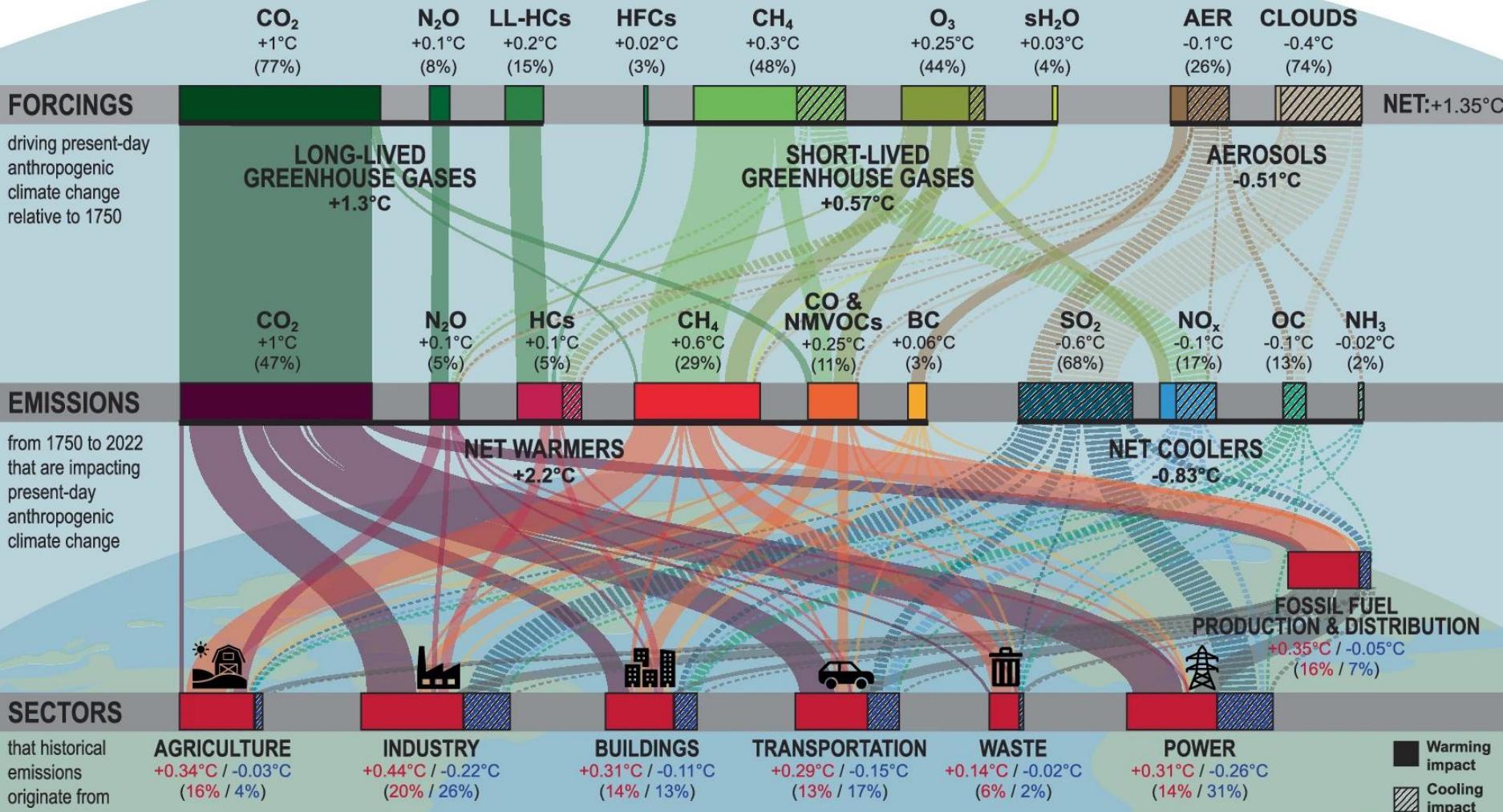


Sustainability and Chemistry

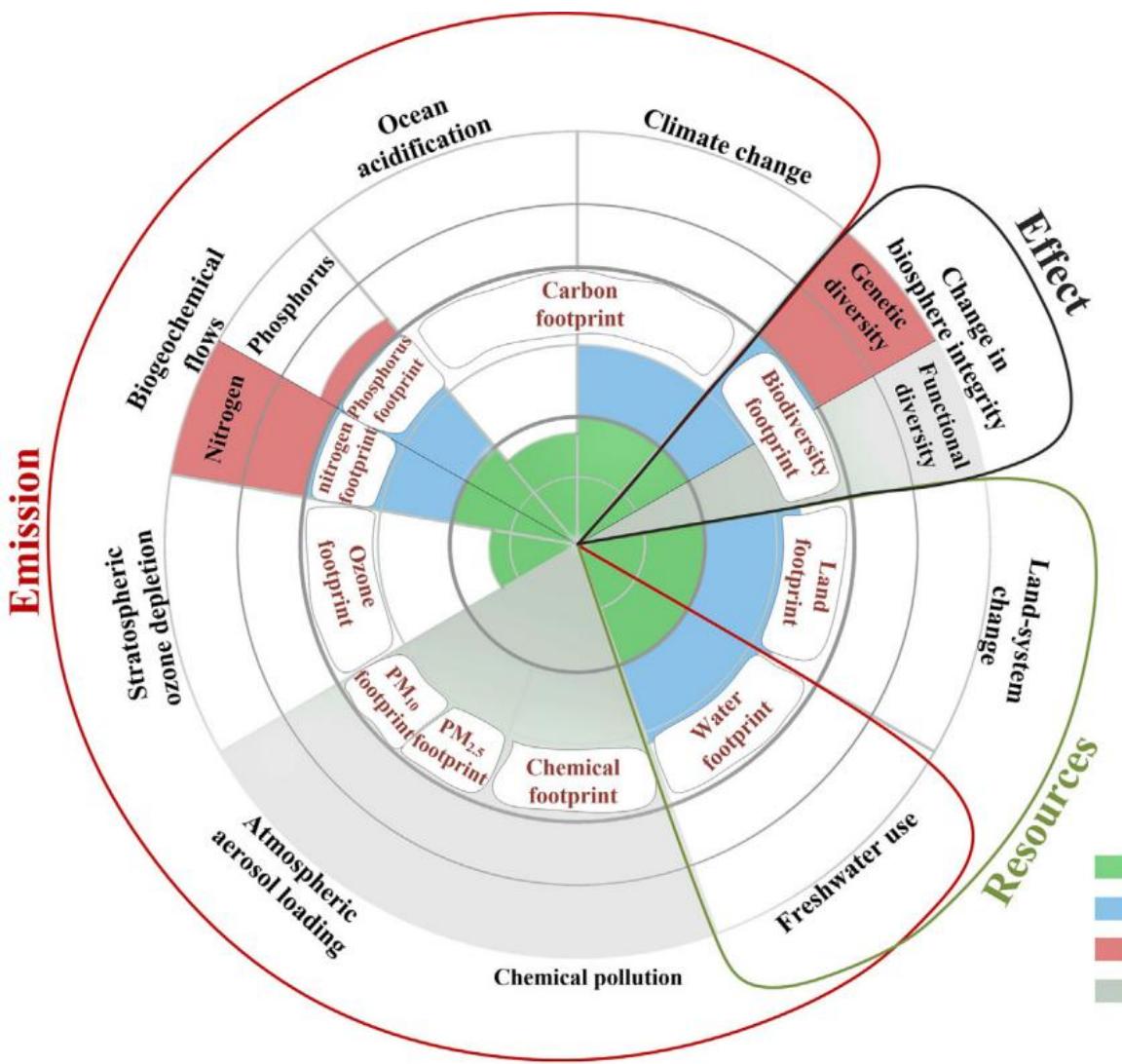
CH5106: L7

Instructors: Sayam Sengupta
Swaminathan Sivaram
Amitava Das

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.

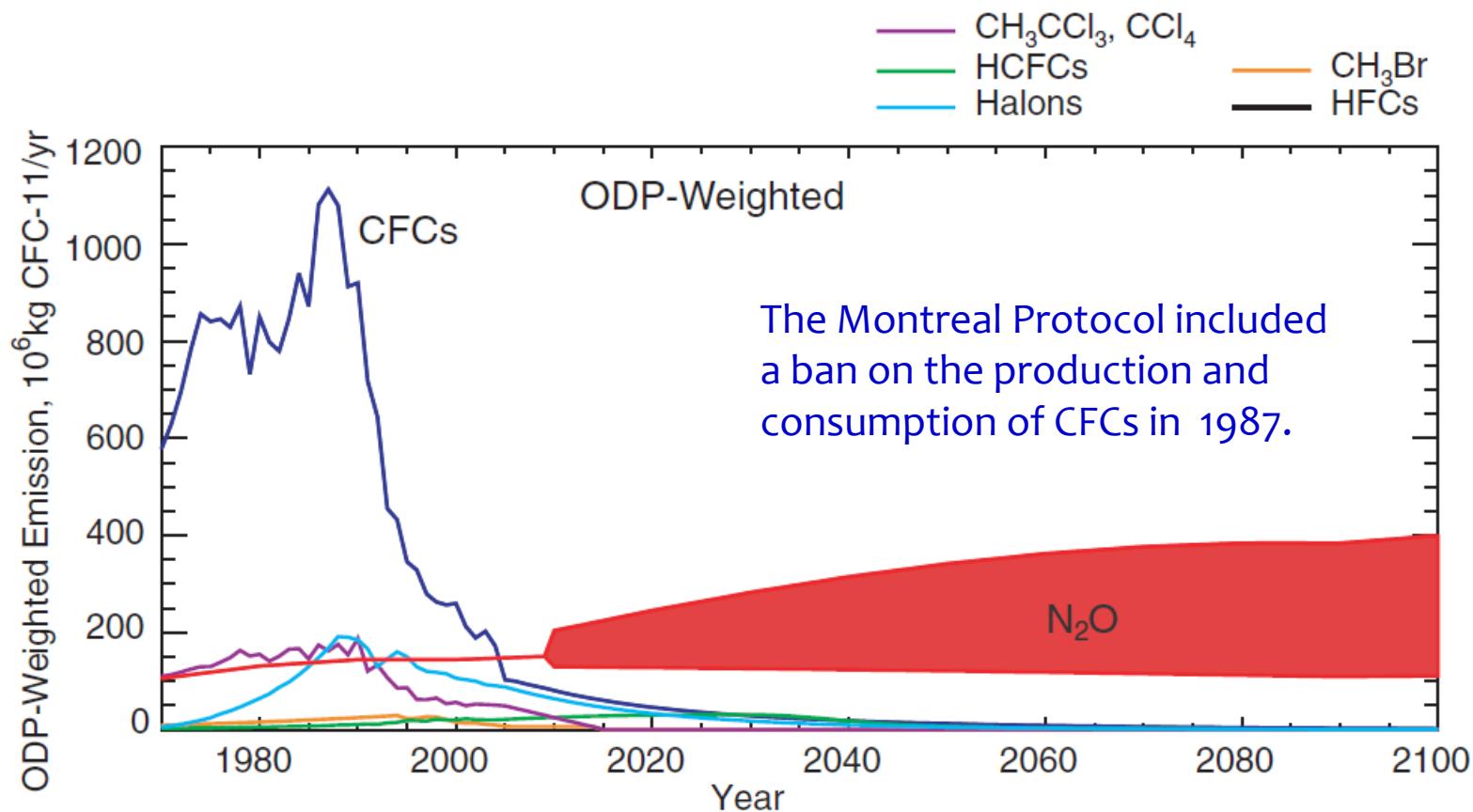


Halogenated Compounds [LL-HCs: long-lived HCs] including Chlorofluorocarbons (CFCs), Hydrochlorofluorocarbons (HCFCs), Hydrofluorocarbons (HFCs); CH₄: Methane; O₃: Tropospheric & Stratospheric Ozone; sH₂O: Stratospheric Water Vapor; AER: Aerosol direct effects; Clouds: Aerosol-induced cloud effects; 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.



