Exhibit 2b, #27

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Persistence of Metribuzin and Metabolites in Two Subarctic Soils

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ABSTRACT

Persistence and leaching of ^{14}C-metribuzin [4-amino-6-(1,1-dimethyl)-3-(methylthio)-1,2,4-triazin-5(4*H*)-one] and metabolites were determined in Tanana (loamy, mixed, nonacid Pergelic Cryaquept) and Beales (sandy, mixed Typic Cryochrept) silt loam soils under irrigated potato (*Solanum tuberosum* L.) and dryland barley (*Hordeum vulgare* L.) conditions in the subarctic. Overall, dissipation of total ^{14}C (metribuzin and metabolites) was significantly slower ($P > 0.05$) in Tanana than Beales soil over the first 105 d, but by 468 d, the ^{14}C remaining (51% of applied) did not differ ($0.05 < P$) between soils. Initial degradation of metribuzin was rapid in both soils but was not significantly different between soils ($0.05 < P$). At 35 d after application 24% of applied metribuzin remained. At the end of the study (468 d), 5.0% of the applied metribuzin was still present. Unextractable residues accounted for the greatest amount of ^{14}C remaining in the soils. Of the extractable metabolites, greater amounts of desaminometribuzin were found in both soils than diketometribuzin or desaminodiketometribuzin. More water moved through the irrigated than nonirrigated soil as evidenced by bromide movement. Also, more ^{14}C moved to 15 to 22.5 cm depth in the irrigated than in the nonirrigated soil, but <1% of applied ^{14}C was detected below 22.5 cm for both soils and irrigation treatments. Rapid metribuzin degradation in combination with sorption processes minimized leaching of total metribuzin residues through these subarctic surface soils.

In field studies, some herbicides have been shown to degrade slower at high latitudes than at lower latitudes. For instance, Conn and Cameron (1988) found that 61% of triallate [*S*-(2,3,3-trichloro-2-propenyl)-bis(1-methylethyl)carbamothioate] applied was present at the end of the growing season in subarctic soils, while only 10 to 19% remained 5 mo after application in England (Fryer and Kirkland, 1970). Conn and Knight (1984) found that approximately twice as much trifluralin [2,6-dinitro-*N*, *N*-dipropyl-4-(trifluoromethyl)benzenamine] remained at the end of 1 yr in Alaska than in the same time in Saskatchewan (Smith and Hayden, 1976) and Manitoba (Prichard and Stobbe, 1980), Canada. Metribuzin [4-amino-6-(1,1-dimethyl)- 3-(methylthio)-1,2,4-triazin-5(4*H*)-one] persisted longer in Alaska (12% remaining after 115 d) (Conn and Cameron, 1988) than at Watkinsville, GA (Banks and Robinson, 1982) where all metribuzin had degraded within 40 d after application.

Long herbicide persistence in the high latitudes of the subarctic is because of cold soils. Subarctic soils can be frozen for 6 to 7 mo and summer soil temperatures at 5 cm and deeper are below 15°C most of the time (Siddoway et al., 1984; Knight and Lewis, 1986). Soil temperature plays a major role in determining rates of microbial degradation. For instance, dissipation half-life of metribuzin, which is microbially degraded (Moorman and Harper, 1989), was 16 d at 35°C and 377 d at 5°C (Hyzak and Zimdahl, 1974).

Degradation in subsurface soils is also generally reported to be slower than in surface soils. Temperature and moisture have been shown to affect degradation in subsurface soils (Bouchard et al., 1982). Decreased microbial populations and activities in subsurface soils compared to surface soils result in a decreased rate of degradation (Moorman and Harper, 1989).

As herbicide persistence increases, the potential for herbicide leaching also increases. Thus, the potential for herbicide leaching in the subarctic is higher than at lower latitude locations with similar soil texture and organic C content and rainfall. However, no studies have been conducted under subarctic conditions of leaching of pesticides such as metribuzin, which is commonly used for weed control in subarctic potato and spring barley production systems. Also, no studies have reported leaching of metribuzin metabolites under field conditions. Therefore, research was conducted to determine the dissipation of metribuzin and metribuzin metabolites in two soils under subarctic conditions near Fairbanks and Delta Junction, AK.

MATERIALS AND METHODS

Study Sites

Experiments were conducted at the Univ. of Alaska Agricultural and Forestry Experiment Station farms located at Fairbanks (latitude 65°N) and at Delta Junction (latitude 64°N). The climate at both sites is strongly continental and characterized by temperature extremes from −50 to 35°C. The mean annual temperature is −2.2°C at Fairbanks and −3.3°C at Delta Junction. Soils are frozen for 6 to 7 mo each year and when not frozen exhibit a sharp temperature gradient with depth. Temperatures at 15 cm seldom reach 15°C (Knight and Lewis, 1986). The average annual precipitation is 298 mm at Fairbanks and 390 mm at Delta Junction. More than 60% of the precipitation falls as rain. Potential evaporation has been calculated at 466 mm for Fairbanks and 450 mm for Delta Junction (Patrick and Black, 1968).

