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# Evaluation of the Studies on Decline of Pesticide Residues

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A specifically designed field trial was carried out in an apple orchard by applying Reldan 50 EC (active ingredient, chlorpyrifos-methyl) according to registered uses in Hungary to study the variability of results derived from supervised field trials. Two types of composite samples (A, size 24; and C, size 12) were taken at days 0, 3, 7, 10, and 14 after application to study the uncertainty of estimated residue values derived from supervised trials. In the case of type A the sampling officer selected the fruits from the specified quadrant of the tree, whereas for type C the fruits were taken from the vicinity of the marked position at consecutive sampling times. An evaluation model applying various formulas for the linearization of the decline curves of pesticide residues was applied, which enabled using the statistics of linear regression for calculating the best fit and confidence intervals for the experimental data. The results indicated that the uncertainty of sampling contributed ∼84−90% of the combined uncertainty of the results (24−30%). In the decline studies performed simultaneously on the same field, the estimated time required to decrease the initial concentration to half ranged from 0.64 to 4.7 days. Despite the fact that the sample size of type C is half that of type A, both sampling methods provided similar results.

**KEYWORDS: Field trials; pesticide residue decline; uncertainty of sampling; statistical evaluation; uncertainty of estimated concentration and time**

## INTRODUCTION

The dissipation rate of a pesticide after application is important information for the assessment of the behavior of its residues. The time required to decrease the residues to half of their initial concentration, or less frequently to $^1/_5$ or $^1/_{10}$ of the initial concentration, is used to compare the persistence of the residues under different climatic or growing conditions. The decline curve may also be used to estimate the time required for decreasing the average residues below a specified level. On the basis of that information the preharvest interval can be adjusted to ensure that the residue content of the harvested crop will comply with a maximum residue limit (MRL).

The dissipation rate is usually determined by taking samples at various time intervals after the application of the pesticide in supervised trials carried out in such a way that treatments in the trials correspond to the intended use of the pesticide. Because the residue levels in crop units or small increments of grains and soil cores differ to a large extent (average CV is ∼80−100%), the variability of residues in composite samples is inevitably large (*1*, *2*) (estimated average CVs are ∼20−30%). Because of the uncertainty of sampling, the residues measured during the decline studies vary around the true average residue value and may distort the course of the decline curve. An awareness of the expected variability of residues is necessary. Consideration of the spread and variability of the residues helps to avoid misleading interpretations of small differences or drawing definite conclusions from a single calculated value.

The disappearance of pesticide residues from the treated objects is influenced by several physical, chemical, and biochemical processes, which can rarely be described with a simple relationship. The most probable value at a given time can be estimated by applying various curve-fitting computer programs.

On the basis of residue data from supervised field trials, Timme, Frehse, and Laska (*3*) developed an evaluation model applying various formulas for the linearization of the decline curves to obtain a linear relationship between the measured residue ($R$) and the time ($t$) elapsed ($R' = a + bt$). Thus, the statistics of linear regression can be used for calculating the best fit and confidence intervals for the experimental data. The model values are back-transformed to reconstruct the decline curve in its original form. To facilitate the practical application of the model, a computer program was developed and validated according to the requirements of GLP (*2*). The model selects that transformation which provides the best fit based on the sum of squares of the residuals. The residue−time correlation is characterized with the coefficient of determination and the significance of the correlation at 95% level. The time required for decreasing the residues to half ($T$/2) or other fractions of the initial value (e.g., $T$/5 or $T$/10) are calculated with confidence intervals. In addition, the expected average, minimum, and maximum residues at specified times within the duration of the

