Terziotti, Silvia, Hoos, A.B., Harned, D.A., and Garcia, A.M, 2010, Mapping watershed potential to contribute phosphorus from geologic materials to receiving streams, southeastern United States

Abstract

As part of the southeastern United States SPARROW (SPAtially Referenced Regressions On Watershed attributes) water-quality model implementation, the U.S. Geological Survey created a dataset to characterize the contribution of phosphorus to streams from weathering and erosion of surficial geologic materials. SPARROW provides estimates of total nitrogen and phosphorus loads in surface waters from point and nonpoint sources. The characterization of the contribution of phosphorus from geologic materials is important to help separate the effects of natural or background sources of phosphorus from anthropogenic sources of phosphorus, such as municipal wastewater or agricultural practices. The potential of a watershed to contribute phosphorus from naturally occurring geologic materials to streams was characterized by using geochemical data from bed-sediment samples collected from first-order streams in relatively undisturbed watersheds as part of the multiyear U.S. Geological Survey National Geochemical Survey. The spatial pattern of bed-sediment phosphorus concentration is offered as a tool to represent the best available information at the regional scale. One issue may weaken the use of bed-sediment phosphorus concentration as a surrogate for the potential for geologic materials in the watershed to contribute to instream levels of phosphorus—an unknown part of the variability in bed-sediment phosphorus concentration may be due to the rates of net deposition and processing of phosphorus in the streambed rather than to variability in the potential of the watershed's geologic materials to contribute phosphorus to the stream. Two additional datasets were created to represent the potential of a watershed to contribute phosphorus from geologic materials disturbed by mining activities from active mines and inactive mines.

Introduction

The largest reservoir of phosphorus (P) in the environment is minerals in sedimentary rocks (Mueller and Helsel, 1996). Although, in general, phosphorus compounds in rock minerals are relatively insoluble and do not readily move in runoff or groundwater, erosion of surface soil and rock may be a substantial source of suspended phosphorus in streams in some areas where sedimentary rock is exposed, where soils derived from sedimentary rock exist (Dillon and Kirchner, 1975), or especially where deposits of phosphorus minerals are mined. Phosphate mineral deposits in consolidated material in the southeastern United States generally are of two types—phosphate nodules (oolites, or grains incorporated in sedimentary rocks) and accumulations in residuum derived from the weathering of bedrock (U.S. Geological Survey, 1968). In addition, ore-grade deposits of phosphate minerals are present in formations of large areal extent in Florida and Tennessee (two areas where phosphate output is the largest in the Nation) and in formations of smaller areal extent in North Carolina and Alabama. Data describing phosphate mineral content of ore material are available for many mined areas; however, these data cannot be used to characterize the mass of P contributed from the watershed without additional information on density and distribution of the ore material within the host rock. Phosphorus concentrations in streambed sediment, however, may represent average phosphorus levels in the surficial geologic material of the contributing watershed and delivery of this material to the stream (Cannon and others, 2003).

The U.S. Geological Survey (USGS) created a dataset to characterize the potential for a watershed to contribute phosphorus to streams from weathering and erosion of surficial geologic materials. The motivation for creating this dataset was to support calibration of a phosphorus-transport model (SPARROW—SPAtially Referenced Regressions On Watershed attributes) for streams in the southeastern United States. SPARROW (Schwarz and others, 2006) provides estimates of total nitrogen and phosphorus loads in streams from point and nonpoint sources, including background, or naturally occurring, sources. The data also may be useful for a variety of other purposes, including understanding regional background variations in surface-water phosphorus concentrations and developing nutrient criteria.

Mapping Watershed Potential to Contribute Phosphorus from Geologic Materials

In order to create a map of bed-sediment phosphorus concentration values that can be applied to the entire Southeast, values of phosphorus were compiled and summarized by geologic map units. The source data for phosphorus concentration, the method of deriving geologic map units, and the identification of phosphorus mine locations are described below.

Bed-Sediment Phosphorus Concentration Source Data

The USGS National Geochemical Survey (NGS) compiles data on geochemistry of stream-channel sediment (first-order streams) and soil in order to construct geochemical maps and refine estimates of baseline concentrations of chemical elements (U.S. Geological Survey, 2004). Phosphorus data are incorporated into the NGS data base primarily from the re-analysis of a subset of samples collected between 1976 and 1980 for the National Uranium Resource Evaluation (NURE) Program (Averett, 1984) and analyses of new samples collected during 1997–1999 and 2004–2006 by the USGS and collaborating State agencies. In the Southeast, the NGS contains nine datasets based on NURE samples (Alabama I, Alabama II, Coastal 98, Coastal 99, Kentucky, South Carolina, 2000, 2002, and 800) for a total of 6,842 samples, and nine State datasets (Alabama, Florida I, Florida II, Georgia, Mississippi I, Mississippi II, States 2006a, States 2006b, and Tennessee) for a total of 3,280 samples (U.S. Geological Survey, 2004). Thus, 10,122 bed-sediment samples were available across the southeastern U.S. for mapping bed-sediment phosphorus concentration (BSPconc; fig. 1).

