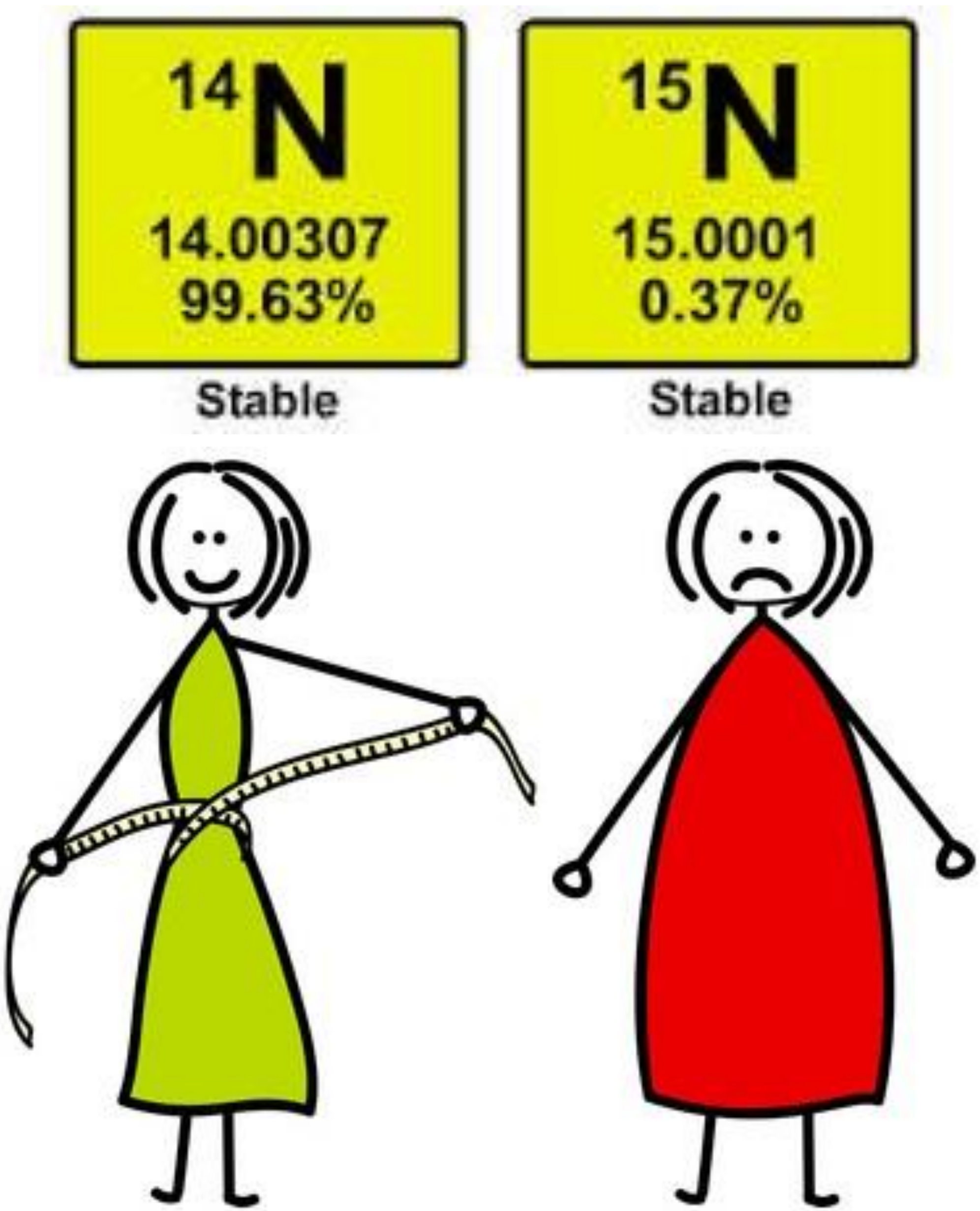
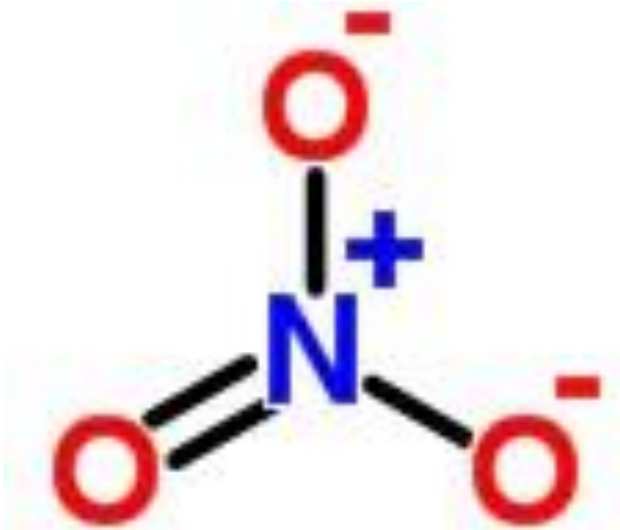
Just like there are fat people and skinny people, there are fat and skinny atoms. Fat atoms act exactly like skinny atoms but contain an extra neutron or two in their nucleus. This makes 'em less energetic. Nitrogen comes in two flavors: ^{14}N (called N-fourteen), the skinny or lighter isotope, and ^{15}N, the fatter or heavier version. During biological transformations (assimilation, nitrification, denitrification) the lighter isotope is preferentially used – it's easier for an organism to use the more energetic version.

