ALPHA 132

PAINTED APPLE MOTH

… where did it come from ?

The painted apple moth is very small … only about two centimetres across its wingspan. It's not much to look at, although the caterpillar is pretty spectacular, with its spines and red stripes.

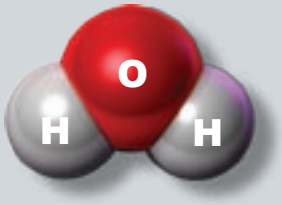
The caterpillar's spines are poisonous, but the main concern with the painted apple moth and caterpillar is that they are voracious … they'll eat anything and everything. Biosecurity NZ rates them as a serious threat to native bush as well as gardens, forestry and crops – a threat to our economy as well as the environment.

A **Painted Apple Moth** caterpillar.

When painted apple moths were discovered in Auckland in 1999, with multiple discoveries in 2001, Biosecurity NZ took this threat very seriously. The seven captured moths were not found close to the port areas but in various suburbs on either side of Auckland city. The places they were found were close to bush, commercial orchards and market gardens.

Biosecurity NZ engaged in an extensive spraying campaign to get rid of painted apple moth. There were many complaints about this, particularly from people who said the spraying caused asthma attacks either for themselves or their children. The spraying cost several million dollars, but it did appear to clear the painted apple moths from the area. But just four weeks short of a two-year clear period, a painted apple moth was found in Otahuhu. This was very serious, and the big question was; is this a local moth which has somehow survived the spray programme, or is it a recent arrival? How could Biosecurity find out? This is where the science comes in.

Iso-trace is a commercial laboratory set up within the University of Otago's Centre for Innovation. The main instrument they use is called an IRMS, an Isotope Ratio Mass Spectrometer, and Iso-trace works only with light stable isotopes such as ,oxygen, hydrogen, sulphur, nitrogen and carbon. The IRMS accurately measures very small differences in stable isotope amounts, and presents the information as a ratio. Researchers are looking at the difference in the 4th and 5th and 6th decimal places. The information is presented as a ratio of the sample relative to a standard, and the units are called per mil (parts per thousand).



Water is made from two hydrogen atoms (H) and one oxygen atom (0).

All the elements present in the material world consist of light and heavy isotopes, with the bulk of each element being comprised of the lightest isotope. The ratio of heavy to light isotopes in any given sample can act as a "fingerprint" for its location. Here is an example of how this might work looking at water, using the hydrogen isotopes present in water molecules. Water molecules are up of oxygen and hydrogen, and isotrace can measure both of these as they both have multiple light stable isotopes.

Hydrogen comes in three types – ^{1}H, ^{2}H, and ^{3}H – depending on whether it has zero, one or two neutrons. ^{3}H is radioactive so Iso-trace doesn't measure this isotope. ^{2}H is also known as deuterium (D), ^{1}H is just known as hydrogen (H). Most hydrogen is ^{1}H (99.98%) so most water molecules are made up of only this kind of hydrogen.

A **Hydrogen** atom contains one proton in its nucleus.

So what's the difference between isotopically light (H_2O) and heavy (HDO) water? H_2O boils at a lower temperature, melts at a lower temperature, and has a lower density. This is because the forces of attraction between the heavier HDO molecules are stronger so it takes more energy to break them.

