Bull. Environm. Contam. Toxicol. 20, 170-173 (1978)

Formation and Persistence of N-Nitrosobutralin in Soil

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It was recently discovered (FAN, et al., 1976) that commercial formulations of trifluralin (α,α,α-trifluoro-2,6-dinitro-N,-N-dipropyl-p-toluidine), one of the leading herbicides in the United States, contained up to 150 ppm of N-nitrosodipropylamine. A broad implication of this discovery is that secondary amines may be nitrosated to produce nitrosamines during the manufacture of many of the dinitroaniline herbicides. The secondary amine may be a precursor of the herbicide as was the case with trifluralin, or, in some cases, could be the herbicide itself. A dinitroaniline herbicide that is also a secondary amine is butralin (4-(1,1-dimethylethyl)-N-(1-methylpropyl)-2,6-dinitrobenzenamine).

We report here a 6-month study that demonstrates: 1 - butralin can be converted to a nitrosamine in a soil high in nitrite, and 2 - nitrosobutralin (4-(1,1-dimethylethyl)-N-(1-methylpropyl)-N-nitroso-2,6-dinitrobenzenamine) is persistent in soil (detectable after 6 months). The observed nitrosation in soil is probably of little significance because of the high levels of nitrite required. The persistence of the nitrosamine, on the other hand, assumes added significance if nitrosated pesticides have been formed during the manufacture of dinitroaniline herbicides and thus have been inadvertently applied to soils.

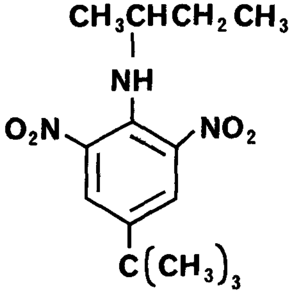
Experimental

Duplicate 1-kg portions of air-dried Matapeake loam were treated with benzene solutions of ^{14}C-butralin (supplied by Amchem Products, Inc., Ambler, Pa. 19002, 1 μCi, 2 mg in 2 ml benzene) and aqueous solutions of ammonium nitrate (285 mg in 5 ml H_2O, 100 ppm N). Two other soil samples were similarly prepared except sodium nitrite (493 mg in 5 ml H_2O, 100 ppm N) was substituted for ammonium nitrate. After the solvents had evaporated, each of the soil samples was thoroughly mixed, treated with 226 g H_2O (70% field capacity) and stored in a greenhouse in a beaker protected from light with aluminum foil. Water was added periodically to replace that lost by evaporation. Samples (100 g dry wt) were removed at intervals and were extracted by shaking first overnight with 300 ml of 3:1 ethyl acetate-benzene, then overnight with 300 ml of methanol. Portions of each extract were counted by standard liquid scintillation methods to determine recovery of ^{14}C. Other portions were chromatographed on silica gel 60 F-254 thin-layer chromatographic (TLC) plates. Plates were developed with benzene,

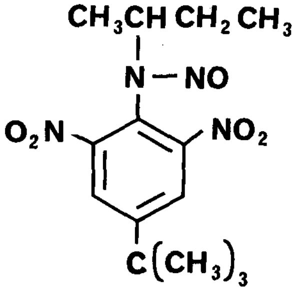
0007-4861/78/0020-0170 $01.00

exposed to No-screen medical X-ray film, and, finally, spots corresponding to butralin (Rf.59) and nitrosobutralin (Rf.43) were scraped and counted. Other minor spots (Rf's .47, .31, 0) were present, and were scraped and counted to determine total recoveries, but were not investigated further.

