Oxygen as a tracer for fossil fuel CO₂ emission sources

Author: Bernice KUIJPERS

Supervisors: Prof. Dr. Wouter PETERS
Dr. Ingrid van der LAAN-LUIJKX

March 15, 2018
Abstract

The combustion processes involved in fossil fuel burning lead to emittance of carbon dioxide and consumption of oxygen. The fact that every fuel type has a specific oxidative ratio, makes oxygen a potential tracer for fossil fuel carbon dioxide. Fluctuations in atmospheric oxygen concentration are modelled using WRF-chem. In order to do so, an average oxidative ratio is calculated per emission category for the Netherlands. To complete the modelling of oxygen, biosphere and ocean exchanges are included. The model outcomes are validated using measurements from Weybourne (UK) and Lutjewad (NL) of October 2014. Even though Weybourne is situated outside the Netherlands, the model reached an index of agreement of 0.75 for that location. Most discrepancies in the simulation of the compound concentrations are found to be due to errors in the meteorological circumstances and wind direction.

Furthermore, study area Rijnmond (NL) is analysed in more detail. The information about the usage of distinct fuel types of various point sources in Rijnmond allowed for a more veracious modelling of oxygen in that area, using the (known) oxidative ratios of point sources within the domain. This results in lower oxidative ratios and higher oxygen concentrations as compared to the simulation done with the average oxidative ratio of the Netherlands. Unfortunately, results at Rijnmond cannot yet be validated due to the absence of oxygen measurements in the area. A measurement campaign as part of the RINGO project (ICOS n.d.) is however planned to start in the near future, which will allow for more insight in the potential of modelling oxygen as a tracer for fossil fuel carbon dioxide in urban areas.
Preface

The report presented here is the result of the work I did for my Master thesis at the Meteorology and Air Quality group at Wageningen University. During my study, my interest in climate and atmospheric composition grew as I learned more about atmospheric science. Whilst looking for a subject for my Master thesis, Wouter Peters introduced me to Ingrid van der Laan-Luijkx, who sparked my interest for atmospheric oxygen leading me to write the following thesis.

I would like to thank both my supervisors for their support and guidance. I want to express my gratitude to Ingrid van der Laan-Luijkx for her day-to-day supervision and the content related discussions I had with her, which really contributed to my learning process. The calm manner in which Ingrid interacts made me feel comfortable and she really contributed to my confidence during my research. Furthermore, I’d like to thank Wouter Peters for his weekly supervision, overall keeping track of my progress, and intermediate feedback. I appreciate being invited to join the RINGO meeting at Groningen University, involving me in the project and increasing my insight in the relevance of my research. Together, my supervisors created an environment in which I was able to develop myself.

I would also like to thank Ingrid Super, for the WRF-chem model setup and the scripts she provided at the start of my research. Furthermore, Michiel van der Molen as well as Kees van den Dries spent considerable time and effort in helping me with my first model runs, which I very much appreciate.

Valuable data in the form of APO fields and the COFFEE dataset were made available by Christian Rödenbeck and Christoph Gerbig, respectively, which greatly contributed to the analysis done in this research. Furthermore, oxygen measurements at Lutjewad were made available by Charlotte van Leeuwen, Elise Broekema, and Harro Meijer, and measurements at Weybourne by Thomas Barningham, Penelope Pickers, and Andrew Manning. Both datasets were crucial in validating the created model.

Finally, I would like to express my gratitude to my friends and fellow students at the Meteorology and Air Quality department, for their scientific and mental support and at times much needed supply of chocolate. Largely because of you, I will look back on my time working on my thesis with much joy and laughter. Thank you.
Contents

List of Figures 5

List of Tables 6

1 Introduction 7

1.1 Background theory 8

1.1.1 Carbon reservoirs 8

1.1.2 Oxidative ratios 9

1.1.3 Expressing atmospheric oxygen 11

1.2 Research area and WRF-Chem 13

1.3 Research justification and research objectives 14

2 Methods 16

2.1 Case study 16

2.2 Modelling framework and settings 17

2.3 Modelling strategy 18

2.3.1 Modelling CO₂ emissions, photosynthesis, and respiration 18

2.3.2 Modelling O₂ uptake and release 20

2.3.3 Ocean-atmosphere O₂ exchange 21

2.4 Analysis of the results 21

2.4.1 Converting O₂ data to ppm concentrations 21

2.4.2 Calculating and analysing outcoming Oxidative Ratios 22

3 Wind direction - statistical analysis of the model performance 24

3.1 WRF version 3.2.1 vs version 3.9.1 27

3.1.1 Update in the Revised MM5 Monin-Obukov scheme 28

3.2 Location comparison 30

3.3 4x4 km vs 1x1 km horizontal resolution 33

3.4 Wind direction nudging 34
4 Partitioning fluctuations in atmospheric O\(_2\)  
4.1 O\(_2\) fluctuation partitioning  
4.1.1 Diurnal cycles  
4.2 Total O\(_2\) fluctuation and model validation  
4.2.1 Zweth, Rijnmond  
4.2.2 Lutjewad, Groningen  
4.2.3 Weybourne, North Norfolk  
5 Simulating (fossil fuel) CO\(_2\), fossil fuel O\(_2\), and fossil fuel oxidative ratios  
5.1 Fossil fuel CO\(_2\), O\(_2\), and OR\(_{ff}\) at Rijnmond  
5.1.1 CO\(_2\) concentrations  
5.1.2 Dominant CO\(_2\) emission sources  
5.1.3 Fossil fuel O\(_2\) and OR\(_{ff}\)  
5.2 Fossil fuel CO\(_2\), O\(_2\), and OR\(_{ff}\) at the north of Groningen  
5.2.1 CO\(_2\) concentrations  
5.2.2 Dominant CO\(_2\) emission sources  
5.2.3 Fossil fuel O\(_2\) and OR\(_{ff}\)  
5.3 Fossil fuel CO\(_2\), O\(_2\), and OR\(_{ff}\) at North Norfolk  
5.3.1 CO\(_2\) concentrations  
5.3.2 Dominant CO\(_2\) emission sources  
5.3.3 O\(_2\) fluctuations and OR\(_{ff}\)  
5.4 CO\(_2\) emission events  
5.4.1 CO\(_2\) events at Zweth  
5.4.2 CO\(_2\) events at Lutjewad  
5.4.3 CO\(_2\) events at Weybourne  
6 Source specific OR\(_{in}\)  
6.1 O\(_2\) fluctuations and OR\(_{ff}\)  
6.2 CO\(_2\) emission events  
7 Discussion
7.1 Model uncertainties and recommendations .......................... 74
    7.1.1 Ocean exchange ............................................. 74
    7.1.2 Biosphere exchange ......................................... 75
    7.1.3 Fossil fuel burning ......................................... 75
    7.1.4 Uncertainties in advection ................................. 75
    7.1.5 Initial conditions, boundary conditions, and entrainment .. 76
    7.2 Recommendations for future analysis .......................... 77

8 Conclusion ............................................................. 79

9 Research outlook ................................................... 81
List of Figures

1. Global Carbon Dioxide budget .................................................. 8
2. Carbon reservoirs and fluxes .................................................. 9
3. Anticorrelation between atmospheric O$_2$ and CO$_2$ ................. 10
4. Sources and sinks of O$_2$ and CO$_2$ ........................................ 12
5. Map of Rijnmond ............................................................... 14
6. Map of the north of Groningen and North Norfolk ....................... 17
7. Map of the model domains .................................................... 17
8. Wind direction as modelled by WRF version 3.2.1, version 3.9.1, and observed .................................................. 24
9. Observed versus simulated wind direction for WRF version 3.2.1 and version 3.9.1 .................................................. 27
10. Map showing an example of days with 'well' and 'badly' simulated wind direction .................................................. 31
11. Observed and simulated wind direction at Rotterdam, Lauwersoog, and Eindhoven .................................................. 32
12. Comparison of wind direction observations, and as modelled on a 4x4 and 1x1 km horizontal resolution .................................................. 34
13. Comparison of observed wind direction and as modelled with and without observation nudging .................................................. 35
14. Partitioning of the fossil fuel, biosphere, and ocean sources/sinks at Zweth, Rijnmond .................................................. 38
15. Partitioning of the fossil fuel, biosphere, and ocean sources/sinks at Lutjewad, north of Groningen .................................................. 39
16. Partitioning of the fossil fuel, biosphere, and ocean sources/sinks at Weybourne, North Norfolk .................................................. 40
17. Diurnal cycles of fossil fuel, biospheric, and oceanic O$_2$ uptake at the three study areas .................................................. 42
18. Time series of total O$_2$ uptake at Zweth, Rijnmond .................................................. 43
19. Time series of total CO$_2$ concentrations, modelled and observed at Zweth, Rijnmond .................................................. 44
<table>
<thead>
<tr>
<th>Page</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>Time series of total O&lt;sub&gt;2&lt;/sub&gt; uptake, modelled and observed at Lutjewad, north of Groningen.</td>
</tr>
<tr>
<td>21</td>
<td>Time series of total CO&lt;sub&gt;2&lt;/sub&gt; concentrations, modelled and observed at Lutjewad, north of Groningen.</td>
</tr>
<tr>
<td>22</td>
<td>Time series of total O&lt;sub&gt;2&lt;/sub&gt; uptake, modelled and observed at Weybourne, North Norfolk.</td>
</tr>
<tr>
<td>23</td>
<td>Time series of total CO&lt;sub&gt;2&lt;/sub&gt; concentration, modelled and observed at Weybourne, North Norfolk.</td>
</tr>
<tr>
<td>24</td>
<td>Time series and wind rose of CO&lt;sub&gt;2&lt;/sub&gt; concentrations at Zweth, Rijnmond.</td>
</tr>
<tr>
<td>25</td>
<td>Map of average CO&lt;sub&gt;2&lt;/sub&gt; emissions over domain 4 and relative importance of the SNAP emission categories at Zweth, Rijnmond.</td>
</tr>
<tr>
<td>26</td>
<td>Maps of average ffCO&lt;sub&gt;2&lt;/sub&gt;, ffO&lt;sub&gt;2&lt;/sub&gt;, and OR&lt;sub&gt;ff&lt;/sub&gt; over Rijnmond.</td>
</tr>
<tr>
<td>27</td>
<td>Average diurnal cycle of a) ffCO&lt;sub&gt;2&lt;/sub&gt; and ffO&lt;sub&gt;2&lt;/sub&gt; concentration, and b) OR&lt;sub&gt;ff&lt;/sub&gt; in Zweth for October 2014.</td>
</tr>
<tr>
<td>28</td>
<td>Time series and wind rose of CO&lt;sub&gt;2&lt;/sub&gt; concentrations at Lutjewad, north of Groningen.</td>
</tr>
<tr>
<td>29</td>
<td>Map of average CO&lt;sub&gt;2&lt;/sub&gt; emissions over domain 3 and relative importance of the SNAP emission categories at Lutjewad, north of Groningen.</td>
</tr>
<tr>
<td>30</td>
<td>Maps of average ffCO&lt;sub&gt;2&lt;/sub&gt;, ffO&lt;sub&gt;2&lt;/sub&gt;, and OR&lt;sub&gt;ff&lt;/sub&gt; over the Netherlands.</td>
</tr>
<tr>
<td>31</td>
<td>Average diurnal cycle of ffCO&lt;sub&gt;2&lt;/sub&gt;, ffO&lt;sub&gt;2&lt;/sub&gt;, and OR&lt;sub&gt;ff&lt;/sub&gt; in Weybourne, North Norfolk.</td>
</tr>
<tr>
<td>32</td>
<td>Time series and wind rose of CO&lt;sub&gt;2&lt;/sub&gt; concentrations at Weybourne, North Norfolk.</td>
</tr>
<tr>
<td>33</td>
<td>Relative importance of the SNAP emission categories at Weybourne, North Norfolk.</td>
</tr>
<tr>
<td>34</td>
<td>Maps of average ffCO&lt;sub&gt;2&lt;/sub&gt;, ffO&lt;sub&gt;2&lt;/sub&gt;, OR&lt;sub&gt;ff&lt;/sub&gt;, and OR according to COFFEE over domain 2.</td>
</tr>
<tr>
<td>35</td>
<td>Average diurnal cycle of ffCO&lt;sub&gt;2&lt;/sub&gt;, ffO&lt;sub&gt;2&lt;/sub&gt;, and OR&lt;sub&gt;ff&lt;/sub&gt; in Weybourne, North Norfolk.</td>
</tr>
<tr>
<td>36</td>
<td>Map of source specific OR&lt;sub&gt;in&lt;/sub&gt; values as model input over Rijnmond.</td>
</tr>
<tr>
<td>37</td>
<td>Maps of ffO&lt;sub&gt;2&lt;/sub&gt; and OR&lt;sub&gt;ff&lt;/sub&gt; at Rijnmond simulated using source specific OR&lt;sub&gt;in&lt;/sub&gt;.</td>
</tr>
<tr>
<td>38</td>
<td>Diurnal cycle of ffCO&lt;sub&gt;2&lt;/sub&gt;, ffO&lt;sub&gt;2&lt;/sub&gt;, and OR&lt;sub&gt;ff&lt;/sub&gt; at Zweth simulated using source specific OR&lt;sub&gt;in&lt;/sub&gt;</td>
</tr>
<tr>
<td>A1</td>
<td>Wind direction error versus wind speed for WRF version 3.2.1.</td>
</tr>
<tr>
<td>A2</td>
<td>Observed versus simulated wind direction at Rotterdam and Lauwersoog.</td>
</tr>
</tbody>
</table>
List of Tables