Soil Characteristics

The Fairbanks soil is Tanana silt loam and the Delta Junction soil is a Beales silt loam. Soils were collected from four profiles at each site and the composited soil was analyzed using methods reported in Graham and Conn (1992) for particle size, organic matter, and pH. These data and metribuzin sorption coefficients, K_f, 1/n, and K_{oc}, determined using the batch equilibration method, are summarized in Table 1. Coefficients from sorption isotherms were calculated using the linearized form of the Freundlich equation $\log x/m = \log K_f + (1/n) \log C$ where x/m is μmol herbicide sorbed per kg soil, C is μmol herbicide

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Abbreviations: a.i., active ingredient; K_f, intercept of the sorption isotherm; 1/n, slope of the sorption isotherm; K_{oc}, K_f corrected for soil organic C content; LSC, liquid scintillation counting; DA, desaminometribuzin; DK, diketometribuzin; DADK, desaminodiketometribuzin.

Table 1. Soil physical and chemical properties of Tanana and Beales silt loam soils.†

Soil	Depth	Clay	Silt	OC	pH	K_f	1/n	K_{oc}
	cm	%				$\mu mol^{-1/n} L^{1/n} kg^{-1}$		$\mu mol^{1-1/n} L^{1/1} kg^{-1}$
Tanana	0–15	14	71	3.8	6.5	1.3	0.92	34
	30–45	11	63	0.69	7.4	0.36	0.90	51
Beales	0–15	8.0	50	6.4	4.7	2.4	0.92	38
	30–45	8.0	25	0.74	5.1	0.30	0.90	51

† Data from Graham and Conn (1992).

per liter of supernatant solution after equilibration, and K_f and 1/n are intercept and slope of the sorption isotherm. K_{oc} is K_f corrected for soil organic C content.

Experiment Design

The study incorporated a randomized complete block design with two crop/soil moisture regimes (irrigated potato and dryland barley), two locations (Fairbanks and Delta Junction) and five blocks for each crop/moisture regime at each site. The plots were 4.6 × 9.1 m.

In 1990, 'Datal' barley (78 kg ha^{-1}) was planted into barley stubble using a no-till drill on 9 May at Delta Junction and on 11 May at Fairbanks. Fertilizer was banded between the rows at a rate of 101 kg ha^{-1} N, 56 kg ha^{-1} P_2O_5, and 45 kg ha^{-1} K_2O. Following disking, 'Shepody' potato were planted at Delta Junction on 14 May and at Fairbanks on 17 May 1990. Rows were 0.9-m apart and seed pieces were placed at 0.3-m intervals in the row using a single row assist feed planter. Granular fertilizer was applied at the rate of 146 kg ha^{-1} N, and 291 kg ha^{-1} of both P_2O_5 and K_2O by the planter in a band beside and below the seed. Potassium bromide, used to trace water movement, was applied at a rate of 98 kg ha^{-1} to the plots at Fairbanks on 17 May and Delta Junction on 18 May 1990 using a CO_2 backpack sprayer calibrated to deliver 355 L ha^{-1} at 208 kPa.

Field lysimeters were constructed by pushing four 10.2 cm diam., 91-cm long acrylonitrile butadiene plastic pipes into the soil of each plot using downward hydraulic pressure supplied from the blade of a crawler-type tractor. These lysimeters were installed on 5 June at Delta Junction and on 6 June 1990, at Fairbanks. An aliquot (1.0 mL) of ^{14}C-labeled metribuzin (2.26 kBq) (Mobay Chemical Corp.[1], Agric. Chem. Div., Kansas City, MO 64120) was applied dropwise to the surface of the soil in each lysimeter at Delta Junction on 6 June and at Fairbanks on 8 June 1990. The specific activity for metribuzin [5-^{14}C] was 770 MBq $mmol^{-1}$ and radiochemical purity was >97%, as determined by thin-layer chromatography.

Commercial metribuzin formulation (Sencor 75 DF) (Mobay Chemical Corp., Agric. Chem. Div., Kansas City, MO 64120) was applied to potato and barley plots on the same days that the lysimeters were installed, prior to emergence for potato and at the three to five leaf stage for barley. A CO_2 backpack sprayer was used to apply 0.83 kg a.i. ha^{-1} to barley and 1.0 kg a.i. ha^{-1} to potato. The sprayer was calibrated to deliver 239 L ha^{-1} at 208 kPa.

Potato plots were irrigated weekly based on gravimetric soil moisture measurements made from three soil cores in each location that were sectioned into 0 to 15, 15 to 30, and 30 to 45 cm depth increments. Moisture release curves generated for each depth increment and study site were used to determine the amount of water to add to bring the soil to field capacity. A single line of RAIN BIRD sprinklers (1800 series, MPR-15SQ) (RAIN BIRD Inc., Glendora, CA 91740) delivering 69.1 mm h^{-1} of rain at 208 kPa and 4.6 m spacing was used to irrigate the potato plots. A series of cans was used to measure the amount of water distributed by the irrigation system and to determine when the pre-determined amount of water had been applied to the plots.

Barley and potato were planted at Delta on 21 to 22 May and at Fairbanks on 23 to 24 May 1991, using the same seeding and fertilizer rates and implements described for 1990. No additional potassium bromide or herbicide was applied. The irrigation method for potato was the same as in 1990.

Soil Sampling and Preparation

Replicate lysimeters were removed on 11 July, 15 Aug., 19 Sept. 1990; and 21 May and 17 Sept. 1991. The lysimeters were capped and kept at −20°C until analysis. Soil cores were obtained for bromide analysis on the same dates as lysimeter removal using a "zero contamination" JMC probe (22 mm diam.) (Clements Assoc. Inc., Newton, IA 50208). Three samples were obtained in each plot to 90-cm depth. Bromide samples were kept at −20°C in acetate liners until analyzed.