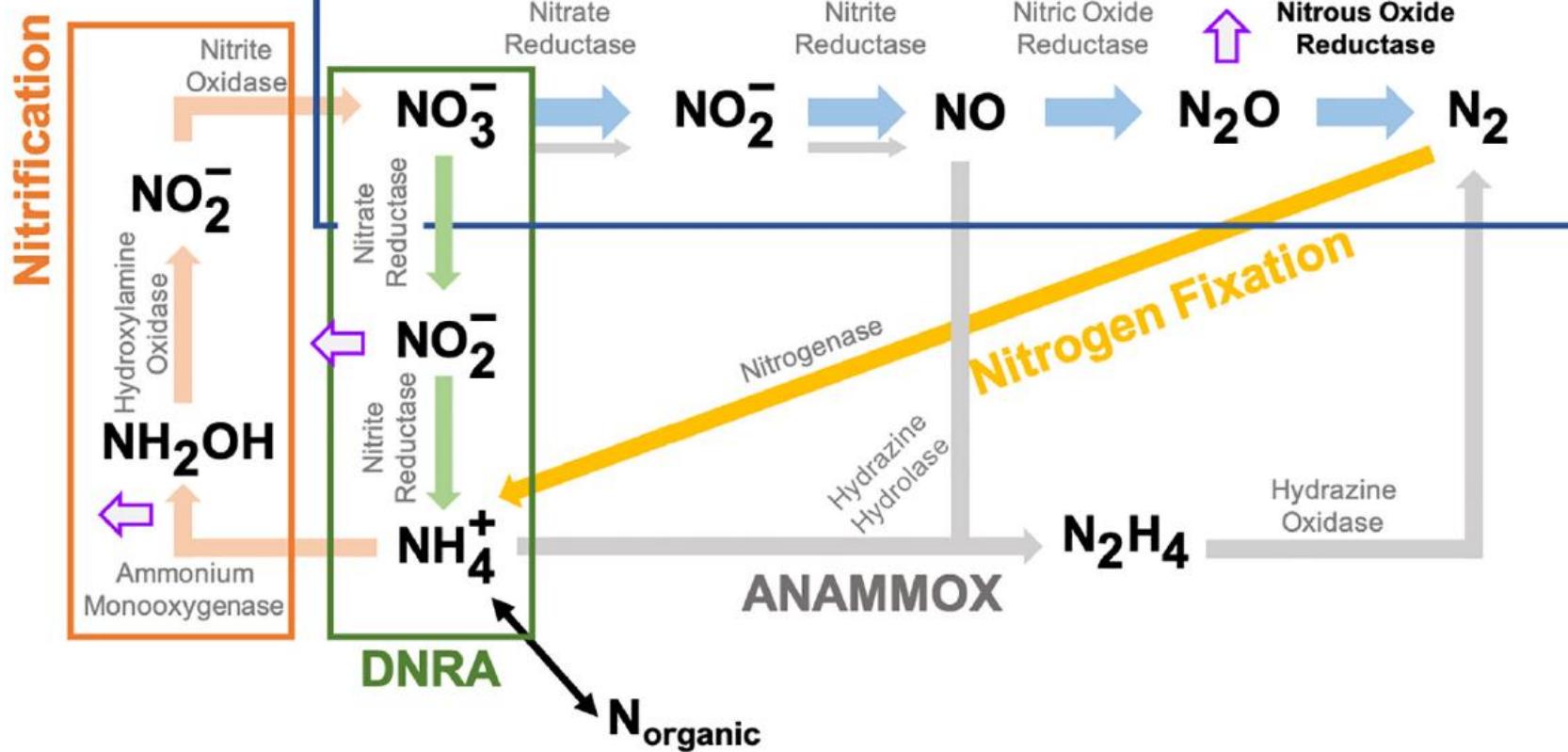
Planetary boundaries and environmental footprints (updated from Steffen et al. (2015b)): Matching environmental footprint indicators based on planetary boundaries. **The outer red line circles emission footprints, green indicates resource consumption footprints, and black indicates composited footprints.**
Science of the Total Environment
785 (2021) 147383

- Below boundary
- In zone of uncertainty
- Beyond zone of uncertainty
- Boundary not quantified yet



Historical and projected ODP-weighted emissions of the most important ODSs and non-CO₂ greenhouse gases. Non-N₂O 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](#)

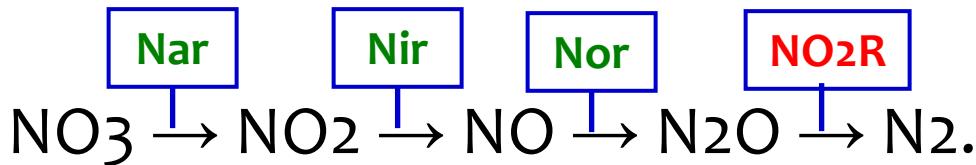
DENITRIFICATION



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 .

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.

N_2O reduction is highly exergonic ($\Delta G^\circ = -339.5 \text{ kJ mol}^{-1}$), and this molecule is a stronger oxidant than N_2 , as seen by its redox potential ($E^\circ (\text{pH 7.0}) = 1.35 \text{ V}$). Although this reaction is thermodynamically favourable, **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](#)

For nitrous oxide (N_2O) in its **ground electronic state**, the **spin multiplicity** is 1.

- The ground-state electron configuration of N_2O 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.

N_2O 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: N_2O absorbs UV light (< 200 nm), it can dissociate:

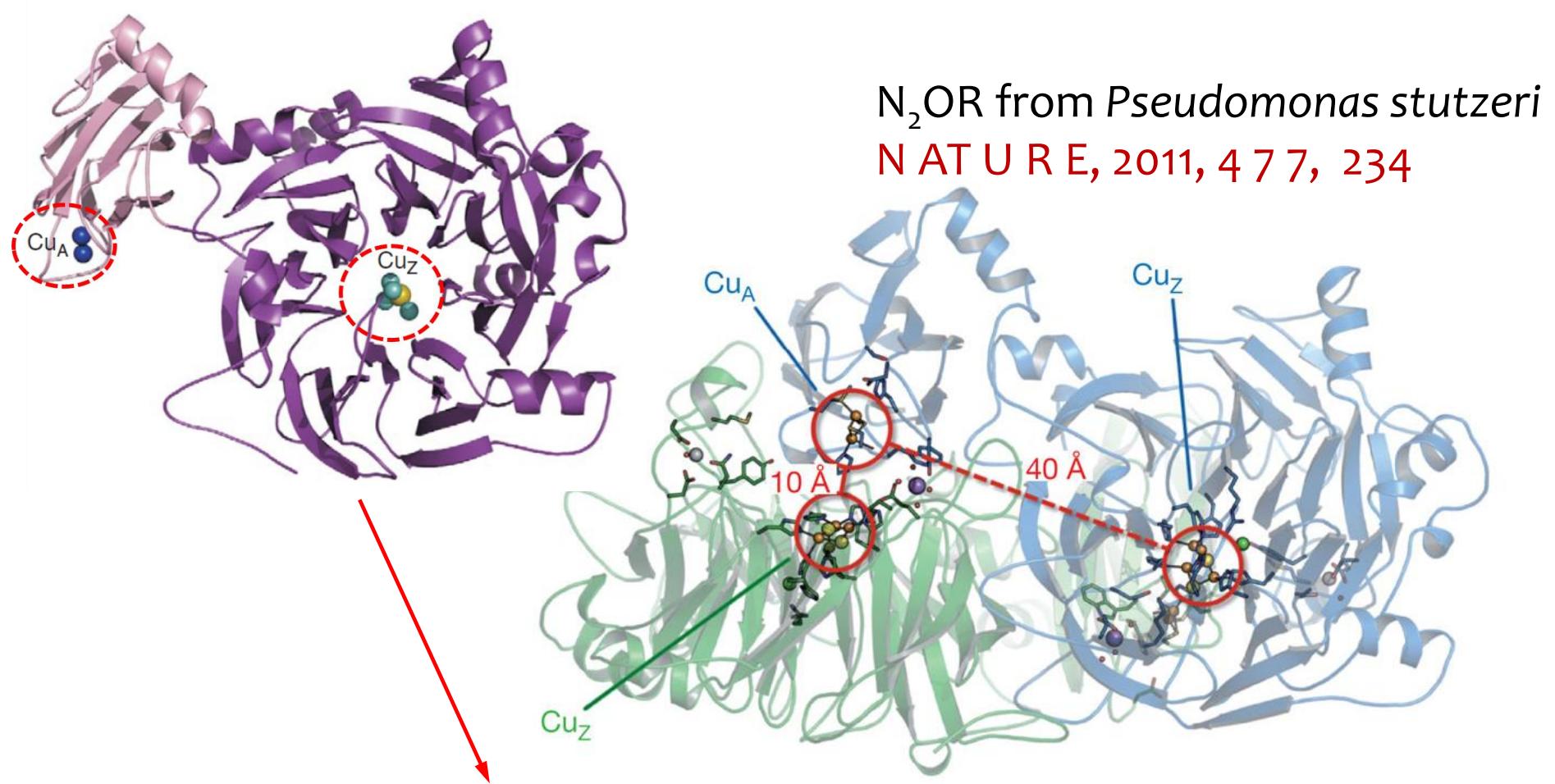


The $\text{O}({}^3\text{P})$ channel is spin-forbidden from the singlet ground state.

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

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}_o : pH 7:0 is +1.35V; $\Delta G'_o = -339.5\text{ kJ}\cdot\text{mol}^{-1}$), its activation energy barrier of 250 kJ·mol⁻¹ leads to substantial kinetic stability and chemical inertness.

