5. For all the considered characteristics, the general tendencies (when the risk of 'non-conformity' is acceptable) are in accord with the bibliography.

In the case of old ceramic suction cups [22], the influencing processes may be divided into screening and adsorption, the intensity and part of each depending on the compound characteristics. The bias is extreme for kresoxym-methyl and terbuthylazine.

Concerning B_1 'storage in suction cup', the bias is particularly significant for glyphosate ($B_1 = 19\%$). First, we note that processes of volatilization would not influence the concentration [11]. As the suction cups are old, microbial growth may

Table 5. Risk of 'no-conformity' (in bold, significant at 10% risk).

	B_1 (%)	B_4 (%)
Solubility	85	30
Log (K_{oc})	2	41
Log (K_{ow})	11	35
Half-life hydrolysis	36	13
Half-life photolysis	86	94

have occurred, and so losses through biodegradation may have occurred (table 1). However, the final measured concentrations of a degradation product are low (the average concentration for the main metabolite acid aminomethylphosphonic (AMPA) is $0.7\,\mu g\,L^{-1}$ against $C_{Fsi} = 80\,\mu g\,L^{-1}$ for glyphosate). Thus, no degradation exists, or the first steps of the degradation process are exceeded. Adsorption processes on organic matter existing in these old cups could also be at stake, as shown by the risk of 'non-conformity' for log (K_{oc}) (2%).

Storage in a freezer for 3 months (B_4) is a critical step, during which several processes may take place [11]. Four compounds (cymoxanil, kresoxym-methyl, carbendazim, and terbuthylazine) have a significant bias ($B_x < 65\%$). Only the glyphosate, glufosinate, diuron, simazine, and pyrimethanil are not affected. Table 5 particularly shows the influence of the 'half-life for hydrolysis processes' parameter and a more slight influence of factors such as solubility, log(K_{oc}) and log(K_{ow}). As many studies [11, 24, 33] have predicted, several reactions can occur during the storage time. Losses through adsorption, and particularly through the transformation reaction, appear to be predominant.

4.2. *Critic of global data acquisition*

Figure 4 shows the evolution of global biases B_{SS}. The quality of acquisition of C_{SS} data is rather poor (except for pyrimethanil) with an average $B_{SS} = 48\%$ (figure 4) and

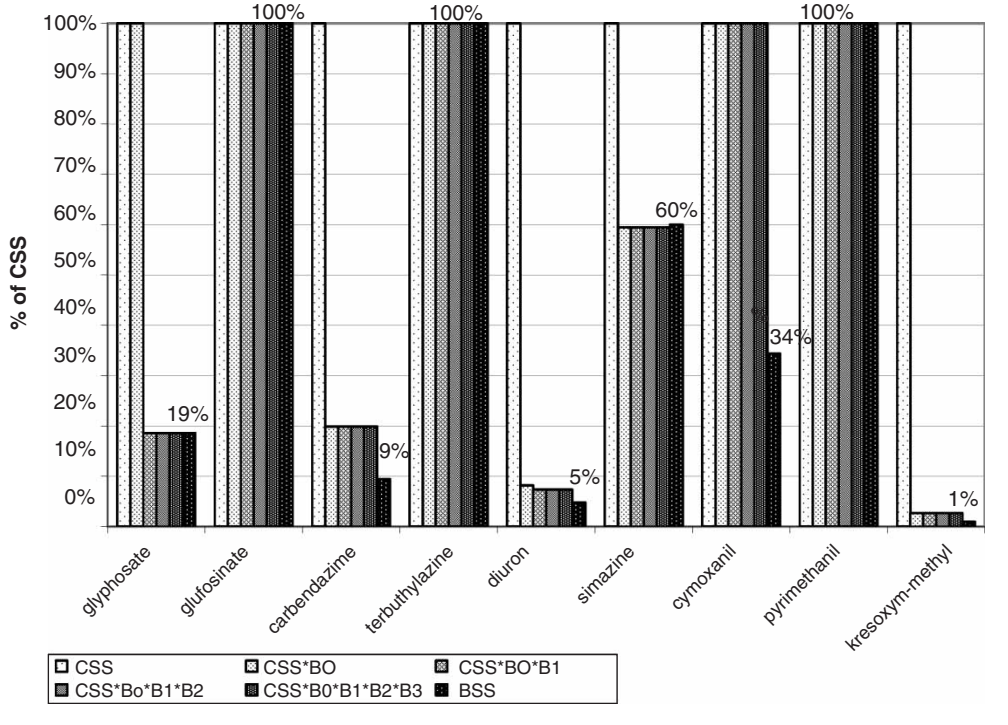

Figure 4. Bias evolution during C_{SS} (concentration of pesticide X in soil solution) data acquisition; B_i is the bias due to step i of data acquisition and B_{ss} the announced value of C_{ss} after all the steps with $C_{SS} = 1$.

