Residence Time, Chemical and Isotopic Analysis of Nitrate in the Groundwater and Surface Water of a Small Agricultural Watershed in the Coastal Plain, Bucks Branch, Sussex County, Delaware

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Introduction
Resource managers need a practical perspective on travel time of groundwater to streams, detailed understanding of the sources of nitrogen for targeting management efforts and to better quantify water-quality improvements.
State of Delaware  
2010 Combined Watershed Assessment Report (305(b)) and Determination for the Clean Water Act Section 303(d) List of Waters Needing TMDLs

Department of Natural Resources and Environmental Control  
April 1, 2010

Bucks Branch has some of the highest measured concentrations of total nitrogen in any stream in the State (Delaware Department of Natural Resources and Environmental Control, 2010) and most of the nitrogen is in the form of nitrate.
Introduction

The vast majority of nitrogen inputs in this part of Sussex County, Delaware are from manure and fertilizer.
Purpose/Objectives

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Concentrations of sulfur hexafluoride ($SF_6$), dissolved gases and silica in groundwater and surface water to determine the apparent age of groundwater in the aquifer and to estimate the average residence time of groundwater discharging to streams.
Purpose/Objectives

The purpose of this study was to present (1) estimated residence times of groundwater and (2) and provide a chemical and isotopic analysis of nitrate in the groundwater and surface water of the Bucks Branch watershed. Major-ion chemistry and the nitrogen and oxygen isotopic composition of nitrate in groundwater and stream water during base flow to evaluate the potential sources of nitrogen and to describe biogeochemical processes.
The study area is located approximately 32 miles (mi) west of the Atlantic Ocean shoreline in Sussex County, Delaware.

**Bucks Branch** drains 7.02 square miles (mi²), and is a tributary to the Nanticoke River located on the Delmarva Peninsula, which eventually drains into the Chesapeake Bay.
Study Area

A. 1968

Bucks Branch watershed boundary

B. 1997

Bucks Branch watershed boundary

Aerial photograph by Agricultural Stabilization and Conservation Service, 1968

Aerial photograph by Earth Data (formerly PhotoScience), 1997
Channelization and dredging (ditching) of streams affects the nearby water table, impairs the functional properties of the aquatic ecosystem, reduces canopy cover.
Methods
Mass Balance

Land Use
(ag, residential, etc.)

Biota
(plants, bacteria, etc.)

Atmospheric
(rain, etc.)

INPUTS

Upper Chester Showcase Watershed
Mass Balance

**INPUTS**

- Land Use
  - (ag, residential, etc.)
- Biota
  - (plants, bacteria, etc.)
- Atmospheric
  - (rain, etc.)

**Upper Chester Showcase Watershed**

**OUTPUTS**

- Surface Water
  - (gage, synoptics, etc.)
- Groundwater
  - (deep and shallow, etc.)
Methods

Stream Synoptic (n = 7, 5)
High/Low Baseflow Conditions
Field Parameters
Major Ions (DNREC)
N & O Isotopes (USGS)

Groundwater Synoptic (n = 10)
Sampled Once
Field Parameters
Major Ions (DNREC)
N & O Isotopes (USGS)
Dissolved Gases (USGS)
Residence Time of Groundwater
Residence Time of GW

The apparent age of groundwater sampled ranged from 13 to 30 years, with a median age of **18 years**.

The residence time of groundwater contributing to the stream during base flow was based on an empirical model using simple linear regression of groundwater ages and silica concentrations in groundwater.
The estimated residence time of groundwater contributing to stream flow for the entire Bucks Branch watershed represented by the outlet and is approximately **19 years**.

This value is comparable to the median age of **18 years** for groundwater.
Chemical and Isotopic Analysis of Nitrate
The surficial aquifer had **oxic conditions** with dissolved oxygen levels greater than 0.5 mg/L.

The **lack of reducing conditions** for effective removal of nitrate by microbes coupled with the high rate of nitrogen input often leaves any effects of possible loss of nitrate indistinguishable.

Nitrate exceeded the USEPA **drinking-water standard** (10 mg/L as N) in 60 percent of the groundwater wells and at 42 percent of the surface-water sites.
Fertilizer, manure and soil organic matter produce an acidity that is often neutralized with lime (crushed dolomite) \([\text{CaMg(CO}_3\text{)}_2]\).

A similar relation of NO\(_3\) was found with potash (KCl) and specific conductance.

**Graph**

- Title: Calcium + magnesium, in milligrams per liter vs. Concentration of nitrate as N, in milligrams per liter
- Equation: \(\text{Ca} + \text{Mg} = 1.44 \times \text{NO}_3 + 0.13\)
- \(\text{R}^2 = 0.98\)
- \(p < 0.0001\)
The relative abundance of cations and anions in ground water present a pattern commonly seen in \textit{water affected by agriculture}.
Isotopic Composition of Nitrate

This linear relation between the N and O isotopes in flow path studies has been shown to be an indication of denitrification in groundwater.
Isotopic Composition of Nitrate

EXPLANATION

- **Surface-water sampling site and identifier**: SW1
- **Nitrate concentration, in milligrams per liter**: 11.0 (8.43)
- **Nitrogen-isotope ($\delta^{15}N$) composition, per mil**

**Bucks Branch watershed**

- SW7: 4.9 (10.4)
- SW6: 6.1 (8.7)
- SW4: 10.2 (6.47)
- SW3: 12.9 (7.7)
- SW2: 10.3 (7.37)
- SW1: 11.0 (8.43)
Summary and Conclusions

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- Median age of sampled groundwater is 18 years and the estimated residence time of groundwater contributing to the stream-flow for the entire Bucks Branch watershed at the outlet is approximately 19 years.
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• Concentrations of nitrate exceeded the USEPA drinking-water standard (10 mg/L) in 60 percent of groundwater samples and 42 percent of surface-water samples.
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• Nitrogen and oxygen isotopes ($\delta^{15}$N and $\delta^{18}$O) of nitrate in groundwater and surface water indicate some loss of nitrate through denitrification, but this process is not sufficient to remove all of the nitrate and concentrations of nitrate remain elevated.
Possible Next Steps

- Monthly (Baseflow) Sampling
- Event (Storm) Sampling
- Major Ions, Nutrients
- N & O Isotopes
- Continuous WQ (Temp, pH, SC, DO)
- Nitrate Sensor

Nitrate
Possible Next Steps

- High/Low Baseflow Conditions
- Field Parameters
- Major Ions, Nutrients
- N & O Isotopes
- Nitrate Sensor

Seasonal Synopotics
Possible Next Steps

- Bi-Monthly Sampling of Shallow Wells (WQ, Levels)
- Continuous Water Quality (Temp, SC, Nitrate)
- Geoprobe Synoptics
- Track Inputs
Monitoring the Water Quality Response of Conservation Practices in Small Watersheds
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