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**Table 1.** Linear Transformations Applied for Residues Measured in Decline Studies (*1*)

| function | transformation for residue value | transformation for time | best fit (%) |
|---|---|---|---|
| 1st order | log $R$ | none | 35 |
| 1.5th order | $1/\sqrt{R}$ | none | 6 |
| 2nd order | $1/R$ | none | <5 |
| root function 1st order, (sqrt 1st order) | Log $R$ | $\sqrt{t}$ | 35 |
| root function 1.5th order | $1/\sqrt{R}$ | $\sqrt{t}$ | 11 |
| root function 2nd order | $1/R$ | $\sqrt{t}$ | 8 |

trial can be calculated. It is recommended that the model be used only for predicting values for short time periods beyond the sampling interval, given that the quality of the fit is adequate. At the time of its publication, the practical applicability of the model was tested on the results of 420 supervised field trials. The transformations performed by the program and the percentage of the cases in which the respective transformation provided the best fit is given in **Table 1**. Owing to its simplicity, this model was used to compare the applicability of two sampling methods applied in the decline studies for estimating the expected residue ranges at different times after application, as part of an extensive trial carried out with apple to determine the residues in individual fruits and validate various sampling methods.

The results and evaluation of the decline studies are reported in this paper. The details of the environmental conditions and validation of the analytical procedure are not directly relevant to the study; therefore, they are not included in this paper.

## MATERIALS AND METHODS

**Layout and Treatment of Experimental Site.** A well-maintained 12-year-old, typical commercial apple orchard of 20 ha was selected for the site of the experiment near Nyíregyháza in eastern Hungary. The trees were planted in 6 × 3 m blocks. The experimental plot included the area between the 33rd and 37th rows. Each row consisted of 149 trees. The majority of the trees were of the Csányi Jonathan variety with Golden Delicious at approximately every 15th tree.

A day before the treatment, every 10th tree was labeled to indicate the numbers of the row and the tree in order to easily identify the appropriate tree for taking samples. The Golden Delicious trees and those that were very small or dead were marked on the map of the plot, and they were disregarded in the sampling operations. The treatment was carried out according to the study plan, following normal farming practice, with a Hardi TC 1082 mist blower. The first 111 trees of the rows were treated, and the sections from the 112th to the 119th tree formed the buffer zone, whereas the section from the 120th to the 149th tree was kept for untreated control. The treated area was one ha. The outer rows (33 and 37) and the first and last three trees of the treated field were not included in the sampling area.

The sprayer was calibrated a day before the application. The actual dose rate applied was 1.493 L of Reldan 50 EC/ha in 796.5 L spray volume corresponding to 757 g of chlorpyrifos-methyl/ha, which was in accord with the target rate of 750 g of active ingredient (ai)/ha and 800−1000 L/ha spray volume. The lower range of the registered volume was chosen because the canopy of the trees could not hold more spray.

**Sampling.** During this trial, composite samples were taken following two different sampling designs (types A and C) at 0, 3, 7, 10, and 14 days after application of the pesticide. Seven persons trained in sampling repeated the sampling procedures from seven sampling sites independently. At days 0 and 14, 319−320 apples were taken randomly from the whole treated area (sample type B) and analyzed individually (*2*).

The sampling sites were selected by drawing random numbers with Statgraphics statistical software. For the purpose of allocation of random numbers, the treated trees in rows 34−36 were numbered continuously from 1 to 333. Thus, for instance, the random numbers 66, 166, and 266 indicated the 66th tree in row 34, the 55th tree in row 35, and the 44th tree in row 36, respectively. When a number drawn corresponded with the first and last three trees of the rows, or selected a nonrepresentative tree, it was disregarded and the next random number was used.

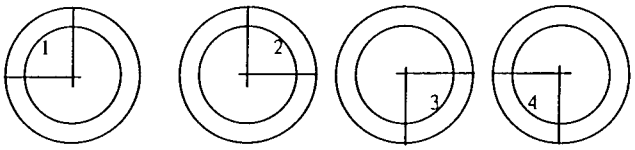


**Figure 1.** Cluster of four trees representing one sampling site and the sampled quadrants for type A samples.

*Composite sample type A* consisted of 24 apples each. Each sample was taken from four adjacent trees representing the standard plot design with four trees according to supervised field trial protocols. The fruits were taken from a different single quadrant from each tree in order to sample all four quadrants as illustrated in **Figure 1**. Six apples were collected from the whole quadrant, including its top, middle, and bottom, interior and periphery segments, approximately proportional to the abundance of fruit. Altogether 24 fruits were collected from one sampling site (the cluster of four trees). During consecutive samplings, the same quadrants were sampled from each tree, but on each occasion the fruits were selected from the quadrants at the discretion of the sampling officer.

