Cape Verde Atmospheric Observatory (CVO)

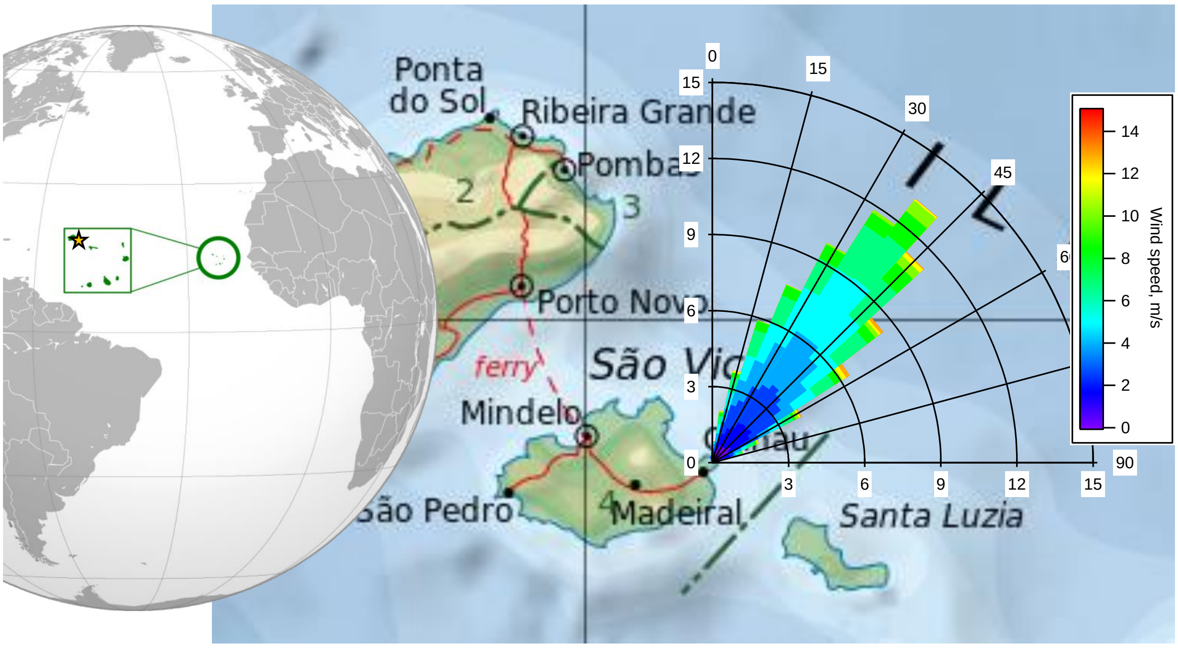

Figure S1. Location of CVO on the globe, and within the Cape Verde archipelago. Also shown is the wind rose data (centred on the site) for the data used in the analysis of NO_x data.

Box model description

The Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC) atmospheric chemistry box model (Emmerson and Evans, 2009) is used to interpret the NO_x observations. It use the Kinetic PreProcessor (KPP-2.1, Damian et al., 2002) to solve ordinary differential equations generated from the reactions and their kinetic information (Sandu and Sander, 2006).

Rate information is assimilated from; Master Chemical Mechanism for near explicit organic reactions (MCMv3.3.1, Bloss et al., 2005; Jenkin et al., 1997, 2003, 2015; Saunders et al., 2003); inorganic rates at taken from IUPAC (Atkinson et al., 2004, 2007) and JPL (Burkholder et al., 2015) evaluated databases and are detailed in tables below; clear sky photolysis rates are calculated by the Tropospheric Ultraviolet and Visible model (TUV, www2.acom.ucar.edu/modeling/tuv-download; Madronich, 1993).

Table ST1. Rates of O_x reactions used in DSMACC model.