1. CO₂ emission categories with corresponding OR_{iin} ............................................. 19
2. Statistics for wind direction as modelled by WRF version 3.2.1 and version 3.9.1 ............................................. 25
3. Statistics for wind direction as modelled by WRF version 3.2.1 and version 3.9.1 at wind speeds > 3 m/s ............................................. 26
4. Statistics for wind direction as modelled by WRF version 3.2.1, version 3.9.1, and version 3.9.1 without surface layer scheme updates ............................................. 30
5. Statistics for wind direction at Rotterdam, Lauwersoog, and Eindhoven ............................................. 32
6. Statistics for wind direction as modelled by WRF with and without observation nudging ............................................. 36
7. Statistics of O₂, CO₂, and wind direction model performance at Lutjewad, north of Groningen ............................................. 47
8. Statistics of modelled O₂, CO₂, and wind direction at Weybourne, North Norfolk ............................................. 49
9. Minimum and maximum ffCO₂ and ffO₂, the corresponding OR_{iff}, and prevailing wind direction per CO₂ event at Zweth ............................................. 66
10. Minimum and maximum ffCO₂ and ffO₂, the corresponding OR_{iff}, and prevailing wind direction per CO₂ event at Lutjewad ............................................. 67
11. Minimum and maximum ffCO₂ and ffO₂, the corresponding OR_{iff}, and the prevailing wind direction per CO₂ event at Weybourne ............................................. 67
12. Emission events at Zweth using the source specific OR_{iin} ............................................. 72
A1. Model settings overview ............................................. 88
A2. Statistics of wind speed for WRF version 3.2.1 ............................................. 88
A3. Overview of all statistics for wind direction ............................................. 89
A4. Overview of statistics for O₂, CO₂, and wind direction at the three study areas ............................................. 90
A5. Adapated model files and scripts ............................................. 91
1 Introduction

There is a general agreement in the scientific community that humans have a major influence on the recent changes recorded in the climate (Cook et al. 2013). Questions that arise from this are mainly related to how the climate will change in the future and what can and should be done about it. An important contributor to anthropogenic climate change is the emission of greenhouse gases, such as carbon dioxide (CO₂) and methane (CH₄). Emission of these greenhouse gases cause global temperatures to rise, which is expected have adverse effects for humans as well as many other species on Earth (IPCC - Intergovernmental Panel on Climate Change 2013).

In order to successfully reduce and verify anthropogenic greenhouse gas emissions, it is important to know what causes increases and decreases in these emissions. For instance, how would emissions change during a cold winter, if house-hold electricity and gas are more smartly managed, or if electric cars instead of petrol cars are driven? To answer these kind of questions, high resolution temporal and spatial information is needed (Pickers 2016). Especially urban areas are important in this, since about 70% of all anthropogenic CO₂ emissions originate from cities (Nicole 2010). Monitoring as well as modelling of urban and regional concentrations of CO₂ and co-emitted species has therefore received a lot of attention (Huszar, Belda, and Halenka 2016; Lopez et al. 2013; Q. J. Zhang et al. 2015). ¹⁴CO₂ can be used as a tracer to separate fossil fuel CO₂ and CO₂ from the biosphere, as CO₂ emitted from fossil fuels does not contain ¹⁴CO₂. Furthermore, ¹³C:¹²C ratios in combination with ¹⁴C concentrations can be used to separate various fossil fuel sources (Djuricin, Pataki, and Xu 2010; Zondervan and Meijer 1996). Carbon monoxide (CO) can also be used as a tracer to quantify fossil fuel CO₂, due to the co-emittance of CO as fossil fuels are combusted (Lopez et al. 2013). The CO₂ co-emitted species often have a distinct emission ratio for specific source types (Djuricin, Pataki, and Xu 2010; Lopez et al. 2013). The emission ratios thus provide information about the dominant emission sources. Eulerian as well as Gaussian models (and a combination these methods) are being developed as to use emission ratios to provide insight in emission sources (Super et al. 2017). A relatively novel tracer for fossil fuel CO₂ sources is oxygen (O₂). Introducing O₂ as a tracer for fossil fuel CO₂ can potentially contribute to the information these models generate about the emission sources for fossil fuel CO₂. The general aim of this research is to study and...
improve the knowledge about the importance of various fossil fuel types in urban areas. This will be attempted by implementing atmospheric O$_2$ as a tracer in an emission model, validating the model using measurements, and finally studying the modelled results. Before going into more detail about the research objectives in Section 1.3, relevant theory concerning atmospheric O$_2$ will be discussed and information about the research area and used model will be provided in Section 1.1 and Section 1.2.

1.1 Background theory

1.1.1 Carbon reservoirs

On relatively short (i.e. non-geological) timescales, the global carbon cycle consists of four main carbon reservoirs: the atmosphere, oceans, terrestrial biosphere (including soils), and fossil fuels (Figure 1). In the past 50 years, there has been a significant transfer of carbon from fossil fuels to the atmosphere by human activities. About 44% of the released carbon stays in the atmosphere, as the remaining carbon is taken up by the oceans or the terrestrial biosphere (Figure 2) (Le Quéré et al. 2016).

![Figure 1: Overview of the global carbon dioxide budget. The carbon reservoirs are shown along with their contribution to the atmospheric carbon in gigatonnes of carbon per year (Le Quéré et al. 2016).](image-url)

CO$_2$ interacts with the terrestrial biosphere mainly through photosynthesis and respiration.
As plants photosynthesize, CO\(_2\) is taken up and O\(_2\) is released into the atmosphere. Fossil fuel combustion releases CO\(_2\) into the atmosphere while using O\(_2\) from the atmosphere. The atmospheric O\(_2\) and CO\(_2\) are thus anti-correlated to each other due to photosynthesis and respiration by the terrestrial biosphere and fossil fuel combustion (Figure 3). As opposed to the terrestrial sink and fossil fuel source, however, carbon uptake by the oceans does not directly influence atmospheric O\(_2\) concentrations. Atmospheric carbon is taken up through the solubility of CO\(_2\). This process is known as the solubility pump. The dissolved carbon is taken up by marine organisms which – when they die – sink and transport the carbon to the deeper oceans. This process is known as the biological pump. Due to these processes, along with the physical mixing of the oceans and the change in ocean pH acting as a buffer, the oceans are expected to take up about 26% of the carbon released into the atmosphere (Le Quéré et al., 2016). The main O\(_2\) flux from the oceans results from outgassing, mainly influenced by changes in the oceans heat budget (Randerson et al., 2006).

**Figure 2:** Most important carbon reservoirs and fluxes influencing the atmospheric CO\(_2\) and O\(_2\) concentrations. The changes in atmospheric O\(_2\) and CO\(_2\) are shown in the ‘Atmosphere’ box. In these formulas F is the CO\(_2\) emission from fossil fuel combustion, B is the net land biosphere sink, O is the net ocean CO\(_2\) sink, and Z is the net air-sea O\(_2\) flux. \(\alpha_F\) and \(\alpha_B\) are the oxidative ratios for fossil fuel combustion and net biosphere exchange, respectively (I. Van Der Laan-Luijkx, 2010).

### 1.1.2 Oxidative ratios

Because of the processes underlying the anti-correlation described in Section 1.1.1, high precision atmospheric O\(_2\) measurements along with atmospheric CO\(_2\) measurements can be used
to separate out oceanic and terrestrial carbon fluxes (R. F. Keeling and Shertz [1992]). The terrestrial carbon fluxes can be further distinguished by their differences in oxidative ratios. Terrestrial photosynthesis and respiration occurs through the following process (Seibt et al. [2004]):

$$CO_2 + H_2O \leftrightarrow CH_2O + O_2.$$  \hspace{1cm} (1)

In this process, on average 1.1 moles of O$_2$ are consumed per mole of CO$_2$ emitted and vice versa. The average oxidative ratio of the terrestrial biosphere is thus $\alpha_B = 1.1$ (Severinghaus [1995]). This oxidative ratio can vary over spatial and temporal scales, largely dependent on the elements involved in the oxidation process.

For fossil fuel combustion, the oxidative process is described as (R. F. Keeling and A. C. Manning [2014]):

$$C_xH_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O.$$  \hspace{1cm} (2)

The oxidative ratios for fossil fuel combustion can be distinguished for the three main types of fossil fuel: solids (e.g. coal), liquids (e.g. oil), and gases (e.g. natural gas). The average ratios for these types of fossil fuel are $\alpha_F = 1.17, 1.44$, and $1.95$, respectively (R. F. Keeling [1988]). Cement production is also an anthropogenic source of atmospheric CO$_2$. The processes involved in cement production, however, do not consume oxygen. The oxidative ratio of cement...
production is therefore 0. A global average value for the oxidative ratio of fossil fuel combustion of $\alpha_F = 1.4$ is mainly used (R. F. Keeling [1988]). However, due to the differences in the fossil fuel sources used in different countries and over the seasons, this value can vary in space and time.

