- Player, T. J. In Free Radicals, Lipid Peroxidation and Cancer; McBrien, D. C. H., Slater, T. F., Eds.; Academic: London, 1982; p 173.
- Ramarathnam, N.; Osawa, T.; Namiki, M.; Tashiro, T. J. Sci. Food Agric. 1986, 37, 719.
- Su, J.-D.; Osawa, T.; Namiki, M. Agric. Biol. Chem. 1986, 50, 199.
 Su, J.-D.; Osawa, T.; Kawakishi, S.; Namiki, M. Agric. Biol. Chem. 1987, in press.
- Wilbur, K. M.; Bernheim, F.; Shapiro, O. W. Arch. Biochem. 1949, 24, 305.
- Witting, L. A. Free Radicals in Biology; Pryor, W. A. Ed.; Aca-

demic: New York, 1980; Vol. IV, p 295.

- Wood, A. W.; Wang, H. T.; Chang, R. L.; Newmark, H. L.; Lehr, R. E.; Yagi, H.; Sayer, J. M.; Jerina, D. M.; Conney, A. H. Proc. Natl. Acad. Sci. U.S.A. 1982, 79, 5513.
- Yaeger, L. L.; Bjorksten, J. In Autoxidation in Food and Biological Systems; Simic, M. G., Karel, M., Eds.; Plenum: New York, 1980; p 405.

Received for review May 6, 1986. Revised manuscript received April 23, 1987. Accepted June 13, 1987.

Environmental Impact of Agricultural Nitrogen and Phosphorus Use

Andrew N. Sharpley,* S. J. Smith, and J. W. Naney

The impact of fertilizer application on the amount of nitrogen (N) and phosphorus (P) in surface runoff from 20 watersheds and ground water from 45 shallow wells (<20-m water tables) has been assessed for the past several years on agricultural land in the Southern Plains. The major proportion of N and P transported in surface runoff was in the particulate form (averaging 64 and 75%, respectively). Soluble and total P concentrations from unfertilized and fertilized watersheds were consistently greater than the critical levels associated with accelerated eutrophication (10 and 20 μ g L⁻¹, respectively). In most cases, nitrate- and ammonium-N concentrations in ground water were within acceptable limits for potable use (10 mg L⁻¹ NO₃-N) and for fish (2.5 mg L⁻¹ NH₄-N). In general, therefore, these agricultural practices had little environmental impact on ground water quality, although P enrichment of surface runoff may stimulate accelerated eutrophication of small lakes and impoundments in the Southern Plains. Measures to reduce the environmental impact of agricultural N and P use are discussed.

The transport of nitrogen (N) and phosphorus (P) in surface runoff from agricultural land, increased by fertilizer applications, often controls the biological productivity of surface waters (Loehr, 1974; Schindler, 1977; Vollenweider and Kerekes, 1982). Although both N and P have been associated with accelerated eutrophication, most attention has focused on P. This results from the fact that exchange of N between the atmosphere and a waterbody and fixation of atmospheric N by some blue-green algae, can be sufficient to prevent N from limiting biological productivity. Thus, for most lakes, P is often the limiting element and its control is of prime importance in reducing the accelerated eutrophication of a water body. As a result, Sawyer (1947) and Vollenweider (1971) proposed critical soluble (SP) and total P (TP) concentrations of 10 and 20 μ g L⁻¹ respectively, which if exceeded may accelerate the eutrophication of lakes and impoundments.

Due to the rapid fixation of fertilizer P by surface soil material, ground water contamination by fertilizer material is often associated with nitrate-N (NO₃-N). This results from the fact that N fertilizer application to agricultural land exceeds that of the other mineral elements (Hargett and Berry, 1985). In the ammonium-N (NH₄-N) form, N is fairly immobile in soil. However, under most conditions NH₄-N is converted to NO₃-N, which can readily move with soil water. Nitrate-N not utilized by the crop, incorporated into soil organic matter, or denitrified, can leach from the soil profile into the ground water where it has the potential to pose an environmental hazard. Acceptable

limits of NO_3 -N concentration of 10 and 100 mg L⁻¹ have been established for human and livestock consumption, respectively, and NH_4 -N concentrations above 0.5 and 2.5 mg L⁻¹ may be harmful to humans and fish, respectively (U.S. EPA, 1973).

