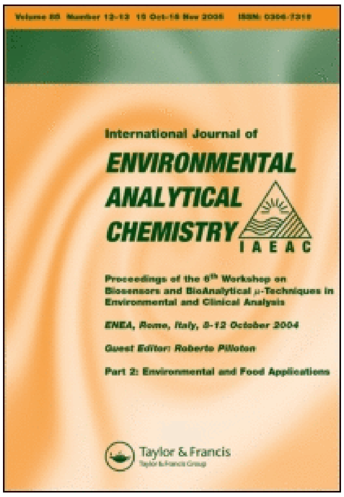

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R. A. Baumann[a]; V. M. 't Hart-De Kleijn[a]; R. Hoogerbrugge[a]
[a] Laboratory of Organic-Analytical Chemistry, National Institute of Public Health and Environmental Protection, Bilthoven, The Netherlands

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EVALUATION OF A SAMPLING METHOD USED FOR THE ANALYSIS OF CHLOROPHENOXY HERBICIDES, N-CONTAINING PESTICIDES AND PAHs IN RAIN WATER

R. A. BAUMANN, V. M. 't HART-DE KLEIJN
and R. HOOGERBRUGGE

Laboratory of Organic-Analytical Chemistry, National Institute of Public Health and Environmental Protection, P.O. Box 1, 3720 BA Bilthoven, The Netherlands

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The influence of a sampling method for rain water on the quality of the analytical results obtained for pesticides and polycyclic aromatic hydrocarbons (PAHs) was studied. Also the possibility of applying a single sampling method for the analysis of a selected group of chlorophenoxy herbicides, nitrogen containing pesticides and PAHs was evaluated.

A conservation experiment was performed using 8 bottles of rain water with known amounts of the components which were sampled at regular time intervals (0, 4, 6 and 8 weeks). The influence of 6 discrete parameters was investigated by varying these parameters using a two level factorial experimental design. The selected parameters were the amounts of the three analysed groups of compounds, the addition of copper sulphate (to eliminate algal growth), the type of rain gauge and the use of open or closed conservation bottles. The samples from the conservation bottles were analysed both on the amount of pesticides and PAHs.

Using the present sampling technique the addition of copper sulphate appeared to have a negative influence on the stability of cyanazine and a positive effect on the stability of the chlorophenoxy herbicides. Other parameters which had systematic effects were the fact whether open or closed container bottles were used and the type of rain gauge.

KEY WORDS: Rain water, pesticides, sampling method, factorial design.

INTRODUCTION

In the Netherlands rain water is monitored for the presence of a wide range of chemical compounds. The Dutch National Precipitation Chemistry Network (LMR) is in operation since 1978 as a joint research project of the National Institute of Public Health and Environmental Protection (RIVM) and the Royal Dutch Meteorological Institute (KNMI)[1]. Among others, main objectives of the LMR are: 1) regional and nation-wide monitoring of wet deposition fluxes and 2) notification and quantification of trends in wet deposition fluxes.

The LMR comprises of 14 monitoring stations. On 3 sites (De Bilt, Leiduin and Rotterdam) rain water samples are collected for the analysis of polycyclic aromatic hydrocarbons (PAHs), up to 1991, and organochlorine pesticides (hexachlorocyclohexanes). The sampling frequency for the PAHs is two weeks; two samples are combined to one 4 weekly sample. The sampling frequency for the pesticides is 4 weeks. The sampling is performed by collecting the rain water for a certain amount of time in a conservation bottle which is positioned in a rain gauge.

Due to the lack of data for the occurrence of pesticides in dutch rain water, other than organochlorine pesticides, an inventory research was carried out in May-October 1988[2,3]. This investigation was primarily focussed on the presence and variation in concentrations of some polar pesticides e.g. bentazone, atrazine, simazine, metolachlor en metazachlor[4]. These compounds were chosen because of their possible occurrence in drinking water. In some rain water samples bentazone, atrazine and simazine were found in concentrations exceeding 0.1μg/l.

Because the 1988 project had an urgent character, it was not possible to investigate the qualitative and quantitative aspects of the sampling method as well as the conservation of the samples. Contrary to ground and surface water, rain water is sampled during a prolonged period of one or several weeks, while the sample stays in the collection device under field conditions.