1.1.3 Expressing atmospheric oxygen

As described above, the atmospheric $O_2$ concentration is affected by exchange with components in the carbon cycle. Changes in atmospheric $O_2$ are often expressed as changes in the ratio $O_2/N_2$ in per meg. This is because the changes in atmospheric oxygen are relatively small compared to its total mole fraction, i.e. 0.20946 (R. F. Keeling, A. C. Manning, et al. [1998]). Atmospheric nitrogen ($N_2$) is much less variable, which means that the $O_2/N_2$ ratio mainly represents the $O_2$ concentration and is less sensitive to changes in other atmospheric gases (R. F. Keeling and Shertz [1992]). A change of 1 ppm $O_2$ without changes in other gases causes a change of $\delta(O_2/N_2) = 6.04$ per meg, where an exchange of $O_2$ for an equal amount of $CO_2$ causes a change of $\delta(O_2/N_2) = 4.77$ per meg. Changes in $O_2/N_2$ ratio are expressed as:

$$\delta(O_2/N_2) = \frac{(O_2/N_2)_{sample} - (O_2/N_2)_{reference}}{(O_2/N_2)_{reference}}. \quad (3)$$

To separate the oceanic component from the measured $O_2$ levels, a tracer called Atmospheric Potential Oxygen (APO) is used. APO is defined as the $O_2/N_2$ ratio if all methane ($CH_4$) and carbon monoxide ($CO$) were oxidised to $CO_2$ and converted to $O_2$ through photosynthesis. This means that variations can be caused only by oceanic $CO_2$ uptake and partly by fossil fuel emissions. Biological processes are thus excluded. APO can be expressed as (Stephens et al. [1998]):

$$APO = \delta \frac{O_2}{N_2} - \frac{\alpha_B}{X_{O_2}} CO_2 - \frac{0.9}{X_{O_2}} CH_4 + \frac{0.6}{X_{O_2}} CO, \quad (4)$$

in which $X_i$ is the mole fraction of the molecule $i$ (e.g. 0.20946 for $O_2$). To model changes in APO due to changes in $O_2$, $N_2$, or $CO_2$, equation 4 can be written as (Stephens et al. [1998]):

$$\Delta APO = \frac{\Delta O_2}{X_{O_2}} - \frac{\Delta N_2}{X_{N_2}} + \frac{\Delta CO_2}{X_{CO_2}} M, \quad (5)$$

in which $M$ is the total number of moles. Equations 4 and 5 include the influence of $CH_4$.
and CO on APO. If these species are not taken into account, equation 5 can be combined with the global carbon and oxygen budget equations as shown in Figure 2. This results in a global APO budget (Andrew C. Manning and Ralph F. Keeling 2006):

$$\Delta APO = (\alpha_F - \alpha_B)F + \alpha_BO + Z,$$

(6)

where $F$ is the atmospheric CO$_2$ from fossil fuels, $O$ is the atmospheric CO$_2$ sink due to the ocean, and $Z$ is the net O$_2$ air-sea exchange (A. C. Manning and R. F. Keeling 2006). If $F$ and $Z$ are known (or can be estimated), the land and ocean carbon sinks can be calculated. A graphical representation of this is shown in Figure 4 (R. F. Keeling and A. C. Manning 2014). Figure 4 also shows the increase in atmospheric CO$_2$ due to fossil fuel combustion, and the mitigation of these concentrations due to ocean and land uptake.

**Figure 4:** Increase in atmospheric CO$_2$ and decrease in $\delta$(O$_2$/N$_2$) due to fossil fuel combustion, along with the mitigating effects of uptake by the land and ocean components. The dots represent 6-monthly averages of $\delta$(O$_2$/N$_2$) and CO$_2$ from Alert, Canada, La Jolla, California, USA, and Cape Grim, Tasmania, Australia (R. F. Keeling and A. C. Manning 2014).

As mentioned above, APO still includes influence of some fossil fuel combustion. There-
fore, a modified version $\Delta \text{APO}^*$ is suggested, which is only sensitive to air-sea exchange (Sirignano et al. [2010]):

$$\Delta \text{APO}^* = \Delta \text{APO} - \left(\alpha_F - \alpha_B\right)F. \quad (7)$$

Because the oxidative ratio for fossil fuel combustion ($\alpha_F$) varies in space (depending on what kind of fossil fuel is used), I. T. Van Der Laan-Luijkx et al. (2010) performed a modelling study to estimate regional oxidative ratios. The REgional MOdel (REMO) (Chevillard et al. [2002]) is an atmospheric transport model which uses hourly $\text{CO}_2$ and $\text{O}_2$ fluxes from the $\text{CO}_2$ release and Oxygen uptake from Fossil Fuel Emissions Estimate (COFFEE) dataset as input (Steinbach et al. [2011]). COFFEE combines $\text{CO}_2$ emissions from the Emission Database for Global Atmospheric research (EDGAR) (Olivier and Berdowski [2001]) and fossil fuel type specific oxidative ratios from the EN energy statistics (http://www.data.un.org) to model the distribution of the oxidative ratios from fossil fuel combustion.

### 1.2 Research area and WRF-Chem

The aim of this research is to find the $\text{CO}_2$ emission sources in urban areas by incorporating $\text{O}_2$ as a tracer for urban fossil fuel emissions. To achieve this, the model setup by Super et al. (2017) will be used as a starting point. This setup models $\text{CO}_2$ mole fractions in the Rijnmond area. This area will therefore also be used as the study area in this research. The Rijnmond area is shown in Figure 5. It includes Rotterdam as the major urban area, a large harbour, and an industrial area. To model the mole fractions and oxidative ratios in the study area, the Eulerian model Weather Research and Forecasting (WRF-Chem) V3.2.1 is used (Skamarock et al. [2008]). Four domains are defined which have a horizontal resolution of 48x48, 12x12, 4x4, and 1x1 km respectively. Domain 1 covers the largest part of Europe, domain 2 covers the Netherlands, Belgium, Luxembourg, Germany, and part of the UK, domain 3 zooms into the Netherlands, and domain 4 shows the Rijnmond area in more detail (Figure 7).

$\text{O}_2$ measurement campaigns at Rijnmond were planned to start in December 2017. In the end this was not realised, though measurements are planned to start in the near future. Due to the uncertainty in availability of the data, study areas containing Weybourne and Lutjewad were studied as a backup. $\text{O}_2$ measurements have been conducted at Weybourne and Lutjewad for
several years. $O_2$ data from these stations are thus useful to validate the model. Weybourne is located in North Norfolk on the east coast of the United Kingdom, in model domain 2. Lutjewad is located on the north coast of the Netherlands, in model domain 3. More information about the study areas are given in Section 2.1.

![Figure 5: Map of the Rijnmond area (light blue) including the city of Rotterdam (dark blue), the harbour area (yellow), and the glasshouse agricultural sector (green). The prevailing wind direction during October 2014 is indicated by the black arrow (Super et al. 2016).](image)

### 1.3 Research justification and research objectives

In the past, research has been done on continuously measuring atmospheric $O_2$ and $CO_2$ concentrations in order to partition $CO_2$ emissions from the terrestrial biosphere and oceans, and quantify fossil fuel $CO_2$ emissions. $O_2$ measurements can be useful in characterising and monitoring the fossil fuel mix in urban areas based on the different oxidative ratios (R. F. Keeling and A. C. Manning 2014). A combination of atmospheric $O_2$ measurements and modelling could improve the quantification of $CO_2$ emissions in cities. $O_2$ has however not yet been integrated in regional fossil fuel emission models and can be considered an under-exploited tool for quantifying fossil fuel $CO_2$ emissions in urban areas.

The aim of this research is therefore to incorporate $O_2$ as a tracer in an atmospheric model to study the importance of the various fossil fuel types within the study area. As a starting point for this research, the urban area Rijnmond will be used. The three main objectives of this research are:
1. Implementing O$_2$ as a tracer for fossil fuel CO$_2$ in WRF-Chem.

2. Validating the model outcomes by comparing them with O$_2$ concentration measurements from the study areas.

3. Using the developed model to investigate the fossil fuel sources of atmospheric CO$_2$ in Rijnmond.

From these main objectives, the following research questions are defined:

- How do the modelled O$_2$ concentrations compare to the measured concentrations at the Weybourne and Lutjewad?

- Following from the oxidative ratios found in WRF-Chem, what are the fossil fuel sources of atmospheric CO$_2$ in Rijnmond, the north of Groningen, and North Norfolk?

O$_2$ concentrations are modelled using WRF-chem. The methods used to implement O$_2$ in the model are described in Chapter 2. This chapter therefore mainly deals with the first research objective. In Chapter 2, the approach to calculating oxidative ratios for further analysis is also specified. Chapter 3 gives insight in the model’s performance in simulating the wind direction for the chosen case study. In Chapter 4, the importance of the three main sources and sinks (i.e. the ocean, the biosphere, and fossil fuels) in atmospheric O$_2$ concentration is elaborated on for the three study areas (Rijnmond, the north of Groningen, and North Norfolk). In chapter 4, the second research objective is also addressed by validating the modelled O$_2$ concentrations using measurements conducted at Lutjewad and Weybourne. Chapters 5 and 6 will focus on oxygen fluctuations due to fossil fuel burning in order to achieve the third research objective. In Chapter 5 the modelled fossil fuel CO$_2$, fossil fuel O$_2$, and the fossil fuel oxidative ratios that follow from this are analysed. Furthermore, specific events where high CO$_2$ concentrations were simulated are analysed in order to find the emission sources responsible. Finally, in Chapter 6, the results of a second strategy in modelling fossil fuel O$_2$ in Rijnmond are analysed and compared to earlier results, which may in the future be validated using measurements conducted at Zweth.
2 Methods

2.1 Case study

The main study area, Rijnmond (Figure 5), is located in a flat terrain near the west coast of the Netherlands. It includes one of the most industrialized parts of the country, containing an industrial area (Botlek) and one of the largest harbours in the world (Europoort). The area is highly urbanised with more than 1.4 million inhabitants (CBS, 2017) over 807.5 km². The bottom-up estimated emissions in Rijnmond are about 35 Mt CO₂ per year (PRTR 2015), where the harbour is identified as the largest CO₂ emitter. The main sources of CO₂ are energy production and industrial processes. These are often point sources, which result in 80% of the total CO₂ emissions (Super et al. 2017). At first instance, the month of October 2014 will be studied, which - according to Super et al. (2017) - is a month with various moments of high CO₂ concentrations. The wind direction (Chapter 3), and various CO₂ emission sources (Chapter 5) will be analysed for the month of October 2014. The emission sources are linked to oxygen uptake. The implementation of this will be described in more detail in Section 2.3.

As mentioned in Section 1.2, regions North Norfolk and the north of Groningen can be used as extra study areas, because of the availability of O₂ observations during the month of October 2014 at Weybourne and Lutjewad - as opposed to Zweth, of which O₂ data is not yet available. Groningen is located in the north of the Netherlands. Measurement site Lutjewad is located on the coast (shown in Figures 6a and 7), in a more rural area than Rijnmond. The municipality in which the measurement site is located contains about 10 thousand inhabitants over 240 km² (CBS 2017). Carbon emissions in the direct surroundings of Lutjewad are limited, with about 0.5 Mt CO₂ per year in the surrounding area about the same size as North Norfolk and Rijnmond (RIVM 2016). Potential emission sources that can influence concentrations at Lutjewad are the city of Groningen and the city of Leeuwarden. Groningen city is located about 40 km southeast of the measurement site, and Leeuwarden is located about 45 km southwest.

North Norfolk is located at the east coast of the UK. The measurement site at Weybourne is situated about 40 km north of the city of Norwich (as shown in Figure 6b). The area is less urbanized compared to Rijnmond, with only about 104 thousand inhabitants (ONS 2016) over 962.5 km². Carbon emissions are around 0.7 Mt CO₂ per year (BEIS 2015). There are three gas
production plants in the area, located about 20 km east of Weybourne, which are responsible for about 35% of all CO\textsubscript{2} emissions in the area.

![Maps](image)

**Figure 6:** Maps showing a) study area the north of Groningen containing measurement site Lutjewad, and b) study area North Norfolk containing measurement site Weybourne.

