

Sustainability and Chemistry

CH5106: L6

Instructors: Sayam Sengupta
Swaminathan Sivaram
Amitava Das

Trade of economically and physically scarce virtual water in the global food network

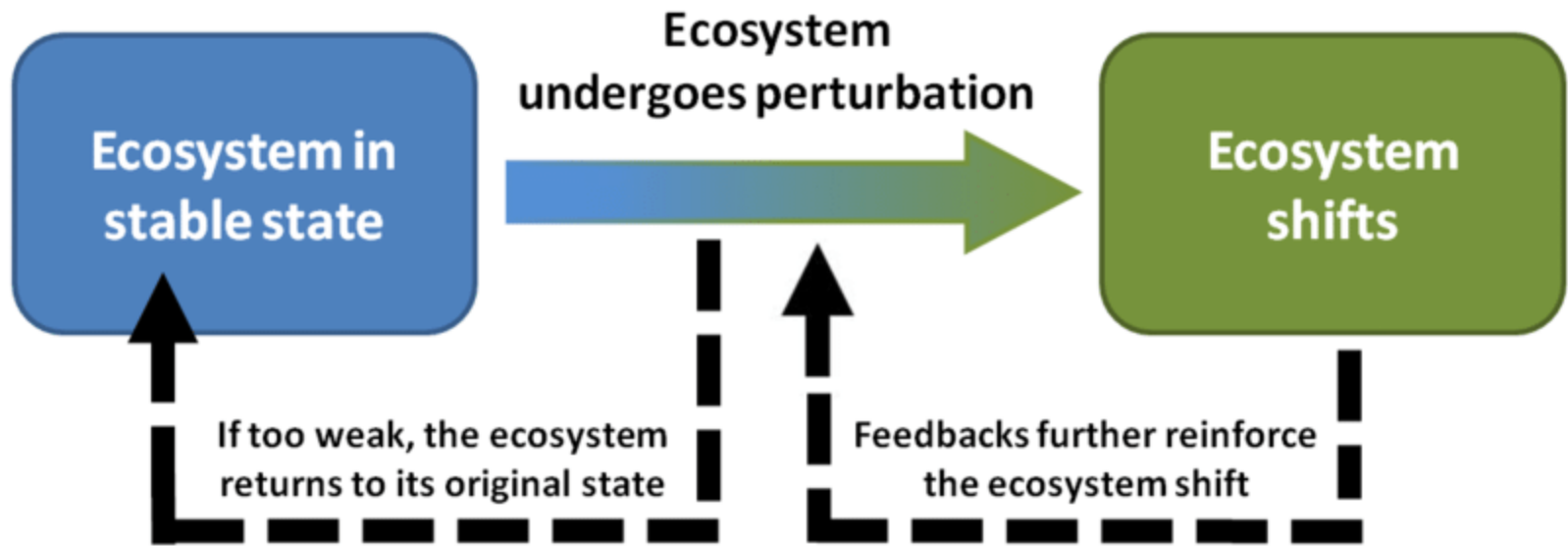
Sci Rep 11, 22806 (2021). <https://doi.org/10.1038/s41598-021-01514-w>

The **virtual water (VW) trade** in food refers to the volume of water used to produce crops exchanged in the global market. When assessing a country's water abundance or scarcity in the context of international virtual water trade, scholars typically consider only physical water availability, overlooking *economic water scarcity*—constraints imposed by socio-economic conditions.

A newly proposed **composite water scarcity index** (CWSI) that combines physical and economic water scarcity.

39% of virtual water volumes are exported from countries with a higher CWSI than that of the destination country. Such unfair routes occur both from low- to high-income countries and among low- and middle-income countries themselves.

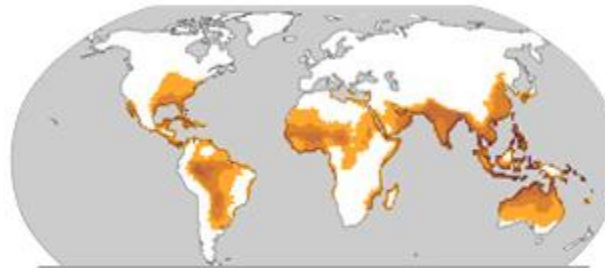
The application of the CWSI reveals a shift in status—from net exporter to net importer—for some wealthy countries, and vice versa for certain low- and middle-income countries. It enables quantification of the extent to which virtual water (VW) exchanges follow environmentally and economically inequitable routes, thereby informing the development of fair compensation policies.



Ecosystems typically exist in stable, recognizable states maintained by balanced biological, physical, and chemical interactions. While minor disturbances can be absorbed with resilience, major or prolonged disruptions may push the system past a critical threshold, triggering a shift to an alternative stable state. This new state often differs markedly in structure and function, reinforced by self-sustaining feedbacks that lock in the altered condition.

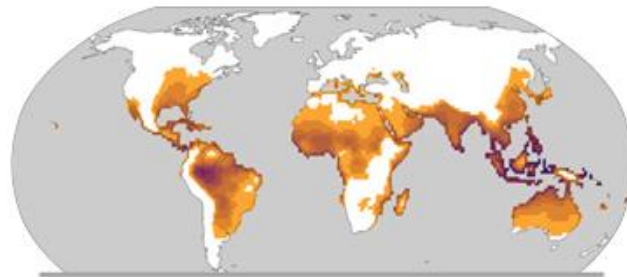


Heat-humidity risks to human health

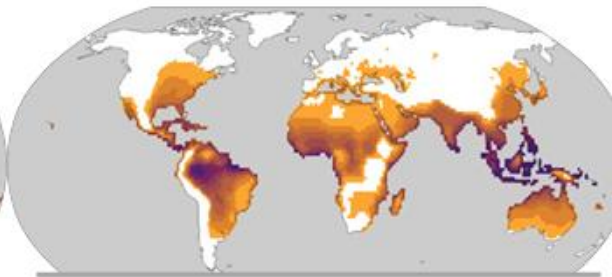


Historical 1991–2005

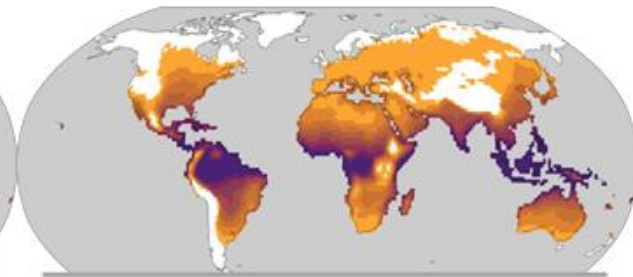
Days per year where combined temperature and humidity conditions pose a risk of mortality to individuals



1.7 – 2.3°C



2.4 – 3.1°C



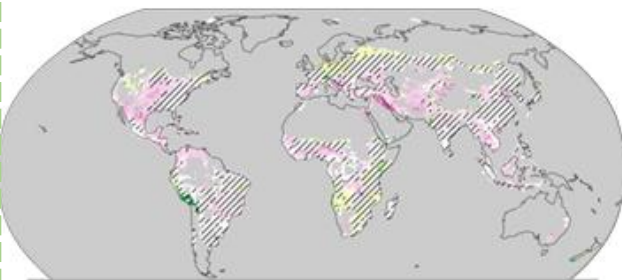
4.2 – 5.4°C

³Projected regional impacts utilize a global threshold beyond which daily mean surface air temperature and relative humidity may induce hyperthermia that poses a risk of mortality. The duration and intensity of heatwaves are not presented here. Heat-related health outcomes vary by location and are highly moderated by socio-economic, occupational and other non-climatic determinants of individual health and socio-economic vulnerability. The threshold used in these maps is based on a single study that synthesized data from 783 cases to determine the relationship between heat-humidity conditions and mortality drawn largely from observations in temperate climates.

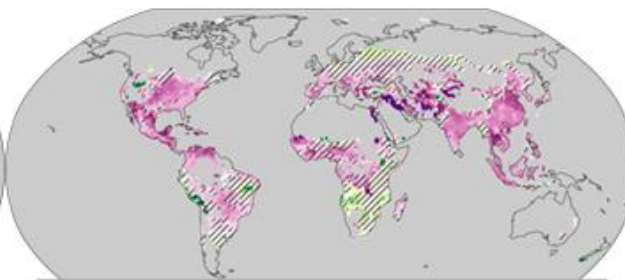
Food production impacts



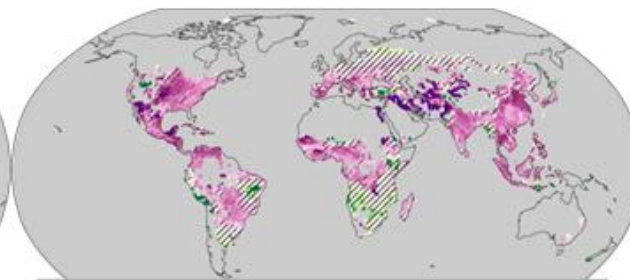
Maize yield Changes (%)



1.6 – 2.4°C

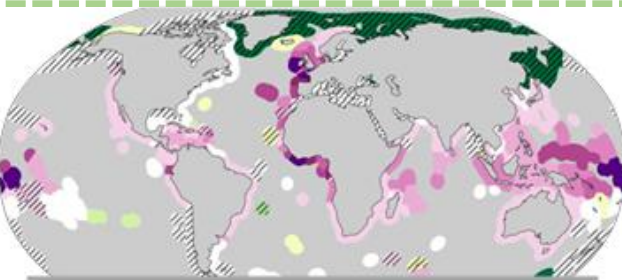


3.3 – 4.8°C

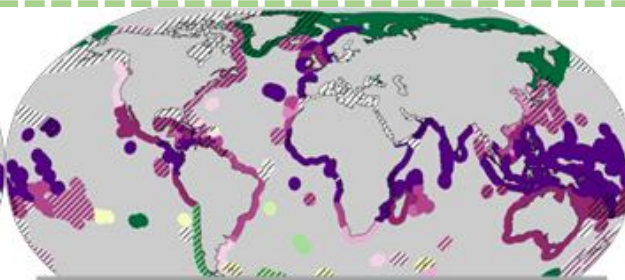


3.9 – 6.0°C

⁴Projected regional impacts reflect biophysical responses to changing temperature, precipitation, solar radiation, humidity, wind, and CO₂ enhancement of growth and water retention in currently cultivated areas. Models assume that irrigated areas are not water-limited. Models do not represent pests, diseases, future agro-technological changes and some extreme climate responses.