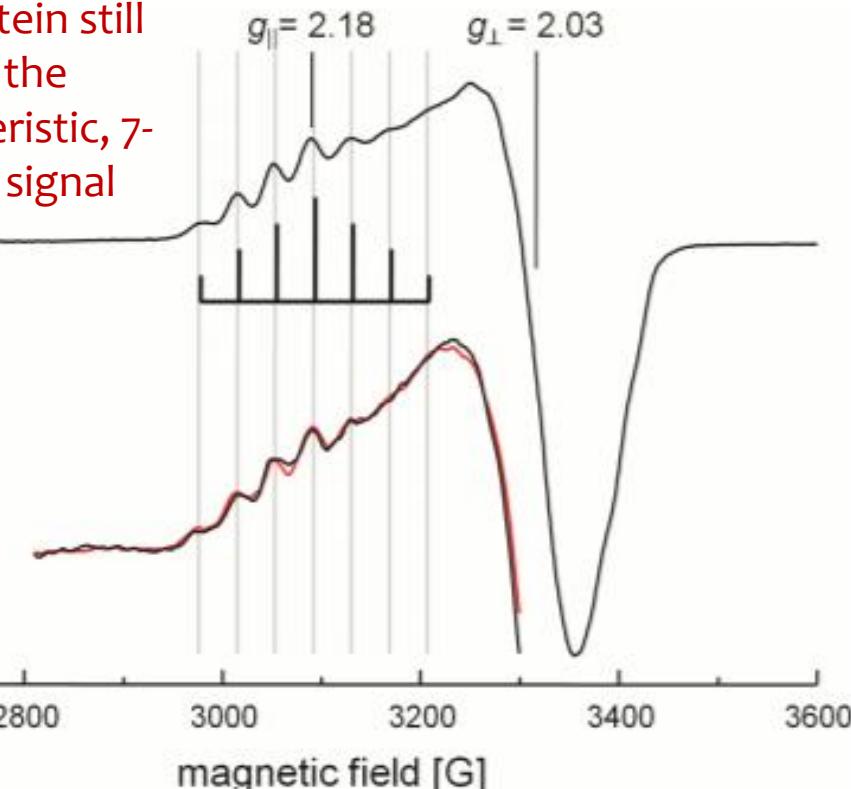
The biological reduction of N₂O to N₂ is catalyzed by a specialized enzyme, nitrous oxide reductase (usually referred as NO₂R), a periplasmic, homodimeric metalloprotein of 130 kDa that contains with two distinct multinuclear Cu centers per subunit, a binuclear Cu_A ET site, and a catalytic Cu_Z center, a novel μ_4 -sulfide-bridged tetranuclear Cu cluster. N₂O reductase (N2OR) catalyzes the final step of denitrification, that is, the two-electron reduction of N₂O to N₂.



Ribbon diagram of a monomer of *N₂OR* from *Achromobacter cycloclastes* showing two domains, a C-terminal cupredoxin domain (left, in lighter shade) carrying the CuA center (dark blue spheres) and the N-terminal -propeller domain (right, darker shade) with the catalytic CuZ 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)

CuA is of a characteristic, pink colour in the mixed-valent $[\text{Cu}_{\text{A}1}(1.5):\text{Cu}_{\text{A}2}(1.5)]$ 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 CuA1–CuA2 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.

Nuclear Spins of Copper

- Both isotopes of Cu are NMR-active:

- ^{63}Cu (69% natural abundance), $I = 3/2$
- ^{65}Cu (31% natural abundance), $I = 3/2$

Both isotopes contribute to the hyperfine splitting in EPR.

Hyperfine Splitting Rule

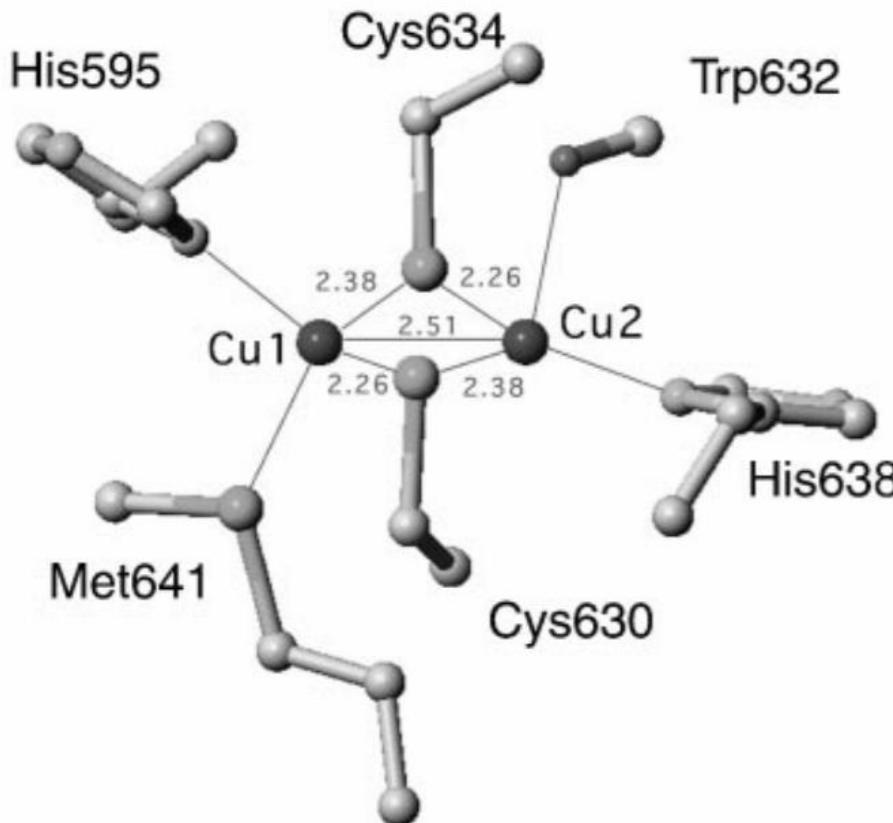
For one electron delocalized over **two equivalent Cu-nuclei** with spin I

The number of hyperfine lines is $(N) = 2nl+1$

n : number of equivalent nuclei.

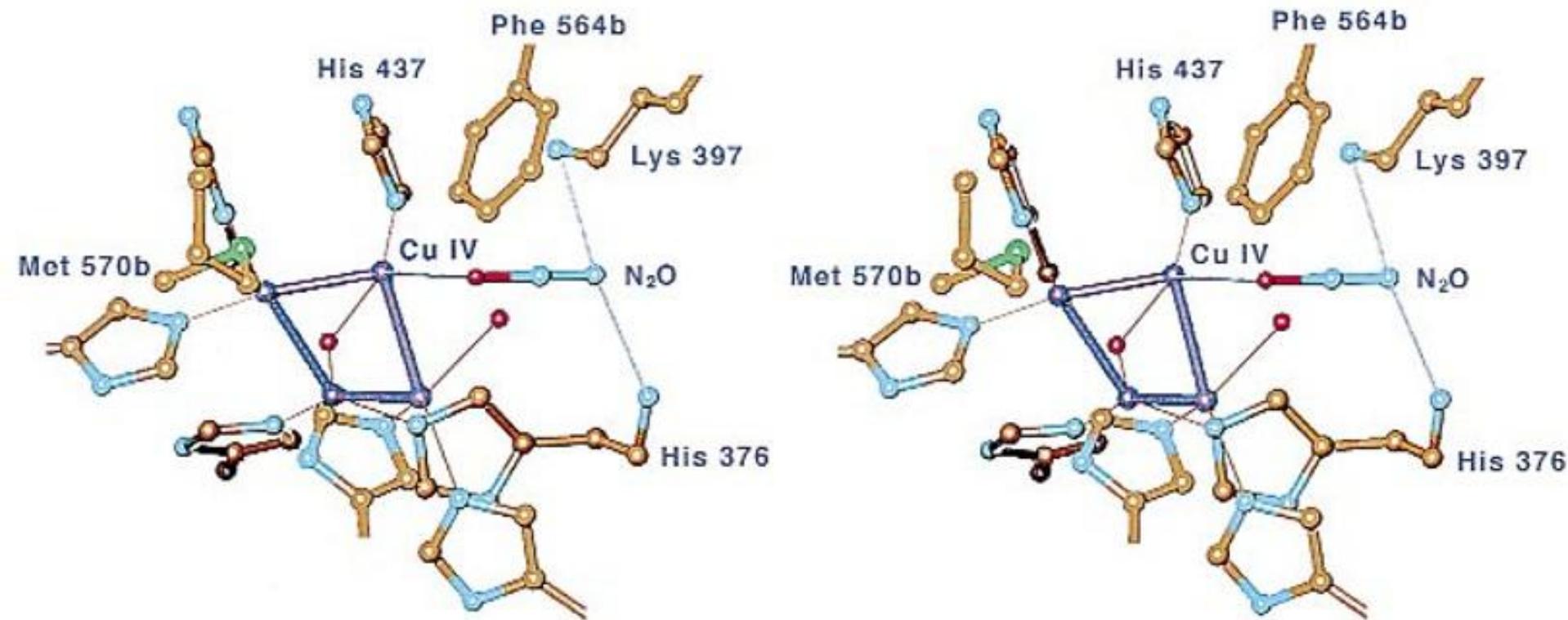
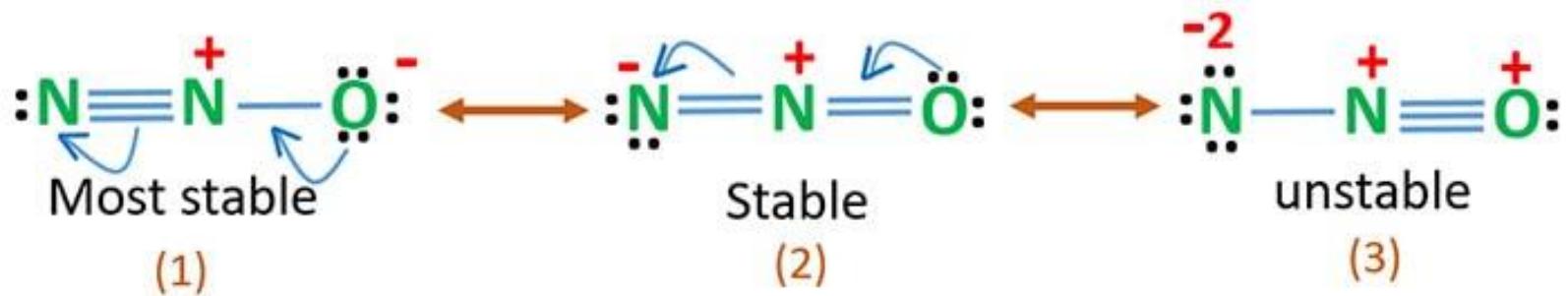
- Here: $n = 2$ and $I = 3/2$.