The soil columns were thawed at room temperature for 16 h. A table saw was used to make two longitudinal cuts most of the way through the plastic and a utility knife was used to complete the cuts. The top half of the plastic column was removed. The soil in each column was sectioned into five depth intervals: 0 to 7.5; 7.5 to 15; 15 to 30; 30 to 45 and 45 to 60 cm. Subsamples were taken from each depth from each column for determination of soil moisture, total radioactivity, and metribuzin and metabolites. Samples were held at −15°C until analysis.

Chemical Extraction and Analyses

Three subsamples in soil at each sampling time from each depth and replicate were analyzed for ^{14}C using a Packard 306 Sample Oxidizer (Packard Instruments Co., Downers Grove, IL 60515). Soil (0.4 g) was mixed with 0.1 g of microcystalline cellulose and placed in a paper cone and combusted for 2 min. Carbon dioxide was trapped in 8 mL of CARBO-SORB. This solution was mixed with 12 mL of PERMAFLUOR E+ (Packard Instruments Co., Downers Grove, IL 60515) and radioactivity (^{14}C) was determined by liquid scintillation counting (LSC) using a Packard 2250CA Tri-carb scintillation analyzer (Packard Instruments Co., Downers Grove, IL 60515).

To determine extractable ^{14}C in soil, duplicate 12-g soil samples were mixed with 12 mL of 0.01 *N* $CaCl_2$ in 50-mL glass centrifuge tubes and shaken for 48 h on platform shaker at 325 rpm. After centrifuging (759 × *g* for 30 min), the supernatant was decanted, weighed, and transferred to a 20-mL scintillation vial. To determine total ^{14}C activity in this supernatant, 1 mL of supernatant was transferred to a 7-mL scintillation vial, 5 mL of scintillation counting solution was added, and ^{14}C activity was determined.

After $CaCl_2$ extraction, the soil remaining in the centrifuge tube was extracted again with 36 mL 4:1 methanol/water (v/v). After shaking for 6 h, the tubes were centrifuged and the supernatant transferred to a 50-mL conical tube. An additional 33 mL of 4:1 methanol/water (v/v) was added to the soil and the mixture was shaken for 16 h. After this mixture was centrifuged, the two supernatants were combined and the methanol evaporated using compressed air and a 50°C water bath until only water remained. Carbon-14 in the remaining aqueous

[1] Mention of a trademark, vendor, or proprietary product does not constitute a guarantee or warranty of the product by USDA and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

Table 2. Dissipation of ^{14}C in Tanana silt loam soil.

Crop	Depth	Days after application 35	70	105	349	468
	cm	% of ^{14}C applied remaining				
Potato	0–7.5	49.7 ± 11.6†	64.3 ± 11.9	78.7 ± 27.0	27.4 ± 8.5	32.4 ± 1.0
	7.5–15	6.66 ± 4.01	5.61 ± 6.04	ND‡	4.93 ± 0.10	10.6 ± 4.58
	15–22.5	0.70 ± 0.33	0.43 ± 0.15	1.40 ± 0.34	1.65 ± 0.64	2.49 ± 0.20
	22.5–30	0.40 ± 0.12	0.25 ± 0.04	ND	0.47 ± 0.36	0.39 ± 0.14
	30–45	0.50 ± 0.29	0.36 ± 0.15	ND	0.17 ± 0.17	0.32 ± 0.11
	45–60	0.16 ± 0.11	0.33 ± 0.10	0.48 ± 0.13	0.03 ± 0.02	ND
	Total	58.9 ± 7.1	71.2 ± 6.8	80.8 ± 13.4	33.2 ± 8.3	46.2 ± 3.8
Barley	0–7.5	103.1 ± 36.0	58.3 ± 42.3	78.1 ± 36.4	81.65 ± 5.40	59.4 ± 20.8
	7.5–15	2.0 ± 1.2	5.67 ± 2.52	ND	2.73 ± 1.11	5.85 ± 2.98
	15–22.5	0.22 ± 0.03	0.38 ± 0.11	1.22 ± 0.50	0.15 ± 0.21	0.41 ± 0.18
	22.5–30	0.15 ± 0.03	0.24 ± 0.06	ND	0.03 ± 0.05	0.07 ± 0.04
	30–45	0.19 ± 0.05	0.30 ± 0.12	0.39 ± 0.21	ND	ND
	45–60	0.10 ± 0.07	0.03 ± 0.05	0.24 ± 0.11	ND	0.01 ± 0.01
	Total	106.0 ± 36.7	64.0 ± 43.1	79.9 ± 36.2	84.6 ± 6.8	65.8 ± 22.8

† Mean and standard deviation.
‡ ND = not detected.

fraction was determined on a 1-mL aliquot as previously described.

The ^{14}C in the soil remaining after extraction was determined by combustion as previously described. This ^{14}C was considered bound residue. Percent moisture of this soil was determined by drying another portion of each sample to constant weight at 60°C after allowing methanol to evaporate.

