Persistence of Hexazinone and Metsulfuron-methyl in a Mixed-Wood/Boreal Forest Lake

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The persistence of hexazinone and metsulfuron-methyl herbicides was investigated in an experiment using in situ enclosures deployed in a mixed-wood/boreal forest lake. Dissipation studies provided evidence that aqueous residues of hexazinone may persist (DT_{50} = 131–280 days) under conditions typical of northern lentic systems in the mixed-wood/boreal forest. Although dissipation rates of hexazinone differed depending upon initial concentrations (10^4 and 10^3 $\mu g\ L^{-1}$), such differences were of little practical significance. In contrast, concentration-dependent dissipation of metsulfuron-methyl was of practical significance with slow rates (DT_{50} > 84 days) observed for 10^3 $\mu g\ L^{-1}$ concentrations and more rapid rates (DT_{50} = 29.1 days) at environmentally realistic initial concentrations approximating 10 $\mu g\ L^{-1}$. The unexpectedly slow dissipation of hexazinone observed in this study was postulated to result from the influence of low light intensity and short day length on the primary degradation pathway—photolysis. Further study of hexazinone dissipation and impact in relevant northern aquatic systems subject to photolytic inhibition is warranted.

Hexazinone and metsulfuron-methyl are the active ingredients of Velpar L and Escort DF herbicides, respectively. Hexazinone has recently received aerial registration for use in Canadian forest vegetation management at maximum rates of 4.0 kg of ai ha^{-1} (Campbell, 1991). Metsulfuron-methyl, an experimental herbicide with a similar potential use pattern, has a much lower maximum label rate (0.12 kg of ai ha^{-1}), reflecting its inherently higher phytotoxicity. In Canadian forest regeneration, herbicides are typically applied aerially. Thus, contamination of aquatic systems of forested watersheds may occur through a variety of input mechanisms, including accidental overspray, drift, surface runoff, and leaching, with lower concentrations expected in the receiving water, respectively. Since both hexazinone and metsulfuron-methyl are characterized by high water solubility and low octanol–water partition coefficients (Table I), a relatively high potential for off-site movement into aquatic systems via runoff or leaching exists. The general literature on fate and impact of forest herbicides in lentic ecosystems has recently been reviewed (Thompson et al., 1992a).

Because metsulfuron-methyl has only recently been introduced as an experimental forest herbicide, field data on aquatic fate are lacking. On the basis of laboratory studies, metsulfuron-methyl appears to exhibit behavior similar to that of other members of the sulfonylurea class of herbicides, for example, chlorsulfuron (Glean) and sulfometuron-methyl (Oust) (Beyer et al., 1988; Blair and Martin, 1988). As weak acids with pK_a values ranging between 3.3 and 5.2, sulfonylureas exist in natural aqueous media as a mixture of the undissociated and dissociated (anionic) forms (Beyer et al., 1988). The ratio of the two forms found in natural waters is dependent upon pH, which thus exerts a significant influence on environmental fate. The primary mechanism of degradation for metsulfuron-methyl and other sulfonylureas in aqueous systems is hydrolysis, the rate of which is significantly reduced under cool temperatures and intermediate pH (5–8) (Beyer et al., 1988). The major hydrolytic degradation product, methyl 2-(aminosulfonyl)benzoate, may subsequently undergo microbial degradation of the phenyl ring (Joshi et al., 1985; Anderson and Dulka, 1985). Sulfonylureas exhibit high water solubilities and low octanol–water partition coefficients (K_{ow}), both of which are significantly affected by pH (Beyer et al., 1988). The high water solubility (3300 and 9500 mg L^{-1}) and low octanol–water partition coefficient (K_{ow} = 9.3–11.9 and 0.014) for hexazinone and metsulfuron-methyl, respectively, suggest a low potential to sorb or partition into organic matrices at the pH of most surface waters.

