Persistent organic pollutants (POPs) are organic substances that have characteristics of persistence in the environment; transboundary movement, or the ability to travel long distances through air and water; toxicity; and bioaccumulation in living things. Perfluorooctane sulfonate (PFOS), a toxic chemical that never breaks down, was added to the Stockholm Convention on POPs and was listed in the Annex B restrictions with many exemptions to continue using PFOS. This study focused on the occurrence of PFOS in the water system of Bangkok, Thailand, including the Chao Phraya and Bang Pakong Rivers, tap water in industrial zones and residential areas, drinking water, and industrial wastewater. Seasonal effect of PFOS between dry season and wet season was also observed for more than 3 years. Solid phase extraction (SPE) coupled with HPLC-ESI-MS/MS was used for the analysis of these compounds. PFOS was detected in most water samples. The average concentration of PFOS in the Chao Phraya River (urban area) was 1.70 ng/L, whereas lower concentrations were detected in the Bang Pakong River (suburban area), residential tap water, and bottled drinking water, with averages of 0.7, 0.4, and 0.5 ng/L, respectively. Higher concentrations (an average of 25.1 ng/L) were found in industrial tap water, whose sources were from surface water near the industrial zones. Much higher concentrations were detected in industrial wastewater, with the maximum of 6,100.8 ng/L. These results indicated that industrial wastewater was one of the major sources of PFOS contamination in the water system of the city of Bangkok. This study provided data on the spatial occurrence, its seasonal effect, and distribution of PFOS in the water environment of Bangkok and surrounding areas, which need continuous attention to this emerging contaminant. © 2013 American Society of Civil Engineers.