Evaluating the Source of Pb and Sr in North Carolina Surface Waters

By
Paige Cary

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University of North Carolina at Chapel Hill

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Dr. Drew S. Coleman, Thesis Advisor

Abstract

Lead and strontium concentrations and isotopic compositions of surface water samples collected across the state of North Carolina have been evaluated to determine the predominate contributor of each element to the water. Strontium isotope systematics in NC surface waters are reflective of the underlying bedrock geology and the influence of seawater in the Coastal Plain. The lead isotopic data is decoupled from the strontium data and displays no trends with relation to bedrock geology, though there may be some evidence of natural lead contribution to river waters in the Blue Ridge Belt. Most lead isotope ratios fall within or very close to the range for eastern U.S. leaded gasoline, suggesting that the source of lead in North Carolina surface waters is primarily anthropogenic.

Introduction

A recent study of Sr and Pb isotope ratios along the Neuse River Basin of North Carolina conducted by Watts et al. (2018) revealed the necessity of analyzing the Pb isotope data of NC rivers in order to determine the major contributing source of Pb to NC surface waters. It was found that whereas $^{87}Sr/^{86}Sr$ ratios vary in response to geologic and environmental influences from the headwaters of the Neuse, downstream, $^{206}Pb/^{207}Pb$ ratios remain invariant along the length of the Neuse River. Furthermore, $^{206}Pb/^{207}Pb$ ratios of Neuse River samples fall within the range for eastern U.S. leaded gasoline, suggesting that Pb in the Neuse River Basin is derived from an anthropogenic source.

It is possible to pinpoint the source(s) of dissolved constituents in natural waters by comparing the isotopic signatures of those constituents to those of their suspected sources. $^{87}Sr/^{86}Sr$ values at the head of the Neuse River fall around 0.705, which is consistent with

subsurface diabase dikes through which groundwater flows and feeds the surface water (Watts et al., 2018). $^{87}Sr/^{86}Sr$ ratios rise as the Neuse River flows through the Coastal Plain (Figure 1) and level off at the coast at around 0.709, the modern approximation for the $^{87}Sr/^{86}Sr$ ratio of seawater (Palmer and Edmond, 1989). The consistency of $^{87}Sr/^{86}Sr$ ratios with subsurface geology and their reflection of the influence of seawater along the Neuse River Basin lead Watts et al. (2018) to suggest that the sources of Sr to the Neuse River are primarily geologic and environmental.

These isotopic fingerprinting methods can be applied to naturally occurring dissolved solutes as well as environmental contaminants, as evidenced by studies which relate Pb isotopes in Atlantic Ocean waters to multiple continental sources (Noble et al, 2015; Veron et al, 1994). Lead isotope ratios along the Neuse River are consistent with U.S. leaded gasoline (Watts et al., 2018). We conducted a statewide survey of Pb and Sr isotopes and concentrations of NC river waters in order to determine whether the same patterns in Pb and Sr isotopes documented along the Neuse River are present across NC river basins as a whole.

