



Figure 1 | Schematic diagram of planetary spin-orbit resonances. **(a)** A planet on a concentric, circular orbit in synchronous rotation. **(b)** A planet on an eccentric, elliptical orbit in a 3:2 spin-orbit resonance. Snapshots proceed counter-clockwise from the top left. Wieczorek *et al.*¹ use numerical simulations to show that Mercury could have once had a synchronous rotation with the Sun. The planet could have been knocked out of this stable orbit by a large impact, causing it to later slow into its present-day 3:2 spin-orbit resonance.

initially been captured into a synchronous rotation with the same side always facing the Sun. However, a large impact on Mercury at a later stage could have instantaneously knocked the planet well out of this stable resonance. The present 3:2 rotation state is found to be the most likely end point of this complex evolution.

Calculations aside, we may be able to read some of Mercury's history from its surface. If Mercury spent a significant amount of time in synchronous rotation, the distribution of asteroid impacts on its surface should not be uniform. Close to the

gravitational pull of the Sun, asteroids and comets generally approach on elongated, almost parabolic orbits. Their trajectories therefore tend to intersect Mercury's orbit at high angles. This means that more craters would have formed at the locations of eternal midnight and noon (by inbound and outbound bodies, respectively) and fewer at the boundary between the sides of perpetual day and night. Counts of the largest and oldest craters, representative of earlier periods in Mercury's history, tentatively support this picture. This implies that Mercury once experienced relentless

heat on the side on which the Sun never set, and eternal night on the other, until one of the last large impacts knocked it out of that state. Further data from the MESSENGER spacecraft — a NASA space probe currently orbiting Mercury and surveying its surface — will test this hypothesis more rigorously. If it proves correct, the synchronous history of Mercury may have profound implications for the thermal history of its surface.

Past synchronous rotation would also mean that Mercury is likely to have formed spinning in the opposite direction to its orbital motion, like Venus and Uranus currently do. This matches the prevailing picture that the solid planets formed from a merging of large planetesimals, with a post-formation spin axis oriented randomly⁵.

Wieczorek *et al.*¹ suggest that Mercury's current slow rotation is not primordial. Instead, it is probably the product of a long evolution within slowing cosmic clockwork, assisted by occasional kicks from interplanetary collisions. □

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ATMOSPHERIC CHEMISTRY

Natural atmospheric acidity

Formic acid exerts a significant influence on atmospheric chemistry and rainwater acidity. Satellite observations and model simulations suggest that terrestrial vegetation accounts for around 90% of the formic acid produced annually.

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Formic acid is one of the largest sources of acidity in the global atmosphere¹.

This acid is found in remote as well as polluted regions, and is an important component of the complex, and poorly understood, soup of organic matter present in the atmosphere². Although it contributes to the acidity of precipitation, formic acid is quickly consumed by microbes, so does not lead to the harmful effects of acid rain. However, formic acid has a significant effect on aqueous-phase chemistry in the atmosphere. Aqueous reactions in

cloud droplets and on aerosols influence atmospheric composition, for instance through the production and loss of radicals that affect ozone, the activation of halogens and the formation of secondary organic aerosols^{3–5}. Many of these reactions are highly dependent on pH and are thus sensitive to formic acid levels. Writing in *Nature Geoscience*, Stavrakou and co-workers⁶ use satellite measurements to investigate the global sources and sinks of atmospheric formic acid, and suggest that this acid can account for 50% or more

of rainwater acidity in many continental regions of the world.

The name 'formic acid' originates from the Latin word *formica*, meaning ant. Formicine ants secrete formic acid for defence purposes, but are only a minor source of this acid to the atmosphere globally. The photochemical oxidation of volatile organic compounds (VOCs) is thought to represent the largest global source, although it is uncertain exactly how much formic acid is produced in this way. However, the VOC isoprene, emitted

by terrestrial vegetation, is thought to be the main precursor compound. The mechanism of isoprene oxidation is a key uncertainty in chemical models: recent chamber studies suggest that isoprene yields five to ten times more formic acid than previously assumed⁷. Other notable formic acid precursors include biogenic and anthropogenic compounds such as 2-methyl-3-buten-2-ol, acetylene, monoterpenes and other alkenes; their contributions are even less well defined than that of isoprene.