In an experiment performed in the time period Dec. 89–Feb. 90, the quality of analytical results obtained for PAHs and a selected group of pesticides, was evaluated. A second research goal was wether it would be possible to apply a combined sampling method for both PAHs and pesticides. As we are interested in the quantitation of wet deposition fluxes and not in measuring a concentration of pesticides and/or PAHs in a single shower, stability parameters were chosen according to the procedures that were in operation in the sampling scheme of the LMR at that time.

The influence of several of these sampling parameters was studied using an experimental design. The measurements were organized as a conservation experiment. At regular time intervals samples from the conservation bottles were analysed both on the amount PAHs and the amount of pesticides.

The results obtained for the PAHs are described in an RIVM report[5], and will also be published in a separate scientific paper. In this paper the results obtained for a number of nitrogen containing pesticides and chlorophenoxyacid herbicides are discussed.

The statistical evaluation of the measurement results yields some conclusions with respect to the influence of the selected parameters on the analytical results. The objective to describe the quality of the results seemed reasonably achieved by this single set of experiments. However, comparison with an earlier triazine conservation experiment seems to imply that the influence of the matrix and of ambient conditions, like the temperature, cannot be excluded and should be incorporated explicitly in this type of experiments.

Table 1 Parameters incorporated in the factorial design.

Factor no.			
1	Addition of copper sulfate	0 no	1 yes
2	high/low level [PAH]	0 low	1 high
3	high/low level [CPA]	0 low	1 high
4	high/low level [N-cont. pest.]	0 low	1 high
5	Open or closed bottle	0 open	1 closed
6	Type of rain gauge	0 open	1 wet-only

EXPERIMENTAL

Factorial design

The main objective of the factorial design was to find out how the measured quantity of each component is related to the deposited quantity, and which factors influence this relation. A very important parameter is the possible loss of components during the sampling process, when the rain water is stored in the conservation bottle of the rain gauge. Thus, 0, 4, 6 and 8 weeks were chosen as sampling intervals. Six other parameters were selected that could influence the results. These parameters, given in Table 1, were the amounts of the three analysed groups of compounds, the addition of copper sulphate (to eliminate algal growth), the type of rain gauge and the use of open or closed conservation bottles. It is obvious that a large number of other factors like the temperature during sampling, the presence and size distribution of particles in the collected rain water, and other matrix effects can influence the results. However, because such factors are difficult to control in an experiment, they were not incorporated in the study.

When a complete factorial design is made, the number of measurements is the product of the number of levels of all the factors that are taken into account. In our case, for 6 factors on two levels plus one factor (storage time) at 4 levels, $2^6*4=256$ analyses for each group of components have to be carried out. Because of this very large number of determinations, a partial factorial design, given in Table 2, was chosen in which the 6 factors from Table 1 can be calculated independently from each other[6,7]. Factor no. 7 is determined by interactions of the other 6 factors, it is given to complete the table.

Table 2 Composition of the factorial design.

factors	*1*	*2*	*3*	*4*	*5*	*6*	*7*
rain gauge no.							
1	0	0	0	0	1	1	1
2	0	0	1	1	0	0	1
3	0	1	0	1	1	0	0
4	0	1	1	0	0	1	0
5	1	0	0	1	0	1	0
6	1	0	1	0	1	0	0
7	1	1	0	0	0	0	1
8	1	1	1	1	1	1	1
9	1	0	0	0	0	1	1

With this set-up it is possible to conclude that one factor has a significant effect on an analytical result while the effect of the other factors is negligible. To evaluate interactions of factors, a more complete factorial design, e.g. more analyses, are necessary.

This partial design was based on the availability of 9 rain gauges, 5 of the wet-only type and 4 of the open type. Gauge no. 9 was not absolutely necessary but was used as a control.

Conservation experiment

A volume of 47 l rain water was obtained by mixing samples from different sites of the LMR. This quantity was analysed for the pesticides that were selected for the conservation experiment. None of these compounds was found in concentrations above the limit of determination.

Nine aliquots of 5 l were taken, and the different compounds were added according to factors nos. 1 to 4 of Table 2. Each aliquot was added to a brown glass bottle and stored in a rain gauge in the field, also according to Table 2. Care was taken that no precipitation could enter the glass bottles during the experiment.

Addition of PAHs, pesticides and copper sulphate Because the majority of the PAHs can be found in measurable quantities in "blank" rain water, the blank level was chosen as low concentration level. For the high concentration level, quantities between 30 and 210 ng/l per component, concentrations found previously in dutch rain water[8,9], were added.

