Centre for **Sustainable & Circular** Technologies

MONASH University

UNIVERSITY OF BATH

Bath Monash Global PhD Programme in Sustainable & Circular Technologies

Project Title:	Chemical sensing of nitrous oxide – A pollutant of concern in multiple environmental contexts
Supervisors at Bath:	Dr Simon E. Lewis (lead, chemistry)
Supervisors at Monash:	A/Prof. Kellie L. Tuck (lead, chemistry), Dr Vincent Cadarso Busto (Mech. Eng.)
Home Institution (Bath):	Oct 2022 – Oct 2024; Oct 2025-end
Indicative period at Host Institution (Monash):	Oct 2024 – Oct 2025 (can be flexible)

Project Summary (to include a brief description of the relevance to sustainable & circular technologies)

Background

Nitrous oxide (N_2O, so-called "laughing gas") has a significant negative environmental impact – it is the most potent ozone-depleting substance in the 21st century and has a Global Warming Potential (GWP) nearly 300x that of CO_2. Since the industrial revolution, atmospheric N_2O levels have increased by almost 25%, due to human activities.

So far, no fluorescent/luminescent chemosensors for N_2O have ever been reported. N_2O concentration is designated an "essential ocean variable" by the Global Ocean Observing System, but currently can only be monitored through research ship-based observations. A fluorescent chemosensor would be applicable in "lab-on-a-chip" autonomous buoy networks, so allowing much greater spatial and temporal resolution for marine N_2O monitoring.

Scientific Programme

The chemical inertness and poor coordination ability of N_2O mean harsh reaction conditions are usually required, but a few examples of N2O reacting spontaneously are known. The Aldridge group used a "Frustrated Lewis Pair (FLP)" to form a chemosensor with good selectivity for N_2O, but its readout is colorimetric, so its limit of detection is not low enough to detect environmentally relevant concentrations. Instead, we are targeting fluorescent/luminescent sensors due to the intrinsically higher sensitivity typically observed for such sensors. At its heart this project will focus primarily on design and synthesis of novel molecules to be evaluated as chemosensors/chemodosimeters for N_2O. Interest in and prior experience of synthetic organic chemistry is therefore an important criterion for candidates. Prior knowledge/experience of fluorescence/luminescence, marine science and environmental science more broadly is advantageous but not essential.

The second strand of the project, ***to be pursued at Monash***, draws on the expertise of the Tuck group in the area of Luminescent lanthanide-based complexes. These have long luminescence lifetimes that greatly exceed the fluorescence lifetime of organic molecules. Time-gated experiments allow removal of the shorter- lived background fluorescence, resulting in output being solely due to the luminescence of the lanthanide complex. This is especially significant for this project, as environmental samples often contain fluorescent molecules, which give rise to false positive identification or an over-estimate of concentration.

Thirdly, *also at Monash*, the application of the developed chemosensors in "lab-on-a-chip" devices will be undertaken, jointly with Dr Vincent Cadarso Busto. In the longer term, at-sea trials of such devices could be undertaken by the Ocean Technology and Engineering group at the UK National Oceanographic Centre, with whom we have an ongoing collaboration.

Relevance to Sustainable and Circular Technologies:

Climate breakdown is the defining sustainability issue of our lifetimes. At the recent COP26 meeting yet more countries pledged timescales on which they will reach "net zero" carbon emissions. However, this focus on CO_2 must not come at the expense of efforts to also mitigate other greenhouse gases. While the quantities of these other gases of concern (N_2O, CH_4, HFCs, SF_6) are lower, they have GWP values which are orders of magnitude greater than CO_2. Hence they are highly significant drivers of global heating. Efforts towards mitigating emissions of these gases must be underpinned by a comprehensive understanding of both their natural fluxes and anthropogenic emissions. However, in the case of N_2O such understanding is lacking, compared to CO_2. Just as the oceans are a huge carbon sink, the amount of N_2O (and N_2O precursors, *i.e.* nitrogen in other oxidation states) in the oceans would cause unsurvivable heating were it to enter the atmosphere. While most marine N_2O remains sequestered (currently), annual ocean emissions are estimated to be ≈ 3 Mt (≡ 1 $GtCO_2e$). Human activity can significantly influence these emissions, with agricultural nitrogenous runoff affecting the extent of archaeal nitrification as well as microbial denitrification (both of which involve N_2O as an intermediate). As noted above, there is a pressing need to acquire more detailed and granular data on oceanic N_2O levels to enable greater understanding of N_2O fluxes – only on this basis can informed decisions be made about where N_2O mitigation efforts should best be targeted. In order to acquire such datasets, there is a real need for new methods of monitoring N_2O in a rapid and cost-efficient manner that can be deployed in autonomous monitoring systems. This is the problem that our proposal seeks to address.

Further reading

Lewis *et al.*, *Analyst*, 2020, *145*, 6262, doi:10.1039/d0an01404d

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Tuck et al., *Coord. Chem. Rev.* 2018, *375*, 191, doi:10.1016/j.ccr.2017.11.018

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Lewis *et al.*, *Front. Chem. Sci. Eng.*, 2020, *14*, 90, doi:10.1007/s11705-019-1790-7

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