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**Continuous and flask observations of atmospheric  $\delta O_2/N_2$  and  $CO_2$  at Lutjewad station, the Netherlands, and Mace Head station, Ireland**

**APO meeting, September 18-20, 2015**

*Scripps, La Jolla, Ca*

**Charlotte van Leeuwen, Bert Scheeren, Ingrid van der  
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Centre for Isotope Research (CIO)

Energy and Sustainability Research Institute Groningen (ESRIG)

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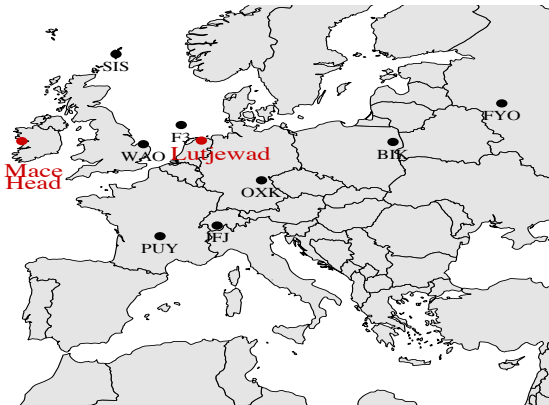


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# Atmospheric O<sub>2</sub> in Europe



Lutjewad: in operation since 2000

- sea level, mast intake at 60 m above ground
- flasks taken 1-2 per week
- “local background” conditions:
- $^{222}\text{Rn} < 3 \text{ Bq/m}^3$  and  $[\text{CO}] < 200 \text{ ppb}$

Mace Head: flask pairs filled once per week for CIO since 1999

- sea level, intake at  $\approx 10 \text{ m}$  above sea level
- only sampled in background conditions

Flask measurements at CIO: 2.5 l flasks, LH valves, filled at ambient pressure duplicate/triplicate measurements using an Micromass DI Optima

Additionally,  $[\text{CO}_2]$ ,  $[\text{CH}_4]$ ,  $[\text{CO}]$  measured using a HP6890N GC until 2013, thereafter with a Picarro



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## System Performance

O<sub>2</sub> DI Optima

flask precision (duplicates)  $\leq 4$  per meg

internal scale stability  $\approx 2$  per meg

Cylinder precision (single mm) :  $\approx 10$  per meg until Jan 2015

Calibration on the “Scripps” scale depends on infrequent and few cylinder measurements...

CO<sub>2</sub> GC and Picarro

Accuracy  $< 0.1 \text{ ppm}$  (WMO X2007 scale)