2.2 Modelling framework and settings

As mentioned in Section 1.2, WRF-Chem V3.2.1 is used to simulate CO\textsubscript{2} and O\textsubscript{2} concentrations in the study areas. As initial and boundary conditions in WRF-Chem, meteorological fields from
the National Centers for Environmental Prediction (NCEP) Final (FNL) Operational Global
Analysis (National Centers for Environmental Prediction/National Weather Service/NOAA/U.S
2000) are used. These initial and boundary conditions have a horizontal resolution of 1x1° and a
temporal resolution of 6 hours. CO₂ initial and boundary conditions are taken from the 3D mole
fractions of CarbonTracker Europe (Van Der Laan-Luijkx et al. 2017). These have a horizontal
resolution of 1x1° and have 25 vertical levels, and are therefore both horizontally and vertically
interpolated onto the WRF-Chem grid.

Four domains are defined as shown in Figure [7]. The outer domain is situated over Europe,
domain 2 is zoomed into the Netherlands and contains the study area North Norfolk. Domain 3
covers only the Netherlands, and domain 4 is zoomed into the Rijnmond area. These domains
have a horizontal resolution of 48x48, 12x12, 4x4 and 1x1 km respectively, and a vertical reso-
lution of 29 eta levels. The lowest model layer is 40 m deep, and the lowest 1 km is divided in 8
levels. The Yonsei University boundary layer scheme (Hong, Noh, and Dudhia 2006) is used as
this scheme has proven to be most reliable over the Netherlands (Bozhinova et al. 2014; Daniels
et al. 2016; Steeneveld, Ronda, and Holtslag 2014). Furthermore, the Dudhia scheme is used
as shortwave radiation scheme (Dudhia 1989), the Rapid Radiation Transfer Model (RRTM) is
used as longwave radiation scheme (Mlawer et al. 1997), and the Unified Noah Land-Surface
Model is used as surface physics scheme (Ek 2003). An overview of the model settings and
schemes used is given in Table [A1] in the Appendix.

2.3 Modelling strategy

In order to achieve the first research objective, and model O₂ concentrations in WRF-chem, a
few steps are taken to add to the current model setup. These steps are described in Sections
2.3.1 to 2.3.3; the modelling of CO₂ sources and sinks, the implementation of O₂ uptake and
release due to these CO₂ sources and sinks, and the implementation of O₂ ocean exchange.

2.3.1 Modelling CO₂ emissions, photosynthesis, and respiration

To model emissions in WRF-chem, several emission databases are used. The TNO-MACC
III inventory for 2011 provides fossil fuel and biofuel emissions at a horizontal resolution of
0.123x0.0625°, which are used for the simulations in domain 1 to 3. The emissions for domain 4 are taken from the Dutch Emission Registration, and compiled by the Netherlands Organisation for Applied Scientific Research (TNO) to a 1x1 km resolution emission map. Area sources are added to the lowest surface level, whereas point sources are given a vertical distribution based on plume rise calculations by Bieser et al. (2011). The emissions are categorized using the Standardized Nomenclature for Air Pollutants (SNAP) classification. SNAP distinguishes 10 emission categories (shown in Table I), which are classified according to the power developed by the combustion processes (mostly categories 01, 02, and 03), the technical characteristics of the process (categories 04 and 05), or the condition of use of the fuel types (mainly the mobile sources, categories 07 and 08) (EUROSTAT 2005). In the model setup by Super et al. (2017), categories 03 and 04, and categories 05, 06, and 09 are combined, since they would separately be too small to distinguish.

**Table 1:** CO₂ emission categories along with the description of the SNAP classifications. Estimations of the average oxidative ratios for the Netherlands are given for every category.

<table>
<thead>
<tr>
<th>CO₂ emission category (SNAP and biogenic)</th>
<th>Description</th>
<th>$OR_{O₂:CO₂}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Combustion in energy and transformation industries</td>
<td>-1.762</td>
</tr>
<tr>
<td>02</td>
<td>Non-industrial combustion plants</td>
<td>-1.460</td>
</tr>
<tr>
<td>03</td>
<td>Combustion in manufacturing industry</td>
<td>-1.460</td>
</tr>
<tr>
<td>04</td>
<td>Production processes</td>
<td>-1.460</td>
</tr>
<tr>
<td>05</td>
<td>Extraction and distribution of fossil fuels and geothermal energy</td>
<td>-1.4</td>
</tr>
<tr>
<td>06</td>
<td>Solvent and other product use</td>
<td>-1.4</td>
</tr>
<tr>
<td>07</td>
<td>Road transport</td>
<td>-1.536</td>
</tr>
<tr>
<td>08</td>
<td>Other mobile sources and machinery</td>
<td>-1.536</td>
</tr>
<tr>
<td>09</td>
<td>Waste treatment and disposal</td>
<td>-1.4</td>
</tr>
<tr>
<td>10</td>
<td>Agriculture</td>
<td>-</td>
</tr>
<tr>
<td>Biofuel emissions</td>
<td></td>
<td>-1.07</td>
</tr>
<tr>
<td>Photosynthesis</td>
<td></td>
<td>-1.1</td>
</tr>
<tr>
<td>Respiration</td>
<td></td>
<td>-1.1</td>
</tr>
</tbody>
</table>

Furthermore, biofuels are distinguished as a separate category, as well as uptake and release of CO₂ by the biosphere through photosynthesis and respiration. Photosynthesis and respiration are calculated by the SiBCASA model for nine different land use types at a 1x1° resolution. This is scaled to the land use map, and the modelled short wave radiation and temperature in WRF-chem as described by Super et al. (2017).
2.3.2 Modelling O₂ uptake and release

Within the various categories (as shown in Table 1), exchange between O₂ and CO₂ takes place. Therefore, per (combined) emission category, an average oxidative ratio (OR_{in}) is calculated based on the fuel mix used in the Netherlands and the relevant oxidative process as described in equation 2 (derived from Emissiefactoren, 2017; LNG, 2017; RvO, 2016; Wikipedia, 2017; Wikipedia, 2017a). In this study, processes that consume or emit O₂ in exchange with CO₂ are given a negative OR. This means that the OR for fossil fuel burning, photosynthesis, and respiration are negative. For photosynthesis and respiration an OR_{in} for the biosphere of -1.1 is assumed. The average values for OR_{in} per emission category are shown in Table 1. These are used to calculate the uptake of O₂ as ‘negative emissions’ per SNAP category in WRF-chem through:

\[ \Delta O_2 = \Delta CO_2 \cdot OR_{in}. \] (8)

This results in negative values for \(\Delta O_2\), except for the photosynthesis term. The sum of \(\Delta O_2\) per category (i.e. the total fluctuation in O₂ concentration) is therefore often negative. Negative concentrations can however not be modelled in WRF-chem, therefore the background value of O₂ is in first instance set to a constant of 1000 ppm. This way, increases as well as decreases can be simulated, and the background value can easily be corrected for in the analysis. The changes in fossil fuel O₂ concentration, along with the corresponding increases in fossil fuel CO₂ can again be converted to values for OR_{ff} for specific events and at specific locations, which can be studied.

The values for OR_{in} can be assigned using two different methods; either by assigning an OR_{in} to CO₂ emissions per emission category, or by assigning an OR_{in} to each grid cell based on activities in that cell. The differences between the two methods will be elaborated on in the coming paragraph, and the results will be compared in Chapter 6.

As explained above, average OR_{in} values are calculated and assigned per CO₂ category. For the SNAP categories, these values are based on average fuel mixes used in the Netherlands. However, for some point sources in Rijnmond, the specific fuel type that is used is known. With this information, a more accurate OR_{in} value can be established for the grid cell in which the point source is located. Therefore, as a second experiment, OR ratios are firstly based
on the used fuel type of the point sources (if the information is known), and secondly on the SNAP categories. Therefore, the OR\textsubscript{in} ratio is calculated per grid cell, which is then used to calculate changes in O\textsubscript{2} concentration. O\textsubscript{2} production or consumption through photosynthesis, respiration, and biofuel burning are - similar to the first method - calculated using the calculated average OR as shown in Table 1. The method used in this experiment will only affect O\textsubscript{2} concentrations in the 4\textsuperscript{th} domain, since specific fuel type information is only known over Rijnmond, and thus does not affect simulated O\textsubscript{2} concentrations in North Norfolk or the north of Groningen.

2.3.3 Ocean-atmosphere O\textsubscript{2} exchange

The atmospheric O\textsubscript{2} concentration does not only fluctuate through fossil fuel burning and exchange with the biosphere. The ocean can also act as an O\textsubscript{2} source or sink as described in Section 1.1.1. This exchange is however not directly correlated to CO\textsubscript{2} uptake by the ocean. O\textsubscript{2} uptake by the ocean is implemented in WRF-chem through Atmospheric Potential Oxygen (APO) inversions as modelled by Rödenbeck et al. (2008). APO is used to express the oceanic O\textsubscript{2} uptake or release, and thus exclude all biological processes and most of the fossil fuel influences (Section 1.1.3). APO inversions by Rödenbeck et al. (2008) are implemented as initial condition and boundary condition in WRF-chem, and thus added to the constant 1000 ppm background value as described before. 6-hourly APO inversions are available on a global scale on a 5x3.8° horizontal resolution and 26 vertical levels. For more information about the APO inverse modelling please refer to Rödenbeck et al. (2008).

2.4 Analysis of the results

Once O\textsubscript{2} is implemented into the WRF-chem setup, the model results need to be validated and further analysis can be done. The most important steps applied in the model validation and further analysis are discussed below.

2.4.1 Converting O\textsubscript{2} data to ppm concentrations

In order to validate the model, O\textsubscript{2} simulations are compared to O\textsubscript{2} observations. Due to the relatively small changes in O\textsubscript{2} concentration compared to its background, changes in O\textsubscript{2} con-
centration are expressed as changes in \((O_2/N_2)\) ratio compared to a reference concentration in per meg (as described in Section 1.1.3). In order to compare the simulated and observed values, the observed values thus have to be converted to \(O_2\) concentrations in ppm. Since the changes in \(O_2\) concentrations are assumed to be due to exchange with \(CO_2\), measurement data is converted using:

\[
O_2 \ [ppm] = \frac{O_2/N_2 \ [permeg]}{4.77}.
\] (9)

Before applying this equation, the APO values that represent ocean exchange are converted to \(O_2/N_2\) using (Wilson 2012):

\[
\delta(O_2/N_2) = \delta APO = 1.1 \cdot \frac{CO_2 - 350}{X_{O_2}},
\] (10)

in which 1.1 is oxidative ratio typically used for the land biosphere, \(CO_2\) is the simulated \(CO_2\) concentration in ppm, 350 is an arbitrary reference, and \(X_{O_2}\) is the standard mole fraction of \(O_2\) in air (i.e. 0.209392).

