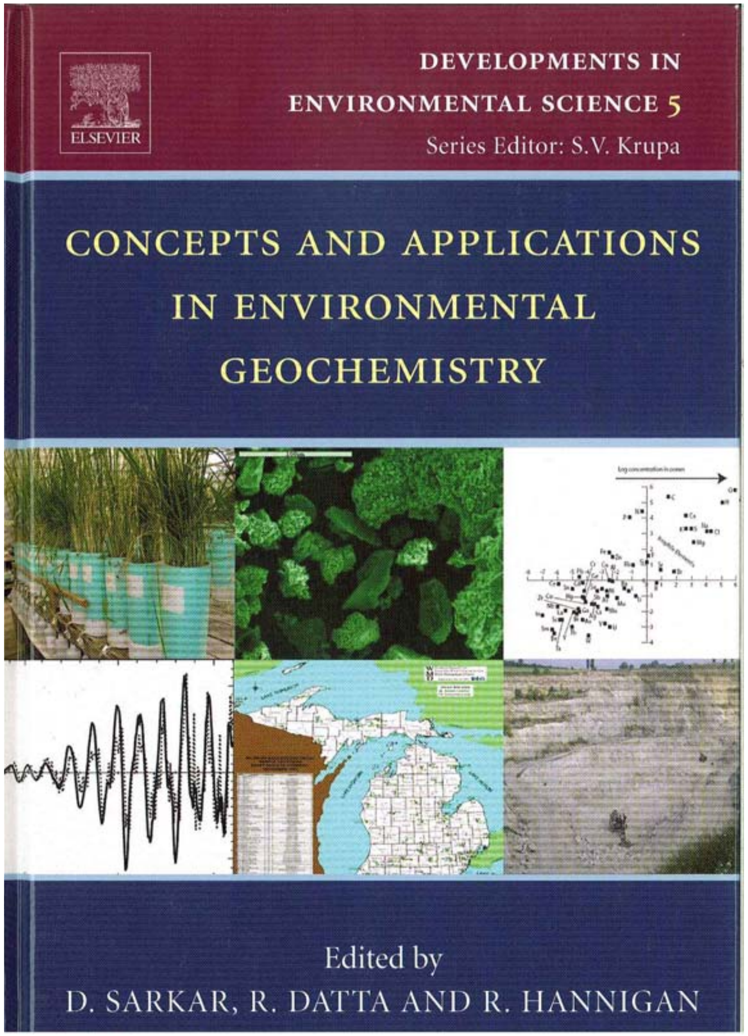


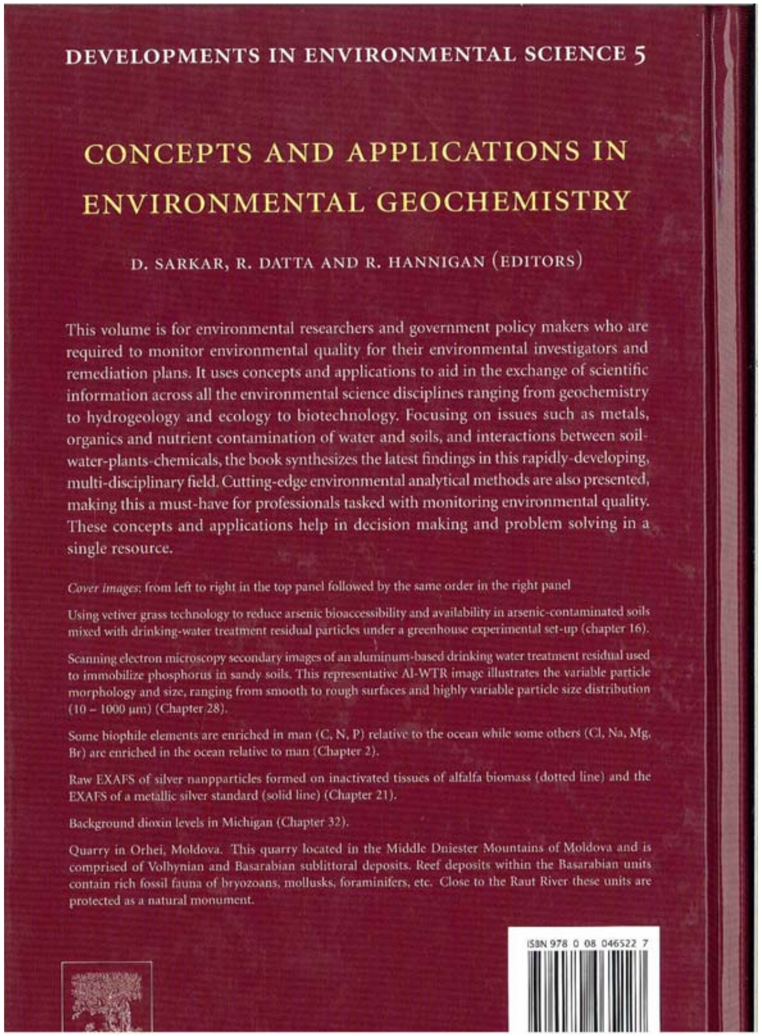
ELSEVIER

DEVELOPMENTS IN
ENVIRONMENTAL SCIENCE 5

Series Editor: S.V. Krupa

CONCEPTS AND APPLICATIONS IN ENVIRONMENTAL GEOCHEMISTRY

Edited by
D. SARKAR, R. DATTA AND R. HANNIGAN



DEVELOPMENTS IN ENVIRONMENTAL SCIENCE 5

CONCEPTS AND APPLICATIONS IN ENVIRONMENTAL GEOCHEMISTRY

D. SARKAR, R. DATTA AND R. HANNIGAN (EDITORS)

This volume is for environmental researchers and government policy makers who are required to monitor environmental quality for their environmental investigators and remediation plans. It uses concepts and applications to aid in the exchange of scientific information across all the environmental science disciplines ranging from geochemistry to hydrogeology and ecology to biotechnology. Focusing on issues such as metals, organics and nutrient contamination of water and soils, and interactions between soil-water-plants-chemicals, the book synthesizes the latest findings in this rapidly-developing, multi-disciplinary field. Cutting-edge environmental analytical methods are also presented, making this a must-have for professionals tasked with monitoring environmental quality. These concepts and applications help in decision making and problem solving in a single resource.

Cover images: from left to right in the top panel followed by the same order in the right panel

Using vetiver grass technology to reduce arsenic bioaccessibility and availability in arsenic-contaminated soils mixed with drinking-water treatment residual particles under a greenhouse experimental set-up (chapter 16).

Scanning electron microscopy secondary images of an aluminum-based drinking water treatment residual used to immobilize phosphorus in sandy soils. This representative Al-WTR image illustrates the variable particle morphology and size, ranging from smooth to rough surfaces and highly variable particle size distribution (10 – 1000 μm) (Chapter 28).

Some biophile elements are enriched in man (C, N, P) relative to the ocean while some others (Cl, Na, Mg, Br) are enriched in the ocean relative to man (Chapter 2).

Raw EXAFS of silver nanpparticles formed on inactivated tissues of alfalfa biomass (dotted line) and the EXAFS of a metallic silver standard (solid line) (Chapter 21).

Background dioxin levels in Michigan (Chapter 32).

Quarry in Orhei, Moldova. This quarry located in the Middle Dniester Mountains of Moldova and is comprised of Volhynian and Basarabian sublittoral deposits. Reef deposits within the Basarabian units contain rich fossil fauna of bryozoans, mollusks, foraminifers, etc. Close to the Raut River these units are protected as a natural monument.

ISBN 978 0 08 046522 7

Elsevier
Radarweg 29, PO Box 211, 1000 AE Amsterdam, The Netherlands
Linacre House, Jordan Hill, Oxford OX2 8DP, UK

First edition 2007

Copyright © 2007 Elsevier Ltd. All rights reserved

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means electronic, mechanical, photocopying, recording or otherwise without the prior written permission of the publisher

Permissions may be sought directly from Elsevier's Science & Technology Rights Department in Oxford, UK: phone (+44) (0) 1865 843830; fax (+44) (0) 1865 853333; email: permissions@elsevier.com. Alternatively you can submit your request online by visiting the Elsevier web site at http://www.elsevier.com/locate/permissions, and selecting *Obtaining permission to use Elsevier material*

Notice
No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made

Library of Congress Cataloging-in-Publication Data
A catalog record for this book is available from the Library of Congress

British Library Cataloguing in Publication Data
A catalogue record for this book is available from the British Library

ISBN: 978-0-08-046522-7
ISSN: 1474-8177

For information on all Elsevier publications
visit our website at books.elsevier.com

Printed and bound in Italy

07 08 09 10 11 10 9 8 7 6 5 4 3 2 1

Working together to grow
libraries in developing countries
www.elsevier.com | www.bookaid.org | www.sabre.org
ELSEVIER BOOK AID International Sabre Foundation

Contents

Section I: Today's Environmental Geochemistry—A Review of New Concepts and Innovative Practices

Section II: Geochemistry in Surface- and Groundwater Research

Section III: Lithosphere–Hydrosphere Interactions: Applications of Geochemical Principles

Section IV: Geochemistry in Soils Research

Section V: Environmental Biogeochemistry—Concepts and Case Studies

Section VI: Application of Geochemical Principles in Environmental Quality and Remediation Research

Section VII: Applications of New Analytical and Quantitave Methods in Environmental Geochemistry Research

Section VIII: Conclusion

List of Contributors

P.A. Abanda	Mid-South Community College, West Memphis, AR, USA
Hassan Y. Aboul-Enein	Pharmaceutical and Medicinal Chemistry Department, Pharmaceutical and Drug Industries Research Division, National Research Centre, Dokki, Cairo, Egypt
Honey Aggarwal	Department of Biotechnology & Environmental Sciences, Thapar Institute of Engineering & Technology (Deemed University), Patiala, Punjab, India
Imran Ali	Department of Chemistry, Jamia Millia Islamia (Central University), Jamia Nagar, New Delhi, India
C. Brannon Andersen	Department of Earth and Environmental Sciences, Furman University, Greenville, SC, USA
Andrea Anderson	Department of Earth and Environmental Sciences, University of Texas at San Antonio, San Antonio, TX, USA
S. Banerjee	Center for Study of Man and Environment, Sector II, Salt Lake City, Kolkata, India
M.L. Barrico	Department of Botany, University of Coimbra, Coimbra, Portugal
Tracy D. Branam	Indiana Geological Survey, Indiana University, Bloomington, IN, USA
B. Brocks	Towson University Geochemistry Laboratory, Towson University, Towson, MD, USA
Yong Cai	Department of Chemistry & Biochemistry and Southeast Environmental Research Center, Florida International University, University Park, Miami, FL, USA

REFERENCES

Alikhan, M.A., Bagatto, G., Zia, S., 1990. The crayfish as a biological indicator of aquatic contamination by heavy metals. Water Res. 24(9), 1069–1076.