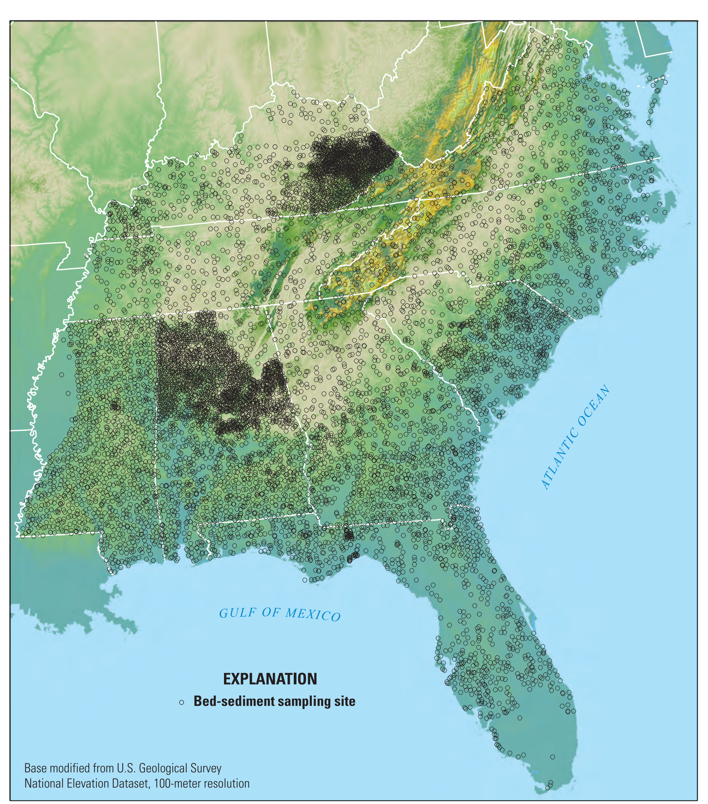


Figure 1. Locations of stream sites sampled for bed-sediment phosphorus concentrations in the southeastern United States as part of the U.S. Geological Survey National Geochemical Survey.

Streams for bed-sediment sampling in the Southeast for the NURE program were selected randomly from topographic maps marked with grids that cover 10 to 30 square kilometers (km^2), with an average density of one site per 13 km^2. If possible, no sites were selected that were closer than 1.5 kilometer (km) to another site, and the area drained was no more than three times the area of the grid so that the maximum size of a basin draining to a site would be 90 km^2. The largest headwater stream within the grid was chosen if the site was accessible to field personnel (Bolivar, 1980), and an attempt to sample most streams draining from 8 to 26 km^2 (3 to 10 square miles) was made (Ferguson and others, 1976). Samples were collected upstream from roads, ponds or other disturbances that could have altered the sampling results, and samples were collected outside of populated areas (Information Systems Programs, Energy Resources Institute, 1985) in order to accurately represent the local-scale variation in sediment mineral composition with surficial geology or other geographical characteristics. In the development of datasets for the NGS, NURE samples in most areas were selected randomly for re-analysis in order to achieve a density of approximately one sample per 289 km^2; however, in densely sampled areas in Kentucky and Alabama, all of the NURE samples were re-analyzed.

In order to verify that samples were in general from small, undisturbed basins, basin drainage area and watershed percentage of developed and agricultural area at each sampling site in the Southeast SPARROW study area (7,421 of the 10,122 sampling sites) were examined using the National Hydrography Dataset Plus (NHDPlus, 2009). The NHDPlus maintains tables that include cumulative drainage area and basin characteristics derived from the 1992 National Land-Cover Data (NLCD; Vogelmann and others, 2001) for every stream segment. Because most samples were taken before 1997, the 1992 land-cover data were most appropriate to use for evaluating anthropogenic effects.