The only field study pertinent to aquatic fate of sulfonylureas (Michael and Neary, 1987) indicated that sulfometuron-methyl was relatively nonpersistent in streamwater following applications to forested watersheds in Florida and Mississippi. In the latter site, maximum sulfometuron residues (44 $\mu g\ L^{-1}$) in streams protected by a buffer zone declined to <1 $\mu g\ L^{-1}$ within 29 days after application, although trace levels below the quantitation limit were detected until 63 days posttreatment. Two field studies on the environmental fate and persistence of hexazinone pertinent to northern lentic aquatic systems have been reported. Solomon et al. (1990) reported DT_{50} values of 3.8 and 3.7 days and DT_{95} values of 42 and 21 days, respectively, for two rates (4.0 and 0.4 kg ha^{-1}) of hexazinone applied to in situ enclosures in a highly acidic (pH 4.5) bog lake of northern Ontario. Consistent with laboratory data, only minimal residues associated with plastic enclosure liners or natural sediments were observed. Initial aqueous concentrations (167.5 and 16.74 $\mu g\ L^{-1}$) declined to below detectable levels 21 and 42 days postapplication (limits of detection for hexazinone in water were not reported). In contrast, a more rapid dissipation (DT_{50} < 24 h) of initially high (820 $\mu g\ L^{-1}$) residues was observed by Legris and Couture (1987) in a shallow (25 cm) pond directly oversprayed with hexazinone at a nominal rate of 3.6 kg ha^{-1}. Minimal sorption to sediments was also reported, with residue maxima of 0.172 $\mu g\ g^{-1}$. On the basis of laboratory studies, photolysis and biotransformation are considered the primary degradative mechanisms for hexazinone in aquatic systems, with hydrolysis being relatively unimportant (Rhodes, 1980a,b). Pho-

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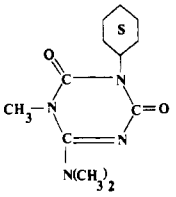
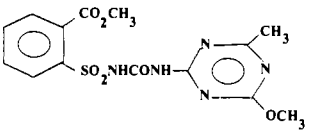
Table I. Physicochemical Characteristics of Hexazinone and Metsulfuron-methyl Herbicides

characteristic	hexazinone	metsulfuron-methyl
trade name	Velpar L	Escort
chemical family	*s*-triazine	sulfonylurea
Chemical Abstracts Service Registry	51235-04-2	74223-64-6
empirical formula	$C_{12}H_{20}N_4O_2$	$C_{14}H_{15}N_5O_6S$
mol wt	252.3	381.4
pK_a	1.09–1.23	3.3
K_{ow}	9.3–11.9	0.018
water solubility at 25 °C, mg L^{-1}	3300	9500
max application rate (forestry), kg ha^{-1}	4.0	0.12
EEC,[a] $\mu g\ L^{-1}$	800	24
96-h LC_{50} (*Daphnia magna*), mg L^{-1}	151.6	>150
96-h LC_{50} (*Selenastrum capricornutum*), $\mu g\ L^{-1}$	22.5	not available
mode of action	PS inhibition[b]	ALS inhibition[b]
chemical structure		

[a] Expected environmental concentration (EEC) based on direct overspray of water body (0.5-m depth) at full application rate. [b] Photosynthetic (PS) and acetolactate synthetase (ALS) inhibition, respectively.

tolytic degradation is known to be substantially affected by water type, with enhanced rates of photolysis observed in natural waters, water and sediment mixtures, or waters amended with photoinitiators (riboflavin, anthraquinone) as compared to distilled water. The high water solubility (33 g L^{-1}) and low sorption characteristic for this compound (Freundlich isotherm constants K = 0.2 and 1.0 for soils of 1.4 and 4.0% organic matter, respectively; Rhodes, 1980a,b) explain the low sediment sorption, which has been observed in both laboratory and field studies as noted above. Hexazinone may be degraded through a variety of different pathways yielding eight known metabolites (Rhodes, 1980a,b). The demethylated or hydroxylated products are most commonly observed in the field.

The proposed use patterns for metsulfuron-methyl and hexazinone in control of competing vegetation in Canadian forestry, together with their potential mobility, result in a risk of aquatic contamination. The paucity of field data pertinent to lentic systems in the mixed-wood/boreal forest, combined with data demonstrating the significant influence of environmental variables on degradation rates, dictates the need for investigation of the fate and impact of these compounds under typical use scenarios. As a component of a larger study designed to address these data gaps, the aqueous persistence of hexazinone and metsulfuron applied at various rates to in situ enclosures deployed in a lake typical of northern mixed-wood/boreal forest watersheds was studied. Results of the fate study are reported here, while the impact of observed residues on phytoplankton and zooplankton communities is detailed elsewhere (Thompson et al., 1992b,c).