In other words, the lighter isotope (^{14}N) becomes more concentrated in the transformed product, while greater amounts of the heavier isotope (^{15}N) are left behind. For example, when nitrate is denitrified into nitrogen gas by bacteria the gas ends up having less of the heavier ^{15}N isotope while the remaining nitrate becomes isotopically heavier (more ^{15}N). The whole process of discriminating between isotopes is called "fractionation."



The fractions in fractionation are very small. Unlike our own population, there are relative few fat nitrogen atoms: 99.6% of all nitrogen atoms are of the lighter (or skinner) ^{14}N flavor; only 0.4% are fat. Isotopic analysis, measuring the relative proportion of heavy to light atoms in a sample, yields very small numbers and to make things easier results are expressed in comparison with known standards: air in the case of nitrogen (and a specific kind of water known as SMOW for oxygen).

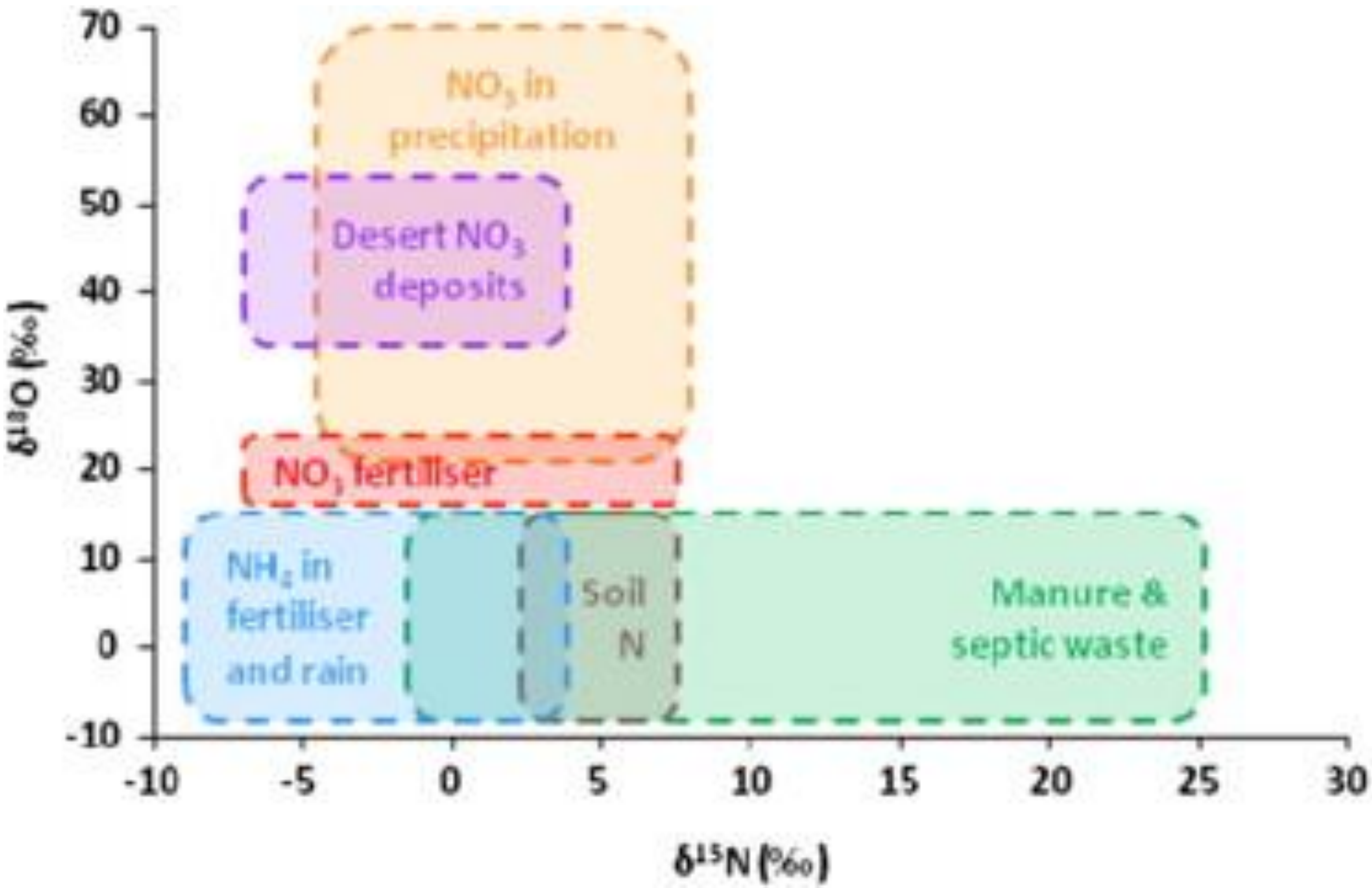
The isotopic proportion term for nitrogen is $\delta^{15}N$ (say delta N-fifteen) and the unit is ‰ (per mil). A positive $\delta^{15}N$ simply means that a sample contains relatively more fat nitrogen than air; a negative $\delta^{15}N$, less fat nitrogen than air. The more fat nitrogen, the greater the $\delta^{15}N$ value.