Of the 7,421 sampling sites within the SPARROW study area, 5,560 could be assigned with confidence (within 200 meters) to an individual stream segment on the 1:100,000-scale NHDPlus. The size distribution of watersheds for these sites confirms that the sites drain small areas; half of the sites drain areas smaller than 9.1 km^2 and 90 percent of the sites drain areas smaller than 47 km^2 (table 1). Presumably these values would be even lower had all 7,421 sampling sites been included in the analysis; the lack of association with the 1:100,000-scale NHDPlus that caused 1,861 sites to be excluded from the analysis was, in most cases, due to location of the excluded site on a first-order stream too small for representation by 1:100,000 hydrography. The distribution of land-cover characteristics of watersheds for the 5,560 sampling sites confirms that the majority of the sites represent basins with little urban development; that is, land cover is less than 0.1-percent developed in half of the watersheds and less than 5-percent developed in 90 percent of the watersheds. Although some of the sites are affected by agricultural activity (land cover is more than 50-percent agricultural for 10 percent of the sites), the majority of the sites are relatively undisturbed (less than 12-percent agricultural in half of the watersheds).

Table 1. Basin drainage areas and percentages of agricultural land and developed land for National Geochemical Survey stream sites sampled for bed-sediment phosphorus content in the southeastern United States.

Percentile	Cumulative drainage area, in square kilometers	Agricultural land	Developed land	Forested land
		Percentage in 1992		
10th	2.2	0	0	2
25th	4.2	2.1	0	18.9
50th	9.1	12	0.1	37.9
75th	19.3	30.5	0.9	53.2
90th	46.6	50.3	5.1	67.2
Mean	**56.4**	**19.2**	**2.4**	**36.9**

Based on the characteristics of the target stream population, several assumptions can be made about the bed-sediment BSPconc from this dataset:

- BSPconc values from the majority of these sites represent conditions with minimal anthropogenic sources in the watershed, and consequently, the average values of BSPconc for different subregions indicate spatial variation in the potential of the upstream watershed to contribute P from naturally occurring geologic materials to the receiving stream channel.
- BSPconc values represent the potential contribution of P from the local area adjacent to the sampling site (Bolivar, 1980).
- BSPconc values represent streambed conditions in small headwater stream channels.

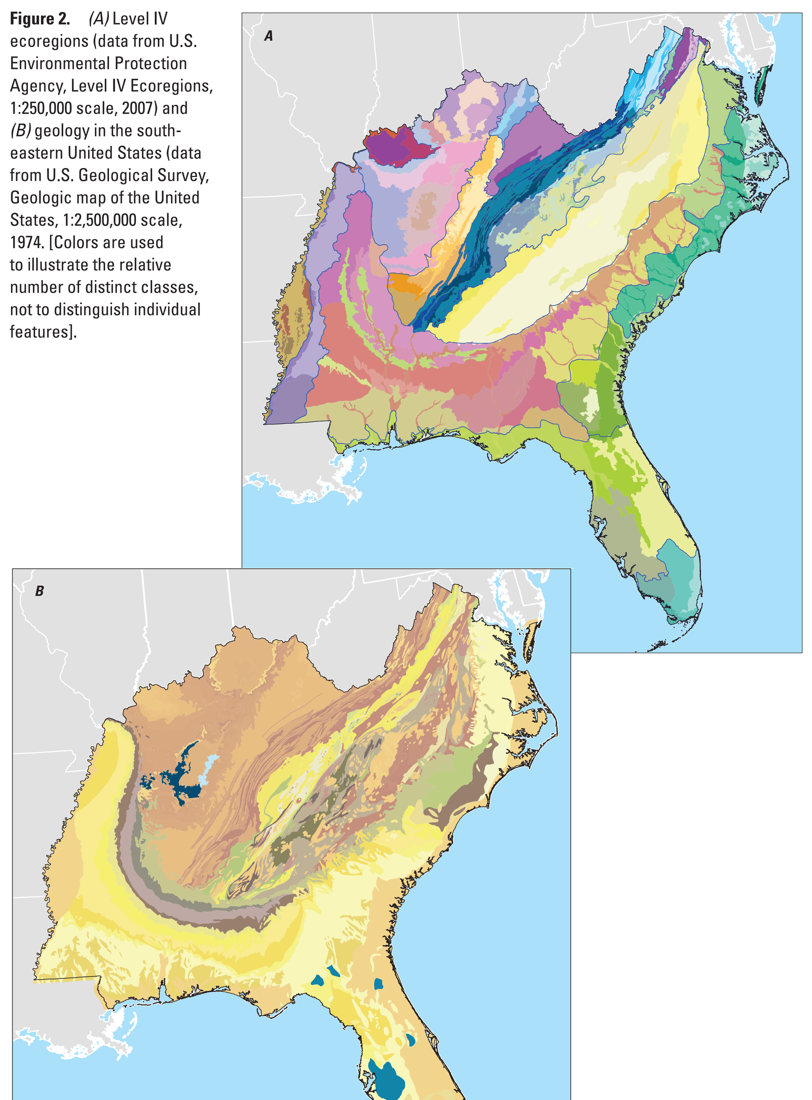
All three of these assumptions are critical to the interpretation and application of the data in this report.