0.9 – 2.0°C



3.4 – 5.2°C

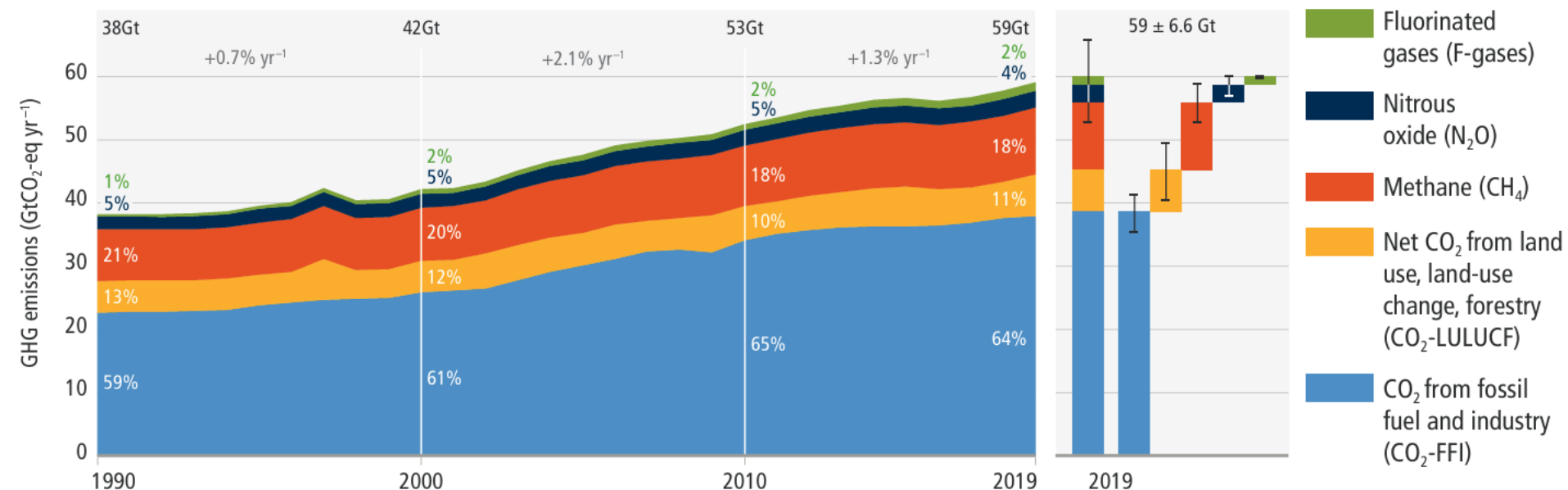
- Areas with little or no production, or not assessed
- Areas with model disagreement

Fisheries yield (Maximum catch potential) Changes (%)



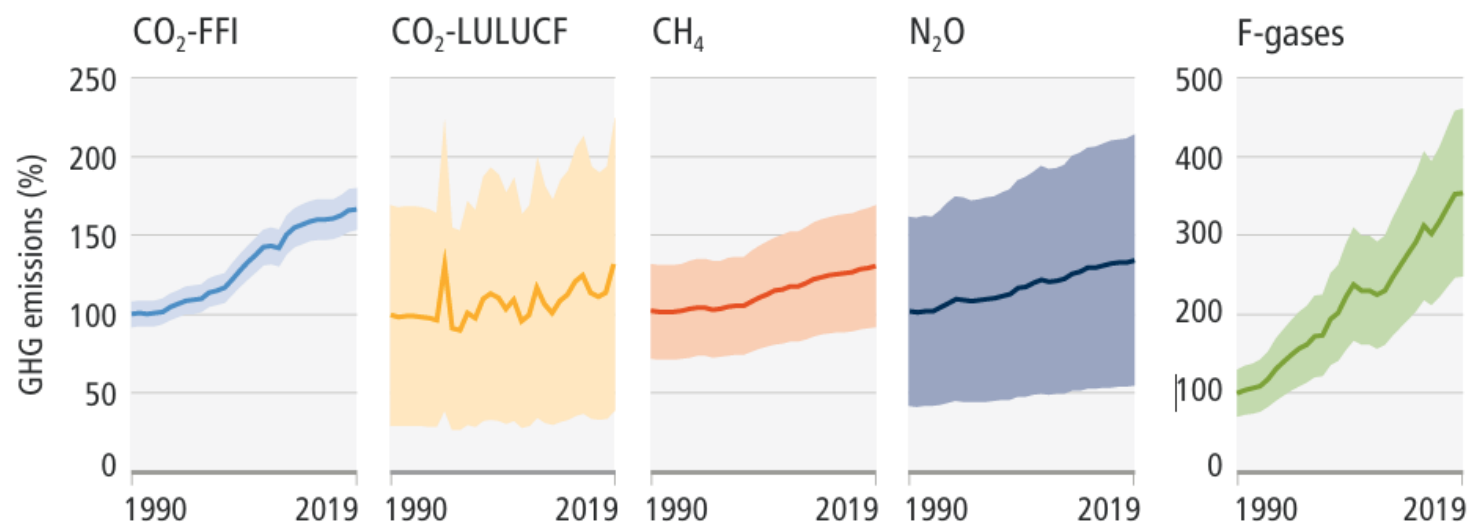
Global net anthropogenic emissions have continued to rise across all major groups of greenhouse gases.

a. Global net anthropogenic GHG emissions 1990–2019⁽⁵⁾



The solid line indicates central estimate of emissions trends. The shaded area indicates the uncertainty range.

































The solid line indicates central estimate of emissions trends. The shaded area indicates the uncertainty range.



Greenhouse Gas (GHG)	Atmospheric Lifetime (yrs)	Global Warming Potential (GWP)	Primary Current Sources	High GWP gases
Carbon dioxide (CO ₂)	50-200	1	Fossil fuel use, land use, cement	
Methane (CH ₄)	12±3	21	Fossil fuel use, agriculture	
Nitrous oxide (N ₂ O)	120	310	Mostly agriculture, ~1/3 are anthropogenic	
Hydrofluorocarbons (HFCs)	1.5 to 209	150 to 11,700	Alternative to ozone depleting substances	
Perfluorocarbons (PFCs)	2,600 to 50,000	6,500 to 9,200	Primary aluminum production; semiconductor manufacturing	
Sulfur Hexafluoride (SF ₆)	3,200	23,900	Used in electric power transmission, magnesium and semiconductor industries	

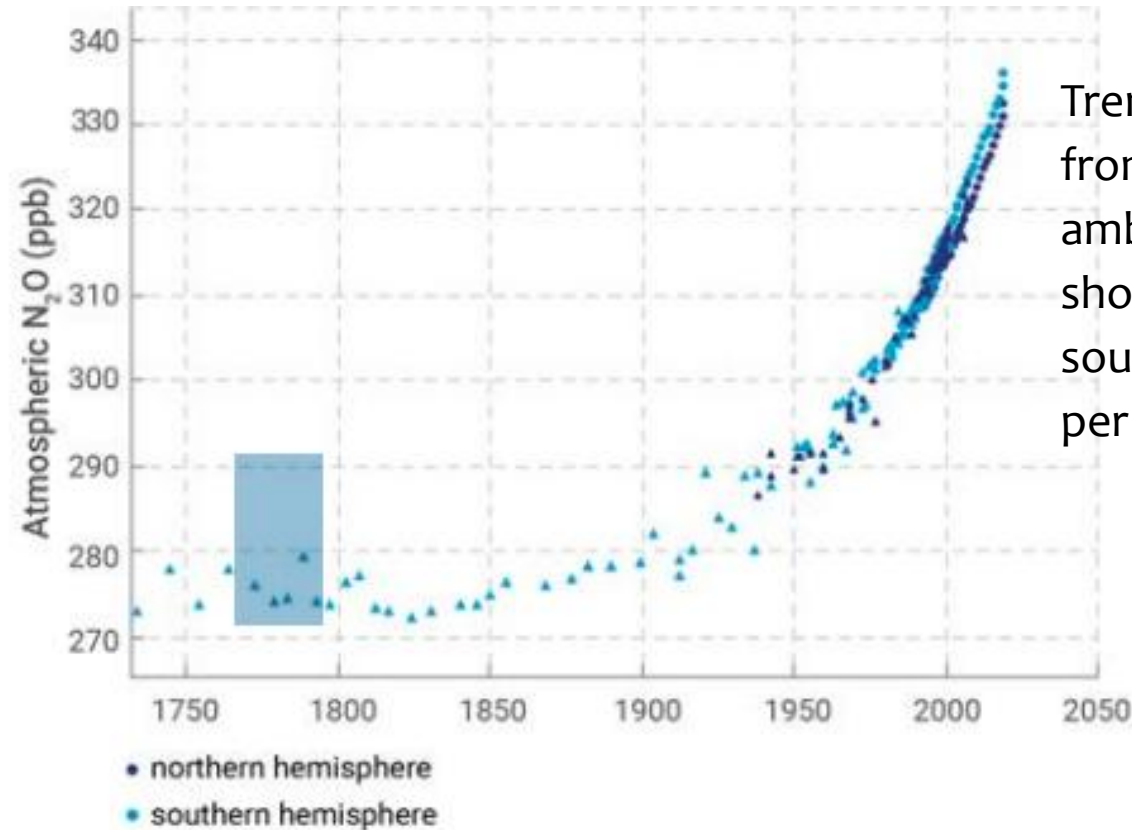
<https://www.global-climate-change.org.uk/6-5-2.php>

The Kyoto Protocol fixed the use of GWP values published by the IPCC in 1996 in its Second Assessment Report. Since then, the IPCC has updated its GWP values four times, in 2001, 2007, 2013, and 2021. The result has been a proliferation of GWP values out there that leads to a lot of confusion.