### 2.4.2 Calculating and analysing outcoming Oxidative Ratios

Once \(O_2\) fluctuations are modelled, the information can be used to calculate fossil fuel oxidative ratios \((OR_{ff})\), and identify the dominant fossil fuel sources in the study areas. This analysis can be done for the average over October 2014, as well as for specific times. In order to study a specific \(CO_2\) emission event information is needed about the maximum \(CO_2\) concentration measured during the event, as well as the background \(CO_2\) concentration before the event. If the peak in \(CO_2\) is due to fossil fuel burning, the \(CO_2\) peak will correspond to a low in \(O_2\) concentration. The magnitude of the decrease in \(ffo_2\) along with the magnitude of the increase in \(ffCO_2\) concentration yields an \(OR_{ff}\) for that specific event following (this is the same principle as rewriting Eq. 8):

\[
OR_{ff} = \frac{\Delta(ff)O_2}{\Delta(ff)CO_2}.
\] (11)

The value for \(OR_{ff}\) that is found yields information about the important fossil fuel sources in case of the specific emission event. This, in combination with meteorological conditions during the event can identify the origin of the high \(CO_2\) concentrations simulated during the event. An \(OR_{ff}\) including influences from the biosphere (and the ocean) can also be generated using Eq.
The \( \Delta O_2 \) and \( \Delta CO_2 \) that is used is than calculated as changes as opposed to the background value, taken into account uptake and release by the biosphere and ocean.
3 Wind direction - statistical analysis of the model performance

Modelled compound concentrations (i.e. tracers) are greatly influenced by local sources, as well as the transport of compounds emitted elsewhere. In this transport, the modelled wind direction plays an important role. For this research, the WRF-chem setup as developed by Super et al. (2017) will be used as a starting point to model CO$_2$ mole fractions. Ultimately, O$_2$ will be added as a tracer to the model setup. Super et al. (2017) found that the main discrepancy in their model performance on simulating CO and CO$_2$ concentrations around Rotterdam was due to errors in the simulated wind direction. They used a combination of WRF-chem version 3.2.1 and the Gaussian plume model OPS (Operational Priority Substances) to simulate the CO and CO$_2$ mixing ratios. The analysis in this chapter is a follow up to those conclusions by Super et al. (2017). To gain more insight in the WRF model performance, in the following sections the wind direction simulation of WRF version 3.2.1 will be discussed, the used model version will be compared to a more recent model version (Section 3.1), the performance between various locations within the domain will be compared (Section 3.2), and the model performance using a finer horizontal resolution will be analysed (Section 3.3). Furthermore, observation nudging will be attempted to improve the simulations (Section 3.4).

Figure 8: Wind direction for October 2014 at Rotterdam airport as measured by KNMI and simulated by WRF version 3.2.1 and version 3.9.1.

The wind direction for October 2014 simulated by WRF (at a 4x4 km grid size), along with the observations by KNMI at Rotterdam airport are shown in Figure 8. The observations agree with observations done at other KNMI sites in the area, such as Rotterdam Geulhaven and
Cabauw; the mean and standard deviation do not vary more than 5° between the surrounding measurement stations. The average simulated wind direction over the month overestimates the wind direction by about 15°, simulating slightly more westerly winds. The trend in the wind direction is similar between the simulations and observations. South-easterly winds (around 130-160°) are sometimes mistaken for more southerly winds, such as on the 10th, and 14th and 15th of October. Wind speed tends to be overestimated by WRF. A statistical analysis of the wind speed is added to the Appendix (Table A2).

Statistical analysis is done on the observed (O) and simulated (P) wind direction values, of which the most important quantitative measures are shown in Table 2. The same tables including the number of values (N), regression parameters (intercept a and slope b of the linear regression), Mean Average Error (MAE), and systematic and unsystematic Root Mean Square Error (RMSE_s and RMSE_u, respectively) are added to the Appendix (Table A3). In Table 2 all modelled values are included. In literature it is found, however, that WRF is less successful in simulating wind directions when wind speeds are low (Jimenez and Dudhia 2013, Papanastasiou, Melas, and Lissaridis 2010). This is because low wind speed values can induce errors in the physical parameterization processes during the model application (Papanastasiou, Melas, and Lissaridis 2010). Furthermore, when wind speeds are low, they are often also more difficult to measure accurately, resulting in less reliable observation values. When plotting the difference in simulated and observed wind direction against wind speed for October 2014, a larger disagreement between simulated and observed values can indeed be identified at the lower wind speed range (Figure A.1, Appendix). In Table 2 therefore, similar to the study by Jimenez & Dudhia (2013), all directions simulated at wind speeds lower than 3.0 m/s are excluded and considered ‘low wind speeds’. At these times, observed wind speeds are generally also below 3.0 m/s.

To accompany the qualitative indices in Tables 2 and 3, the relation between the simulated

### Table 2: Most important quantitative measures of wind direction model performance for WRF version 3.2.1 and WRF version 3.9.1. Where $\bar{O}$ and $\bar{P}$ is the mean of the observed and simulated values, $sd_O$ and $sd_P$ the standard deviation of the observed and simulated values, RMSE the root mean square error, and $d$ the index of agreement. Terms $d$ and $R^2$ are dimensionless, the remaining terms have unit °.

<table>
<thead>
<tr>
<th>WRF-chem version</th>
<th>$\bar{O}$</th>
<th>$\bar{P}$</th>
<th>$sd_O$</th>
<th>$sd_P$</th>
<th>RMSE</th>
<th>$d$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>66.3</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>3.9.1</td>
<td>189</td>
<td>206</td>
<td>63.0</td>
<td>56.5</td>
<td>58.2</td>
<td>0.761</td>
<td>0.337</td>
</tr>
</tbody>
</table>
Table 3: Same as Table 2, only here wind direction values simulated with wind speeds larger than 3 m/s are taken into account.

<table>
<thead>
<tr>
<th>WRF-chem version</th>
<th>$\bar{O}$</th>
<th>$\bar{T}$</th>
<th>$sd_O$</th>
<th>$sd_T$</th>
<th>RMSE</th>
<th>$\delta$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1</td>
<td>197</td>
<td>212</td>
<td>50.6</td>
<td>46.2</td>
<td>48.3</td>
<td>0.752</td>
<td>0.307</td>
</tr>
<tr>
<td>3.9.1</td>
<td>201</td>
<td>212</td>
<td>50.8</td>
<td>48.8</td>
<td>41.5</td>
<td>0.827</td>
<td>0.460</td>
</tr>
</tbody>
</table>

and observed wind directions are displayed in Figure 9 (a). The average values $\bar{O}$ and $\bar{T}$ in Tables 2 and 3 show that the average wind direction is overestimated by about 15°. Even though the simulated wind direction becomes more westerly when low wind speeds are excluded, so does the observed wind direction. The general wind direction simulations over the month are thus not improved due to this selection. The standard deviations ($sd_O$ and $sd_T$) show that the variability is underestimated by the model; the model thus shows less variability in wind direction than the observations. Figures 8 and 9 show the relation between the observed and simulated wind direction. Even though a clear relation is apparent, there are also outliers. A large number of these outliers are simulated at low wind speeds. Furthermore, it is important to notice that the outliers observed around 0-50° and simulated around 330-360° look like they are far from the ideal regression line, but are in fact not necessarily far of. This, since a wind direction simulated at 350° is in reality only 20° from a wind direction observed at 10. The RMSE is sensitive to extreme values, and is therefore generally regarded as a high estimate of the MAE (Table A3 Appendix) (Willmott 1982). The relatively low RMSEs compared to RMSEu (Table A3 Appendix), indicates that the errors in the model simulations are largely unsystematic. Overall, the values for index of agreement ($\delta$, ranging from 0 to 1) and $R^2$ indicate a relatively low model performance. Super et al. (2017) calculated statistics on the daytime (08:00-17:00 LT) average values of a three month period (from October to December). The daytime averages are not analysed here, since this leaves a too low value for $N$, decreasing the reliability of the quantitative measures. The outcome of the quantitative statistics on wind direction in this study are however in the same order of magnitude as the statistics by Super et al. (2017). The $R^2$ and RMSE that follow from the wind speed do improve by about 20% as only daily averages are taken into account. This suggests that daily averages in wind speed are captured better by WRF than hourly fluctuations, since individual wind speeds simulated from 8:00 to 17:00 LT do not match observations significantly better than wind speeds simulated for other times.
Figure 9: Relation between the simulated and the observed wind direction for WRF model version 3.2.1 (a) and version 3.9.1 (b). The wind directions simulated at wind speeds lower than 3 m/s are shown in red (and shifted slightly), and directions simulated at wind speeds higher than 3 m/s are shown in blue. An ideal regression line is shown in black.

From this, it can indeed be concluded that WRF has some difficulties simulating the correct wind direction, which are most apparent at low wind speeds. On average over the month, simulated wind directions are more westerly than observations. Furthermore, WRF underestimates variations in the wind direction by about 6° on average. The errors are mainly unsystematic, and are therefore difficult to correct for.

3.1 WRF version 3.2.1 vs version 3.9.1

In their research Super et al. (2017) used WRF-chem version 3.2.1, whereas the currently latest available version of WRF is version 3.9.1. We investigate the possible changes and improvements in wind direction simulations between those versions. Again, the simulated wind directions will be compared to observations at Rotterdam airport (Figure 8). Figure 8 does not show striking differences between wind direction as modelled by the two WRF versions: both versions show a similar trend and thus generally follow the KNMI observations. From Figure 8 it is difficult to determine which model version actually performs better in simulating wind direction. The quantitative measures are again shown in Tables 2 and 3 (extended in Appendix Table A3). The average values and standard deviations do not improve significantly as simulations are done by the later model version. The RMSE and MAE do improve by about 12% and 20% respectively as the later model version is used. This improvement increases to about 14% and
26% as wind speeds lower than 3 m/s are excluded. d and R² also improve when version 3.9.1 is used, however, this improvement is relatively smaller when low wind speeds are excluded from the model run.

Overall, WRF version 3.9.1 performs better in simulating wind directions than version 3.2.1. Both model versions are less successful in simulating wind directions with relatively low wind speeds. Version 3.2.1, however, seems to have more difficulty in simulating wind directions at low wind speeds than version 3.9.1.

A low model performance at low wind speeds would indicate poorer model performance at stable conditions, for instance during the night. The difference between simulations and observations are however not systematically larger at night. In the update to WRF version 3.7, the Revised MM5 Monin-Obukov scheme, which is used in this study as a surface layer scheme (Table A1, Appendix), is adapted to better represent the roughness length of water bodies (Ucar 2015). This could have its effect on the wind direction simulated above the ocean at low wind speeds. At Rotterdam, the wind often originates from the sea located only about 30 km West. Winds simulated at Rotterdam airport are thus influenced by the winds simulated above the North Sea. This improvement in the surface layer scheme could explain the increased model performance in the later model version.

3.1.1 Update in the Revised MM5 Monin-Obukov scheme

As mentioned in Section 3.1, the Revised MM5 Monin-Obukov scheme was updated with WRF model version 3.7. This could explain the changes in model performance between version 3.2.1 and 3.9.1. In this subsection the changes made in the surface layer scheme will be further explained, and it will be investigated whether these changes are actually responsible for the difference in model results.

During the WRF version 3.7 update, the heat and moisture exchange coefficients over water were adapted; from version 3.7 on, exchange coefficients are calculated using COARE 3.0 instead of Carlson-Boland (UCAR 2014). The adaptation is implemented through the change in determination of the roughness length (z₀) of water surfaces. z₀ is calculated using Charnock’s (1955) expression plus a smooth flow limit, following Smith (1988):
\[ z_0 = \frac{\alpha u^2}{g} + \frac{0.11\nu}{u_s}, \]  

(12)

in which \( u_s \) is the friction velocity, \( \alpha \) is Charnock’s parameter (with a value of 0.0185 m in the used surface layer scheme), \( g \) is the gravitational constant, and \( \nu \) is the kinematic viscosity.

Version 3.2 made use of a constant value for the smooth flow limit of 1.59e\(^{-5} \) m in calculation of \( z_0 \). In version 3.7, this constant is replaced by a calculation of the flow limit in equation 11 with a value for \( \nu \) of 1.5\(^{-5} \) m\(^2\)/s. Because of the dependence of the smooth flow limit on \( u_s \), \( z_0 \) increases when \( u_s < 0.104 \) m/s, and decreases \( z_0 \) when \( u_s > 0.104 \) m/s. This generally results in lower values for \( z_0 \), since in practice \( u_s \) has values of about 0.2 m/s and larger (Vickers, Mahrt, and Andreas 2015). Due to the surface layer scheme updates, wind speeds close to the surface ocean are thus generally higher. The adaption also has its effect on the heat and moisture exchange coefficients and consequently reduces moisture and heat fluxes over water surfaces.