particularly because of the part of B_0 'passage through ceramic suction cup wall, with an average B_X of 66%. For four compounds (glyphosate, kresoxym-methyl, terbuthylazine, and carbendazime) with $B_{SS} < 20\%$, the data acquisition of pesticide concentration in soil solution must be revised, and the data correction appears to be critical. However, the use of other suction cups with other materials (e.g. Teflon-quartz) does not seem to limit the bias concerning pesticides (data not shown) contrary to explanations from various studies [27, 32]. In the same way, cleaning the devices does not appear to be a solution (data not shown), as the adsorption site would become free again. Finally, the use of other devices could be contemplated (lysimeter, etc.). For glyphosate, in particular, the bias B_0 is not known (specific experiment in progress), and the dominant bias is B_1.

5. Conclusions

Measuring and acquiring a reliable measurement are essential preconditions to any research aimed at modelling the processes of transfers in the natural environment. The data acquisition can be complex: this is the case with the sample of soil solution to assess the concentrations of various solutes. Specifically concerning the determination of the pesticide concentrations in solution, the necessary precision is more significant because the concentrations concerned are weak (lower than $10\,\mu g\,L^{-1}$). Knowledge of the sources and the magnitude of uncertainty and error therefore remains essential for the decision-maker to assess to which extent decisions can be made with confidence from data and modelling results.

In this study, the bias induced by measurement strategy for the concentration of various pesticides is quantified for soil solution. Each possibility of data loss has been analysed and tested. The 'passage via a PTFE sampling tube' and 'transport in an icebox' steps appear to create no bias during the acquisition of 'pesticide concentration' data. The 'passage through ceramic cup' step is particularly problematic for carbendazim, terbuthylazine and kresoxym-methyl ($B_o < 20\%$) and, to a lesser extent, for simazine (no data for glyphosate). The influencing processes may be divided into screening and adsorption, the intensity and the part of each depending on compound characteristics [22]. Compounds with a high value of K_{ow} (glyphosate particularly with glyphosate $B_1 = 19\%$) would be affected during storage in suction cups, and the adsorption on the organic matter present in those old cups would be at stake. Storage in a freezer for 3 months (B_4) is a critical step where several processes may take place. Four compounds (cymoxanil, kresoxym-methyl, carbendazim, and terbuthylazine) have a significant bias ($B_X < 65\%$). Only the glyphosate, glufosinate, diuron, simazine, and pyrimethanil are not affected. Losses through adsorption, and particularly through transformation reactions, may be predominant for certain sensitive compounds.

Globally, the acquisition chain of 'concentration in soil solution' data would need to be revised because it creates an important bias (on average, 48% of the initial concentration is finally detected). The critical step is particularly the sampling by ceramic suction cups (except for cymoxanil and pyrimethanil). The use of other devices could be envisaged (Teflon-quartz suction cup, lysimeter, etc.) without total proof of quality being shown.

We are aware of the limits of this approach. Indeed, bias is theoretically assessed from a large number of measurements [8]. Other experiments with two more replications would therefore be necessary to quantify the bias of an acquisition method more precisely. Moreover, laboratory experiments are simply a particular view of in situ reality (i.e. ceramic cup tested in a solution) and will never represent its particular conditions (i.e. behaviour of ceramic cups in soil). However, if a bias is detected in laboratory experiments, it must exist in the field, and advice can be proposed to approach perfect data acquisition chain quality. Thus, compounds can be favoured or avoided when certain devices are used (i.e. in our case, terbuthylazine and kresoxym-methyl with ceramic cups), strategies can be proposed (i.e. a limited holding time for cymoxanil and kresoxym-methyl), and material can be confirmed (i.e. passage through a Teflon sampling tube) or validated (i.e. transport in an icebox). If it is impossible to decrease bias (i.e. in our case, we cannot use any materials other than suction cups), then data correction may be contemplated. While using a probabilistic approach, the quantified biases should also be accepted and be effective in the models to improve their precision and relevance [3].

In any case, it is difficult to extrapolate from this study because other situations need new experiments depending on data-acquisition parameters. Moreover, faced with the variability of compounds and the data-acquisition situation, no perfect material appears to exist [38]. All situations should be also tested.

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