Although once treated as simple downstream transporters of material, river networks are now recognized for their role in transformation, storage, and removal of carbon and nutrients during transport. Linkages between channel geomorphic structure and the biogeochemistry and ecology of lotic ecosystems are known to be important. Specifically, the physical structure of streams can influence rates of primary production and ecosystem respiration, as well as the balance between the two, and has both direct and indirect effects on the retention of inorganic nutrients. The overarching goal of this research was to develop a better understanding of the relationships among geomorphology, metabolism, and nutrient dynamics in large rivers by taking advantage of natural changes in river form associated with broad-scale geologic transitions in the Cahaba River, AL. Geomorphic structure resulting from these broad transitions, in turn, constrain longitudinal distribution of different aquatic primary producers. Evaluation of spatial and temporal patterns of gross primary production and ecosystem respiration conducted at several stations along the Cahaba River found there was an important effect of regional geology on metabolism. Along the Fall Line of the Cahaba River, extensive shoal habitat supports expansive crops of submerged and emergent macrophytes and attached and suspended algae. We assessed changes in primary producer composition and productivity over a growing season, relating these patterns to riverine nitrate retention and found the identity and characteristics of primary producers have potentially significant consequences for nutrient dynamics. In the Coastal Plain effects of regional geology on metabolism was expressed through strong seasonal changes in plankton productivity, which drives high rates of gross primary production and ecosystem respiration as evidenced by a multi-fold increase in metabolism during periods of high plankton biomass. Our evaluation of the fate and biogeochemical implications of phytoplankton production in the Coastal Plain, confirmed it played an important role in fueling water column processing and provided evidence of delivery of phytoplankton to the sediments, increasing local retention of labile organic carbon, and decreasing downstream export. Overall, this research contributes to our understanding of river ecosystem metabolism and nutrient retention by highlighting the complexity and variability of interactions among the proximate and distal factors influencing rates of biogeochemical cycling.