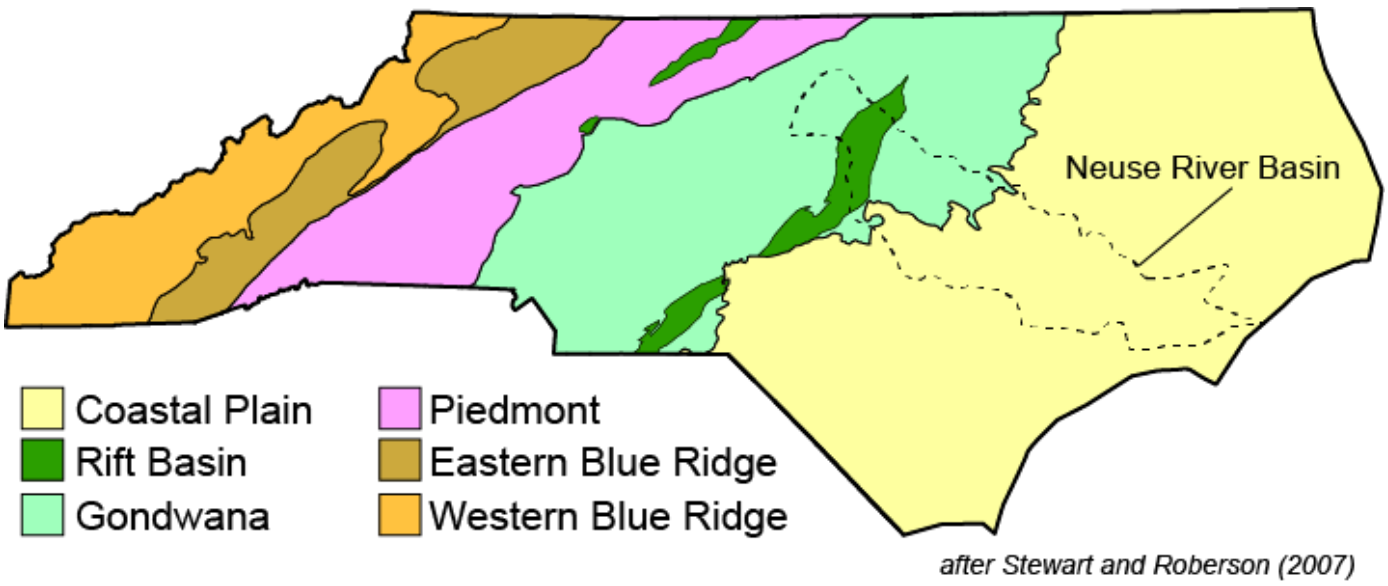

Figure 1. General geologic map of North Carolina with the Neuse River Basin outlined.

Geologic Setting

The rivers of North Carolina flow through a number of diverse rock types. The geology of North Carolina can be simplified into a series of belts and terranes which grade into one another moving west to east (Figure 1). The Blue Ridge Belt is the westernmost and oldest of these geologic units, located within the Appalachian Mountains, and consisting primarily of Precambrian and Early Paleozoic metaigneous and metasedimentary rocks, particularly granitic gneisses, paragneisses, and schists (Hatcher and Goldberg, 1991).

Adjacent to the Blue Ridge Belt is the Piedmont Terrane, which consists of Middle to Late Proterozoic basement rock and Paleozoic metamorphic and plutonic rocks (Horton and McConnell, 1991). East of the Piedmont Terrane are the Gondwanan Terranes, which encompass the Charlotte Belt, the Carolina Slate Belt, and the Raleigh Belt. The Gondwanan Terranes consist primarily of Paleozoic metamorphic and plutonic rocks (Stuckey, 1965). Located within the Gondwanan Terranes is the Triassic Rift Basin, consisting of Triassic sedimentary deposits cut by Jurassic diabase dikes (Ragland, 1991). The Coastal Plain is comprised of unconsolidated gravels, sands, silts, and clays ranging in age from the Cretaceous to the present (Stuckey, 1965).

In general, the geology of North Carolina decreases in age from west to east. Because these geologic units align themselves approximately northeast-southwest moving laterally across the state, much of the data presented in this paper is plotted against longitude in order to detect potential trends in the data related to the underlying geology.

Methods

Surface water samples were taken across the state of North Carolina from streams flowing over a range of diverse geologic settings, from the mountains to the Coastal Plain. In total, 49 water samples have been collected for this project.

All samples were collected in flux cleaned polyethylene bottles. The samples were passed through 0.45 μm filters and acidified with clean HNO_3 upon collection. For Sr isotopic and concentration analysis, 10-15 mL of water was spiked with a tracer enriched in ^{84}Sr, then dried down and dissolved in 3.5N HNO_3. For Pb isotopic and concentration analysis, 30-40 mL of water was spiked with a ^{205}Pb tracer and dissolved in 1.1 HBr. Samples were passed through element-specific ion exchange chromatography columns in order to isolate each element for analysis.

