



HYDROLOGY

Tropical rain recycling

Thom Rahn

The behaviour of water in the atmosphere is a poorly understood part of the hydrological cycle. Applying the principles of isotope chemistry to satellite data provides a powerful approach for improving the situation.

Water is arguably our most precious resource. It moves through Earth's system in many ways, beginning with its evaporation from the oceans into the atmosphere. There, air masses mix, and droplets coalesce and fall. Some of this precipitation goes straight back into the ocean, while some enters the terrestrial water cycle as rain or snow. Terrestrial water re-evaporates or is stored in glaciers, recharges aquifers or is carried by rivers back to the sea. The processes behind this delivery of a water molecule from ocean to cloud to rain droplet (or snowflake), and eventually back to the ocean, are highly complex. On page 528 of this issue, Worden *et al.*¹ unravel a little more of the mystery behind the journey.

The authors' study takes its cue from the seminal work of Harmon Craig², who in 1961 found that the stable isotopes of hydrogen and oxygen (expressed in terms of the ratios $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$) follow a simple linear relationship in all precipitation, regardless of where the water was collected. This relationship, along with maps of the distribution of ^2H and ^{18}O in precipitation, has helped to a degree in tracking water through the atmosphere. Along the way, it has illuminated phenomena as diverse as the source regions of groundwater recharge, the pathways of migratory bird species, and the provenance of mineral assemblages resulting from the evaporation of water.

But whereas measuring the isotopic content of rainfall and snow is a straightforward process, analysing isotopic ratios in the vapour

from which this precipitation condensed is another matter altogether. One option is to collect samples with a mechanical cold trap and return them to a laboratory for conventional analysis³; another is to measure isotopes *in situ* using laser-based optical methods^{4,5}. Both approaches have their merits, but have been little used to date. A third option is to determine the isotopes in water from space through satellite-based spectrometric analysis. This has been accomplished previously for ^2H , but only for the upper troposphere (the lowest portion of Earth's atmosphere) and lower stratosphere^{6,7}, or for clear-sky conditions over the Pacific Ocean⁸. Worden *et al.*¹ go one better by retrieving globally distributed profiles of ^2H in water using the Thermal Emission Spectrometer onboard NASA's Aura satellite. These yield the first comprehensive map of the ^2H distribution of water vapour in the troposphere.

The history of this water vapour can be illuminated by comparing Worden and colleagues' measurements with theoretical expectations. In the simplest model, tropical ocean waters evaporate, and are lifted to cloud height by convection and transported poleward, where progressive 'rainout' depletes the air mass of moisture. Because the lighter stable isotopes evaporate preferentially, the initial vapour is depleted in the heavier isotopes ^2H and ^{18}O (Fig. 1, overleaf) when compared with its oceanic origin. As this vapour condenses into clouds to form precipitation, the heavier isotopes become concentrated again in the

liquid phase, further depleting the remaining cloud water vapour (blue curves in Fig. 1) and removing the heavier isotopes from the atmosphere. When the remaining dry and depleted air is mixed with freshly evaporated moist air, its isotopic composition and moisture content move back towards equilibrium with the ocean (the orange curves). In this simple model, air parcels cycling in the atmosphere are represented by the orange and blue regions of Figure 1, depending on whether they are dry or moist.

But as those of us who live in arid regions of the world can verify, rain sometimes does not make it to the ground at all: some of the precipitation is certainly recycled within the atmosphere. If the isotopic composition of a parcel of water vapour is strongly influenced by the re-evaporation of rainfall, it would be expected to be moister, but more depleted in heavy isotopes because of its recycled origin (green area in Fig. 1).

Worden *et al.*¹ identify such an additional ^2H depletion in approximately half of the water vapour in moist air (that is, air in regions dominated by precipitation rather than evaporation) that they sample over tropical oceans. According to their data, on average about 20% of tropical precipitation over the ocean must have re-evaporated before reaching the surface — in some cases, the value exceeds 50%. Although this recycling of precipitation via re-evaporation is not a new idea^{9,10}, it is beautifully illustrated by these measurements.

The degree of re-evaporation depends on the ambient relative humidity. Because a droplet plummets from a cold, saturated cloud through to warmer, generally unsaturated air below, one might expect re-evaporation to be fairly ubiquitous. Perhaps surprisingly, only about half of Worden and colleagues' data from moist tropical air, and very few of their extratropical data, confirm the effect. The lack of re-evaporation in these cases is possibly due to earlier cooling, and the resulting increase in relative humidity,

