

Soil Residues Following Repeat Applications of Diuron, Simazine, and Terbacil¹

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Abstract: Diuron, simazine, and terbacil were applied in field plots annually from 1981 to 1995. Soil was sampled at selected times after herbicide application in 1993, 1994, and 1995 to determine herbicide residue changes with time and soil depth. Diuron residues were found mainly in the upper 20 cm of soil; residue concentration decreased exponentially with time. Less than 1% of the initial concentration after application in summer was present the following spring. Terbacil residues were found in soil below the upper 20 cm. Terbacil degraded more slowly than diuron, and residues in spring were less than 30% the level of the previous summer. Simazine plus hydroxysimazine soil residues were present in all depths to 100 cm and were higher than diuron or terbacil at these depths. Simazine plus hydroxysimazine residues in spring were nearly 40% the level of the previous summer. With all three herbicides, soil residues were greatest in the upper 20 cm of soil during 2 to 3 wk following application. Data confirmed that diuron did not leach, whereas simazine can migrate through the soil. Terbacil migrated intermediately in depth relative to diuron and simazine. After 15 annual applications, herbicide residues were present but were not accumulating.

Nomenclature: Diuron, *N'*-(3,4-dichlorophenyl)-*N,N*-dimethylurea; simazine, 6-chloro-*N,N'*-diethyl-1,3,5-triazine-2,4-diamine; desethylsimazine, 2-chloro-4-(ethylamino)-6-amino-*s*-triazine; di-desethylsimazine, 2-chloro-4,6-diamino-*s*-triazine; hydroxysimazine, 2-hydroxy-4,6-bis(ethyl-amino)-*s*-triazine; terbacil, 5-chloro-3-(1,1-dimethylethyl)-6-methyl-2,4(1*H*,3*H*)-pyrimidinedione.

Additional index words: Herbicide movement.

Abbreviations: DAT, days after herbicide treatment; GC-MS, gas chromatography-mass spectrometry; HPLC-PDA, high-performance liquid chromatography with photodiode array detector; MS, mass spectrometry; ODS, octadecyl silane; SFE, supercritical fluid extraction.

INTRODUCTION

Diuron, simazine, and terbacil have been registered over 30 yr and have been applied repeatedly over many years in fruit orchards. These herbicides can accumulate in soil (Heeney et al. 1981; Machado-Neto and Victoria-Filho 1995) and may reduce vigor of nontarget species (Hogue and Neilsen 1988). Environmental pollution may also occur when herbicides such as simazine leach from soil and contaminate groundwater (Cohen et al. 1986).

Previous research demonstrated that these herbicides did not leach readily from the soil and did not accumulate in large quantities. Diuron and simazine can be biologically degraded and serve as a resource for some soil microbe populations (Behki and Khan 1994; Sheets 1964), but most biological activity is in the upper 20 cm of soil (Tworkoski and Welker 1996). While diuron, si-

mazine, and terbacil do not leach readily from soil (Dawson et al. 1968), repeated applications over several decades may contribute to residue accumulation in soil below the depth of high microbial activity, photodegradation, and oxidation. The objective of this research was to quantify residues of diuron, simazine, and terbacil from soil depths to 1 m where these herbicides were applied annually to the soil surface for more than 10 yr.

MATERIALS AND METHODS

Field. Plots (1.5 by 10 m) were selected in a randomized complete block design with four replications near Kearneysville, WV. A 3-m grass strip was maintained between replicates. Beginning in Spring 1981, simazine (Princep, 80% WP),³ diuron (Karmex, 80% dispersible granule), and terbacil (Sinbar, 80% WP) were applied at 4.5 kg ai/ha each year to separate plots. Soil was not

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³ Mention of a trademark, vendor, or proprietary product throughout this paper does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

Table 1. Properties of Hagerstown silt loam (fine, mixed, mesic typic Hapludalf) from experiment sites to 1-m depths.