		2023 vs 1990		2023 vs 2005		2023 vs 2022	
	Power Industry		+96%		+36%		+2%
	Industrial Combustion and Processes		+91%		+41%		+2%
	Buildings		+1%		+3%		+1%
	Transport		+78%		+26%		+4%
	Fuel Exploitation		+48%		+23%		+2%
	Agriculture		+20%		+15%		0%
	Waste		+56%		+37%		+2%
	All sectors		+62%		+28%		+2%

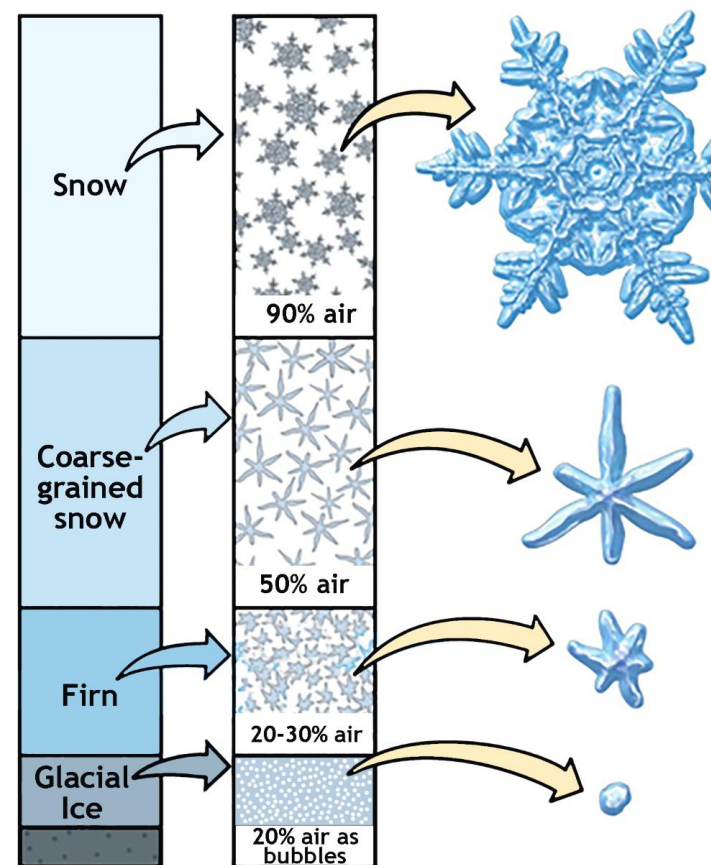
Publication: GHG emissions of all countries; 2024 report

https://edgar.jrc.ec.europa.eu/report_2024#



Trends in atmospheric N_2O levels derived from ice core or firn air (triangle) and ambient air (circle) measurements, shown for the northern (dark blue) and southern (light blue) hemispheres, parts per billion by volume.

Estimated global emissions and uncertainties based on the atmospheric levels assuming a constant lifetime of N_2O of 116 ± 9 years, nitrous oxide and CO_2 equivalent, megatonnes per year.

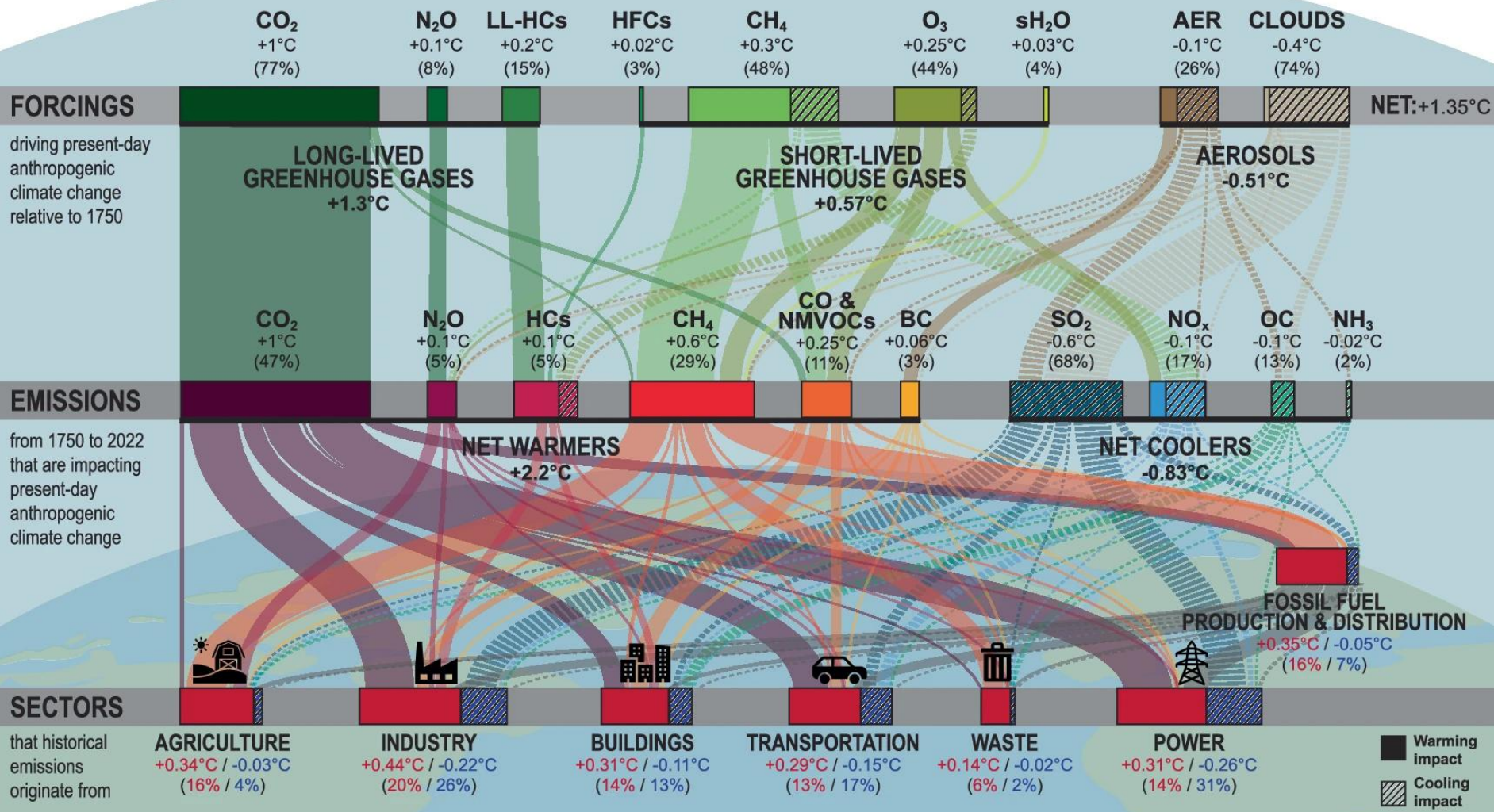


Firn is the intermediate stage between snow and ice. A porous layer found on glaciers and ice sheets. It plays a crucial role in regulating glacier dynamics and provides valuable insights into past atmospheric composition.

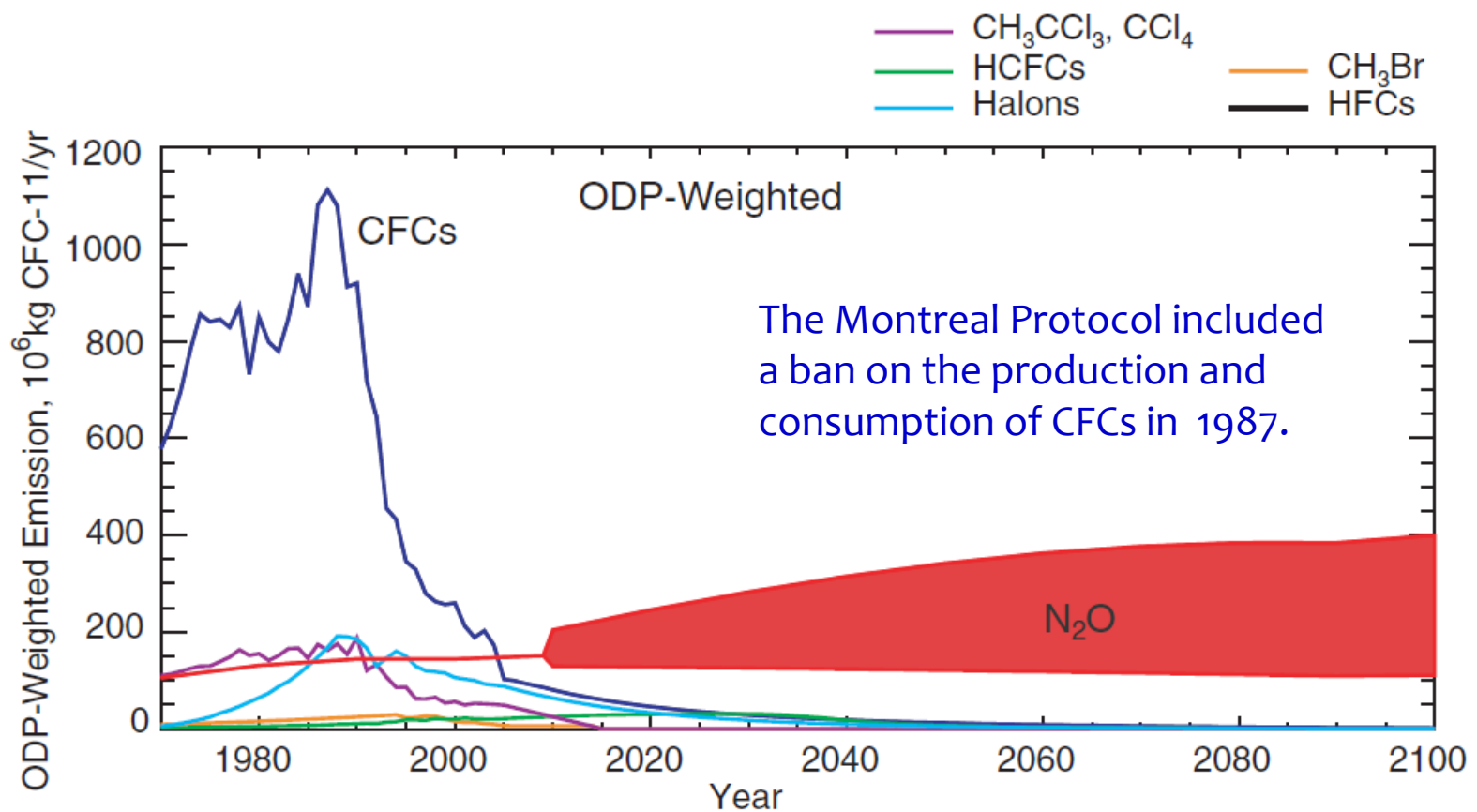
Findings from the new Global Nitrous Oxide Assessment (N_2O) warns that without urgent action on rising N_2O emissions, there is no viable pathway to limiting global warming to 1.5°C , and provides tangible tools to reduce emissions by more than 40% from current levels.