Thus, $N=2(2)(32)+1=7$ lines

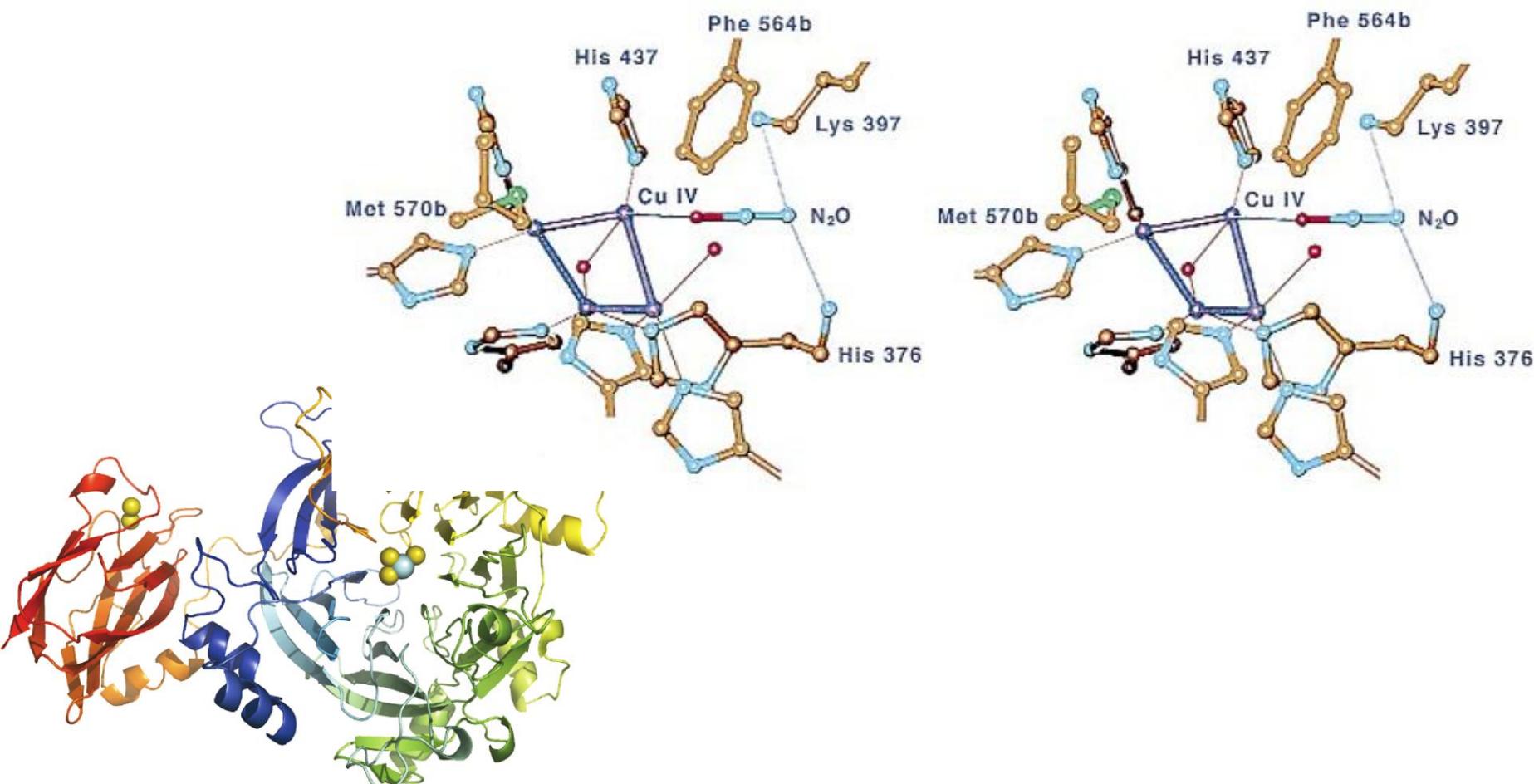


The Cu₂S₂ (cysteine) core: Cu1–Cys630 and Cu2–Cys634 ...the terminal histidine–copper bond lengths are 2.03 Å (Cu1–His595) and 1.98 Å (Cu2–His638). The axial thioether sulphur of Met641 is at 2.45 Å from Cu1, whereas the other axial ligand, the backbone carbonyl oxygen of residue Trp632, is at 2.57 Å 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.

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 $^{\text{IV}}\text{Cu}$ through its O-atom; (ii) two electrons are transferred to $^{\text{IV}}\text{Cu}$ 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 $^{\text{IV}}\text{Cu}$, 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.



What kind of science is sustainability science?

Science that enables us to pursue the goals of sustainable development.

Sustainable development is one that meets the needs of the present without compromising the ability of future generations to meet their own needs.

Many assume that economic interests and environmental interests are in conflict.

But new research makes the case that the perception of development vs. conservation is not just unnecessary, but actively counterproductive to both ends.

One needs to understand that economic and environmental goals are NOT mutually exclusive.

“The impression that economic and environmental goals are mutually exclusive has contributed to a lack of connection among some of the sectors best equipped to solve such interconnected problems.”

The Science of Sustainability: The Way Forward [Proc R Soc B 280: 20122845.
<http://dx.doi.org/10.1098/rspb.2012.2845>]



Global supply chains are undergoing significant realignments, driven by geopolitical conflicts and shifting economic priorities. Many businesses are reassessing their sourcing strategies, adopting nearshoring practices, and building more resilient, localized production hubs. These shifts are particularly evident in subsectors such as petrochemicals and speciality chemicals, where supply delays and dependencies can critically affect downstream industries.

In Asia, countries like India, China, and Vietnam are emerging as major chemical manufacturing hubs, benefiting from cost advantages and supportive government policies. At the same time, Western economies are investing in domestic manufacturing capacity to reduce reliance on imports and strengthen strategic autonomy.

Rise of Specialty and Performance Chemicals

The specialty chemicals segment is witnessing strong growth, driven by rising demand for tailored, high-performance, and environmentally friendly products. Key areas include personal care ingredients, food additives, electronic materials, and water treatment solutions—industries marked by continuous innovation.

Unlike bulk or commodity chemicals, speciality chemicals command higher profit margins and are less exposed to price volatility. By 2025, this segment is expected to be a major growth engine for the industry. Companies investing in R&D, fostering customer collaboration, and addressing niche market needs are gaining a clear competitive edge.

Performance Chemicals

- These are **specialty chemicals** designed for specific applications, where their performance (rather than sheer volume) is the key value driver.
- Unlike commodity chemicals (produced in bulk, like sulfuric acid or chlorine), performance chemicals are manufactured in lower volumes but sold at higher margins because they deliver tailored properties.
- They are often **custom-formulated** for particular industries such as automotive, construction, agriculture, coatings, cosmetics, water treatment, and electronics.

Examples:

- Surfactants (detergents, emulsifiers)
- Adhesives and sealants
- Dyes and pigments
- Water treatment chemicals
- Lubricating oil additives
- Cosmetic and personal care ingredients
- Electronic chemicals

Top 5 Growth Drivers (2025)

- 1. Sustainability & Green Chemistry** – Rising demand for bio-based, recyclable, and low-carbon chemicals as regulations and customer preferences shift.
- 2. Specialty Chemicals Expansion** – Growth in high-value segments (personal care, electronics, food additives, water treatment) with higher margins and innovation focus.
- 3. Digitalization & Industry 4.0** – Adoption of AI, IoT, and predictive analytics to optimize operations, reduce downtime, and improve supply chain efficiency.
- 4. Regional Manufacturing Hubs** – Growth of India, China, and Southeast Asia as cost-competitive production centers, supported by government incentives.
- 5. End-Use Market Growth** – Strong demand from pharmaceuticals, EV batteries, renewable energy, and construction materials.

Top 5 Challenges (2025)

- 1. Geopolitical & Trade Disruptions** – Supply chain vulnerabilities due to conflicts, sanctions, and protectionist trade policies.
- 2. Energy & Feedstock Volatility** – Fluctuations in oil, gas, and raw material prices affecting margins.
- 3. Stringent Environmental Regulations** – Pressure to decarbonize, phase out hazardous chemicals, and comply with global ESG standards.
- 4. R&D and Innovation Costs** – High investment needed to develop specialty and sustainable solutions, with long commercialization timelines.
- 5. Talent Shortages** – Difficulty in attracting and retaining skilled workforce in areas such as digital technologies, process innovation, and sustainability.

2024 chemical industry outlook

The chemical industry should balance short- and long-term goals to weather the uncertainty in the current landscape and position itself for the future.

By mid-2023, several chemical companies significantly revised their expectations. Multiple factors contributed to sluggish demand for chemicals globally, including a recession in Europe, inflation in the United States, and a smaller-than-expected rebound in demand from China. Chemical output grew less than 1% year over year and many companies have turned their focus to reducing costs and improving efficiencies to help offset this reduction in output.

To help companies begin to strategize about addressing these issues, the following trends have been investigated in the 2024 chemical industry outlook:

Demand drivers

Regional dynamics

Digital and artificial intelligence

Circular economy

Sustainability and trust

Demand drivers: Energy transition drives chemical demand

The energy transition poses complex challenges that require a comprehensive approach to deliver sustainable, reliable, and affordable solutions for reducing carbon emissions. Driving this transition depends on a strong understanding of emerging technologies, evolving regulatory frameworks, and shifting investment landscapes.

To illustrate the scale, annual global investment in the energy transition reached **\$2.1 trillion in 2024**. This unprecedented level of investment underscores not only the magnitude of the challenge but also the opportunities it presents for companies across the energy production and process industries.

<https://www.aiche.org/resources/publications/cep/2025/april/key-drivers-energy-transition-electrification-and-other-clean-energy-solutions>

Global energy investment is set to rise to **\$3.3 trillion in 2025** amid economic uncertainty and energy security concerns.

Demand drivers: Energy transition drives chemical demand

The energy transition is generating a wave of manufacturing activity that depends on chemicals and materials for support. New government policies and incentives have spurred investment in the energy transition of 2021 and 2022.

The Infrastructure Investment in 2021: US\$70 billion to electric vehicle (EV) infrastructure and clean energy transmission.

In 2022: US Congress passed the Creating Helpful Incentives to Produce Semiconductors (CHIPS), infusing another US\$469 billion in tax incentives and funding into sectors such as domestically manufactured semiconductors, lithium-ion batteries, solar panels, and other clean energy technologies, as well as the components and material inputs for these products. Healthcare is another dominant sector that drives the demand and investments.