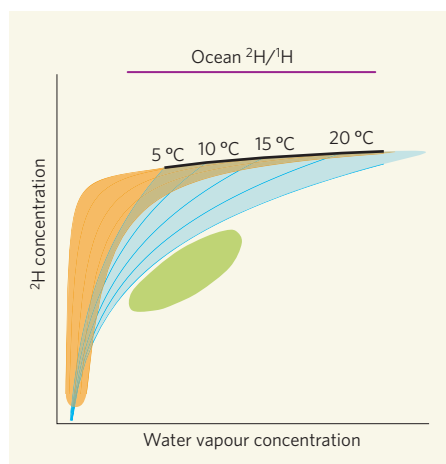


Figure 1 | Stable isotopes in water vapour. The isotopic composition of ocean water defines the baseline ratio of hydrogen isotopes $^2\text{H}/^1\text{H}$ (purple line). As water evaporates from the ocean, its isotopic composition becomes depleted in heavier isotopes, such as ^2H , and moves towards the black curve. Warmer air holds more moisture, as indicated by the sea surface temperatures at the time of evaporation. Condensation in clouds causes the remaining water vapour to become further depleted in the heavy isotopes; the ^2H proportion descends down the blue curves. As dry air high in the atmosphere depleted in ^2H (bottom left-hand corner) mixes with freshly evaporated ocean air, it is moistened; the isotopic composition becomes more enriched in heavy isotopes, moving up along the orange curves. Rainwater that evaporates before it reaches the ocean again is moister and more depleted in heavy isotopes than water vapour resulting from straight evaporation from and condensation into the oceans (green area). These characteristics are detected by Worden *et al.*¹ in about half of their moist-air observations over the tropical oceans.

as the air was advected from warmer regions. By contrast, the water vapour with the greatest signature of re-evaporation is evidence of condensation from local convection.

Potentially even more significant for our understanding of the processes that deliver fresh water to land is that water vapour over tropical continental land masses is, on average, less depleted in ^2H than it is over the tropical oceans. In addition, a proportion is even more enriched than is water vapour in equilibrium with the oceans. These results can be accounted for only by one of two mechanisms. First, relatively enriched water vapour that evaporates from the ocean is transported to land at low altitudes, and is convectively lofted. Alternatively, previous continental precipitation is recycled, with an isotopic composition reflecting a potentially complex history of condensation and evaporation.

Of course, both processes could work in parallel. Future research addressing the seasonal variability of the distribution of ^2H in continental water vapour, and the addition of an ^{18}O data set, will help to resolve the question of whether transport of oceanic air or

recycling of continental precipitation is dominant. Meanwhile, the data provided by Worden *et al.*¹ offer an invaluable insight into the global water cycle. Understanding all aspects of the hydrological cycle will be crucial as we proceed into a future with an uncertain climate, where potable water will become an ever more precious resource. ■

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ORGANIC CHEMISTRY

Catalytic gold rush

Steven P. Nolan

Despite gold's reputation as an inert element, chemists have mined a rich seam of catalytic reactions that use this metal. The latest example stakes out gold's claim as a versatile catalyst.

At the turn of the nineteenth century, the small outpost of Dawson, located at the juncture of the Yukon and Klondike rivers, saw a record population explosion. This was caused by a simple cry: “Gold!” A similar gold fever has recently overtaken chemists, who have discovered that this supposedly inert metal can catalyse a wide array of chemical reactions. A striking example of this has now been described by Forsyth and colleagues¹ in *Angewandte Chemie*. They have used a gold-catalysed reaction as the key step in the synthesis of an elaborate organic molecule, so cementing the use of this metal in mainstream chemistry.

It is surprising that gold has taken so long to find a place in catalysis. The reason for the delay is nothing to do with cost, as might be expected — many metals commonly used as catalysts (such as platinum, rhodium and iridium) are much more expensive than gold.

Much of the blame must be attributed to the long-held assumption that gold is unreactive. But gold salts have been known for some time to have a high affinity for carbon–carbon triple bonds (known as alkyne bonds). The simple reactions of these salts with alkynes are the basis of the present gold rush².

Compounds such as gold chloride (AuCl) are now frequently assessed by chemists as catalysts for new chemical transformations^{3,4}. This has led to the development of an impressive array of organic reactions^{2–6} that provides a foundation for Forsyth and colleagues' work. Gold salts can promote chemical transformations at room temperature with reaction times of just minutes. This contrasts with other metal-catalysed reactions that require higher temperatures and reaction times of hours or even days.

Forsyth and colleagues¹ now report the use

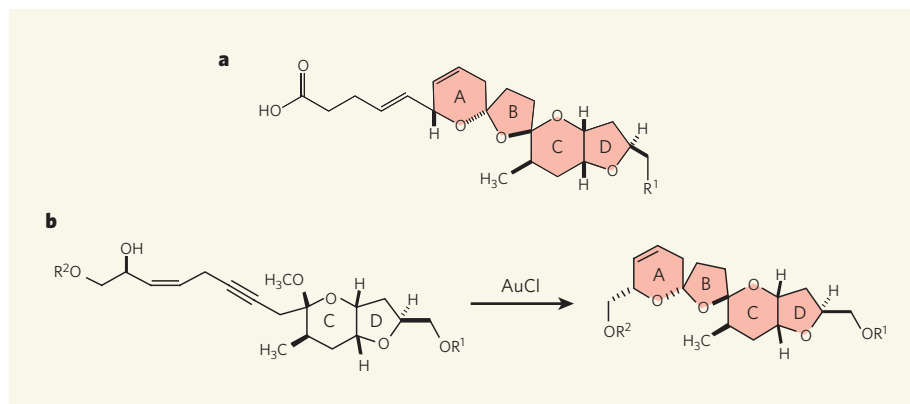


Figure 1 | Gold catalysis in organic synthesis. **a**, Azaspiracids are a family of marine toxins, the core structure of which is shown here. The ring subunits are commonly labelled A–D as shown; R_1 represents the various structures found for each specific azaspiracid. **b**, Forsyth and colleagues¹ use a reaction catalysed by gold chloride (AuCl) to construct rings A and B. R_2 represents a chemical group that may be converted into the side chain found in azaspiracids.