Knowledge of the natural baseline quality of groundwaters is an essential prerequisite for understanding pollution and for imposing regulatory limits. The natural baseline of groundwaters may show a range of concentrations depending on aquifer mineralogy, facies changes, flow paths and residence time. The geochemical controls on natural concentrations are discussed and an approach to defining baseline concentrations using geochemical and statistical tools is proposed. The approach is illustrated using a flowline from the Chalk aquifer in Berkshire, UK where aerobic and anaerobic sections of the aquifer are separately considered. The baseline concentrations for some elements are close to atmospheric values whereas others evolve through time-dependent water–rock interaction. Certain solutes (K, NH4+), often considered contaminants, reach naturally high concentrations due to geochemical controls; transition metal concentrations are generally low, although their concentrations may be modified by redox controls. It is recommended that the baseline approach be incorporated into future management strategies, notably monitoring.