The range of As concentrations found in natural waters is large, ranging from less than 0.5  $\mu$ g l-1 to more than 5000  $\mu$ g l-1. Typical concentrations in freshwater are less than 10  $\mu$ g l-1 and frequently less than 1  $\mu$ g l-1. Rarely, much higher concentrations are found, particularly in groundwater. In such areas, more than 10% of wells may be 'affected' (defined as those exceeding 50  $\mu$ g l-1) and in the worst cases, this figure may exceed 90%. Well-known high-As groundwater areas have been found in Argentina, Chile, Mexico, China and Hungary, and more recently in West Bengal (India), Bangladesh and Vietnam. The scale of the problem in terms of population exposed to high As concentrations is greatest in the Bengal Basin with more than 40 million people drinking water containing 'excessive' As. These large-scale 'natural' As groundwater problem areas tend to be found in two types of environment: firstly, inland or closed basins in arid or semi-arid areas, and secondly, strongly reducing aquifers often derived from alluvium. Both environments tend to contain geologically young sediments and to be in flat, lowlying areas where groundwater flow is sluggish. Historically, these are poorly flushed aguifers and any As released from the sediments following burial has been able to accumulate in the groundwater. Arsenicrich groundwaters are also found in geothermal areas and, on a more localised scale, in areas of mining activity and where oxidation of sulphide minerals has occurred. The As content of the aquifer materials in major problem aguifers does not appear to be exceptionally high, being normally in the range 1-20mg kg-1. There appear to be two distinct 'triggers' that can lead to the release of As on a large scale. The first is the development of high pH (>8.5) conditions in semi-arid or arid environments usually as a result of the combined effects of mineral weathering and high evaporation rates. This pH change leads either to the desorption of adsorbed As (especially As(V) species) and a range of other anion-forming elements (V, B, F, Mo, Se and U) from mineral oxides, especially Fe oxides, or it prevents them from being adsorbed. The second trigger is the development of strongly reducing conditions at near-neutral pH values, leading to the desorption of As from mineral oxides and to the reductive dissolution of Fe and Mn oxides, also leading to As release. Iron (II) and As(III) are relatively abundant in these groundwaters and SO4 concentrations are small (typically 1 mg l-1 or less). Large concentrations of phosphate, bicarbonate, silicate and possibly organic matter can enhance the desorption of As because of competition for adsorption sites. A characteristic feature of high groundwater As areas is the large degree of spatial variability in As concentrations in the groundwaters. This means that it may be difficult, or impossible, to predict reliably the likely concentration of As in a particular well from the results of neighbouring wells and means that there is little alternative but to analyse each well. Arsenic-affected aquifers are restricted to certain environments and appear to be the exception rather than the rule. In most aquifers, the majority of wells are likely to be unaffected, even when, for example, they contain high concentrations of dissolved Fe.