# Nitrogen and Phosphorus in Streams in Agricultural Watersheds

# Exhibits





**Coverage:** Nitrate data from 130 stream sites; total nitrogen data from 133 stream sites. Stream sites are in watersheds where agriculture is the predominant land use. These watersheds are within 36 major river basins studied by the USGS NAWQA program.

Trend analysis has not been conducted because these data represent one cycle of sampling. For more information about uncertainty, variability, and statistical analysis, view the technical documentation for this indicator.

Data source: Mueller and Spahr, 2005



# Exhibit 2. Phosphorus in streams in agricultural watersheds of the contiguous U.S., 1992-2001

**Coverage:** Orthophosphate data from 132 stream sites; total phosphorus data from 129 stream sites. Stream sites are in watersheds where agriculture is the predominant land use. These watersheds are within 36 major river basins studied by the USGS NAWQA program.

Trend analysis has not been conducted because these data represent one cycle of sampling. For more information about uncertainty, variability, and statistical analysis, view the technical documentation for this indicator.

Data source: Mueller and Spahr, 2005

# Introduction

Nitrogen is a critical nutrient that is generally used and reused by plants within natural ecosystems, with minimal "leakage" into surface or ground water, where nitrogen concentrations remain very low (Vitousek et al., 2002). When nitrogen is applied to the land in amounts greater than can be incorporated into crops or lost to the atmosphere through volatilization or denitrification, however, nitrogen concentrations in streams can increase. The major sources of excess nitrogen in predominantly agricultural watersheds are fertilizer and animal waste; other sources include septic systems and atmospheric deposition. The total nitrogen concentration in streams consists of nitrate, the most common bioavailable form; organic nitrogen, which is generally less available to biota; and nitrite and ammonium compounds, which are typically present at relatively low levels except in highly polluted situations. Excess nitrate is not toxic to aquatic life, but increased nitrogen may result in overgrowth of algae, which can decrease the dissolved oxygen content of the water, thereby harming or killing fish and other aquatic species (U.S. EPA, 2005). Excess nitrogen also can lead to problems in downstream coastal waters, as discussed further in the N and P Loads in Large Rivers indicator.

Phosphorus also is an essential nutrient for all life forms, but at high concentrations the most biologically active form of phosphorus (orthophosphate) can cause water quality problems by overstimulating the growth of algae. In addition to being visually unappealing and causing tastes and odors in water supplies, excess algal growth can contribute to the loss of oxygen needed by fish and other animals. Elevated levels of phosphorus in streams can result from fertilizer use, animal wastes and wastewater, and the use of phosphate detergents. The fraction of total phosphorus not in the orthophosphate form consists of organic and mineral phosphorus fractions whose bioavailability varies widely.

This indicator reports nitrogen and phosphorus concentrations in stream water samples collected from 1992 to 2001 by the U.S. Geological Survey's (USGS's) National Water Quality Assessment (NAWQA) program, which surveys the condition of streams and aquifers in study units throughout the contiguous U.S. Specifically, this indicator reflects the condition of 129 to 133 streams draining watersheds where agriculture is the predominant land use (the exact number of sites with available data depends on the analyte), according to criteria outlined in Mueller and Spahr (2005). These watersheds are located in 36 of the 51 NAWQA study units (i.e., major river basins). Sites were chosen to avoid large point sources of nutrients (e.g., wastewater treatment plants). At each stream site, samples were collected 12 to 25 times each year over a 1–to–3–year period; this indicator is based on a flow–weighted annual average of those samples. Related indicators report the concentrations of nitrogen and phosphorus in small wadeable streams, regardless of land use (in contrast to this more focused indicator), and <u>nitrate concentrations in ground water in agricultural watersheds</u>.