MATERIALS AND METHODS

Lake Site Description Site Selection. Greenwater Lake, ON, Canada (46°53′30″ N, 84°2′75″W) is a 3.0-ha lake located approximately 80 km northwest of Sault Ste. Marie, ON. The lake site was chosen for this study as being typical of small, mixed-wood/boreal, lentic ecosystems that might be inadvertently oversprayed or otherwise exposed to herbicides as the result of their use in forest vegetation management. The study, initiated on August 1, 1989, was conducted during the late summer and fall to mimic typical timing of operational aerial spray programs. Water temperatures, conductivity, pH, and dissolved oxygen were monitored throughout the course of the study using a Hydrolab DataSonde 2000 submersible datalogger (Hydrolab Corp., Austin, TX). Nutrients and other water chemistry characteristics (e.g., ex. NH_3, NO_3/NO_2 as N, total organic carbon, total inorganic carbon, Ca, Mg, Cl, K, SO_4, SiO_2) were determined on the basis of depth-integrated samples taken throughout the course of the study, filtered (0.45 μm), and analyzed using a Technicon IIC+ autoanalyzer (Technicon Inc., Tarrytown, NY). Total Kjeldahl nitrogen in these samples was quantified, under contract, by Enviroclean laboratories (Enviroclean, a unit of Lavalin Engineers Inc., London, ON). Only general characteristics of the lake site at the time of experiment initiation are summarized here (Table II), since a detailed description of water quality assessments in relation to herbicide treatment will be the subject of a future publication. Irradiation measurements made subsequent to the study were obtained using a LI-COR LI-188b integrating quantum photometer equipped with a single PY 7708 pyronometer and potentiometer with range set at $\times 10^3$ and an integration time of 100 s.

Table II. Characteristics of the Greenwater Lake Experimental Site

characteristic	description[a]	characteristic	description[a]
location	Laverendrye township, ON (46° 53 N; 84° 03 W)	dissolved oxygen, mg L^{-1}	7.2–8.0
lake type	dimictic, mesotrophic	pH range	6.7–7.3
bottom sediments	organic, flocculent	temp, °C	22 (at 2-m depth)
depth range across enclosures, m	3.4–4.7	conductivity, MS cm^{-1}	0.03
Secchi disk depth, m	3.4–4.7	NH_3, ppb	59.7
		total P, ppb	19.0

[a] Reported values are ranges or averages observed at initiation of the experiment on Aug 1, 1989.

Experimental Design, Chemical Application, and Aqueous Residue Sampling. In situ enclosures constructed of impervious polyethylene sidewalls suspended from wood/styrofoam floats and anchored into natural bottom sediments served as individual experimental units for this study (Figure 1). Enclosures were deployed in a shallow (mean depth 4.3 m) bay of Greenwater Lake, where bottom slope was minimal and sediments were suitable for sealing of the enclosures.

Hexazinone and metsulfuron-methyl, as the formulated products Velpar L (240 g of ai L^{-1}; 24% ai) and Escort DF (60% ai), were applied to triplicate enclosures at various treatment levels covering the full range of expected environmental concentrations (EEC), from drift to accidental direct overspray scenarios (refer to Table V for nominal values). Herbicides were applied to individual enclosures using two backpack sprayers (Model 4F, R&D Sprayers Inc., Opelousas, LA), each assigned to a specific chemical and equipped with a 2-m hand-held boom with a single open-orifice nozzle pressurized by CO_2 at 210 kPa. Total amounts

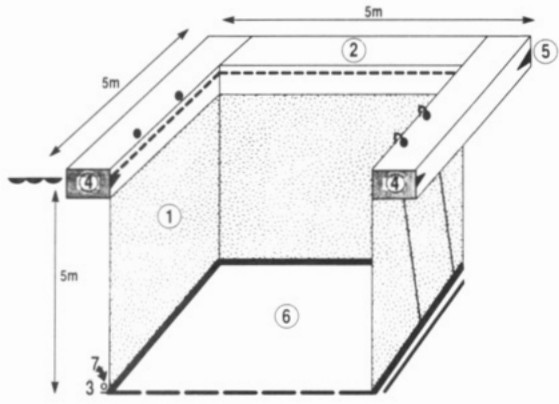


Figure 1. Design detail of in situ enclosure: (1) 6-mil polyethylene liner; (2) 17.8 × 35.6 cm wooden float; (3) 2.5 × 2.5 × 0.32 cm angle iron; (4) polyethylene-encased styrofoam flotation; (5) 15.2-cm leaf hinge with clevis pin; (6) natural sediment bottom; (7) 0.32 cm diamater elastic shock cord.