Aqueous supernatants from the $CaCl_2$ and methanol/water extractions were individually extracted with chloroform to separate the polar and nonpolar ^{14}C-compounds. Each supernatant was transferred to a 125-mL separatory funnel and extracted three times using 5 mL of chloroform each time. The chloroform extract was dried by passing it through phase separatory paper into a 50-mL conical tube. Carbon-14 activity in chloroform was determined from total chloroform weight and counting radioactivity in 1-g solution with 15 mL of scintillation cocktail. Unextractable ^{14}C remaining in each aqueous phase was considered to be unidentified polar metabolites. To determine ^{14}C activity in the water, the total weight of water was determined and then 1 g of water was transferred to a 7-mL scintillation vial, 5 mL of cocktail added, and counted using LSC.

Bromide was measured in 50 g moist soil in 100 mL of distilled water using an Orion Model 94-35 bromide electrode (Orion Research Inc., Boston, MA 02129) and a single junction reference electrode with an expanded scale pH meter. A standard curve was developed relating bromide concentration to corresponding millivolt readings from the bromide electrode. Bromide concentrations were determined by relating the millivolt readings to the standard curve.

HPLC Separation of Metribuzin and Metabolites

One drop of decanol was added to the chloroform extract, the chloroform evaporated, and 1 mL of methanol added. The resulting solution was passed through a 0.45 μm nylon filter. The samples were then evaporated to near dryness and redissolved in 0.5 mL of 1:1 (v/v) methanol/water. Standards of metribuzin, desaminometribuzin (DA), diketometribuzin (DK), and desaminodiketometribuzin (DADK) were used to determine retention times on a Hewlett Packard 1090 HPLC (Hewlett-Packard Co., Avondale, PA 19311) equipped with a diode array detector, and Adsorbosphere-C18-5 micron column (Alltech Assoc. Inc., Deerfield, IL 60015) (250 × 4.6 mm i.d.). The mobile phase was methanol:0.05% acetic acid (43:57, v/v) with a flow rate of 1.0 mL min^{-1}. Injection volume was 100 μL. Retention times for DK, DADK, metribuzin, and DA were 10.4, 13.1, 21.4, and 23.2 min, respectively. A fraction collector was used to collect metribuzin and metabolites after passing through the HPLC column. Carbon-14 activity of each fraction was determined by LSC.

Statistical Analysis

The experiment was analyzed as a randomized complete block design with two crop/soil moisture regimes and two

Table 3. Dissipation of total ^{14}C in Beales silt loam soil.

Crop	Depth	Days after application 35	70	105	349	468
	cm	% of ^{14}C applied remaining				
Potato	0–7.5	59.8 ± 33.5†	35.00 ± 9.5	45.3 ± 17.9	50.9 ± 15.6	39.1 ± 9.3
	7.5–15	0.31 ± 0.09	0.60 ± 0.44	0.92 ± 0.80	2.22 ± 1.32	6.09 ± 3.83
	15–22.5	0.21 ± 0.06	0.12 ± 0.09	0.18 ± 0.08	0.50 ± 0.50	8.82 ± 6.13
	22.5–30	0.10 ± 0.05	0.18 ± 0.17	0.20 ± 0.20	ND‡	0.10 ± 0.04
	30–45	0.19 ± 0.09	0.03 ± 0.05	0.10 ± 0.10	ND	0.05 ± 0.05
	Total	60.6 ± 16.7	36.0 ± 4.7	46.8 ± 8.9	53.6 ± 17.4	46.2 ± 4.3
Barley	0–7.5	68.1 ± 37.9	31.3 ± 16.1	41.2 ± 23.5	27.9 ± 0.0	44.3 ± 19.1
	7.5–15	0.31 ± 0.26	0.13 ± 0.13	2.45 ± 1.27	1.77 ± 0.11	2.38 ± 1.73
	15–22.5	0.20 ± 0.24	0.01 ± 0.01	0.38 ± 0.16	0.01 ± 0.02	1.05 ± 0.12
	22.5–30	0.05 ± 0.06	0.03 ± 0.03	0.14 ± 0.11	ND	ND
	30–45	0.05 ± 0.09	0.06 ± 0.06	0.10 ± 0.10	ND	ND
	Total	68.7 ± 38.0	31.5 ± 16.3	44.3 ± 24.5	29.7 ± 0.1	47.7 ± 20.8

† Mean and standard deviation.
‡ ND = not detected.

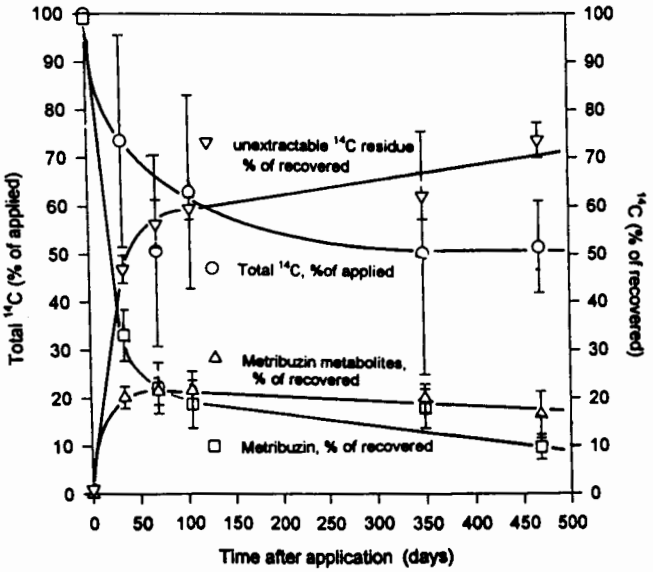

Fig. 1. Dissipation of ^{14}C-metribuzin in Beales and Tanana silt loam soils. Error bars are standard deviations about the mean.

locations (soils) with five blocks. A separate analysis of variance was performed for each sampling date. Percent data were arc-sine transformed prior to analysis.