The nonpoint pollution of lakes and impoundments via the contamination of surface and ground water with fertilizer N and P is now recognized as one of the nation's major water quality problems. For example, in 1984, the EPA reported to Congress that 6 of 10 EPA regions found nonpoint sources to be the principal remaining cause of water quality problems and that virtually every state reported some kind of problem related to these sources (U.S. EPA, 1984). More specifically, the southwestern United States, a large and important farming and ranching area, is undergoing greater rural and urban demands on its water supplies as the population increases. As a result, there has been a renewed urgency in obtaining detailed information on surface and ground water supplies associated with current and proposed agricultural management practices. Although several studies have documented the effect of N and P fertilizer applications on surface and ground water quality in the corn belt region of the midwest United States (Burwell et al., 1975, 1977; Hanway and Laflen, 1974; Schuman et al., 1973a,b), little information is available for the southwest, especially Oklahoma and Texas.

This paper presents the results of an 8-year monitoring program of 20 watersheds and 45 shallow wells (<20-m water table depth) in Oklahoma and Texas, to assess the impact of agricultural practices on N and P levels in surface and ground water quality in this area. In some cases, wells were located on watersheds not monitored for surface runoff quantity and quality.

Water Quality and Watershed Research Laboratory, USDA—ARS, Durant, Oklahoma 74702-1430.

Table I. Watershed Management Characteristics (1977-1984)

	water-	атеа	slope		ferti ap	lizer pl ^e			
	shed	ha	%	crop type ^a	Ν	Р			
			El F	Reno OK					
	FR1	16	26	native grass					
	FR2	1.0	2.9	native grass	29	2			
	FR3	1.6	3.2	native grass		-			
	FR4	1.6	3.6	native grass ^b	29	2			
	FR5	1.6	3.5	wheat	75	16			
	FR6	1.6	2.9	wheat	76	12			
	FR7	1.6	2.9	wheat	56	13			
	FR8	1.6	2.7	wheat	56	13			
			Rie	esel, TX					
	Y	122 2.6		mixed"	74	38			
	Y2	53	2.9	mixed	40	30			
	Y6	6.6	3.2	cotton/oats/	45	24			
	Y8	8.4	2.2	sorghum	96	19			
	Y10	7.5	1.9	rotation	82	28			
	Y14	2.3	1.4	Klein grass					
	W10	1.1	2.1	coastal Bermuda					
				grass					
	SW11	8.0	1.0	wintergreen	82				
				hardinggrass					
Woodward, OK									
	W1	4.8	7.0	native grass					
	W2	5.6	8.2	native grass	6	2			
	W3	2.7	8.6	wheat ^c	95	23			
	W4	2.9	7.4	wheat ^{c}	85	23			

^aScientific names of crops are as follows: cotton, Gossypium hirsutum L.; oats, Avena sativa L.; sorghum, Sorghum sundanese (Piper) Stapf; wheat, Triticum aestivum L.; klein grass, Panicum coloratum L.; wintergreen hardinggrass, Phalaris acquatica L.; coastal Bermuda grass, Cynodon dactylon L. ^bBurned March 1979, 1981, 1983. ^cPlanted from native grass to wheat in fall 1978. ^d 60% Bermuda grass pasture and 40% a 3-year rotation of cotton, oats, and sorghum. ^eUnits kg ha⁻¹ per year.

MATERIALS AND METHODS

The management characteristics of the 20 watersheds, representing major agricultural practices in this area, are detailed in Table I. The major soil types on the El Reno, OK, Reisel, TX, and Woodward, OK, watersheds are Kirkland silt loam (fine, mixed, thermic, Udertic Paleustolls), Houston Black clay (fine, montmorillonitic, thermic, Udic Pellusterts), and Woodward loam (coarse-silty, mixed, thermic, Typic Ustochrepts), respectively. Watershed runoff was measured by precalibrated flumes or weirs equipped with FW-1 stage recorders and flow-weighted samples collected from each runoff event as detailed previously (Sharpley et al., 1982).

The principal geologic and management features of the well locations, as they relate to ground water studies, are given in Table II. At each location, the watersheds represent characteristic settings where ground water quality may be affected by changes in land use and management



Figure 1. Mean annual flow-weighted concentration and amount of N transported in surface runoff as a function of watershed management practice.

practices. The water table depths generally ranged from 3 to 20 m, with the wells sampled on a seasonal basis. Additional details about the wells and locations have been given in previous publications (Naney et al., 1984; Smith et al., 1983, 1987). For all watersheds, fertilizer N and P applications were made in conjunction with recommended soil test results.