The assessment shows that N_2O is currently the most significant ozone-depleting substance being emitted, risking exposing much of the world's population to higher UV levels and an increase in skin cancers and cataracts.

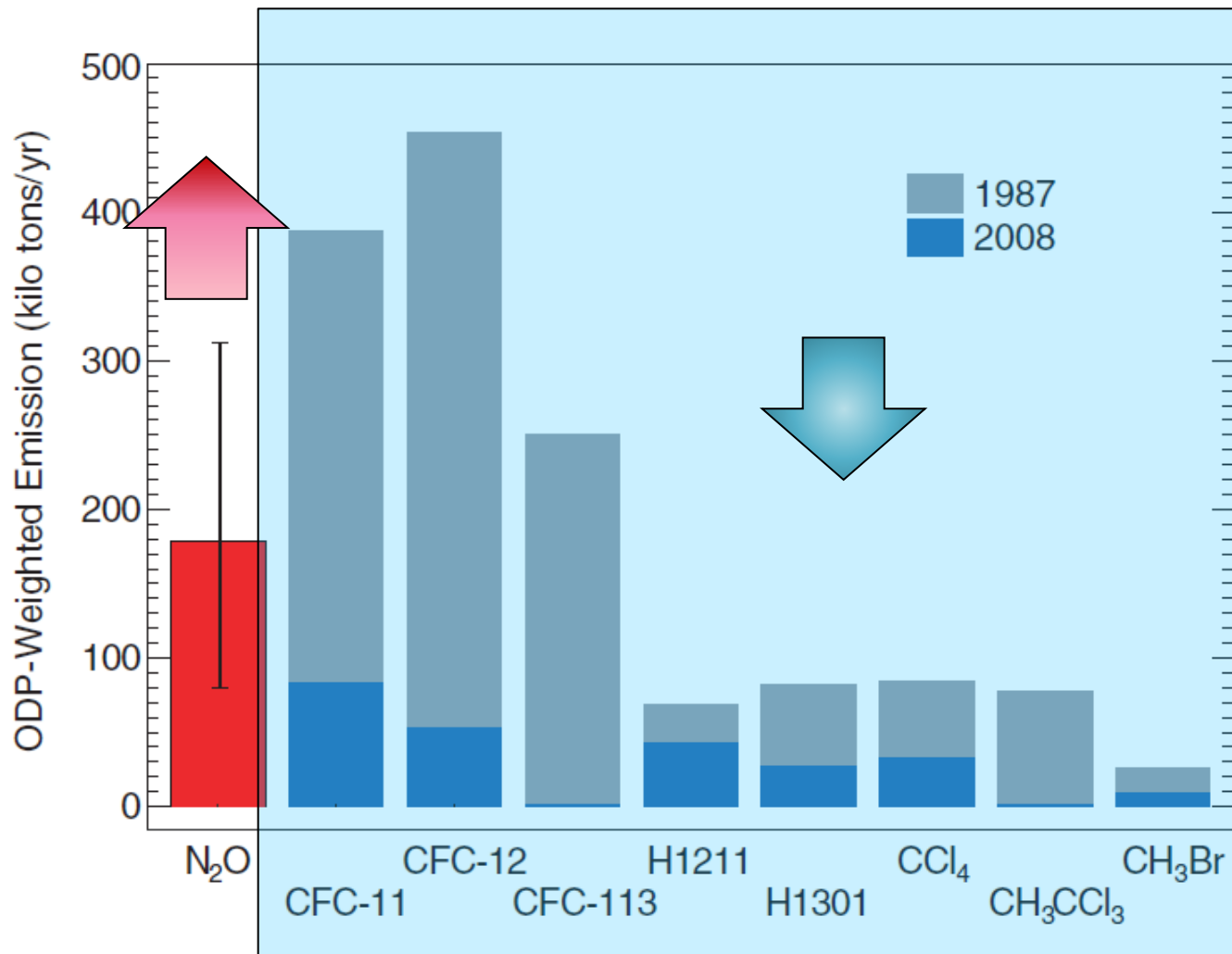
A **Sankey diagram** is a flow diagram where the width of each arrow (or band) is proportional to the quantity of the flow it represents. It's often used to show how resources like energy, money, or materials move through a system.



Halogenated Compounds [LL-HCs: long-lived HCs] including Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs), Hydrofluorocarbons (HFCs); CH₄: Methane; O₃: Tropospheric & Stratospheric Ozone; sH₂O: Stratospheric Water Vapor; AER: Aerosol direct effects; Clouds: Aerosol-induced cloud effects; CO & NMVOCs: Carbon Monoxide & Non-Methane Volatile Organic Carbons; BC: Black Carbon; SO₂: Sulfur Dioxide; NO_x: Nitrogen Oxides; OC: Organic Carbon; NH₃: Ammonia. Sector to emissions data taken from the analysis herein (including emissions contributions to net temperature change), emissions to forcings data taken from ref. ². Biomass burning and land use changes not included. Agriculture includes energy-use emissions from forestry and fisheries. Power represents power generation.



Historical and projected ODP-weighted emissions of the most important ODSs and non- CO_2 greenhouse gases. Non- N_2O ODS emissions are taken from WMO ([Global Ozone Research and Monitoring Project Report No. 50, Geneva, Switzerland, 2007](#)). Hydrofluorocarbon (HFC) projections are taken from Velders et al. [Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 10949](#) & [Science, 2009, 326, 123-125](#)



Ozone depleting potential (ODP) is a measure of how much damage a chemical can cause to the ozone layer compared with a similar mass of trichlorofluoromethane (CFC-11). **CFC-11, with an ODP of 1.0**, is used as the base figure for measuring ozone depleting potential.

Montreal Protocol included a ban on the production and consumption of CFCs in 1987.

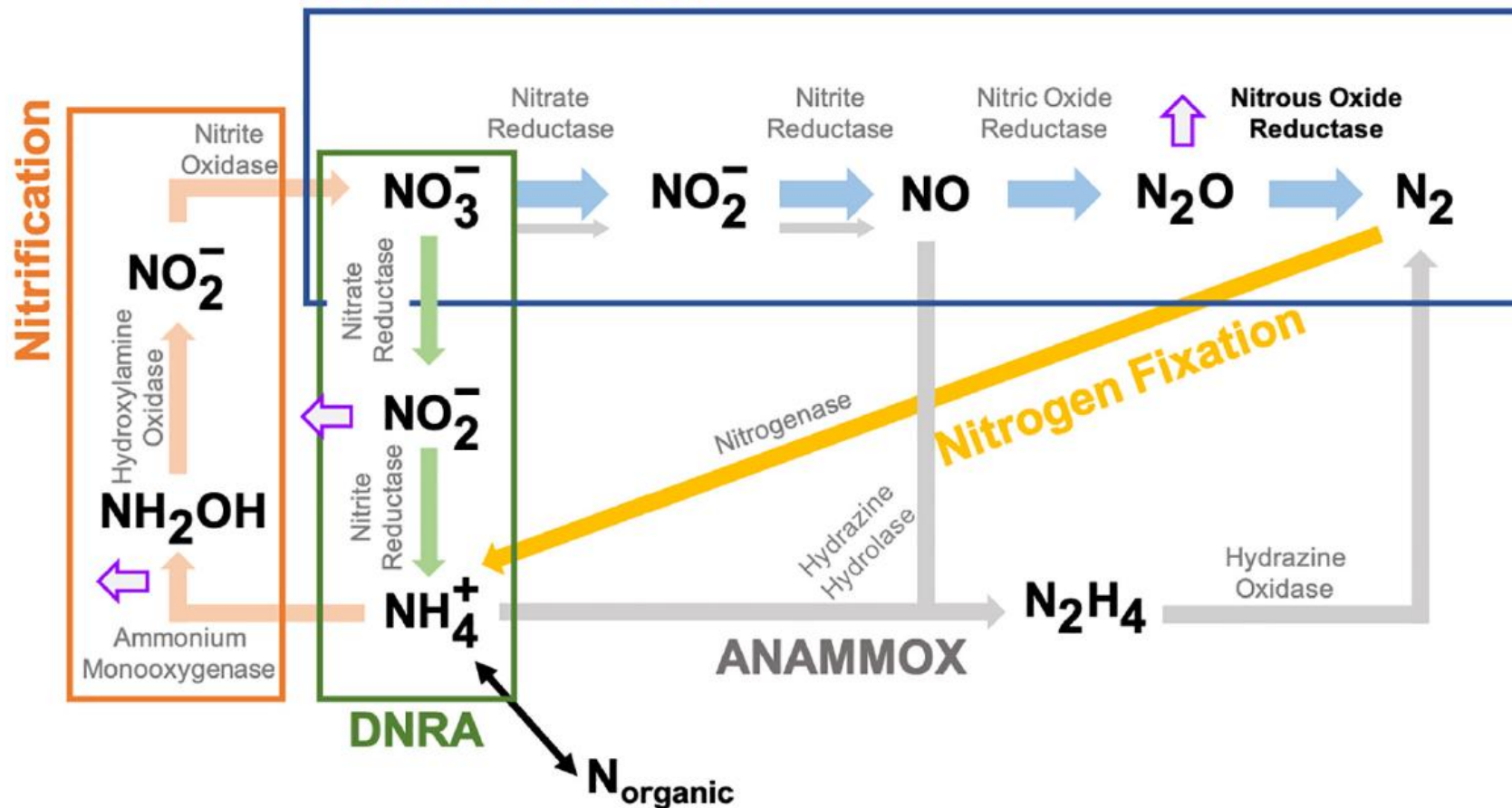
Comparison of annual N₂O ODP-weighted emissions with emissions of other Ozone Depleting Substances (ODSs). A report from the Global Monitoring Division, Earth System Research Laboratory, National Oceanic and Atmospheric Administration for CFC-11, CFC-12, Halon 1211 (H1211), Halon 1301 (H1301), and CH₃Br; all other emissions are taken from WMO. [Science](#), 2009, 326, 123-125

Aircraft engines operating at high altitudes emit significant amounts of **water vapour (H_2O)** as a combustion byproduct, along with **nitrogen oxides (NO_x)** that can oxidise to form **nitric acid (HNO_3)**. In the **cold lower stratosphere**, particularly at polar or high-latitude regions, the addition of H_2O increases the local relative humidity, and in combination with HNO_3 , can lead to the condensation of **nitric acid trihydrate (NAT: Type I)** or water–ice particles (**Type II**). These particles constitute **polar stratospheric clouds (PSCs)**.