of herbicide to be applied to individual enclosures were calculated on the basis of the desired nominal concentration and the estimated enclosure volume (4.2 m width × 4.9 m length × X depth), where depth was taken as the average of four soundings about the perimeter of the specific enclosure 2 days prior to treatment. Immediately prior to application, premeasured amounts of herbicide were vigorously mixed in 12-L stainless steel spray tanks containing 3 L of distilled water. With the nozzle held approximately 30 cm above the water surface to minimize drift, the chemical was applied in two passes (opposite directions) over the entire surface of the enclosure (20.58 m^2). Applications of each chemical were made by progressing from lowest to highest concentration, with spray tanks and booms flushed with distilled water between rates to minimize error resulting from residual carry-over.

Initial concentrations in each of the 27 enclosures were quantified by sampling approximately 3 h postapplication to verify the nominal concentrations for impact studies. In addition, dissipation rates were determined at high and intermediate concentrations of hexazinone (10^4 and 10^3 $\mu g\ L^{-1}$) and metsulfuron-methyl (10^3 and 100 $\mu g\ L^{-1}$), respectively. For dissipation studies, sampling was conducted on days 0, 1, 3, 7, 10, and 14, with weekly sampling thereafter until termination of the study at freeze-up (77 days postapplication).

Aqueous residues were sampled using an integrating sampler constructed of an aluminum tube (25 mm o.d. × 3.7 m long) fitted with a poly(vinyl chloride) check valve. A single integrated sample was taken from each enclosure to a constant depth of 3 m. An aliquot (900 mL) of the field sample was transferred directly into a 1-L Nalgene screw-cap bottle which had been prerinsed with acetone. Samples were frozen (−10 °C) within 6 h and stored frozen until extraction and analysis. On the basis of physicochemical characteristics of these two compounds and ^{14}C-radiolabeled tracer studies conducted in our laboratories, adsorption to sampling materials was considered negligible.

Analytical Methods. Aqueous residues of hexazinone were quantified using gas–liquid chromatography with thermoionic specific detection (GLC-TSD) similar to the method previously reported by Solomon et al. (1990). Briefly, subsamples (50–500 mL depending upon expected concentration) were sequentially extracted by liquid–liquid partition with four portions of ethyl acetate (typically 75 mL). The combined organic fractions were filtered through anhydrous sodium sulfate (~5 g) and collected in a 250-mL round-bottom flask. Following sample concentration to approximately 2–3 mL via rotary evaporation (Buchi RE20 rotary evaporator, water bath 60 °C), samples were brought to a constant volume in ethyl acetate. Aliquots of the final sample were serially diluted as required to yield peak areas within the linear range of the detector, and a 2-μL aliquot was injected to GLC-TSD for quantification against an appropriate external standard in ethyl acetate (1.0 $\mu g\ mL^{-1}$) prepared from a neat analytical standard (99.9%; supplied courtesy of E. I. du Pont de Nemours and Co., Wilmington, DE).

Metsulfuron-methyl residues were quantified using a gas–liquid chromatographic technique with electron-capture detection as previously reported (Thompson and MacDonald, 1992). Following titration to pH 3.0 with 5% sulfuric acid, metsulfuron-methyl residues were partitioned from a subsample (100–500 mL depending upon expected concentration) into 100 mL of methylene chloride. The extract, concentrated to approximately 5 mL by rotary evaporation (Buchi RE20 rotary evaporator, water bath 65 °C), was transferred to a centrifuge tube with exhaustive rinsing using ethyl acetate (3 × 5 mL) and brought to a constant volume of 10 mL by evaporation under nitrogen prior to Florisil fractionation to separate the parent compound from the primary metabolite. Residues of intact metsulfuron-methyl were converted to methyl 2-(aminosulfonyl)benzoate (SULF) by aqueous, acid hydrolysis (1 h at 90 °C). Subsequent to hydrolytic conversion, SULF was partitioned and reconstituted in an exact volume of ethyl acetate and a 2-μL aliquot was injected to GLC-ECD for quantitation against an internal standard of chlorsulfuron (99.9%; supplied courtesy of Du Pont), which was added to the original aqueous subsample prior to extraction.