All watershed and well samples for chemical analysis were refrigerated at approximately 4 °C after collection. Aliquots of each sample were centrifuged and filtered (0.45 μ m). Nitrate- and NH₄-N and SP were determined on the filtered samples. Aliquots of the unfiltered samples were removed for Kjeldahl N (TKN) and TP analysis. Chemical analysis for NO₃-N, NH₄-N, and TKN were made by standard methods described in the Federal Water Pollution Control Manual (U.S. Department of the Interior, 1971). Nitrate-N was determined with brucine sulfanilic acid and NH₄-N and TKN with Nessler's reagent and micro-Kjeldahl digestion apparatus, respectively. Total N (TN) was calculated as the sum of NO_3 -N and TKN. Soluble P was determined on filtered samples by the colorimetric method of Murphy and Riley (1962) and TP by digestion of unfiltered samples with perchloric acid (O'Connor and Syers, 1975). U.S. EPA (1973, 1976) publications were used as guides for water quality standards.

RESULTS AND DISCUSSION

Surface Runoff. Annual flow-weighted concentrations of NO_3 -N, NH_4 -N, TN, SP, and TP averaged for 1977–1984, for each watershed are presented in Table III. Due to the conversion of NH_4 - to NO_3 -N and subsequent ease of movement of NO_3 -N with infiltration water in the

Table II. Principal Watershed Features Related to Ground Water Quality Studies for Soluble N and P Assessment

site	no. wells	drilled depth, m	major land use ^a	geologic age	stratigraphy	lithology
Chic ka sha El Reno	11 10	10-40 10-25	native grass, wheat native grass, wheat, grain sorghum	quaternary quaternary permian permian	terrace deposits, alluvium terrace deposits El Reno group Cloud Chief formation, Whitehorse El Reno	sand, gravel sand, gravel shale, sandstone gypsum, shale, sandstone
Ft. Cobb	2	15-30	peanuts, grain sorghum	quaternary	group alluvium Whitehorse group	sand, silt
Woodward	22	3–9	improved grasses, wheat, alfalfa	quaternary permian	terace deposits Whitehorse group	sand, gravel shale, sandstone

^a Scientific names of crops not listed in Table I: alfalfa, Medicago sativa L.; peanuts, Arachis hypogaea L.

Table III. Mean Annual Flow-Weighted Concentration (mg of N L^{-1} , μ g of P L^{-1}) and Amount (kg ha⁻¹ per year) of Nitrate, Ammonium, and Total N and Soluble and Total P in Runoff from the Watersheds Averaged for 1977-1984

<u></u>	nitrat	nitrate-N		ammonium-N		total N		soluble P		l P	
watershed	concn	amt	concn	amt	concn	amt	concn	amt	concn	amt	
				F	Reno OK						
FR1	0.24	0.08	0.21	0.14	3.18	1.71	120	0.081	230	0.05	
FR2	1.29	1.35	1.64	0.90	4.28	3.35	140	0.129	290	0.21	
FR3	0.17	0.09	0.19	0.12	1.82	1.12	80	0.143	190	0.11	
FR4	1.87	0.73	1.06	0.43	7.61	2.13	20	0.076	300	0.11	
FR5	1.33	0.72	0.50	0.45	7.65	6.27	220	0.154	1510	1.75	
FR6	1.58	1.38	0.65	0.19	10.33	6.00	320	0.097	1700	0.93	
FR7	1.76	0.81	0.53	0.19	6.39	2.41	310	0.116	1020	0.36	
FR8	2.27	1.11	0.49	0.21	8.54	3.61	430	0.146	1140	0.52	
					0.01	0.0-				0.02	
				F	Reisel, TX						
Y	2.11	2.12	0.17	0.19	4.59	4.65	160	0.175	580	0.62	
Y2	2.01	2.16	0.10	0.12	4.51	4.83	140	0.125	730	0.77	
Y6	3.56	2.70	0.21	0.07	7.62	3.57	70	0.519	920	0.98	
Y8	3.24	2.94	0.05	0.05	6.77	5.94	70	0.063	1170	0.95	
Y10	2.35	4.63	0.09	0.07	8.84	12.01	80	0.079	1410	2.59	
Y14	1.05	1.93	0.54	1.72	3.47	6.64	100	0.178	370	0.35	
W10	0.49	0.68	0.14	0.20	1.77	2.39	90	0.091	180	0.20	
SW11	3.16	2.25	0.65	0.43	6.13	5.51	32	0.110	980	0.92	
Woodward OK											
W 1	0.30	0.02	0.26	0.02	5.26	0.21	160	0.011	670	0.05	
W2	0.26	0.05	0.21	0.02	5.30	0.91	170	0.022	1670	0.33	
w3	0.73	0.14	0.28	0.05	14.20	1.92	370	0.030	3070	0.30	
W4	0.29	0.05	0.29	0.03	5.28	1.11	230	0.022	1150	0.16	
-											

soil profile, away from the zone of removal in runoff, NO_3 and NH_4 -N concentrations and amounts were low. From 22 to 93% of the TN transported was particulate (sediment bound), with an average value of 64% for all watersheds. Particulate N represents sorbed NH_4 -N and organic N.

