Dissolved organic matter (DOM) affects arsenite [As(III)] toxicity by altering its sorption equilibrium at the cell wall interface. A better understanding of such mechanism is of great importance to assess As(III) ecotoxicity in aquatic systems. Batch experiments were conducted to study the effects of DOM on the regulation of As(III) sorption and toxicity in the diatom Navicula sp. The influence of humic acid (HA) on As(III) toxicity was assessed by measuring algal growth, chlorophyll a, and reactive oxygen species (ROS), whereas As(III) mobility across the cell wall was estimated by determining the concentration of intracellular, cell-wall-bound, and free As(III) ions in cell media. Results showed that the effects of HA on arsenite toxicity varied depending on various combinations of As(III)-HA concentrations. EC50 had an approximate threefold increase from 8.32 (HA-free control) to 22.39 μM (at 20 mg L(-1) HA) when Navicula sp. was exposed to 1.0-100.0 μM of As(III), compared to an overall low complexation ratio of HA-As(III) in a range of 0.91-6.00 %. The cell wall-bound and intracellular arsenic content decreased by 19.8 and 20.3 %, respectively, despite the lower arsenite complexation (2.10 ± 0.16 % of the total As). Meanwhile, intracellular ROS was decreased by 12.6 % in response to 10.0 μM As(III) and 10 mg L(-1) HA vs. the HA-free control. The significant contrast indicated that complexation alone could not explain the HA-induced reduction in arsenite toxicity and other factors including HA-cell surface interactions may come into play. Isotherms describing adsorption of HA to the Navicula sp. cells combined with morphological data by scanning electron microscopy revealed a protective HA floccule coating on the cell walls. Additional Fourier transform infrared spectroscopic data suggested the involvement of carboxylic groups during the adsorption of both HA and As(III) on the Navicula sp. cell surface. Collective data from this study suggest that cell wall-bound HA can moderate As(III) toxicity through the formation of a protective floccule coating occupying As(III) sorption sites and decreased effective functional groups capable of binding As(III). Our findings imply that As(III) toxicity can be alleviated due to the increased hindrance to cellular internalization of As(III) in the presence of naturally abundant DOM in water.