Concentrations of Pb and Sr, and isotopic ratios were determined by isotope dilution thermal ionization mass spectrometry (ID-TIMS). Isotopic ratios of Sr were normalized to $^{86}Sr/^{88}Sr = 0.1194$ assuming exponential fractionation behavior. Replicate analyses of NBS-987 standard yielded $^{87}Sr/^{86}Sr = 0.710266 \pm 0.000016$ (2σ; n = 20) which provides the best estimate of uncertainty in Sr ratios. Lead isotopic ratios were corrected for fractionation assuming 0.14% ± 0.07%/amu on the basis of replicate analyses of NBS-981. Uncertainty in Pb isotopic ratios is dominated by fractionation uncertainty.

Results

$^{87}Sr/^{86}Sr$ values range from 0.704 to 0.721. A plot of $^{87}Sr/^{86}Sr$ versus longitude (Figure 2a) shows how the Sr isotopic composition NC of surface waters changes from west to east across the state. $^{87}Sr/^{86}Sr$ ratios reach a maximum value of approximately 0.721 in the Blue Ridge Belt, decreasing to the east and reaching a minimum of about 0.704 in the Gondwanan

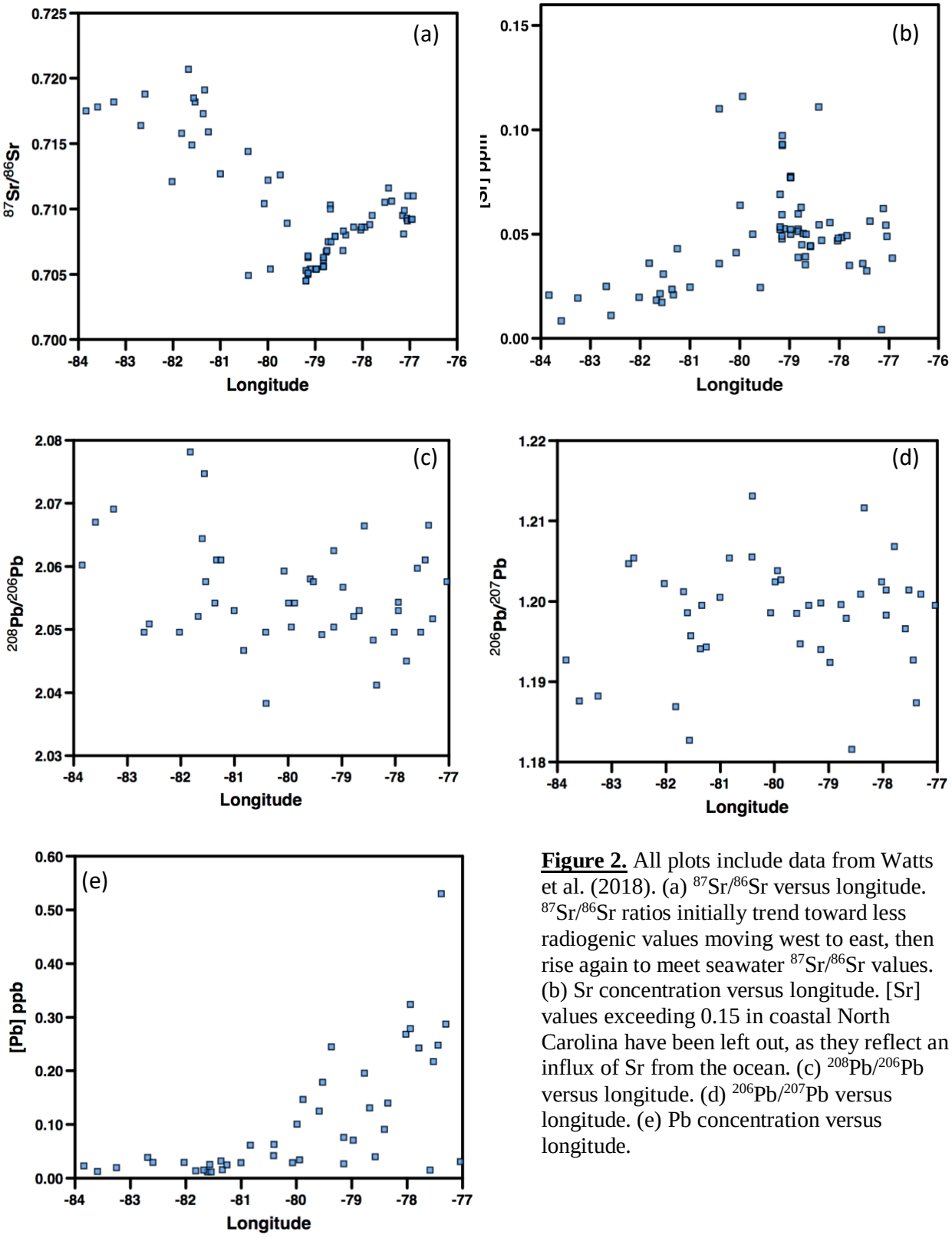

Figure 2. All plots include data from Watts et al. (2018). (a) $^{87}Sr/^{86}Sr$ versus longitude. $^{87}Sr/^{86}Sr$ ratios initially trend toward less radiogenic values moving west to east, then rise again to meet seawater $^{87}Sr/^{86}Sr$ values. (b) Sr concentration versus longitude. [Sr] values exceeding 0.15 in coastal North Carolina have been left out, as they reflect an influx of Sr from the ocean. (c) $^{208}Pb/^{206}Pb$ versus longitude. (d) $^{206}Pb/^{207}Pb$ versus longitude. (e) Pb concentration versus longitude.

Terranes and the Triassic Basin. $^{87}Sr/^{86}Sr$ ratios then rise again through the Coastal Plain and level off between 0.709 and 0.712.

Sr concentration values range from 0.004 to 0.76 ppm. Sr concentrations rise with decreasing $^{87}Sr/^{86}Sr$ ratios. Figure 2b does not include samples with Sr concentrations higher than 0.15, as they are located in estuaries and reflect an influx of ocean Sr. Excluding these samples, the maximum Sr concentration values coincide with the minimum $^{87}Sr/^{86}Sr$ values.

The Pb isotopic data display no trend with respect to longitude (Figures 2c and 2d). $^{208}Pb/^{206}Pb$ values range from 2.038 to 2.078, and $^{206}Pb/^{207}Pb$ values range from 1.182 to 1.213. The concentration of Pb ranges from 0.012 to 0.53 ppb. The concentration of Pb increases significantly, though gradually, from west to east, and there is a considerable spread in concentration values in the eastern part of the state (Figures 2e and 3).