To investigate whether these changes are responsible for the improvement in wind direction at low wind speeds in version 3.9.1 as opposed to version 3.2.1, the surface layer physics file in WRF version 3.9.1 was adapted so that the calculations of the moisture and heat flux above water surfaces are done according to the equations used in version 3.2.1. The results are added to Table 4 (extended in the Appendix). The model performance parameters show that the wind simulation of version 3.9.1 without the update improve as the wind directions simulated at low wind speed are excluded, similar to version 3.2.1. Furthermore, the number of values excluded due to a simulated wind speed lower than 3.0 m/s increases by 146 values as the update is removed from the model. There are still some differences between the simulations of the adapted version 3.9.1 and version 3.2.1. The remaining differences between the two models are due to other model updates which affect the simulated wind direction, such as e.g. updates in the YSU boundary layer scheme.
Table 4: Most important quantitative measures of wind direction model performance for WRF version 3.9.1 without the surface layer scheme updates from version 3.7. Results of version 3.2.1 are repeated for clarity. The statistics are shown of all values, as well as only the values simulated at wind speeds > 3 m/s. It can be seen that just as is the case with version 3.2.1, the model performance improves as values at low wind directions are excluded.

<table>
<thead>
<tr>
<th>WRF-chem version</th>
<th>( \bar{\phi} )</th>
<th>( \bar{P} )</th>
<th>sd(_{\phi} )</th>
<th>sd(_P )</th>
<th>RMSE</th>
<th>( d )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.1</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>66.3</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>3.9.1</td>
<td>189</td>
<td>206</td>
<td>63.0</td>
<td>56.5</td>
<td>58.2</td>
<td>0.761</td>
<td>0.337</td>
</tr>
<tr>
<td>3.9.1 - update</td>
<td>190</td>
<td>202</td>
<td>62.3</td>
<td>51.4</td>
<td>57.9</td>
<td>0.730</td>
<td>0.271</td>
</tr>
</tbody>
</table>

3.2 Location comparison

The statistical analysis as presented in Section 3.1.1 shows the differences in wind direction simulation by WRF version 3.2.1 and version 3.9.1. The simulations are compared to observations conducted at Rotterdam airport. It can be discussed whether the model performance based on observations and simulations conducted for Rotterdam are representative for the entire domain (domain 3 in Figure 7), which covers the Netherlands as a whole. The model performance of version 3.2.1, the version which will be used in this study, at Rotterdam will be compared to the performance at Eindhoven and Lauwersoog (as shown in Figure 10). The observation site at Eindhoven is, similarly to Rotterdam, situated in an urbanized area, but is located more inland in Noord-Brabant. Lauwersoog is situated closely to the measurement station at Lutjewad, where \( O_2 \) measurements are being conducted which might be useful for further analysis of the model performance of simulating \( O_2 \) in this or future research. The observation site is located in Groningen, on the north coast of the Netherlands. In Figure 11, the simulated and observed wind direction for all three locations for October 2014 is shown. A similar trend for the three locations can be seen, although there are also several moments in which the simulated wind direction varies within the domain (also depicted in Figure 10).
A statistical analysis of the model performance at the three locations is shown in Table 5. At all sites, simulated winds are more westerly than the observed winds, and deviations from the general wind directions are underestimated. The simulations at Lauwersoog statistically match the observations best, whereas the simulations at Eindhoven show the poorest results. In Eindhoven, the simulated mean is the largest (+25° compared to observations), and deviations from the mean are smallest (-10.3° compared to observations). The $sd_O$ and $sd_P$ at Lauwersoog similar those calculated for Rotterdam, suggesting that the poorer model performance at Rotterdam as expressed by $d$ and $R^2$ are mainly due to the stronger overestimation in the general wind direction (hence winds coming more from the west in the simulations as compared to observations). At Lauwersoog, the $sd_P$ is largest, and RMSE is lower than at the other sites. Furthermore, the amount of simulations with wind speeds lower than 3.0 m/s is limited. The improvement in model performance when low wind speeds are excluded is lower for this station compared to the other stations. This suggests that the better model performance at Lauwersoog is due to the larger wind speeds at the coast. It should be noted that lower wind speeds also make the observations of wind direction less reliable, which can have its effect on the calcu-
lated statistical measures.

![Wind Direction Graphs](image)

**Figure 11**: Wind direction for October 2014 as simulated by WRF and observed by the KNMI at Rotterdam (a), Eindhoven (b), and Lauwersoog (c) for October 2014.

**Table 5**: Most important quantitative measures of wind direction model performance at Rotterdam, Eindhoven, and Lauwersoog.

<table>
<thead>
<tr>
<th>Location</th>
<th>$\bar{O}$</th>
<th>$\bar{P}$</th>
<th>sd$_{O}$</th>
<th>sd$_{P}$</th>
<th>RMSE</th>
<th>d</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rotterdam</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>66.3</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>Eindhoven</td>
<td>187</td>
<td>212</td>
<td>58.7</td>
<td>48.4</td>
<td>61.1</td>
<td>0.673</td>
<td>0.224</td>
</tr>
<tr>
<td>Lauwersoog</td>
<td>190</td>
<td>198</td>
<td>63.6</td>
<td>58.1</td>
<td>50.4</td>
<td>0.820</td>
<td>0.448</td>
</tr>
</tbody>
</table>

Overall, WRF’s performance in simulating wind directions, and consequently the transport of compounds, does not show striking differences, but can vary over the third domain. The simulations analyzed so far are done at a 4x4 km horizontal resolution. In Section 3.3, the model performance at this horizontal resolution is compared to simulations done at a 1x1 km horizontal resolution.
3.3 4x4 km vs 1x1 km horizontal resolution

The compound concentrations modelled by (Super et al. [2017], as well as in this study, are finally simulated in a smaller domain covering the Rijnmond area only (domain 4, Figure [7]). This domain has a horizontal resolution of 1x1 km. Therefore, the wind directions simulated at this resolution will be compared to the wind directions as previously simulated and analyzed in this chapter. The comparison of simulations is shown in Figure [12]. Furthermore, the quantitative statistics are shown in Table [A3] in the Appendix. It can be seen that there is very little difference between the simulations at the two resolution sizes. This is the case for wind direction, as well as wind speed (not shown). Studies have shown that a model’s performance can be improved by using a finer horizontal resolution, but may also be similar, or even worse (Carvalho et al. [2012]). This is due to uncertainties in the performance of the various physical parameterizations and their responses to grid resolution (Pleim et al. [1995], Wu et al. [2008], Y. Zhang et al. [2006]). Increasing grid resolution may improve the simulation of fine-scale processes (Mass et al. [2002], Westphal [2001]) but does not necessarily correlate to better model accuracy (Gego et al. [2005]). Furthermore, computational costs of finer resolutions are often much higher. Therefore it is important to outweigh the improvement of results to the computational costs. In this study, however, even though the simulated wind directions do not improve in domain 4 as opposed to domain 3, it will still be worthwhile to simulate compound emissions at a 1x1 km horizontal resolution. This, as Dekker (2014) shows, that to successfully model compound emissions in an urban area, a horizontal resolutions of 1x1 km is needed.
3.4 Wind direction nudging

From the analyses done in Sections 3.1 to 3.3, it becomes apparent that WRF has issues in simulating the correct wind directions, especially at lower wind speeds. Simulated compound concentrations depend largely on the transport of the compound and thus the wind direction. A potential way to improve the simulated wind direction is by observation nudging. In observation nudging, artificial tendency terms are introduced to gradually ‘nudge’ the model towards observations (Pettersson 2016). In order to investigate the potential use of observation nudging in this study, observation nudging of the wind direction is implemented in domain 1 (Figure 7). The most important nudging settings are the nudging weight, the horizontal radius of influence, and the time window. A nudging strength of $6.0 \times 10^{-4}$ s$^{-1}$ is used. This effects the strength to which a simulated value is pulled towards an observation in units of inverse seconds (for more information: Pettersson (2016)): the larger the nudging strength, the smaller the error is that remains after a certain amount of time. The horizontal radius of influence is set to 250 km. This means that simulations up until 250 km from an observation point are influenced by that observation. The influence is however larger if the location of the observation is close to the simulated grid cell than if the grid cell were further away. Finally, since observations are hourly, the time window is set to 1 h. This means that the nudging strength is largest at the time of observation, and decreases to 0 up until half an hour before and after the observation. The observational data that is used for the wind direction nudging is obtained from the Integrated Surface Database (ISD) from the National Oceanic and Atmospheric Administration (NOAA). The ISD contains
global hourly and synoptic observations over land and water (NOAA, 2014). Observation nudging using similar datasets have improved forecasts in other experiments, although impacts are not equally positive in various situations (Liu et al. 2007; Macpherson, Deblonde, and Aparicio 2008).

Statistics of the wind nudging data are shown in Table 6 (extended in Appendix Table A3). The observation nudging was conducted only at surface levels and in the 1st domain. This mainly reduces the standard deviation of the simulated values. The time series of the wind direction with and without observation nudging in Figure 13 shows that the model runs are similar, and differences are often difficult to distinguish. The model does not show clear improvements towards the KNMI observations due to the nudging. From this, it can be concluded that, for the used nudging strength, observation nudging is not useful to improve wind direction simulations.

There is still discussion in literature on the combination of nudging settings to simulate without over-manipulating the data (Bullock et al. 2014; Li et al. 2016; Liu et al. 2007). In this case, the effect of observation nudging is not significantly positive enough to improve simulations, and a greater nudging weight would increase the chance of losing important mesoscale features created by the model, or creating noise in the model results (Deng et al. 2008). Therefore, observation nudging will not be applied in order to obtain further results in this study.

*Figure 13:* Observations and simulation of the wind direction as modeled by WRF with and without observation nudging applied.
Table 6: Most important quantitative measures of wind direction model performance for WRF version 3.2.1, without and with observation nudging applied.

<table>
<thead>
<tr>
<th></th>
<th>$\bar{O}$</th>
<th>$P$</th>
<th>$sd_O$</th>
<th>$sd_P$</th>
<th>RMSE</th>
<th>d</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without nudging</td>
<td>190</td>
<td>207</td>
<td>57.5</td>
<td>57.3</td>
<td>57.64</td>
<td>0.720</td>
<td>0.257</td>
</tr>
<tr>
<td>With nudging</td>
<td>190</td>
<td>210</td>
<td>57.5</td>
<td>52.3</td>
<td>55.6</td>
<td>0.739</td>
<td>0.310</td>
</tr>
</tbody>
</table>
4 Partitioning fluctuations in atmospheric O\textsubscript{2}

The first research objective (as stated in Section 1.3) is to implement O\textsubscript{2} as a tracer for fossil fuel CO\textsubscript{2} (ffCO\textsubscript{2}) in WRF-chem. To do so, fossil fuel O\textsubscript{2} (ffO\textsubscript{2}) is simulated as negative emissions as a result of CO\textsubscript{2} emissions as described in Section 2.3.1. To complete the modelling of O\textsubscript{2}, uptake and release as a response to biospheric processes (i.e. respiration and photosynthesis), as well as uptake and release by the ocean (hereafter referred to as O\textsubscript{2\textsubscript{bio}} and O\textsubscript{2\textsubscript{oc}}) are included in the model. To gain an overview of the importance of these O\textsubscript{2} sources and sinks in the modelling of O\textsubscript{2}, partitioning of the ocean, biosphere, and fossil fuel components is elaborated on in this chapter (Section 4.1). The total of the modelled fluctuations in O\textsubscript{2} is compared to measurements in Lutjewad (NL) and Weybourne (UK) in order to validate the model results (Section 4.2). After the various O\textsubscript{2} sources and sinks are explored in this chapter, ffO\textsubscript{2} and its use as a tracer for fossil fuel sources are analysed in more detail in Chapters 5 and 6.