The low and high concentration level for the pesticides, nitrogen containing pesticides as well as chlorophenoxy herbicides, was about 200 ng/l, and 1000 ng/l, respectively. The precise values of the spiked amounts are given in Table 3. The estimated precision is ±3%.

When necessary, 100 ml of a copper sulphate solution of 5 g/l CuSO4. 5 H2O in diluted sulphuric acid (pH=2) was added to a conservation bottle[10], resulting in a final copper sulphate concentration of 100 mg/l. In this case, 4.9 l rain water instead of 5 l was used.

Type of rain gauge The experiment was performed with 2 different types of rain gauges[1]. The wet-only gauge is closed from the atmosphere during dry periods, and the conservation bottle is kept in the dark. The rain water that is collected with this gauge has a chemical composition that closely resembles the true composition of the rain water.

The open rain gauge can collect dry deposition from gasses and aerosols during dry periods. This dry deposition can (partly) dissolve with rain water collected afterwards. The conservation bottle is also kept in the dark.

Experimental set-up The conservation experiment took place from december 1989 until february 1990. During this period the temperature outdoors fluctuated between 0 and 10°C. The samples that were stored in closed bottles were kept under a nitrogen atmosphere.

At the beginning of the experiment (t = 0 weeks) and after 4, 6 and 8 weeks respectively, 1010 ml was collected from the rain gauges for analysis. After collection samples were kept at +4°C in the dark in brown glass bottles. For analysis of the nitrogen containing pesticides and chlorophenoxy herbicides, samples, blanks and recoveries were extracted respectively derivatized within two days after sampling.

Table 3 Recoveries, additions (ng/l) and estimated effects in percentage of the added amount.

Nitrogen containing pesticides

Component	Desethylatrazine	Simazine	Atrazine	Cyanazine	Metazachlor	average	RSD
recovery (low)	91.9%	99.4%	99.7%	113.6%	112.6%	103.4%	9.3%
recovery (high)	90.5%	96.9%	96.7%	105.4%	99.7%	97.8%	5.4%
average RSD recovery	4.2%	4.8%	4.5%	4.4%	3.9%		
Additions (ng/l)							
Samples (low)	186	220	160	110	210		
Samples (high)	1240	1507	1060	714	1388		
Average effects							
average effect PAH	5.7%	3.6%	2.8%	0.5%	1.6%	2.8%	2.0%
average effect copper	−7.6%	−4.0%	−4.7%	−9.8%	0.1%	−5.2%	3.8%
average effect bottle (closed-open)	−4.7%	−4.4%	−4.0%	−0.4%	−2.0%	−3.1%	1.8%
average effect CPA	1.3%	−1.8%	−1.0%	0.2%	−2.8%	−0.8%	1.6%
average effect triazines	−14.3%	−7.8%	−10.4%	3.2%	6.7%	−4.5%	9.0%
average effect gauge (wet-only—open)	6.1%	4.2%	4.0%	3.5%	3.9%	4.3%	1.0%
estimate 0 weeks	96.7%	95.6%	101.2%	86.7%	99.8%	96.0%	5.7%
decrease/week	−0.8%	0.2%	0.1%	−3.2%	−0.4%	−0.8%	1.4%
estimate after two weeks	95.1%	96.1%	101.4%	80.3%	99.0%	94.4%	8.3%
RSD with respect to linear model	13.2%	6.4%	6.2%	11.7%	4.8%	8.4%	
Result first study							
recovery (low)	88.2%	93.4%	93.7%	107.3%	102.3%	97.0%	7.7%
recovery (high)	88.2%	94.1%	94.9%	101.7%	99.7%	95.7%	5.3%
estimate 0 weeks	95.4%	105.4%	100.4%	91.6%	103.3%	99.2%	5.7%
decrease/week	0.0%	−0.6%	−0.3%	−2.3%	−0.6%	−0.8%	0.9%
average effect copper	−12.7%	−9.1%	−6.2%	−30.9%	−4.6%	−12.7%	10.6%
average effect bottle (closed-open)	−3.8 %	−3.4%	−4.2%	1.9%	−0.3%	−2.0%	2.6%
average effect triazines	0.9%	−0.1%	1.6%	−0.7%	0.8%	0.5%	0.9%
average effect gauge (wet-only—open)	5.5%	6.6%	4.4%	14.7%	4.9%	7.2%	4.2%