Formic acid is also emitted directly by vegetation. However, the flux is bidirectional. Thus the net effect can be either emission or uptake, depending on the ambient concentration^{8,9}. Other sources include biomass and biofuel burning, soils, agriculture and fossil fuel combustion. The contribution of the latter is likely to be minor, given that atmospheric formic acid has been shown to be composed mainly of modern carbon¹⁰. The total source of formic acid to the atmosphere was recently estimated to be 55 Tg yr⁻¹, about twice as large as earlier estimates¹¹.

Using measurements from the Infrared Atmospheric Sounding Interferometer (IASI) satellite sensor, onboard Europe's MetOp-A satellite, combined with a global chemical model, Stavrou and co-workers⁶ present evidence for a severe and widespread underestimation of formic acid sources to the atmosphere. Their study confirms recent work using aircraft and ground-based observations, which also found evidence for a missing source of formic acid¹¹. Importantly, the satellite data pinpoint biogenic emissions, particularly from boreal and tropical forests, as the most likely cause of the discrepancy between observations and model predictions (Fig. 1).

Stavrou and co-authors infer that 100–120 Tg of formic acid is produced globally each year — two to three times that estimated from known sources, with about 90% originating from the terrestrial biosphere. This is a large source: for context, it is a significant fraction of the estimated global emissions of isoprene (500–600 Tg yr⁻¹), the dominant VOC emitted to the atmosphere, and comparable to the combined emissions of all anthropogenic VOCs (100–200 Tg yr⁻¹). If these findings are borne out by future work, the importance of formic acid could have been significantly underestimated: using this revised budget, Stavrou *et al.* estimate that formic acid alone can account for as much as 60–80% of rainwater acidity over Amazonia and for up to 30–50% over the United States in summer.

A key unresolved issue is whether this additional formic acid is caused by direct



Figure 1 | Boreal forest from above. Stavrou and colleagues⁶ show that temperate and boreal forests are key hotspots for the production of formic acid. Using satellite data and a global chemical model, they show that the global production of formic acid is two to three times larger than previous estimates suggest, and that terrestrial vegetation accounts for around 90% of the annual production. Other sources include fossil fuel combustion, agriculture and biomass burning.

emissions from vegetation, or oxidation of other biogenic VOCs. *In situ* flux measurements provide little evidence for the former^{8,9}, although the data are too sparse to be certain. If oxidation of precursor VOCs is the source, this raises questions regarding their identity. The high concentrations of formic acid measured by IASI over mid- and high-latitude forests suggest that monoterpenes and related compounds may be involved, based on the geographic distribution of their emissions. However, as Stavrou and co-authors⁶ point out, resolving the satellite–model discrepancy on the basis of monoterpene oxidation would require unrealistic yields of formic acid, based on present estimates of monoterpene emissions. Other unidentified precursors may be responsible. Identifying the specific origin of this apparently biogenic formic acid will be important for representing the associated chemical effects in atmospheric models. Furthermore, acetic acid and other organic acids are also known to be important sources of atmospheric acidity¹; present estimates of their sources may also be incorrect.

The updated estimate provided by Stavrou and co-workers⁶ clearly reduces the overall bias in formic acid sources based on the IASI satellite observations. However, capturing the vertical profiles of formic acid apparent in airborne measurements proved difficult in their model simulations. This discrepancy no doubt results, in part, from the comparison of a 4° × 5° global model to point measurements, but probably also reflects outstanding uncertainties regarding the sources and sinks of formic acid. For example, laboratory experiments show that formic acid is produced as organic aerosols age^{12,13}. The atmospheric significance of aerosol aging is uncertain, but observed correlations do suggest some link between organic aerosol chemistry and formic acid¹¹. The rate at which formic acid is emitted during biomass burning, and produced photochemically as the smoke plumes age, is another important uncertainty.

Stavrou and co-authors⁶ show that terrestrial vegetation is a much greater source of formic acid than previously assumed. Although intense source regions of formic acid have been identified, the nature of this source remains uncertain. Two more IASI instruments are scheduled to be launched aboard upcoming MetOp satellites (in 2012 and 2017), and should extend the formic acid data record. Combined with new *in situ* mass spectrometry techniques¹⁴, and with complementary space-based measurements from the Tropospheric Emission Spectrometer¹⁵ aboard NASA's Aura satellite, these instruments should yield a more in-depth understanding of organic acids and their chemical effects in the atmosphere. □

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