RESULTS AND DISCUSSION

Carbon-14 Dissipation

Overall dissipation of ^{14}C was significantly slower ($P > 0.05$) in the Tanana silt loam soil than in the Beales soil over the first 105 d after application. At 105 d after application, 80% of applied ^{14}C remained in Tanana soil compared to 45% in Beales soil (Tables 2 and 3). However, by 468 d after application, amounts of ^{14}C remaining in both soils were not significantly different. An average of 51% of applied ^{14}C could be accounted for in both soils throughout the soil profile from 70 to 468 d after application (Fig. 1). The loss of ^{14}C probably is because of a combination of mineralization to $^{14}CO_2$, leaching, and volatilization. Moorman and Harper (1989) reported up to 20% of ^{14}C-ring-labeled metribuzin mineralized to $^{14}CO_2$ in a laboratory experiment. Leaching, discussed in detail below, could not be confirmed to be a major process contributing to ^{14}C loss from the soils. Averaged over both soils, <1.0% of applied ^{14}C was detected below 22 cm at any of the five sampling times from 35 to 468 d after application. Volatilization was not measured in our experiment.

Carbon-14 Movement

Throughout the 468 d of the experiment, the majority of the ^{14}C was found at the 0 to 7.5 cm depth (Tables 2 and 3). However, at 35 d after application, ^{14}C was found to depths of 60 and 45 cm in Tanana and Beales soils, respectively. Amounts of ^{14}C, too small to positively identify whether metribuzin or metabolites, were also found throughout the soil profile during the course of the experiment. For instance, through 105 d after application, <2% of the applied was found below 15 cm in both soils compared to 2 to 7% and 0.1 to 3% at depth 7.5 to 15 cm in the Tanana and Beales soils, respectively. At 349 and 468 d after application, the greatest amounts of ^{14}C detected deeper than in the top 7.5 cm of soil were found at depth 7.5 to 15 cm in both soils but did not exceed 11% of applied. Less than 1% of the applied ^{14}C was found below 22 cm.

These results are in agreement with those reported by Burgard et al. (1994) where metribuzin appeared to remain in the top 15 cm of soil under irrigated potato production loamy sand in east-central Minnesota in spite of water movement to the bottom of the analyzed profile (90−105 cm). In other studies, metribuzin did not leach past 30 cm in non-irrigated sandy loam (Nicholls et al., 1982; Walker, 1978) or furrow-irrigated clay (Hyzak and Zimdahl, 1974) and reached 38 cm in irrigated sandy loam soil (Jones et al., 1990). In contrast, Logan et al. (1994) found small amounts of metribuzin in tile drain water. These studies determined movement of parent metribuzin only, while our study determined movement of total ^{14}C metribuzin residues, that is, parent and metabolites.

In our study, bromide was applied 20 d prior to metribuzin application. On the day of metribuzin application,

Table 4. Bromide distribution in Tanana silt loam soil.

Crop	Depth	Days after metribuzin application							
		0	10	38	69	105	349	406	465
	cm	mg kg⁻¹							
Barley	0–7.5	16.9 ± 5.9†	23.3 ± 10.0	1.9 ± 0.6	2.9 ± 1.2	3.1 ± 3.1	1.4 ± 0.3	1.8 ± 0.9	3.9 ± 1.5
	7.5–15	–‡	–	4.5 ± 2.3	6.9 ± 2.0	2.0 ± 0.6	2.3 ± 0.4	3.4 ± 1.6	5.1 ± 1.3
	15–22.5	3.0 ± 1.6	1.4 ± 1.1	9.7 ± 3.0	5.4 ± 1.1	4.4 ± 1.5	5.4 ± 1.5	3.5 ± 1.3	4.3 ± 1.4
	22.5–30	–	–	1.7 ± 1.2	0.8 ± 0.2	5.0 ± 1.2	4.1 ± 1.1	2.8 ± 0.8	3.0 ± 1.6
	30–45	2.2 ± 1.4	0.5 ± 0.2	0.7 ± 0.1	0.5 ± 0.1	2.6 ± 0.8	2.6 ± 1.4	2.4 ± 0.7	2.8 ± 2.7
	45–60	1.4 ± 0.6	0.5 ± 0.2	0.7 ± 0.1	0.6 ± 0.2	0.7 ± 0.2	0.4 ± 0.1	1.4 ± 0.3	0.8 ± 0.4
	Total	23.5	25.7	19.2	17.1	17.8	16.2	15.3	19.9
Potato	0–7.5	21.7 ± 5.9	22.4 ± 5.8	3.3 ± 4.6	1.1 ± 0.5	2.8 ± 1.3	5.6 ± 2.3	0.9 ± 0.4	0.6 ± 0.3
	7.5–15	–	–	5.9 ± 2.7	4.1 ± 3.1	0.6 ± 0.2	2.2 ± 1.0	0.8 ± 0.3	0.4 ± 0.3
	15–22.5	3.4 ± 0.8	0.8 ± 0.2	3.6 ± 2.2	3.9 ± 1.6	1.5 ± 1.5	2.8 ± 1.4	0.6 ± 0.3	0.6 ± 0.3
	22.5–30	–	–	0.6 ± 0.2	1.9 ± 1.6	3.5 ± 2.9	2.0 ± 0.7	0.7 ± 0.4	0.6 ± 0.4
	30–45	2.1 ± 0.7	0.5 ± 0.2	0.5 ± 0.2	1.4 ± 1.6	2.1 ± 1.0	1.8 ± 0.8	0.9 ± 0.8	0.6 ± 0.5
	45–60	2.0 ± 1.3	0.6 ± 0.1	0.7 ± 0.2	0.7 ± 0.3	1.3 ± 0.7	1.3 ± 1.0	0.9 ± 0.7	0.6 ± 0.4
	Total	29.2	24.3	14.6	13.1	11.8	15.7	4.8	3.4