Chlorophenoxy herbicides

Component	MCPP	MCPA	2,4-D	average	RSD
recovery (low)	104.8%	121.9%	115.9%	114.2%	8.7%
recovery (high)	103.9%	108.7%	106.8%	106.5%	2.4%
average RSD recovery	19.0%	26.4%	24.0%	23.1%	3.8%
Additions (ng/l)					
Samples (low)	223	203	219		
Samples (high)	930	845	912		
Average effects					
average effect PAH	−9.2%	1.2%	3.8%	−1.4%	6.8%
average effect copper	15.2%	32.0%	28.3%	25.2%	8.8%
average effect bottle (closed-open)	7.4%	26.8%	23.3%	19.1%	10.4%
average effect CPA	−23.3%	−24.2%	−5.7%	−17.8%	10.4%
average effect triazines	7.0%	−1.3%	−2.4%	1.1%	5.1%
average effect gauge (wet-only—open)	18.6%	11.6%	9.0%	13.1%	4.9%
estimate 0 weeks	101.4%	90.6%	95.7%	95.9%	5.4%
decrease/week	0.8%	−3.9%	−8.2%	−3.8%	4.5%
estimate after two weeks	103.0%	82.8%	79.3%	88.4%	12.8%
RSD with respect to linear model	5.6%	13.8%	1.8%	8.7%	

A small scale conservation experiment took place in the summer of 1989. The results of this preliminary work are used only for an estimation of the representativity of this project in the paragraph on accuracy and representativity of the results.

Analytical methods

All used chemicals were analytical grade unless stated otherwise. Alfa-(2,3,4,5,6) pentafluorobenzyl bromide (lot no. 58220) was obtained from Pierce (Oud Beijerland, The Netherlands).

Nitrogen containing pesticides Atrazine, cyanazine, desethylatrazine, metazachlor and simazine were selected for the experiment. An aliquot of 500 ml rain water was extracted with 1 × 100 ml and 2 × 50 ml dichloromethane, respectively. The combined extracts were filtered over anhydrous sodium sulphate and evaporated to dryness with Kuderna-Danish. The residue was dissolved in 1 ml n-hexane. An aliquot of this solution was injected into a Carlo Erba gaschromatograph equipped with an NPD 40 detector under the following conditions

Column:	fused silica, stationary phase DB 5, 30 m length, I.D. 0.525 mm., film thickness 1.5 μm.
Injectortemp:	220°C.
Detectortemp:	250°C.
Carrier-gas:	helium, column head pressure 40 KPa
Make-up gas:	helium, column head pressure 100 KPa
Oven temp:	temp. 1: 80°C (2 min.), rate 1: 30°C/min.; temp. 2: 170°C (hold 15 min.), rate 2: 10°C/min. temp. 3: 215°C (hold 0 min.), rate 3: 15°C/min. temp. 4: 250°C (hold 15 min.).
Injection:	4 μl splitless.

Quantitation of the components was by external standards. Limits of determination were in the range 5–20 ng/l.

Chlorophenoxycarboxylic acids (2,4-Dichlorophenoxy)acetic acid (2,4-D), (2-methyl-4-chlorophenoxy) acetic acid (MCPA) and 2-(4-chloro-2-methylphenoxy)propionic acid (MCPP) were selected for the experiment. 4-(4-Chloro-2-methylphenoxy)butanoic acid (MCPB) was used as internal standard.

The chlorophenoxy herbicides react with pentafluorobenzyl-bromide (PFB-Br) in a two phase derivatisation reaction to form PFB derivatives.

An aliquot of 50 μl internal standard solution (120 ng/ml MCPB in milli-Q water), 1 ml fosfate buffer (pH 7.4), 3 ml katalyst solution (4.5 g tetrahexylammonium hydrogen sulphate in dichloromethane) and 20 μl PFB-Br (reagent) were added to 9 ml rain water.

This mixture was shaken for 50 min. Hereafter, 350 μl 6N HCl was added and the mixture was again shaken for 1 min. After separation of the organic and aqueous phases, the dichloromethane layer was transferred to a tube containing a small quantity of anhydrous sodium sulphate. This tube was shaken for 30 sec. and after clearing of the mixture, 2.0 ml was transferred to a second tube. The dichloromethane was evaporated with a nitrogen stream at room temperature. The residue was dissolved in 200 µl n-hexane. An aliquot of 3 µl was injected into the GC-MS system under the following conditions

gas chromatograph:	Finnigan 9610
mass spectrometer:	Finnigan 4500 (NCI)
column:	fused silica, length: 25 m, i.d.: 0.25 mm, coated with CP Sil 19 CB, film thickness: 0.25 µm
injector temperature:	250°C
oven temperature:	temp. 1: 70°C (1 min), rate 1: 15°C/min, temp.2: 220°C, rate 2: 5°C/min, temp.3: 260°C (30 min)
carrier gas:	helium, column head pressure 7 psi
injection:	3 µl splitless

The limit of determination was 0.1 µg/l for all components.