Anderson, M.B., Preslan, J.E., Jolibois, L., Bollinger, J.E., George, W.J., 1997. Bioaccumulation of lead nitrate in Red Swamp Crayfish (Procambarus clarkia). J. Hazard. Mater. 54, 15–29.

Baker, B., 1998. Mercury in fish: Agencies work to find common ground. Bioscience 48(11), 900.

Campbell, L.M., Osano, O., Hecky, D.G., 2003. Mercury in fish from three rift valley lakes (Turkana, Naivasha and Baringo), Kenya, East Africa. Environ. Pollut. 125, 281–286.

Dickson, G.W., Briese, L., Geisy, J.P., 1979. Tissue metal concentrations in two crayfish species co-habitating a Tennessee cave stream. Oecologia 44, 8–12.

DiStefano, R.J., Neves, R.J., 1991. Response of the crayfish *bartonii bartonii* to acid exposure in southern Appalachian streams. Can. J. Zool. 69, 1585–1591.

Geisy, J.P., Bowling, J.W., Kania, H.J., 1980. Cd and zinc accumulation and elimination by freshwater crayfish Cambarus robustus and Cambarus bartoni. Can. J. Zool. 63, 2313–2322.

Hart, B.T., 1982. Uptake of trace metals by sediments and suspended particulates: A review. Hydrobiologia 91, 299.

Hasiotis, S.T., 1999. Crayfish fossils and burrows from the upper triassic chinle formation, Canyonlands National Park, Utah. Paleontol. Res. 2, 83–90.

Hasiotis, S.T., Mitchell, C.E., 1993. A comparison of crayfish burrow morphologies: Triassic and Holocene paleo- and neoichnological evidence, and the identification of their burrowing signatures. Ichnos 2, 291–314.

Hasset, J.M., Jennett, J.C., Smith, J.E., 1980. Heavy metals accumulation by algae. In: Baker, R.A. (Ed.), Contaminants and Sediments, Vol. 2, pp. 409–424.

Hobbs, H.H., 1989. An illustrated checklist of American crayfishes (Decapoda: Astacidae, Cambaridae, and Parastacidae). Smithson. Contrib. Zool. 480, 236.

Holdich, D.M., Lowery, R.S., 1988. Freshwater Crayfish, Biology, Management, and Exploitation. Timber Press, Portland, OR.

Khan, A.T., Forester, D.M., Mielke, H.W., 1995. Heavy Metal Concentration in Two Populations of Crayfish. Vet. Human Toxicol. 37(5), 426–428.

Mason, R.P., Laporte, J., Andres, S., 2000. Factors controlling the bioaccumulation of mercury, methylmercury, arsenic, selenium, and cadmium by freshwater invertebrates and fish. Arch. Environ. Contam. Toxicol. 38(3), 283–297.

Mirenda, R.J., 1986. Acute toxicity and accumulation of zinc in the crayfish, *Orconectes virillis* (Hagen). Bull. Environ. Contam. Toxicol. 37, 387–394.

Mwangi, S.M., Alikhan, M.A., 1993. Cadmium and nickel uptake by tissues of Cambarus bartoni (Astacidae, Decapoda, Crustacea): Effects on copper and zinc stores. Water Res. 27(5), 921–927.

Naqvi, S.M., Howell, R.D., Sholas, M., 1993. Cadmium and lead residues in field-collected red swamp crayfish (Procambarus clarkia) and uptake by alligator weed, Alternanthera philoxiroides. J. Environ. Sci. Health, B 28(4), 473–485.

Roel, M.J., Orth, D.J., 1993. Trophic basis of production of stream-dwelling Smallmouth Bass, Rock Bass, and Flathead Catfish in relation to Invertebrate Bait Harvest. Trans. Am. Fisher. Soc. 122, 46–62.

Wright, D.A., Welbourn, P.M., 1993. Effects of mercury exposure on ionic regulation in the crayfish Orconectes propinquus. Environ. Pollut. 82(2), 139–142.

Developments in Environmental Science, Volume 5
D. Sarkar, R. Datta and R. Hannigan (Editors)

ISSN: 1474-8177/DOI:10.1016/S1474-8177(07)05024-3

Chapter 24

Relations among land cover, vegetation index, and nitrate concentrations in streams of the Enoree River Basin, piedmont region of South Carolina, USA

Suresh Muthukrishnan, Gregory P. Lewis and C. Brannon Andersen

Abstract

Globally, high nitrate concentrations and fluxes in rivers are correlated with human population density and can lead to eutrophication of estuaries and coastal oceans. Although elevated nitrate concentrations often are associated with agricultural land cover, urban land cover also can contribute substantially to elevated nitrate concentrations in streams and rivers. In the piedmont region of the southeastern United States, urban areas typically are located in the headwater areas of watersheds. Because headwaters account for the majority of stream channel length in a watershed, the effect of urbanization on the biogeochemical cycling of nitrogen is magnified. We examined the relations between stream nitrate concentrations, land cover, and vegetation density in watersheds of nineteen tributaries of the Enoree River in northwestern South Carolina, USA. Based on data from 134 sample localities, stream nitrate concentrations generally increased with increasing urban land cover and decreased with increasing forest cover and vegetation density (normalized density vegetation index). Although watersheds with the highest percent urban land cover typically had the highest nitrate concentrations, nitrate concentrations were most variable spatially in drainage basins with 5 to 20% urban land cover. The relations between land cover, vegetation density, and nitrate concentrations are complicated by variation in the intensity of urbanization and spatial location of urban and forested land within the drainage basin of each sample locality. Artificial ponds in urban areas appear to play an important role in lowering stream nitrate concentrations and contribute to the spatial variability of nitrate concentrations.

24.1. Introduction

Globally, nitrate concentrations in rivers correlate positively with human population density (Peierls et al., 1991). Furthermore, human activities have increased greatly the flux of nitrogen, especially nitrate–nitrogen, from terrestrial to aquatic ecosystems within the last two centuries (Meybeck, 1982; Meybeck and Helmer, 1989; Vitousek et al., 1997; Galloway and Cowling, 2002). Elevated nitrate concentrations and fluxes in river water threaten drinking water quality and contribute to eutrophication of estuaries and coastal oceans (Vitousek et al., 1997). Humans have increased nitrate loading to rivers in several ways. For example, both agricultural non-point sources and point-source inputs from wastewater treatment plants (WWTPs) contribute nitrates to rivers (Vitousek et al., 1997; Paul and Meyer, 2001). Atmospheric deposition of nitrogen to watersheds also appears to contribute to river nitrogen (Jaworski et al., 1997). Clearing forest vegetation for timber, agriculture, urban development, or other purposes reduces the uptake and storage of nitrogen in plant biomass, thereby allowing more nitrogen to enter streams and rivers (e.g., Likens et al., 1970).

Land use and land cover in watersheds often are effective predictors of water quality in rivers (e.g., Hunsaker and Levine, 1995) because they integrate the effects of various human activities. Previous studies have incorporated remote sensing data and geographical information systems (GIS) with field-based data to better understand the relationships between land use/land cover and biophysical processes. Satellite data and aerial photographs are commonly used to create land use/land cover, vegetation density, and biodiversity data (Stoms and Estes, 1993; Filoso et al., 2003). Satellite data also have been used widely in assessing the health and density of vegetation biomass using several indices, including the commonly used normalized density vegetation index (NDVI) (Tucker and Sellers, 1986; Bannari et al., 1995; Ji and Peters, 2003). GIS has been used commonly to organize and display data and to study spatial and temporal relations between variables such as water chemistry and land use and land cover within a watershed (Ballester et al., 2003).

Based on previous studies of land cover and land use, elevated stream nitrate concentrations are associated with both agriculture and urban land covers. For example, agricultural land use contributes significant amounts of nitrogen in large watersheds such as the Mississippi, the Seine, and the Changjiang (Moreau et al., 1998; Roy et al., 1999; Goolsby, 2000; Rabalais et al., 2002; Zhiliang et al., 2003), as well as in smaller watersheds such as the River Vilaine (Moreau et al., 1998). Agricultural sources contribute 20% or more of the dissolved inorganic nitrogen in rivers within these watersheds. In some cases, however, streams in urbanized watersheds have higher nitrate concentrations than streams in agricultural watersheds (e.g., Boyle et al., 1997; Douglas et al., 2002). In contrast, streams draining forested watersheds typically have very low nitrate concentrations (Clark et al., 2000).

In regions undergoing rapid urban development, several types of land cover may be found within a single watershed (e.g., urban residential, urban commercial, forested, agricultural). This variety of land covers may increase the variability of nitrate concentrations within the watershed. Thus, the distribution of land use and land cover in watersheds may be important in controlling the concentration of nitrogen in streams.

In this study, we examined the relations among stream nitrate concentrations, land cover and vegetation density in tributary watersheds of the 1893 km^2 Enoree River basin in the Piedmont Province of South Carolina, USA (Fig. 24.1). Water samples were collected from localities representing drainage areas from about 0.2 km^2 to 307 km^2. Remote sensing and GIS were used to develop land use and land cover data, to calculate NDVI, to delineate drainage areas for individual sample

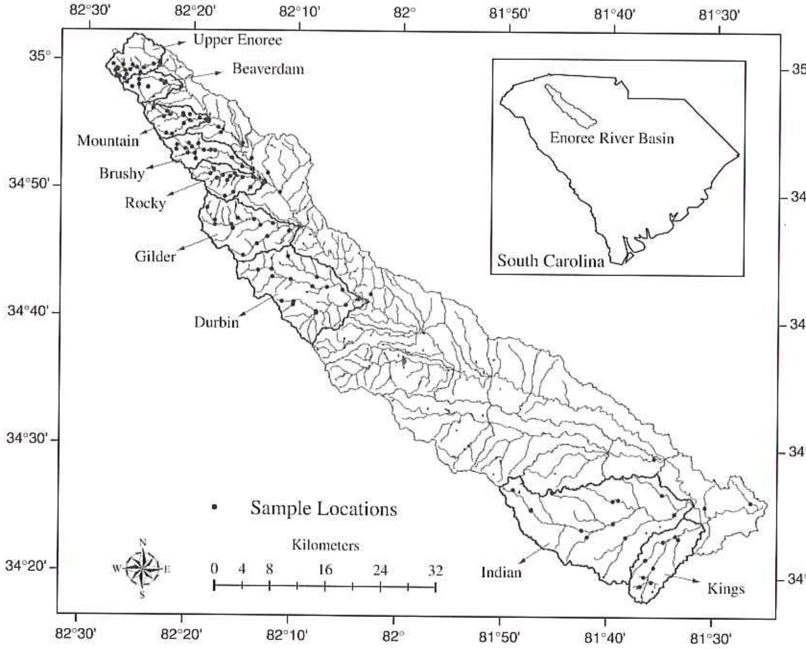


Figure 24.1. Location map of watersheds and sample localities within the Enoree River Basin.

localities, and to analyze the spatial distribution of urban land cover and vegetation within the drainage area of each sampling site.

