

CROSS MEDIA INPUTS TO EASTERN US WATERSHEDS AND THEIR SIGNIFICANCE TO ESTUARINE WATER QUALITY

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ABSTRACT

Extensive research on Chesapeake Bay estuary, its drainage basin, and its airshed have now demonstrated that atmospheric deposition and diffuse land discharges are the largest sources for many parameters affecting estuarine water quality. For example, phosphorus and sediments are transported to the Bay largely in overland storm flows, nitrate largely in atmospheric deposition and in ground water, many pesticides and other toxic materials in surface waters and atmospheric deposition, and silicate primarily in ground water. Concerns over point sources such as sewage treatment outfalls and industrial outfalls have led to greatly improved treatment methods, alleviating the relative magnitude of these sources. The realization of the magnitude and importance of diffuse sources has led to research on improved land use practices, including better patterns of land use in the Chesapeake Bay landscape. One example is the use of and improved management of forested riparian buffer zones in the coastal plain part of the drainage basin.

KEYWORDS

Water quality; land use; atmospheric deposition; riparian forest; nutrients; diffuse sources; sediments; toxics; ground water; storm water.

INTRODUCTION

In recent years Chesapeake Bay and many other estuaries in the eastern United States have experienced serious problems with oxygen depletion (Officer *et al.*, 1984). The principal cause of this problem has been overenrichment with nitrogen, and phosphorus (Correll, 1987). Most of the nitrogen is delivered as diffuse inputs from agricultural runoff and atmospheric deposition (Correll, 1987; Fisher and Oppenheimer, 1991). Historically, most of the phosphorus was delivered as point sources, but in recent years point sources have been diminished as a result of improved treatment and diffuse sources have become a dominant factor (Lung, 1986). Surface runoff from row crops dominates the diffuse sources of phosphorus (Jordan *et al.*, 1986a; Correll *et al.*, in press). An often overlooked nutrient is silicate, which is required for the productivity of a number of organisms, especially diatoms (Anderson, 1986). Essentially all of the silicate inputs to Chesapeake Bay originate as the products of soil mineral weathering and are transported in ground water to rivers and thence to the estuary (D'Elia *et al.*, 1983). As nitrogen and phosphorus enrichments have increased, silicate limitations are suspected to exert a strong influence on phytoplankton species composition, especially in the lower part of Chesapeake Bay in the summer and fall.

Another major water quality problem in Chesapeake Bay is contamination with toxic materials. Many of these are introduced as point sources. An example was a large introduction of kepone into the James River (Bender and Huggett, 1984). Others such as PCB's are introduced both in point sources and by atmospheric deposition (Helz and Huggett, 1987). Still others, such as the widely used agricultural herbicide atrazine, are introduced in overland storm water flows and in atmospheric deposition (Correll *et al.*, 1978; Wu 1981). Once herbicides such as atrazine enter tidal waters they become highly concentrated in natural organic surface slicks (Wu *et al.*, 1980) and cause widespread mortality to submersed vascular plants (Correll and Wu, 1982).

The fine particulates or suspended sediments which are introduced to the estuary as a result of soil erosion cause very high turbidity. The combination of soil particulates and high phytoplankton populations limits sunlight penetration in Chesapeake Bay (Pierce *et al.*, 1986; Gallegos *et al.*, 1990). Thus primary productivity is sometimes light-limited in this nutrient-enriched estuarine system (Harding *et al.*, 1986).

Thus, the problems encountered in attempts to manage and improve Chesapeake Bay water quality are complex, with diverse sources and transport mechanisms. Although considerable research has been conducted on these issues, we still are limited by the lack of adequate understanding of the overall Chesapeake Bay system, which includes not only the 12,000 km² estuary and the coastal ocean adjacent to its mouth, but also its 178,000 km² drainage basin and larger areas of poorly defined airshed. We will focus on diffuse sources of nutrients, sediments and atrazine, an agricultural herbicide; and on how variations in weather, and differing geology, land use patterns, and riparian vegetation affect nutrient delivery to Chesapeake Bay.