RESULTS AND DISCUSSION

Nitrogen containing pesticides

All analytical results were corrected for recoveries (Table 3) measured in milli-Q water. With quantitation, the different recoveries at the low and high concentration level were taken into account. A summary of the analytical results is presented in Table 3. Data are given as a percentage of the spiked amount.

The results with respect to conservation-time are described using a linear model as is illustrated in Figures 1 and 2. For each component the amount after 0 weeks, the decrease-rate and the RSD with respect to the linear model are summarized in Table 3.

The effects of the different factors on the measured concentrations are calculated as the difference between the average for each parameter on the high and the low level, respectively. Because of the set-up of the factorial design that rules out correlation between parameter effects, apart from possible interactions, the difference of these averages is a good estimate of the effect of the specific parameter. In Table 3 the average effects of the selected factors for each compound are given, averaged for the whole group of nitrogen containing pesticides.

The factors chlorophenoxyacid herbicides (CPA) (–0.8±1.6%) and nitrogen containing pesticides (–4.5±9.0%) do not systematically influence the analytical results; the factor PAH (2.8±2.0%) can have a small impact.

The 3 factors that do have influence on the final analytical results are the addition of copper (–5.2±3.8%), open or closed bottle (–3.1±1.8%) and open or wet-only rain gauge (4.3±1.0%).

It can be concluded from the data given in Table 3 that for all nitrogen containing pesticides, except metazachlor (+0.1%), the presence of copper leads to an increased

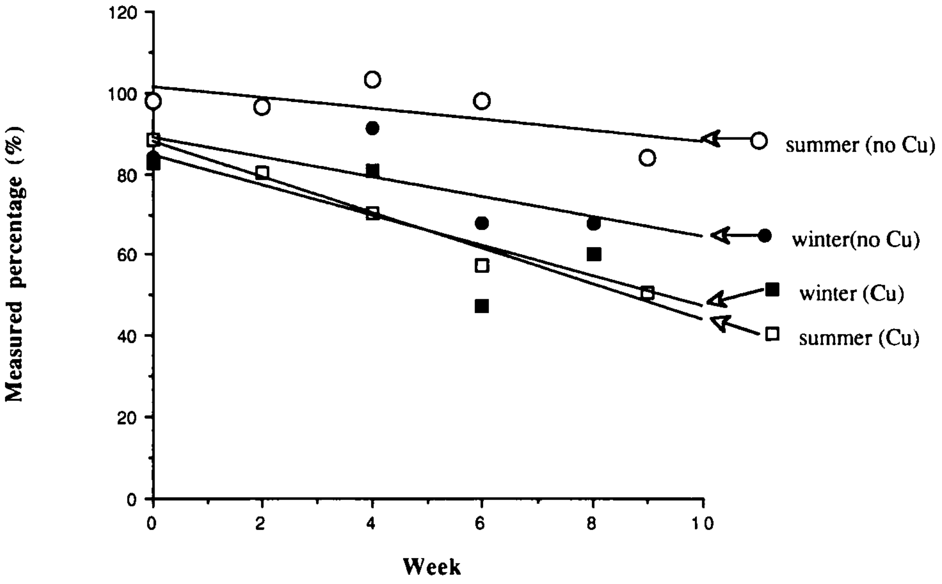

Figure 1 Measured percentage cyanazine as function of the conservation time. Both the results of the first (summer 1989) and the second experiment (winter 1989–90) are shown, with and without the copper addition.