† Mean and standard deviation.
‡ 7.5 to 15 cm were composited with 0 to 7.5 cm depth at 0 and 10 d after application.

Table 5. Bromide distribution in Beales silt loam soil.

Crop	Depth	Days after metribuzin application							
		0	7	35	69	104	349	406	468
	cm	mg kg^{-1}							
Barley	0–7.5	30.1 ± 3.1†	15.2 ± 4.7	14.2 ± 2.0	21.8 ± 8.1	0.7 ± 0.4	2.4 ± 1.1	0.9 ± 0.6	2.8 ± 1.1
	7.5–15	–‡	–	0.6 ± 0.2	0.8 ± 0.4	1.6 ± 1.4	3.4 ± 1.7	1.9 ± 1.4	3.6 ± 1.0
	15–22.5	0.6 ± 0.1	0.4 ± 0.1	0.4 ± 0.0	0.5 ± 0.1	3.4 ± 1.0	2.8 ± 1.5	0.8 ± 0.5	1.4 ± 0.4
	22.5–30	–	–	0.3 ± 0.0	0.4 ± 0.1	1.5 ± 1.2	0.7 ± 0.2	0.8 ± 0.8	0.4 ± 0.1
	30–45	0.5 ± 0.0	0.3 ± 0.0	0.4 ± 0.0	0.4 ± 0.0	0.9 ± 0.7	0.4 ± 0.2	0.4 ± 0.2	0.2 ± 0.1
	45–60	0.5 ± 0.1	0.3 ± 0.0	0.5 ± 0.1	0.6 ± 0.1	0.8 ± 0.6	–	0.3 ± 0.1	0.2 ± 0.0
	Total	31.7	16.2	16.4	24.5	9.1	9.7	5.1	8.6
Potato	0–7.5	34.1 ± 12.1	32.5 ± 5.6	20.3 ± 3.9	3.7 ± 0.8	11.6 ± 5.0	20.5 ± 12.1	2.1 ± 1.2	0.5 ± 0.2
	7.5–15	–	–	1.8 ± 1.6	0.9 ± 0.2	3.3 ± 1.3	3.0 ± 1.0	3.9 ± 0.9	0.3 ± 0.1
	15–22.5	0.43 ± 0.2	0.8 ± 0.9	0.4 ± 0.1	0.4 ± 0.3	1.6 ± 1.0	1.3 ± 0.4	2.4 ± 1.2	0.3 ± 0.1
	22.5–30	–	–	0.4 ± 0.1	0.3 ± 0.0	0.7 ± 0.3	1.0 ± 0.8	1.1 ± 0.8	0.4 ± 0.3
	30–45	0.44 ± 0.1	0.3 ± 0.1	0.4 ± 0.1	0.3 ± 0.1	0.7 ± 0.2	1.0 ± 0.5	0.5 ± 0.2	0.7 ± 0.3
	45–60	0.7 ± 0.3	0.4 ± 0.1	0.5 ± 0.0	0.5 ± 0.1	0.8 ± 0.2	–	–	0.6 ± 0.3
	Total	35.7	34.0	23.8	6.1	18.7	26.8	10.0	3.1

† Mean and standard deviation.
‡ 7.5 to 15 cm were composited with 0 to 7.5 cm depth at 0 and 7 d after application.

bromide was detected throughout the profile; however, 73 and 95% of bromide in the profile was in the top 15 cm of Tanana and Beales soils, respectively (Tables 4 and 5). An average of 93% of the bromide in the profiles of both soils under both cropping systems was in the surface 15 cm 7 to 10 d after metribuzin application.

By 38 d after metribuzin application, bromide had moved to lower depths of the Tanana soil. Averaged over both crops, 70% of the bromide in the profile was in the 7.5 to 22.5 cm depth (Table 5). By Day 105, 45% of the bromide was at the 22.5 to 45 cm depth. In contrast, at Day 104 in the Beales soil, 54 and 12% of the bromide was at depth 15 to 30 cm in barley and potato, respectively. More bromide remained after 465 d under dryland barley ($P > 0.01$) than under irrigated potato production (Tables 4 and 5), suggesting that more water moved through the profile under irrigated conditions. In both soils, more ^{14}C moved to the 15 to 22.5 cm depth under irrigated conditions (Tables 2 and 3), however, irrigation did not move ^{14}C below 22.5 cm.