Delineating Geologic Map Units

The BSPconc values were grouped into geologic map units (GMUs), defined by using regional-scale geologic features, and averaged to a single value for each GMU. The grouping and averaging accomplished two objectives: (1) creating a continuous surface of BSPconc throughout the Southeast regardless of sample-site density, and (2) minimizing the effect of BSPconc values that are affected by human activity. As previously discussed, the site-selection strategy for the bed-sediment data networks in NGS favor sites in relatively undisturbed areas; in practice, however, the BSPconc results at some sites may be affected by anthropogenic sources. Potential bias introduced by these sites was minimized by averaging values from many sites within a GMU.

The GMUs were created by delineating zones with similar lithochemistry based on geologic age (King and Beikman, 1974) and geomorphic setting (indicated by level IV ecoregions; U.S. Environmental Protection Agency, 2007). The digital maps of geologic age and level IV ecoregions were overlain and merged to create unique GMUs for each combination of geologic age and ecoregion. This combination creates units with similar geologic properties and accounts for regional variations reflected by ecoregions. Additional boundaries representing known phosphate-rich formations in Tennessee and Florida were incorporated to refine the GMU boundaries in these areas (Smith and Whitlatch, 1940, p. 8, 15; Clawges and Price, 1999; fig. 2).

Figure 2. *(A)* Level IV ecoregions (data from U.S. Environmental Protection Agency, Level IV Ecoregions, 1:250,000 scale, 2007) and *(B)* geology in the southeastern United States (data from U.S. Geological Survey, Geologic map of the United States, 1:2,500,000 scale, 1974. [Colors are used to illustrate the relative number of distinct classes, not to distinguish individual features].



Delineating Areas Affected by Phosphate Mining

In this analysis, P derived from geologic material that has been extracted from a subsurface deposit and placed on the land surface was characterized separately from P derived from naturally occurring geologic materials in a watershed. The mapped location and description of phosphate mines from the Mineral Resources Data System (MRDS; U.S. Geological Survey, 2005b) were used to identify all possible areas where disturbed geologic materials may affect instream P concentration. The MRDS dataset contains 839 mine sites, active and inactive, in the southeastern United States. The determination of mine status is based on information from the active mines and mineral plants in the U.S. dataset (U.S. Geological Survey, 2005a), which identifies 19 of the 839 phosphate mines sites as active mines.

Only two active mine operations were identified outside of Florida, one in Mississippi and one in North Carolina. Boundaries of mined land for these operations were estimated by using aerial photography (fig. 3*A*). High-resolution imagery was used to identify the parcels and delineate the boundary for the mined areas.

Because delineations of inactive mine operations were not available outside of west-central Florida, and because the land use at the inactive mine locations has been altered making it difficult to identify using current aerial photography, an estimate of the area associated with an inactive phosphate mine was based on active mining operations within a GMU. The mean area value of mined land (area classified as barren land in the NLCD (Homer and others, 2004) observed for a subset of mine operations within the GMU was assigned to inactive phosphate mine locations (fig. 3*B*). For example, inactive mine operations in central Tennessee were assigned a mined-land area of 0.1 km^2, whereas inactive mine operations in southwestern Florida were assigned a mined-land area of 4.3 km^2. The areal extent was represented as a circular area centered over the coordinate of the point location (from MRDS), with radius sized to match the assigned area (for example, radii of 35 or 1,171 meters to correspond with assigned areas of 0.004 or 4.3 km^2).

For mining operations in west-central Florida, boundaries of mined land were estimated by using a combination of geospatial datasets describing location of land parcels and barren land cover (fig. 3*C*). The Mandatory Phosphate Mine Boundaries geospatial dataset from the Florida Department of Environmental Protection (2007) was used to delineate land parcels identified as inactive and active mining operations. The parcels from this layer were combined with the set of parcels of land disturbed by phosphate mining prior to 1975 (Zellar-Williams, Inc., and Conservation Consultants, Inc., 1980), some of which represent mines that are still active. Areas of actual mining activities within each of these parcels were identified and coded by using the areas classified as barren in the NLCD. For parcels identified by the Mandatory Phosphate Mine Boundaries not included in the Zellar-Williams parcels, only the sections that were classified as barren were considered to represent the areal extent of mined land. For parcels identified by the Zellar-Williams report, which explicitly delineate disturbed land, the entire parcel area (not just NLCD barren land) was used to represent the areal extent of mined land.