The surface runoff loss of N is summarized in Figure 1, according to watershed land use (Table I). With cultivation of native grass, NO3-N and TN concentrations increased. In contrast, NH₄-N concentrations decreased, possibly due to an increased conversion of NH₄-N to NO₃-N with cultivation. The greater TN concentration of runoff from the wheat watersheds may result in part from the generally larger amounts of fertilizer N applied (105 kg of N ha⁻¹ per year). In terms of N load, however, greater runoff losses resulted in a larger NO₃-N and TN load from the rotationally cropped watersheds compared to the other land use watershed (Figure 1). Even so, TN loss represented a small proportion of fertilizer N applied (3 and 9% averaged for the wheat and rotation watersheds, respectively). As the transport of fertilizer N and P could not be distinguished from soil N and P, the proportion of applied fertilizer transported in runoff represents a maximum value, assuming the N and P loss was derived solely from the applied fertilizer.

In general, SP loss represented a small proportion of the TP loss (Table III). Particulate P accounted for 40–93% of the TP transported in runoff, with an average value of 75% for all watersheds. Although the concentration of SP and TP in runoff from the watersheds studied may be altered by sorption-desorption, dilution, sedimentation, and resuspension during transport to a lake, the values were consistently greater than critical P concentrations associated with accelerated eutrophication (10 and 20 μ g L^{-1} for SP and TP, respectively). This was the case even for the unfertilized watersheds, where natural soil fertility levels were high enough to enrich surface runoff P concentrations. Mean annual flow-weighted concentrations and loads of SP and TP for the period 1977-1984 are summarized in Figure 2 according to land use. Although the concentration of SP in surface runoff from wheat was greater than that from land under native grass or rotational cropping, little difference in P load between land uses was



Figure 2. Mean annual flow-weighted concentration and amount of P transported in surface runoff as a function of watershed management practice.

observed (Figure 2). A dramatic increase in TP concentration and load was associated with cultivation of native grass, due to an increased loss of soil and associated P. Although P loss in surface runoff from agricultural land can result in water quality deterioration, the losses are not of agronomic importance. For example, the TP loss from the wheat and rotational watersheds represented a small proportion of the fertilizer P applied (8 and 4% for the wheat and rotational watersheds, respectively).

In any discussion of the impact of P transport in runoff on lake water quality and eutrophication, consideration must be given to the bioavailability (availability to algal uptake) of the transported P. Although SP is immediately bioavailable, particulate P can represent a long-term source of P to a water body, dependent on the physical and chemical characteristics of both the soil and water body. Rapid chemical extraction procedures, which simulate algal removal of particulate P, have been proposed for the routine determination of particulate P bioavailability and include NaOH (Logan et al., 1979; Sagher et al., 1975;

Table IV. Soluble N (mg L⁻¹) and P (μ g L⁻¹) Concentrations in Ground Waters at Various Locations in Oklahoma as Affected by Land Use

					NO ₃ -N		NH ₄ -N		soluble P	
location	period	use ^a	wells	no. observns	mean	range	mean	range	mean	range
Chickasha	1979-1982	native grass	2	9	0.5	0.1-0.9	0.34	0.00-1.99	75	7-239
El Reno	1983-1986	native grass	3	21	1.8	0.0 - 11.9	0.04	0.01 - 0.08	25	4-77
Woodward	1983-1985	native grass	3	15	3.6	1.4 - 8.6	0.09	0.00 - 0.65	9	2 - 14
Woodward	1981-1985	alfalfa	1	12	6.6	0.8 - 8.3	0.22	0.05 - 1.60	0	0
Woodward	1981 - 1985	Bermuda grass	4	46	6.5	0.1 - 10.4	0.12	0.00 - 0.44	6	1 - 25
Woodward	1980-1985	eastern gama grass	6	70	2.4	0.0 - 12.9	0.16	0.00 - 1.04	5	4-7
Woodward	1980 - 1985	love grass	2	20	8.3	2.6 - 13.5	0.07	0.00 - 0.14	4	17
Woodward	1982 - 1985	old world bluestem	1	10	16.1	11.3 - 18.8	0.09	0.01 - 0.28	3	0-8
El Reno	1983-1986	grain sorghum/wheat	3	14	2.6	0.2 - 8.8	0.05	0.01 - 0.27	38	11-63
Ft. Cobb	1983-1985	grain sorghum	1	5	1.7	0.7 - 2.5	0.06	0.00 - 0.17	35	16-61
Ft. Cobb	1983-1985	peanut	1	5	1.8	0.0-3.5	0.04	0.00 - 0.12	94	71-103
Chickasha	1979 - 1982	wheat	5	9	1.2	0.1 - 4.1	0.50	0.00 - 2.83	160	19 - 294
El Reno	1979-1986	wheat	1	16	0.7	0.0 - 2.5	0.46	0.05 - 1.61	857	2-8506
Woodward	1981 - 1985	wheat	, 2	25	3.5	2.2 - 7.0	0.10	0.01 - 0.58	50	2-129
El Reno	1983-1986	min-till wheat	3	21	8.6	1.5 - 17.7	0.03	0.00-0.09	28	3-52
Woodward	1983-1985	min-till wheat	3	15	1.0	0.0-6.9	0.07	0.00 - 0.11	17	7-59
Chickasha	1979-1982	farmsteads	3	9	` 4.1	0.2 - 18.4	0.50	0.00-3.30	31	13-53
Chickasha	1979-1982	oil field	1	9	0.3	0.0-0.36	0.05	0.00-0.11	13	9-16