		O_X reactions	
#	Reaction	Rate	Reference
1	$O + O_2 \rightarrow O_3$	$(6.00 \times 10^{-34}$ $[O_2][O_2](TEMP/300)^{-2.6}))$ + $(5.60 \times 10^{-34}$ $[O_2][N_2](TEMP/300)^{-2.6}))$	(Burkholder et al., 2015)
2	$O + O_3 \rightarrow 2O_2$	8.00×10^{-12} $e^{(-2060/TEMP)}$	(Burkholder et al., 2015)
2	O^1D + $M \rightarrow$ O + M	$(3.30 \times 10^{-11}$ $[O_2]e^{(55/TEMP)})$ + $(2.15 \times 10^{-11}$ $[N_2]$ $e^{(110/TEMP)})$	(Burkholder et al., 2015)
2	$O^1D + H_2O \rightarrow 2OH$	1.63×10^{-10} $[H_2O]$ $e^{(60/TEMP)}$	(Burkholder et al., 2015)
5	$O^1D + O_3 \rightarrow O$	2.40×10^{-10} $[O_3](0/TEMP)$	(Burkholder et al., 2015)

Table TS2. Rates of HO_x reactions used in DSMACC model.

HO_x reactions

#	Reaction	Rate	Reference
1	$O + OH \rightarrow H + O_2$	$1.80 \times 10^{-11}\, e^{(180/TEMP)}$	(Burkholder et al., 2015)
2	$O + HO_2 \rightarrow OH + O_2$	$3.00 \times 10^{-11}\, e^{(200/TEMP)}$	(Burkholder et al., 2015)
3	$O + H_2O_2 \rightarrow OH + HO_2$	$1.40 \times 10^{-10}\, e^{(-2000/TEMP)}$	(Burkholder et al., 2015)
4	$H + O_3 \rightarrow OH + O_2$	$1.40 \times 10^{-10}\, e^{(-470/TEMP)}$	(Burkholder et al., 2015)
5	$H + HO_2 \rightarrow 2OH$	$7.20 \times 10^{-11}\, e^{(0/TEMP)}$	(Burkholder et al., 2015)
6	$OH + O_3 \rightarrow HO_2 + O_2$	$1.70 \times 10^{-12}\, e^{(-940/TEMP)}$	(Burkholder et al., 2015)
7	$OH + OH \rightarrow O + H_2O$	$1.80 \times 10^{-12}\, e^{(0/TEMP)}$	(Burkholder et al., 2015)
8	$OH + HO_2 \rightarrow H_2O + O_2$	$4.80 \times 10^{-11}\, e^{(250/TEMP)}$	(Burkholder et al., 2015)
9	$OH + H_2O_2 \rightarrow HO_2$	$2.90 \times 10^{-12}\, e^{(-160/TEMP)}$	(Atkinson et al., 2004)
10	$OH + H_2 \rightarrow H_2O + H$	$2.80 \times 10^{-12}\, e^{(-1800/TEMP)}$	(Burkholder et al., 2015)
11	$OH + CO \rightarrow HO_2$	$1.44\times10^{-13} \times (1+([M]/4.2\times10^{19}))$	(Atkinson et al., 2004)
12	$HO_2 + O_3 \rightarrow OH + O_2$	$1.00 \times 10^{-14}\, e^{(-490/TEMP)}$	(Burkholder et al., 2015)
13	$2HO_2 \rightarrow H_2O_2$	$(2.20 \times 10^{-13} \times (1 + (1.40 \times 10^{-21}\, e^{(2200/TEMP)} \times [H_2O]) \times e^{(600/TEMP)}) + (1.90 \times 10^{-33} [M] \times (1 + (1.40 \times 10^{-21}\, e^{(2200/TEMP)} \times [H_2O]) \times e^{(980/TEMP)})$	(Atkinson et al., 2004)

Table TS3. Rates of NO_x reactions used in DSMACC model.