These clouds provide surfaces for **heterogeneous chemical reactions** that convert inactive chlorine reservoir species (e.g., ClONO_2 , HCl) into active, ozone-depleting forms (e.g., ClO).

Additional read: A significant ozone depletion could result from the formation of additional polar stratospheric clouds produced by the injection of H_2O and HNO_3 by the aircraft engines. [Journal of Atmospheric Chemistry volume 18, pages103–128\(1994\)](#)

DENITRIFICATION



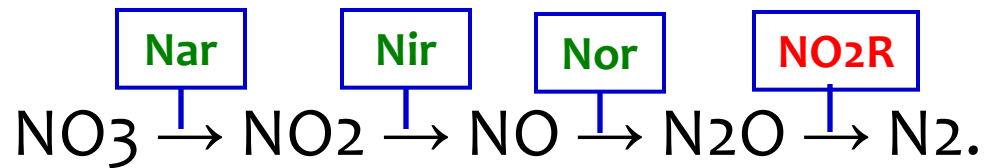
ANAMMOX: Anaerobic NH_4^+ oxidation, **DNRA:** Dissimilatory nitrate reduction to NH_4^+

In O_2 -limited environments (anaerobic conditions), denitrifying bacteria can switch from O_2 -dependent respiration to nitrate (NO_3^-) respiration in which the NO_3^- is sequentially reduced via nitrite (NO_2^-), nitric oxide (NO) and N_2O to N_2 .

N_2O accumulates during biological nitrogen removal from wastewater as a byproduct of nitrification by ammonia oxidizing bacteria and/or as a result of incomplete denitrification by heterotrophic denitrifying bacteria in the activated sludge (Schreiber et al Front. Microbiol., ., 2012, 3, 372).

A significant proportion of the rise in atmospheric N_2O is microbial in origin. This implies that the enzyme responsible for reduction, **nitrous oxide reductase (NO₂R)**, does not always carry out the final step of denitrification either efficiently or in synchrony with the rest of the pathway. FEMS Microbiol. Letts. 365, 2018, fnx277

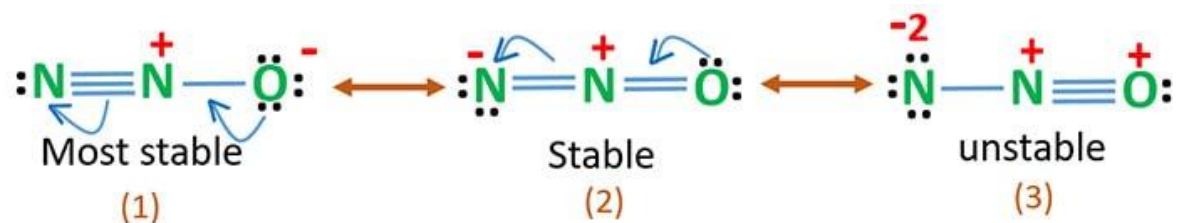
Under anaerobic conditions, denitrifying organisms perform the reduction of inorganic NO_3^- or NO_2^- in sequential steps that involve the abstraction of an oxygen atom at each step, with the production of gaseous molecules at intermediate stages:



Each step is catalyzed by a distinct enzyme—nitrate reductase (Nar), nitrite reductase (Nir), nitric oxide reductase (Nor), and nitrous oxide reductase (N_2OR)—located either in the inner membrane or the periplasm of various α -, β -, γ -, and ϵ -proteobacteria.

N₂O is a linear asymmetrical molecule, and its electronic and structural properties can be described with the resonance structures.

N₂O reduction is highly exergonic ($\Delta G^\circ = -339.5 \text{ kJ mol}^{-1}$), and this molecule is a stronger oxidant than N₂, as seen by its redox potential ($E^\circ (\text{pH } 7.0) = 1.35 \text{ V}$). Although this reaction is thermodynamically favorable, a high activation barrier (250 kJ mol^{-1}) makes this process kinetically unfavorable--consistent with a spin-forbidden process. J. Am. Chem. Soc. 1987, 109, 5539-5541



The reduction of N₂O to molecular nitrogen (N₂) requires two protons and two electrons, according to Eq. (1):



This is a challenging reaction to be catalyzed by a metalloenzyme, as nitrous oxide is not just kinetically inert to decomposition but also a poor transition metal ligand, due to its weak σ -donating and π -accepting properties

For **nitrous oxide (N₂O)** in its **ground electronic state**, the **spin multiplicity** is 1.

- The ground-state electron configuration of N₂O has **all electrons paired** → total spin quantum number $S=0$.
- Spin multiplicity is given by $2S+1 = 1$ [**singlet state**]. This is the stable atmospheric form.

N₂O can be excited via **UV absorption** or photodissociation, leading to various states:

State	Notation	Spin multiplicity	Notes
First excited singlet	$^1\Delta, ^1\Pi$	1	Spin-allowed from ground state via electric dipole transitions. Short-lived.
First excited triplet	$^3\Delta, ^3\Pi$	3	Spin-forbidden from ground state; often accessed via intersystem crossing.
Rydberg states	ns, np	1 or 3	Higher energy; lead to ionization or dissociation.

Photodissociation Pathways & Multiplicity: N₂O absorbs UV light (< 200 nm), it can dissociate:
N₂O → N₂ (singlet) + O(¹D) → Both products singlet (multiplicity 1)

N₂O → N₂ (singlet) + O(³P) → O atom triplet state (multiplicity 3)

The O(³P) channel is spin-forbidden from the singlet ground state.

Triplet channels lead to slower, spin-forbidden reactions; singlet channels are faster but require higher-energy UV photons

- In quantum mechanics, spin selection rules for electronic transitions state

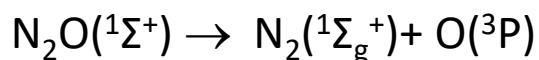
$$\Delta S = 0$$

The total electron spin must be conserved during the transition/ reaction.

If a reaction or transition changes the spin state (e.g., singlet \rightarrow triplet or triplet \rightarrow singlet), it is spin-forbidden.

- Spin-forbidden processes occur more slowly than spin-allowed ones because they rely on **spin-orbit coupling** to mix states of different spin multiplicities.
- Often occur through **intersystem crossing (ISC)**—a non-radiative process that changes multiplicity.
- Important in **atmospheric chemistry**

For **N₂O photodissociation**:



N₂O reduction is thermodynamically favored ($\text{N}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N}_2 + \text{H}_2\text{O}$; E^{Red}_0 : pH 7:0 is + 1:35V; $\Delta G'_0 = -339.5 \text{ kJ}\cdot\text{mol}^{-1}$), its activation energy barrier of 250 kJ·mol⁻¹ leads to substantial kinetic stability and chemical inertness.

The biological reduction of N₂O to N₂ is catalyzed by a specialized enzyme, nitrous oxide reductase (usually referred as NO₂R), a periplasmic, homodimeric metalloprotein of 130 kDa that contains with two distinct multinuclear Cu centers per subunit, a binuclear Cu_A ET site, and a catalytic Cu_Z center, a novel μ₄-sulfide-bridged tetranuclear Cu cluster. N₂O reductase (N₂OR) catalyzes the final step of denitrification, that is, the two-electron reduction of N₂O to N₂.

The crystal structures of N₂OR from *Pseudomonas nautica* and *Paracoccus denitrificans* at 2.4 Å and 1.6 Å resolutions, have revealed a novel μ_4 -sulphide-bridged tetranuclear Cu₄ cluster.