| Depth | Particle size | | | Organic | | |
|--------|---------------|------|------|---------|--------|-----|
| | Sand | Silt | Clay | Acidity | Matter | CEC |
| cm | | | | | | |
| 0-20 | | | | | | |
| 20-40 | | | | | | |
| 40-60 | | | | | | |
| 60-80 | | | | | | |
| 80-100 | | | | | | |

disturbed and no crop was planted. Herbicides were applied over the top with a four-nozzle boom equipped with Delavan LF-5 tips on 50.8-cm spacing in a carrier volume of 549 L/ha. Herbicides were applied between the first weeks of May and June each year. In addition to herbicide treatments, control plots were maintained by mowing once each year during winter. The composition of the vegetation growing on experimental plots is reported in a companion paper (Tworkoski et al. 2000). Average weekly soil temperatures were recorded during 1993 and 1994, the years that soil residues were analyzed. Soil physical and chemical properties were determined.⁴

Soil. Soil was collected from each plot to a depth of 1 m using a 6.35-cm diam soil probe.⁵ The soil type was a Hagerstown silt loam (fine, mixed, Mesic Typic Hapludalf) (Table 1). Soil was sampled three times during 1993 and 1994: 1 wk before herbicide treatment (all depths), 14 d after treatment (DAT) (1994) or 21 DAT (1993) (10-cm depth only), and 58 DAT (1994) or 63 DAT (1993) (all depths). Soil was collected once in 1995, 98 DAT. The soil probe was cleaned between samples and only soil from the inner portion of the core was used for residue analysis. The soil was separated into five groups by depth: 0 to 20, 20 to 40, 40 to 60, 60 to 80, and 80 to 100 cm. Each group was analyzed separately and will be referred to by the midpoint depths, 10, 30, 50, 70, and 90 cm. The soil was air dried for 1 d, sieved through 2-mm mesh, homogenized, and stored at -3 C.

Chemicals. Analytical grade herbicide standards were obtained from the U.S. EPA, Pesticides & Industrial Chemicals Repository, Research Triangle Park, NC; Chem Service, West Chester, PA; and Axact Standards, Inc., New York, NY.

Supercritical Fluid Extraction. All supercritical fluid extraction (SFE) (HP 7680) used 4.0 g soil with 1 ml 0.35 N HCl added 1 h before extraction to ensure at least 15% moisture content. For diuron and terbacil, extraction conditions were modified from Wheeler and McNally (1989)—density, 0.79 g CO₂/ml; pressure, 351 bar; extraction temperature, 80 C—with 2% methanol as modifier. Static extraction was executed for 10 min followed by dynamic extraction for 13 min (5.7 thimble volumes). Extracts were collected on an octadecyl (C₁₈) silane (ODS) trap at 40 C and herbicides were eluted from the trap in 1.3 ml methanol.

Extraction conditions for simazine and simazine degradation products, were modified from Janda et al. (1989)—density, 0.9 g CO₂/ml; pressure, 350 bar; extraction temperature, 50 C—with 5% methanol as modifier. Static extraction was executed for 5 min followed by dynamic extraction for 15 min (5.5 thimble volumes). Extracts were collected on an ODS trap at 45 C, and herbicides were eluted from the trap in 1.3 ml methanol. Extraction efficiency was determined by applying formulated herbicides to soil so that the soil was thoroughly wet and then dried for 24 h. Mean recoveries (± standard deviation) of diuron, simazine, desethylsimazine, di-desethylsimazine, hydroxysimazine, and terbacil were 51.4 ± 5.3%, 46.9 ± 9%, 23.4 ± 4.4%, 6.0 ± 1.7%, 51.7 ± 5.2%, and 70.9 ± 5.6%, respectively. Recovery with SFE was lower than with organic solvent extraction, but the consistently low coefficients of variation for most analytes demonstrated that results were reliable and could be normalized (Tworkoski et al. 1996).