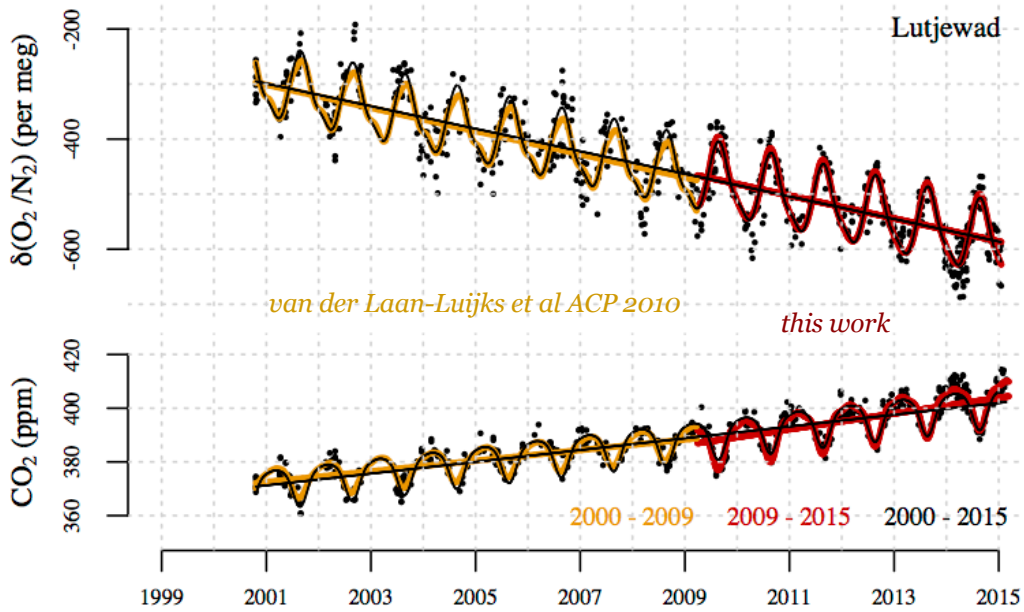


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# Observations: flasks

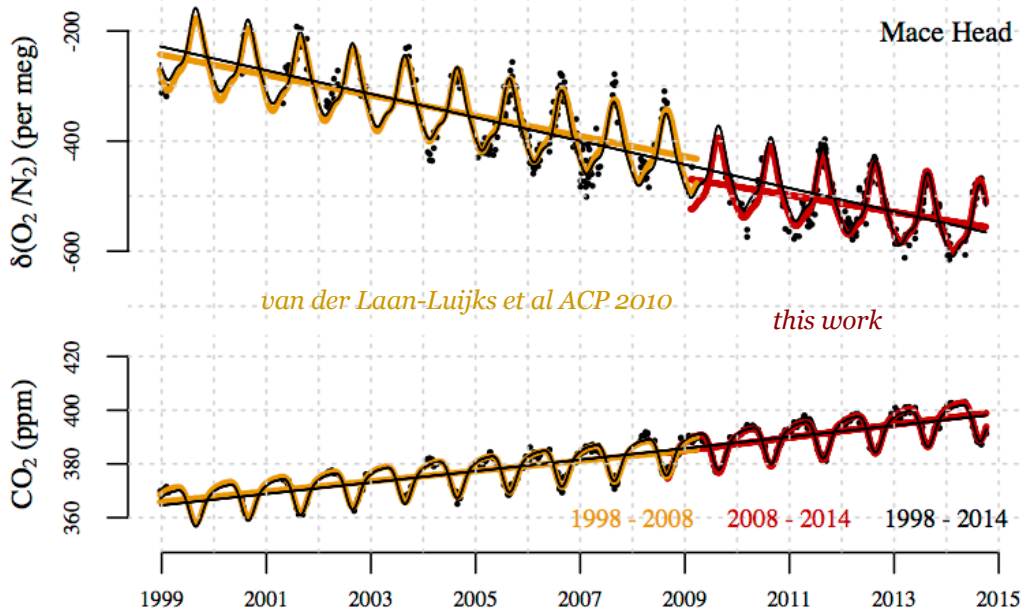


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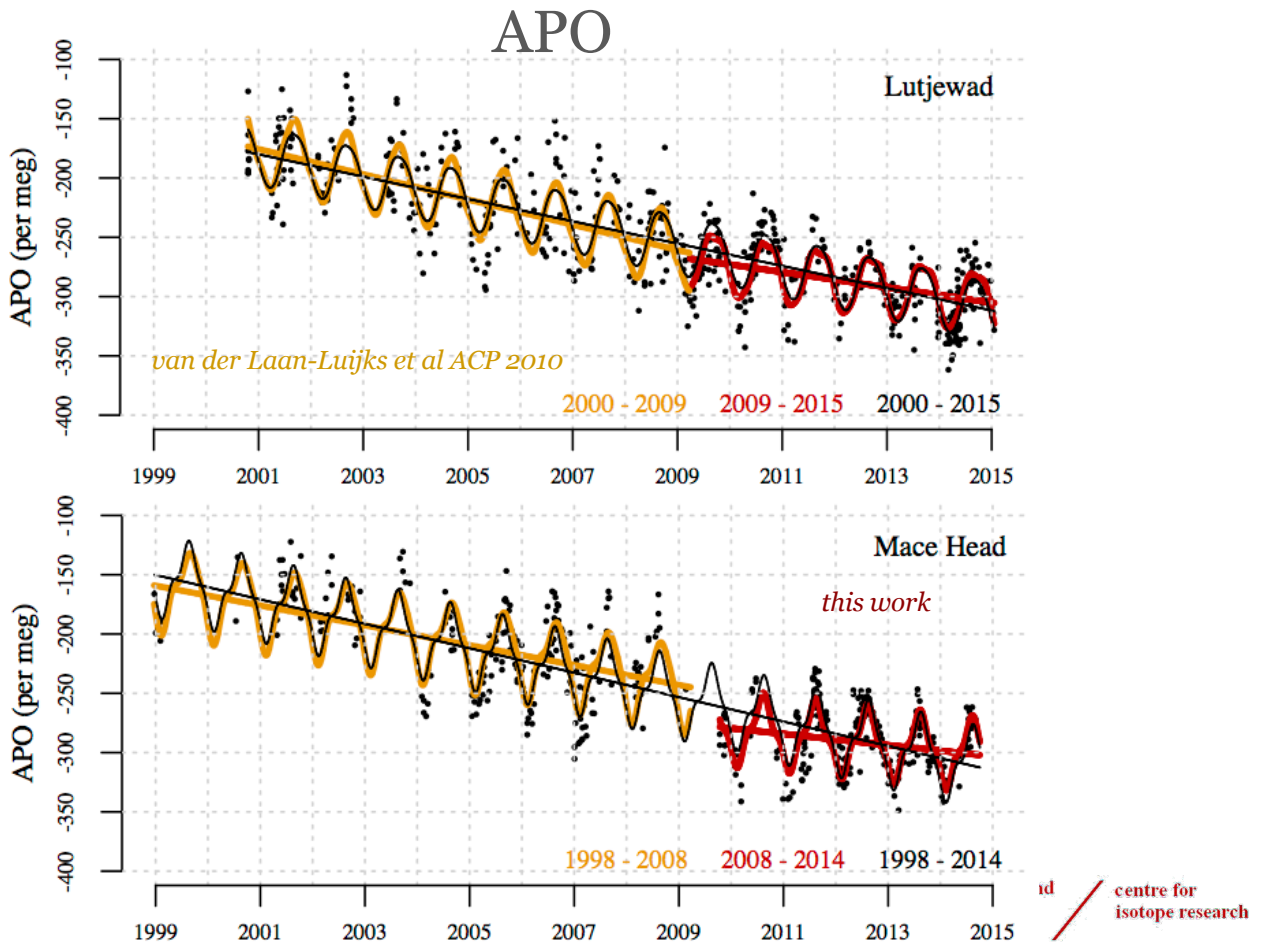