NO_x reactions

#	Reaction	Rate	Reference
1	$O + NO \rightarrow NO_2$	$5.00 \times 10^{-11}\, (TEMP/300)^{-0.3}$	(Atkinson et al., 2004)
2	$O + NO_2 \rightarrow NO_3$	$1.30 \times 10^{-31}\, (TEMP/300)^{-1.5}\, [N_2]$	(Atkinson et al., 2004)
3	$O + NO_3 \rightarrow NO_2 + O_2$	$1.00 \times 10^{-11}\, e^{(0/TEMP)}$	(Burkholder et al., 2015)
4	$O + NO_2 \rightarrow NO + O_2$	$5.10 \times 10^{-12}\, e^{(210/TEMP)}$	(Burkholder et al., 2015)
5	$H + NO_2 \rightarrow OH + NO$	$4.00 \times 10^{-10}\, e^{(-3400/TEMP)}$	(Burkholder et al., 2015)
6	$OH + HONO \rightarrow NO_2 + H_2O$	$2.50 \times 10^{-12}\, e^{(260/TEMP)}$	(Atkinson et al., 2004)

7	$HO_2 + NO \rightarrow OH + NO_2$	$3.30 \times 10^{-12}\ e^{(270/TEMP)}$	(Burkholder et al., 2015)
8	$HO_2 + NO_2 \rightarrow HO_2NO_2$	1.40×10^{-31} (TEMP/300)$^{-3.1}$ [N^2]	(Atkinson et al., 2004)
9	$HO_2 + NO_3 \rightarrow OH + NO_2$	$4.00 \times 10^{-12}\ e^{(0/TEMP)}$	(Atkinson et al., 2004)
10	$NO + O_3 \rightarrow NO_2 + O_2$	$3.00 \times 10^{-12}\ e^{(-1500/TEMP)}$	(Burkholder et al., 2015)
11	$NO + NO_3 \rightarrow NO_2 + NO_2$	$1.50 \times 10^{-11}\ e^{(170/TEMP)}$	(Burkholder et al., 2015)
12	$NO_2 + O_3 \rightarrow NO + 2O_2$	$1.20 \times 10^{-13}\ e^{(-2450/TEMP)}$	(Burkholder et al., 2015)
13	$NO_2 + NO_3 \rightarrow NO + NO_2 + O_2$	$4.50 \times 10^{-14}\ e^{(1260/TEMP)}$	(Burkholder et al., 2015)
14	$2NO_3 \rightarrow 2NO_2 + O_2$	$8.50 \times 10^{-13}\ e^{(-2450/TEMP)}$	(Burkholder et al., 2015)
15	$NO_2 + NO_3 \rightarrow N_2O_5$	3.60×10^{-30} (TEMP/300)$^{-4.1}$ [N_2]	(Atkinson et al., 2004)
16	$N_2O_5 \rightarrow NO_3 + NO_2$	1.30×10^{-3} (TEMP/300)$^{-3.5}$ $e^{(-11000/TEMP)}$ [N_2]	(Atkinson et al., 2004)
17	$OH + NO \rightarrow HONO$	7.40×10^{-31} (TEMP/300)$^{-2.4}$ [N_2]	(Atkinson et al., 2004)
18	$OH + NO_2 \rightarrow HNO_3$	3.20×10^{-30} (TEMP/300)$^{-4.5}$ [N_2]	(Atkinson et al., 2004)
19	$OH + NO_3 \rightarrow HO_2 + NO_2$	$2.00 \times 10^{-11}\ e^{(0/TEMP)}$	(Atkinson et al., 2004)
20	$HO_2NO_2 \rightarrow NO_2 + HO_2$	$4.10 \times 10^{-5}\ e^{(-10650/TEMP)}$ [N_2]	(Atkinson et al., 2004)
21	$OH + HNO_3 \rightarrow NO_3 + H_2O$	1.50×10^{-13}	(Atkinson et al., 2004)
22	$OH + HO_2NO_2 \rightarrow NO_2$ + prods	$3.20 \times 10^{-12}\ e^{(690/TEMP)}$	(Atkinson et al., 2004)

Table TS4. Rates of Bromine reactions used in DSMACC model.