24.2. Study area

24.2.1. *Climate and hydrology*

The Enoree River basin is located within the lower Broad River basin, which in turn comprises the northern half of the Santee River basin, one of the United States Geological Survey's National Water Quality Assessment Program watersheds. The Enoree River basin is classified as sixth-order (Strahler, 1952).

The climate of the region is subtropical, with daily high temperatures averaging 22°C and daily lows averaging 11°C. Rainfall averages 120 cm per year with a distinctly rainy winter and dry late summer and fall (Camp, 1960, 1975; Camp et al., 1960, 1975). During the period of the study, South Carolina experienced the most severe drought since the mid-1950s, and many rivers in the Piedmont Province, including the Enoree River, experienced record low discharges and few storm events during the summer months (Andersen et al., 2001; Andersen et al., 2004).

24.2.2. *Geology, soils, and vegetation*

The Enoree River basin is underlain by igneous and high-grade metamorphic rocks of the Inner Piedmont and Charlotte belts that are comprised mainly of silicate minerals (see review and references in Andersen et al., 2001). These minerals have low solubility, resulting in relatively dilute stream waters with conductivities often $< 100\,\mu\mathrm{S\,cm^{-1}}$ (Andersen et al., 2001). The soils in the area are predominantly ultisols, with some alfisols in the southern third of the basin (Camp, 1960, 1975; Camp et al., 1960, 1975). Forests are typically second-growth and are composed mainly of pines (*Pinus* spp.) and/or hardwoods, especially oaks (*Quercus* spp.), hickories (*Carya* spp.), red maple (*Acer rubrum*), sweet gum (*Liquidambar styraciflua*), and tulip poplar (*Liriodendron tulipifera*). Pine plantations are especially common in the southern half of the basin.

24.3. Methods

24.3.1. *Sample collection and analysis*

Grab samples were collected four to seven times at each of 134 localities in 19 tributary watersheds during June through August 1999 or 2000 (Fig. 24.1, Table 24.1). Nine of the watersheds had multiple sample

Table 24.1. Nitrate and land cover data for sample drainages in the Enoree River basin

Locality	Year			Nitrate ($mg\,l^{-1}$)			Percent Land Cover			
		n	Area (km^2)	Mean	Minimum	Maximum	Urban	Forested	Grass	NDVI
Upper Enoree River										
UE01	1999	8	0.63	2.93	2.46	3.76	40.0	24.6	34.9	111
UE02	1999	10	0.71	3.23	2.51	4.10	38.1	24.7	37.3	112
UE03	1999	7	1.72	1.41	1.09	1.64	9.8	37.1	53.0	120
UE04	1999	9	0.74	2.72	1.72	8.95	38.3	25.2	36.4	112
UE05	1999	6	1.75	1.11	0.77	1.83	10.5	37.2	52.4	120
UE06	1999	8	7.38	1.71	1.13	2.33	9.6	45.2	44.6	124
UE07	1999	7	0.27	5.35	3.46	13.59	15.6	20.3	64.1	110
UE08	1999	5	0.58	0.75	0.00	1.04	3.8	32.0	64.4	123
UE09	1999	8	18.07	1.67	1.41	2.07	9.8	47.5	42.5	126
UE10	1999	7	10.05	1.27	0.93	1.53	13.5	42.1	44.0	123
UE11	1999	6	0.63	4.53	0.85	12.67	43.4	16.0	40.4	114
UE12	1999	6	0.18	2.05	1.65	2.31	0.0	40.2	59.8	129
UE13	1999	7	1.63	0.39	0.26	0.52	0.5	57.4	40.8	129
UE14	1999	8	34.55	1.53	1.13	1.76	6.1	51.1	42.6	128
UE15	1999	8	19.13	1.64	1.12	2.51	9.3	47.9	42.6	126
UE16	1999	5	1.77	2.63	2.35	2.96	34.1	25.1	41.0	118
UE17	1999	7	13.55	2.52	0.91	7.85	10.5	46.5	42.8	125
UE18	1999	5	0.20	1.76	1.34	2.89	36.7	14.2	50.0	118
UE19	1999	4	2.10	1.42	1.16	1.67	1.6	64.7	33.7	131
Beaverdam Creek										
BD01	1999	7	24.38	1.54	1.27	2.52	8.3	58.2	33.4	130
BD02	1999	7	15.05	0.44	0.15	1.73	11.3	51.6	36.9	127
BD03	1999	7	0.34	1.56	1.40	1.84	0.0	49.6	50.4	128
BD04	1999	7	1.55	0.84	0.32	2.07	4.0	47.2	48.4	125
BD05	1999	7	13.76	1.33	0.70	1.54	12.4	51.5	36.0	127
BD06	1999	7	0.72	1.26	1.09	1.70	5.5	61.8	32.3	131
BD07	1999	7	0.92	1.84	1.62	2.35	3.7	57.9	38.0	130
BD08	1999	7	7.08	2.08	1.75	2.66	21.2	54.0	24.5	126
BD09	1999	7	3.90	1.75	1.39	2.37	4.1	73.2	22.7	135
BD10	1999	7	0.44	1.13	0.44	1.32	8.1	64.0	28.0	129
BD11	1999	5	0.83	3.37	2.74	3.60	60.6	24.2	14.3	108
Mountain Creek										
MC01	2000	6	30.36	1.75	0.83	5.39	23.9	53.0	22.8	127
MC02	1999	7	29.56	1.45	1.17	2.24	24.3	53.6	22.2	127
MC03	1999	7	29.03	1.34	1.14	1.55	23.4	53.6	22.6	127
MC04	1999	7	24.54	1.13	0.01	2.04	20.1	55.8	24.0	129
MC05	1999	7	14.58	0.66	0.09	3.26	5.9	72.6	21.1	136
MC06	1999	7	7.95	1.33	1.03	1.67	0.0	96.2	4.9	143
MC07	1999	7	1.02	2.15	1.68	2.65	40.7	23.5	35.6	121
MC08	1999	7	8.41	0.72	0.43	1.30	42.8	30.0	27.2	118
MC10	1999	7	1.36	1.98	1.72	2.39	0.0	98.7	1.3	144
MC11	1999	7	3.77	1.64	1.42	2.13	34.1	38.9	23.7	123
MC12	1999	7	1.93	1.39	1.25	1.54	9.6	43.0	47.4	126
MC13	1999	7	0.89	0.57	0.44	0.66	0.0	67.0	33.1	136

Table 24.1. (*Continued*)

Locality	Year			Nitrate (mg l^{-1})			Percent Land Cover			
		n	Area (km^2)	Mean	Minimum	Maximum	Urban	Forested	Grass	NDVI
MC14	1999	7	2.69	0.82	0.58	1.42	30.9	46.1	20.6	124
MC16	1999	7	0.68	1.41	1.07	2.21	30.8	27.6	41.1	122
MC17	1999	6	2.93	0.26	0.14	0.34	0.0	92.5	6.9	142
Brushy Creek										
BY01	2000	7	38.20	1.96	1.74	2.55	64.7	21.0	14.1	112
BY02	2000	7	36.11	2.05	1.66	2.52	64.9	20.5	14.3	113
BY03	2000	7	32.06	2.20	1.83	2.70	65.4	21.1	13.1	113
BY04	2000	7	24.99	2.46	2.14	3.04	68.3	20.8	10.7	113
BY05	2000	7	23.25	2.48	2.29	2.99	67.8	21.5	10.4	113
BY06	2000	7	21.39	2.54	2.30	2.98	68.4	21.5	9.8	113
BY07	2000	7	1.83	5.93	5.30	8.24	61.7	24.0	14.2	113
BY08	2000	7	13.73	2.88	2.65	3.25	67.8	22.8	9.1	112
BY09	2000	7	1.22	1.34	0.80	2.33	72.0	7.8	20.2	112
BY10	2000	7	1.80	3.32	2.96	3.92	76.0	19.8	4.2	114
BY11	2000	7	2.19	1.31	1.09	1.56	69.9	23.9	6.2	116
BY12	2000	7	6.12	2.13	1.68	2.73	64.4	23.5	11.8	111
BY13	2000	7	3.25	3.37	3.05	3.69	82.0	14.1	3.9	110
BY14	2000	7	0.64	5.73	4.95	7.83	84.4	9.6	5.9	108
BY15	2000	7	1.94	5.41	5.14	5.98	66.1	15.2	18.7	103
Rocky Creek										
RC01	1999	7	36.37	2.23	1.77	3.41	50.2	21.9	26.8	108
RC02	1999	7	30.78	2.47	1.79	3.54	52.4	20.9	25.6	107
RC03	1999	7	29.02	2.34	2.04	2.63	53.3	20.7	24.8	107
RC04	1999	7	18.34	2.23	1.73	2.80	56.4	20.2	22.2	109
RC05	1999	7	13.55	2.46	2.05	2.87	59.9	20.3	18.9	110
RC06	1999	6	3.45	5.11	2.05	6.06	68.8	15.2	16.0	116
RC07	1999	7	3.98	3.31	2.77	3.77	68.3	15.0	16.5	104
RC08	1999	7	2.93	1.27	0.60	2.69	47.9	18.3	32.9	112
RC09	1999	7	5.87	2.14	1.74	2.46	55.4	21.2	23.3	99
RC10	1999	7	3.75	2.03	1.67	2.63	59.1	21.7	19.0	97
RC11	1999	7	0.86	2.42	1.30	7.88	30.5	12.2	57.7	103
RC12	1999	7	1.21	0.78	0.34	1.36	34.2	12.2	51.2	106
RC13	1999	7	1.76	1.83	0.63	2.84	34.5	27.3	35.7	113
Gilder Creek										
GC01	1999	7	81.26	2.48	1.84	3.01	35.9	28.0	35.8	113
GC02	1999	7	4.89	1.63	1.13	2.48	6.4	62.1	28.4	126
GC03	1999	7	50.41	2.53	2.26	3.05	49.9	19.1	30.9	109
GC04	1999	7	17.14	1.68	1.44	2.03	20.2	35.7	43.8	119
GC05	1999	7	11.15	2.61	2.26	3.59	22.2	39.3	38.4	120
GC06	1999	7	40.28	3.00	2.54	3.88	54.7	17.1	27.9	108
GC07	1999	7	3.46	3.86	2.82	4.32	45.1	20.6	34.3	111
GC08	1999	7	4.40	5.63	3.48	6.44	50.6	11.8	37.0	104
GC09	1999	7	20.04	3.55	2.99	4.37	60.4	14.0	25.5	105
GC10	1999	7	6.99	1.32	0.91	1.91	45.3	21.6	32.2	110
GC11	1999	7	2.47	2.81	1.93	3.57	79.7	5.2	14.5	98

Table 24.1. (*Continued*)