High-Performance Liquid Chromatography-Photodiode Array Detector. For all herbicides, methanol extracts from SFE were dried under reduced pressure and dissolved in 200 µl methanol, and 50 µl was injected in a Shimadzu⁶ high-performance liquid chromatograph, which was equipped with a Hewlett-Packard (HP)⁷ Lichrospher 100 RP-18 (5 µm) column, an autoinjector, and a photodiode array detector for high-performance liquid chromatography-photodiode array detector (HPLC-PDA) analysis. The gradient used was 10 to 25% acetonitrile in the first 6 min, 25 to 65% acetonitrile from 6 to 21 min, 65 to 100% acetonitrile from 21 to 23 min, and a methanol rinse before returning to start conditions (Steinheimer 1993). Fractions (0.5 ml) were collected, dried, and dissolved in methanol for mass spectrometry (MS, full-scan mode) verification of herbicide identity. The system and data analysis were controlled by the Shi-

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⁵ Giddings Machine Co., Inc., Fort Collins, CO 80522.

⁶ Shimadzu Scientific Instruments, Inc., Columbia, MD 21046.

⁷ Hewlett-Packard Co., Wilmington, DE 19808.

madzu EZChrom Chromatography Data System. Retention times and absorption maxima were: simazine, 14.98 min, 222 nm with minor peak at 265 nm; di-desethylsimazine, 3.82 min, 207 nm with minor peak at 255 nm; desethylsimazine, 9.72 min, 215 nm with minor peak at 261 nm; hydroxysimazine, 14.92 min, 221 nm; terbacil, 14.91 min, 213 and 280 nm; diuron 16.73 min, 210 and 251 nm with minor peak at 290 nm.

The quantitation limit of simazine and its degradation products was 1.0 ng/ μ l. Quantitation limits for terbacil and diuron were 10 and 5.0 ng/ μ l, respectively. The coefficients of determination for all standard curves were greater than 0.99 for a range from the quantitation limit to 50.0 ng/ μ l for simazine and diuron and 100.0 ng/ μ l for terbacil.

Gas Chromatography–Mass Spectrometry. Diuron, simazine, simazine degradation products, and terbacil were analyzed using an HP 5890 gas chromatograph with an HP 5971 mass-selective detector and autosampler for gas chromatography–mass spectrometry (GC-MS) analysis. The MS interface temperature was 315 C and a 100-ms dwell time was used. Approximately 25% of the herbicides that were quantitated by HPLC-PDA were confirmed for identity by MS in the full-scan mode. Periodically, the MS detector was operated quantitatively in selected ion monitoring (SIM) mode with the following ions being collected: 219 (diuron), 201 (simazine), 145 (di-desethylsimazine), 173 (desethylsimazine), and 161 (terbacil). Hydroxysimazine was not quantitated because it could not pass through the GC and, even with derivatization (methylation), it could not be quantitated by GC-MS. An isocyanate degradation product of diuron provided a reproducible standard curve, which was used to quantitate diuron since intact diuron is nearly impossible to recover with the GC parameters used (Grob 1981). Separation of herbicides was accomplished with a fused silica capillary column (15 m by 0.53 mm with a 0.50- μ m film thickness⁸). Gas chromatography conditions were: He carrier gas head pressure of 100 kPa; 260 C injector temperature; oven temperature ramp from 80 to 178 C (30 C/min), 178 to 190 C (2 C/min), and 190 to 310 C (30 C/min). Retention times of diuron, simazine, di-desethylsimazine, desethylsimazine, and terbacil were 15.4, 15.5, 14.7, 15.2, and 16.3 min, respectively.

The quantitation limit of simazine and its degradation products was 0.1 ng/ μ l. Quantitation limits for terbacil and diuron were 0.5 and 5.0 ng/ μ l, respectively. The coefficients of determination for all standard curves were