		Bromine reactions	
#	Reaction	Rate	Reference
1	$Br + O_3 \rightarrow BrO + O_2$	$1.70 \times 10^{-11}\ e^{(-800/TEMP)}$	(Atkinson et al., 2007)
2	$BrO + NO_2 \rightarrow BrNO_3$	5.20×10^{-31} ((TEMP/300.)$^{-3.2}$)[M]	(Burkholder et al., 2015)
3	$BrNO_3 \rightarrow BrO + NO_2$	$2.80 \times 10^{13}\ e^{(-12360/TEMP)}$	(Orlando and Tyndall, 2002)
4	$BrO + HO_2 \rightarrow HOBr + O_2$	$4.50 \times 10^{-12}\ e^{(500/TEMP)}$	(Atkinson et al., 2007)
5	$Br + HO_2 \rightarrow HBr + O_2$	$4.80 \times 10^{-12}\ e^{(-310/TEMP)}$	(Burkholder et al., 2015)
6	$HBr + OH \rightarrow Br + H_2O$	1.10×10^{-11}	(Atkinson et al., 2007)

7	$BrO + NO \rightarrow Br + NO_2$	$8.70 \times 10^{-12}\ e^{(260/TEMP)}$	(Atkinson et al., 2007)
8	$2BrO \rightarrow 2Br + O_2$	$2.36 \times 10^{-12}\ e^{(40/TEMP)}$	
9	$2BrO \rightarrow Br_2 + O_2$	$2.79 \times 10^{-14}\ e^{(860/TEMP)}$	
10	$Br + HCHO \rightarrow HBr + HO_2$	$1.70 \times 10^{-11}\ e^{(-800/TEMP)}$	(Burkholder et al., 2015)
11	$Br + NO_3 \rightarrow BrO + NO_2$	1.60×10^{-11}	(Burkholder et al., 2015)
12	$HOBr + NO_3 \rightarrow BRO + HNO_3$	$2.7 \times 10^{-12}\ e^{(300/TEMP)\wedge 2.66}$	*This work*

Table TS5. Rates of Iodine reactions used in DSMACC model.

		Iodine reactions	
#	Reaction	Rate	Reference
1	$I + HO_2 \rightarrow HI$	$1.50 \times 10^{-11}\ e^{(-1090/TEMP)}$	(Atkinson et al., 2007)
2	$IO + NO_2 \rightarrow INO_3$	7.70×10^{-31} ((TEMP/300)$^{-5.}$)[M]	(Atkinson et al., 2007)
3	$INO_3 \rightarrow IO + NO_2$	$1.10 \times 10^{15}\ e^{(-12060/TEMP)}$	(Atkinson et al., 2007)
4	$OH + HI \rightarrow I$	3.00×10^{-11}	(Burkholder et al., 2015)
5	$IO + NO \rightarrow NO_2 + I$	$7.15 \times 10^{-12}\ e^{(300/TEMP)}$	(Atkinson et al., 2007)
6	$I + O_3 \rightarrow IO + O_2$	$2.30 \times 10^{-11}\ e^{(-870/TEMP)}$	(Burkholder et al., 2015)
7	$IO + HO_2 \rightarrow HOI + O_2$	$1.40 \times 10^{-11}\ e^{(540/TEMP)}$	(Atkinson et al., 2007)
8	$HOI + OH \rightarrow IO$	2.00×10^{-13}	(Mössinger and Cox, 2001)
9	$2IO \rightarrow I + OIO$	$(5.40 \times 10^{-11}\ e^{(180/TEMP)}) \times 0.38$	(Atkinson et al., 2007; Bloss et al., 2001)
10	$2IO \rightarrow 2I + O_2$	$(5.40 \times 10^{-11}\ e^{(180/TEMP)}) \times 0.11$	(Atkinson et al., 2007; Bloss et al., 2001)
11	$OIO + NO \rightarrow IO + NO_2$	$1.10 \times 10^{-12}\ e^{(542/TEMP)}$	(Plane et al., 2006)
12	$I_2 + NO_3 \rightarrow INO_3 + I$	1.50×10^{-12}	(Atkinson et al., 2007)
13	$I + NO_3 \rightarrow IO + NO_2$	1.00×10^{-10}	(Atkinson et al., 2007)
14	$HOI + NO_3 \rightarrow IO + HNO_3$	$2.70 \times 10^{-12}\ e^{(300/TEMP)\wedge 2.66}$	(Saiz-Lopez et al., 2016)

Table TS6. Rates of mixed halogen reactions used in DSMACC model.