Locality	Year			Nitrate (mg l^{-1})			Percent Land Cover			
		n	Area (km^2)	Mean	Minimum	Maximum	Urban	Forested	Grass	NDVI
GC12	1999	7	4.33	1.69	1.20	2.50	52.2	19.2	28.6	108
GC13	1999	7	1.58	1.83	0.75	2.58	60.7	10.5	28.1	102
GC14	1999	7	4.59	3.09	2.98	3.29	25.9	25.9	48.1	113
Durbin Creek										
DB01	2000	7	131.25	10.65	7.70	15.00	8.4	40.8	50.7	120
DB02	2000	7	48.22	0.99	0.71	1.51	5.5	39.6	54.9	119
DB05	2000	7	77.25	16.92	14.95	19.68	10.5	41.9	47.4	120
DB06	2000	7	48.31	28.66	23.07	37.57	14.8	39.4	45.6	119
DB07	2000	7	18.42	2.08	1.65	2.50	5.3	39.7	55.0	119
DB08	2000	7	41.76	30.86	25.49	33.44	17.1	36.1	46.7	118
DB09	2000	7	3.67	7.60	6.43	8.56	13.2	23.9	63.0	109
DB10	2000	6	13.05	1.19	0.92	1.65	8.4	34.7	56.9	116
DB11	2000	7	16.52	1.44	1.06	1.93	7.8	32.9	59.1	116
DB12	2000	6	2.47	1.42	0.82	2.19	11.0	21.8	67.3	109
DB13	2000	7	4.23	2.12	1.30	2.91	18.1	26.8	55.2	113
DB14	2000	7	1.49	9.50	7.06	10.76	36.3	24.5	39.2	111
DB15	2000	7	33.30	1.79	1.48	2.01	20.5	31.9	47.4	116
DB16	2000	7	16.90	2.06	1.89	2.44	19.4	33.5	46.8	116
DB17	2000	7	6.65	1.91	1.78	2.35	28.2	21.1	50.8	112
DB18	2000	7	9.15	1.91	1.48	2.76	29.4	38.6	31.5	118
Indian Creek										
IR01	2000	7	228.42	0.64	0.42	1.40	1.2	81.5	17.2	130
IR04	2000	7	14.71	0.43	0.37	0.48	0.2	96.9	2.9	131
IR05	2000	7	7.68	0.51	0.26	0.83	0.3	99.0	0.5	132
IR06	2000	7	121.11	0.54	0.29	0.71	1.3	79.5	19.1	130
IR07	2000	7	9.54	0.82	0.67	1.00	0.6	56.9	42.5	125
IR08	2000	7	32.44	0.80	0.49	1.05	3.4	76.1	20.4	128
IR10	2000	7	16.97	0.52	0.38	0.72	0.5	84.7	14.9	131
IR11	2000	7	62.93	0.73	0.59	1.09	1.2	75.8	22.9	
IR13	2000	7	17.47	0.72	0.38	0.88	0.7	66.1	33.0	126
IR14	2000	7	2.09	0.69	0.47	0.96	1.0	65.0	33.9	127
IR15	2000	7	0.52	2.08	0.90	2.69	5.9	17.9	76.4	121
IR16	2000	7	4.42	0.84	0.68	0.98	0.2	54.7	45.1	122
Kings Creek										
KC01	2000	7	45.55	0.90	0.50	1.25	2.8	75.2	21.7	128
KC02	2000	7	8.15	0.72	0.48	1.10	0.2	82.3	17.1	129
KC03	2000	7	12.27	0.75	0.59	0.87	1.3	75.9	23.1	130
KC04	2000	7	4.07	0.84	0.70	1.10	3.6	64.9	31.5	127
KC05	2000	7	17.76	0.91	0.65	1.04	5.9	69.6	23.9	126
KC06	2000	7	1.25	0.78	0.68	0.89	8.9	81.3	9.9	126
KC07	2000	7	2.16	1.03	0.06	2.21	9.7	64.0	24.7	124
KC08	2000	7	2.18	1.35	1.21	1.50	5.9	74.3	18.3	126
Other										
AB01	2000	4	29.39	2.69	1.76	3.09	14.3	26.2	59.4	113
AC01	2000	8	5.80	2.77	2.43	3.68	26.6	20.2	53.2	104

Table 24.1. (*Continued*)

Locality	Year			Nitrate ($mg\,l^{-1}$)			Percent Land Cover			
		n	Area (km^2)	Mean	Minimum	Maximum	Urban	Forested	Grass	NDVI
CC01	1999	6	4.24	2.90	2.61	3.29	64.9	13.1	22.1	115
CH01	1999	6	4.83	3.82	3.12	4.69	70.1	12.6	17.4	107
DC01	2000	7	11.15	2.63	1.87	3.10	21.5	39.8	38.7	115
DL01	2000	7	7.24	3.05	1.66	7.84	11.2	53.9	34.7	127
DN01	2000	7	307.03	2.00	0.53	6.38	4.7	67.1	27.8	128
SC01	2000	7	9.21	0.36	0.29	0.40	0.2	82.6	17.0	129
UC01	2000	7	5.15	0.48	0.22	0.72	0.0	90.6	9.4	130
UT01	2000	6	10.35	2.38	1.99	2.83	40.1	18.1	41.2	107

localities; the other ten each had a single sample locality near its confluence with the Enoree River. Samples were collected and processed following the methods of Andersen (2001) and Andersen et al. (2001). Nitrate and nitrite concentrations were measured using a Dionex 120 ion chromatograph. Nitrite concentrations are not reported because 95% of the concentrations were below the detection limit of $0.050\,mg\,l^{-1}$. Although ammonium was not measured, we assumed the concentrations also were negligible based on subsequent analyses of a number of watersheds in the region (G.P. Lewis and C.B. Andersen, unpublished data). Additional major cation and anion results for 116 sample localities are tabulated in Andersen et al. (2001). A complete dataset is available from the authors. Chemical composition reliability was checked using the charge balance method of Freeze and Cherry (1979). In this study, the mean, maximum, and minimum nitrate concentrations for each locality were used for analysis. Mean nitrate concentration data from each sample site were used to analyze the effect of land use and vegetation density on nitrate concentrations in the context of the corresponding drainage area. Because we lacked stream discharge data, we could not determine relationship of nitrate fluxes with land use or vegetation density.

SigmaStat v. 3.1 was used to perform statistical analyses (Systat Software, 2004). Nitrate concentrations in forested watersheds within the Enoree River basin are known to vary significantly from year to year, particularly between drought and non-drought years (Keaton et al., 2005). Because some samples were collected in 1999 and some in 2000, a paired *t*-test was used to determine if the mean nitrate concentrations for seven localities sampled in both years differed significantly. Although mean nitrate concentrations in 1999 were slightly higher than mean concentrations in 2000 (Fig. 24.2), the means did not differ significantly ($p = 0.14$). Therefore, we combined the two datasets for analysis. We used Kruskal-Wallis One Way Analysis of Variance on Ranks tests to determine if the median nitrate concentrations, land cover percentages, and NDVI values differed significantly among the nine tributary watersheds with multiple sample localities. This non-parametric test was used because the data failed either the Kolmogorov-Smirnov test for normality or a test for equal variance. We used standard linear regression analysis on log-transformed data to test for significant relations among nitrate concentrations, land covers, and NDVI.

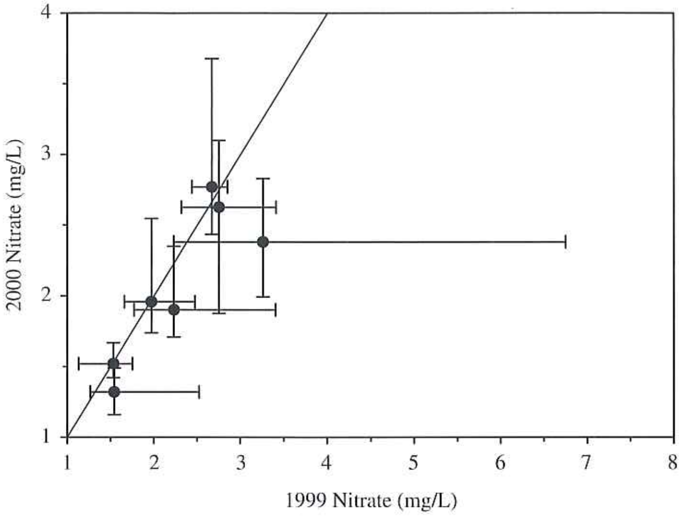


Figure 24.2. Comparison of nitrate concentrations for seven sample localities where water samples were collected in both 1999 and 2000. Filled circles represent the mean nitrate concentrations and bars represent the range of concentrations.

24.3.2. Watershed delineation

A digital elevation model (DEM) was used to delineate the drainage area corresponding to each of the 134 sample localities (Fig. 24.1, Table 24.1). An "Hydrology Analysis" extension (ESRI, 2005) was used with ArcGIS system to process the DEM, identify flow directions and sinks, fill the sinks, and then calculate flow accumulations for each grid cell. Once flow direction and flow accumulation layers were generated, the contributing drainage area for any specific point within the watershed was calculated by clicking on the points of interest, which in our case were the sampling localities. Once the watershed was delineated, total area of each basin was calculated by multiplying the total number of grid cells within the watershed by the grid dimension, which was 30 m × 30 m, or $0.009\,\mathrm{km}^2$.

24.3.3. Land cover

A Landsat 7 ETM+, 30-m spatial resolution imagery (path/row/year-month-date are 17/36/2000-06-01 and 18/36/2000-06-10) covering the area of the Enoree River basin was obtained. A combination of supervised and unsupervised classification (ISODATA algorithm with 10 iterations and 0.95 convergence threshold with the initial clustering means derived from training dataset collected using supervised sampling method) methods, along with post-classification clumping and sieving were used to develop land cover data for the entire basin. Final classification for the entire Enoree basin included the following land cover types: water, commercial/industrial, agricultural, high-density residential, low-density residential, grass/pasture, and forest. Ground truth information and aerial photographs taken in 1999 were used to verify the classification results. Also, on November 16, 2003, each sample locality in the Brushy Creek watershed, which had the greatest diversity in land use, was visited and field-checked for agreement with land cover data. At each sample locality, agreement was found between qualitative field assessment and digital land cover data.

24.3.4. Normalized difference vegetation index

The spectral reflectance values from the Landsat ETM+ image were used to compute the normalized difference vegetation index (NDVI), one of more than twenty existing vegetation indexes that gauge small differences between the amount, distribution, and vitality of green biomass (Chen and Brutsaert, 1998; Boone et al., 2000; Jensen, 2000). We selected NDVI because it is widely used and has been shown to detect changes in the amount of green biomass and chlorophyll content (Bannari et al., 1995; Jensen, 2000). We used bands 4 (infrared, 0.75–0.90 μm) and 3 (red, 0.63–0.69 μm) of the Landsat ETM+ data because plant reflection and absorption of radiation are greatest in these wavelengths. The NDVI values for each pixel were calculated using the relationship

$$\mathrm{NDVI} = \left(\frac{(\mathrm{ETM\ Band4} - \mathrm{ETM\ Band3})}{(\mathrm{ETM\ Band4} + \mathrm{ETM\ Band3})}\right)$$

The computed NDVI values ranged from −1.0 to 1.0, where vegetated areas will typically have values higher than zero and other non-vegetated areas, such as water, snow, or barren areas, will have negative values.

