CNP Ratio

One of the more important concepts in biologically based site remediation is the mole ratio of carbon/nitrogen/phosphorous elements in bacteria and using this ratio in the design of nutrient dosage for bio-stimulation/bio-augmentation type treatments.

The earliest reference I can find on CNP is the work done in 1934 by Alfred Redfield. Redfield took samples of phytoplankton from the across the Atlantic, Pacific and Indian Oceans. He developed a CNP ratio (also termed the Redfield ratio) of 106:16:1 for phytoplankton that was directly correlated to the nutrient balance in the three oceans.

One of the later ratios in publication includes one that describes the top five elements in bacteria the C:H:O:N:P ratio and reminds us of the importance of oxygen in cell formation. That ratio is $C_{64}H_{85}O_{23}N_{13}P$. Most commonly used in practice is the CNP ratio of 100:10:2. Those of us in the industry need to be careful on how we apply this ratio. For some sites with very limited contaminant mass or for sites where a co-metabolite is necessary to establish relevant bacteria mass the carbon will be total carbon of the contaminant or added co-metabolite. But for sites with significant contaminant mass that will be directly assimilated by the bacteria, use of the total contaminant mass to determine the mass of nutrient to be added will lead to gross over dosing of nutrients into the aquifer with potential detrimental impacts to surrounding drinking water and/or surface water.

For those sites with contamination adsorbed to soil the hydrocarbon mass can be in the range of several tons. The design criteria for nutrient dosage then must become the maximum bacterium mass that can be sustained via the treatment scenario being applied. Some of the higher concentrations attributed to bio-stimulation or bio-augmentation are on the order of 10^5 and maximum of around 10^7 cells per milliliter. Based on a bacteria density of 1.1 g/cm^3 we can estimate a range of 4 mg/L up to a maximum of 400 mg/L as our MLSS (mixed liquor suspended solids), with 50% of that mass being attributed to carbon. Use of 200 mg/L as a maximum carbon concentration to limit nutrient dosage to impacted areas would help to limit the potential for nitrate formation in surrounding drinking water and reducing algae blooms in surface waters connected through fractures or porous soil structures.

Some very recent studies show that restrictions on phosphate dosage can serve to increase the metabolic/respiration rates of aerobic bacteria. Since adenosine triphosphate (ATP) is the only available method of internal energy storage, maintaining a lean phosphate concentration could be forcing bacteria to expend the energy generated from respiration rather than storing it. Also, certain forms of nitrogen can have a chronic toxicity impact on cell division (can slow or even stop it). In short, too much nutrient can be rate limiting.

Nutrient addition to groundwater should be approached from the perspective of providing only the nutrients required to form the maximum potential population while including potential site sources of nitrogen and phosphate in the design. Most of our hydrocarbon sites have been in shallow aquifers which are frequently impacted by leaking sanitary sewers, septic leach-fields and overly fertilized lawns or farmland. In most cases, these impacts are seasonal or may only impact specific areas of a plume so nutrient dosage must be regulated independently to each sparge well.

Once the bacteria population is established additional nutrients are rarely necessary. Nitrogen and phosphorus are used in development of many of the enzymes used in the contaminant oxidation/reduction reactions but are not consumed. Depending upon the dissolved oxygen concentration being maintained in the treatment zone, nitrogen can be lost through off-gassing during denitrification. In aerobic treatment, the primary element in demand is oxygen. Stoichiometric indicate 2.3 moles of oxygen is required to oxidize a mole of carbon. In practice the assumption is a minimum of 5 pounds of oxygen per pound carbon. In design, we are using 10 pounds of oxygen per pound carbon to determine the amount of time required for treatment. In most cases, this has shown to be a conservative estimate and leads to closure of even some of the heaviest contaminated sites in two to three years of treatment.

In summary, except for the application of oxygen necessary for aerobic respiration, nutrient dosage should follow the adage that "less is more" both from the standpoint of protecting area receptors and to optimize growth and overall metabolic rates. A lean bacterium is a healthy bacterium.

Figure 1 - Pseudomona aeruginosa