4.1 O\textsubscript{2} fluctuation partitioning

O\textsubscript{2} is the second most abundant molecule in the atmosphere, with a relative abundance of about 20.9%. Small scale fluctuations in atmospheric O\textsubscript{2} concentration can be used to partition and quantify the land and ocean carbon sinks in the carbon budget at described in Section 1.1. Since only fluctuations on a scale of ppm appear and are important in this partitioning, the O\textsubscript{2} background concentration is not implemented in the model. The variation in concentration that remains, is due to O\textsubscript{2} uptake or release by the ocean, biosphere, and (fossil) fuel burning.

The fluctuations as modelled per component (i.e. the ocean, biosphere, and fossil fuel burning) vary over the three study areas. The three components as simulated for Zweth (Rijnmond, NL) are shown in Figure 14. Figure 14a shows a time series of the O\textsubscript{2} fluctuations. O\textsubscript{2} is mainly depleted from the atmosphere during October 2014. As can be expected in an urban area, most of the O\textsubscript{2} fluctuations are due to fossil fuel burning (as also shown in Figure 14b). Fossil fuel burning is responsible for 53.7% of all O\textsubscript{2} uptake in Zweth, with a average of -9.6 ppm as opposed to the background concentration. There is however a lot of fluctuation in the importance of the fossil fuel component over time, as it is driven by the ffCO\textsubscript{2} emissions in the nearby area.

O\textsubscript{2} fluctuations due to the biosphere is the second largest component at Zweth. The effect
of the biosphere can be divided in uptake of O\textsubscript{2} due to respiration, and release of O\textsubscript{2} due to photosynthesis. The biosphere is a net O\textsubscript{2} sink over the studied month (October 2014). It is responsible for 43.8\% of the total O\textsubscript{2} uptake, with an average of -7.8 ppm as opposed to the background. Even though fluctuations in the biospheric uptake and release are not as large as the fluctuations due to the fossil fuel component, they are still easily distinguished in the dataset, indicating that the biosphere is not a constant sink over time. In spring and summer months, this component is expected to act as a O\textsubscript{2} source, due to the increased amount of photosynthesis.

The final component responsible for O\textsubscript{2} variation in the atmosphere is the ocean. In Zweth, the ocean in responsible for 2.4\% of the total O\textsubscript{2} uptake, with an average of -0.4 ppm. Not only uptake of O\textsubscript{2} takes place, as on occasion, the ocean acts as a O\textsubscript{2} source in Zweth. This is due to due to the alternation of outgassing and uptake of O\textsubscript{2}, dependent on solubility changes in the ocean (Rödenbeck et al. 2008). Relatively slow equilibrium rates in this solubility of O\textsubscript{2} in the ocean cause relatively little variation in the total O\textsubscript{2} concentration due to the ocean over the examined time scale. Over longer time scales, the ocean has a larger influence on atmospheric O\textsubscript{2} as new equilibria are reached with changing climates (R. F. Keeling and A. C. Manning 2014).

As a second study area, O\textsubscript{2} fluctuations at Lutjewad are analysed. Lutjewad is a rural station, located on the north coast of Groningen (NL). Even though the modelled total O\textsubscript{2} fluctuations are smaller due to the more remote location, the fossil fuel component is cumulatively still the
largest (49.0%, Figure 15b), with an average O₂ uptake of -5.7 ppm. The fluctuations of the ffO₂ at Lutjewad are smaller than the ffO₂ at Zweth. This is because CO₂ emissions are less severe at Lutjewad, and emission concentrations are more diluted. Furthermore, due to the coastal location of Lutjewad, inversions are less severe. This decreases the trapping of air with low O₂ concentrations.

The biosphere is almost equally important as fossil fuel burning in the total O₂ uptake in Lutjewad, with an average of -5.4 ppm. It is responsible for 46.4% of all O₂ taken up. It is important to note that the prevailing wind direction is southwest. Air modelled at this location has thus travelled over land before reaching Lutjewad, increasing the importance of the fossil fuel and land biosphere components. The ocean is again a relatively small component, responsible for 4.6% of the total O₂ fluctuations. Even though the wind originates from the land, the oceanic component is still larger for Lutjewad than for Zweth (with an average uptake of -0.5 ppm), due to the coastal location of the study area.

In Weybourne total O₂ fluctuations are smallest as shown in Figure 16. This is mainly due to the relatively small amount of fossil fuel burning in the area. Weybourne is the only study area in which the biosphere is a more important component than fossil fuel burning (62.5% vs 31.5% of the modelled total O₂ fluctuations). Fossil fuel burning causes an average uptake of -2.9 ppm, whereas the biosphere causes an average net uptake of -5.7 ppm O₂.

The ocean causes an uptake of -0.5 ppm on average. The O₂ fluctuations at Weybourne
due to the biosphere and ocean are thus similar in magnitude to those at Lutjewad, showing the similarities between the two sites (i.e. coastal background stations). O\textsubscript{2} concentrations at Lutjewad are however more influenced by fossil fuel burning than concentrations at Weybourne.

Figure 16: a) Time series of O\textsubscript{2} fluctuations due to fossil fuel burning (blue), land biosphere activity (orange), and the ocean (green), and b) cumulative importance of fossil fuel burning, land biosphere activity, and the ocean for October 2014 at Weybourne (North Norfolk, UK).

Overall it can be stated that during the autumn month of October 2014, all three components act as a net sink of atmospheric O\textsubscript{2}. In summer months, the biosphere is likely to turn into a source of atmospheric O\textsubscript{2}. The total uptake of O\textsubscript{2} (mainly due to fossil fuel burning) is then expected to be mitigated by the biosphere. In the case of Weybourne, biological activity in summer is even likely to result in a net increase in O\textsubscript{2} concentrations. On the short time scales as modelled here, O\textsubscript{2} fluctuations due to the ocean are relatively small, especially in urban areas. The main difference between the three study areas in O\textsubscript{2} uptake is to be found in the amount of fossil fuel burning in the nearby area upwind.

4.1.1 Diurnal cycles

The times series in Figures 14a to 16a show variation in the amount of O\textsubscript{2} uptake over time. From these figures a clear diurnal cycle is however not easily distinguished. Figure 17 shows the average diurnal cycle of the three components for the three measurement sites over the studied month. ffO\textsubscript{2} is expected to decrease during the day due to increased anthropogenic activity and thus ffCO\textsubscript{2} emissions, and increase again at night. The decrease is mitigated by boundary layer mixing and entrainment with air from the free troposphere with higher concentrations.
This decrease during the day is simulated at Zweth and Weybourne (Figure 17a). In Zweth commuting hours around 8:00 and 18:00 LT can be distinguished. At Weybourne, $ffO_2$ is larger, with a relatively small average amplitude (0.5 ppm). The diurnal average $ffO_2$ at Lutjewad does not show the expected cycle: $ffO_2$ is largest during the day and lower at night with an amplitude of about 2 ppm. The $ffCO_2$ emissions around Lutjewad are smaller than those around Zweth. It could thus be the case that the effect of boundary layer mixing and entrainment at this location overpowers the increase in $ffCO_2$ emissions, causing an increase in $ffO_2$ during the daytime.

The average diurnal cycle of $O_{bio}$ is shown in Figure 17b. A clear diurnal cycle can be seen for Zweth and Weybourne, with the lowest concentrations at night and in the morning due to plant respiration at night. During the day, photosynthesis becomes relatively more important, releasing oxygen and causing an increase in $O_{bio}$. In Zweth, the total effect of the biosphere is larger than in Weybourne (i.e. the lower average $O_{bio}$). This is likely due to the more inland location of the site. $O_{bio}$ in Lutjewad also shows a low in the early morning. The amplitude of the cycle is however smaller at this site compared to the other sites. This means that there is less difference between the photosynthesis and respiration term simulated at Lutjewad.
Figure 17: Average diurnal cycles of O\textsubscript{2} uptake due to a) fossil fuel burning (ffO\textsubscript{2}), b) biospheric activity (O\textsubscript{2\textsubscript{bio}}), and c) the ocean (O\textsubscript{2\textsubscript{oc}}) in Zweth (blue), Lutjewad (orange), and Weybourne (green).

The diurnal variation in O\textsubscript{2\textsubscript{oc}} as shown in Figure 17c is minimal for all three sites. A diurnal cycle in ocean uptake/outgassing is however not expected due to its slow response time. The figure does show the similarity in O\textsubscript{2\textsubscript{oc}} between coastal sites Lutjewad and Weybourne, and the slightly lower impact in the more inland site Zweth. It should be noted that the uptake and release of O\textsubscript{2} from the ocean is modelled based on the Atmospheric Potential Oxygen (APO) fluxes as modelled by Rödenbeck et al. (2008). This model has a coarse spatial scale of 3.8x5.0°, meaning that the resolution of the ocean O\textsubscript{2} fluxes are not very precise and more regional scale differences between the sites could be missed.

4.2 Total O\textsubscript{2} fluctuation and model validation

The combination of ffO\textsubscript{2}, O\textsubscript{2\textsubscript{bio}}, and O\textsubscript{2\textsubscript{oc}} results in a total fluctuation in O\textsubscript{2} concentration as opposed to the background concentration. This total fluctuation over the month, as well as the diurnal averages are analysed for each study area. In case of Lutjewad and Weybourne,
measurements of both atmospheric CO₂ and O₂ concentration are compared to the simulated results in order to assess the model performance.

4.2.1 Zweth, Rijnmond

As is apparent from Section 4.1, fossil fuel burning in the industrial area and harbour nearby has the largest influence on variation in atmospheric O₂ at Zweth. The steep lows shown in Figure 18a can be largely attributed to O₂ uptake due to fossil fuel burning. However, the biosphere does still play a significant role in the total uptake of atmospheric O₂. The average diurnal cycle as shown in Figure 18b shows a low around 8:00 LT, and a high just after midnight. The total O₂ concentration has an average of -17.3 ppm with an amplitude of 3.3 ppm. Again it becomes clear that fossil fuel burning is the most important component at this site, with highs and lows at corresponding times (as depicted in Figure 17b). However, the total concentration is still influenced by the biosphere (see Figure 17b), diminishing the low O₂ concentration in the afternoon and causing a small peak through photosynthesis. The increase in total O₂ in the afternoon is also partly attributed to the effect of boundary layer mixing and entrainment. Air entrained from the free troposphere contains more O₂ than the air within the boundary layer, resulting in an increase in O₂ at the surface.

Figure 18: a) Time series of the total O₂ fluctuations and b) diurnal average of total O₂ as opposed to the background, as modelled for Zweth during October 2014. The shading represents the standard deviation of the simulated averages.
In addition to the $O_2$ concentrations simulated at Zweth, the $CO_2$ concentrations are shown in Figure 19. This figure also contains data of hourly observations in Zweth. It can be seen that the model often underestimates $CO_2$ concentrations. The diurnal cycle simulated at Zweth follows a similar trend as the average diurnal cycle of the observations. The amplitude in the cycle is however underestimated, as becomes especially apparent during the night and (early) morning. This shows the difficulty the model has in representing stable conditions at night.