ATMOSPHERIC DEPOSITION

Both Chesapeake Bay and its drainage basin are within the region of North America where acidic deposition is a serious problem (Wisniewski and Keitz, 1983; Shin and Carmichael, 1992). The annual average volume-weighted bulk precipitation at the Rhode River site on the mid-western shore of The Bay had a pH of 4.17 over the eleven years from 1974 through 1984 and reached a minimum pH of 3.88 in 1981 (Correll *et al.*, 1987; Weller *et al.*, 1986; Table 1). During this period average annual rainfall volume was 116 cm, which is about 8 cm above the long-term average. This bulk precipitation contributed an average flux of 5.14 kg ha⁻¹ yr⁻¹ of nitrate nitrogen and 3.04 kg ha⁻¹ yr⁻¹ of ammonium nitrogen. Peak nitrate deposition was in 1983, when nitrate plus ammonium bulk precipitation was 10.65 kg ha⁻¹.

TABLE 1 Volume-Weighted Mean Bulk Precipitation At The Rhode River Site

Parameter	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	Average
Volume (cm)	110	142	116	86	119	151	89	102	115	138	110	116.2
pH	4.45	4.47	4.29	4.35	4.45	4.07	3.95	3.88	4.26	4.13	4.16	4.17
NO ₃ (kg N ha ⁻¹)	3.25	4.65	5.57	3.52	6.20	6.04	4.28	5.24	5.21	7.53	5.04	5.14
NH ₄ (kg N ha ⁻¹)	-	-	-	-	3.02	2.80	1.95	3.09	2.72	3.12	4.56	3.04

Dry atmospheric deposition is very difficult to measure and appropriate values to use in budgets are much more speculative. In one case dry deposition of nitrate and ammonium were assumed to be equal to wet or bulk deposition (Fisher and Oppenheimer, 1991). When wet or dry deposition occurs directly on the surface of the estuary it is clearly a source of readily available nitrogen. However, when the deposition occurs on the drainage basin, much of this nitrogen is removed from the water before it is discharged into the estuary. For example, from 1974-1978 the total discharges of nitrate and ammonium from the Rhode River watershed due to all combined sources were only 22% and 5.9%, respectively, of bulk deposition on the drainage basin (Correll and Ford, 1982; Table 2). This

was true despite the fact that these basins were also receiving dry deposition and had 35% of their

TABLE 2 Integrated Annual Rhode River Watershed Area Yield Discharge

Parameter	1974	1975	1976	1977	Average
Discharge (cm)	20.8	40.0	28.3	12.2	25.3
Nitrate (kg N ha ⁻¹)	0.70	1.33	1.26	0.38	0.92
Diss. NH ₄ (kg N ha ⁻¹)	0.11	0.28	0.23	0.10	0.18

area devoted to row crops and pasture land. One basin, entirely covered with mature hardwood deciduous forest, where the only external nitrogen source was atmospheric deposition, discharged only 3.4% as much nitrate and 3.3% as much ammonium as was deposited in bulk precipitation over a four year period (Weller *et al.*, 1986). Thus it would be prudent to be cautious in concluding that very much of the nitrogen deposited from the atmosphere on the drainage basin actually reaches the Chesapeake. However, the atmospheric wet deposition of nitrogen which occurs directly on the estuarine waters is still an important input. For the Rhode River this was estimated to exceed all drainage basin inputs in 6 out of 7 years (Correll and Ford, 1982). Only during unusually wet seasons did land runoff exceed direct atmospheric bulk precipitation on the estuarine surface! For Chesapeake Bay as a whole, Fisher and Oppenheimer (1991) estimated direct wet deposition to the tidal waters as 6.5 million kg yr⁻¹.