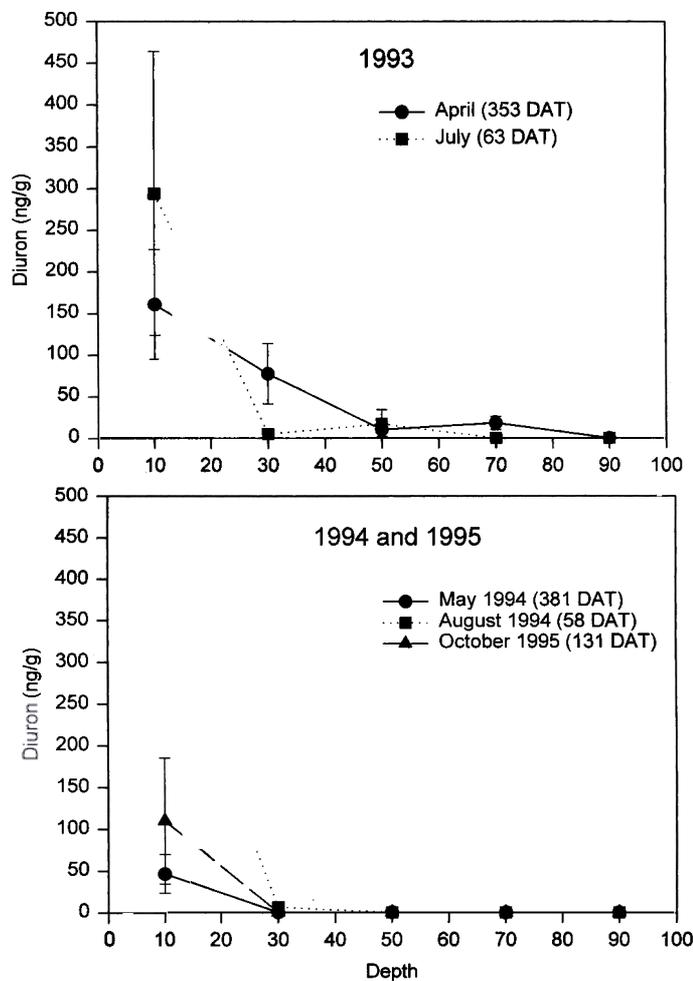


Figure 1. Relationship between diuron residues and soil depth at selected times.

greater than 0.98 for a range from the quantitation limit to 50.0 ng/ μ l.

RESULTS AND DISCUSSION

Herbicide Residues and Soil Depth. Soil was sampled to 100-cm depths in April and July 1993, May and August 1994, and October 1995. Interactions prohibited combining diuron data across sampling dates. Diuron residues decreased with depth in an exponential pattern (Figure 1, Table 2). Only samples from the April 1993 sampling date had diuron residues below the 50-cm depth. No diuron residues were found at depths greater than 70 cm. These results reinforce previous findings that large amounts of diuron do not leach from the upper 10 cm of soil (Dawson et al. 1968; Foy et al. 1996; Hill et al. 1955; Weldon and Timmons 1961).

Simazine residues were present in soil from most depths (Table 3). The biorefractory behavior of simazine

⁸ Supelco, Inc., Bellefonte, PA 16823.

Table 2. Coefficients of the regression for the relationship between soil residue concentrations of diuron and terbacil and soil depth at different time after treatment.^a

| Herbicide | Year | Month | b ₀ | b ₁ | r ² | |
|-----------|------|-------|----------------|----------------|----------------|------|
| Diuron | | | 4.0977 | -0.0415 | 0.30 | |
| | | | 4.1943 | -0.0558 | 0.50 | |
| | | | 1994 | 2.1016 | -0.0300 | 0.35 |
| | | | 4.4694 | -0.0617 | 0.56 | |
| Terbacil | 1995 | | 2.4101 | -0.0344 | 0.34 | |
| | | | 1993 | 6.4257 | -0.0245 | 0.25 |
| | 1994 | | 6.0286 | -0.0348 | 0.19 | |
| | | | 5.0009 | -0.0503 | 0.34 | |
| | | | 6.3924 | -0.0728 | 0.55 | |
| | | | 1995 | 5.1710 | -0.0583 | 0.39 |

^a The data were fitted to the equation $dC/dD = -kC$ by taking the natural log at the soil herbicide concentration and regressing it against depth.

can contribute to its persistence and may have led to leaching, despite its low water solubility (3.5 ppmw). Simazine residues were similar at all soil depths in April 1993, May 1994, and October 1995. Simazine residues decreased with depth only in July 1993 (63 DAT) and August 1994 (58 DAT). In July 1993 (63 DAT), simazine residues decreased linearly with depth [simazine soil residue (ng/g) = 503 - 1.1 (depth in cm); r² = 0.25; n = 20]. In August 1994 (58 DAT), simazine residues decreased linearly with depth [simazine soil residue (ng/g) = 679 - 4.6 (depth in cm); r² = 0.44; n = 17].