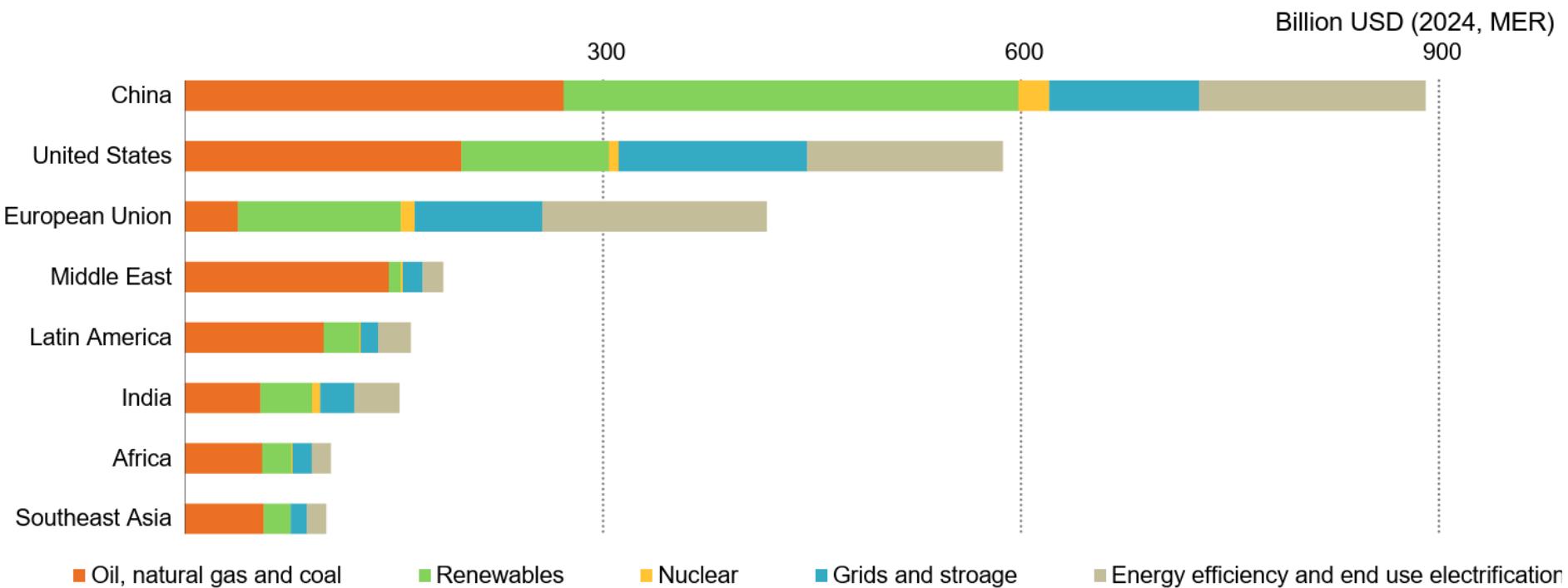
So, while total demand for chemicals was soft in 2023, demand for chemicals and materials that are needed to support the energy transition is expected to rise in 2024 and beyond as the impact of these policies reverberates through the economy. <https://www2.deloitte.com/us/en/insights/industry/oil-and-gas/chemical-industry-outlook.html>

Impact on demand

How might the energy transition impact overall demand in 2024? In 2023, an estimated US\$2.8 trillion was invested globally in energy, with more than 60% invested in clean energy technology, such as renewables, EVs, and battery storage.

China sets the pace, as energy security drives spending growth

Energy investment by region, 2025



More than one-quarter of global energy investment takes place in China. Most of the growth in spending in recent years has been in fossil fuel importing countries looking to bolster their energy security by accelerating transitions

IEA. CC BY 4.0.

The chemical industry should balance short- and long-term goals to weather the uncertainty in the current landscape and position itself for the future

Over the last three years, stakeholder pressure and government policies have incentivized investment in the energy transition. As a result, there appears to be an acceleration in the convergence of sectors related to the energy transition. For instance, some oil and gas companies are moving into critical minerals mining and processing, agriculture, and chemicals to secure clean energy supply chains. Meanwhile, some chemical companies are moving into lithium processing, battery manufacturing, and clean ammonia for similar reasons. Therefore, while there are new opportunities for chemical companies, the industry is also competing with other industries that often have stronger cash flows, such as large oil and gas companies.

<https://www.deloitte.com/us/en/insights/industry/chemicals-and-specialty-materials/chemical-industry-outlook/2024.html>

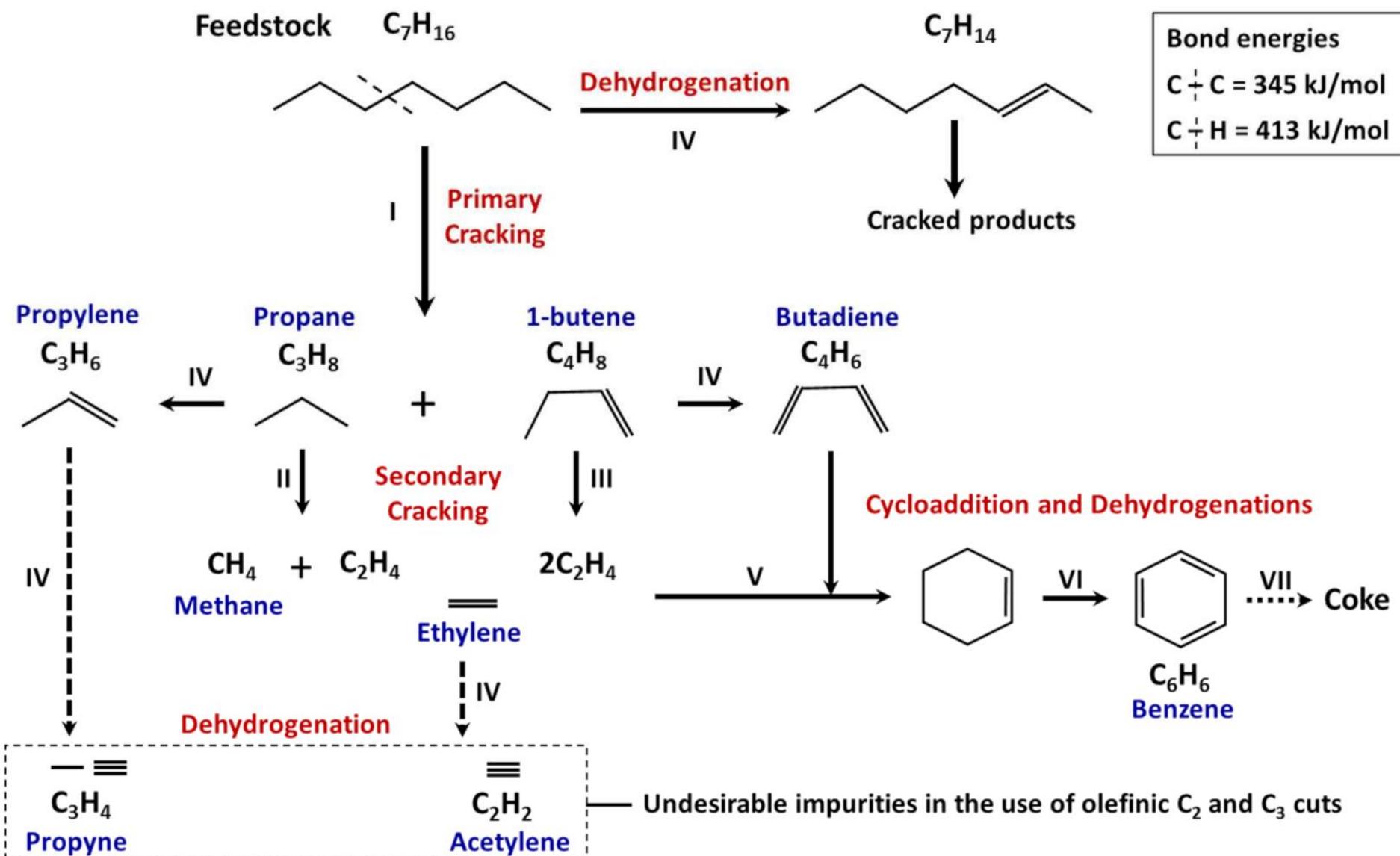
Market share battle for olefins and polyolefins

One aspect in which regional dynamics are changing the landscape is olefins and polyolefins. In 2023, China completed more than 20 petrochemical projects, pushing its global share of petrochemical capacity up to 25%. [Refiners in China have moved away from fuels toward petrochemicals in anticipation of declining demand for fossil-based transport fuels.](#) China expanded capacity down the supply chain as it moved toward self-sufficiency, adding ethylene, propylene, polyethylene, and polypropylene capacity.

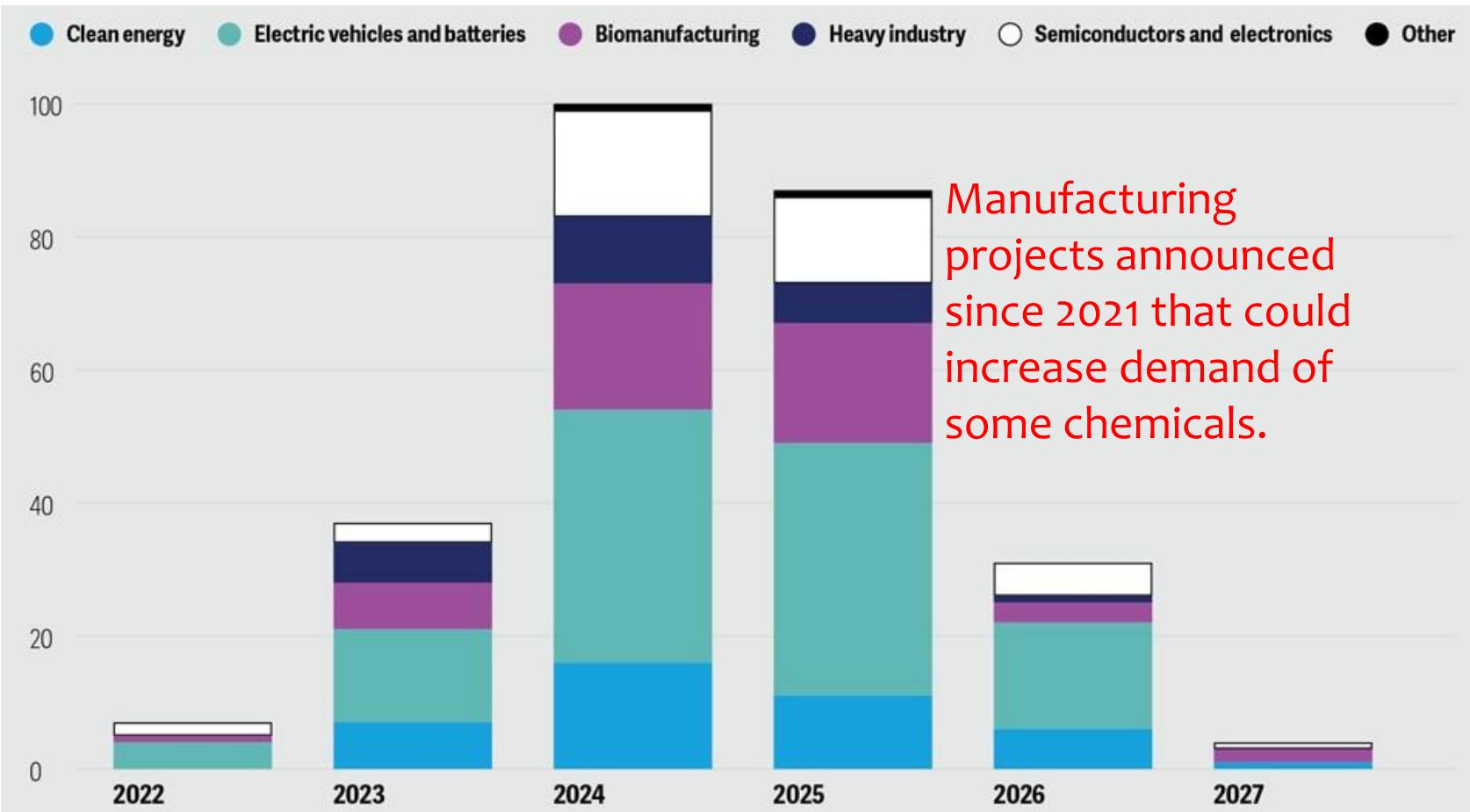
Olefins and polyolefins are changing the landscape because they are both a major source of industrial emissions and an essential enabler of the low-carbon economy.