Figure 3. Representations of the areal extent of mined land within a phosphate-mine operation. *(A)* Based on aerial photography, active mine delineation in North Carolina (red lines indicate areal extent of mined land); *(B)* based on average size of barren land polygons within a geologic map unit, inactive mines in Tennessee (yellow lines represent the geologic map unit boundaries); and *(C)* based on land parcels and barren land cover, active and inactive mines in west-central Florida (red lines indicate areal extent of mined land).

Characterization of Bed-Sediment Phosphorus Concentration Using Geologic Map Units

By overlaying and merging digital maps of geologic age, level IV ecoregions, and boundaries of local formations, a set of 608 GMUs were delineated for the Southeast. GMUs smaller in area than 30 km^2 were combined with an adjacent GMU to remove the artifact of numerous small units created along the edges of the intersecting map layers. The GMUs with fewer than three stream sites were considered to have insufficient data points to define a representative mean value and, therefore, were classified as "data poor." The 278 GMUs in the data-poor classification compose only about 8 percent of the study area. An algorithm was developed to compute new values for the data-poor GMU by averaging the data-poor value with the mean BSPconc value from other GMUs with at least one of the following prioritized criteria: (1) GMUs within the same level III ecoregion and of the same geologic age as the data-poor GMU; (2) GMUs with the same geologic age (regardless of ecoregion) and adjacent to the data-poor GMU; or if these first two conditions fail, (3) using BSPconc values from all adjacent GMUs to calculate a mean BSPconc value for the data-poor GMU. A final test was conducted to determine if the new BSPconc value assigned to the data-poor GMU differed by more than 500 parts per million (ppm) from the original GMU BSPconc values. If this was the case, mean BSPconc values using all three conditions were calculated, and the BSPconc value closest to the original value was used. The areal extent and location of the data-poor GMUs are summarized in table 2 and displayed in figure 4, respectively.

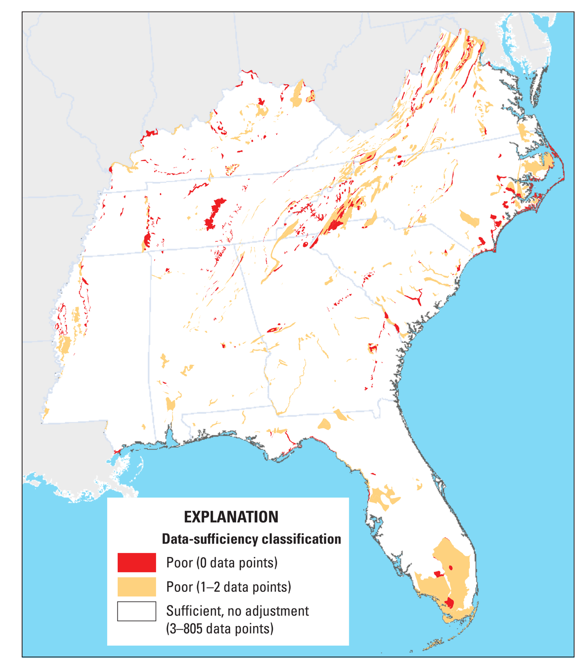
The spatial pattern in BSPconc was evaluated with respect to the GMU boundaries using one-way ANOVA and the Tukey multiple-comparison test. The GMUs explained 56 percent of the total variation in BSPconc, and distributions between some GMUs were sufficiently different (at alpha = 0.1) to enable division into distinct groupings. Figure 5 displays the mean BSPconc from phosphorus values of bed-sediment samples collected in undisturbed, headwater streams within a GMU .

Table 2. Data sufficiency classification and methods for assigning average bed-sediment phosphorus concentrations to geologic mapping units.

[GMU, geologic map unit; BSPconc, bed-sediment phosphorus concentration; definition of data sufficiency classification: sufficient—sufficient number of sampling points (three or more) within the GMU to represent the average condition and no adjustments to mean value, poor—insufficient number of sampling points (less than three) to represent the average condition and adjustment to the original mean value was applied; percentages may not add up to 100 because of rounding]

Data sufficiency classification	Number of GMUs in classification	Area, in square kilometers	Percentage of study area	Method for assigning an average BSPconc value for the GMU
Sufficient	329	993,908	91.7	Average the BSPconc of samples from within the GMU
Poor	244	85,652	7.9	Average the BSPconc of samples from within the GMU with average BSPconc from GMUs in same level III ecoregion that have the same geologic age
Poor	26	3,279	0.3	Average the BSPconc of samples from within the GMU with average BSPconc from adjacent GMUs with the same geologic age (regardless of ecoregion)
Poor	9	667	0.1	Average the BSPconc of samples from within the GMU with average BSPconc from adjacent GMUs (regardless of geologic age and ecoregion)
Total	**608**	**1,083,506**	**100**	

Figure 4. Geologic map units for which mean value of bed-sediment phosphorus concentration was adjusted because of insufficient bed-sediment sampling sites.