These values then were scaled (which is a simple way to amplify small difference between two NDVI values) in order to enhance the visual differences in density of vegetation in the given area using the following relationship:

$$\mathrm{ScaledNDVI} = 100(\mathrm{NDVI} + 1)$$

After scaling, NDVI values ranged from 0 to 200, in which values 100 and below indicated a lack of vegetation, while values above 100 indicated the presence of vegetation, with higher numbers representing denser vegetation cover.

24.4. Results

The sample localities drained watersheds ranging in area from 0.2 to $307\,\mathrm{km}^2$ (Table 24.1) with considerable variation in land cover. In the nine tributary watersheds with multiple sample localities, the drainages were hierarchical and nested. As such, the chemical composition of the downstream localities and their relations to land cover represent an integration of the upstream localities.

24.4.1. Nitrate concentrations

Median nitrate concentrations differed significantly ($p < 0.001$) among the nine tributary watersheds with multiple sample localities. Nitrate concentrations ranged from below the detection limit of $0.05\,\mathrm{mg\,l^{-1}}$ to greater than $30\,\mathrm{mg\,l^{-1}}$. The highest concentrations occurred downstream of a wastewater treatment plant discharging into Durbin Creek. The highest nitrate concentration unaffected by a known point-source was about $13\,\mathrm{mg\,l^{-1}}$. Brushy Creek, Rocky Creek, Gilder Creek, and Durbin Creek watersheds had the highest mean and median concentrations of nitrate (Fig. 24.3). Durbin Creek had relatively high mean and median nitrate concentrations even when the sample localities downstream of the wastewater treatment plant were removed from analysis. The mean concentration of nitrate in Durbin Creek was above the 75th percentile value because of two headwater sample localities that had mean nitrate concentrations greater than $7\,\mathrm{mg\,l^{-1}}$. The lowest mean and median nitrate concentrations were found in the mostly forested Indian Creek and Kings Creek. The Upper Enoree, Beaverdam Creek, and Mountain Creek watersheds had intermediate nitrate concentrations, typically between 1 and $3\,\mathrm{mg\,l^{-1}}$. The ten watersheds with a single sample locality each (grouped as "other" in Fig. 24.3) had mean nitrate concentrations ranging from

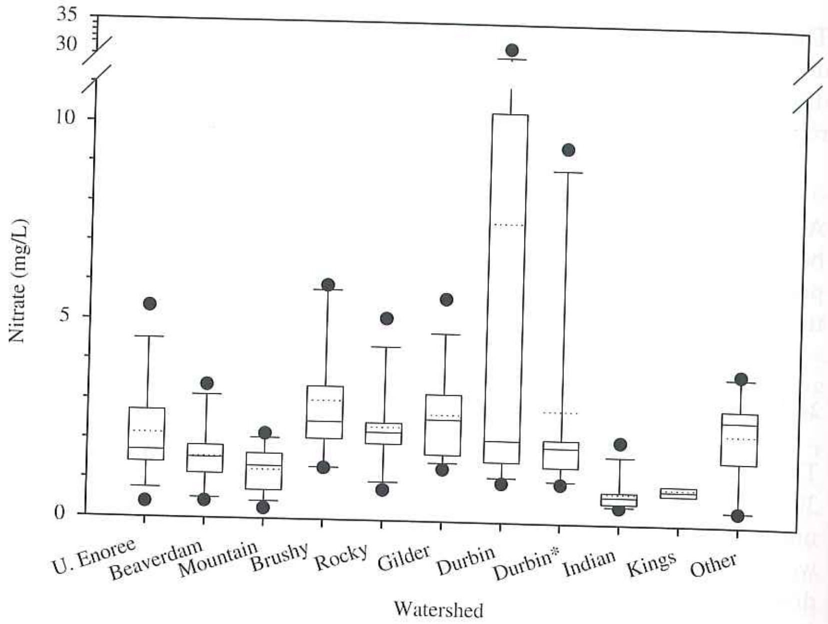


Figure 24.3. Mean nitrate concentrations in streams of tributary watersheds of the Enoree River basin. Watersheds are listed in the downstream direction. "Other" refers to ten watersheds with only a single sample locality. "Durbin" includes four sample localities downstream of a wastewater treatment plant; "Durbin*" removes those four localities. In the box plot, the median is represented by a solid horizontal line, the mean by a dotted horizontal line, the limits of the box represents the 25th and 75th percentiles, the bars represent the 5th and 95th percentiles, and the filled circles represent outliers.

less than $0.50\,\mathrm{mg\,l^{-1}}$ to greater than $3.0\,\mathrm{mg\,l^{-1}}$. In Brushy Creek, Rocky Creek, Gilder Creek, and Durbin Creek (excluding WWTP-affected samples), the highest nitrate concentrations occurred in headwater streams with small drainages, although the overall correlation between nitrate concentrations and drainage areas for all sample localities was very weak and not statistically significant ($p = 0.076$).

24.4.2. Land cover

The Enoree River basin as a whole had 9% ($170\,\mathrm{km^2}$ out of $1893\,\mathrm{km^2}$ area) of its drainage area classified as urban, 58% as forested, and 33% as grass/pasture land covers. The majority of the urban land cover was concentrated along the headwater regions of the Enoree River basin and was strongly influenced by the expansion of the Cities of Greenville and Spartanburg. Qualitative analysis of aerial photographs and ground truthing indicates that the vast majority of the grass/pasture land cover is grass in urban areas and pasture or hayfields in rural areas. Row crops constitute only a small percentage of the grass/pasture land cover, and intensive feedlot operations are absent.

For urban, forested, and grass/pasture land covers, the percentage of cover differed significantly ($p < 0.001$) among the nine tributary watersheds with multiple sample localities (Fig. 24.4). Proportionally, the Brushy, Rocky, and Gilder Creek watersheds were the most urbanized and the least forested (Fig. 24.5). The Beaverdam, Indian, and Kings Creek watersheds were the most forested watersheds. The Upper Enoree, Mountain, and Durbin Creek watersheds were dominated by mixtures of forest and grass/pasture with lesser amounts of developed land cover.

Proportionally, watershed land cover formed either an urban to grass/pasture gradient or a grass/pasture to forested gradient (Fig. 24.5). The relations among the various land covers were complex and non-linear (Fig. 24.6). In particular, the relation between forested and urban land cover was inverse but non-linear.

24.4.3. NDVI of drainage areas

The NDVI indicates the density of vegetation cover, or "greenness" of a watershed (Fig. 24.7). The weighted mean NDVI differed significantly ($p < 0.001$) among the nine tributary watersheds with multiple sample localities (Fig. 24.4). Among all drainage basins, the weighted mean NDVI values ranged from 97 to 144. Watersheds with NDVI value less than 100 were completely developed with little or no vegetation cover. Although no significant relationship ($p = 0.47$) was observed between weighted mean NDVI of a watershed and the watershed area, the NDVI values for watersheds smaller than $20\,\mathrm{km^2}$ showed maximum variation. NDVI showed a significant, negative correlation ($p < 0.001$) with percentage of urban land cover and a significant, positive correlation ($p < 0.001$) with percentage of forested land cover but showed no significant relationship ($p = 0.07$) with percentage of grass/pasture land cover (Fig. 24.8). Spatially, highest NDVI values were observed alongside the streams where minimally disturbed riparian vegetation was present (Fig. 24.9). The lowest NDVI values were observed in the headwater regions of the watersheds where intense development resulted in loss of vegetative cover around the streams. The Upper Enoree, Beaverdam, Indian and Kings Creeks had more areas with contiguous and densely forested vegetation cover (darker shades of gray in Fig. 24.9) compared to Brushy, Rocky, Gilder, and Durbin Creeks (lighter shades of gray in Fig. 24.9).

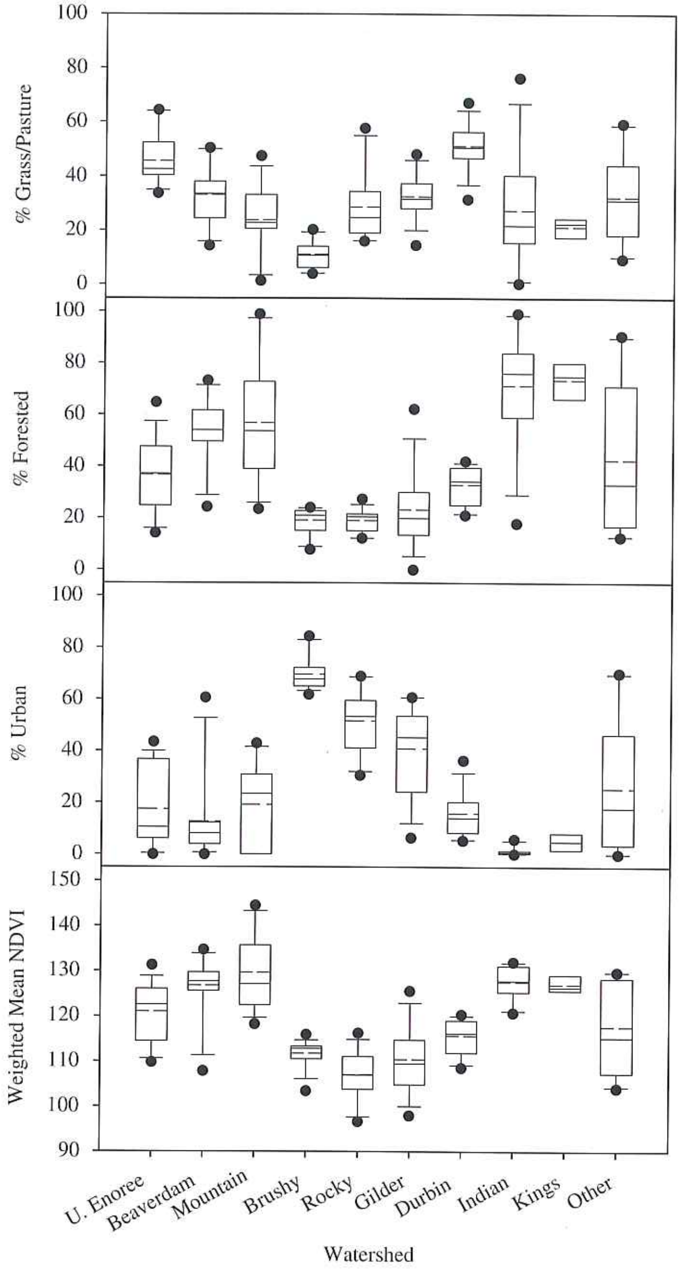


Figure 24.4. Land cover of sample locality drainages in the tributary watersheds of the Enoree River basin. Note that weighted NDVI values are most similar to the percent forested land cover.