Specifications for analytical instrumentation and materials are provided in Table III. The theoretical method detection limits (MDL = ts, where t is the critical value of $t_{0.01,5}$ and s is the standard deviation of blank response) were calculated according to the recommendations of Kirchmer (1988) and based on the standard deviation of blank response for the complete analytical procedure. Both analytical methods were validated in-house using blank water samples fortified with known amounts of analytical standards prior to analysis of actual field samples.

Time to 50% dissipation (DT_{50}) of hexazinone and metasulfuron-methyl residues were estimated by linear regression of observed concentrations with time postapplication.

RESULTS AND DISCUSSION

Analytical Method Validation and Verification of Initial Concentrations. Results of the method validation study (Table IV) indicate that both hexazinone and metsulfuron-methyl analytical techniques were efficient, precise, and highly sensitive (MDL = 2 and 0.01 $\mu g\ L^{-1}$, respectively). On the basis of precision estimates (<12% CV) for the lowest fortification rates tested, limits of quantitation (LOQ) established for this study were 10 $\mu g\ L^{-1}$ for hexazinone and 0.05 $\mu g\ L^{-1}$ for metsulfuron-methyl. As such, the analytical methods were suitable for accurate quantitation of all initial test concentrations, as well as for residues down to levels approximating 10% of the initial concentrations chosen for dissipation studies.

Untreated control enclosures showed no residue levels above the MDL on any sampling day. In general, mean concentrations observed on day 0 were highly correlated (r^2 = 0.94 and 0.99) to nominal levels of metsulfuron-methyl and hexazinone treatments, with reasonable variability (average CV = 13.3 and 24.5%, respectively). However, enclosures treated with hexazinone at the 10 and 10^4 $\mu g\ L^{-1}$ concentrations showed higher than expected mean concentrations (33 and 1.634×10^4 $\mu g\ L^{-1}$) and relatively high variability (26.7 and 9.38% CV) (Table V). Since concentrations on day 1 for these same replicate enclosures were 8.0 (8.4% CV) and 1.134×10^4 $\mu g\ L^{-1}$ (3.74% CV), respectively, the high residue levels and variability observed on day 0 may be reasonably attributed to incomplete and differential mixing of hexazinone in these enclosures within the 3-h period between application and initial sampling. Similarly, higher than expected day 0 concentrations were observed for metsulfuron-methyl at nominal levels of 10^3 and 10 $\mu g\ L^{-1}$ with observed mean concentrations on day 1 [1140 (17.6% CV) and 10 $\mu g\ L^{-1}$ (19.0% CV)] being much closer to expected values. In contrast, the variability and higher than expected concentration for metsulfuron-methyl at the 100 $\mu g\ L^{-1}$ nominal level were largely the result of a high observation (210 $\mu g\ L^{-1}$) in one of three enclosures. Thus, observations on days 0 and 1 verified the expected nominal concentrations as

Table III. Specifications for Analytical Instrumentation Used in Quantitation of Hexazinone and Metsulfuron-methyl Residues

specification	hexazinone method	metsulfuron method
chromatograph	Varian Vista 6000	Varian Vista 6000
detector	thermoionic specific	electron capture
autosampler	Varian 8000	Varian 8000
injection technique	hot splitless	hot on-column
injection volume, μL	2	2
column type	DB-5 1-μm film (0.25 μm × 30 m)	DB-17 1 μm film (0.53 μm × 15 m)
carrier gas	nitrogen (1.5 mL min^{-1})	nitrogen (1 mL min^{-1})
makeup gas	nitrogen (30 mL min^{-1})	nitrogen (29 mL min^{-1})
detector gases	air (176 mL min^{-1}) hydrogen (4.3 mL min^{-1})	
operating temp, °C		
injector	200	250
column	75–250 (at 30 °C min^{-1})	100–200 (at 20 °C min^{-1}) 220–250 (at 30 °C min^{-1})
detector	300	325
linearity range, ng injected	0.1–10	0.001–0.1
method detection limits (water), μg L^{-1}	2	0.01

Table IV. Results of In-House Validation of Hexazinone and Metsulfuron-methyl Analytical Methods

fortification level, μg L^{-1}	n	mean recovery, %	SD[a]	CV[b]
		Hexazinone		
10^4	3	104.3	2.65	2.54
100	4	81.0	0.18	0.22
10	4	107.0	3.84	3.59
		Metsulfuron-methyl		
50	6	92.0	5.2	5.7
0.5	6	83.9	4.2	5.0
0.05	6	97.9	10.9	11.1

[a] Standard deviation. [b] Coefficient of variation.