# Observations: flasks



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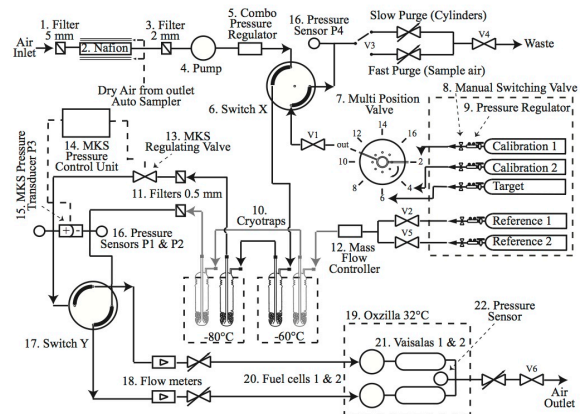
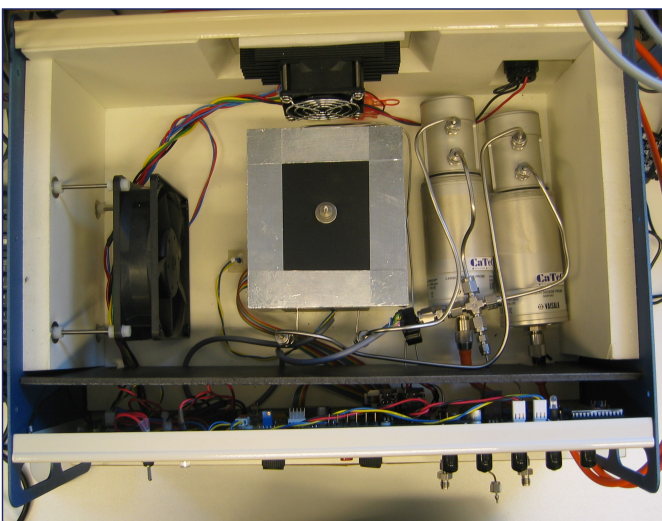
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## Lutjewad continuous measurements