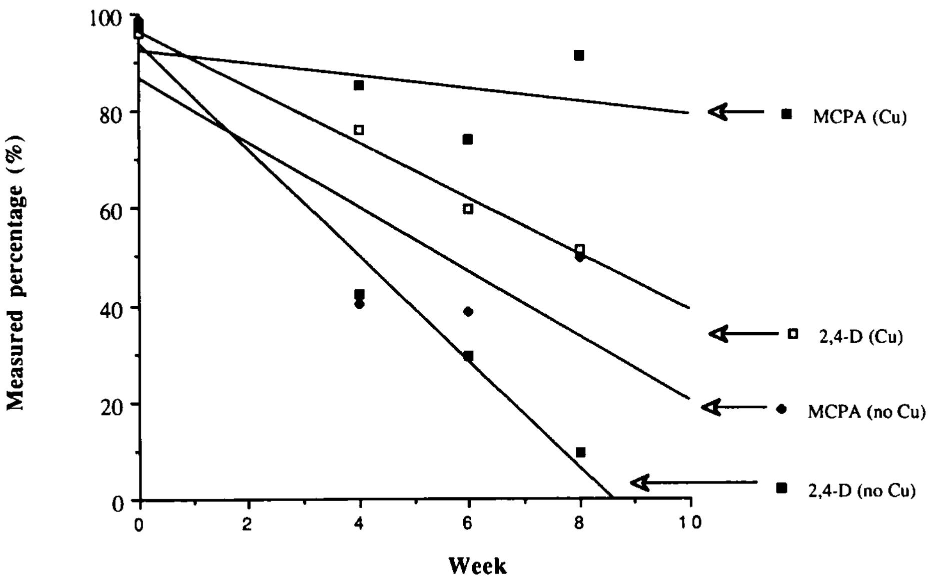

Figure 2 Measured percentages MCPA and 2,4-D as function of the conservation time, with and without copper addition.

degradation, average between –4.0 and –9.8%. The relation of the presence, respectively absence of copper and the cyanazine concentration in time is shown in Figure 1. The degradation rate may be influenced by the chemical composition of the rain water e.g. by matrix effects and/or by the temperature during the field experiment (summer vs. winter). The influence of the temperature on the degradation rate of some pesticides in soil was described by Rüdel *et al.*[11]. They found that half-live values of simazine and chlortoluron could differ up to a factor of 2.5 when laboratory and field experiments were compared. From the results obtained from an earlier triazine conservation summer experiment, also given in Table 3 it can be concluded that the relation between the presence and absence of copper and the concentration of the pesticides in time is different than found in the present winter experiment. As an example, the mean effect for cyanazine is –9.8% (winter) vs. –30.9% (summer). In the paragraph on accuracy and representativity of the results this phenomenon will be discussed in more detail. To illustrate the observed differences, the curves for cyanazine of the earlier summer experiment are incorporated in Figure 1.

In a sterility test[12], it was found that addition of 20 mg Cu/l was not sufficient to maintain the sterility of rain water for a period exceeding 2 days. To inhibit the microbiological activity in rain water for 1 or 2 months, an addition of at least 100 mg/l is necessary.

The factor open or closed bottle has a small influence on the concentration-time relation. The fact that in closed bottles a lower concentration in time is found than in open bottles could indicate that the sample matrix water has a higher evaporation rate than the pesticides.

With both the summer and winter conservation experiment, a small difference between the used rain gauges was observed. Use of the wet-only type resulted in an average of about 5 % higher concentration values compared to the open type. This implies that the construction of the rain gauge can influence the final analytical result. It can not be excluded that a difference in volatilization of pesticides plays a role. During the conservation experiment both gauges were closed from the atmosphere to prevent deposition.

The small effect of the factor PAH on the analytical results is possibly related to a matrix effect. In rain water samples a background concentration of some PAHs is frequently measured. If these compounds interfere with the analysis of the nitrogen containing pesticides, a variation in the background concentration could lead to a variation in the analytical results, specially at the low concentration level. Because of the chosen factorial design, these interactions could not be studied explicitly.

A more detailed discussion on the accuracy and representativity of the results obtained for the analysis of the nitrogen containing pesticides is given in the corresponding paragraph.

Chlorophenoxyacid herbicides (CPA)

Also for this group of compounds, all analytical results were corrected for recoveries (Table 3) measured in milli-Q water. Calculation of the results for the CPAs was identical with the method that was applied for the nitrogen containing pesticides.

In Table 3 the mean effects of the selected factors for each compound are given, averaged for the whole group of CPAs.

The factors PAH (–1.4±6.8%) and nitrogen containing pesticides (1.1±5.1%) have no influence on the analytical results. The 4 factors that do have an influence are the addition of copper (25.2±8.8%), open or closed bottle (19.1±10.4%), the concentration of CPA (17.8±10.4%) and open or wet-only rain gauge (13.1±4.9%).

In the case of the CPAs, the presence of copper in the rain water samples has a stabilising effect. The decrease of concentration with time is lower when copper is added. In Figure 2 this is visualized for MCPA and 2,4-D.