The method can be considered as an approximate stratified random sampling. The quadrants represent the strata, which may receive different pesticide deposits because of the movement of the sprayer. The fruits were selected from the quadrant according to the judgment of the sampling officer without following a random design. Therefore, the sampling method is not truly random. The residues were not measured separately in the individual quadrants because the fruit taken was composited to determine the average residue.

The random number drawn represented the first tree of the cluster of four trees except if the selected number fell within the last four trees in a row of the sampling area. In the latter case the last four trees of the sampling area were selected for the cluster. The selected number was discarded if it fell within an already selected cluster. The row/tree numbers of the starting trees of the clusters were 34/36, 35/14, 35/35, 35/72, 36/10, 36/30, and 36/66, respectively.

*Sample type C* consisted of 12 apples each. Taking into consideration the prior information (*5*) on the uneven distribution of the residues on various spatial positions of the trees, for the purpose of sampling, the trees were divided into six imaginary segments representing the following positions: OH, outer high; IH, inner high; OM, outer middle; IM, inner middle; OL, outer low; IL, inner low. The high, middle, and low sections divided the height of canopy into approximately three equal parts. The outer part amounted to about one-third of the diameter of the cross section of the canopy as illustrated in **Figure 1**.

For collecting one sample of type C, 12 trees and one imaginary segment on each tree were randomly selected. Thus, 7 times 12 trees were randomly selected for taking 7 composite samples. Those trees that had already been selected for other composite samples were omitted, and the next random number was used to select a tree. The positions from which the fruits were first taken were labeled, and the fruits were taken from the vicinity of the marked position at consecutive sampling times. Because the sampling positions for the first primary samples were selected randomly and the same positions were used for taking the fruits at the consecutive sampling occasions, all samples taken can be considered random and used to estimate the unbiased mean residue.

The principal difference between sample types A and C is that the primary samples were taken from the vicinity of fixed locations at consecutive sampling days in case of type **C** samples, whereas in type A samples only one-fourth of the tree was specified and the six apples were picked according to the judgment of the sampling officer.

The samples were collected in plastic bags and transported to the laboratory within 1 h after sampling, where the samples were placed into deep-freezer as received and stored at ≤−18 °C until analysis.

**Table 2.** Residues (Milligrams per Kilogram) Measured in Composite Samples of Types A and C

| sampling method | days after appl | sampling site 1 | 2 | 3 | 4 | 5 | 6 | 7 | av residue | CV |
|---|---|---|---|---|---|---|---|---|---|---|
| A | 0 | 0.27 | 0.13 | 0.098 | 0.17 | 0.10 | 0.20 | 0.17 | 0.164 | 0.37 |
| | 3 | 0.14 | 0.072 | 0.050 | 0.092 | 0.066 | 0.052 | 0.073 | 0.078 | 0.40 |
| | 7 | 0.036 | 0.024 | 0.035 | 0.027 | 0.034 | 0.047 | 0.024 | 0.032 | 0.25 |
| | 10 | **0.043** | 0.024 | 0.033 | **0.033** | 0.026 | 0.023 | 0.020 | 0.029 | 0.28 |
| | 14 | 0.033 | **0.028** | 0.018 | 0.025 | 0.019 | **0.025** | **0.024** | 0.025 | 0.21 |
| order | | sqrt 1st | sqrt 1st | sqrt 1st | sqrt 1st | 1.5th | sqrt 1.5th | sqrt 1.5th | | 0.30[a] |
| $r'^{2}$[b] | | 0.75 | 0.95 | 0.98 | 0.94 | 0.99 | 0.99 | 0.98 | | |
| $S_{cor}$[c] | | 0.53 | 0.096 | 0.11 | 0.093 | 0.12 | 0.12 | 0.11 | | |
| C | 0 | 0.173 | 0.18 | 0.153 | 0.127 | 0.146 | 0.221 | 0.152 | 0.164 | 0.18 |
| | 3 | 0.097 | 0.094 | 0.101 | 0.066 | 0.089 | 0.097 | 0.051 | 0.095 | 0.37 |
| | 7 | 0.043 | 0.036 | 0.037 | 0.03 | 0.026 | 0.038 | 0.029 | 0.036 | 0.24 |
| | 10 | 0.022 | 0.026 | 0.037 | 0.028 | 0.022 | 0.023 | 0.020 | 0.026 | 0.24 |
| | 14 | 0.017 | 0.023 | 0.018 | 0.024 | 0.022 | **0.027** | 0.019 | 0.021 | 0.17 |
| order | | 1st | 1st | 1st | sqrt 1st | 1st | sqrt 1st | sqrt 1st | | 0.24[a] |
| $r'^{2}$ | | 0.98 | 0.90 | 0.97 | 0.97 | 0.90 | 0.98 | 0.99 | | |
| $S_{cor}$ | | 0.11 | 0.072 | 0.11 | 0.11 | 0.073 | 0.11 | 0.12 | | |