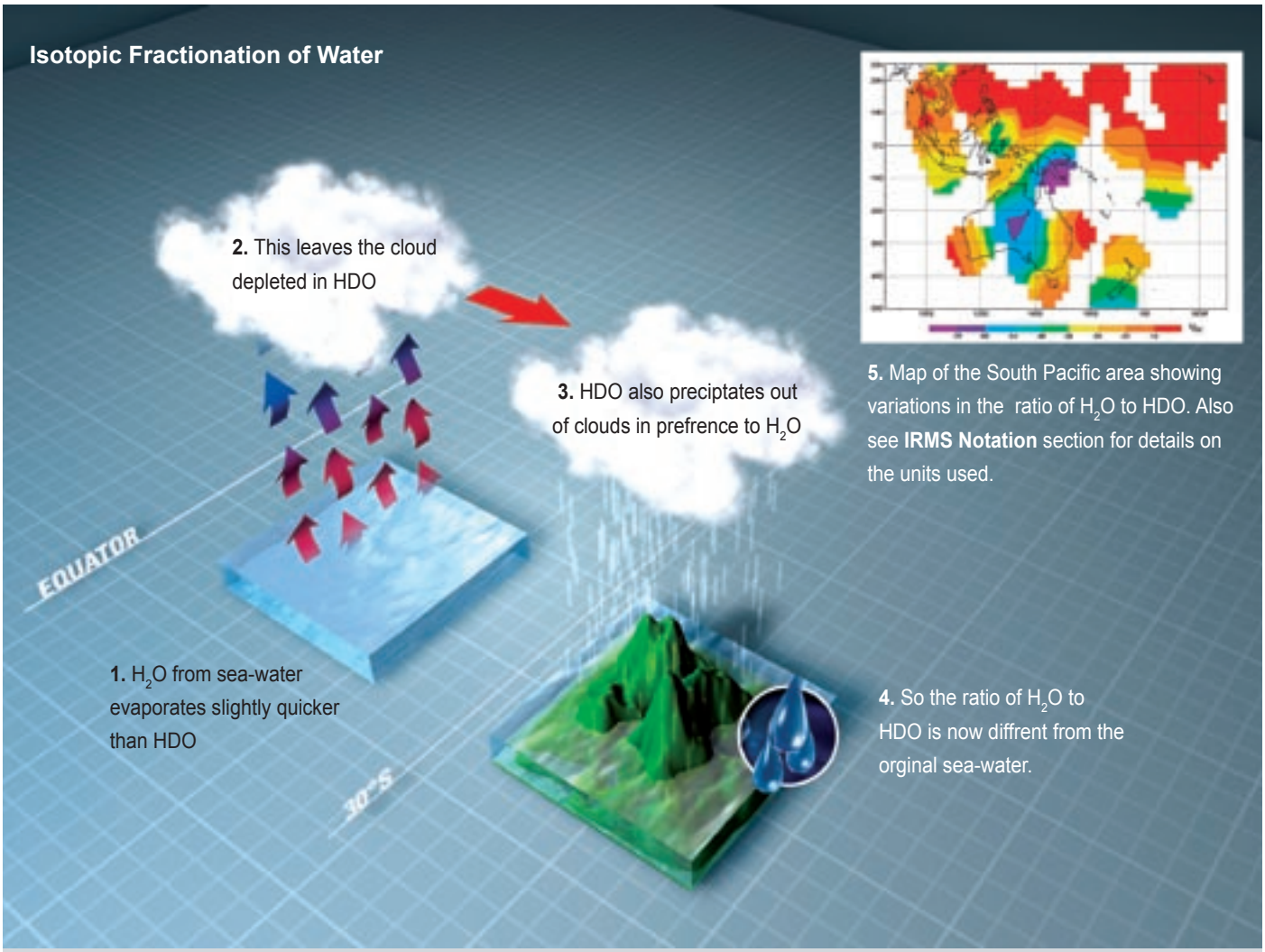
Now let's consider clouds… As water evaporates from the ocean to make clouds, H_2O evaporates slightly quicker than HDO, so the proportion of HDO in the cloud is less than in the waster from which it evaporated. As the cloud travels its cyclonic path it precipitates (rains) with the HDO precipitating in preference to the H_2O. This means the ratio of H_2O to HDO is greater than when the cloud formed.

As the cloud travels, the water it contains has less and less HDO, so although that HDO is most inclined to precipitate out, there's less and less of it available, so the rain has less and less HDO - less deuterium - in its make-up. The rain that falls has less and less HDO, depending on how far into the cloud's traveling pattern it is. Cloud-traveling patterns are determined by meteorological forces and currents, and can be mapped. That means that you can actually map the globe in terms of the ratio of deuterium to hydrogen isotope for precipitation (rain). Similar maps are available for oxygen isotopes. How does this help us in our investigation of the painted apple moth?

While a **Dueterium** atom contains one proton and one neutron in its nucleus.

Water is absorbed by plants and the hydrogen isotopes are incorporated into their tissue. Bugs then eat the plants that have absorbed the water and the isotopic fingerprint of the water is incorporated into the tissues of the bug (or in this case, the caterpillar). The isotopic fingerprint changes by a known amount during this process so scientists are able to compare the isotopic fingerprint from their sample to the isotopic fingerprint of the water absorbed by the caterpillar.