**Oxzilla + Vaisala = Oxzala**



Use of Oxzilla II pioneered by Stephens et al. (2007), Thompson et al. (2007) and Patecki & Manning (2007). Also used by van der Laan-Luijckx et al, 2010 on the F3 North Sea gas platform

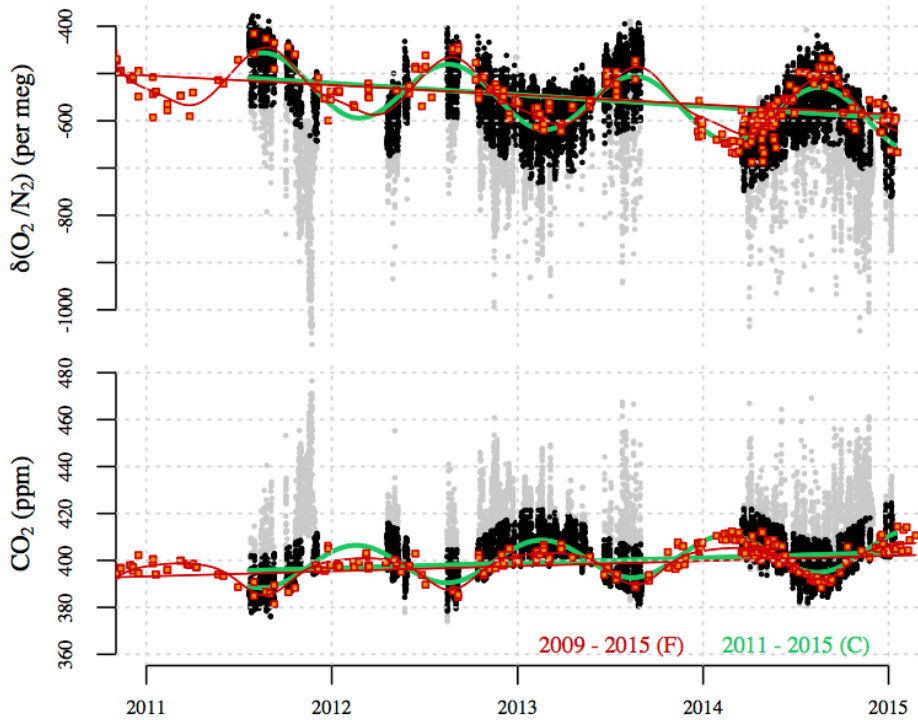


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# Lutjewad continuous and flasks

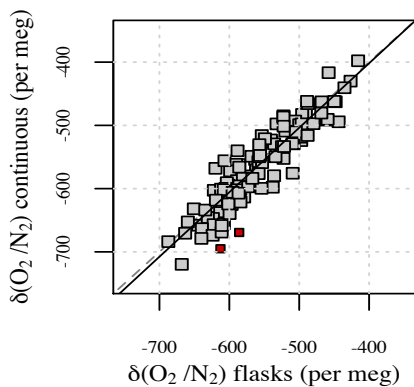
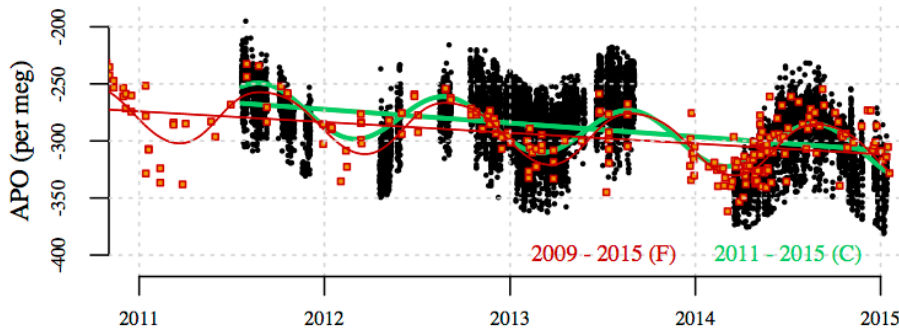


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# Lutjewad continuous and flasks APO



flask-continuous comparison

good average agreement, but large scatter:  
 25 per meg instead of expected  $\approx 12$  per meg  
 caused by flask handling ??