For nitrogen, the indicator reports the percentage of streams with average concentrations of nitrate and total nitrogen in one of five ranges: less than 1 milligram per liter (mg/L); 1-2 mg/L; 2-6 mg/L; 6-10 mg/L; and 10 mg/L or more. This indicator measures nitrate as N, i.e., the fraction of the material that is actually nitrogen. Measurements actually include nitrate plus nitrite, but because concentrations of nitrite are typically insignificant relative to nitrate, this mixture is simply referred to as nitrate. Naturally occurring levels of nitrate and total nitrogen vary substantially across the country, and statistical analyses of water quality data suggest that appropriate reference levels range from 0.12 to 2.2 mg/L total N, such that some streams in the lowest category (less than 1 mg/L) may still exceed recommended water quality criteria (U.S. EPA, 2002).

Concentrations of total phosphorus and orthophosphate (as P) are reported in four ranges: less than 0.1 mg/L, 0.1–0.3 mg/L, 0.3–0.5 mg/L, and 0.5 mg/L or more. There is currently no national water quality criterion for either form to protect surface waters because the effects of phosphorus vary by region and are dependent on physical factors such as the size, hydrology, and depth of rivers and lakes. Nuisance algal growths are not uncommon in rivers and streams below the low reference level (0.1 mg/L) for phosphorus in this indicator, however (Dodds and Welch, 2000), and statistical analyses of water quality data suggest that more appropriate reference levels for total P range from 0.01 to 0.075 mg/L, depending on the ecoregion (U.S. EPA, 2002). Some streams in the lowest category may exceed these recommended water quality criteria. The border between the U.S. and Mexico spans approximately 2,000 miles, from the Pacific Ocean to the Gulf of Mexico. The area is subjected to a unique blend of increased industrial development (especially on the Mexican side of the border), intense pressures because of the shifting and growing population related to this development, and an arid climate that can exacerbate many air quality problems. Ozone and particulate matter are air pollutants of particular concern (U.S. EPA, 2003).

## What The Data Show

Average flow-weighted nitrate concentrations were 2 mg/L or above in about 60 percent of stream sites in these predominantly agricultural watersheds (Exhibit 1). About 13 percent of stream sites had nitrate concentrations of at least 10 mg/L (the slightly smaller percentage of streams with total N above 10 mg/L is an artifact of the flow-weighting algorithm). Nearly half of the streams sampled had total nitrogen concentrations in the 2–6 mg/L range, and 78 percent had concentrations of 2 mg/L or above.

Nearly half of the streams in agricultural watersheds had average annual flow-weighted concentrations of orthophosphate (as P) of at least 0.1 mg/L (Exhibit 2). Approximately 85 percent of the streams had concentrations of total phosphorus of 0.1 mg/L or above, while 13 percent had at least 0.5 mg/L total phosphorus.

- These data represent streams draining agricultural watersheds in 36 of the major river basins (study units) sampled by the NAWQA program in the contiguous U.S. While they were chosen to be representative of agricultural watersheds across the United States, they are the result of a targeted sample design, and may not be an accurate reflection of the distribution of concentrations in all streams in agricultural watersheds in the U.S.
- This indicator does not provide information about trends over time, as the data in Mueller and Spahr (2005) only represent the first cycle of the NAWQA program. NAWQA has completed its second cycle of sampling (2002-2011) and has initiated a third cycle.

## Data Sources

Summary data for this indicator were provided by USGS's NAWQA program. These data have been published in Mueller and Spahr (2005), along with the individual sampling results on which the analysis is based.

#### References

Dodds, W.K., and E. Welch. 2000. Establishing nutrient criteria in streams. J. No. Am. Benthol. Soc. 19:186-196.

Mueller, D.K., and N.E. Spahr. 2005. Water-quality, streamflow, and ancillary data for nutrients in streams and rivers across the nation, 1992–2001: U.S. Geological Survey data series 152. <u>http://pubs.usgs.gov/ds/2005/152/</u>

U.S. EPA (United States Environmental Protection Agency). 2005. National estuary program—challenges facing our estuaries. Key management issues: Nutrient overloading. <u>https://www.epa.gov/nep/how-national-estuary-programs-address-environmental-issues</u>.