Evidence for simazine movement into soil has been inconsistent. Skroch et al. (1975) and Dawson et al. (1968) found little or no simazine below the top 15 cm of soil. However, simazine is classified as a leacher and has been detected in groundwater (Cohen et al. 1986; EPA 1992). Soil properties and environment likely affect simazine movement. Leaching to lower depths may occur in coarse soils with low organic matter, and simazine residues can cause damage to sensitive crops such as peach [*Prunus persica* (L.) Batsch] (Majek et al. 1984). Organic matter and warm, wet conditions facilitate decomposition of 2-chloro-s-triazines (Erickson and Lee 1989; Sheets 1970). Therefore, simazine may persist longer in soil where sunlight does not penetrate and where microbial populations are low. Persistence of atrazine [6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine] increased with soil depth to 60 cm. Below 60 cm, atrazine dilution probably occurred so that detection was limited (Sheets 1970). In the current study, simazine and simazine degradation products persisted in the deep soil.

Hydroxylation and dealkylation are major processes in the degradation of simazine. Simazine degrades to hydroxysimazine by chemical hydrolysis (Erickson and Lee 1989) and to dealkylated products by bacterial ac-

Table 3. Simazine residues in soils sampled at 0 to 100 cm deep during 1993, 1994, and 1995.

| Date sampled | Days after treatment | Simazine residue ^{a,b} depth (cm) | | | | |
|----------------------|----------------------|---|-----|-----|-----|--------|
| | | 10 | 30 | 50 | 70 | 90 |
| — ng/g soil dry wt — | | | | | | |
| April 1993 | 353 | 443 bc | 499 | 514 | 472 | 432 ab |
| June 1993 | 21 | 1,509 a | NM | NM | NM | NM |
| July 1993 | 63 | 520 bc | 370 | 495 | 512 | 337 ab |
| May 1994 | 381 | 331 c | 490 | 422 | 282 | 317 b |
| June 1994 | 14 | 1,392 a | NM | NM | NM | NM |
| Aug. 1994 | 58 | 704 b | 579 | 617 | 555 | 584 a |
| Oct. 1995 | 131 | 479 bc | 504 | 517 | 567 | 441 ab |

^a Within a column, means followed by the same letter do not differ at the 0.05 level of significance according to Waller-Duncan K-ratio *t* test. Simazine residues did not differ with date at depths 30, 50, and 70 cm.

^b NM, not measured.

tivity (Behki and Khan 1994). It is likely that hydroxysimazine was the dominant molecule in the simazine-hydroxysimazine fraction from shallow soil that was identified by HPLC-PDA. Simazine and hydroxysimazine had similar absorbance spectra and retention times. Hydroxysimazine may not be phytotoxic, but it degrades slowly and persists in soil (Khan and Marriage 1979). The water solubility of hydroxysimazine is probably lower than simazine due to pH-dependent tautomerism. Therefore, the simazine-hydroxysimazine fraction from deeper soil was probably simazine or hydroxysimazine that was formed after leaching. Dealkylated simazine residues do not persist. No dealkylated simazine was found in orchard soils treated with simazine for up to 9 yr (Kahn and Marriage 1979). Sorenson et al. (1993) determined that dealkylated products of atrazine did not accumulate in soil and could leach into groundwater. In the current experiment, no significant quantities of dealkylated simazine were found.

Depth, DAT, and the interaction of depth and DAT affected terbacil residues. Terbacil residues decreased with depth following an exponential pattern (Figure 2, Table 2). In general, terbacil concentrations approached zero at depths below 40 cm. In July 1993 (63 DAT), terbacil residue concentrations were high at all depths and dropped below 200 ng/g soil at depths below 60 cm but were not zero. These results generally agree with findings that terbacil did not leach readily in soil (Marriage et al. 1977; Skroch et al. 1975).

Herbicide Soil Residues and Time After Application.