[a] Average CV. [b] $r'^{2}$, coefficient of determination. [c] $S_{cor}$, significance of correlation.

**Sample Processing and Extraction.** The composite samples were thawed in a microwave oven at 500 W for 30 min. The whole sample was chopped in a kitchen machine into a pulp containing peel pieces of 3−6 mm. To keep the uncertainty of sample processing as low as possible, portions of 400 g of apple (the maximum amount that could be processed) were transferred into a kitchen blender and blended with 100 mL of water to obtain a homogeneous pulp (*6*). A portion of 125 g of the homogenate (equivalent to 100 g of sample) was removed from the blender for analysis. This portion was mixed with 11.7 g of sodium hydrogen carbonate and 117 g of anhydrous sodium sulfate and extracted with 100 mL of EtAc containing diazinon as internal standard (0.495 mg/mL for day 0 and 3 samples and 0.0495 mg/mL for day 7, 10, and 14 samples), with an Ultra Turrax at high speed for 3 min. The extract was left to settle until the clean supernatant solution appeared on the top. A 10 mL portion of the supernatant was filtered through cotton wool into a graduated test tube, which was tightly closed with a glass stopper and stored in a refrigerator at ∼4 °C for GLC analysis.

**GC analysis** was performed at 200 °C isothermal temperature on a CP-SIL 5 CB 15 m × 0.53 mm wide-bore capillary column with a nitrogen−phosphorus specific thermionic detector.

The characteristic parameters of the system were as follows: effective plate number for chlorpyrifos-methyl, 11000; selectivity of the detector (P/C) measured with tributyl phosphate/eicosane, 27000; retention times of chlorpyrifos-methyl, ∼4 min, and diazinon, ∼3 min.

**Recovery studies**, performed as part of the method validation altogether with 20 analytical portions at 0.023, 0.11, 0.23, and 0.79 mg/kg fortification levels, resulted in an overall average recovery of 82.6% with a coefficient of variation (CV) of 10.6%. The estimated limit of quantification was 0.005 mg/kg. Separate experiments were performed to compare the residues in fresh samples and in deep-frozen ones after thawing. The thawing in a microwave oven did not affect the field-incurred residue levels, and storage of dried extracts in the refrigerator did not result in observable loss of residues. At the time of the analysis of samples, the individual recoveries from spiked analytical portions were 73.5, 84.3, 82.2, 77,4, and 76.1%, giving an average of 78.7% and a CV of 5.65%. The difference between the results of method validation and performance verification tests was not significant. The reported results were not corrected for recovery.

## RESULTS AND DISCUSSION

The validation of the analytical method applied covered the residue range measured in the samples. Its performance parameters enabled the accurate detection of residues present. The residues measured in composite samples are shown in **Table 2**. The average CVs of residues in composite samples taken with methods A and C were 30 and 24%, respectively. As the relative standard uncertainty of the results is ∼30%, the residues measured can be expressed with two significant figures. Neither the mean values obtained with sampling methods A and C at a given sampling time nor the average CVs were significantly different.