The future of petrochemicals in India looks promising, with the domestic chemicals market projected to attract investments exceeding US\$87 billion over the next decade. India is expected to contribute more than 10% to global petrochemical growth during this period. [\[Report EY India, 23 Aug 2024\]](#)

Main reactions involved in the cracking of higher alkane:



The chemical industry underpins more than 75% of all emissions-reduction technologies required to achieve global net-zero targets by 2050. For example, it supplies battery materials for electric vehicles, refrigerants for heat pumps, epoxy, polyurethane, and lubricants for wind turbines, and speciality solvents for semiconductors. Growing demand from these sectors is expected to stimulate chemical production in 2024, with over 100 new projects projected to come online during the year.



Source: Deloitte analysis of the White House's Investing in America website (accessed September 26, 2023), press releases, and news articles.

Olefins and polyolefins are reshaping the industrial and energy transition landscape. As essential building blocks of modern life—used in packaging, automotive parts, construction, medical devices, textiles, and renewable energy infrastructure—their scale and ubiquity mean that any shift in their production or recycling carries global consequences.

The chemical sector faces a critical duality: olefin production via fossil fuel-based steam cracking (~550 °C) is among the most energy- and carbon-intensive processes, while polyolefins—though essential—dominate plastic consumption and pollution. Yet, the industry is also a key enabler of decarbonization. Rapid innovation in recycling, process electrification, and bio- or CO₂-derived feedstocks is reshaping sustainability pathways. Meanwhile, polyolefins' lightweight, durable properties make them vital to low-carbon technologies, including solar panels, wind turbines, hydrogen pipelines, and electric vehicles.

While polyolefins present challenges in waste management, their properties make them indispensable in decarbonization technologies and circular economy models.

With billions in global investment flowing into clean technologies, olefins and polyolefins stand at the intersection of industrial transformation and sustainable growth, making them pivotal to the future low-carbon economy.

Polyolifins can also be key enablers of decarbonization because of their lightweight, durable, and versatile properties.

1. Lightweighting and Energy Efficiency

2. Renewable Energy Infrastructure: Solar panels, Wind turbines

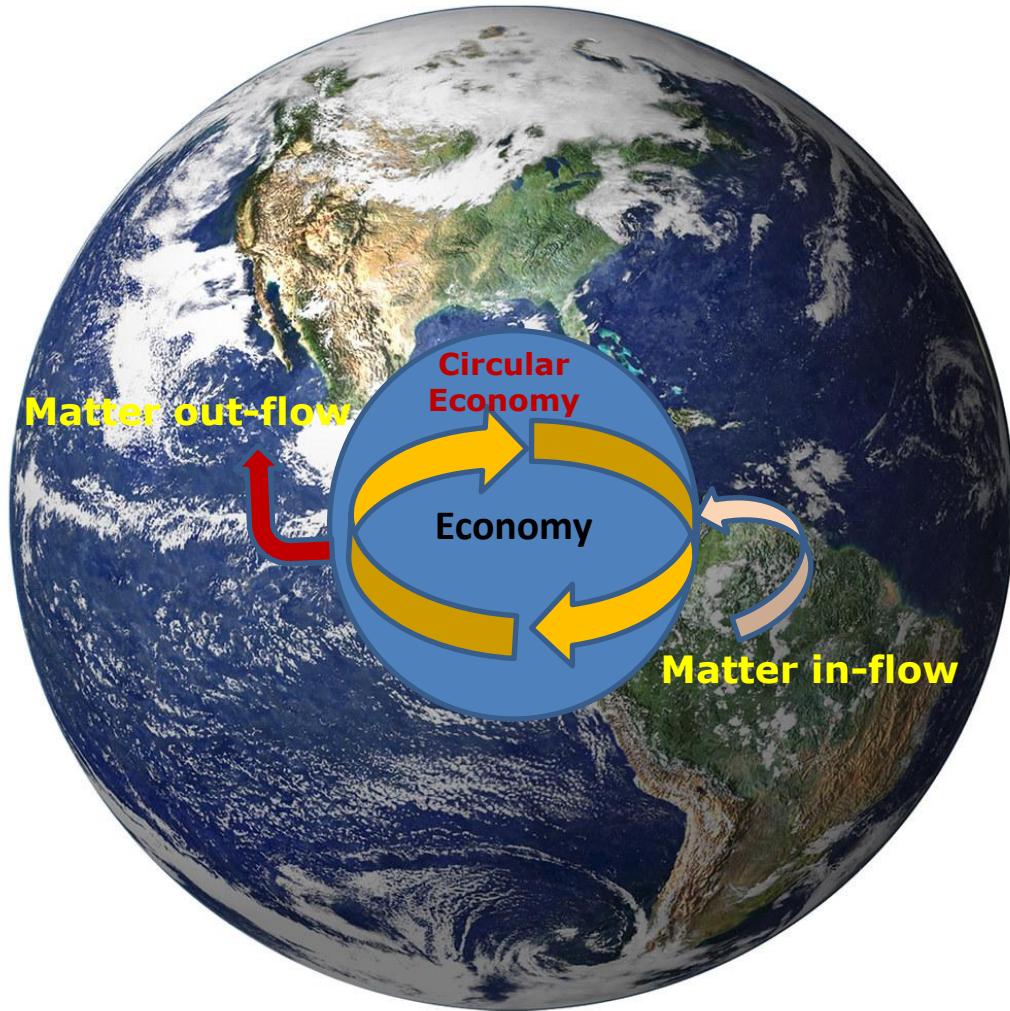
3. Hydrogen Economy & Energy Transport

- Pipes and tanks for hydrogen distribution and storage.
- Lower material weight reduces embodied energy in construction and operation. (Low ISO-GWP)

4. Circular Economy Potential: Chemical and mechanical recycling. Bio-based and CO₂-derived feedstocks can further decarbonize production.

5. Durability and Extended Lifetimes: Low lifecycle emissions.

In short, While polyolefins present challenges in waste management, their properties make them indispensable in decarbonization technologies and circular economy models.



Chemicals are everywhere in our daily life

They play a fundamental role in most of our activities and well-being.

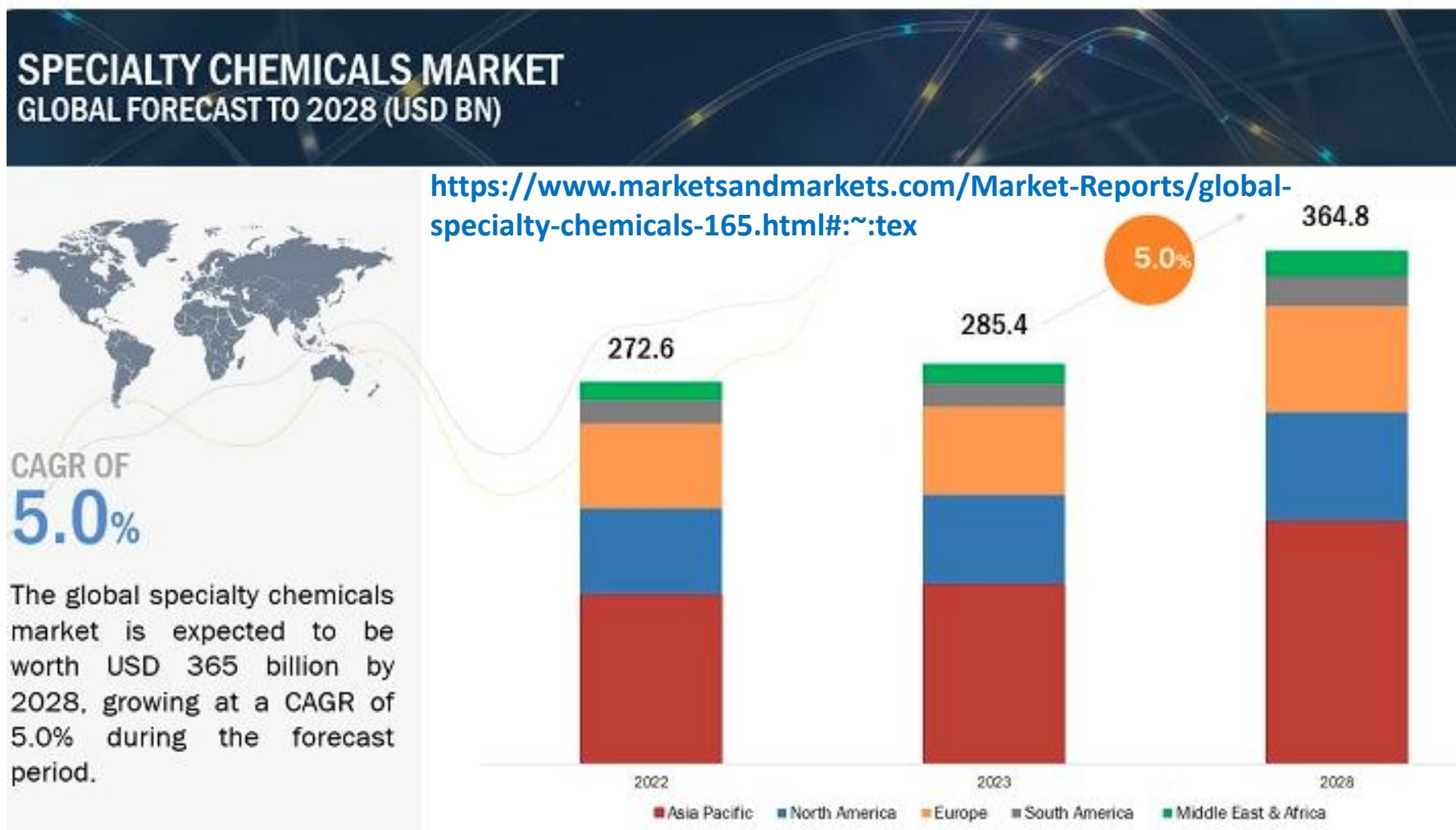
- 157,000: Individuals listed on chemicals identified by CAS numbers, according to the most comprehensive global inventory to date with 2000 new chemicals added every year
- 75,000: Mixtures, polymers, and substances of unknown or variable composition.
- 120,000: Substances that could not be conclusively identified.
- 60,000 chemicals “that are not well understood and regulated”
- \$7,800,000,000,000: The value of the global production of synthetic chemicals is estimated to **\$7.8 trillion a year**. That's almost a billion dollars every hour. Or the combined GDP of Japan and the UK.
- 700 synthetic chemicals in our body that are not naturally part of the human body chemistry.