To evaluate diuron dissipation with time, diuron soil concentrations at each depth were regressed against DAT. Since diuron residues were close to zero at depths below 10 cm regardless of DAT, only the regression at the 10-cm depth is presented. Diuron residues declined at the

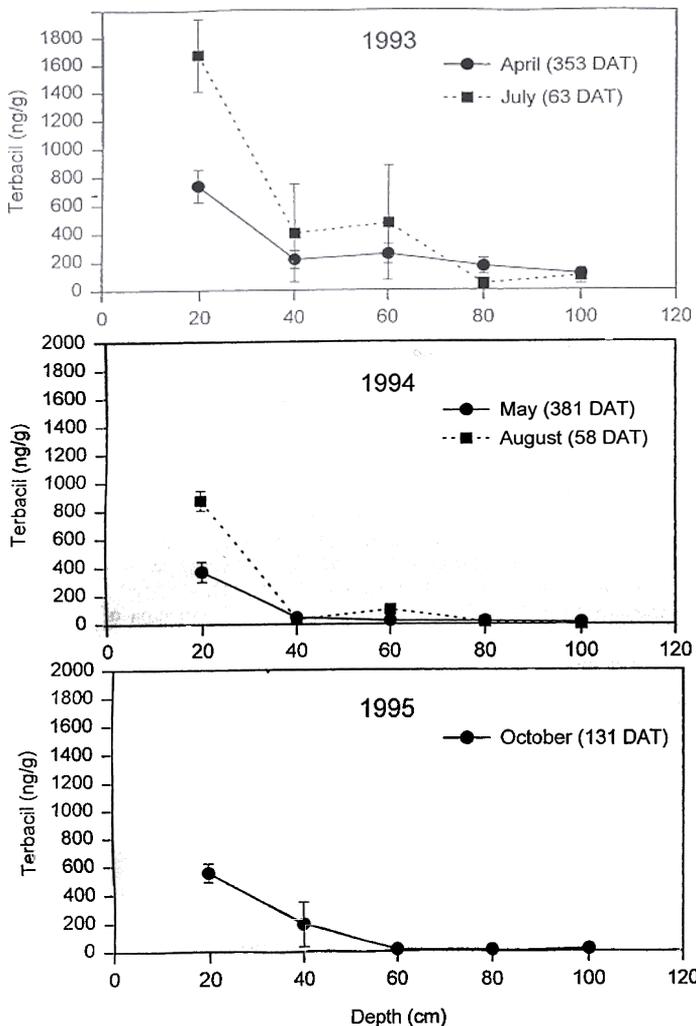


Figure 2. Relationship between terbacil residues and soil depth at selected times.

10-cm depth with increased time after treatment and by 125 DAT, diuron residues were close to zero (Figure 3, Table 4).

Reviewing 10 yr of research, Sheets (1964) found no evidence that diuron accumulated in soil when applied annually for 2 to 4 yr at rates of 2.2 to 4.5 kg/ha. *N*-phenyl urea herbicides hydrolyze readily in the environment, but there is a possibility that degradation products, such as 3,4-dichloroaniline, can occur. Our results are confirmation that repeated applications of diuron over 13 yr do not lead to soil accumulation. However, crop injury may occur when they are planted within 12 mo of diuron application at 4.5 kg/ha (Sheets 1964).

Soil was sampled only to the 10-cm depth in June 1993 and June 1994. Simazine residue concentrations at the 10-cm depth were affected by sampling date, with the highest concentrations in June 1994 (14 DAT) and