Metribuzin Degradation

Initial dissipation of metribuzin was rapid in both soils. At 35 d after application, an average of 33% of ^{14}C remaining in the soil was metribuzin (24% of initially applied metribuzin) (Fig. 1). Of ^{14}C remaining 105 d after application, an average of 19% was metribuzin (equivalent to 10% of initially applied metribuzin). There was no metribuzin dissipation over the winter months while the soil was frozen; 18% of ^{14}C remaining in the soil was metribuzin at 349 d after application (9% of initially applied metribuzin). Dissipation resumed during the spring. At the end of the experiment, 10% of remaining ^{14}C was metribuzin (5% of initially applied metribuzin). These data are similar to those of Conn and Cameron (1988) who found 13% of applied metribuzin remained 1 yr after application in the surface 15 cm of Volkmar (coarse-silty over sandy or sandy-skeletal, mixed Aquic Chryochrepts) and Beales silt loam soils. Burgard et al. (1994) found 17% of metribuzin applied to a loamy sand soil remaining in the top 45 cm of soil 1 yr after application.

Metribuzin made up a larger fraction of the remaining ^{14}C in the Beales than in the Tanana silt loam (Tables 6 and 7) on all sampling dates although not significantly different on all sampling dates. The lower pH of the Beales soil (4.7) vs. the Tanana soil (6.5) may have contributed to slower metribuzin degradation. Ladlie et al. (1976) found that dissipation of metribuzin decreased with a decrease in soil pH from 6.7 to 4.6.

Metribuzin degraded to several metabolites, including DA, DK, and DADK (Tables 6 and 7). There were also unknown nonpolar and polar metabolites. In the surface soils, the greatest amount of ^{14}C was in the form of unextractable ^{14}C residues ($P < 0.01$). Greater amounts of DA were found in both soils than DK or DADK ($P <$

Table 6. Product distribution of ^{14}C in 0 to 7.5 cm depth Beales silt loam soil as a function of time.

Crop	Days after application	Metribuzin	DA	DK	DADK	Unknown	Polar	Unextractable
		% of ^{14}C remaining						
Potato	35	39.6 ± 10.7†	7.5 ± 3.0	1.5 ± 0.3	1.2 ± 0.8	0.4 ± 0.3	6.8 ± 1.4	43.1 ± 6.2
	70	24.9 ± 9.8	5.6 ± 1.2	1.5 ± 0.5	1.6 ± 0.6	1.4 ± 1.5	7.3 ± 1.2	57.8 ± 8.1
	105	24.5 ± 6.2	6.0 ± 2.4	1.8 ± 0.8	1.9 ± 0.6	1.2 ± 0.8	8.0 ± 1.6	56.5 ± 4.9
	349	16.6 ± 1.3	8.6 ± 4.1	0.8 ± 0.2	2.1 ± 0.1	1.7 ± 0.7	9.2 ± 1.1	61.1 ± 3.9
	468	12.3 ± 2.5	3.5 ± 0.2	0.9 ± 0.4	1.7 ± 0.3	0.7 ± 0.5	7.0 ± 0.7	74.0 ± 2.9
Barley	35	35.0 ± 4.8	8.0 ± 4.5	1.9 ± 0.4	1.4 ± 0.6	0.7 ± 0.3	7.1 ± 1.6	46.0 ± 4.9
	70	28.1 ± 5.2	8.9 ± 4.5	1.8 ± 0.7	1.9 ± 1.1	0.7 ± 0.5	9.5 ± 2.8	49.2 ± 9.1
	105	20.4 ± 4.0	6.3 ± 3.0	1.4 ± 0.2	1.8 ± 0.5	0.7 ± 0.5	7.8 ± 0.5	61.7 ± 4.9
	349	18.7 ± 4.5	8.1 ± 2.3	0.8 ± 0.4	2.7 ± 0.6	0.5 ± 0.2	9.4 ± 0.3	60.0 ± 8.2
	468	11.5 ± 1.6	3.7 ± 1.1	0.9 ± 0.5	2.4 ± 0.9	0.4 ± 0.3	9.2 ± 1.7	72.0 ± 4.0

† Mean and standard deviation.

Table 7. Product distribution of ^{14}C in 0 to 7.5 cm depth Tanana silt loam as a function of time.

Crop	Days after application	Metribuzin	DA	DK	DADK	Unknown	Polar	Unextractable
		% of ^{14}C remaining						
Potato	35	29.5 ± 6.8†	6.0 ± 2.3	2.1 ± 1.0	1.8 ± 0.3	1.3 ± 0.9	10.4 ± 0.7	49.0 ± 4.8
	70	16.4 ± 3.7	5.9 ± 1.5	1.7 ± 0.7	2.4 ± 0.8	0.8 ± 0.6	11.9 ± 1.1	60.9 ± 2.8
	105	12.5 ± 2.6	5.2 ± 2.7	1.5 ± 0.8	3.4 ± 1.1	1.3 ± 0.9	15.1 ± 3.2	61.0 ± 5.4
	349	14.5 ± 10.3	2.8 ± 1.3	0.7 ± 0.6	1.1 ± 0.4	1.2 ± 1.1	10.4 ± 0.8	69.3 ± 7.8
	468	8.9 ± 0.3	2.9 ± 1.8	0.3 ± 0.1	0.7 ± 0.1	0.5 ± 0.3	8.1 ± 0.6	78.6 ± 1.9
Barley	35	28.2 ± 1.9	9.5 ± 3.1	1.3 ± 0.2	2.0 ± 0.4	1.8 ± 0.4	7.9 ± 1.4	49.4 ± 5.3
	70	19.3 ± 4.7	5.1 ± 2.4	1.3 ± 0.7	3.1 ± 0.8	1.0 ± 0.9	12.7 ± 1.6	57.5 ± 3.6
	105	17.7 ± 5.0	5.2 ± 2.0	1.5 ± 0.9	2.8 ± 0.6	0.8 ± 0.6	13.0 ± 1.8	59.1 ± 4.5
	349	24.1 ± 4.3	2.5 ± 1.8	1.6 ± 0.6	2.0 ± 0.3	1.5 ± 1.2	9.8 ± 0.7	58.5 ± 2.5
	468	6.5 ± 0.0	5.2 ± 0.0	1.3 ± 0.0	2.8 ± 0.0	2.3 ± 0.0	11.8 ± 1.7	70.1 ± 0.0