[Environ. Sci. Technol. 2020, DOI: [10.1021/acs.est.9b06379.22600](https://doi.org/10.1021/acs.est.9b06379.22600)]

- About USD 6.2 trillion in 2024 (global chemicals market value, estimate). [PR Newswire](#)
- For context, **world chemical sales were €5.195 trillion in 2023** (latest audited global figure), implying a modest uptick into 2024. [\[2024 Facts and Figures - cefic\]](#)
- Longer-term signals: UNEP notes the sector could approach **~US\$10 trillion by 2030** (doubling from 2017), underscoring continued growth.

[Chemical Industry Outlook worth \\$6,324 billion by 2025 - Exclusive Report by MarketsandMarkets](#)

The Global specialty chemicals market @ 2023: 285.4 billion
Projected market @ 2028: 364.8 billion
[5% Compound Annual Growth Rate]



Compound annual growth rate (CAGR)

$$\text{CAGR} = \left[\left(\frac{\text{Ending Investment Amount}}{\text{Start Amount}} \right)^{\frac{1}{\text{Number of Years}}} - 1 \right]$$

Approximate Number of Chemicals by Category (Daily Life Context)

1. Household & Personal Care

1. **Surfactants, fragrances, preservatives, colorants, solvents**
2. **~ 3,000–5,000 chemicals** used in formulations globally.

2. Food & Agriculture

1. **Fertilizers, pesticides, herbicides, insecticides, food additives (colors, flavors, stabilizers, preservatives)**
2. **~ 5,000–7,000 chemicals** in active use.

3. Healthcare & Pharmaceuticals

1. **Active Pharmaceutical Ingredients (APIs), excipients, diagnostic reagents, medical polymers**
2. **~ 10,000–12,000 chemicals** (including APIs and excipients).

4. Textiles & Apparel

1. **Fibers, dyes, finishing chemicals, coatings**
2. **~ 8,000–10,000 chemicals** (especially dye intermediates and auxiliaries).

5. Electronics & Communication

1. **Semiconductor chemicals, photoresists, solvents, adhesives, rare earths**
2. **~ 2,000–3,000 chemicals** in specialized applications.

6. Energy & Transportation

1. **Fuels, lubricants, additives, composites, polymers**
2. **~ 4,000–6,000 chemicals** (including petrochemical derivatives).

7. Construction & Infrastructure

1. **Cement additives, polymers, adhesives, paints, sealants**
2. **~ 3,000–5,000 chemicals** actively used.

Persistent, Bioaccumulative, and Toxic (PBT) Chemicals:

1. Persistent (P):

A chemical is considered **persistent** if it resists degradation in the environment (through processes such as hydrolysis, photolysis, or biodegradation). It typically remains in soil, water, air, or organisms for long periods, leading to long-term exposure.

2. Bioaccumulative (B):

A chemical is **bioaccumulative** if it tends to build up in the tissues of living organisms (often in fatty tissues) over time, rather than being excreted or metabolized efficiently. Bioaccumulation can occur through food chains, leading to higher concentrations in predators (biomagnification).

3. Toxic (T):

A chemical is **toxic** if it causes harmful effects to organisms, including humans, at relatively low concentrations. Toxicity may involve carcinogenicity, mutagenicity, reproductive toxicity, endocrine disruption, or organ-specific damage.

In short, **PBT chemicals** are long-lasting in the environment, accumulate in organisms, and are harmful to health or ecosystems (e.g. polychlorinated biphenyls (PCBs), dioxins, and certain pesticides (like DDT)

1. Persistence (P)

A chemical is considered **persistent** if it resists degradation in the environment.

- **REACH (EU criteria):**

- Half-life in **marine water** > 60 days
- Half-life in **fresh or estuarine water** > 40 days
- Half-life in **marine sediment** > 180 days
- Half-life in **freshwater/estuarine sediment** > 120 days
- Half-life in **soil** > 120 days

REACH: A European Union regulation concerning the Registration, Evaluation, Authorisation, and restriction of **Chemicals**

- **Very Persistent (vP):**

- Half-life in **marine, freshwater, or estuarine water** > 60 days
- Half-life in **sediment or soil** > 180 days

2. Bioaccumulation (B):

A chemical is **bioaccumulative** if it builds up in living organisms.

- **Measured by bioconcentration factor (BCF) or bioaccumulation factor (BAF):**
- **B (Bioaccumulative):** BCF or BAF > 2,000
- **vB (Very Bioaccumulative):** BCF or BAF > 5,000

3. Toxicity (T): A chemical is considered **toxic** if it causes harmful effects at low concentrations.

- **REACH (EU criteria):**
- Chronic **NOEC (No Observed Effect Concentration)** for aquatic organisms < **0.01 mg/L**
- Evidence of **carcinogenicity, mutagenicity, or reproductive toxicity (CMR, category 1A or 1B)**
- Evidence of **chronic toxicity** in mammals

EPA stands for the **United States Environmental Protection Agency**

U.S. EPA Criteria (similar but slightly different focus):

- **Persistence:** Half-life in water, sediment, or soil consistent with above thresholds.
- **Bioaccumulation:** BAF or BCF > **1,000** often considered bioaccumulative.
- **Toxicity:** Based on **acute and chronic toxicity data**, including potential for endocrine disruption, neurotoxicity, carcinogenicity, etc.

A systematic and computer-aided workflow was developed to facilitate the chemical redesign for reduced persistency. The approach includes elements of Essential Use, Alternatives Assessment and Green and Circular Chemistry and ties into goals recently formulated in the context of the EU Green Deal.

Chemical pollution has consequently been identified as one of the five main drivers of global biodiversity loss. Chemical pollution ('novel entities' in planetary boundaries) MUST not be breached. Studies reveal that the planetary boundary is exceeded. Worldwide, initiatives to reduce the impact of chemicals are lagging, underlining the urgent need for more ambitious action ([United Nations Environment Programm, 2019](#), [Wang et al., 2020](#)).

The organophosphate chemical triisobutyl phosphate (TiBP) was used as a case study for exploration of the approach, as its emission to the environment was expected to be inevitable when used as a flame retardant. TBP is a highly polar solvent. It is mainly used as an antifoaming agent in various aqueous systems where it can destroy foam and act as a foam inhibitor.

Tri-n-butyl phosphate (TnBP), a typical alkyl organophosphate ester is widely used as an emerging flame retardant for polybrominated diphenyl ethers alternatives, but the potential toxicity and mechanism are unclear. In this study, the reproductive toxicity of TnBP and its related mechanisms were explored using the *Caenorhabditis elegans* (*C. elegans*) model.

After TnBP (100–1000 µg/L) exposure: TnBP toxicity in *C. elegans* arises from a combination of oxidative stress, DNA damage, apoptosis, and mitochondrial dysfunction, with SKN-1/Nrf2, CEP-1/p53, and xenobiotic metabolism pathways playing central roles. [[Ecotoxicol Environ Saf. 2021, 227, 112896](#); [Environ Sci Pollut Res Int. 2023, 30, 85578-85591](#)]

Exposure to environmentally relevant concentrations of TnBP impaired gonad development (crucial for sexual differentiation and reproduction, involving a complex interplay of genetic and environmental factors) and reduced reproductive capacity in *C. elegans*. [[Ecotoxicology and Environmental Safety 227 \(2021\) 112896](#)]

Tri-n-butyl phosphate (TBP) detected in all environmental matrices.

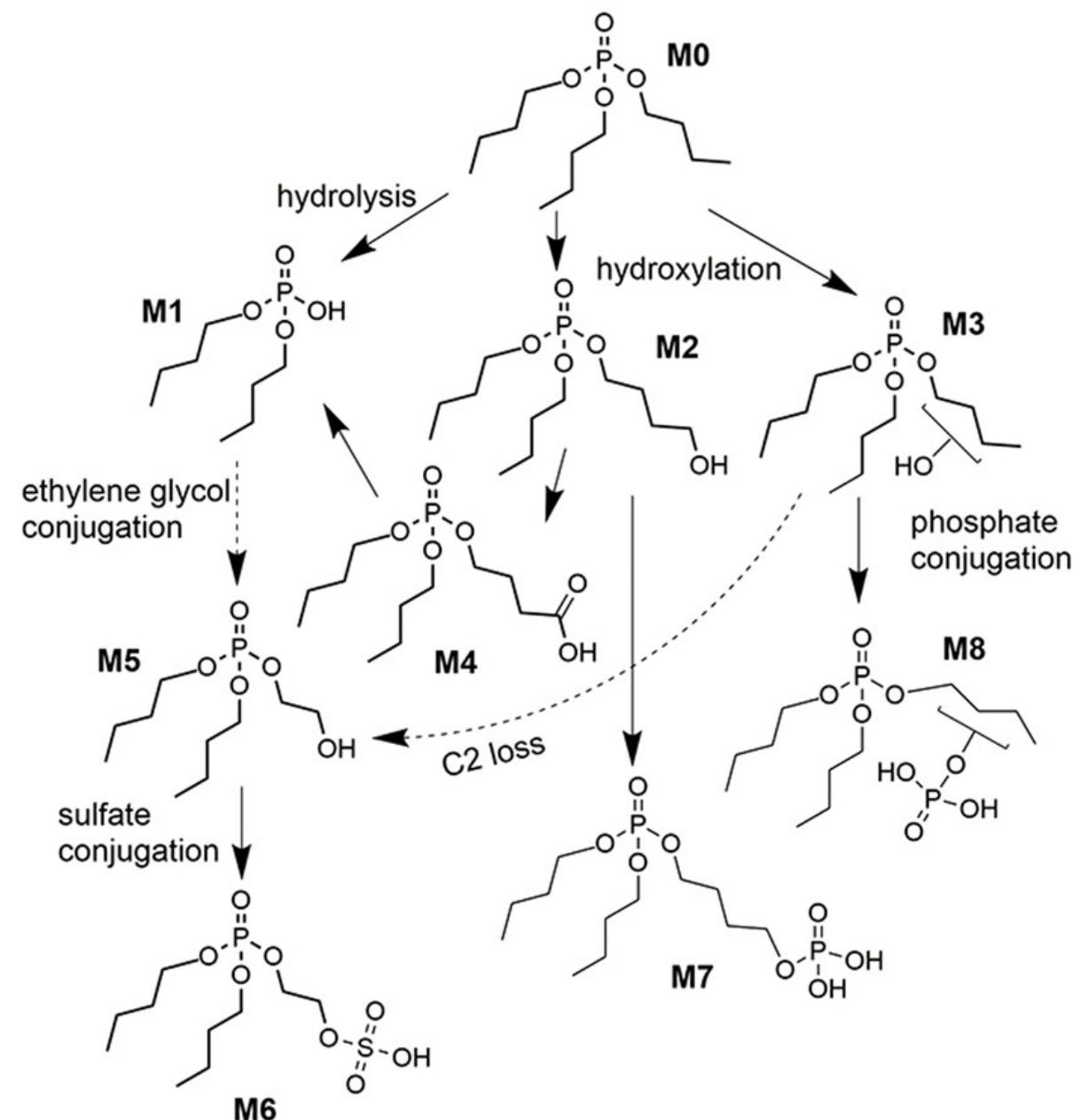
TnBP, when metabolized in the earthworm (*Perionyx excavatus*), does not show overt toxicity, unlike in *C. elegans*:

TBP
tributyl phosphate:
plasticizer
industrial solvent
anti-foaming agent



Metabolism of TBP in the earthworm, *Perionyx excavatus*

Reproductive toxicity, Estrogen-disrupting effects of TnBP
Ecotoxicol. Environ. Safety 2021, 227, 112896; Environ Pollut. 2018, 234, 389-395



Metabolism of TnBP in *Perionyx excavatus*:

Studies indicate that *Perionyx excavatus* can metabolize TBP through **phase I and phase II detoxification pathways**, likely involving **hydrolysis and conjugation reactions**. These processes convert TBP into **less harmful metabolites** that can be excreted, thereby preventing accumulation and toxic effects. Unlike in *C. elegans*, where TnBP induces oxidative stress, apoptosis, and DNA damage, the earthworm's **efficient biotransformation capacity** appears to mitigate toxicity. This highlights species-specific differences in organophosphate metabolism and suggests that *P. excavatus* may tolerate environmental TBP exposure without significant impairment.

The bioaccumulation potential of TnBP in earthworm-soil ecosystem is low at 10 mg kg^{-1} and 50 mg kg^{-1} of TBP. Various phase I and phase II biotransformation products were identified in earthworms. Phase I metabolites include DBP, TBP-OH and TBP-OOH. Novel phase II metabolites were identified: ethanol DBP and its sulfate conjugate, and the phosphate conjugate of hydroxylated TBP, suggesting a unique enzyme system in *P. excavatus* for xenobiotic metabolism.

For hydrophobic xenobiotics, the major detoxification pathway is by bonding of highly polar compounds, thus making them hydrophilic, which can then be easily excreted.

[Environmental Pollution; 2018, 234, 389-395](#)

Tri-n-butyl phosphate (TnBP) Exposure:

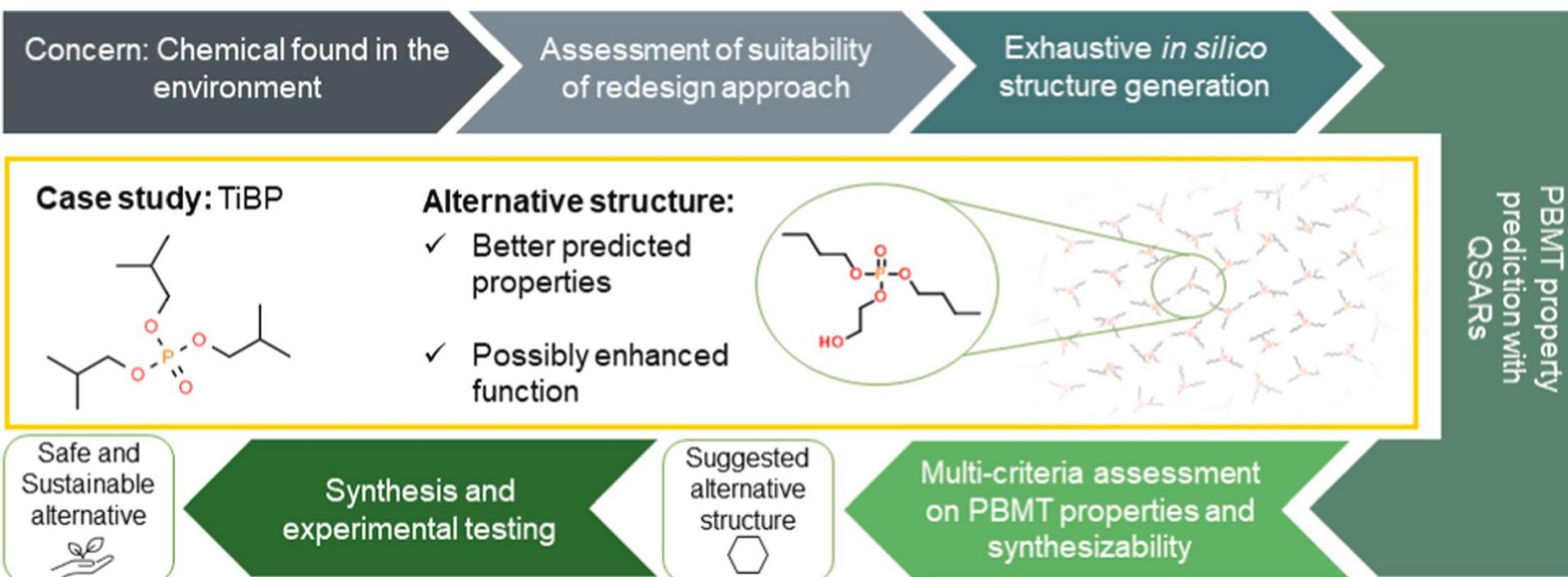
The production volume of TnBP is estimated at 3,000 – 5,000 tonnes worldwide. The major uses of TnBP in industry are as a component of aircraft hydraulic fluid and as a solvent for rare earth extraction and purification. No current consumer product uses of TnBP have been identified. The primary occupational exposure to TnBP results from its use as an ingredient in aircraft hydraulic fluids. The potential for exposure to TBP varies with the type of maintenance activity but is almost always via a dermal pathway.

$$BCF = \frac{\text{Concentration}_{\text{Biota}}}{\text{Concentration}_{\text{Water}}}$$

A bioconcentration factor (BCF) is a measure of how much a substance accumulates in an organism's tissues to the concentration of the substance in the surrounding environment.

BCF can also be related to the octanol-water partition coefficient, K_{ow} . The octanol-water partition coefficient (K_{ow}) is correlated with the potential for a chemical to bioaccumulate in organisms and can be predicted via software for **structure-activity relationship (SAR)** or through the linear equation

Chemosphere, 2022, 296, 134050



Systematic, computer-aided approach to redesign for less persistent chemicals

Quantitative structure-activity relationship

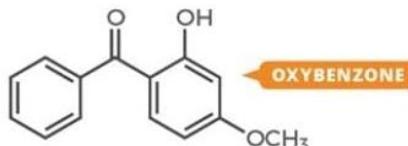
Persistence (P), bioaccumulation (B), mobility (M) and toxicity (T) potency properties

SUNSCREEN AND CORAL REEF DAMAGE

Sunscreen protects our skin from the sun, but there's also evidence that some of the lotion's ingredients may damage coral reefs. Here we look at the responsible compounds and efforts to combat the problem.

SUNSCREEN COMPOUNDS

Sunscreens use various compounds to protect our skin. These include inorganic pigments like titanium dioxide and organic compounds that absorb the ultraviolet radiation.



Oxybenzone and octinoxate are used in 70–80% of sunscreens. Sunscreen washes off when you swim or shower and can end up in the oceans.

 **14,000 METRIC TONS**
The estimated mass of sunscreen released into the world's oceans every year

OXYBENZONE IN SEAWATER SAMPLES

US VIRGIN ISLANDS



OXYBENZONE CONCENTRATION

75-1,400 µg/L

HAWAII



OXYBENZONE CONCENTRATION

0.8-19.2 µg/L



EFFECTS ON CORAL

Coral gets stressed by pollution and changes in temperature, leading to coral bleaching. During bleaching, the algae that live on the coral and provide it with food leave or die.



Studies suggest that the organic compounds used in sunscreens, such as oxybenzone, can cause coral bleaching, making coral more susceptible to disease and death.

COMBATING THE PROBLEM



HAWAII

BANNED



PALAU

BANNED

Hawaii will ban the sale of sunscreens containing oxybenzone and/or octinoxate in 2021. The Pacific nation of Palau will ban sunscreens containing these and eight other ingredients in 2020.



The evidence against these ingredients is largely limited to laboratory-based studies, which may not reflect conditions on reefs.

MINERAL SUNSCREEN ACTIVE INGREDIENTS

TITANIUM DIOXIDE, TiO₂
ZINC OXIDE, ZnO

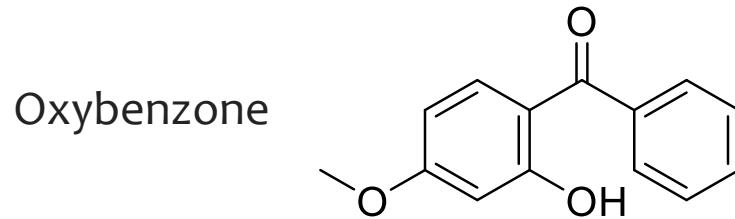
Sunscreens based on solely inorganic minerals are considered to be safer for reefs. Chemists are also trying to develop naturally derived sunscreens.

Journal of Science Policy and Governance, 2024, 24,
<https://doi.org/10.3812/6/JSPG240106>

Science, 2022, 376, 644-648



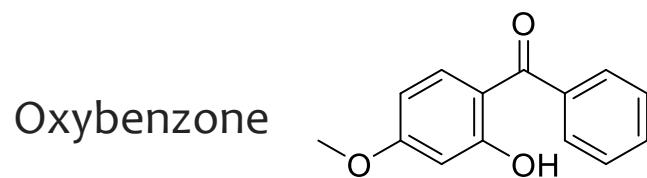
Although oxybenzone protects against UV-induced (290 to 370 nanometers) photo-oxidation, both the anemone and a mushroom coral formed oxybenzone-glucoside conjugates that were strong photo-oxidants. Algal symbionts sequestered these conjugates, and mortality correlated with conjugate concentrations in animal cytoplasm. Many commercial sunscreens contain structurally related chemicals, and understanding metabolite phototoxicity should facilitate the development of coral-safe products.



The concentration of oxybenzone at a coral reef can vary widely, depending on factors such as tourist activity and water conditions. Coral-bleaching events on Australia's Great Barrier Reef, for example, have been linked more closely to trends in water temperature than to shifts in tourist activity. "Mass bleaching happens regardless of where the tourists are," Hughes says. "Even the most remote, most pristine reefs are bleaching because water temperatures are killing them."



The metabolic products of oxybenzone-based sunscreen threaten the survival of bleached corals, which have already lost their symbiotic algal partners that could have helped minimize the toxic effects of the chemicals. [Science, 2022, 376, 578-579]



A possible relaxation mechanism is the rotation of excited OH groups toward the bulk (water or aq. phase) and the formation of a hydrogen bond after which energy dissipation occurs rapidly due to the increased anharmonicity of the OH vibrational potential. [PNAS, 2013, 18780-18785]