Nitrate is not an atom, it's a molecule: a molecule consisting of one nitrogen atom and three oxygen atoms. Just as the nitrogen in a nitrate molecule can be either fat or skinny, any of the oxygen atoms can also be fat or skinny. The skinny or light oxygen atom is called ^{16}O (oxygen-sixteen), the fat or heavy version ^{18}O (oxygen-18). As with nitrogen, the vast majority of oxygen atoms are skinny (99.8% are skinny, 0.2% are fat).

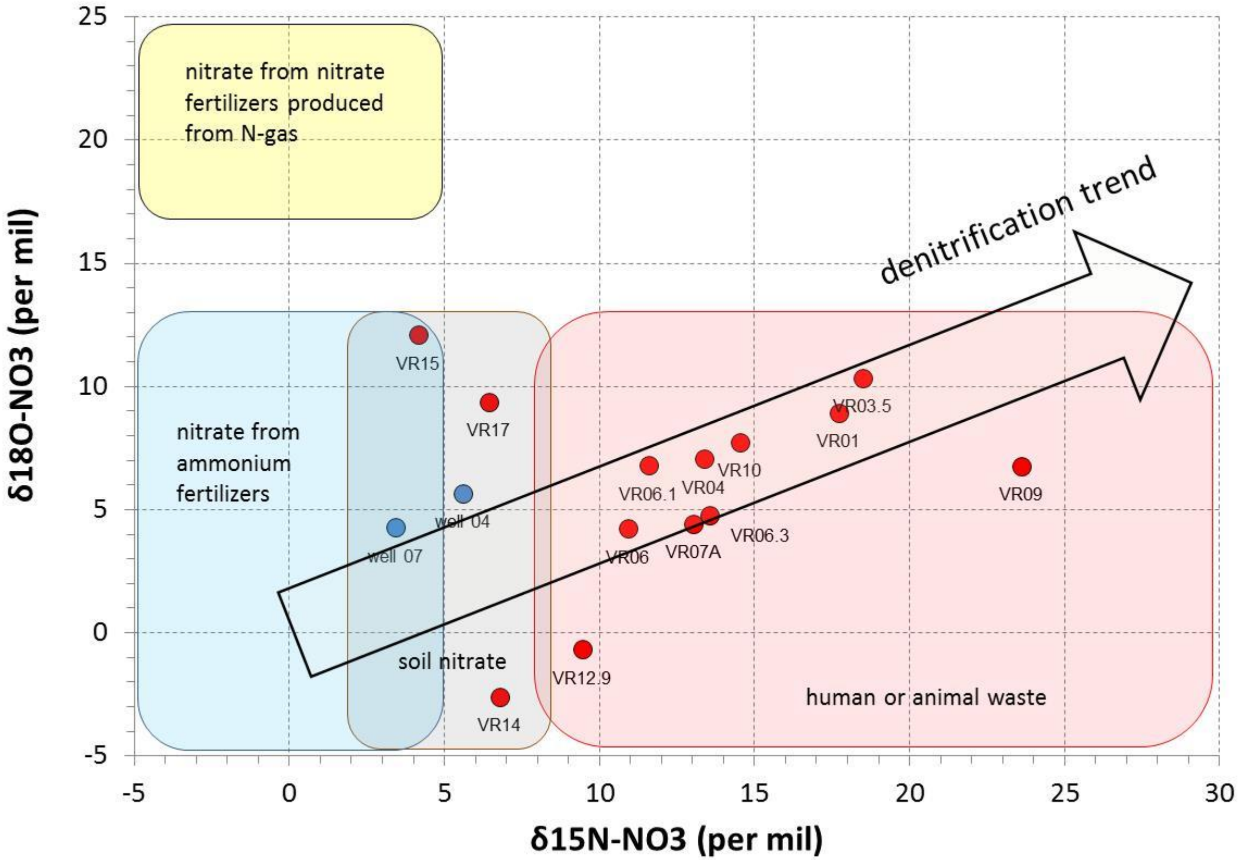
And as with nitrogen, biological processes fractionate between different oxygen isotopes. But so can physical processes. For example, evaporation, which requires energy to transform a water molecule from liquid to vapor leaves more of the heavier ^{18}O behind, while rainfall, which represents the loss of energy as vapor becomes liquid, has a higher percentage of the less energetic fat guys. As there are fat nitrogen or oxygen atoms, there are also fat nitrate molecules (usually containing either a fat nitrogen or a fat oxygen, very, very rarely more than one fat atom – if there is only a 0.2% chance of running into a fat oxygen in a nitrate molecule, the chance of running into two fat oxygen in the same molecule is 0.0004%, a chance of only four in a million).