Characterization of Contribution of Phosphorus to Streams from Geologic Materials Disturbed by Mining Activities

During phosphate mining activity, phosphate-rich mineral deposits are disturbed and can affect the concentration of P in nearby streams. Estimates of the potential of an upstream watershed to contribute P to streams from runoff from areas of disturbed geologic materials can be developed as a simple function of areal extent of mined land in the watershed, or as a combined function of areal extent of the mined land and the level of phosphate enrichment in the mined deposit. Following the second approach, a series of graded step functions was developed by assigning zero for areas mapped as undisturbed and by assigning a gradient of values in disturbed areas that reflects the varying levels of phosphate enrichment in mined deposits. A value for potential was assigned to each mined area in the Southeast by associating the estimated mined-area polygon with the overlapping GMUs. The method may assign a value to a mine based on bed-sediment sampling sites outside the estimated mined-area polygon (fig. 6*A*, *B*), depending on the location of the maximum BSPconc in the GMU relative to the polygon.

The status of a mining operation was used to weight the value associated to a mine. An active mine is assigned the maximum value within the GMU that its areal extent overlaps, whereas an inactive mine is assigned a value midway between the maximum and mean value of the GMU that its areal extent overlaps. This is illustrated in figure 6*C*, for a GMU for which the maximum BSPconc for bed-sediment sampling sites is 9,176 ppm and the average BSPconc is 708 ppm. The GMU contains mine polygons that fall in both active and inactive mining activity zones; active mines were assigned the value 9,176 ppm (GMU maximum) and inactive mines were assigned the value of 4,942 ppm (average of 9,176 and 708 ppm).

This approach makes two assumptions, both with unknown validity: (1) ore of similar phosphate-mineral content is extracted from mines within the same GMU, and (2) the BSPconc for at least one sample within the GMU reflects the influence of phosphate-mining activity. Estimates of BSPconc therefore, may be less reliable in areas with high density of mined land, as the density of geochemical survey data is insufficient to determine variable loading rates among individual mines or to differentiate contributions from mined-land from contributions from natural, undisturbed land in these areas.

Using Regionalized Bed-Sediment Phosphorus Concentration in Watershed Models to Characterize Contribution of Phosphorus to Streams

Calibration and application of watershed models of instream transport and concentration of P require characterization of the potential of the upstream watershed to contribute P from naturally occurring geologic materials in the watershed to instream (water-column) P flux in the receiving stream. For an empirical watershed model such as SPARROW, characterizing potential contribution in absolute mass units is not necessary; rather, characterizing the relative variability, or gradient, of contribution across the region is sufficient. SPARROW's regression analysis determines the appropriate functional relation between the explanatory variable (for example, BSPconc) and the mass contributed to instream P flux.

The spatial distribution of BSPconc from the NGS dataset, which represents headwater streams draining relatively undisturbed watersheds, is useful for modeling the gradient in potential to contribute P to streambed sediments in headwater streams. The response variable of interest in watershed models, however, generally is contribution to instream flux rather than contribution to streambed sediments, and it is not clear that spatial distribution of BSPconc is useful in modeling instream P flux. Instream P flux and BSPconc in headwater streams are influenced by several of the same factors—variation in availability of P in geologic materials in the watershed and variation in basin rates of erosion and transport of P to the edge of the stream. BSPconc is influenced further by variation in the rates of net deposition and processing of P in the streambed (McDowell and Sharpley, 2001; Walling and others, 2003). The spatial pattern of BSPconc, therefore, is useful as a surrogate for watershed contribution to instream P flux only under the assumptions of (1) equal rates across all headwater streams in the region, (2) net deposition from the water column, and (3) processing within the streambed sediment. Such assumptions are challenged by known variability among headwater streams in frequency of flushing, occurrence of low dissolved-oxygen conditions, and aquatic-plant processing. The spatial pattern of BSPconc is offered as a tool, representing the best available information at the regional scale, with the caveat that the surrogate relation is weakened by not accounting for variability in headwater streams in the rates of net deposition and processing of P in the streambed.