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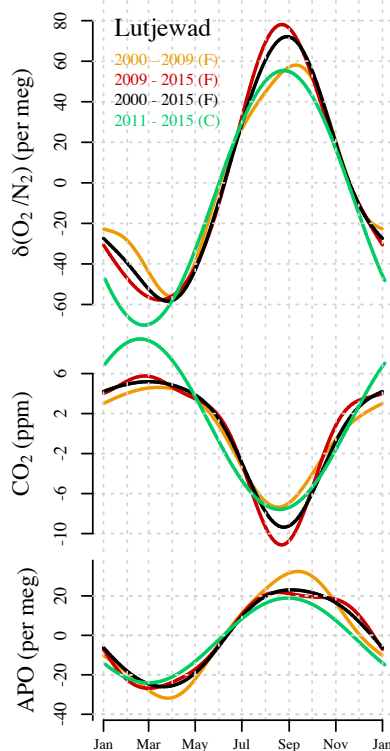
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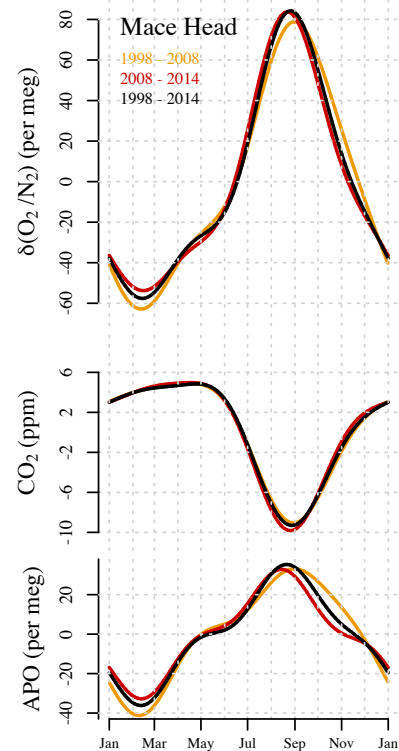
# Trend analysis

Location	Time period & reference	Trend		
		CO <sub>2</sub>	δO <sub>2</sub> /N <sub>2</sub>	APO
Lutjewad (53.24°N 6.21°E)	2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)	1.97 ± 0.07	-21.0 ± 0.9	-10.6 ± 0.7
	2009 – 2015 [Flasks – CIO] (this work)	2.94 ± 0.09	-20.8 ± 0.8	-6.4 ± 0.5
	2000 – 2015 [Flasks – CIO] (this work)	2.19 ± 0.03	-20.5 ± 0.3	-9.4 ± 0.2
	2011 – 2014 [Continuous – CIO] (this work)	2.20 ± 0.05	-24.4 ± 0.4	-12.0 ± 0.2
Mace Head (53.20°N 9.54°W)	2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)	1.90 ± 0.04	-18.5 ± 0.7	-8.4 ± 0.7
	2009 – 2015 [Flasks – CIO] (this work)	2.41 ± 0.04	-15.3 ± 0.9	-4.7 ± 0.8
	2000 – 2015 [Flasks – CIO] (this work)	2.12 ± 0.01	-21.4 ± 0.3	-10.3 ± 0.2
Weybourne (52.95°N 1.12°E)	Jan 2009 – April 2012 [Continuous] (Wilson, 2012)	2.41 ± 0.07	-25.3 ± 0.4	-13.4 ± 0.1
F3 (54.51°N 4.44°E)	2006 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)	2.11 ± 0.04	-27.1 ± 0.6	-13.2 ± 0.5
Jungfrauoch (46.33°N 7.59°E)	2007 – 2011 [Flasks – CIO] (van der Laan-Luijkx et al., 2013)	1.94 ± 0.18	-23 ± 3	xxx
	2007 – 2011 [Flasks – MPI] (van der Laan-Luijkx et al., 2013)	1.83 ± 0.17	-17.3 ± 1.5	xxx
	2007 – 2011 [Flasks – Bern] (van der Laan-Luijkx et al., 2013)	1.76 ± 0.17	-29 ± 3	xxx
Fyodorovskoye (56.27°N 32.55°E)	1998 – 2008 [Flasks 100 m – CIO] (van der Laan et al., 2014)	1.98 ± 0.15	-16.1 ± 2.0	-8.5 ± 1.8
Bialystok (53.13°N 23.01°E)	Aug 2005 – Jun 2008 [Continuous] (Popa et al., 2010)	2.0 ± 0.5	-23 ± 3	-12.2 ± 0.9