U.S. EPA. 2002. Summary table for the nutrient criteria documents. Accessed November 2007. <a href="https://www.epa.gov/sites/production/files/2014-08/documents/criteria-nutrient-ecoregions-sumtable.pdf">https://www.epa.gov/sites/production/files/2014-08/documents/criteria-nutrient-ecoregions-sumtable.pdf</a> (3pp, 140K).

Vitousek, P., H. Mooney, L. Olander, and S. Allison. 2002. Nitrogen and nature. Ambio 31:97-101.

## **Technical Documentation**

## Identification

1. Indicator Title

Nitrogen and Phosphorus in Streams in Agricultural Watersheds

2. ROE Question(s) This Indicator Helps to Answer

What are the trends in the extent and condition of fresh surface waters and their effects on human health and the environment? What are the trends in the critical physical and chemical attributes of the nation's ecological systems?

3. Indicator Abstract

This indicator reports nitrogen and phosphorus concentrations in water samples taken from streams in predominantly agricultural watersheds between 1992 and 2001. These two nutrients occur naturally in fresh surface waters, but they can occur at elevated concentrations as a result of human activities. Nutrient availability influences the health of aquatic ecosystems.

4. Most Recent Update

05/2008

# Data Sources

5. Data Sources

This indicator is based on data collected by the U.S. Geological Survey's (USGS's) National Water Quality Assessment (NAWQA) program.

6. Data Availability

Summary data for this indicator were provided by USGS's NAWQA program. These data have been published in Mueller and Spahr (2005), along with the individual sampling results on which the analysis is based. The table at <a href="http://pubs.usgs.gov/ds/2005/152/data/Cycle\_L\_sw\_nuts\_summary\_data.xls">http://pubs.usgs.gov/ds/2005/152/data/Cycle\_L\_sw\_nuts\_summary\_data.xls</a> (MS Excel, 589K) presents the results of flow-weighting, while the official data report in Mueller and Spahr (2005) also lists the land use classification assigned to each sampling site. This indicator reports on the subset of sites classified as "agricultural."

# Methodology

7. Data Collection

This indicator is based on measurements of nitrate plus nitrite, total Kjeldahl nitrogen (N), dissolved orthophosphate, and total phosphorus (P) in water samples from streams.

#### Survey Design

The data for this indicator were collected between 1992 and 2001 as part of the NAWQA program, which set out to examine 51 study areas (i.e., major river basins) across the contiguous 48 states. This program was specifically designed to sample streams draining "representative" watersheds of each of the major land use types, sometimes referred to as "indicator" sites. NAWQA's overall sample design represents a comprehensive effort to assess the nation's water quality through study units spread across the contiguous 48 states, as shown in the map on NAWQA's Web site (http://water.usgs.gov/nawqa/).

This indicator reports nutrient concentrations in streams draining watersheds where agriculture was considered the primary land use, according to a standard set of criteria described in Mueller and Spahr (2005) (in particular, see <a href="http://pubs.usgs.gov/ds/2005/152/htdocs/data\_report\_ancillary.htm">http://pubs.usgs.gov/ds/2005/152/htdocs/data\_report\_ancillary.htm</a>). "Agricultural" watersheds are those that are more than 50 percent cropland or pasture and no more than 5 percent urban. Classifications were based on the National Land Cover Dataset (NLCD). Agricultural watersheds were sampled in 36 of NAWQA's 51 study

units; the other study units did not have any stream samples that were representative of agricultural watersheds. NAWQA also sampled several forested and urban streams, which can provide some useful context for the agricultural data.

The 9-year NAWQA study period was divided into three-year cycles, with approximately one-third of the study units intensely sampled during each cycle. Within each study unit, major streams were sampled for nutrients 12 to 25 times per year over the period of intense monitoring, and less frequently in other years. For this indicator, the analysis used NAWQA data from only the 1 to 3 years of most intense monitoring at each site. Samples from 129 to 133 streams in agricultural watersheds were analyzed for nitrate (nitrate plus nitrite, as N), total N, orthophosphate (as P), and total P. The exact number of sites varied due to data availability:

- Nitrate: 130
- Total N: 133
- Orthophosphate: 132
- Total P: 129

Because of NAWQA's scientific sampling design, results are considered to be fairly representative of conditions in agricultural watersheds nationwide. This broad national indicator is not specifically designed to target sensitive populations or ecosystems. It may be relevant to sensitive populations, however, to the extent that certain threatened or endangered species may be particularly sensitive to elevated nutrient levels and related changes in the trophic state of waterbodies.