To estimate the contribution of the sampling to the overall average uncertainty of the results (30% for sample type A and 24% for sample type B), we have to take into account the uncertainty of the sample processing and analysis. The efficiency of the chopper used for sample processing had been tested previously (*7*) with the same variety of field-treated apple. The sampling constant ($K_s$)

$$K_s = m \times \mathrm{CV}\%^2 \qquad (1)$$

defined as the mass of single increment ($m$), which must be withdrawn from a well-mixed material to keep the relative sampling uncertainty at 1% with 68% confidence (*8*), was estimated to be 21 kg.

The corresponding sample-processing uncertainty of 14.5% for 100 g of analytical portion [$\sqrt{(21000/100)} = 14.49$] would have been too high for this experiment; therefore, an additional homogenization of a 400 g portion with a blender was included in the procedure. The sampling constant after homogenization of chopped apple in a blender in the presence of water was reported to be ∼0.15 kg (*9*). The combined uncertainty of sample processing can be calculated as

$$\mathrm{CV}_{Sp2} = \sqrt{\frac{K_{S1}}{m_1} + \frac{K_{S2}}{m_A}} \qquad (2)$$

where $K_{S1}$ and $K_{S2}$ are the sampling constants for chopping and blending, respectively, $m_1$ is the mass of chopped sample material taken for further homogenization in a blender, and $m_A$ is the portion of the homogenized sample that is analyzed. Inserting the corresponding values ($K_{S1}$ = 21000 g, $K_{S2}$ = 150 g, $m_1$ = 400 g, $m_A$ = 100 g) into eq 2, we obtain $\mathrm{CV}_{Sp2}$ = 7.35% for the two-step sample-processing uncertainty.

The variability of results ($R$), which may be attributed to the uncertainty of random sampling ($\mathrm{CV}_S$), can be calculated (*10*, *11*) by taking into account the average relative uncertainties of

**Table 3.** Estimated Residue Values (Milligrams per Kilogram) at Sampling Days 0, 10, and 14 with Their Confidence Intervals and Range Based on Sample Type A

| sample | measured residue (g/kg) | estimated residue values (mg/kg) mean | min | max | range |
|---|---|---|---|---|---|
| | | Day 0 | | | |
| 1 | 0.27 | 0.289 | 0.068 | 1.227 | 1.159 |
| 2 | 0.13 | 0.132 | 0.032 | 0.542 | 0.510 |
| 3 | 0.098 | 0.102 | 0.053 | 0.195 | 0.142 |
| 4 | 0.17 | 0.176 | 0.047 | 0.658 | 0.611 |
| 5 | 0.10 | 0.103 | 0.073 | 0.157 | 0.084 |
| 6 | 0.20 | 0.201 | not available[a] | | |
| 7 | 0.17 | 0.166 | 0.042 | 0.656 | 0.614 |
| 1–7[b] | 0.164 | 0.157 | 0.079 | 0.311 | 0.232 |
| | | Day 10 | | | |
| 1 | 0.043 | 0.041 | 0.012 | 0.141 | 0.129 |
| 2 | 0.024 | 0.028 | 0.008 | 0.092 | 0.084 |
| 3 | 0.033 | 0.027 | 0.016 | 0.048 | 0.032 |
| 4 | 0.033 | 0.031 | 0.01 | 0.095 | 0.085 |
| 5 | 0.026 | 0.026 | 0.022 | 0.032 | 0.01 |
| 6 | 0.023 | 0.029 | 0.016 | 0.071 | 0.055 |
| 7 | 0.02 | 0.025 | 0.008 | 0.08 | 0.072 |
| 1–7[b] | 0.029 | 0.029 | 0.015 | 0.056 | 0.041 |
| | | Day 14 | | | |
| 1 | 0.033 | 0.029 | 0.008 | 0.107 | 0.099 |
| 2 | 0.028 | 0.021 | 0.006 | 0.075 | 0.069 |
| 3 | 0.018 | 0.022 | 0.012 | 0.039 | 0.027 |
| 4 | 0.025 | 0.023 | 0.007 | 0.074 | 0.067 |
| 5 | 0.019 | 0.018 | 0.016 | 0.022 | 0.006 |
| 6 | 0.025 | 0.023 | 0.013 | 0.055 | 0.042 |
| 7 | 0.024 | 0.017 | 0.005 | 0.06 | 0.055 |
| 1–7[b] | 0.025 | 0.021 | 0.011 | 0.042 | 0.031 |