Some agricultural herbicides including atrazine have sufficiently high vapor pressures to partially vaporize during and subsequent to field application. They are carried long distances in the atmosphere before deposition. Wu (1981) sampled wet deposition at the Rhode River for several years. Atrazine was always detectable in all seasons with peak concentrations of 2.2 µg l⁻¹. Even winter precipitation contained up to 0.97 µg l⁻¹. Similar results were reported by Richards *et al.* (1987) for the northeastern United States with peak concentrations of 1.5 µg l⁻¹. Herterich (1991) reported concentrations up to 1.6 µg l⁻¹ in clouds, and atrazine has been found in concentrations of about 1 µg l⁻¹ even in remote lakes and reservoirs.

LAND DISCHARGES

Land Use Effects

The effects of different land use on the discharge of nutrients and sediments are best revealed by comparing "paired watersheds" for the same time periods so that variation in weather is not a factor. We have extensive data for a series of subwatersheds of the Rhode River subestuary of Chesapeake Bay. They are contiguous small watersheds on the inner part of the Atlantic Coastal Plain geologic province (Correll, 1977). Variations in discharges for the same watersheds among years allows us to determine the effects of differing weather conditions. Some of these results have been summarized in Correll *et al.* (in press). For a given year (Table 3), cropland discharged five times as much total

TABLE 3 Annual Nutrient Discharges of Three Different Rhode River Watersheds Dominated by the Indicated Land Uses (kg ha⁻¹ yr⁻¹)

Parameter	Cropland	Pasture	Forest
Total-N	13.8	5.95	2.74
Dissolved NH ₄	0.45	0.51	0.15
Nitrate-N	6.35	3.20	0.36
Total-P	4.16	0.68	0.63
Orthophosphate-P	1.20	0.32	0.15

N as forest while pasture land had intermediate discharges. Specific nitrogen fractions had differing patterns. Cropland discharged three times as much dissolved ammonium and 18 times as much nitrate as forest. Cropland discharged seven times as much total P and eight times as much phosphate as forest. Over a five year period (Table 4), the combined discharges of all Rhode River subwatersheds varied three-fold among years for total N yr⁻¹ and seven-fold for total N in the spring season. Similar wide interannual variations were observed for other nutrient and sediment parameters. Multiple

TABLE 4 Interannual Variations in Nitrogen Discharges From the Combined Rhode River Study Subwatersheds Over a Five Year Period (kg ha⁻¹ yr⁻¹; Correll *et al.*, in press)

	mean	extremes	mean	extremes
Total-N	1.03	0.32-2.19	2.20	1.11-3.47
Dissolved NH ₄	0.081	0.026-0.176	0.178	0.097-0.275
Nitrate-N	0.364	0.095-0.647	0.916	0.379-1.33

regression models of land use effects on nutrient discharges from Rhode River watersheds indicated that even though only 23% of the watershed was crop land, about half of the total P and over 70% of the total N were discharged from crop land (Jordan *et al.*, 1986a).

The soils of the Rhode River watershed are highly erodible and average slopes are about 5%. Over a study period of about 4 years the average suspended sediment discharge was 5.2 kg ha⁻¹wk⁻¹ (Jordan *et al.*, 1986b). Not only were these sediments derived primarily from crop lands, but the sediments from crop land had a higher phosphorus content (Vaithyanathan and Correll, 1992).

Atrazine is a widely used preemergent agricultural herbicide. In studies on the Rhode River watershed between one and two percent of the applied atrazine was discharged from the watersheds into tidal waters (Correll *et al.*, 1978). Fifty eight percent of the atrazine was discharged in solution. However, during summer thunder storms the atrazine concentration on suspended sediments discharged from these watersheds reached levels of 590 µg g⁻¹ (Correll *et al.*, 1978). Eight Rhode River subwatersheds were found to have atrazine concentrations of up to 40 µg l⁻¹ in their discharges in the summer and up to 10 µg l⁻¹ in the winter (Wu *et al.*, 1983). Atrazine was detectable in discharges from completely forested watersheds, probably due to atmospheric deposition.