The isotopic oxygen concentration is expressed as $\delta^{18}O$ (delta O-eighteen); a positive $\delta^{18}O$ means the sample contains more fat oxygen than SMOW, a negative result means less.



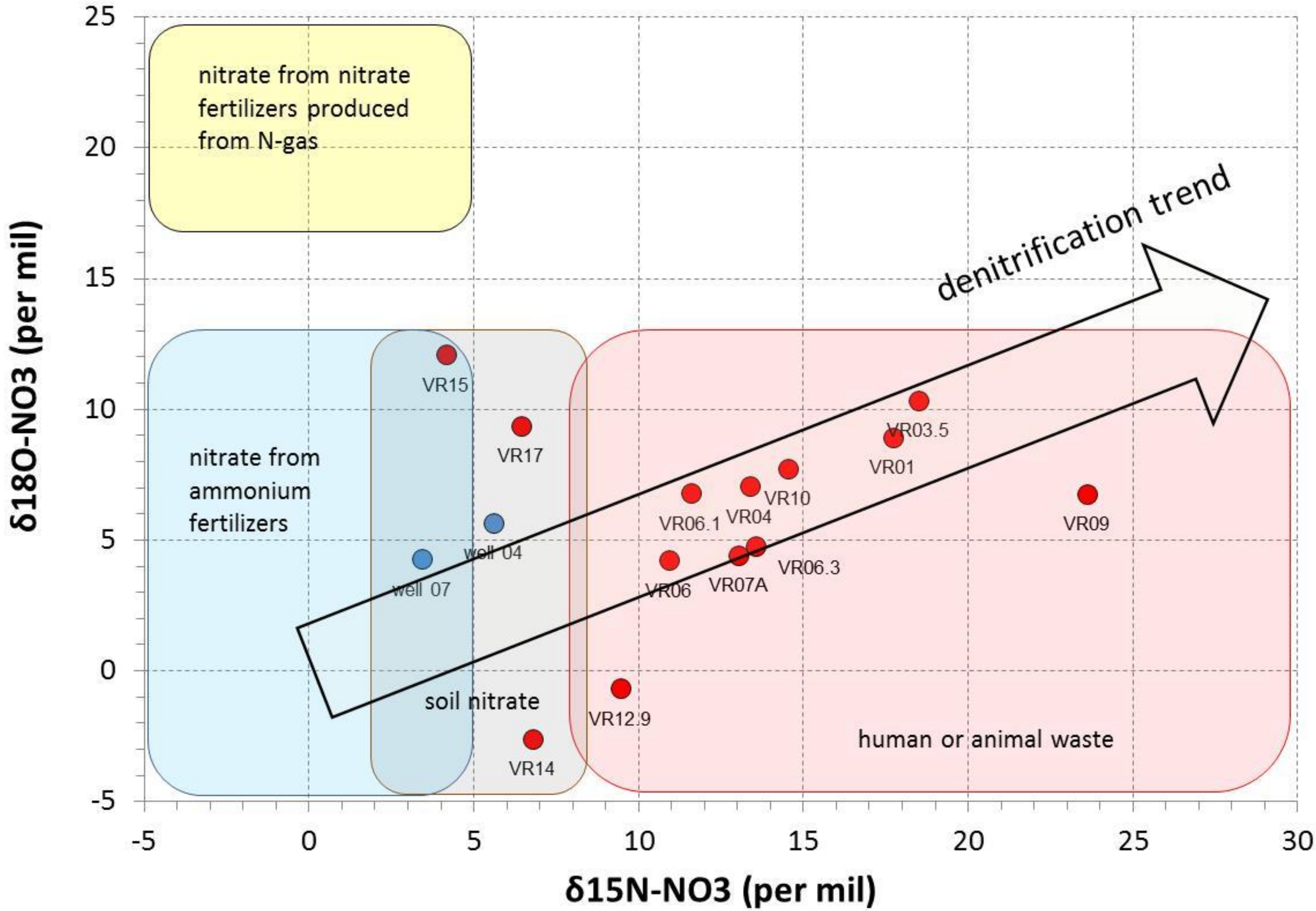
Nitrate molecules in a water sample can be analyzed for the relative proportions of fat to skinny nitrogen, and fat to skinny oxygen. Two isotopic signatures are better than one if our objective is to determine the nitrate source; the chart shows the approximate ranges of $\delta^{15}N$ and $\delta^{18}O$ for different sources.