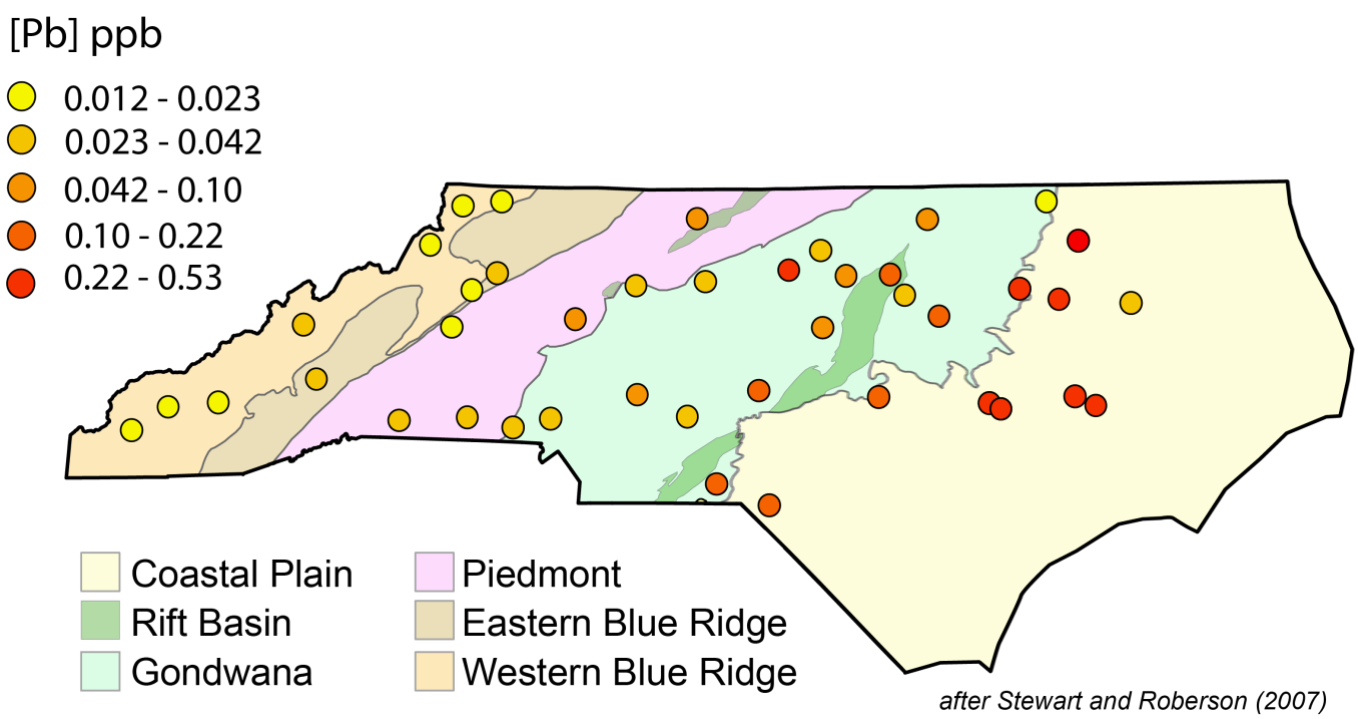

Figure 3. Pb concentration data for the state of North Carolina. Pb concentration increases gradually moving west to east.

Discussion

The Sr isotopic data are reflective of the underlying geology. $^{87}Sr/^{86}Sr$ values are highest (most radiogenic) in the Blue Ridge Belt, which is expected from the oldest rocks in the state. The ratios are also consistent with $^{87}Sr/^{86}Sr$ values of bedrock in the Blue Ridge Belt (Stueber, 1969). $^{87}Sr/^{86}Sr$ ratios trend downward toward the east as the rivers pass through progressively younger geologic units. The isotopic ratios are consistent with bedrock values for the Piedmont and Gondwanan Terranes (Fullagar et al., 1997). The $^{87}Sr/^{86}Sr$ overlap those recorded by Watts et al. (2018) at the headwaters of the Neuse River, and then rise through the Coastal Plain to meet the $^{87}Sr/^{86}Sr$ ratio for seawater, about 0.709. $^{87}Sr/^{86}Sr$ ratios above 0.709 in the Coastal Plain are interpreted as being influenced by agricultural runoff (Watts et al., 2018).

Additionally, $^{87}Sr/^{86}Sr$ values have a tendency to decrease in silicic rocks with increasing Sr concentration (Palmer and Edmond, 1992). This pattern is reflected in our surface water samples (Figures 2a and 2b). Higher Sr concentration values associated with lower $^{87}Sr/^{86}Sr$ ratios in the Gondwanan Terranes may correspond with Jurassic diabase dikes.

The lack of variation of the Pb isotope data with longitude, and therefore geology, is suggestive of an anthropogenic source. This is strongly supported by plotting the Pb isotope data for the surface water samples against Pb isotope data for NC bedrock and U.S. leaded gasoline (Figure 4). The majority of surface water samples fall within or very near the Pb isotope range for U.S. leaded gas. However, there is some indication that natural Pb may be contributing to the Pb isotope ratios of samples in the Blue Ridge Belt, around longitude -82, with noticeably higher $^{208}Pb/^{206}Pb$ ratios than the rest of the samples, which is expected from older rocks in western North Carolina (Figure 2c). Despite the hint of natural Pb which observed in these samples, they are much closer to the range for eastern U.S. leaded gas than values of NC bedrock.