^aScientific names of crops not listed in Tables I and II: eastern gama grass, *Tripsacum dactyloides* L.; love grass, *Eragrostis curula* Beauv.; old world bluestem, *Bothriochloa ischaemum* L. ^bDebris in well.

Dorich et al., 1985), NH₄F (Dorich et al., 1980; Porcella et al., 1970), ion-exchange resins (Armstrong et al., 1979; Heuttl et al., 1979), and citrate-dithionite bicarbonate (CDB) (Logan et al., 1979). Logan et al. (1979) reported that the bioavailable P content of suspended sediment from a Lake Erie tributary ranged from 14-24 to 25-56% of the TP content (500-1200 mg kg⁻¹) as measured by NaOH and CDB extractant, respectively. Similarly, in 2-day and 2-week incubations of suspended stream sediment from agricultural watersheds in northeastern Indiana with algae, Dorich et al. (1985) found 21 and 25%, respectively, of sediment TP to be available, with 98% originating in dissolved and NaOH-extractable fractions. In deposited sediments of a Wisconsin lake Sagher et al. (1975) found that 60-95% of the TP content (600-3900 mg kg⁻¹) was bioavailable (NaOH extraction). In fact, Wildung et al. (1974) reported that the P content of the sediment in several lakes in Oregon was directly related to the biological productivity of surface waters and served as a significant source of P to these waters, supporting increased biological growth. In the case of P availability for submerged macrophyte growth, Carignan and Kalff (1980) found that they depended overwhelmingly on sediments for their P supply. Even under hypereutrophic lake conditions, sediments contributed the major proportion (72%) of P utilized during growth.

Caution must be exercised, however, in relating P bioavailability of sediment material determined by the above chemical extractions and the potential of the sediment to increase algal growth (Lee et al., 1979; Sonzogni et al., 1982). These measures do not include variations in sediment properties or impact of the lake environment on bioavailability, such as differential settling of sediment particles and wind- or other current-induced mixing of the photic surface zone, possibly reducing its depth. Furthermore, aeration of the hypolimnion can have a large effect on P retention capacities of sediments.

Ground Water. Means and ranges of NO₃- and NH₄-N concentrations of well water over the study periods are presented in Table IV. These nutrients are considered to reflect any possible fertilizer N contamination of ground water. It is apparent that, in general, N contents of the wells are within acceptable limits for human (10 and 0.5 mg L⁻¹ NO₃- and NH₄-N, respectively) and livestock and fish consumption (100 and 2.5 mg L⁻¹ NO₃- and NH₄-N,

respectively). There were exceptions, however, for both NO_3 - and NH_4 -N. In the case of NO_3 -N, high well water concentrations were measured mainly on minimum-tilled wheat at El Reno and certain improved grass sites at Woodward. The maximum concentration observed at El Reno was 17.7 mg of NO_3 -N L⁻¹ and 18.8 mg of NO_3 -N L⁻¹ at Woodward. Although these levels are not extremely high, they clearly indicate the potential for NO_3 -N contamination under minimum tillage and intensive grass production.

Due to the increased adoption of minimum tillage, particular attention should be given to its environmental implications regarding ground water. In general, minimum tillage provides a wetter, cooler soil environment, due to the fact that more undisturbed large soil pores and burrows may exist for NO₃-N movement, which may enhance nitrification and NO₃-N leaching potentials (Groffman, 1984; Rice and Smith, 1983; Thomas et al., 1973). There is also less evaporation of soil water and, consequently, less movement of NO₃-N upward toward the soil surface. In the case of the improved grasses at Woodward, the monitored sites were on shallow water table, sandy soils and had received N fertilizer at annual rates of 67–134 kg of N ha⁻¹ for several consecutive years.