The heaviest $\delta^{15}N$ values are found in manure and septic tank wastes (fat N concentrates in waste products, and manure, human and animal, is at the end of a long line of processes as atoms work their way up the food chain); the heaviest $\delta^{18}O$ is found in "wet deposition," the nitrate that accompanies rain.



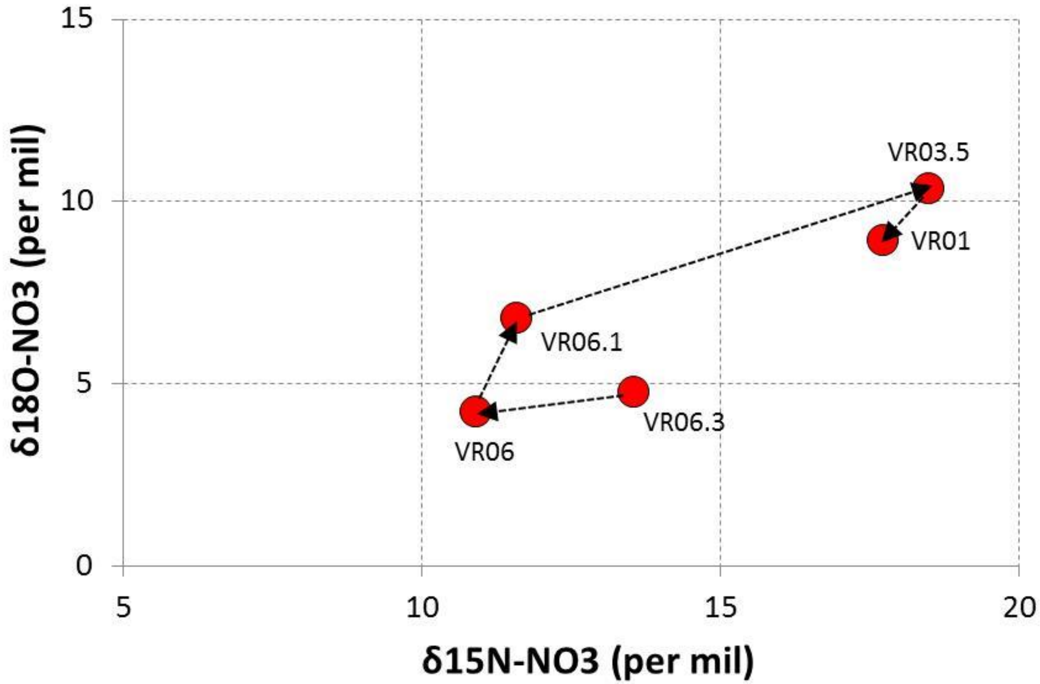
But while knowing two things is better than knowing just one, it still might not be enough to adequately determine the source. The major problem with the SBCK results (shown here) is that the isotopic signature of nitrate can change along the path from source to stream – especially if travel along that path takes considerable time.