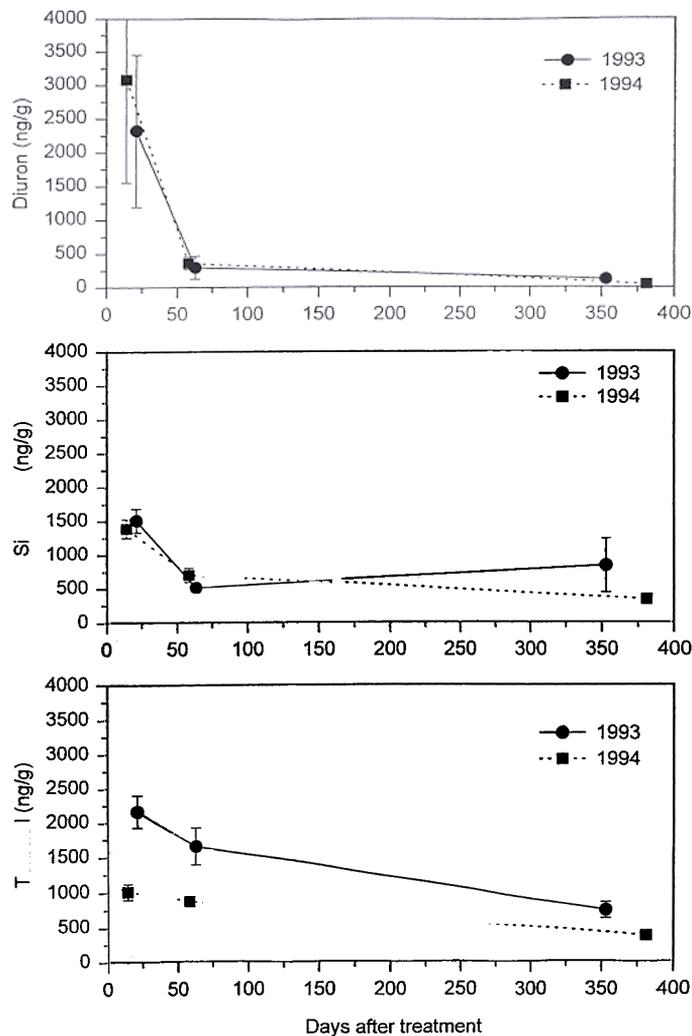


Figure 3. Relationship between diuron, simazine, and terbacil residues at the 10-cm soil depth and days after treatment.

June 1993 (21 DAT) (Figure 3, Table 3). Simazine soil residues decreased with increasing time after treatment (Table 4). Unlike diuron, simazine residues did not approach zero with increasing DAT. However, simazine residues were not increasing during this experiment, sug-

Table 4. Coefficients of the regression for the relationship between soil residue concentrations of diuron, simazine, and terbacil at the 10-cm soil depth and days after treatment.^a

| Herbicide | Year | b_0 | b_1 | r^2 |
|-----------|------|---------|-------|-------|
| Diuron | 1993 | -0.0541 | 0.64 | |
| | 1994 | -0.0113 | 0.67 | |
| Simazine | 1993 | -0.0029 | 0.41 | |
| | 1994 | -0.0033 | 0.74 | |
| Terbacil | 1993 | -0.0031 | 0.77 | |
| | 1994 | -0.0028 | 0.78 | |

^a The data were fitted to the equation $dC/dt = -kC$ by taking the natural log of the soil herbicide concentration and regressing it against days after treatment.

gesting that newly applied simazine was degrading or leaching in soil at a state of equilibrium. We were not able to distinguish simazine from hydroxysimazine, but previous research indicated that simazine was readily hydroxylated and that hydroxysimazine was much more persistent than simazine in soils (Erickson and Lee 1989; Kahn and Marriage 1979). Hydroxylated atrazine binds tightly to soil (Sorenson et al. 1993); thus, it is likely that at shallow depths, hydroxysimazine was the dominant soil residue.

After terbacil treatment, soil residues did not decrease with increasing time at 30, 50, 70, and 90 cm deep. There was a decrease in terbacil concentration with increasing time after application at the 10-cm depth during 1993 (Figure 3, Table 4). In previous research, terbacil residues were primarily terbacil and not intermediate degradation products 1 yr after application (Gardiner et al. 1969). Nearly one-third of the applied terbacil degraded to CO₂ within 7 wk after application, while the remaining terbacil was not degraded. Our results support these findings, in that terbacil soil concentrations decreased with time to a persistent concentration.

This experiment provided a view of the persistence of soil residues of three herbicides that have been commonly used in fruit culture for more than 30 yr. Diuron did not move more than 40 cm into soil and it did not accumulate. Terbacil was more persistent than diuron, but like diuron, significant residues were not found below 60 cm. In contrast, simazine or simazine degradation products were found at 100 cm, the deepest soil depth sampled. Ongoing research will determine whether the soil residues of this experiment will adversely affect growth of newly planted fruit trees.

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