Geological Effects

Direct tests of the effects of geology on diffuse source watershed discharges are almost nonexistent. We have been examining the effects of watershed location within the Atlantic Coastal Plain geological province for several years. Watersheds were selected for study along a transect from the inner to the outer coastal plain. Results from these watersheds were compared with results from long-term Rhode River coastal plain watersheds for the same time periods (Tables 5, 6; Correll, 1991). Outer coastal

TABLE 5 Effects of Location on Atlantic Coastal Plain on Nitrogen and Phosphorus Discharges From Chesapeake Bay Watersheds in the Spring of 1989

Location	Land Use	Total-N (mg l ⁻¹)	Total-P (mg l ⁻¹)	Atomic Ratio (N/P)
Outer Coastal Plain	Forest	0.45	0.04	11
Inner Coastal Plain	Forest	1.0	0.22	4.5
Outer Coastal Plain	Agriculture	4.2	0.22	19
Mid Coastal Plain	Agriculture	3.9	0.63	6.2
Inner Coastal Plain	Agriculture	3.4	1.9	1.8

plain watersheds discharged lower concentrations of phosphorus and higher concentrations of nitrate

than inner coastal plain watersheds. Watersheds at intermediate locations had intermediate discharges. This was true in general as well as for a given land use. Thus a completely forested outer coastal plain drainage discharged significantly less phosphorus than a Rhode River forested drainage basin or another inner coastal plain test basin. As a result the atomic ratios of nitrogen to phosphorus in discharges varied dramatically among these watersheds. In one spring season the average atomic ratio varied from about two for Rhode River agricultural watersheds to about 19 for an outer coastal plain agricultural drainage basin. Differences in discharges for inorganic nitrogen and phosphorus fractions were also large (Table 6). Outer coastal plain forest had 6-fold lower phosphate concentrations than forest on the inner coastal plain. Cropland-dominated outer coastal plain watersheds had only 6 percent of the phosphate and 11 percent of the ammonium concentrations found on agricultural watersheds on the inner coastal plain. However, nitrate concentrations were over four times higher on the outer coastal plain.

TABLE 6 Effects of Location on Atlantic Coastal Plain on Nitrate, Ammonium, and Phosphate Discharges From Chesapeake Bay Watersheds in the Spring of 1989

Location	Land Use	PO ₄ (mg l ⁻¹)	NO ₃ -N (mg l ⁻¹)	NH ₄ -N (mg l ⁻¹)
Outer Coastal Plain	Forest	0.02	0.03	0.05
Inner Coastal Plain	Forest	0.13	0.06	0.09
Outer Coastal Plain	Agriculture	0.05	3.1	0.12
Mid Coastal Plain	Agriculture	0.31	1.9	0.52
Inner Coastal Plain	Agriculture	0.85	0.75	1.05

We are now conducting similar geological comparisons in two spatially important subformations of the piedmont geological province. We believe that these differences among geological areas are primarily due to differences in ground water hydrologic pathways. In the sandy outer coastal plain almost all discharges are as ground water and hydraulic conductivities are very high. Extensive drainage ditches further reduce surface flows. Thus soluble fractions such as nitrate are easily transported, but there is little erosion and transport of phosphorus as particulates.

The transport of nitrate in ground waters to coastal receiving waters is a serious problem in the northeastern United States as well. Results similar to our outer coastal plain findings have been reported for the Cape Cod, MA region (Valiela *et al.*, 1990; Giblin and Gaines, 1990). This topic was reviewed recently by Lowrance and Pionke (1989).