NAWQA provided several references to document the design of the survey upon which this indicator is based. Gilliom et al. (1995) discuss the overall design of the NAWQA program, while Mueller and Spahr (2005) describe how watersheds were classified as to land use.

## Sample Collection

Sampling procedures can be found in Mueller and Spahr (2005), which describes how samples were collected and preserved. Samples were collected using depth and width integrating techniques that ensured these samples represented the entire cross-section of the stream (techniques documented in Shelton, 1994). NAWQA protocols also include criteria for the selection, use, and cleaning of collection equipment.

## Sample Analysis

All samples were analyzed at USGS's National Water Quality Laboratory (NWQL) in Colorado using standard methods, which are fully documented in Mueller and Spahr (2005) and other USGS publications.

## 8. Indicator Derivation

Because nutrient concentrations typically vary with stream flow (volume), NAWQA calculated a flow-weighted mean concentration for each nutrient. This type of calculation uses a regression model to transform non-daily measurements into a mean value that accounts for day-to-day variability in stream flow (volume) over the course of a given year. USGS commonly calculates a flow-weighted mean when the concentration of a given constituent —

in this case, nitrogen or phosphorus — may be correlated with stream flow (i.e., total load is an issue). Models are described and documented in Mueller and Spahr (2005).

NAWQA calibrated the regression models using 1 to 2 years of daily stream flow data from USGS gauges located at or near each of the water quality sampling sites. These gauges are part of a network of thousands of USGS stream gauges located across the U.S. A single gauge may measure volumetric discharge directly using a current meter or indirectly using calculations that can be performed on measurements of stream depth (a unique rating curve for each stream, relating volume to stream height). Collection of stream flow data follows long-standing USGS protocols. For example, see USGS online references regarding depth (stage) gauging (http://pubs.usgs.gov/twri/twri3-A6/ and http://pubs.usgs.gov/twri/twri3a7/); conversion of depth to discharge (http://pubs.usgs.gov/twri/twri3-a1/ and http://pubs.usgs.gov/twri/twri3-a10/); and direct measurement of discharge (http://pubs.usgs.gov/twri/twri3a8/).

9. Quality Assurance and Quality Control

USGS has many procedures in place to ensure the quality of its data. Mueller et al. (1997) describe quality assurance/quality control (QA/QC) procedures for the collection and analysis of stream water quality samples under the NAWQA program. Routine sampling procedures include field blanks and replicates to assess measurement bias and variability (Mueller et al., 1997).

# Analysis

10. Reference Points

Thresholds for ecological effects vary by ecoregion, in part because the effects are dependent on physical factors such as the size, hydrology, and depth of rivers and lakes. For nitrogen, statistical analyses of water quality data suggest that appropriate reference levels in streams range from 0.12 to 2.2 mg/L total N (U.S. EPA, 2002). For phosphorus, statistical analyses suggest that appropriate reference levels range from 0.01 to 0.075 mg/L total P (U.S. EPA, 2002).

Similarly, USGS has established "background" values based on extensive studies of relatively undeveloped watersheds. Flow-weighted concentrations during a 1990–1995 study, for example, were generally low with median basin concentrations of 0.087, 0.26, 0.010, and 0.022 mg/L for nitrate as N, total N, orthophosphate as P, and total P, respectively (Clark et al., 2000). Background levels vary somewhat by region due to factors such as nitrogen deposition and geology (e.g., bedrock rich in phosphorus).

11. Comparability Over Time and Space

The same sampling methods were used at all locations during the study period (1992–2001). No corrections have been made to adjust for spatial or temporal biases.