[a] Due to the large variation of the results, confidence intervals could not be estimated. [b] All 35 data have been taken into account.

the results ($CV_R$ = 24% for sampling method C and 30% for sampling method A), sample processing ($CV_{Sp}$ = 7.35%), and analysis ($CV_A$ = 10.6%) as

$$CV_S = \sqrt{CV_R^2 - CV_{Sp}^2 - CV_A^2} \quad (3)$$

Inserting the above values into eq 3, we obtain $CV_S$ values of 27.1 and 20.2% for sample types A and C, respectively. The calculation indicates that in this experiment the sampling is the major source of the uncertainty of the results (84−90%), and the remaining contribution of the sample processing and analysis of residues [(30 − 27.1)/30 = 9.7% and (24 − 20.2)/24 = 15.7%] to the overall variability of the results is relatively small. Consequently, the uncertainty of the measured and estimated values, summarized in **Tables 2**−**5** can be mainly attributed to the uncertainty of sampling.

The random variation of the results distorts the tendency of the change of the average residue concentration. The residue values exceeding the concentrations previously measured in the decline studies are given in boldface type in **Table 2**.

When the disappearance of the residues is rapid and the decline curve is steep, the random variation may not cause the fluctuation of the measured values, and the decline curve shows a continuous decrease of the residue concentration. The effect of the random variation of the residue content of samples is more pronounced when the disappearance of the residues is slower and the decline curve becomes flatter, as was the case at days 10 and 14 in this study. A value higher than the one observed previously occurred in four cases of seven when sampling method A was used, and it occurred in one case of seven with sampling method C. The results indicate that

**Table 4.** Estimated Residue Values (Milligrams per Kilogram) at Sampling Days 0, 10, and 14 with Their Confidence Intervals and Range Based on Sample Type C

| sample | measured residue (g/kg) | estimated residue values (mg/kg) mean | min | max | range |
|---|---|---|---|---|---|
| | | Day 0 | | | |
| 1 | 0.17 | 0.159 | 0.073 | 0.344 | 0.271 |
| 2 | 0.18 | 0.195 | 0.070 | 0.547 | 0.477 |
| 3 | 0.15 | 0.146 | 0.064 | 0.334 | 0.270 |
| 4 | 0.13 | 0.129 | 0.066 | 0.253 | 0.187 |
| 5 | 0.15 | 0.120 | 0.024 | 0.604 | 0.580 |
| 6 | 0.22 | 0.231 | 0.074 | 0.719 | 0.645 |
| 7 | 0.15 | 0.144 | 0.084 | 0.249 | 0.165 |
| 1–7[a] | 0.164 | 0.147 | 0.064 | 0.614 | 0.550 |
| | | Day 10 | | | |
| 1 | 0.043 | 0.028 | 0.014 | 0.056 | 0.042 |
| 2 | 0.051 | 0.038 | 0.015 | 0.095 | 0.08 |
| 3 | 0.037 | 0.032 | 0.015 | 0.067 | 0.052 |
| 4 | 0.03 | 0.029 | 0.016 | 0.051 | 0.035 |
| 5 | 0.026 | 0.027 | 0.006 | 0.118 | 0.112 |
| 6 | 0.038 | 0.031 | 0.012 | 0.081 | 0.069 |
| 7 | 0.029 | 0.023 | 0.014 | 0.036 | 0.022 |
| 1–7[a] | 0.036 | 0.028 | 0.019 | 0.046 | 0.027 |
| | | Day 14 | | | |
| 1 | 0.017 | 0.014 | 0.006 | 0.03 | 0.024 |
| 2 | 0.023 | 0.019 | 0.007 | 0.055 | 0.048 |
| 3 | 0.018 | 0.017 | 0.008 | 0.04 | 0.032 |
| 4 | 0.024 | 0.022 | 0.012 | 0.04 | 0.028 |
| 5 | 0.022 | 0.015 | 0.003 | 0.078 | 0.075 |
| 6 | 0.027 | 0.021 | 0.008 | 0.06 | 0.052 |
| 7 | 0.019 | 0.016 | 0.01 | 0.026 | 0.016 |
| 1–7[a] | 0.021 | 0.019 | 0.013 | 0.028 | 0.015 |