Riparian Forest Effects

Although cropland drainage basins are responsible for much of the phosphorus and most of the nitrogen discharges in systems like the Rhode River watershed, these discharges would be much larger if it were not for the presence of hardwood deciduous riparian forests along essentially all of the stream channels. Long-term studies of one 16 ha cropland watershed and the first order stream draining it have led to a better understanding of how these cropland/riparian forest landscapes function. One study by Peterjohn and Correll (1984; Table 7) showed that this forest trapped 94% of the suspended sediments in overland storm flows. As a result 84% of particulate organic N, 78% of particulate ammonium, and 85% of particulate total P were removed from overland flows. In this and subsequent studies of shallow ground waters flowing from the cropland through the riparian forest it was shown that for three years an average of 86 % of the nitrate was removed during transit (Correll and Weller, 1989; Peterjohn and Correll, 1986; Table 8). The efficiency of this nitrate removal was highest in the fall (97%) and lowest in the winter (81%). Tree assimilation and storage in accretions of woody biomass could have accounted for about 25% of this nitrate removal, but the available evidence leads us to believe that denitrification is the most important mechanism for nitrate removal in the ground water. Direct evidence for increased rates of nitrous oxide emissions within the forest was obtained, but extreme temporal and spatial variation made the calculation of flux rates

TABLE 7 Changes in Nutrient Concentrations (mg l^{-1}) in Overland Storm Flows From a Cropland on the Rhode River Watershed as it Moved Through a Riparian Hardwood Forest Along a First Order Stream (Peterjohn and Correll, 1984)

Position	Season	Total Susp. Part.	Nitrate N	<u>NH₄-Nitrogen</u>		<u>Organic-N</u>		<u>Total-P</u>	
				Exchang. Part.	Diss.	Part.	Diss.	Part.	Diss.
Entering riparian forest	Spring	8,840	3.73	0.73	3.63	27.7	1.47	3.22	0.26
	Summer	11,500	10.5	0.52	1.17	32.1	2.72	11.9	0.13
	Fall	3,830	1.57	0.30	0.90	16.8	0.78	3.29	0.13
	Winter	1,760	1.99	0.05	0.25	1.32	2.04	0.86	0.32
	Year	6,480	4.45	0.40	1.49	19.5	1.75	4.82	0.21
19 m into riparian forest	Spring	1,380	2.60	0.22	1.23	6.47	1.18	2.31	0.08
	Summer	966	1.93	0.12	0.41	5.06	1.44	2.09	0.09
	Fall	122	0.34	0.04	0.07	2.61	0.53	0.60	0.39
	Winter	176	2.18	0.04	0.16	0.37	1.33	0.06	0.38
	Year	661	1.76	0.10	0.47	3.63	1.12	1.27	0.24
Leaving riparian forest after 50 metres	Spring	372	0.74	0.08	0.40	2.54	1.18	0.45	0.25
	Summer	524	1.03	0.11	0.18	3.46	0.71	1.04	0.18
	Fall	no overland flow reached these samplers in the fall							
	Winter	360	1.05	0.08	0.65	2.02	0.08	--	--
	Year	419	0.94	0.09	0.41	2.67	0.66	0.74	0.22

TABLE 8 Mean fluxes for a period of three years for Water and Nitrate Entering a First Order Stream Riparian Forest on Rhode River Watershed via Precipitation and Cropland Groundwater Drainage and Leaving the Forest via Stream Base Flow and Evapotranspiration (ET). Watershed is Composed of 10.4 ha of rowcrops and 5.9 ha Riparian Forest (Correll and Weller, 1989).

Time Period	<u>Water Volume (cm)</u>				<u>Nitrate (kg season^{-1} or yr^{-1})</u>		
	Precip- itation	Crop drainage	ET	Stream Baseflow	input	output	Input- output
Winter	31.6	30.8	35.1	27.3	117.5	22.0	95.5
Spring	31.7	25.0	34.4	22.3	93.9	9.1	84.8
Summer	24.0	9.8	25.8	8.0	36.4	6.2	30.2
Fall	26.1	2.1	25.9	2.3	15.1	0.4	14.7
Complete Year	113.4	67.8	121.2	59.9	262.9	37.9	225.0

impossible (Correll, 1991). The ground water leaving the crop land is acidic with a mean pH of about 4.5. This acidity is largely due to nitrification of reduced nitrogen in the cropland (Correll *et al.*, 1987). As it traversed the forest the mean pH increased to about 5.5 providing another benefit to stream water quality (Peterjohn and Correll, 1986; Correll and Weller, 1989), since these systems are still too acidic for many fish to successfully spawn (Correll *et al.*, 1987). This increase in pH is due to the both nitrate assimilation by the plants and denitrification (Correll and Weller, 1989). Similar effects of riparian forests have been reported in other locations on the Atlantic Coastal Plain (Lowrance *et al.*, 1984; Cooper *et al.*, 1986).