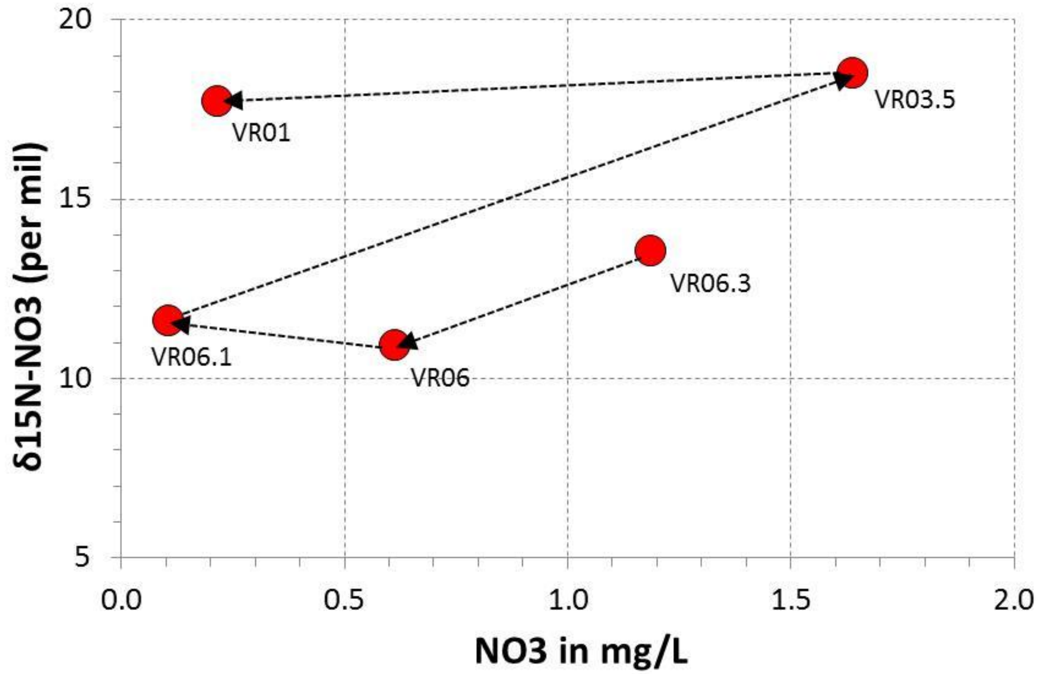
The particular problem with this data is that denitrification (de-ni-tra-fi-ca-tion) of fertilizer nitrogen in a low-oxygen, water-table environment increases both the $\delta^{15}N$ and $\delta^{18}O$ signatures of nitrate along the path indicated by the broad arrow – making it look a lot like manure or septic waste. And we know from the sampling results on upper San Antonio Creek that denitrification within the water-table is taking place. Other processes, such as nitrification of ammonium or biological uptake, or something as simple as mixing nitrate from two or more sources, can modify the isotopic signature and complicate analysis.


nitrate from nitrate fertilizers produced from N-gas
denitrification trend
nitrate from ammonium fertilizers
soil nitrate
human or animal waste
VR15
VR17
well 04
well 07
VR14
VR12.9
VR06
VR07A
VR06.3
VR06.1
VR04
VR10
VR01
VR03.5
VR09
δ18O-NO3 (per mil)
δ15N-NO3 (per mil)
25
20
15
10
5
0
-5
-5
0
5
10
15
20
25
30

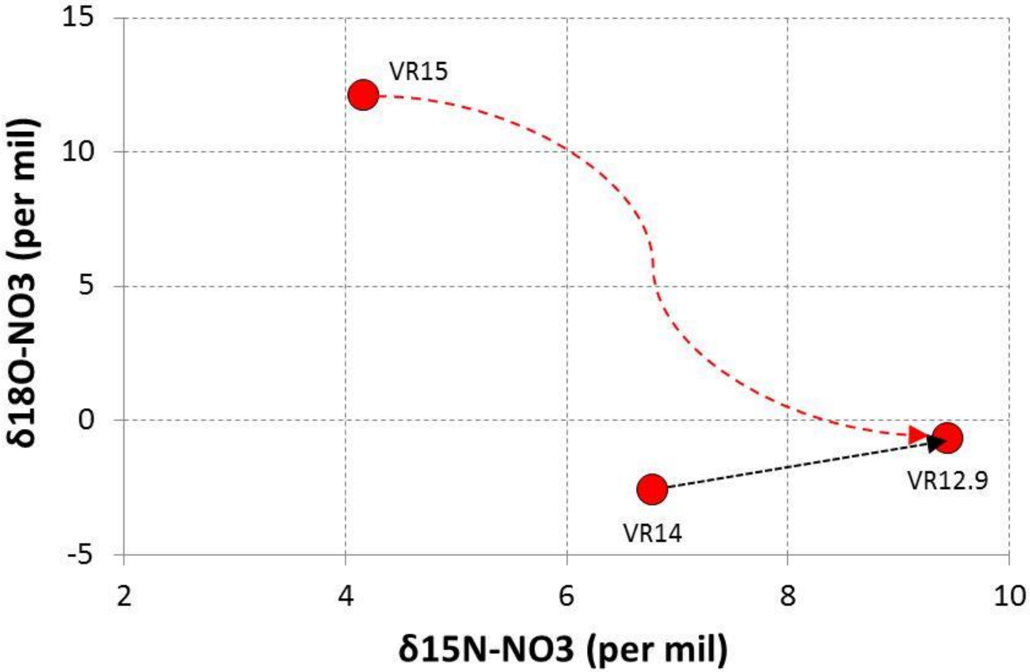
In the slides that follow, I focus in on results for different sections of the watershed. For each section there are two graphs: an upper graph that plots $\delta^{18}O$ vs. $\delta^{15}N$ (as in the graphs shown previously), and a lower graph where $\delta^{15}N$ is plotted against each sample's nitrate concentration (in mg/L).