Table V. Nominal and Mean Actual Aqueous Concentrations of Hexazinone and Metsulfuron-methyl on Day 0

nominal concn, μg L^{-1}	actual concn (mean n = 3), μg L^{-1}	SD[a]	CV[b]
	Hexazinone		
10^4	1.634×10^4	1.53	9.4
10^3	1140	0.08	7.0
100	110	0.011	10.0
10	33	0.008	26.7
	Metsulfuron-methyl		
10^3	1290	0.14	10.9
500	430	0.20	47.0
100	150	0.05	33.3
10	15	0.001	6.6

[a] Standard deviation. [b] Coefficient of variation.

reasonably accurate, with effective replication (i.e., <20% CV n = 3) after full mixing had occurred by day 1.

Aqueous Residue Dissipation. Dissipation of aqueous hexazinone and metsulfuron-methyl residues was tracked over time in each of two different treatment levels as depicted graphically in Figures 2 and 3. The results clearly demonstrate that essentially no dissipation of hexazinone at either the 10^3 or 10^4 μg L^{-1} concentration occurred within the period of observation (35–49 days postapplication). The effective lack of dissipation at either the low or high treatment levels was reflected in the minimal slope estimates (−2.0 to −4.0 and −20.0 to −30.0 μg L^{-1} day^{-1}) generated by linear regression of the data for individual enclosures treated at 10^4 and 10^3 μg L^{-1} nominal concentrations, respectively. Resultant estimates of DT_{50} ranged from 131 to 280 days, depending upon the replicate in question. Although not reported here, hexazinone residues in enclosures treated at 100 and 10 μg L^{-1} also

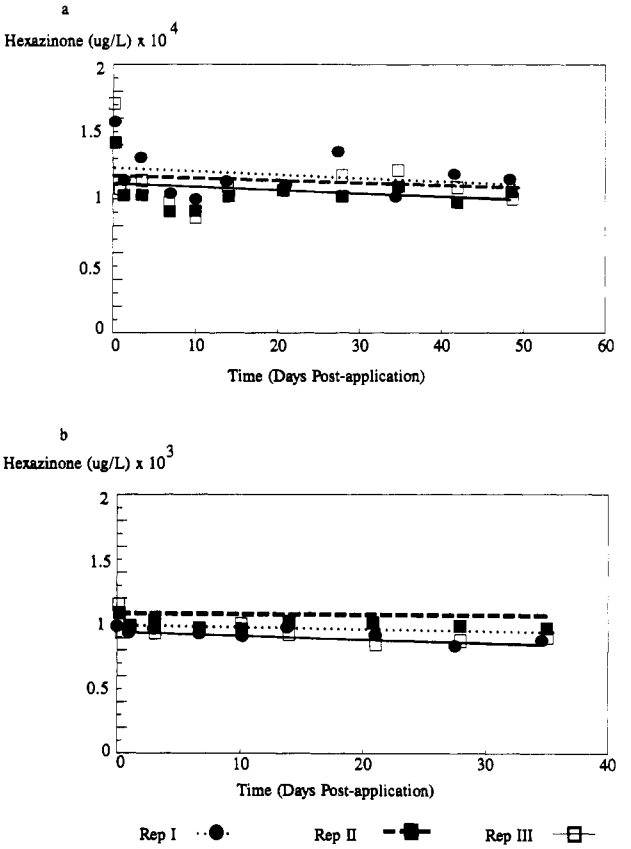


Figure 2. Dissipation of aqueous hexazinones residues in three replicate enclosures treated at (a) 10^4 μg L^{-1} and (b) 10^3 μg L^{-4} nominal levels with associated linear regression of residues vs time postapplication (see Results and Discussion for regression statistics).

showed essentially no dissipation over a 42-day period of observation, confirming the general persistence of hexazinone residues in this study as being independent of initial concentration.

