New applications of continuous atmospheric O_2 measurements: meridional transects across the Atlantic Ocean, and improved quantification of fossil fuel-derived CO_2

By

PENELOPE PICKERS

A thesis submitted to the
School of Environmental Sciences of the
University of East Anglia in partial
fulfilment of the requirements for the
degree of Doctor of Philosophy

School of Environmental Sciences
UNIVERSITY OF EAST ANGLIA

2016

In Memory of Greg Pickers (1949-2016)

Abstract

High precision, continuous measurements of atmospheric O_2 and CO_2 are a valuable tool for gaining insight into carbon cycle processes, and for separating land biospheric, oceanic and fossil fuel fluxes of CO_2. This thesis presents a new atmospheric O_2 and CO_2 measurement system that has been deployed on board a commercial container ship, travelling continuously between Germany (~55°N) and Argentina (~35°S). These data are the first ongoing atmospheric O_2 measurements across the Atlantic Ocean, closing a gap in the global atmospheric O_2 network.

The Atlantic meridional transects of atmospheric O_2 and CO_2 display latitudinally-varying seasonality. The annual mean latitudinal gradient in APO (Atmospheric Potential Oxygen; a tracer derived from O_2 and CO_2 measurements) does not show a pronounced bulge at the equator, in contrast to observations across the Pacific Ocean.

Atmospheric O_2 and CO_2 measurements from Norfolk, UK are used to demonstrate a novel method for quantifying fossil fuel derived CO_2 ($ffCO_2$), using APO data. This APO $ffCO_2$ quantification method is more precise than the frequently-used CO tracer method, owing to a smaller range of APO:CO_2 fossil fuel emission ratios compared to the CO:CO_2 range. A sensitivity analysis of the fossil fuel emission ratios also indicates that the APO method is very likely more accurate than the CO method, and can therefore be used independently of $^{14}CO_2$ measurements (unlike the CO method), which are costly and highly unreliable in many UK regions, owing to nuclear power plant influences.

These new applications of atmospheric O_2 measurements have significant future potential. The shipboard data can be used to test and improve global climate model estimates of meridional oceanic heat and carbon transport in the Atlantic. Using APO to quantify $ffCO_2$ has significant policy relevance, with the potential to provide more accurate and more precise top-down verification of fossil fuel emissions.

List of Contents

List of Figures

List of Tables

Acknowledgements

Having now come to the end of my Ph.D., I can now say that there are two factors that are essential to Ph.D. success: a fair amount of luck, and also a lot of help. Hence, there are many people I would like to thank for the advice, help and support that has been offered to me throughout the last 3½ years.

Firstly, I would like to acknowledge and thank all of the people who helped me to design, build, and test the shipboard O_2 and CO_2 measurement system, in particular: Phil Wilson (UEA), for teaching me the basics of Swagelok in the CRAM lab, for building most of the shipboard system analyser rack and the Blue Box, both of which I inherited when I started my Ph.D., and for filling reference and calibration cylinders; Andy MacDonald (UEA), who introduced me to the art of beautiful tube bending, and who helped me to build the shipboard system regulator manifold and drying rack; Alex Etchells (UEA), who built the 'Nemo' software, and put up with my numerous requests for software 'upgrades'; Dave Blomfield (UEA), who built the ship system electronics box and the aspirated air inlets; Nick Griffin (UEA), who helped me out when I had a pre-cruise electronics emergency; Stuart Rix (UEA) and Gareth Flowerdew (UEA) from the workshop, who helped me to mount all the shipboard system components inside the 19-inch racks, and who also stopped the Blue Box from falling apart (!); and Marica Hewitt (UEA), who helped me with numerous complicated and/or problematic orders, and with all the logistical aspects of deploying and maintaining the shipboard measurement system. I would also like to thank all of the people who came with me to the London Gateway port for the installation and maintenance visits, and in doing so surrendered their Friday evening plans. I am also very grateful to my international colleagues, who provided information that allowed me to compile Table 1.1 in Chapter 1.