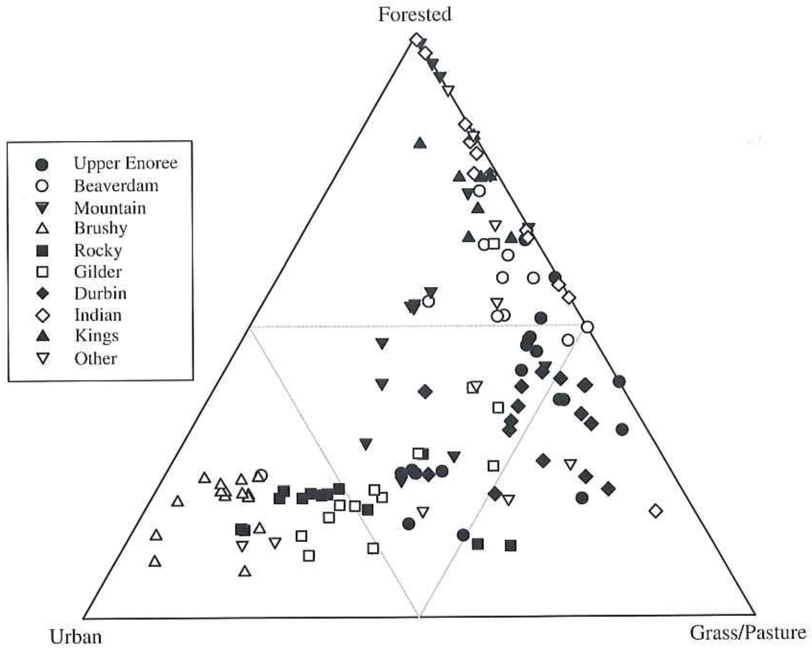


Figure 24.5. Ternary plot showing proportions of land cover for sample locality drainages in the Enoree River basin.

24.4.4. Relations of nitrate with land cover and NDVI

Mean nitrate concentrations showed a significant, positive correlation ($p < 0.001$) with percentage of urban land cover and a significant, negative correlation ($p < 0.001$) with percentage of forested land cover (Fig. 24.10). Mean nitrate concentrations also showed a significant, negative correlation ($p < 0.001$) with mean NDVI (Fig. 24.10). However, mean nitrate concentrations were not significantly correlated with percentage of grass/pasture land cover ($p = 0.17$). Nitrate concentrations were most variable in watersheds with about 5–20% urban land cover (Fig. 24.10).

24.5. Discussion

We interpret land cover in the Enoree River basin to represent the urbanization or reforestation of an originally agricultural (grass/pasture) land cover (Figs. 24.5 and 24.6). Urbanization is correlated with increased

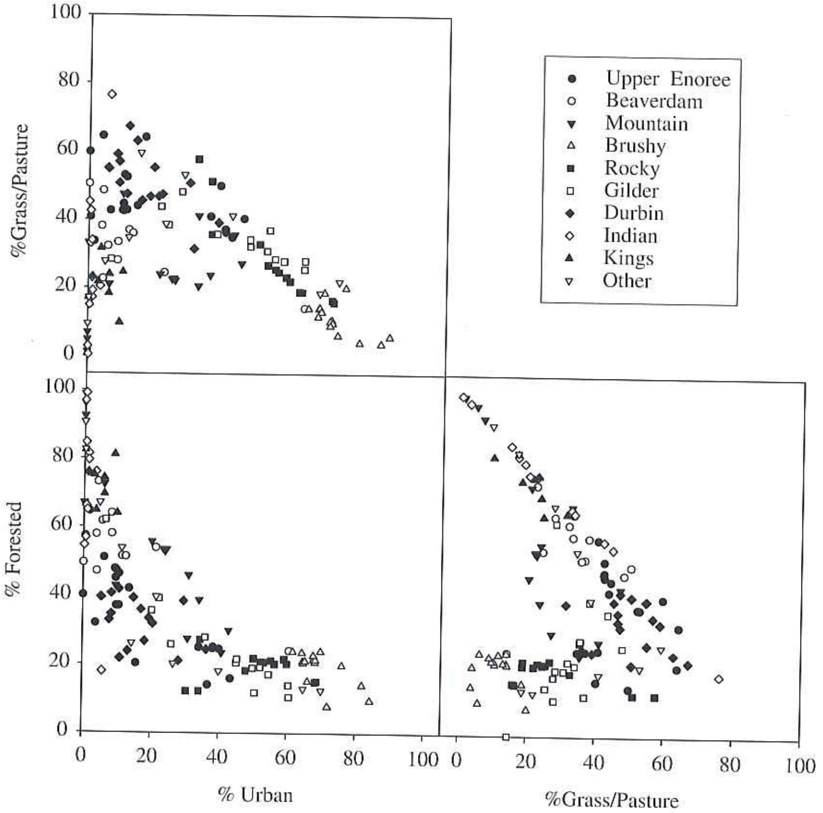


Figure 24.6. Relations between land cover types for sample locality drainages in the Enoree River basin.

nitrate concentrations, whereas reforestation is correlated with decreased nitrate concentrations. Previous studies have shown that nitrate concentrations in forested watersheds are low, especially watersheds undergoing reforestation (Bormann and Likens, 1979; Swank, 1988; Clark et al., 2000). In our discussion, we focus on the relation between urbanization and increased nitrate concentrations.

24.5.1. Potential urban sources of nitrate

In tributary watersheds of the Enoree River basin, other than effluent discharged by a single WWTP, point-source inputs of nitrogen appear insignificant. As a result, land cover is the most important factor controlling stream nitrate concentrations, which were positively correlated

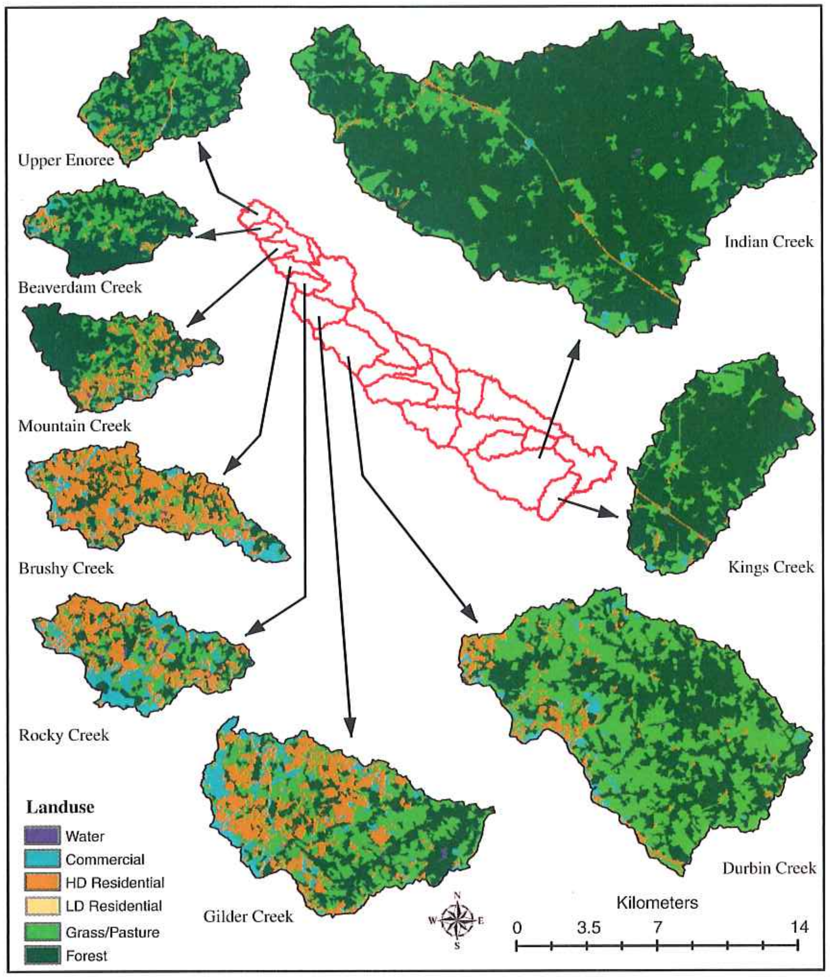


Figure 24.7. Land cover maps for tributary watersheds in the Enoree River basin. Land cover classification is based on satellite images for 2000. See methods for details. For analytical purposes, commercial and high-density (HD) residential land covers are combined as "urban" land cover. The scale in the figure applies to the land cover maps of different watersheds.

with urban land cover in the Enoree River basin. For example, based on the linear regression of nitrate concentration and percentage of urban land cover, watersheds with about 0.02% urban cover would have nitrate concentrations around 0.2–0.4 $\mathrm{mg\,l^{-1}}$, whereas watersheds with $>90\%$ urban cover would be expected to have concentrations around 3 $\mathrm{mg\,l^{-1}}$.

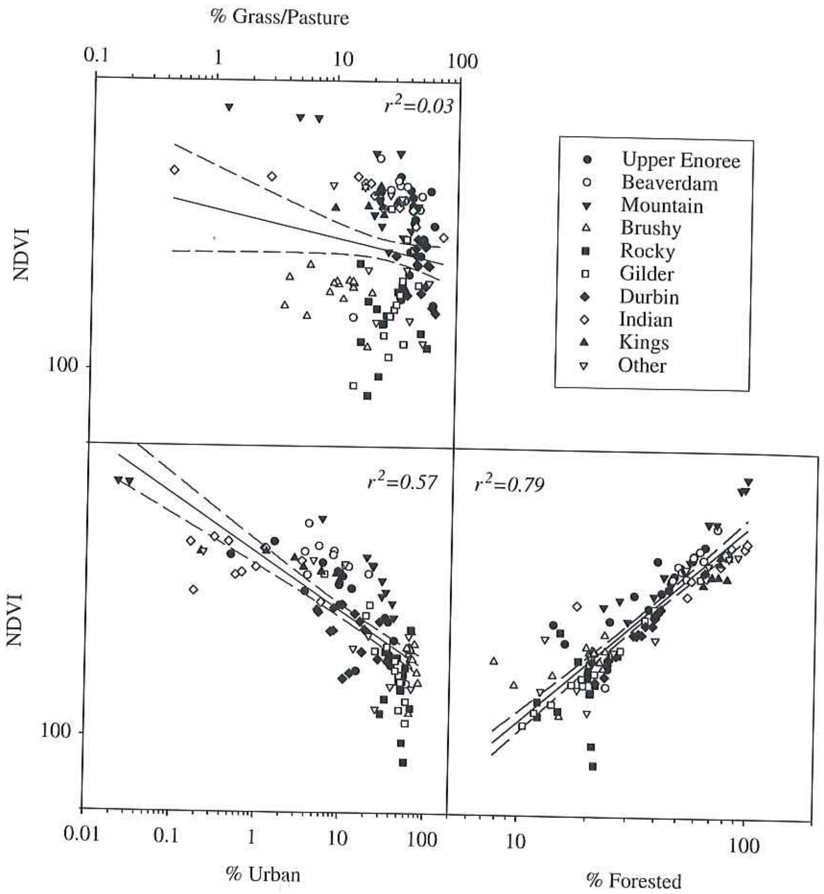


Figure 24.8. Relations between NDVI and land cover. Regression lines are solid and 95% confidence intervals are represented by dashed lines. The NDVI scale is logarithmic. The relationships are statistically significant ($p<0.001$) except for NDVI versus grass/pasture ($p = 0.07$).