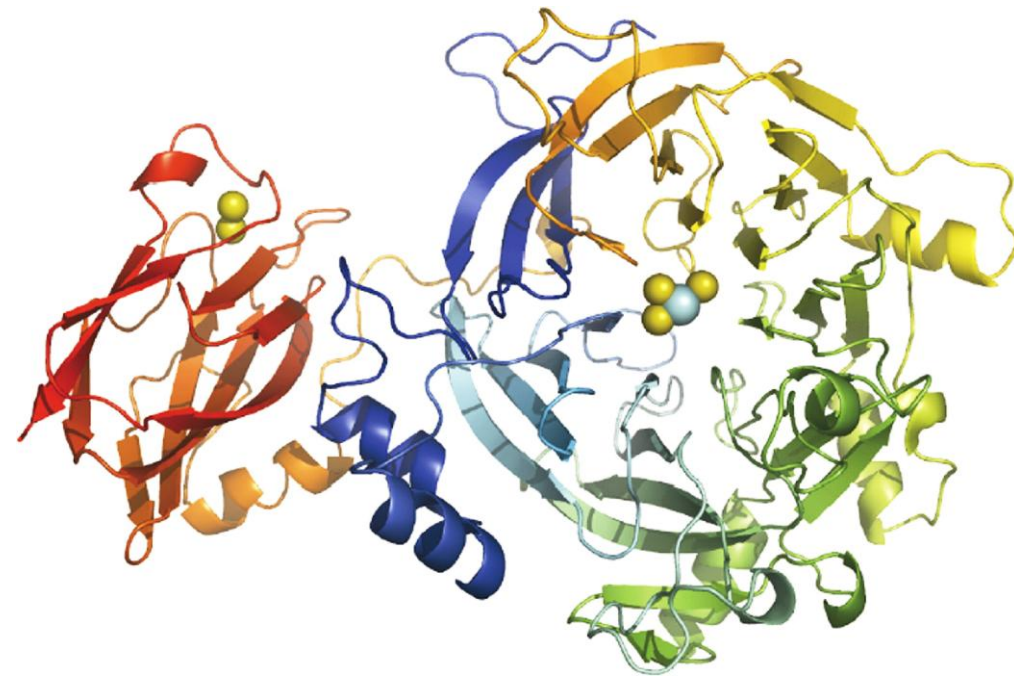
The reduction of nitrous oxide is the last step in the denitrification process of the geo-biological nitrogen cycle:



N₂ORs have been characterised from a wide variety of bacteria including *Achromobacter cycloclastes* (AcN₂OR), *Alcaligenes xylosoxidans* (AxN₂OR), *P. nautica* (PnN₂OR) and *P. denitrificans* (PdN₂OR).^{3,4}

The reduction of N₂O is thermodynamically favourable but it is kinetically inert, and is a poor ligand for transition metals. N₂ORs are a highly conserved protein family of ~130 kDa homodimers containing multiple Cu atoms. Since the original spectroscopic work in the 1980s, more recent, extensive spectroscopic and mutational studies have shown these Cu atoms to be organised into two distinct types of Cu-centres.

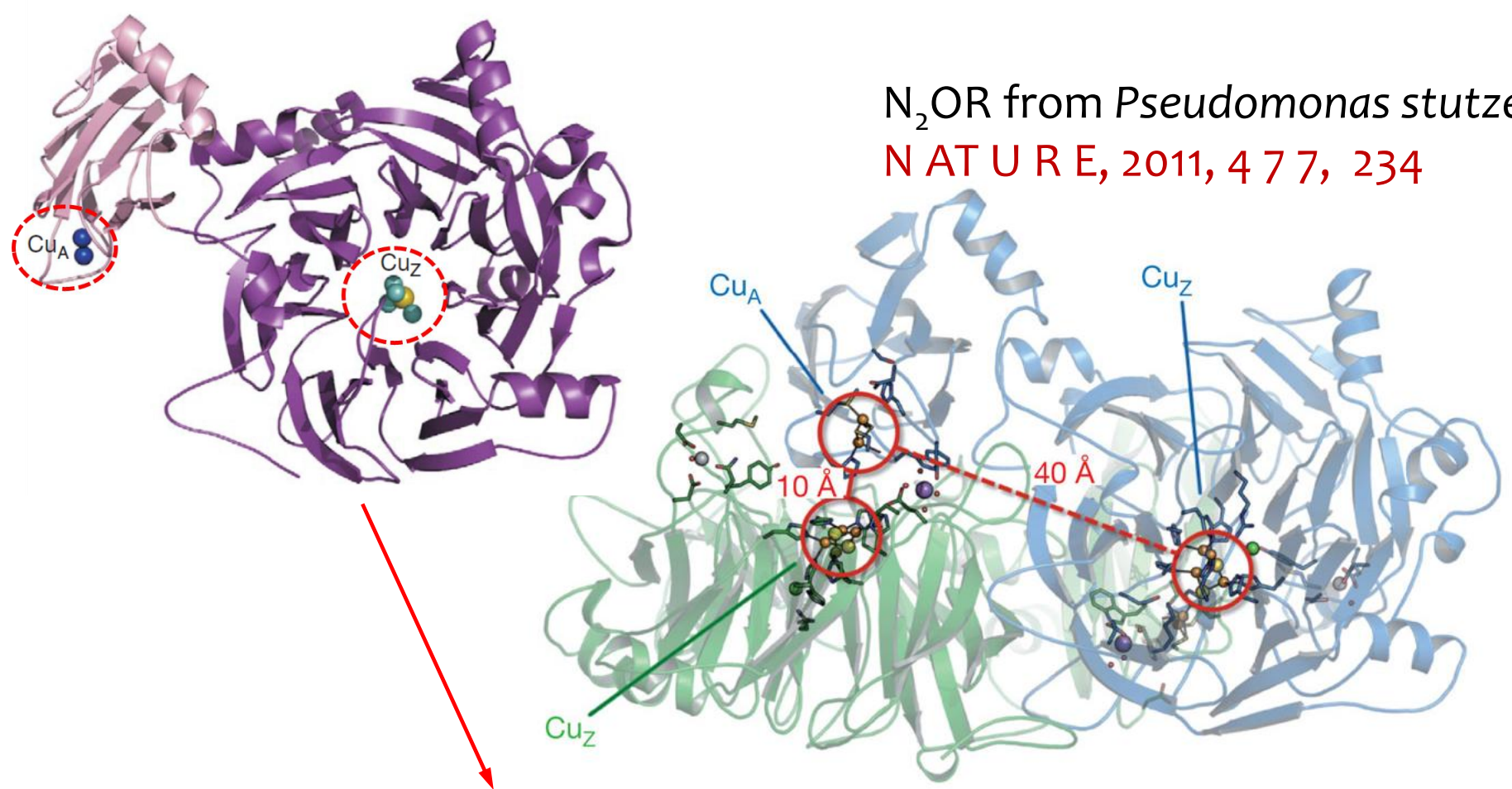
Extensive spectroscopic and mutational studies have shown **these Cu atoms to be organized into two distinct types of Cu centres**. Subsequent X-ray crystal structure analysis of PnN_2OR (from *P. nautica*) and PdN_2OR (*P. denitrificans*) confirmed the presence of two multi-nuclear Cu-centres per monomer. This includes a Cu_A site that, in analogy to the role of this centre in cytochrome c oxidase, is proposed to mediate electron transfer to the second multi-nuclear catalytic Cu_Z centre. The Cu_Z centre is a novel μ_4 -sulphide-bridged tetranuclear Cu cluster ligated by seven His ligands and is the site of N_2O reduction.



Overall structure of a monomer of AcN_2OR showing two domains; a C-terminal domain that contains the Cu_A cluster (left) and an N-terminal domain that contains the catalytic Cu_Z site (right). Copper atoms are shown as yellow spheres.

isolated under aerobic conditions

N_2OR from *Pseudomonas stutzeri*
NAT URE, 2011, 477, 234

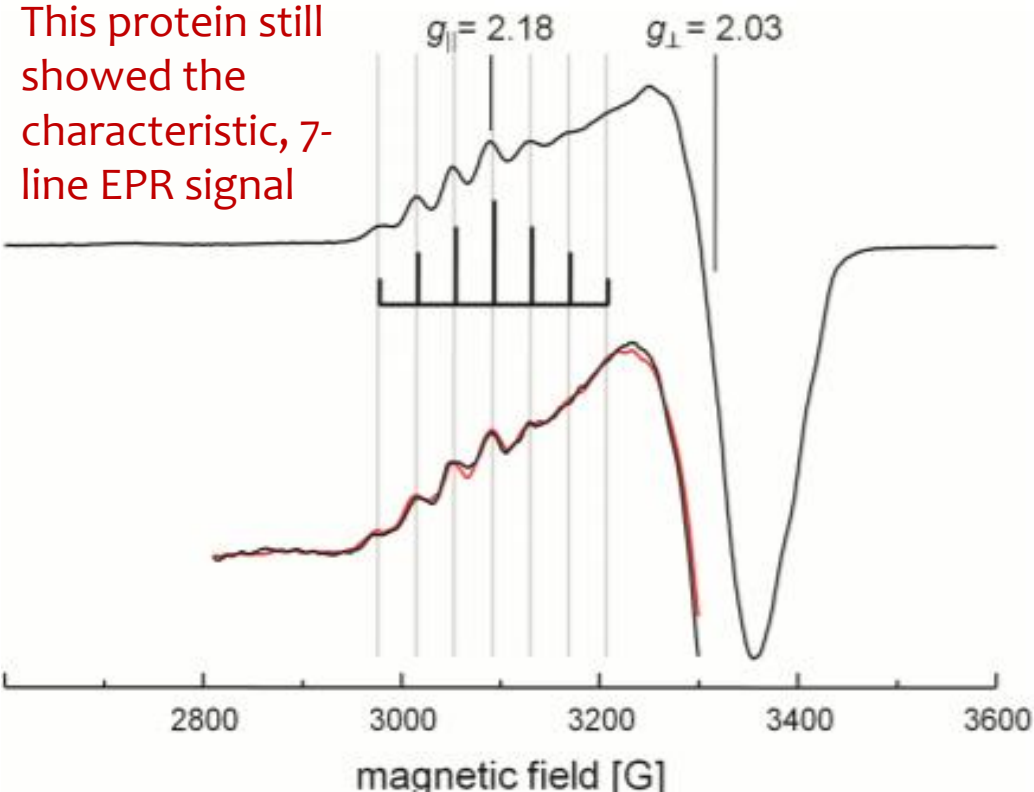


Ribbon diagram of a monomer of N_2OR from *Achromobacter cycloclastes* showing two domains, a C-terminal cupredoxin domain (left, in lighter shade) carrying the Cu_A center (dark blue spheres) and the N-terminal -propeller domain (right, darker shade) with the catalytic Cu_Z center in which copper and inorganic S ions are shown as light blue and dark yellow spheres. (Handbook of Metalloproteins; A. Messerschmidt, Ed.; John Wiley & Sons: Chichester, 2007; Vol. 4, pp 1–15)

The reduction of N₂O is a thermodynamically favorable reaction with $\Delta G = -104.6 \text{ kJ mol}^{-1}$ but its thermo decomposition is kinetically inert owing to a high activation barrier of approximately 250 kJ mol⁻¹. N₂O is a weak σ -donor and weak π -acceptor molecule. However, several complexes of transition metals are able to bind and activate N₂O. However, the M–N₂O complexes reported so far are transient species and is rapidly converted to N₂ and to the corresponding metal-oxidized species. These studies are consistent with a reaction mechanism involving the scission of the NN–O bond [Angew Chem Int Ed. 2010, 49:1018–1024; J Am Chem Soc; 2006, 128, 278–290](#)