[a] All 35 data have been taken into account.

**Table 5.** Estimated *T*/2 Values (Days) with Their Confidence Intervals and Range Based on Sample Types A and C

| sample | transformation | estimated *T*/2 values (days) mean | min | max | range |
|---|---|---|---|---|---|
| | | Sampling Method A | | | |
| 1 | sqrt 1st order | 1.27 | –0.3 | 2.8 | 3.1 |
| 2 | sqrt 1st order | 1.98 | –0.9 | 4.88 | 5.78 |
| 3 | sqrt 1st order | 2.78 | 0.57 | 5 | 4.43 |
| 4 | sqrt 1st order | 1.59 | –0.4 | 3.53 | 3.93 |
| 5 | 1.5th order | 4.27 | 3.23 | 5.3 | 2.07 |
| 6 | sqrt 1.5th order | 0.64 | –1 | 2.26 | 3.26 |
| 7 | sqrt 1st order | 1.33 | –0.2 | 2.88 | 3.08 |
| 1–7[a] | sqrt 1st order | 1.69 | 1.16 | 2.23 | 1.07 |
| | | Sampling Method C | | | |
| 1 | 1st order | 3.98 | 2.71 | 5.25 | 2.54 |
| 2 | 1st order | 4.21 | 2.32 | 6.1 | 3.78 |
| 3 | 1st order | 4.56 | 2.78 | 6.34 | 3.56 |
| 4 | sqrt 1st order | 2.12 | 0.6 | 3.65 | 3.05 |
| 5 | 1st order | 4.69 | 1 | 8.38 | 7.38 |
| 6 | sqrt 1st order | 1.19 | 0.1 | 2.28 | 2.18 |
| 7 | sqrt 1st order | 1.4 | 0.74 | 2.07 | 1.33 |
| 1–7[a] | 1.5th order | 3.24 | 2.4 | 4.08 | 1.68 |

[a] All 35 data have been taken into account.

sampling method C provided a more uniform estimate of the decline curve.

It is worth noting that different transformations (**Table 2**) gave the best fit for the residues measured in the replicate set of samples taken on the same days from the same field. For sample type A the square root 1st order gave the best fit in five cases; in addition, 1.5th and square root 1.5th orders were observed. For type C samples, 4 times the 1st order and 3 times the square root 1st order gave the best fit. The transformations giving the best fit gave significant correlation in all cases. The

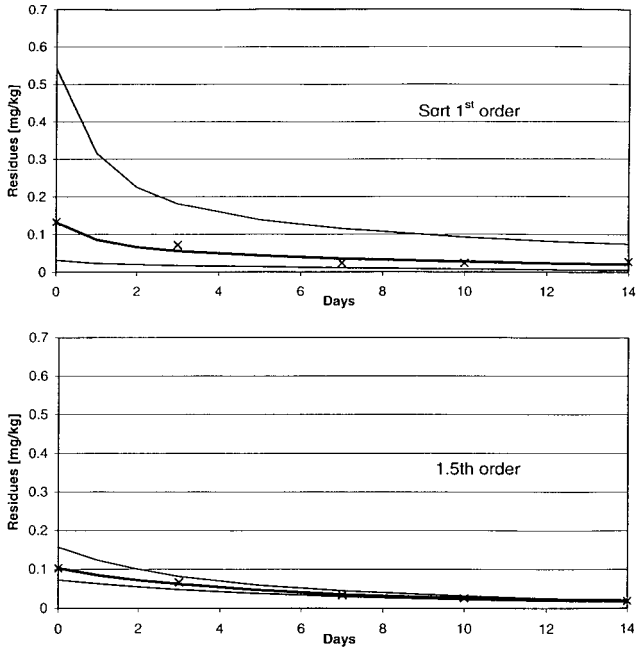


**Figure 2.** Decline curves with confidence intervals from sampling sites A2 (top) and A5 (bottom) obtained with sampling method A. *x* indicates the actually measured residues.