So if you can measure the hydrogen isotopic ratio from the caterpillar you can work out where it got most of its water, which will be where it spent most of its life. In order to get some moth body material that reflects its diet when it was a caterpillar, researchers at Iso-trace used the part of the moth that had been around the longest – the keratin in its wings, which formed when the caterpillar morphed into a moth. (The moths don't eat).



The Hydrogen ratio was –30 per mil, this is consistent with the moth having grown up in a place further towards the Equator than New Zealand. Of the many samples Iso-trace had for comparison, the moth sent by Biosecurity had an isotopic fingerprint closest to one captured in Australia. By contrast the ones that had grown up in Auckland had ratio between -45 and -35 per mil.

Iso-trace was able to confirm for Biosecurity NZ that the captured moth had not survived the expensive spray campaign, but was a recent arrival. This was a great relief to everybody!

IRMS Notation

Stable isotope information is presented as a isotope ratio called per mil. The per mil value is a ratio of a sample compared to a reference material. The hydrogen and oxygen reference material is a water sample called VSMOW (Vienna Standard Mean Ocean Water); the carbon reference material is a piece of fossil limestone called VPDB (Vienna Pee Dee Belemnite); and the nitrogen reference is N_2 of air.

The equation to calculate the isotope ratio is:

$$\delta = \left[\frac{R_{sample}}{R_{reference}} - 1 \right] * 1000$$

Where δ is the isotope ratio of a sample, and R_{sample} and $R_{reference}$ are the ratios of the absolute amounts of the light isotope to the heavy isotope in each of the sample and the reference material, respectively.

The reference material is always the same for each single element, as this is the ratio for the reference material. So the equation will show the relative amounts of the heavy and light isotopes. For example, this equation gives a positive answer if there is more deuterium in the sample than there is in the reference material.

Isotope scientists can measure VERY small changes in the amount of the heavy isotope. To get an idea of how small these differences are, imagine that you are a farmer with a paddock which has one million sheep in it. Isotope ratio measurements would be accurate enough to tell you if there were 15435 or 15436 black sheep amongst them.

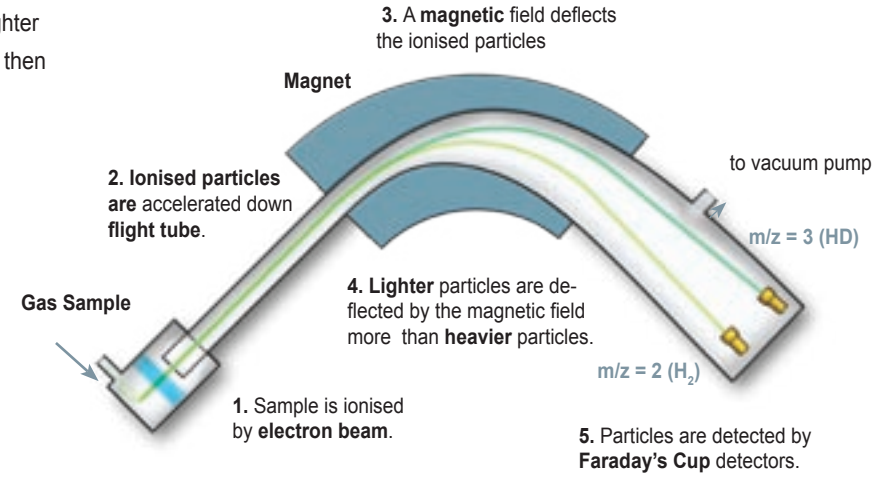
IRMS Instruments

For the stable isotope ratio of a substance to be measured it must first be converted to a suitable gas (see table below). A sample is converted to a gas by combustion (oxidation), reduction or pyrolysis (being blown to bits at very high temperature >1400°C).

Once the gas is formed it is ionised by bombarding it with a stream of electrons before being accelerated through a magnetic field in a curved flight tube. The molecules that contain light atoms are separated from those containing heavy atoms in the flight tube because the lighter molecules are deflected more than the heavy ones. A detector then measures how much of each type of molecule is present.

Element	Gas required for analysis
Hydrogen	H_2
Carbon	CO_2
Nitrogen	N_2
Oxygen	CO_2, CO
Sulphur	SO_2

This detector is called a Faraday's Cup. It's about 5 mm across, and is surface-coated with gold leaf which is then electrically charged. The IRMS has a series of these at different distances from the flight tube, and different ions collect in each one depending on their weight. Fortunately it is the computer that does all the measuring and counting up, and presents the finished results!



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