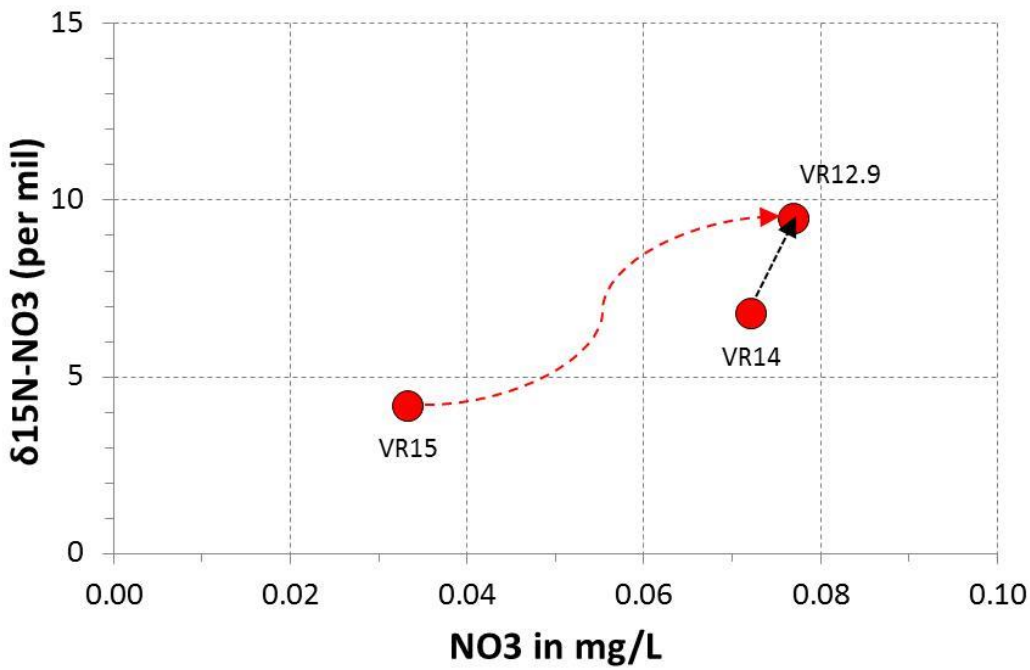
The paths taken by streamflow, from upstream to downstream and from sample to sample, are shown by the dashed arrows. Explanations of what the data are probably showing are located off to the side. As you will see, we picked a bad year and month to sample and there are very few clear-cut answers.