	Mixed halogen reactions		
#	Reaction	Rate	Reference
1	$BrO + IO \rightarrow Br + 0.8\ OIO + 0.2\ I$	$1.50 \times 10^{-11}\ e^{(510/TEMP)}$	(Atkinson et al., 2007)
2	$I + BrO \rightarrow IO + Br$	1.20×10^{-11}	(Burkholder et al., 2015)
3	$Br + IO \rightarrow BrO + I$	2.70×10^{-11}	

Table TS7. Aerosol reactive uptake coefficients (γ) used in DSMACC model. UPTAKE(γ, Temp, Surface Area, Mass).

	Aerosol reactions		
#	Reaction	γ	Reference
1	$N_2O_5 \rightarrow 2 \times p\text{-}NO_3$	0.02	(Crowley et al., 2010)[a]
2	$HNO_3 \rightarrow p\text{-}NO_3$	0.15	(Crowley et al., 2010)[a]
3	$NO_3 \rightarrow p\text{-}NO_3$	0.012	(Crowley et al., 2010)[a]
4	$HOBr \rightarrow 0.5\ Br_2$	0.02-0.80	(Saiz-Lopez et al., 2008)[b]
5	$BrNO_3 \rightarrow HOBr + p\text{-}NO_3$	0.02-0.80	(Burkholder et al., 2015; Saiz-Lopez et al., 2008)[b]
6	$HBr \rightarrow 0.5\ Br_2$	0.02-0.80	(Saiz-Lopez et al., 2008)[b]
7	$HOI \rightarrow 0.5\ I_2$	0.02-0.80	(Saiz-Lopez et al., 2008)[b]
8	$HI \rightarrow 0.5\ I_2$	0.02-0.80	(Saiz-Lopez et al., 2008)[b]
9	$INO_3 \rightarrow HOI + p\text{-}NO_3$	0.02-0.80	(Burkholder et al., 2015; Saiz-Lopez et al., 2008)[b]

[a] Data from IUPAC datasheets of uptake coefficients on Saharan dust.

[b] sensitivity analysis performed on uptake coefficients.