As expected from the rapid fixation of P by soil material and resultant low mobility in the soil profile, well water concentrations of SP were generally low (Table IV). For both NH_4 -N and SP, however, the high concentrations (Table IV) were in most cases due to improperly installed and maintained well casings that allowed surface runoff to flow directly into the wells. Improved well protection techniques eliminated this problem and reduced the nutrient contents to acceptable levels (Naney et al., 1984). CONTROL MEASURES

Control of Fertilizer Loss in Surface Runoff. With proper use and management, fertilizer N and P can have an environmental benefit. Fertilizer-enhanced plant cover can reduce the transport of water, soil, and nutrients in runoff from cultivated infertile or badly eroded soils. The fact that fertilizers can have a positive effect as a conservation tool to minimize runoff was recognized in New Zealand more than 30 years ago (Campbell, 1950). In addition, fertilizer use permits increased production on a reduced acreage, thereby benefiting the environment in several ways. If production is confined to a smaller acreage, total amounts of herbicides and insecticides needed are less.

Control measures are often required, however, to reduce N and P transport in surface runoff. These measures usually involve controlling the fertilizer loss at its source. Nutrient transport may be controlled by increasing ground cover through reduced tillage practices, which result in less soil and associated nurient loss. Of primary importance is increasing fertilizer efficiency. This can be achieved through appropriate fertilizer placement, such as banding, subsurface injection, careful timing, and split applications, so that soil nutrient levels are adquate for crop demands during periods of maximum uptake. Buffer or riparian strips have been effectively used to reduce the transport of particulate nutrients. In addition, small impoundments or reservoirs have been used as effective traps, reducing both soluble and particulate N and P levels as runoff moves from fields to rivers or lakes, improving downstream water quality. The reduction in soluble N and P may be attributed to algal uptake and sorption and that of particulate N and P by sedimentation.

Minimizing Fertilizer Leaching Potential. Due to the low mobility of P in the soil profile, measures to control leaching are generally directed toward NO_3 -N. As was the case for surface runoff control, the basic solution is to increase fertilizer efficiency, supplying only enough to satisfy crop needs above that which the soil does not supply. Maintaining the presence of N at the time of maximum uptake of the crop is especially important and may be accomplished by multiple applications or the use of a nitrification inhibitor. In fact, technology now exists to gear N and P contributions and fertilizer application rates to specific soil areas within a field rather than to a whole field. Additionally, fertilizers can be added in controlled amounts with irrigation water (fertigation) during periods of greater crop demand for N and P.

It should be noted that natural sources such as geologic formations, soil biological processes, and rainfall contribution can increase ground water NO₃-N concentrations. For example, some soil extracts in California have been reported to contain as much as 2000 mg of NO₃-N L⁻¹, primarily due to geologic contributions. Probably the greatest release of NO₃-N to the soil environment occurred when vast areas of the virgin prairies were first brought into cultivation.

Classification of soils by the susceptibility to leaching represents an effective management aid. Such classifications can be made through the use of available soil survey information. In Kansas, soils have been placed into different leaching classes on the basis of soil profile texture and permeability (Kissel et al., 1982). Many ground water contamination problems with fertilizer N and P simply involve direct surface runoff into older, hand-dug or newer, improperly installed, drilled wells. Where possible, agricultural field, feedlot, farmstead, and septic tank drainage should be directed away from the well. In the case of feedlots, NO_3 -N problems mainly occur when the feedlots are not in use and the surface seal breaks down, conditions become aerobic, and NO_3 -N production from the accumlated NH_4 -N is initiated.

Chemical compounds exist that can reduce the transformation of NH_4 - to NO_3 -N. These include nitrification inhibitors (e.g. nitrapyrin, 1-chloro-6,6,6-trimethylpyridine). These chemicals are particularly useful for soils with properties, practices, and weather conditions conducive to excessive leaching. They can temporarily minimize leaching losses on well-drained soils and reduce denitrification losses in heavy soils, especially under extremely wet conditions. For crops that have a fairly sustained N uptake pattern (e.g., forage and turf) controlled-release N fertilizers such as sulfur-coated urea offer an alternative means for minimizing leaching potential. Finally, soils most suspectible to leaching are often those that are irrigated. Proper irrigation design and scheduling can aid considerably in minimizing N leaching.

SUMMARY AND CONCLUSIONS

From this 8-year study of N and P transport in surface runoff and ground water from 20 agricultural watersheds, the following conclusions can be made.

1. The amounts of N transported in surface runoff were small compared to fertilizer N inputs (3-9%) and in many cases were exceeded by amounts in rainfall.