# seasonal cycles



flasks: 3 harmonics  
continuous: 1 harmonic



# seasonal cycle: peak-to-trough amplitudes

Location	Time period & reference	Amplitude		
		CO <sub>2</sub>	δO <sub>2</sub> /N <sub>2</sub>	APO
Lutjewad (53.24°N 6.21°E)	2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)	12.0 ± 0.6	114 ± 8	64 ± 6
	2009 – 2015 [Flasks – CIO] (this work)	16.9 ± 0.8	136 ± 8	49 ± 5
	2000 – 2015 [Flasks – CIO] (this work)	14.5 ± 0.6	130 ± 6	49 ± 5
	2011 – 2014 [Continuous – CIO] (this work)	17.0 ± 0.2	125.6 ± 1.5	43.0 ± 0.8
Mace Head (53.20°N 9.54°W)	2000 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)	14.0 ± 0.3	142 ± 6	74 ± 6
	2009 – 2015 [Flasks – CIO] (this work)	14.8 ± 0.3	137 ± 6	66 ± 5
	2000 – 2015 [Flasks – CIO] (this work)	14.1 ± 0.3	142 ± 5	71 ± 5
Weybourne (52.95°N 1.12°E)	Jan 2009 – April 2012 [Continuous] (Wilson, 2012)	14.9 ± 0.8	134 ± 8	59 ± 6
F3 (54.51°N 4.44°E)	2006 – 2009 [Flasks – CIO] (van der Laan-Luijkx et al., 2010a)	15.2 ± 0.1	144 ± 2	111 ± 2
Jungfrauoch (46.33°N 7.59°E)	2007 – 2011 [Flasks – CIO] (van der Laan-Luijkx et al., 2013)	10.6 ± 0.4	85 ± 4	xxx
	2007 – 2011 [Flasks – MPI] (van der Laan-Luijkx et al., 2013)	10.7 ± 0.3	84 ± 2	xxx
	2007 – 2011 [Flasks – Bern] (van der Laan-Luijkx et al., 2013)	10.3 ± 0.3	69 ± 5	xxx
Fyodorovskoye (56.27°N 32.55°E)	1998 – 2008 [Flasks 100 m– CIO] (van der Laan et al., 2014)	23.2 ± 1.0	131 ± 13	37 ± 8
Bialystok (53.13°N 23.01°E)	Aug 2005 – Jun 2008 [Continuous] (Popa et al., 2010)	25	161	43

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## Discussion / Conclusions



Valuable time series Lutjewad and Mace Head now 15 years long

We need to bring all European records onto the same scale

North Sea is the best known coastal sea in terms of carbon exchange

Wish list: use Weybourne, Lutjewad and F3 either to verify the North Sea Carbon Balance, or using that balance to track the fossil fuel combustion of the numerous North Sea oil and gas rigs

Data will be made available: van Leeuwen, C., Scheeren, H.A., van der Laan-Luijkx, I.T., Kers, B.A.M. and Meijer, H.A.J. – Continuous and flask observations of atmospheric δO<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub> at Lutjewad station, the Netherlands, and Mace Head station, Ireland.



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