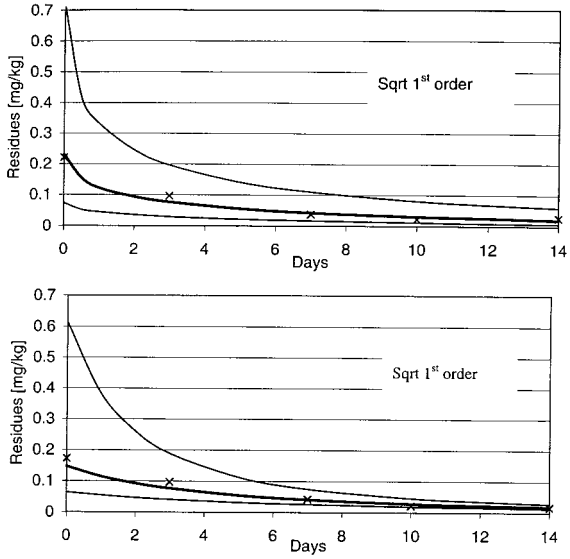


**Figure 3.** Decline curves with confidence intervals from sampling sites C6 (top) and C7 (bottom) obtained with sampling method C. *x* indicates the actually measured residues.

coefficient of determination ($r'^2$) and the significance of correlation ($S_{cor}$) are given in **Table 2**.

By applying the transformation that gave the best fit, the calculated residues and their confidence intervals were transformed back to the original system. Some examples of the estimated decline curves with their confidence intervals are given in **Figures 2** and **3**. The estimated mean residue values and their confidence intervals for days 0, 10, and 14 after treatment and the measured residues are given in **Tables 3** and **4**. **Figures 2** and **3** and the tabulated data clearly indicate the wide range within which residues can be expected. When the combined data sets obtained with seven replicate samples (35 data points) were used for the calculation of decline curves (indicated with 1−7[a] in **Tables 4** and **5**), the estimated confidence intervals, as expected, were much narrower than the range obtained from one set of samples, but they were still relatively large.

Similar variability of residues was observed on all sampling days with both sampling methods, as indicated by the CV values in **Table 2**. Because supervised trials are usually carried out by taking one or two samples at a time, the actual variability of residues cannot be realized. When the results of trials are evaluated, an apparent outlier should not be automatically discarded. The evaluator should have firm experimental evidence to disregard a residue value.

The calculated *T*/2 values, based on the best fit of residue data obtained from decline studies performed simultaneously on the same field, ranged from 0.64 to 4.7 days (**Table 5**). Even the estimates obtained with methods A and C, based on 35 data points for each sampling method, are significantly different. On the basis of sqrt 1st order and 1.5th order transformations the *T*/2 values were 1.7 ± 0.54 days (method A) and 3.2 ± 0.84 days (method C), respectively. The results indicate the expected variation, the uncertainty, of the results obtained from decline studies. Therefore, confidence intervals should always be given when an estimated value is reported. It should be noted that, because of the different ways of transformation of the residue values, *R*, the resulting confidence intervals are not directly comparable if a given set of data is evaluated by different models (*12*).

The seven sets of samples taken from one field indicate that sampling method C requires half of the number of primary samples as method A to provide similar results. It seems worthwhile to test the applicability of method C with additional field trials in comparison with other types of sampling methods. If these trials would confirm the presented findings, substantial savings could be achieved when samples must be shipped over long distances or have to be kept deep-frozen for extended periods before analysis.

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