2. Natural soil fertility levels were high enough to result in soluble and total P concentrations in surface runoff from both unfertilized and fertilized watersheds that were consistently greater than critical levels associated with accelerated eutrophication.

3. Particulate N and P (sorbed and organic forms) accounted for an average 64 and 75% of total N and P, respectively, transported in surface runoff.

4. The respective amounts of N and P transported in surface runoff from the crop rotation watersheds were 1.7 and 1.8 times greater than from fertilized continuous wheat and 2.3 and 4.6 times greater than from unfertilized native grass.

5. In most cases, mean NO₃-N (0.3–16.1 mg L⁻¹) and NH₄-N (0.03–0.50 mg L⁻¹) concentrations in ground water were within acceptable limits for potable use (10 mg L⁻¹ NO₃-N) and for fish (2.5 mg L⁻¹ NH₄-N), and little movement of P to ground water was observed. High N and P concentrations were associated with improperly installed well casings.

6. Land use had little effect on N and P concentrations in ground water, although there appears to be an increased potential for NO_3 -N movement in ground water under minimum tillage and intensive grass production.

In general, therefore, the agricultural management practices studied had little environmental impact on ground water quality, although P enrichment of surface runoff may stimulate the accelerated eutrophication of small lakes and impoundments in the Southern Plains. Measures to reduce the environmental impact of aricultural N and P fertilizer use involve the adoption of minimum tillage practices, which will reduce soil loss and associated N and P in surface runoff. In addition, more efficient fertilizer use, through timing, method of application, chemical additives, and identification of soils susceptible to leaching, will decrease the amount of excess fertilizer N and P not taken up by the crop, which has the potential to be leached from the soil profile. These control measures have recently been implemented on the watersheds studied, following collection of several years of background N and P concentrations and amounts.

ACKNOWLEDGMENT

Technical assistance by ARS personnel at Durant, El Reno, and Woodward, OK, and Temple-Riesel, TX is gratefully acknowledged.

Registry No. N₂, 7727-37-9; P, 7723-14-0.

LITERATURE CITED

- Armstrong, D. E.; Perry, J. R.; Flatness, D. Final Report of the Wisconsin Water Research Center, Madison, WI, 1979.
- Burwell, R. E.; Timmons, D. R.; Holt, R. F. Soil Sci. Soc. Am. Proc. 1975, 39, 523–528.
- Burwell, R. E.; Schuman, G. E.; Heinemann, H. G.; Spomer, R. G. J. Soil Water Conserv. 1977, 32, 226–230.

- Campbell, D. A. Trans. Int. Congr. Soil Sci. 1950, 1, 327-331.
- Carignan, R.; Kalff, J. Science (Washington, D.C.) 1980, 207, 987-989.
- Dorich, R. A.; Nelson, D. W.; Sommers, L. E. J. Environ. Qual. 1980, 9, 557–563.
- Dorich, R. A.; Nelson, D. W.; Sommers, L. E. J. Environ. Qual. 1985, 14, 400–405.
- Groffman, P. M. Soil Sci. Soc. Am. J. 1984, 49, 329-334.
- Hanway, J. J.; Laflen, J. M. J. Environ. Qual. 1974, 3, 351-356.
- Hargett, N. L.; Berry, J. T. TVA Bulletin Y-189, Muscle Shoals, AL, 1985.
- Huettl, P. J.; Wendt, R. C.; Corey, R. B. J. Environ. Qual. 1979, 4, 541-548.
- Kissel, D. E.; Bidwell, O. W.; Kientz, J. F. Kansas State University Agricultural Experimental Station Bulletin 641, Manhattan, KS, 1982.
- Lee, G. F.; Jones, R. A.; Rast, W. In *Phosphorus Management* Strategies for Lakes; Loehr, R. C. Martin, C. S. Rast, W., Eds.; Ann Arbor Science: Ann Arbor, MI, 1979.
- Loehr, R. C. J. Water Pollut. Control Fed. 1974, 46, 1849-1872.
- Logan, T. J.; Oloya, T. O.; Yaksich, S. M. J. Great Lakes Res. 1979, 5, 112-123.
- Murphy, J.; Riley, J. P. Anal. Chim. Acta. 1962, 27, 31-36.
- Naney, J. W.; Smith, S. J.; Berg, W. A. In Water for the 21st Century: Will It Be There? Collins, M. A., Ed.; Freshwater Society Publication; Center for Urban Studies, Southern Methodist University: Dallas, TX, 1984.
- O'Conner, P. W.; Syers, J. K. J. Environ. Qual. 1975, 4, 347-350.
- Porcella, D. B.; Kumagai, J. S.; Middlebrooks, E. J. J. Sanit. Eng. Div., Am. Soc. Civ. Eng. 1970, SA4, 911-926.
- Rice, L. W.; Smith, M. S. Soil Sci. Soc. Am. J. 1983, 47, 1125–1129. Sagher, A.; Harris, R. F.; Armstrong, D. E. University Of Wisconsin
- Water Resources Center Technical Report WIC WRC 75-01, 1975, p 56.
- Sawyer, C. N. J. New Engl. Water Works Assoc. 1947, 61, 109-127.