At the highest nominal concentration of metsulfuron-methyl (10^3 μg L^{-1}), two of the three enclosures (13 and 11) exhibited similar residue dissipation patterns (Figure 3), with residues dissipating slowly (b = −4.0 and −6.0 μg L^{-1} day^{-1}) as a linear function of time (P = 0.0007; r^2 = 0.74 and 0.82). In contrast, residues in the third replicate (enclosure 21) exhibited a precipitous drop from concentrations above 1200 μg L^{-1} on days 0–3 to concentrations approximating 600 μg L^{-1} on days 7 and 10, with dissipation

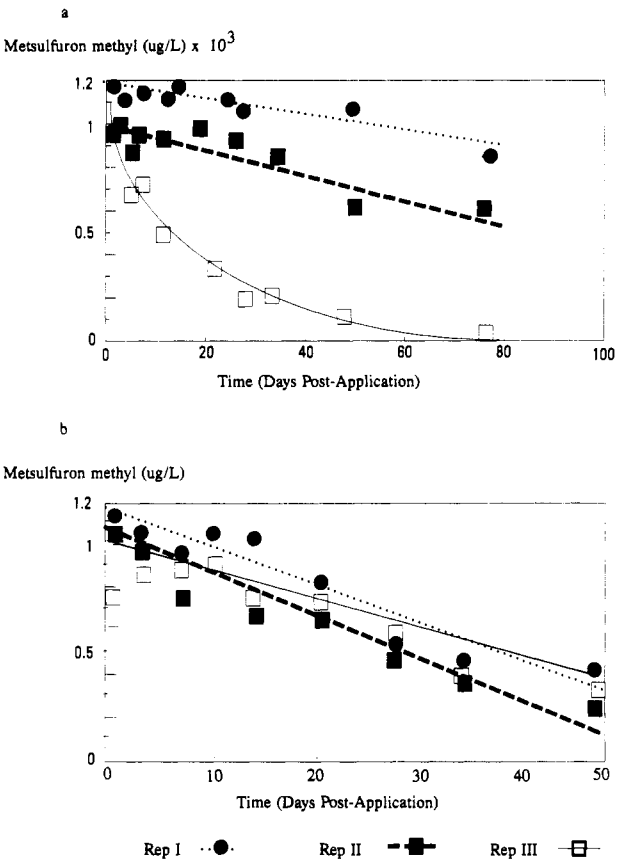


Figure 3. Dissipation of aqueous metsulfuron methyl residues in three replicate enclosures treated at (a) 10^3 μg L^{-1} and (b) 1.0 μg L^{-1}1 nominal levels with linear and exponential regressions of residues vs time postapplication (see Results and Discussion for regression statistics).

best described by an exponential decline function. The precipitous drop in measured concentrations and dissimilarity in dissipation kinetics relative to all other enclosures treated with metsulfuron-methyl suggest that a leak occurred in this enclosure sometime between days 3 and 7. On the basis of results for enclosures 11 and 13, the average DT_{50} estimate for metsulfuron-methyl at 10^3 μg L^{-1} was 118 days (range 84–152 days). In contrast, the mean DT_{50} for enclosures treated with metsulfuron-methyl at 0.01 mg L^{-1} was 29 ± 1.4 days. At the low concentration, all replicates behaved similarly with resultant similarity in linear regression parameters (r^2 = 0.73–0.86; a = 0.11–0.12; b = –2.0 μg L^{-1} day^{-1}). The DT_{50} (29 days) estimated for metsulfuron-methyl at the 10 μg L^{-1} concentration in this study (pH 6.7–7.3) is more rapid than would be predicted solely on the basis of hydrolytic half-life (33 days) reported by Beyer et al. (1988) for metsulfuron-methyl at pH 5 at 25 °C. This discrepancy suggests that other dissipation mechanisms may be active in the decline of metsulfuron-methyl in natural waters. Data reported by Harvey et al. (1985) suggest that the sulfonylurea analogue sulfometuron-methyl is highly susceptible to photolysis (DT_{50} = 3 days). Given the structural similarity of metsulfuron-methyl and sulfometuron-methyl, it is reasonable to expect photolytic degradation of the former similar to that of the latter, even though this mechanism has been described as unimportant in the environmental dissipation of metsulfuron-methyl (Beyer et al., 1988).