With respect to the JC090 cruise, I would like to thank Alberto Naveira Garabato (University of Southampton, UK), for allowing myself and Andrew Manning to 'piggy-back' onto the OSMOSIS project cruise, Alex Forryan (National Oceanography Centre, Southampton, UK), for sharing the JC090 underway data with me, and Dan Comben (National Oceanography Centre, Southampton, UK) who helped to install the inlet lines from the Monkey Island and foremast down to the Met Lab, Martin Bridger (National Environment Research Council, UK) for providing the meteorological data and for I.T. support during the cruise, and Steve Woodward (National Oceanography Centre, Southampton, UK) for arranging the shipping to

Portugal and for helping with other logistical aspects of preparing for the JC090 cruise. I would also like to thank Vas Kitidis (Plymouth Marine Laboratory, UK) for helping to arrange for the pCO_2 measurement system to be turned on for the JC090 cruise, and who provided the pCO_2 data shown in Chapter 3, and Zoë Fleming (National Centre for Atmospheric Science, UK), who produced the NAME footprints for the JC090 cruise. The NEMO-PlankTOM model output presented in Chapters 3 and 5 was provided by Clare Enright (UEA), to whom I am very grateful.

In relation to Chapter 4, I would like to thank Christoph Gerbig (Max Planck Institute for Biogeochemistry, Jena, Germany), for updating the COFFEE dataset to 2014 and providing the data. I would also like to thank the UK Met Office, particularly Andrew Jones and Laura Burgin, for the NAME model training and help that I received when I was getting started with NAME. Leo Earl (UEA) and Mike Salmon (UEA) were very helpful when I was struggling to get NAME set up at UEA and working smoothly, and Zoë Fleming provided me with some sample input files, which were very useful when I was figuring out how to set up my own NAME runs. The Tacolneston data were provided by Dave Oram (CO data; UEA) and Angelina Wenger ($ffCO_2$ from $^{14}CO_2$ data; University of Bristol, UK), and measurements are managed by Simon O'Doherty (University of Bristol, UK) and Bill Sturges (UEA). The Weybourne CO data are maintained by Grant Forster (UEA), who also provided the data.

The shipboard measurements shown in Chapter 5 would not have been possible without the continued generous co-operation of Hamburg Süd and the Cap San Lorenzo crew, who have been extremely helpful throughout the project, and even allowed me to stay on board the ship for a week when I was deploying the shipboard measurement system for the first time. In particular, I would like to thank Nils Klemme, who made the installation on board the Cap San Lorenzo possible, Andreas Buhl, who installed the synflex tubing and cables for the inlet lines, and the engineers who have been changing the chiller traps for me. I would also like to thank the staff at the London Gateway port, DP World and John Good Shipping, especially Colin Hitchcock, Billy Dey, and Helen Woolford, who allow us to visit the ship when it makes berth in the UK, and arrange for the calibration cylinders to be lifted on and off the ship every 8 weeks, so that we can keep the measurement system running. I am also very grateful to Sara Mikaloff-Fletcher (National Institute of Water and Atmospheric Research Ltd, New Zealand) who provided the modelled APO data, and to Yasunori Tohjima (National Institute for Environmental Studies, Japan), for sharing the western Pacific shipboard data with me.

I have been very lucky to have been surrounded by excellent colleagues during my Ph.D., and I would like to thank Thomas 'Barney' Barningham (UEA) for being a great sounding board, when I needed to talk a problem through with someone, Sander van der Laan for some interesting discussions that were very helpful, particularly relating to Chapter 4, and Grant Forster for helping us to keep the measurements at Weybourne running. I would also like to thank Britt Stephens (National Center for Atmospheric Research, Colorado, USA) for his very useful advice about shipboard O_2 measurements, and for all the help with fixing the CRAM Lab VUV analyser.

I have been very fortunate to form some great friendships during my time in 01.37W, in particular Anna Ridley, who introduced me to indoor bouldering (which I highly recommend!), helped to cheer me up when the measurement system was 'broken again', and is as bad as me about talking aloud to oneself in the office. Also, Amanda Hopes, who is the only person I know who is crazier about knitting than me. And of course, I am very grateful to my Mum, for her lasting support and encouragement since I moved to Norwich, and to my Dad, who I am sure would have been very proud.

Last, but certainly not least, I would like to thank my supervisory team: Corinne Le Quéré, who is an incredibly inspiring role model and who helped me to see the 'bigger picture' in my research; Bill Sturges, who has been a fantastic supervisor throughout, always making the time to listen to my measurement system technical woes, and offering insightful advice and lots of encouragement along the way; and finally, Andrew Manning, who is a wonderful person to work with, and to whom I owe the greatest thanks of all.