- Shindler, D. W. Science (Washington, D.C.) 1977, 195, 260-262.
 Schuman, G. E.; Spomer, R. G.; Piest, R. F. Soil Sci. Soc. Am. Proc. 1973a, 37, 424-427.
- Schuman, G. E.; Burwell, R. E.; Piest, R. F.; Spomer, R. G. J. Environ. Qual. 1973b, 37, 299-302.
- Sharpley, A. N.; Smith, S. J.; Menzel, R. G. J. Environ. Qual. 1982, 11, 247–251.
- Smith, S. J.; Menzel, R. G.; Rhoades, E. D.; Williams, J. R.; Eck, H. V. J. Range Manage. 1983, 36, 435–439.
- Smith, S. J. Naney, J. W.; Berg, W. A. In Ground Water Quality and Agricultural Practices; D. M. Fairchild, D. M., Ed.; Lewis Publishing: Chelsea, MI, 1987.
- Sonzogni, W. C.; Chapra, S. C.; Armstrong, D. E.; Logan, T. J. J. Environ. Qual. 1982, 11, 555-563.
- Thomas, G. W.; Blevins, R. L.; Phillips, R. E.; McMahon, M. A. Agron. J. 1973, 65, 736–739.
- Vollenweider, R. A. OECD, Technical Report, Paris, France, 1971. Vollenweider, R. A.; Kerekes, J. *Prog. Water Technol.* **1982**, *12*,
- 5-38.
- Wildung, R. E.; Schimidt, R. L.; Gahler, A. R. J. Environ. Qual. 1974, 3, 133-138.
- U.S. Department of the Interior FWCPA. Methods for Chemical Analysis of Water Wastes; FCN 16020-7/71; National Environmental Research Center, Analysis Contol Laboratory: Cincinnati, OH, 1971.
- U.S. Environmental Protection Agency Water Quality Criteria; U.S. Government Printing Office: Washington, DC, 1973.
- U.S. Environmental Protection Agency Quality Criteria for Water; U.S. Government Printing Office: Washington 1976.
- U.S. Environmental Protection Agency Report to Congress: Nonpoint Source Pollution in the U.S.; U.S. Government Printing Office: Washington, DC, 1984.

Received for review November 20, 1986. Accepted May 18, 1987.

Synthesis and Herbicidal Activity of α -Heterocyclic Carbinol Carbamates

Tai-Teh Wu,* Jamin Huang, Noel D. Arrington, and Gerald M. Dill¹

A series of novel α -benzoxazolylbenzyl carbamates exhibit moderate herbicidal activity in preemergence tests. At 0.5 lb/acre, gramineous crops show tolerance. A total of 53 analogues have been synthesized and their herbicidal activities determined in order to examine the structure-activity relationships. The results indicate very specific structural requirements for herbicidal activity. For optimum activity, there is a specific size requirement for the carbamoyl group and α -phenyl ring substituents. Ortho substituents on the phenyl moiety are necessary for high activity, and meta and para substituents invariably diminish herbicidal activity. A novel ring closure was observed involving attack by the carbamoyl nitrogen at the benzoxazole 2-position, with benzoxazole ring opening, to give a 2-(5-imino)oxazolidinone, which was shown to be herbicidally inactive. This result leads to the conclusion that the ring closure-ring opening process does not contribute to the observed herbicidal activity.

A variety of carbamates are known to possess herbicidal activity (Ashton and Crafts, 1981). However, relatively few heterocyclic carbamates have been reported as herbicides. Recently, a series of herbicidal heterocyclic carbamates involving the isoxazole system was disclosed (Theobald et al., 1981). We now report a series of novel benzylcarbamates substituted with a heterocyclic moiety on the

¹Present address: Monsanto Agricultural Chemical Co., T1G, St. Louis, MO 63166.

 α -carbon, represented by structure 1 (Wu et al., 1986).



The herbicidal activity of the subject class was discovered during a systematic investigation of the herbicidal activity of the benzylcarbamates related to SIRMATE

Research and Development, Union Carbide Agricultural Products Company, Research Triangle Park, North Carolina 27709.