However, we have observed that watersheds with only 5–20% urban land cover had the most variable nitrate concentrations and some of the highest overall concentrations.

High nitrate concentrations in urbanized watersheds could result from several factors, including nitrogen from wet and dry atmospheric deposition, fertilizers added to lawns, septic systems, leaking sewer pipes, and lower nitrogen uptake by vegetation. At present, we lack data to determine the relative contributions of these factors to nitrate concentrations in our study area. Although septic systems are important sources of nitrates in urban areas of other regions (e.g., Hoare, 1984), our observations suggest that houses in the more urbanized watersheds which are within or adjacent to the city of Greenville (Brushy Creek, Rocky Creek, and Gilder Creek) are served by sewer rather than septic systems. Houses in the less urbanized (more rural) and less densely populated watersheds are more likely to have septic systems, although these watersheds tended to have lower nitrate concentrations.

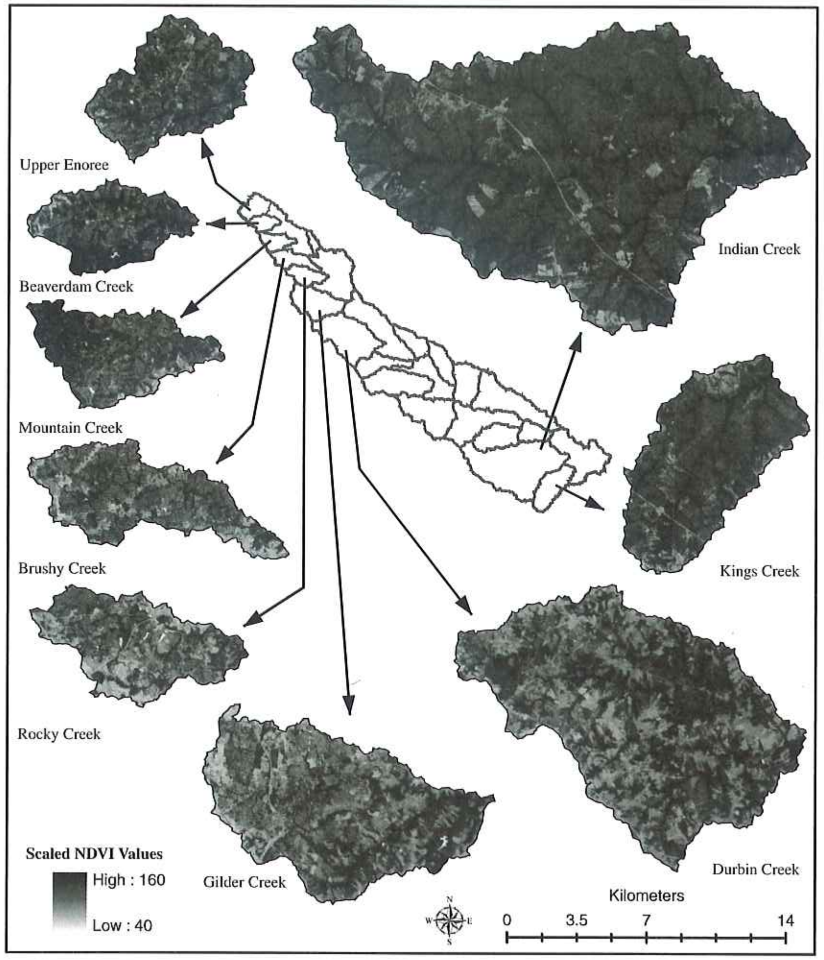


Figure 24.9. Normalized difference vegetation index (NDVI) maps for tributary watersheds in the Enoree River basin. The scale in the figure applies to the landuse map of different watersheds.

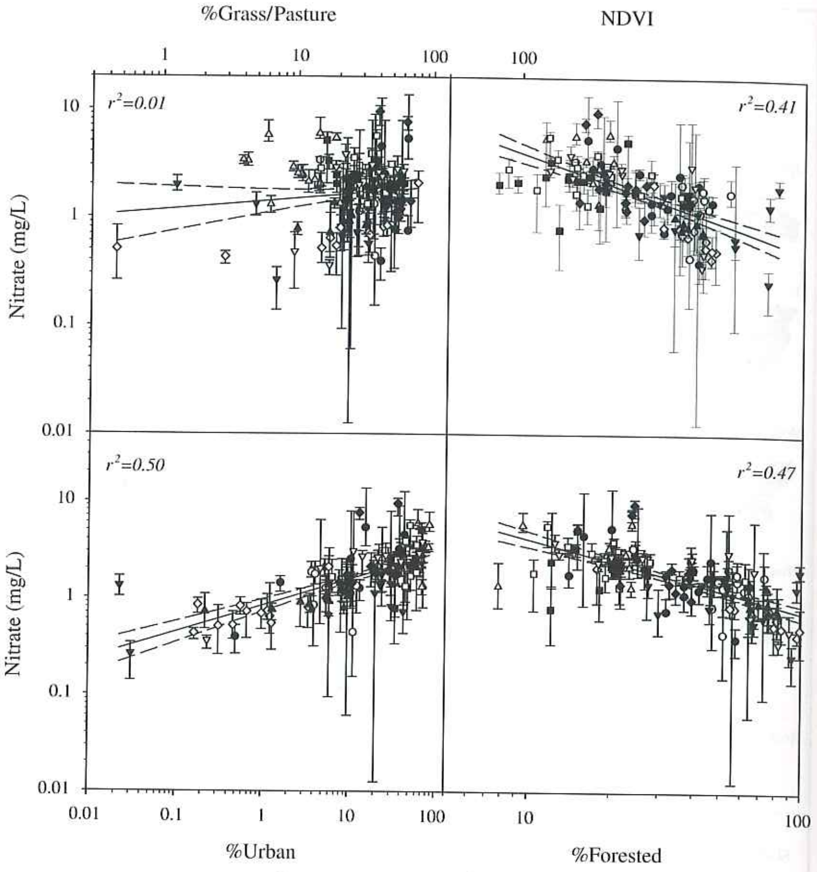


Figure 24.10. Relations between mean nitrate concentrations and land cover for each sample locality. Watersheds are represented by the same symbols as in previous diagrams. Regression lines are solid and 95% confidence intervals are represented by dashed lines. Relationships are statistically significant ($p<0.001$) except for nitrate versus grass/pasture ($p = 0.17$).

The altered hydrology of urban areas also may contribute to high nitrate concentrations in urban streams. Because urban areas have more impervious surface cover than do forests and grasslands, storm flows are greater in urban areas (Paul and Meyer, 2001). As a result, storm flows erode streambeds, accelerating stream channel incision. For example, in the Maryland coastal plain, channel incision of urban streams results in lowered water tables and more deeply oxidized riparian soils (Groffman et al., 2002). These soils thus have lower denitrification potentials and higher nitrification potentials, which contributes to higher nitrate concentrations in soil water moving into the stream channel (Groffman et al., 2002). Urbanization of headwater streams, in particular, may exert an important control on nitrogen transport in streams because small headwater streams make up a large portion of the total river drainage length of a watershed, collecting a majority of the water and dissolved nutrients from the surrounding terrestrial ecosystem (Peterson et al., 2001). We have observed channel incision in streams in the Enoree River basin, as well, but have not yet quantified the degree of incision or its effect on nitrogen biogeochemistry.

24.5.2. Sources of variability in nitrate concentrations

Although we have demonstrated for the Enoree River basin that there are statistically significant, moderately strong relations among nitrate concentrations, land cover, and NDVI, there clearly is much unexplained variation in nitrate concentrations. Variability in the hydrology and biogeochemical functioning of riparian zones may account for some of the nitrate variability. There is abundant evidence from the literature that vegetated riparian zones can reduce the flux of nitrates into stream channels through processes such as uptake by vegetation and denitrification (see review by Hill, 1996). However, if nitrate-laden water moves below the rooting zone, vegetative uptake will not occur (Hill, 1996). Likewise, lack of sufficient organic carbon in anoxic zones in riparian soils may limit the activity of denitrifying bacteria (Hill et al., 2000). As mentioned previously, increased depth of water tables along incised urban stream channels may also limit nitrate removal via denitrification. In our study, at least some of the urban stream reaches were bordered by forested riparian zones, although the widths of these zones varied.

Although NDVI provides a measure of the density of plant biomass in watersheds, it may overestimate plant biomass in the case of urban areas (e.g., residential areas), which have many trees (and thus some canopy cover which would be detected by remote sensing) but little under-story vegetation. For example, in older neighborhoods with larger trees, impervious surfaces such as streets, roofs of houses, or lawns may promote runoff of rainwater in spite of the tree cover. This may explain the strong relation between NDVI and forested land cover, but a relatively weaker relation between NDVI and urban land cover (Fig. 24.8). The overestimation of plant biomass by NDVI, and correspondingly lower assimilation and denitrification potentials, may have contributed to the variability in the nitrate–NDVI relationship.

At present, we are unable to explain the particularly high variability in nitrate concentrations in watersheds with 5–20% urban land cover.

However, among these watersheds is a great variety of spatial arrangements of land cover. For example, in some of these watersheds, the base of the watershed is more densely vegetated and the headwaters are more urbanized. In others, the opposite is true, even though the percentage of urban and forested land covers are similar in these two cases. Thus, the distribution and exact location of vegetation within these watersheds is probably important to the movement of nitrates to the stream channels.

One additional source of variation in nitrate concentrations is the presence of artificial ponds formed behind earthen dams, which are common in the urbanized watersheds (e.g., ponds in residential areas, parks, and golf courses). Such ponds have a major impact on the hydrology of stream systems by increasing the residence time of water, and may affect nutrient cycling (Smith et al., 2002). Nitrate concentrations in streams draining artificial ponds are lower than at other sampling localities in a given watershed. For example, in the Upper Enoree and Rocky Creek watersheds, the lowest nitrate concentrations occurred in streams draining ponds (Table 24.1, sites UE08, UE13, RC08, and RC12). The locality with the lowest nitrate concentration in the Mountain Creek watershed (MC17) also occurred downstream of a small artificial lake, although the lake's inlet stream drained a heavily forested watershed in which nitrate concentrations are typically low even without the influence of ponds (G.P. Lewis and C.B. Andersen, unpublished data). The ability of ponds and lakes to retain nitrates has been documented in other regions and has been attributed to processes such as algal and microbial nitrate assimilation and denitrification (Saunders and Kalff, 2001). In the present study, sample localities downstream of ponds in our study represent a small fraction of all sample localities, and nitrate concentrations increase further downstream of the ponds, possibly due to soil water or groundwater inputs of nitrates. However, ponds are prevalent in the headwater regions of the majority of the watersheds, so the total impact on nutrient cycling remains to be documented.