It is not simple to give an explanation for the stabilizing effect of the copper(II)ions. On one hand the algal and bacterial growth is inhibited. When the CPAs are degraded by microbiological activity, this process can be slowed down considerably. Because this effect is not observed for the nitrogen containing pesticides, it has to be specific for certain components. On the other hand, an ionogenic interaction between the copper ions and the carbonate groups of the CPAs might have a stabilizing effect. To be certain that one of these effects really is in operation, additional experiments have to be performed.

The factor open or closed bottle is acting contrary for the CPAs compared to the nitrogen containing pesticides. When open bottles are used the decrease of concentration with time is higher than with closed bottles. This could indicate volatilization of the compounds.

The large influence of the factor CPA, low vs high spiking level, could point to a concentration dependence of the stability of the CPAs in rain water. This can lead to a considerable complication in the interpretation of the analytical results. A second possibility is that a concentration dependent matrix effect is encountered. In that case, this effect can be minimized by modification of the sample pretreatment and/or the analysis.

The factor type of rain gauge is of influence on the analytical results. The mean difference between the wet-only gauge and the open gauge is about 13%. Also for this components the wet-only meter gives the higher concentration values.

Accuracy and representativity of the results

To describe the accuracy and representativity of the results, the partition in at least three types of accuracy seems necessary, as will be illustrated for the nitrogen containing pesticides.

Recoveries Recoveries in relatively pure (milli-Q) water have a reproducibility with an RSD of about 5%.

Consistency in time For a small decay of concentration with respect to conservation time in combination with the above mentioned reproducibility of the recovery experiments one would expect that the averages of experiments in the same period deviate within a few percent from the calculated linear decay. However, Figure 1 shows much larger deviations indicating that perhaps the recoveries are not representative for the real samples or that on sampling interfering effects occur which cause unexpected systematic deviations. A striking example of such an unexpected deviation is the fact that for all nitrogen containing pesticides the measured amount after 8 weeks of conservation exceeds the amount found after 6 weeks.

The RSD of the recovery measurements of the CPAs are too large to observe such a difference as described above.

Representativity of the matrix Preceeding this experiment a small conservation experiment was conducted in the summer of 1989 on the nitrogen containing pesticides. In general a similar main result, the influence of copper addition on the decay of cyanazine, was found. However, the absolute amount of this effect differs by a factor of about two. This difference is shown in Figure 1 and is mainly caused by the difference in percentage of cyanazine found in the rain water without copper addition. This seems to imply that the difference originates from the matrix differences between the batches of rain water used in both experiments. Therefore precautions seem necessary to generalize results based on a single batch of rain water. Another complication may be changing environmental conditions, like the temperature, which may influence the result and therefore reduce the representativity of a single conservation experiment.

Accuracy indicator.

In the previous paragraph it is shown that the expected accuracy is influenced by the repesentativity of the matrix, which is not known. In order to quantify the information on the accuracy which is present an 'accuracy indicator' is defined as the square root of the quadratic sum of:

- the relative standard deviation of recovery experiments,
- the estimated losses according to the linear model and
- the relative standard deviations with respect to the linear model.

This definition is based on the observation that a correction for the observed losses found in a single set of experiments is not a real option. Then these losses directly influence the accuracy. An improved accuracy can be obtained by repetition of conservation experiments with varying both the matrix composition and the environmental conditions which enables a general description of the decay of the analytes.

The 'accuracy indicator' is shown for several conservation times in Figure 3. Most nitrogen containing pesticides have a very small decay resulting in an accuracy which is not very conservation-time dependent. On the contrary, cyanazine shows an RSD which increases from about 20% (t=0) to more than 40% for a conservation time of 8 weeks. A strong time dependence is also found for two of the CPAs. The results shown in Figure 3 are based on all experimental results and therefore tend to represent the average overall parameter setting. If a sampling technique is selected, then the set of parameters is determined and the average result can be adjusted to this set of parameters by addition of half of the effects presented in Table 3.

Combined sampling

One of the objectives of the research project was the applicability of a combined sampling method for both PAHs and the selected pesticides. In the present sampling regime of the LMR, rain water stays in the rain gauge for an average period of 1 week, and after collection for an average period of 1 week in the refrigerator at 4 °C in a closed bottle.