In summary, results suggest that while aqueous residues of hexazinone were persistent (DT_{50} = 131–280 days) irrespective of initial concentration, metsulfuron-methyl dissipation was clearly concentration dependent, with slow rates (DT_{50} > 84 days) observed for 10^3 μg L^{-1} concentrations and more rapid rates (DT_{50} = 29.1 days) at environmentally relevant initial concentrations approximating 10^4 μg L^{-1}. Although no comparable field data for metsulfuron-methyl exist, results for hexazinone as observed in this study differ markedly from those of previous work. In lentic systems, DT_{50} values of <7 days estimated by Legris and Couture (1987) as well as Solomon et al. (1990) suggest relatively rapid dissipation, in direct contrast to what we have observed.

Disparate persistence estimates for hexazinone in natural waters may reflect differences in environmental parameters, water chemistry, or methods used in estimating DT_{50} values. Given that the primary degradative mechanism for hexazinone is photolysis, the slow dissipation observed in this study may be related to the combination of low light intensity and relatively short day length. Day length at this latitude (Table II) drops dramatically throughout the months of August–October which pertain to our study, as compared to the months of June and July which relate to studies of Solomon et al. (1990) and Legris and Couture (1987). Unfortunately, pyronometer malfunction prevented quantification of irradiance during the course of this study. However, measurements made subsequently (October 10, 1991; 2:00–3:00 p.m.) suggest global sun and sky radiation at the water surface approximating 420 W m^{-2} under full sunlight, 290 W m^{-2} under partial cloud, and 185 W m^{-2} under full cloud. Futher support for this hypothesis is provided via the data of Bouchard et al. (1985), who reported stability (DT_{50} > 260 days) of hexazinone (100 μg L^{-1}) in natural streamwater under dark conditions.

A second possible explanation relates to differences in water chemistry between the various studies; a general description of water quality parameters for our study is provided in Table II. While similar details on water chemistry from previous studies are lacking, the major differentiating characteristics include depth [25 cm for study by Legris and Couture (1987) vs 3.4–4.7 m in our study] and pH [4.5 for the study by Solomon et al. (1990) vs 6.7–7.3 in our study]. Shallow depth in the former study may contribute to more rapid dissipation through enhanced photolysis. The extremely low pH in the bog lake studied by Solomon and co-workers may have resulted in enhanced hydrolysis or photolysis (particularly if high fulvic or humic acid levels characteristic of such lakes acted as photoinitiators). The initially high water temperatures of our study (22 ± 1 °C at 2-m depth) persisted throughout the first 2 weeks and then began to drop consistently with time, reaching 15 °C by 56 days postapplication. Thus, water temperatures during the majority of our study were similar to those observed by Solomon et al. (1990) [water temperatures of Legris and Couture (1988) not reported] and cannot be used to explain the observed differences in dissipation rates.

Finally, a visible reduction in water levels within the lake (i.e., ~1 m) was noted during the initial period of our study during which daytime air temperatures were exceptionally high (25–30 °C). Thus, declining water volumes in enclosures (evidenced by ballooning of sidewalls but not measured) may also be considered as a possible reason for increased persistence, since the overall effect would be to concentrate remaining aqueous residues. If the concentration effect was proportional in rate to dissipation, the net result may be an apparent lack of dissipation. While such a theory is attractive upon first evaluation, it is inconsistent with observation of rapid dissipation concurrently observed for the low metsulfuron-

methyl treatment, the lack of dramatic decline in residues which would be expected when water levels stabilized in September and October, and the fact that other studies, particularly those conducted under warmer conditions in the southern United States, have failed to demonstrate this phenomenon for other similar compounds such as atrazine.

The unexpected and inadequately explained persistence of hexazinone observed in this study appears to warrant further study of herbicide persistence in northern aquatic environments. Future research, necessary to determine if such persistence is common under typical conditions of Canadian forest watersheds, must address the need for detailed monitoring of important environmental parameters such as light intensity (preferably at middepth), duration of irradiance, water temperature, depth, water clarity and quality, and biological productivity such that adequate comparisons to other work may be drawn.

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