24.6. Conclusions

Humans have modified the global biogeochemical cycle of nitrogen substantially. In part, this modification has resulted in a higher flux of nitrogen to the ocean through river systems. In comparison to the contribution of nitrogen by agricultural land use and point-sources to rivers, the impact of urbanization is not well understood. Our study clearly shows that urban land cover is associated with higher concentrations of stream nitrate than forested land cover, well above what is considered normal for undeveloped, forested landscapes. The relation between land cover and stream nitrate concentrations, however, is only moderately strong, in part because of the complex spatial distribution of land cover types within individual watersheds and variation in riparian function and stream morphology. Future research will examine the processes by which urbanization increases stream nitrate concentrations in more detail.

ACKNOWLEDGMENTS

We thank the many students and faculty participants in Furman University's River Basins Research Initiative, especially John Wheeler, Sandy Wheeler, Kenneth Sargent, Christy Gullikson, Neal Gandy, and Tyler Bax. Reviews by Steve Coghlan and Timothy Warner improved the clarity of the manuscript. Funding for this work was provided by the NSF-REU Program (EAR-9820605), South Carolina Department of Health and Environmental Control NPS Program (EQ-9-461), the Associated Colleges of the South, and Furman University.

REFERENCES

Andersen, C.B., 2001. The problem of sample contamination in a fluvial geochemistry research experience for undergraduates. J. Geosci. Educ. 49, 351–357.

Andersen, C.B., Lewis, G.P., Sargent, K.A., 2004. Influence of wastewater treatment effluent on concentrations and fluxes of solutes in the Bush River, South Carolina, during extreme drought conditions. J. Environ. Geosci. 11, 28–41.

Andersen, C.B., Sargent, K.A., Wheeler, J., Wheeler, S., 2001. Fluvial geochemistry of selected tributary watersheds in the Enoree River Basin, SC. South Carolina Geol. 43, 57–71.

Ballester, M.V.R., Victoria, D.C., Krusche, A.V., Coburn, R., Victoria, R.L., Richey, J.E., Logsdon, M.G., Mayorga, E., Matricardi, E., 2003. A remote sensing/GIS-based physical template to understand the biogeochemistry of the Ji-Parana river basin (Western Amazonia). Remote Sens. Environ. 87, 429–445.

Bannari, A., Morin, D., Bonn, F., 1995. A review of vegetation indices. Remote Sens. Rev. 13, 95–120.

Boone, R.B., Galvin, K.A., Smith, N.M., Lynn, S.J., 2000. Generalizing El Nino effects upon Maasai livestock using hierarchical clusters of vegetation patterns. Photogramm. Eng. Rem. Sens. 66(6), 737–744.

Bormann, F.H., Likens, G.E., 1979. Pattern and Process in a Forested Ecosystem. Springer-Verlag, New York, p. 253.

Boyle, C.A., Lavkulich, L., Schreier, H., Kiss, E., 1997. Changes in land cover and subsequent effects on Lower Fraser basin ecosystems from 1827 to 1900. Environ. Manage. 21, 185–196.

Camp, W., 1960. Soil survey of Spartanburg County, SC, U.S. Department of Agriculture, p. 83, and maps.

Camp, W., 1975. Soil survey of Greenville County, SC, U.S. Department of Agriculture, p. 71, and maps.

Camp, W., Jones, W.E., Miford, P.R., Hearn, S.H., Aull, L.E., 1960. Soil survey of Newberry County, SC, U.S. Department of Agriculture, p. 66, and maps.

Camp, W., Meltzer, J.C., Fleming, W.H., Andrew, L.E., 1975. Soil survey of Laurens and Union Counties, SC, U.S. Department of Agriculture, p. 66, and maps.

Chen, D., Brutsaert, W., 1998. Satellite-sensed distribution and spatial patterns of vegetation parameters over a tallgrass prairie. J. Atmos. Sci. 55(7), 1225–1238.

Clark, G.M., Mueller, D.K., Mast, M.A., 2000. Nutrient concentrations and yields in undeveloped stream basins of the United States. J. Am. Water Res. Assoc. 36(4), 849–860.

Douglas, T.A., Chamberlain, C.P., Blum, J.D., 2002. Land use and geologic controls on the major elemental and isotopic (^{15}N and ^{87}Sr/^{86}Sr) geochemistry of the Connecticut River watershed, USA. Chem. Geol. 189, 19–34.

ESRI, 2005. ArcObjects Online: Hydrology Modeling, Last accessed 30 June 2005. Available at http://arcobjectsonline.esri.com/ArcObjectsOnline/Samples/Spatial%20Analyst/Hydrology%20Modeling/HydrologyModeling.htm.

Filoso, S., Martinelli, L.A., Williams, M.R., Lara, L.B., Krusche, A., Ballester, M.V., Victoria, R.L., Camargo, P.B., 2003. Land use and nitrogen export in the Piracicaba River Basin, Southeast Brazil. Biogeochemistry 65, 275–294.

Freeze, R.A., Cherry, J.A., 1979. Groundwater. Prentice-Hall, Englewood Cliffs, NJ, p. 604.

Galloway, J.N., Cowling, E.B., 2002. Reactive nitrogen and the world: 200 years of change. Ambio 31(2), 64–71.

Goolsby, D.A., 2000. Mississippi Basin nitrogen flux believed to cause Gulf hypoxia. EOS T. Am. Geophys. Un. 81(29), 321–327.

Groffman, P.M., Boulware, N.J., Zipperer, W.C., Pouyat, R.V., Band, L.E., Colosimo, M.F., 2002. Soil nitrogen cycle processes in urban riparian zones. Environ. Sci. Technol. 36(21), 4547–4552.

Hill, A.R., 1996. Nitrate removal in stream riparian zones. J. Environ. Qual. 25, 743–755.

Hill, A.R., Devito, K.J., Campagnolo, S., Sanmugadas, K., 2000. Subsurface denitrification in a forest riparian zone: Interactions between hydrology and supplies of nitrate and organic carbon. Biogeochemistry 51, 193–223.

Hoare, R.A., 1984. Nitrogen and phosphorus in Rotorua urban streams. New Zealand J. Mar. Freshwater Res. 18, 451–454.

Hunsaker, C.T., Levine, D.A., 1995. Hierarchical approaches to the study of water quality in rivers. BioScience 45(3), 193–203.

Jaworski, N.A., Howarth, R.W., Hetling, L.J., 1997. Atmospheric deposition of nitrogen oxides onto the landscape contributes to coastal eutrophication in the northeast United States. Environ. Sci. Technol. 31(7), 1995–2004.

Jensen, J.R., 2000. Remote Sensing of the Environment: An Earth Resource Perspective. Prentice-Hall, Saddle River, N.J, p. 544.

Ji, L., Peters, A.J., 2003. Assessing vegetation response to drought in the northern Great Plains using vegetation and drought indices. Remote Sens. Environ. 87, 85–98.

Keaton, M., Haney, D., Andersen, C.B., 2005. Impact of drought upon fish assemblage structure in two South Carolina piedmont streams. Hydrobiologia 545, 209–223.

Likens, G.E., Bormann, F.H., Johnson, N.M., Fisher, D.W., Pierce, R.S., 1970. Effects of forest cutting and herbicide treatment on nutrient budgets in the Hubbard Brook watershed-ecosystem. Ecol. Monogr. 40(1), 23–47.

Meybeck, M., 1982. Carbon, nitrogen, and phosphorus transport by world rivers. Am. J. Sci. 282, 401–450.

Meybeck, M., Helmer, R., 1989. The quality of rivers: From pristine stage to global pollution. Palaeogeogr. Palaeoecol. 75, 283–309.

Moreau, S., Bertru, G., Buson, C., 1998. Seasonal and spatial trends of nitrogen and phosphorus loads to the upper catchment of the river Vilaine (Brittany): Relationships with land use. Hydrobiologia 373/374, 247–258.

Paul, M.J., Meyer, J.L., 2001. Streams in the urban landscape. Ann. Rev. Ecol. Syst. 32, 333–365.

Peierls, B.L., Caraco, N.F., Pace, M.L., Cole, J.J., 1991. Human influence on river nitrogen. Nature 350, 386–387.

Peterson, B.J., Wollheim, W.M., Mulholland, P.J., Webster, J.R., Meyer, J.L., Tank, J.L., Martí, E., Bowden, W.B., Valett, H.M., Hershey, A.E., McDowell, W.H., Dodds, W.K., Hamilton, S.K., Gregory, S., Morrall, D.D., 2001. Control of nitrogen export from watersheds by headwater streams. Science 292, 86–90.

Rabalais, N.N., Turner, R.E., Scavia, D., 2002. Beyond science into policy: Gulf of Mexico Hypoxia and the Mississippi River. BioScience 52(2), 129–142.

Roy, S., Gaillardet, J., Allegre, C.J., 1999. Geochemistry of dissolved and suspended loads of the Seine River, France: Anthropogenic impact, carbonate, and silicate weathering. Geochem. Cosmochim. Ac. 63, 923–938.

Saunders, D.L., Kalff, J., 2001. Nitrogen retention in wetlands, lakes, and rivers. Hydrobiologia 443, 205–2112.

Smith, S.V., Renwick, W.H., Bartley, J.D., Buddemeier, R.W., 2002. Distribution and significance of small, artificial water bodies across the United States landscape. Sci. Total Environ. 299, 21–36.

Stoms, D.M., Estes, J.E., 1993. A remote sensing research agenda for mapping and monitoring biodiversity. Int. J. Rem. Sens. 14, 1839–1860.

Strahler, A.N., 1952. Dynamic basis of geomorphology. Geol. Soc. Am. Bull. 63, 923–938.

Swank, W.T., 1988. Stream chemistry responses to disturbance. In: Swank, W.T., Crossley, D.A. Jr. (Eds.), Forest Hydrology and Ecology at Coweeta. Springer-Verlag, New York, pp. 339–357.

Systat Software, 2004. SigmaStat 3.1 User's Manual. Systat Software Inc., Point Richmond, CA, p. 848.

Tucker, C.J., Sellers, P.J., 1986. Satellite remote sensing of primary production. Int. J. Remote Sens. 7, 1396–1416.

Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.M., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: Sources and consequences. Ecol. Appl. 7(3), 737–750.

Zhiliang, S., Qun, L., Shumel, Z., Hui, M., Ping, Z., 2003. A nitrogen budget of the Changjiang River catchment. Ambio 32, 65–69.