Landfilling is currently the prevailing way of municipal solid waste (MSW) disposal in most countries. Numerous processes interacting in landfills, are responsible for the production of landfill leachate. Apart from many other pollutants the leachate contains metalloids, especially arsenic and antimony. These elements, depending on the properties of landfills, can exist in different chemical species. The knowledge of their speciation is very important, because it can strongly effect the toxicity, mobility and other properties of these elements. High-performance liquid chromatography (HPLC) and mass spectrometry with inductively coupled plasma (ICPMS) has been applied to determination of the speciation of metalloids in landfill leachates. The total concentration of metalloids and distribution of their species are highly variable. It has been observed that a certain fraction of metalloids in landfill leachates can be bound to colloids, which thus affect the mobility and reactivity of these elements in landfill environments. Knowledge of the metalloids speciation enables to assess their impact on the environment and to suggest appropriate technology for possible decontamination of landfill leachates.