Data Layer Products

This study has resulted in three separate spatial data layers. "Pconc_background" characterizes the potential of a watershed to contribute P to streams from geologic materials that are undisturbed by mining or other human activities (fig. 5). "Pconc_active_mined" and "Pconc_inactive_mined" characterize the potential of a watershed to contribute P to streams from geologic materials that have been disturbed by mining activities (fig. 6). The data layers were each allocated to 8,404 individual watershed segments in the southeastern SPARROW study area for use as variables in the model to predict contribution of phosphorus to a stream from these two separate source categories. Data layers are available upon request from the USGS North Carolina Water Science Center (request form available at *http://nc.water.usgs.gov/about/inforequests.html*).

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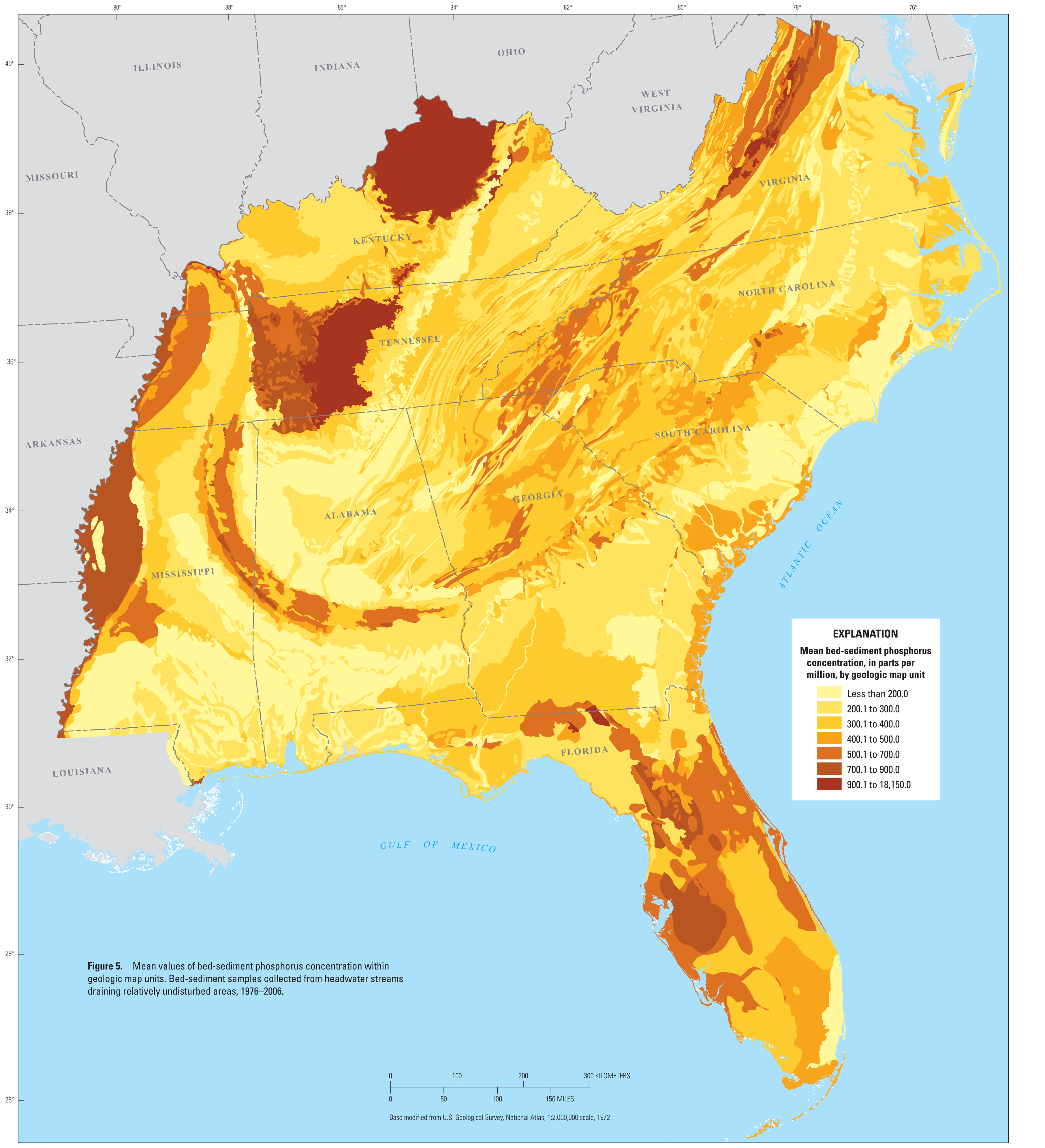
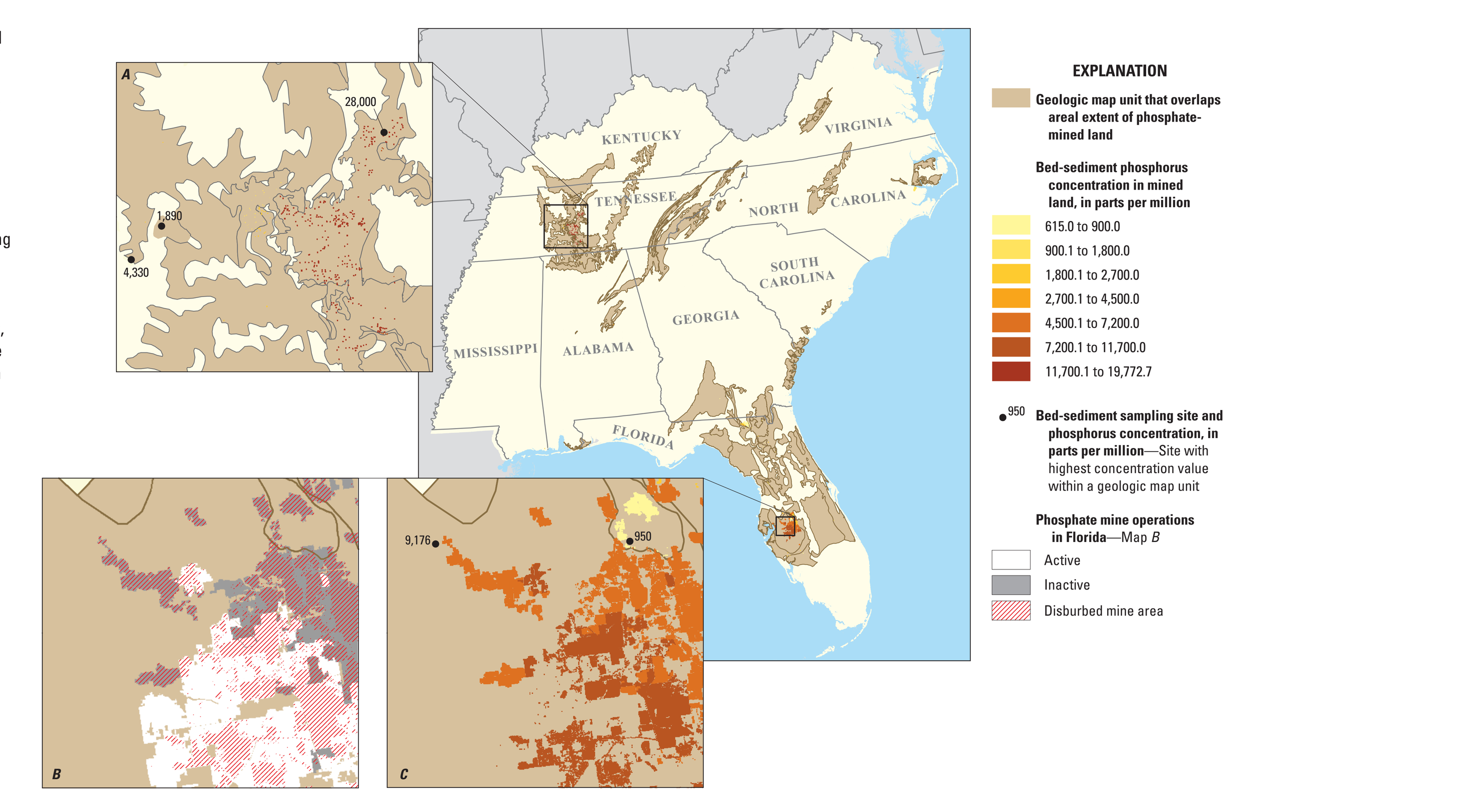


Figure 5. Mean values of bed-sediment phosphorus concentration within geologic map units. Bed-sediment samples collected from headwater streams draining relatively undisturbed areas, 1976–2006.

Figure 6. Areal extent of phosphate-mined land in the southeastern United States and geologic map units that overlap the mined land, with estimates of bed-sediment phosphorus contribution to streams, and *(A)* example in Tennessee showing the locations of phosphate-mined land relative to the locations of three geologic map units that overlap the phosphate-mined land, and the locations of three bed-sediment sampling sites from which the geologic map unit maximum concentration value was derived; *(B)* example in Florida showing parcels that contain inactive and active mine operations, with hachures indicating the disturbed mine areas within the parcels; and *(C)* example in Florida showing how mine operation status is used to weight the value associated to a phosphate-mined land area.



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Mapping Watershed Potential to Contribute Phosphorus from Geologic Materials to Receiving Streams, Southeastern United States

By

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