

# Chapter 4: A California nitrogen mass balance for 2005

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## Box 4.X. Denitrification in Groundwater

Denitrification is the process that converts nitrate ( $\text{NO}_3$ ) to inert nitrogen ( $\text{N}_2$ ) gas through a series of chemical reactions. It is typically a biological process in which micro-organisms, such as bacteria, respire  $\text{NO}_3$  instead of oxygen to meet their metabolic needs. Denitrification can occur when three conditions are met: nitrate is present, oxygen concentrations are low, and a source of electrons (e.g., energy) is available. Denitrifying organisms are ubiquitous in soils and sediments, as well as surface water and groundwater environments; these organisms can also be harnessed to remove nitrate from high nitrogen (N) waters such as in wastewater treatment plants and agricultural runoff. Denitrification is a key transformation in the N cycle as it is the dominant process that converts reactive N back to atmospheric  $\text{N}_2$ . As such, it reduces risks of excess N on human health and the environment (Moran et al. 2011).

In most environments, there are methods, albeit expensive and requiring specialized equipment, for measuring denitrification rates *in situ*. Part of the difficulty is that the product of denitrification,  $\text{N}_2$  comprises almost 80% of the atmosphere. Therefore, it is impossible to detect the small flux of  $\text{N}_2$  from surficial environments where atmospheric air is present. Because of these methodological issues, denitrification is often quantified by difference in mass balance studies because of the difficulties in measuring it directly. In groundwater, denitrification is typically detected by chemical signatures and dissolved excess  $\text{N}_2$  gas left behind by the process. Analysis of the isotopes of nitrogen and oxygen in groundwater  $\text{NO}_3$  can indicate whether denitrification is occurring but may also reflect a signature of the

23 original source (e.g., manure vs. fertilizer) of the  $\text{NO}_3^-$ . Quantifying groundwater denitrification rates  
24 typically involves measuring excess  $\text{N}_2$ . Because groundwater is isolated from the atmosphere, the  $\text{N}_2$   
25 produced by denitrification remains dissolved. This “excess  $\text{N}_2$ ” can be measured and the amount of  
26  $\text{NO}_3^-$  originally dissolved in the water can be determined.

27 Denitrification occurs in groundwater when nitrate-rich water recharged from the surface reaches  
28 portions of the aquifer with low  $\text{O}_2$ . In addition, either organic carbon leached from the surface or  
29 reduced minerals like sulfides need to be present in the sediments or rocks of the aquifer as a source of  
30 energy. In some aquifers, conditions are such that denitrification can convert a significant amount of  
31 the nitrate to  $\text{N}_2$  while in others high  $\text{O}_2$  or a limited supply of energy precludes the complete conversion  
32 of  $\text{NO}_3^-$ . Data on denitrification in groundwater are particularly difficult to obtain and much more  
33 research is needed on the subject (see for example Böhlke and Denver 1995; Fogg et al. 1998; and  
34 Browne and Guldán 2005). It is tentatively agreed by most, that denitrification rates are relatively low in  
35 most groundwater basins in California. The few studies that have been conducted have found that the  
36 aquifers in California do not typically have the combination of conditions that would be conducive for  
37 the removal of all  $\text{NO}_3^-$  by denitrification (Moran et al. 2011; Landon et al. 2011; Green et al. 2008, 2010).  
38 King et al. (2012) suggest that it is practical and sensible to conclude that most  $\text{NO}_3^-$  in California aquifers  
39 used for irrigation and municipal supplies is unlikely to be denitrified. The most prominent exception,  
40 perhaps, are denitrifying conditions found in the vicinity of the major streams and near valley troughs  
41 that have accumulated lake and marshy sediments with significant organic matter (Landon et al. 2011;  
42 Moran et al. 2011). Additional studies using excess nitrogen/argon ( $\text{N}_2/\text{Ar}$ ) ratios, natural N isotopes,  
43 and mass balance calculations could further our understanding of the spatial and temporal variability in  
44 denitrification in California’s groundwater.

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