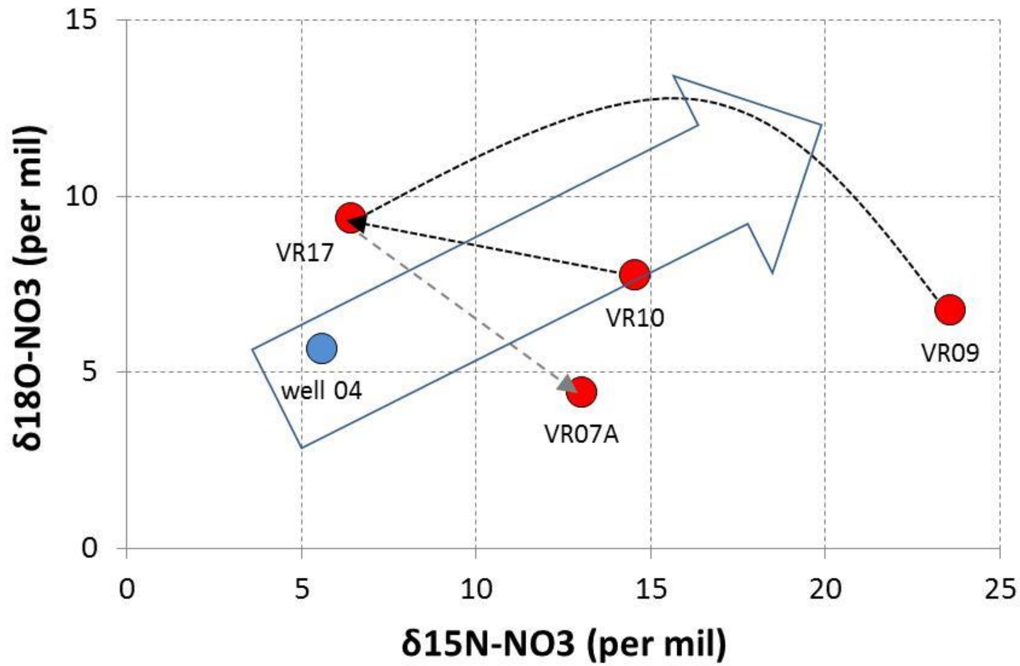


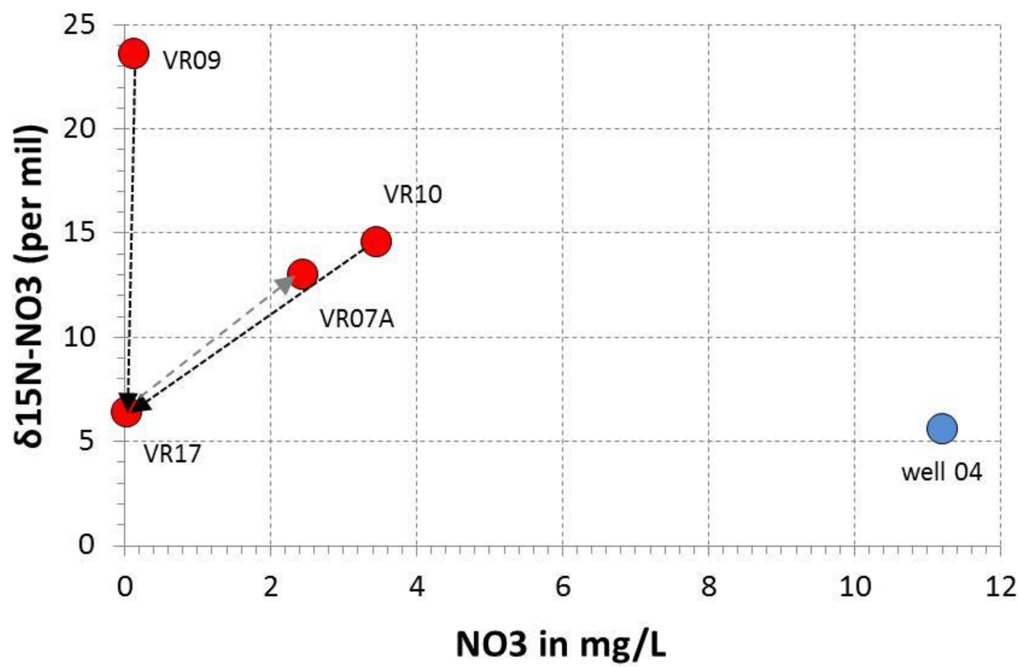
The main stem of the Ventura River story: from above the S. Antonio confluence (VR06.3) to Main Street (VR01). Partially denitrified groundwater originating from suburban land-use surfaces in the river above 06.3. While flowing towards VR06, uptake in the river reduces nitrate concentrations, but since uptake should leave isotopically enriched nitrate the reduction seen is probably related to additional groundwater inflows of lower isotopic content. Flow to VR06.1 indicates the nitrate decrease and isotopic enrichment expected of continued uptake and assimilation. Between VR06.1 and VR03.5 the addition of treated sewage effluent increases both the isotopic signature and the nitrate concentration. From VR03.5 to VR01 nitrate concentrations decrease due to uptake, but the isotopic reduction could be caused by either the addition of 04 water (although the proportional reduction does not fit a simple mixing model) or the entry of ag runoff just above 01 or both.





The upper Ventura River story: from Matilija above the dam (VR15) to Camino Cielo (VR12.9) below the N.Fork confluence. VR12.9 combines water from below Matilija Dam (mostly groundwater/seepage) with N.Fork flow (a minor contributor). These are relatively pristine waters with very low nitrogen concentrations. Water from below the dam is the major contributor with slightly higher nitrate concentrations and a more enriched isotopic signature than the N.Fork. This enrichment probably comes from either denitrification in the water-logged sediments that fill >95% of the reservoir or other groundwater sources. It's interesting that water flowing into the dam is so isotopically different (other chemical parameters also vary). The predominant source of nitrogen in the upper watershed is believed to be atm. deposition, but the possibility exists of some contamination from sparse development along the river bank upstream of VR15.





The San Antonio Creek story: from upper (VR10) to lower S.Antonio at the Ventura confluence (VR07A). Flow at VR17 originates from both VR10 (primarily agricultural) and VR09 (developed and suburban Ojai); VR10 is the dominant contributor. The very different isotopic signature of VR17 from either of these upstream tributaries indicates that flow was probably not continuous between these points and we are looking at some other nearby source. The depleted 15N signature would seem to eliminate the most probable alternative, Lion Canyon: low in nitrate due to appreciable algal uptake, but noted for contamination by cattle and horses. Similarly, flow was not continuous between VR17 and 07A; the water at the 07A comes from the same groundwater source supplying the adjacent Ventura River (VR06.3)(conductivity measurements support this conclusion). Well 04 (data collected Apr.-June 2007), located upstream of VR10, suggests that denitrified, ag-contaminated, groundwater is the probable source of the isotopic signature at VR10; other evidence substantiates appreciable water-table denitrification in drought-years.