† Mean and standard deviation.

0.05) except for Day 349 in Tanana soil. After 70 d in the field, there was generally more DADK than DK in both soils. In contrast, Moorman and Harper (1989) and Webster and Reimer (1976) recovered more DK than DA in surface soils. The differences between our study and those of Moorman and Harper (1989) and Webster and Reimer (1976) are probably not significant, however.

In summary, dissipation of metribuzin appeared to proceed rapidly in subarctic soils and does not appear to readily move downward. It also appears that metabolites of metribuzin do not move in appreciable quantity. Therefore use of this herbicide would not have an adverse impact on environmental quality. The question remains, however, as to whether the bound residues will be slowly available in the future. Additional research is needed on long-term bioavailability of bound residues.

REFERENCES

Banks, P.A., and E.L. Robinson. 1982. The influence of straw mulch on the soil reception and persistence of metribuzin. Weed Sci. 30: 164–168.

Bouchard, D.C., T.L. Lavy, and D.B. Marx. 1982. Fate of metribuzin, metolachlor and fluometuron in soil. Weed Sci. 30:629–632.

Burgard, D.J., R.H. Dowdy, W.C. Koskinen, and H.H. Cheng. 1994. Movement of metribuzin in a sandy loam soil under irrigated potato production. Weed Sci. 42:446–452.

Conn, J.S., and J.S. Cameron. 1988. Persistence and carry-over of metribuzin and triallate in subarctic soils. Can. J. Soil Sci. 68: 827–830.

Conn, J.S., and C.W. Knight. 1984. An evaluation of herbicides for broadleaf-weed control in rapeseed. Efficacy, phytotoxicity, and soil persistence studies. Res. Bull. 62. Agric. For. Exp. Stn., Univ. of Alaska, Fairbanks.

Fryer, J.D., and K. Kirkland. 1970. Field experiments to investigate long-term effects of repeated applications of MCPA, tri-allate, simazine and linuron: Report after 6 years. Weed Res. 10:133–158.

Graham, J.S., and J.S. Conn. 1992. Sorption of metribuzin and metolachlor in Alaskan subarctic agricultural soils. Weed Sci. 40: 155–160.

Hyzak, D.L., and R.L. Zimdahl. 1974. Rate of degradation of metribuzin and two analogs in soil. Weed Sci. 22:75–79.

Jones, R.E., P.A. Banks, and D.E. Radcliffe. 1990. Alachlor and metribuzin movement and dissipation in a soil profile as influenced by soil surface condition. Weed Sci. 38:589–597.

Knight, C.W., and C.E. Lewis. 1986. Conservation tillage in the subarctic. Soil Tillage Res. 7:341–353.

Ladlie, J.S., W.F. Meggitt, and D. Penner. 1976. Effect of soil pH on microbial degradation, adsorption and mobility of metribuzin. Weed Sci. 24:477–481.

Logan, T.J., D.J. Eckert, and D.G. Beak. 1994. Tillage, crop, and climatic effects on runoff and tile drainage losses of nitrate and four herbicides. Soil Till. Res. 30:75–103.

Moorman, T.B., and S.S. Harper. 1989. Transformation and mineralization of metribuzin in surface and subsurface horizons of a Mississippi Delta soil. J. Environ. Qual. 18:302–306.

Nicholls, P.H., A. Walker, and R.J. Baker. 1982. Measurement and simulation of the movement and degradation of atrazine and metribuzin in a fallow soil. Pest. Sci. 12:484–494.

Patrick, J.H., and P.E. Black. 1968. Potential evapotranspiration and climate in Alaska by Thornthwaite's classification. USDA, Forest Serv. Res. Rep. PNW-71. USDA, Washington, DC.

Pritchard, M.K., and E.H. Stobbe. 1980. Persistence and phytotoxicity of dinitroanaline herbicides in Manitoba soils. Can. J. Plant Sci. 60:5–11.

Siddoway, F.H., C.E. Lewis, and R.F. Cullum. 1984. Conservation tillage and residue-management systems for interior Alaska. Agroborealis 16:35–40.

Smith, A.E., and B.J. Hayden. 1976. Field persistence studies with eight herbicides commonly used in Saskatchewan. Can. J. Plant Sci. 56:769–771.

Walker, A. 1978. Simulation of the persistence of eight soil applied herbicides. Weed Res. 18:305–311.

Webster, G.R.B., and G.J. Reimer. 1976. Field degradation of the herbicide metribuzin and its degradation products in a Manitoba sandy loam soil. Weed Res. 16:191–196.