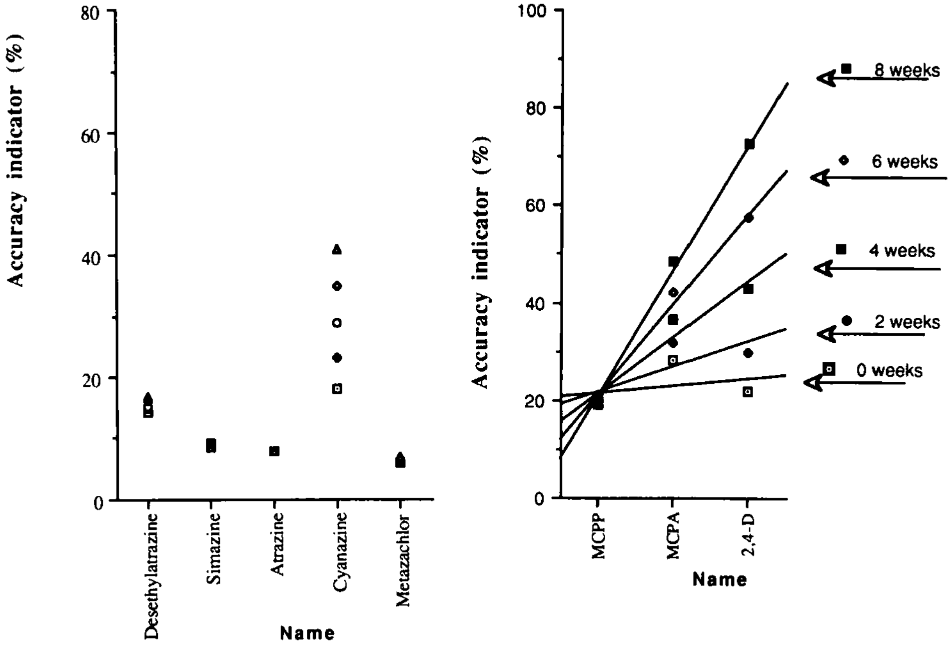

Figure 3 Accuracy indicator for the various pesticides after a conservation-time of 0, 2, 4, 6 and 8 weeks. The indicator is assumed to be a reasonable estimate of the accuracy in the determination of the deposited amounts. A more rigid estimate of the accuracy requires more experiments (see text).

Under this conditions, it can be calculated that the addition of copper sulphate has little effect on the PAHs and the majority of the nitrogen containing pesticides and a negative effect on cyanazine. The addition of copper sulphate has a strong positive effect on the chlorophenoxy herbicides.

When no copper sulphate is added, more than 70% of the amount of all the components will be present in the samples ready for analysis.

The difference in the effect of the factor copper sulphate on the concentration vs. conservation time curve for cyanazine as shown in Figure 1 makes it difficult to correct for this effect. Correction is dependent on the specific rain water matrix and possibly a few other parameters, and therefore hardly feasible in practice.

The use of a combined sampling method is possible, but depends on the uncertainty and the precision of the analyte concentrations that have to be reported.

CONCLUSIONS

Nitrogen containing pesticides The factors addition of copper, open or closed bottle and open or wet-only rain gauge have the largest systematic effect on the decrease in concentration with time. The factor PAH has a small effect on the concentration decrease in time.

Comparison with an earlier summer experiment points to a possible influence of matrix effects and of the ambient temperature on the stability of the compounds under investigation.

Chlorophenoxy herbicides The factors addition of copper, open or closed bottle, CPA concentration and open/wet-only rain gauge have a systematic effect on the changing of the concentration in time for the CPAs. If the influence of the factor CPA is caused by a matrix effect, it can be minimized by modification of the sample clean-up step and/or the method of analysis.

Combined sampling The present sampling procedure results in average losses of PAHs of 20±13%; nitrogen containing pesticides 6±8% and chlorophenoxy herbicides 12±13%.

The (chemical) composition of rain water samples can vary considerably in place and time. This can effect the stability of organic compounds under investigation, and thus the analytical results.

Addition of a fixed concentration of copper sulphate to rain water has a positive effect on the concentration CPAs, resulting in an average 10–15% higher measured concentration. The other investigated components show a small extra decrease when copper sulphate is added.

To give a good estimate of the effect of the addition of a certain amount of copper sulphate to a conservation bottle prior to rain water sampling, additional research has to be carried out. Also the study of addition of other compounds recommended for conservation, as sodium azide and mercury (II) chloride, could lead to more insight in the stability of certain groups of pesticides.

When both the summer and winter conservation experiment are taken into account, correction of analytical data can only be performed if the factor matrix effects and environmental factors such as temperature during sampling are more extensively evaluated.

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