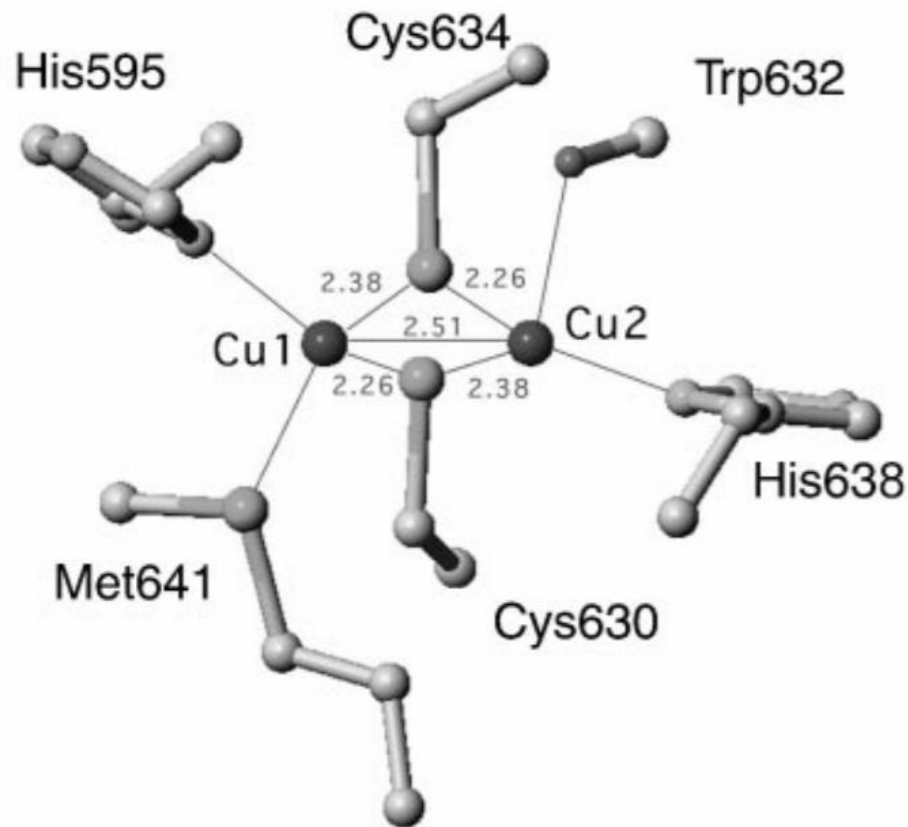
Cu_A is of a characteristic, pink colour in the mixed-valent [Cu_{A1} (1.5):Cu_{A2} (1.5)] state and its conformation was virtually identical in its oxidized form in N₂OR. The spectroscopic hallmark of Cu_A is the narrow 7-line hyperfine splitting in the g_{||} region of the electron paramagnetic resonance (EPR) spectrum that originates from an unpaired electron fully delocalized over two copper nuclei with a nuclear spin I[Cu = 3/2].

The Cu_{A1}–Cu_{A2}
distance was 2.5 Å.
This protein still
showed the
characteristic, 7-
line EPR signal

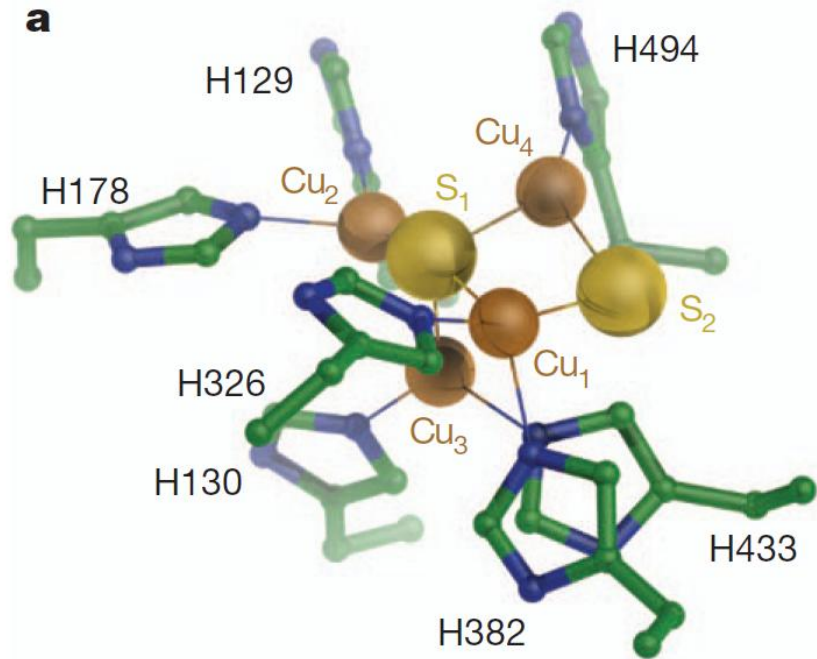
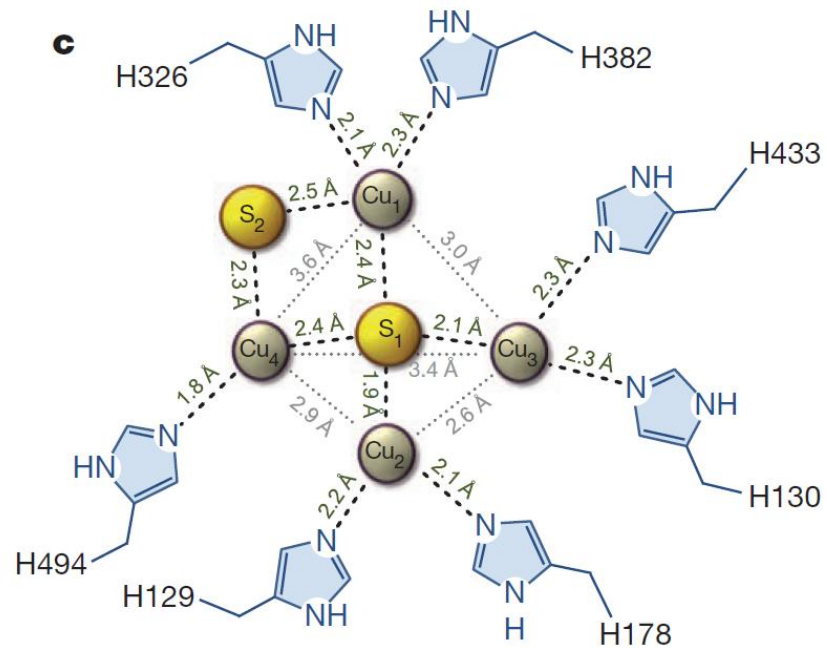


X-band electron paramagnetic resonance (microwave frequencies around 9.4 GHz) spectrum of the sample of *P. stutzeri* N₂OR that was used for crystallization. The characteristic 7-line hyperfine pattern confirms the unpaired electron at the binuclear Cu_A center to be delocalized between the two I=3/2 nuclei.