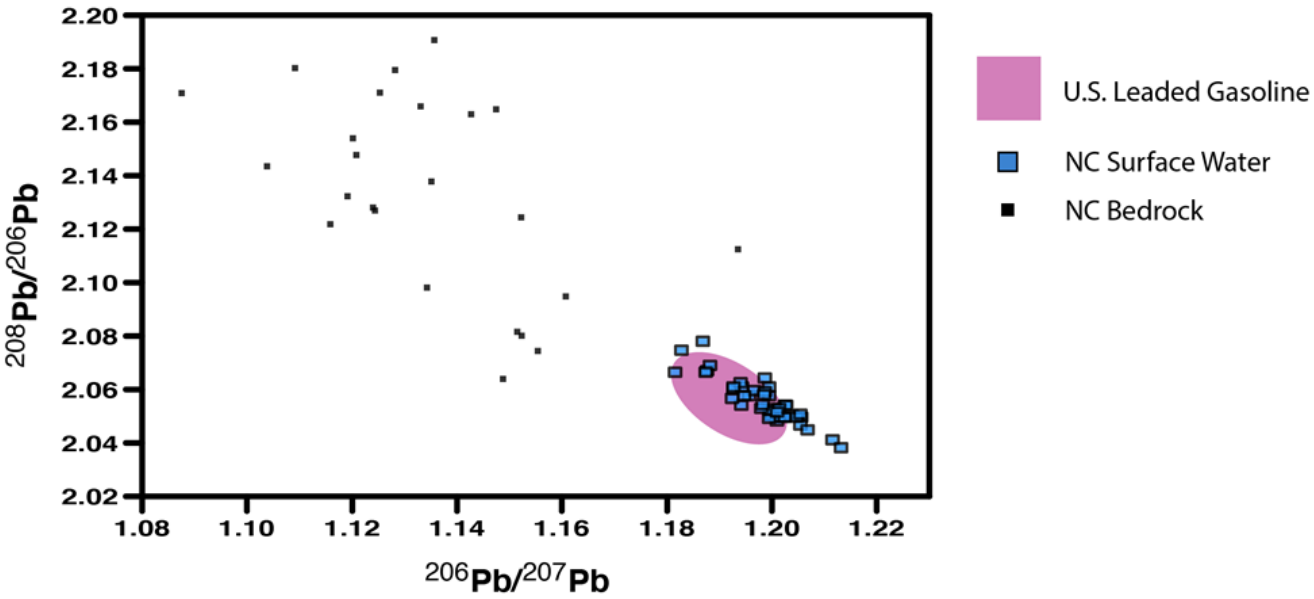

Figure 4. Pb isotope data for NC surface water samples is plotted against whole rock Pb data for NC bedrock from Fisher et al. (2010) and the Pb isotope range for U.S. leaded gas after Komárek et al. (2008).

The United States phased out of its use of leaded gasoline in the 1970's (Nriagu, 1990). Leaded gasoline is no longer in widespread use, though it appears to be the primary contributor of Pb to North Carolina surface waters. It is highly likely that Pb which accumulated in soils while leaded gas was still in use is being leached from the soil by groundwater and incorporated into streams (Teutsch, 2001).

There are several potential explanations for the gradual increase from low to high Pb concentration across the state (Figure 3). The first is that Pb is accumulating in surface waters across North Carolina from west to east. However, this is highly doubtful, since drainage basins in the eastern part of the state are not connected to those in the western part of the state, and there is no way of transferring material between them. The second is that the higher concentrations which we observe in Eastern North Carolina are attributed to higher population density in that part of the state. Though this may be a significant contributing factor, especially considering that the influx of Pb in NC waters is primarily anthropogenic, it cannot account for the gradient

observed between low concentration values in the west and high concentration values in the east.

A more plausible explanation for the low to high concentration gradient across the state is the decrease in elevation and topography over the transition from the mountains to the Coastal Plain. As river gradients decrease across the state, the flowing water has more time to interact with the soil, from which the anthropogenic Pb is likely being leached by river waters. As rivers in the Coastal Plain begin to stagnate, they accumulate more Pb over time, as opposed to quick-flowing streams in the mountains. There is also a much higher percentage of suspended sediment and particulate matter in slow-moving streams in the east, which interacts with the surrounding river waters and potentially contributes to the higher Pb concentrations observed in the east.

Conclusions

$^{87}Sr/^{86}Sr$ values of surface waters across North Carolina are strongly reflective of the underlying geology. Isotope ratios of Pb, however, display no trends with respect to geology, and fall within or very close to the range for eastern U.S. leaded gasoline. This suggests that whereas Sr in North Carolina rivers can be attributed to geologic and environmental factors, Pb is primarily derived from an anthropogenic source.

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