CONCLUSION

The Rhode River watershed and estuary provide a model for the coastal plain landscape of the Chesapeake Bay drainage. An overall landscape level synthesis of our findings on Rhode River nutrient dynamics (Jordan *et al.*, 1986a; Correll *et al.*, in press) found that croplands were responsible for the bulk of the nitrogen discharge from the watershed. However, riparian forests bordering the fields removed 80% or more of most nitrogen and phosphorus fractions in overland storm flows and about 85% of the nitrate in shallow ground water drainage from the fields. Nutrient discharges from these cropland/riparian forest watershed systems still exceeded discharges from pastures and other forests. Bulk precipitation accounted for 31% of the total non-gaseous nitrogen inputs to the landscape. Of these inputs only one percent entered the estuary. Of the total phosphorus inputs to the landscape, seven percent was from bulk precipitation and seven percent of the total inputs entered the estuary. Most of the phosphorus was transported as particulates in surface flows. The largest fraction of nitrogen was transported as nitrate in ground water, emerging as base flow in stream channels. The second largest fraction of nitrogen was transported as particulate organic N in surface flows. Watersheds in the outer coastal plain discharged much less sediment and phosphorus and somewhat higher levels of nitrogen, especially nitrate (Correll, 1991).

The piedmont and Appalachian parts of the Chesapeake Bay watershed are known to account for much more nitrogen and less sediment discharge. Although these are still not well known it is estimated that for the Chesapeake Bay/Watershed system, land discharges from these geological provinces account for about 60% of the total atmospheric, land discharge, and point source loading of total N (Correll, 1987). The inner and mid-coastal plain is the source of most of the suspended sediment loading due to its easily erodible soils, adjacency to the tidal waters, and the lack of dams. Our knowledge base is far from adequate concerning such agricultural chemicals as atrazine, but it is clear that both atmospheric and surface flows are important routes of transport from farms to tidal waters.

Estuarine water quality in systems such as Chesapeake Bay is adversely affected by a wide variety of materials which originate from both point and diffuse sources. These materials are transported into the estuary through the atmosphere, as ground water, and as overland storm flows. Table 9 summarizes some of this information for substances discussed in this paper.

TABLE 9 Sources and Routes of Transfer to Chesapeake Bay of Selected Water Quality Materials

Substance	Sources*	Routings to Chesapeake Bay
Sediments	L - Soil Erosion, Especially From Inner & Mid-Coastal Plain Cropland	Overland Stormflows
Phosphorus	L - Soil Erosion, Especially From Inner & Mid-Coastal Plain Cropland M - Sewage Treatment & Industrial Outfalls	Overland Stormflows Rivers
Silicate	L - Soil Weathering	Ground Water, Either Direct or via Stream Baseflows
Nitrate	L - Combustion of Fossil Fuels L - Leaching of Soils, Especially Croplands M - Sewage Treatment & Industrial Outfalls S - Overland Stormflows From Land	Atmospheric Deposition (Dry & Wet) Ground Water, Either Direct or via Stream Baseflows Rivers Rivers
Ammonium	L - Erosion of Cropland	Overland Stormflows
Atrazine	M - Volatilization of Fertilizers & Manure L - Overland Stormflows from Cropland M - Volatilization of Agricultural Applications	Atmospheric Deposition Surface Flows Atmospheric Deposition

* Relative importance: L = large, M = moderate, S = small

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