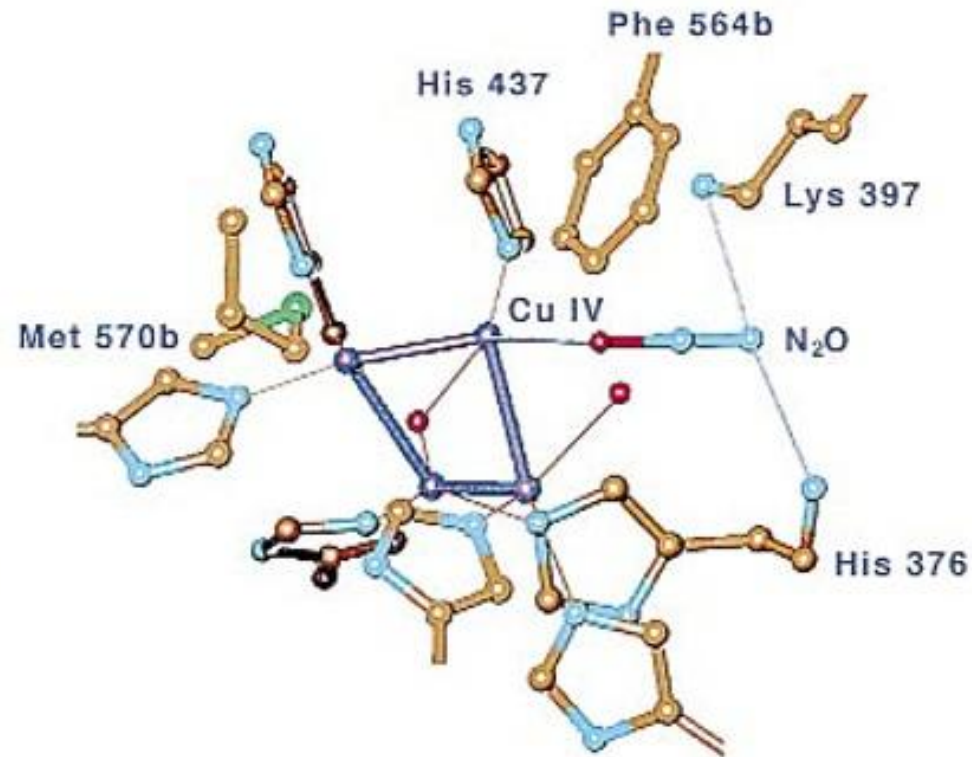
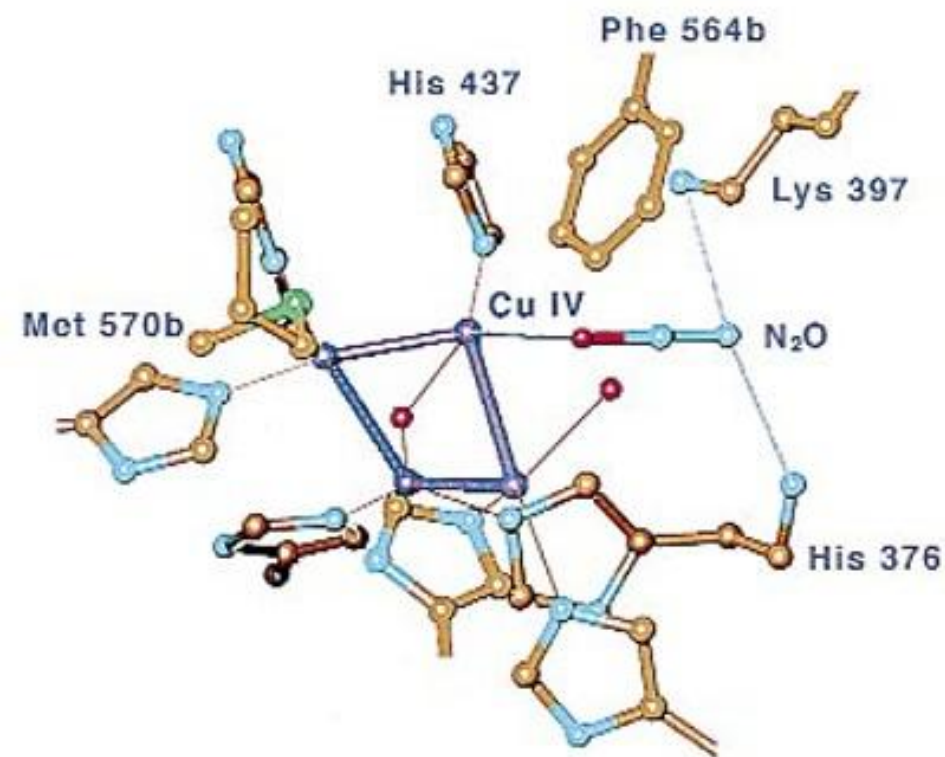
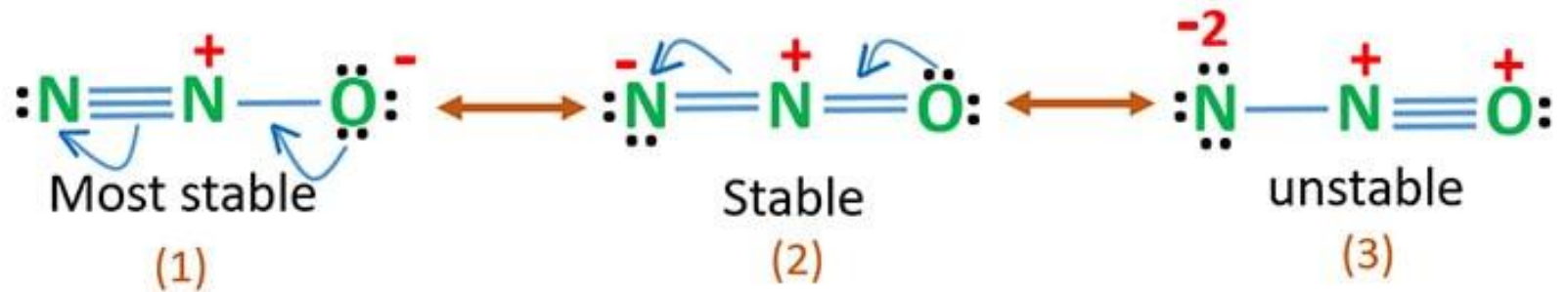
[Nature structural biology, 2000, 7 \(3\), 191-197](#); [Nature, 2011, 477, 234](#).



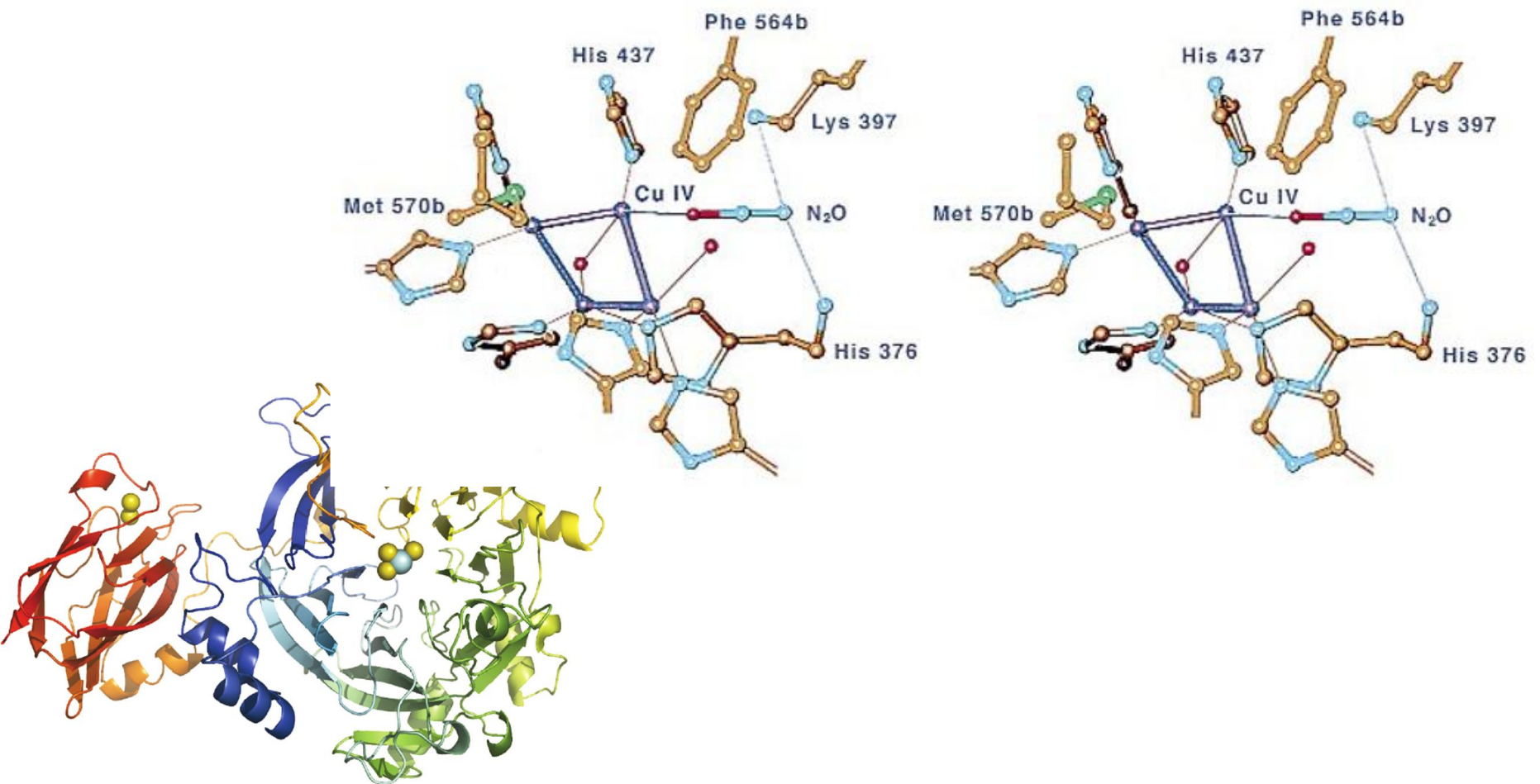
The Cu₂S₂ (cysteine) core: Cu1–Cys630 and Cu2–Cys634 ...the terminal histidine–copper bond lengths are 2.03 Å (Cu1–His595) and 1.98 Å (Cu2–His638). The axial thioether sulphur of Met641 is at 2.45 Å from Cu1, whereas the other axial ligand, the backbone carbonyl oxygen of residue Trp632, is at 2.57 Å from Cu2. The Cu–Cu distance is 2.51 Å. Hydrogen bonds with water molecules couple His638 to certain CuZ ligands across the monomer–monomer interface. Trp632 is also hydrogen-bonded across the interface.

a**c**

The 7-line hyperfine pattern of the X-band electron paramagnetic resonance (EPR) spectrum confirmed the mixed-valent $[\text{Cu}^{1.5+}:\text{Cu}^{1.5+}]$ state of oxidized CuA; [Nature structural biology, 2000, 7 \(3\), 191-197](#)



N_2O binding and reduction mechanism: binding of N_2O molecule at the CuIV of the CuZ cluster. (i) N_2O binds to the oxidized IVCu through its O-atom; (ii) two electrons are transferred to IVCu from the other Cu_A -ions & transferred to the oxygen, which acquires a proton from Lys 397; liberating N_2 ; (iii) the remaining OH^- could either stay on the IVCu , at basic pH as in our structure, or be released after protonation by a second proton from Lys 397, with the formation of a water molecule.



Incomplete denitrification terminating with release of N_2O is a major contributor to the detrimental environmental effects of excessive fertilizer use, and consequently the application of recombinant N_2O reductase (NO_2R) in a suitable host is of major interest for bioremediatory applications.

Nitrous oxide reductase is inhibited under low pH, and is highly sensitive to oxygen. High O_2 concentration and low pH favours N_2O as the end product.

Present emphasis is to elucidate the mechanism of N_2O reduction and on enzyme engineering through a combination of environmental chemistry and synthetic biology to develop biotechnological tools for the efficient bioremediation of N_2O emissions.

(<https://www.slideserve.com/cala/chapter-9-biogeochemical-cycling> and PNAS, 2019, 116 (26), 12822–12827.

Incomplete denitrification terminating with release of N_2O is a major contributor to the detrimental environmental effects of excessive fertilizer use, and consequently the application of recombinant N_2O reductase (NO_2R) in a suitable host is of major interest for bioremediatory applications.

Summary

- Ecological resources are critical to sustainability and our well-being
- Post-industrial revolution we have had unprecedented success in converting ecological resources into economic goods
- Ecological resources are being consumed at a rate which is much faster than nature can replenish back, especially non-renewable fossil fuels for our increasing energy demand
- Conversion of ecological resources into economic resources is putting “newly” created matter into the environment and at rates much faster than our ecology can handle/assimilate
- Science and Technology, until now, has mostly “shifted” the problem into larger scales
- We need to have a “holistic” view to understand what is sustainable
- This requires quantifying sustainability using metrics such as the LCA