To confirm the identity of the product assumed to be nitrosobutralin in the soil experiment, the authentic, unlabelled material was synthesized by nitrosating butralin with N_2O_4, and was purified by recrystallization from methanol (mp 107°). The mass spectrum was consistent with that expected for nitrosobutralin (70ev electron impact m/e 325, 9.8%, M+H ; m/e 294, 100%, M-NO), and its Rf on silica gel TLC was identical to that of the product formed in soil (0.43, benzene). One of the duplicate $NaNO_2$-treated soil samples that had been incubated for 6 months was extracted; after counting, the extract was concentrated to a small volume and then streaked on a 10x20-cm TLC plate. Authentic nitrosobutralin was spotted for comparison, the plate was developed with benzene, and the band corresponding to the Rf of authentic nitrosobutralin was scraped. The silica gel was extracted with acetone, and the extracts were filtered and made up to 10.0 ml. Duplicate 1.0 ml aliquots were counted and produced 101 and 95 cpm, respectively. The remaining 8.0 ml (ca. 800 cpm) was evaporated, 43.75 mg of authentic, unlabelled nitrosobutralin was added, and the mixture was recrystallized twice from methanol. The recovery was 32.37 mg of nitrosobutralin, mp 109-111°. This material was dissolved in 1.00 ml CH_2Cl_2; triplicate 0.20-ml aliquots were counted and averaged 96 cpm (480 cpm/32.37 mg, or 15 cpm/mg). The unrecrystallized material had contained 800 cpm/43.75 mg (18 cpm/mg). That recrystallization did not greatly change the specific activity confirmed the presence of ^{14}C-nitrosobutralin.



Butralin



N-Nitrosobutralin

Results and Discussion

Table 1 lists the recoveries of ^{14}C over 26 weeks. The ^{14}C extractable with ethyl acetate-benzene decreased with time whereas that extractable into methanol remained reasonably constant. Total recoveries ranged from 77% after one week to 42-48% after 26 weeks.

TABLE 1

Total Recoveries of ^{14}C from Matapeake Loam Amended with 1 ppm ^{14}C-Butralin and 100 ppm N as NH_4NO_3 or $NaNO_2$.[a]

Time/wk	Soil Amendment	Extract, % Recovery		Total % Recovery
		EtOAc-Benzene	MeOH	
1	$NaNO_2$	43	34	77
4	$NaNO_2$	40	28	68
4	NH_4NO_3	36	23	59
10	$NaNO_2$	28	23	51
10	NH_4NO_3	28	21	49
26	$NANO_2$	19	29	48
26	NH_4NO_3	17	25	42

[a] Average from duplicate samples

Table 2 shows the recoveries of butralin and nitrosobutralin. After one week, 70% of the added radioactivity was recovered as unchanged butralin; this figure decreased to 35-36% after 6 months. No nitrosobutralin was recovered from soils treated with NH_4NO_3. In the soils treated with $NaNO_2$, however, 4.4% of the added radioactivity was recovered as nitrosobutralin after one week; this percentage decreased to 0.3% after 6 months.

TABLE 2

Recoveries of Butralin and Nitrosobutralin from Incubation of ^{14}C-Butralin in Matapeake Loam Amended with NH_4NO_3 or $NaNO_2$.

Time wk	Soil Amendment	% of Total ^{14}C, Recovered as					
		Butralin			Nitrosobutralin		
		EtOAc-Benzene	MeOH	Total	EtOAC-Benzene	MeOH	Total
1	$NaNO_2$	40	30	70	2.5	1.9	4.4
4	$NaNO_2$	32	n.d.	n.d.	1.6	0	1.6
4	NH_4NO_3	36	n.d.	n.d.	0	0	0
10	$NaNO_2$	22	n.d.	n.d.	1.7	0	1.7
10	NH_4NO_3	24	n.d.	n.d.	0	0	0
26	$NaNO_2$	13	23	36	0.1	0.2	0.3
26	NH_4NO_3	12	23	35	0	0	0

n.d. not determined

In a similar experiment with ^{14}C-atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine), nitrosoatrazine (2-chloro-4-(N-nitroso-N-ethylamino)-6-(isopropylamino)-*s*-triazine) was observed after one week, but was absent in subsequent (4, 10, 26 weeks) samplings (KEARNEY, *et al.*, 1977). Since the lifetime of NO_2^- in aerobic soils is short, it is probable that all of the nitrosobutralin observed in this study was also formed in the first week (perhaps much earlier) and that the nitrosobutralin persisted much longer than did the nitrosoatrazine under the same conditions.

Although high levels of nitrite may briefly accumulate in alkaline soils treated with anhydrous ammonia, its existence in soil in the absence of ammonia is only transitory (BLACK, 1968). Thus the conditions under which nitrosobutralin was formed (100 ppm N as NO_2^-) are very atypical. No nitrosobutralin was observed under more normal soil conditions. Nonetheless, these results do indicate that at least some nitrosated pesticides, if formed in, or added to, soil, may be quite persistent.

References

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