## 12. Sources of Uncertainty

Uncertainty for this indicator stems from a combination of measurement error and other sources. NAWQA has published uncertainty figures for the overall data collection effort, which should be indicative of uncertainty for this indicator. Mueller and Titus (2005) include methods for how to compute confidence intervals around the measured concentrations, and also specifically discuss nutrient data over the period of record for this indicator.

This discussion, as well as the calculation of the uncertainty associated with the regression models used to determine the flow weighted mean annual concentrations, is also summarized in Mueller and Spahr (2005).

Additional uncertainty can be attributed to NAWQA site selection as it is the result of a targeted design as opposed to a statistical survey. Indications of differences between NAWQA agricultural basins and all agricultural basins in the country are not available.

## 13. Sources of Variability

Because uncertainty varies depending on the chemical and analytical method in question, it is difficult to make a single definitive statement about the impact of uncertainty on this indicator. However, because results were averaged over time and generalized over the entire nation, the summary figures reported by this indicator should be considered reasonably accurate. By incorporating flow-weighted averages, the indicator design also accounts for much of the day-to-day and seasonal variability inherent in measurements of chemicals whose concentrations in stream water are linked to stream flow or to the timing of fertilizer application.

There are a few sites for which nitrate appears to exceed total N; this is because the two were modeled independently. The difference is reportedly within the calculated error of the models, however, so it is not statistically significant (Bill Wilber and Dave Mueller, USGS, personal communication, 2005).

# 14. Statistical/Trend Analysis

No trend analysis has been conducted on this indicator, as the NAWQA program has completed only one full sampling cycle to date. The data presented here may serve as a baseline for future surveys.

# Limitations

15. Data Limitations

Limitations to this indicator include the following:

- These data represent streams draining agricultural watersheds in 36 of the major river basins (study units) sampled by the NAWQA program in the contiguous U.S. While they were chosen to be representative of agricultural watersheds across the United States, they are the result of a targeted sample design, and may not be an accurate reflection of the distribution of concentrations in all streams in agricultural watersheds in the U.S.
- 2. This indicator does not provide information about trends over time, as the data in Mueller and Spahr (2005) only represent the first cycle of the NAWQA program. NAWQA has completed its second cycle of sampling (2002-2011) and has initiated a third cycle.
- 3. Drinking water treatment can significantly reduce concentrations of nitrate. Thus, the levels of contaminants reported in this indicator should not be interpreted to represent exposures to people when these waters are used as drinking water supplies.
- 4. The indicator does not represent the very smallest streams—i.e., those that could be classified as first- or second-order.

# References

Clark, G.M., D.K. Mueller, and M.A. Mast. 2000. Nutrient concentrations and yields in undeveloped basins of the United States. J. Am. Water Resources Assoc. 36(4):849–860. <u>http://water.usgs.gov/nawqa/nutrients/pubs/awra\_v36\_no4/</u>.

Gilliom, R.J., W.M. Alley, and M.E. Gurtz. 1995. Design of the National Water-Quality Assessment Program: Occurrence and distribution of water-quality conditions. U.S. Geological Survey Circular 1112.

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Mueller, D.K. and C.J. Titus. 2005. Quality of nutrient data from streams and ground water sampled during water years 1992-2001. U.S. Geological Survey Scientific Investigations Report 2005-5106.

Mueller, D.K., J.D. Martin, and T.J. Lopes. 1997. Quality-control design for surface water sampling in the National Water-Quality Assessment program. U.S. Geological Survey Open-File Report 97-223. <u>http://pubs.usgs.gov/of/1997/223/index.html</u>.

Shelton, L.R. 1994. Field guide for collecting and processing stream water samples for the National Water-Quality Assessment Program. U.S. Geological Survey Open-File Report 94-455.

U.S. EPA (United States Environmental Protection Agency). 2002. Summary table for the nutrient criteria documents. Accessed November 2007. <u>https://www.epa.gov/nutrient-policy-data/ecoregional-criteria-documents</u>.