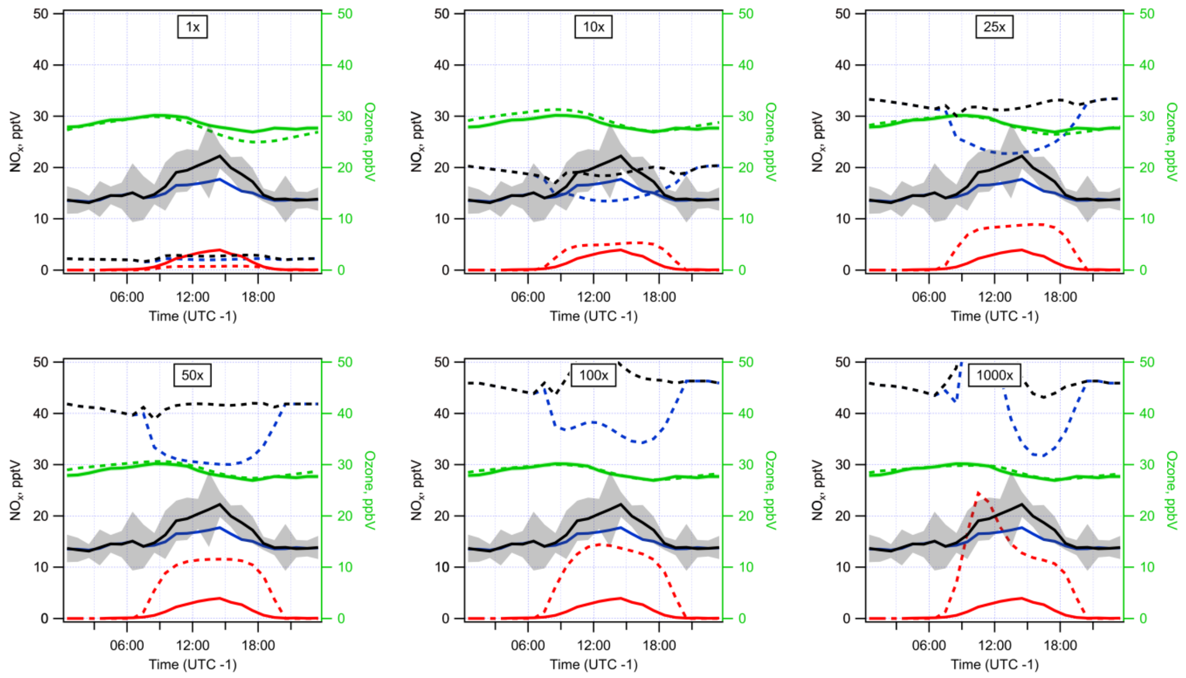

Figure S2. The modelled diurnal profile of NOx at CVO during summer months when photolysis of nitrate is considered. The rate of particulate nitrate photolysis has been scaled to the rate of HNO3 photolysis by factors of 1, 10, 25, 50, 100, and 1000. Observations are solid lines whilst modelled values are shown dashed. Shaded areas are standard error of the observation. O3 – green; NOx – black; NO2 – blue; NO – red.

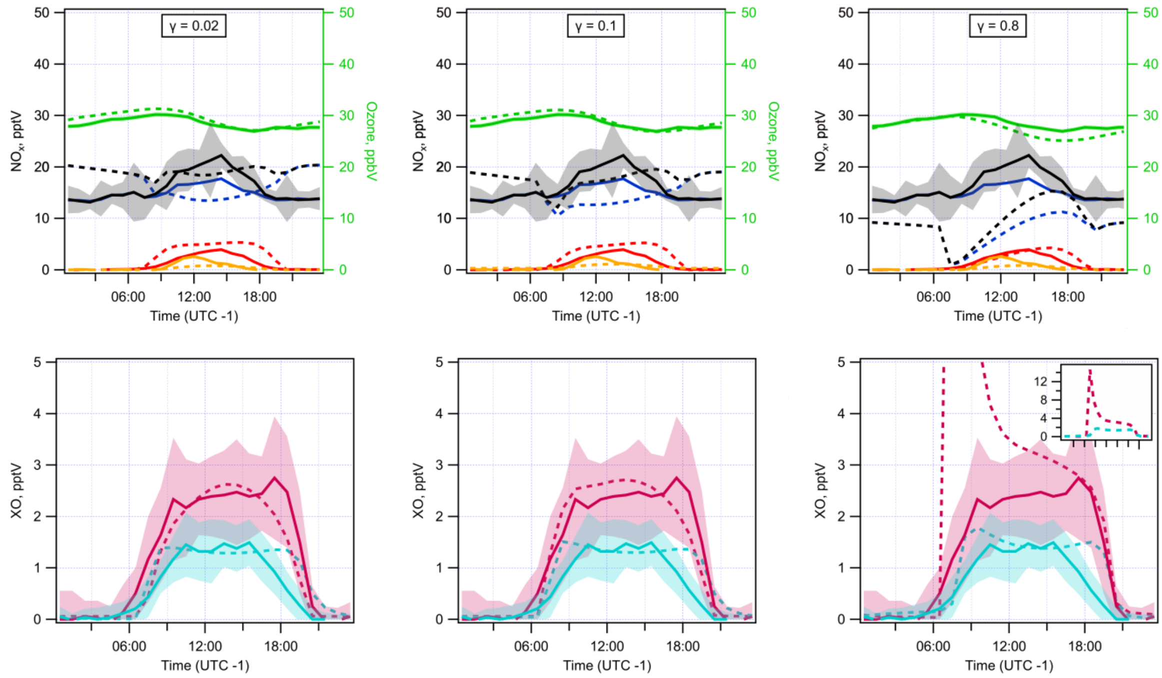

Figure S3. Sensitivity analysis of the effect of changing reactive uptake co-efficients (γ) of reactive halogens (XO, XHO, XONO2, X = Br, I) on NOx (top) and XO (bottom) diurnal behaviour during summer months at CVO. Particulate nitrate photolysis is set at 10 times the rate of gaseous HNO3. Observations are solid lines whilst modelled values are shown as dashed. IO and BrO observations are adapted from Read et al., (2008). Shaded areas are standard error of the observation. O3 – green; NOx – black; NO2 – blue; NO – red; HONO – yellow; IO – turquoise; BrO – purple.

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