The $CO_2$ measurements at Zweth are conducted at ground level, resulting in a large influence of local sources and processes. This can influence the measured $CO_2$ concentration in a way that is not captured by the model simulating on a 1x1 km horizontal resolution. The $O_2$ concentrations shown in Figure 18 are modelled making use of the $CO_2$ emissions. Furthermore, the emitted $O_2$ and $CO_2$ are transported in a similar way. Errors in simulated $CO_2$ are therefore translated into the modelled $O_2$ concentrations. This effect becomes apparent when comparing modelled and observed $O_2$ and $CO_2$ concentrations at Lutjewad and Weybourne in Sections 4.2.2 and 4.2.3, respectively.

**4.2.2 Lutjewad, Groningen**

Changes in simulated $O_2$ concentration at Lutjewad are analysed and compared to observations in order to validate the model. Figure 20a shows the comparison of the simulated and observed $O_2$ fluctuations at Lutjewad in October 2014. Observations at Lutjewad are done at the top of the measurement tower, at 60m height (I. T. Van Der Laan-Luijkx et al. 2010). Variation
in O$_2$ concentration in Lutjewad is limited compared to Zweth due to the smaller amount of fossil fuel burning in the area. O$_2$ exchange through the biosphere is therefore relatively more important at this site. The fluctuations shown here are also smaller due to the increased height (i.e. 60 m compared to surface concentrations). Further analysis done on concentrations at Lutjewad outside of this Section focuses surface concentrations, in order to make the results corresponding to this site optimally comparable to results from the other sites. The change in O$_2$ concentration fluctuates between about -75 ppm and 6 ppm compared to the background value during October 2014. At some moments, the simulated O$_2$ matches the observations quite well (e.g. the 7$^{th}$, 13$^{th}$, 20$^{th}$, 21$^{st}$, 30$^{th}$, and 31$^{st}$ of October). At other times, the modelled and observed values vary quite a lot (in the periods from the 12$^{th}$ to 18$^{th}$ and 25$^{th}$ to 28$^{th}$ of October). In this case, hourly observations of O$_2$ are available, however, the reliability of these values is questionable (I. Van Der Laan-Luijkx 2018). Sample flasks are alternated every 24 hours. Leaking occurred in one of the two flasks causing measurement errors in part of the observations. This means that even though a (statistical) comparison of the observations and simulations possible, solid conclusions cannot be drawn from this. A true validation or rejection of the model is thus not possible based on these figures. Because of the indefinite certainty of the hourly measurements, 3-daily flask data is added to Figure 20a in gray. Even though these measurements are more reliable, only 6 observational values are available from this dataset for October 2014. This makes it impossible to draw hard conclusions about the model performance based on this data. However, the flask data that is available shows similar values as simulated at those moments.

Statistical measures of the model performance in simulating CO$_2$ and O$_2$ concentrations based on the hourly observations are shown in Table 7. A discrepancy is shown in CO$_2$ as well as O$_2$. The average CO$_2$ concentration and standard deviation is underestimated by the model by 4.5 and 2.8 ppm, respectively. These differences are expected to translate to the measures for simulated O$_2$, as those are based on the simulated CO$_2$ and OR$_{in}$. This is also displayed in Figure 21a, where the observed CO$_2$ values are plotted against simulations. At times when the simulated O$_2$ deviates from observations, simulated CO$_2$ also does not agree with CO$_2$ observations. This means that if the errors shown are due to poor model performance, then errors in simulated O$_2$ would be due to errors in simulated CO$_2$ rather than faulty values of OR$_{in}$. 

45
Furthermore (as stated by Super et al. (2017) and further elaborated on in Chapter 3), these discrepancies in CO\textsubscript{2} concentration are often attributed to errors in the simulated wind direction. As a result, the simulated average O\textsubscript{2} is overestimated by 5.4 ppm, and the standard deviation is underestimated by 3.2 ppm. If the these errors have their origin in the simulated CO\textsubscript{2} concentrations, then the amplification in discrepancies can be explained by the multiplication by OR\textsubscript{in} (with an average value of about -1.5). In this case, however, variations between the modelled and observed values are not necessarily due to mistakes in the model, but could also be due to unreliable observations. With this kept in mind, statistical analysis results in an index of agreement of 0.72 and an R\textsuperscript{2} of 0.30 for the modelled O\textsubscript{2} fluctuations and an index of agreement of 0.71 and an R\textsuperscript{2} of 0.30 for the modelled CO\textsubscript{2} concentrations.

**Figure 20:** a) Time series of the total O\textsubscript{2} fluctuations and b) diurnal average of total O\textsubscript{2} as opposed to the background, as modelled and observed at Lutjewad during October 2014. The shading represents the standard deviation of the simulated and observed averages.

**Figure 21:** a) Time series of the total CO\textsubscript{2} and b) diurnal average of total CO\textsubscript{2}, as modelled and observed at Lutjewad during October 2014. The shading represents the standard deviation of the simulated and observed averages.
Table 7: Most important quantitative measures of CO$_2$, O$_2$, and wind direction model performance at Lutjewad.

<table>
<thead>
<tr>
<th></th>
<th>$\bar{O}$</th>
<th>$\mathcal{P}$</th>
<th>sd$_O$</th>
<th>sd$_P$</th>
<th>RMSE</th>
<th>d</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>411.5</td>
<td>407.0</td>
<td>12.2</td>
<td>9.4</td>
<td>11.5</td>
<td>0.71</td>
<td>0.30</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-16.4</td>
<td>-11.0</td>
<td>14.5</td>
<td>11.3</td>
<td>13.5</td>
<td>0.72</td>
<td>0.30</td>
</tr>
<tr>
<td>Wind direction</td>
<td>190</td>
<td>198</td>
<td>63.6</td>
<td>58.1</td>
<td>50.4</td>
<td>0.820</td>
<td>0.448</td>
</tr>
</tbody>
</table>

The simulated daily average values of O$_2$ as shown in Figure 20b do not show a clear diurnal cycle. From midnight on, O$_2$ concentrations increase by about 3.5 ppm until the afternoon, after which they decrease again. The observed values show a similar trend, with (as mentioned above) average values about 5 ppm lower. This is in line with the observed and simulated CO$_2$ concentrations (21b), which also display a lack in diurnal trend and slightly higher average concentrations. This consistency between the simulations and the observations does make the trends shown in Figures 21b, and consequently Figures 20b and 17 more likely to represent reality. The lack in diurnal trend suggests a the signal of a station measuring a background signal. Winds originating mainly from the southwest over the analysed period contradict this, resulting in a signal influenced by fossil fuel burning and biosphere exchange in Figures 20a and 21a. The lack in diurnal trends shown in Figures 20 and 21b may be explained by the relatively small amount of ffCO$_2$ emissions, which are mixed and diluted when they reach Lutjewad, combined with a relatively small amount of boundary layer development and entrainment at the coast, leading to quite constant concentrations during the day. Furthermore, the influence of fossil fuel burning is expected to be lower at 60 m height (at which the air is sampled at this station) as compared to the surface. In order to further investigate whether the lack in diurnal cycles shown in Figures 20 and 21 are due to oceanic influences may be studied by using radon as a tracer to gain insight on the air mass origins at coastal locations (Pszenny and Larson 1990).

4.2.3 Weybourne, North Norfolk

Even though the OR$_{in}$ used as model input are averages per SNAP category for the Netherlands, the changes in O$_2$ concentration in Weybourne (situated in the UK) are also analysed and compared to observations. Figure 22a shows the O$_2$ fluctuations according to the simulations and observations at Weybourne. Weybourne is, similar to Lutjewad, a more rural station than Zweth located on the coast. As a result, the O$_2$ signal is more influenced by biological activity.
During autumn and winter, respiration is generally higher than photosynthesis, resulting in a net uptake of $O_2$ by the land biosphere and therefore amplifying the $O_2$ signal. Figure 22a shows the modelled changes in $O_2$ concentration along with $O_2$ observations at Weybourne, sampled at 10m height (Wilson 2012). The simulations generally follow the same trend as observations, with fluctuations in $O_2$ concentration varying between about -40 ppm and 8 ppm compared to the background value for October 2014. Most of the fluctuations observed are well captured by the model.

Statistical measures of the model performance in simulating CO$_2$ and $O_2$ concentrations are shown in Table 8. The values show that the average concentrations are overestimated by 3.0 ppm by the model. The standard deviation of the modelled $O_2$ concentrations is slightly low compared to the standard deviation of the observations. These differences are smaller for observed and modelled CO$_2$ concentrations. Discrepancies in the modelled CO$_2$ are likely due to the misrepresentation of the wind direction in the model (Chapter 3), whereas the poorer model performance in simulating $O_2$ as compared to CO$_2$ are more likely due to the OR$_{in}$ values. Table 8 thus suggests that the values for OR$_{in}$ is slightly high in Weybourne, as lower value for OR$_{in}$ would result in larger fluctuations from the background value. Even though the hourly observations at Weybourne are more reliable than those from Lutjewad, it should be kept in mind that observations of atmospheric $O_2$ have an uncertainty of about 2 ppm (Barningham 2017).

Figure 22: a) Time series of the total $O_2$ fluctuations and b) diurnal average of total $O_2$ as opposed to the background, as modelled and observed at Weybourne during October 2014. The shading represents the standard deviation of the simulated and observed averages.
Figure 23: a) Time series of the total CO$_2$ and b) diurnal average of total CO$_2$, as modelled and observed at Weybourne during October 2014. The shading represents the standard deviation of the simulated and observed averages.

Table 8: Most important quantitative measures of CO$_2$, O$_2$, and wind direction model performance at Weybourne.

<table>
<thead>
<tr>
<th></th>
<th>$\bar{O}$</th>
<th>$\bar{P}$</th>
<th>$sd_O$</th>
<th>$sd_P$</th>
<th>RMSE</th>
<th>d</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>404.4</td>
<td>404.8</td>
<td>6.0</td>
<td>6.8</td>
<td>5.63</td>
<td>0.78</td>
<td>0.38</td>
</tr>
<tr>
<td>O$_2$</td>
<td>-11.3</td>
<td>-8.3</td>
<td>7.7</td>
<td>6.4</td>
<td>6.7</td>
<td>0.75</td>
<td>0.34</td>
</tr>
<tr>
<td>Wind direction</td>
<td>214</td>
<td>219</td>
<td>58.2</td>
<td>60.3</td>
<td>77.8</td>
<td>0.47</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The simulated average diurnal cycle of O$_2$ (as shown in Figure 22b) shows a similar trend as the observed average values. However, the simulated average is slightly high and the amplitude of the cycle is underestimated. During the nighttime and early morning, the O$_2$ uptake is generally underestimated by a maximum of 4.2 ppm on average, whereas the maximum is better captured by the model. The underestimation in O$_2$ uptake in the average diurnal cycle can have multiple causes. The overestimation of the mean O$_2$ is likely due to an overestimation in OR$_{in}$. The underestimation in diurnal fluctuations in O$_2$ concentration are also shown in the comparison of simulations and observations of the average diurnal cycle of CO$_2$ at Weybourne, as shown in Figure 23b. This suggests that some of the discrepancies between the observed and simulated average diurnal O$_2$ are due to misrepresentations in CO$_2$ concentrations. This could again be due to a poor representation of the wind direction. It could also be that photosynthesis and respiration are underestimated by the model. These processes would mitigate the O$_2$ decrease during the day and reinforce the O$_2$ decrease during the night. Other possible causes could be the misrepresentation of anthropogenic CO$_2$ emissions, or misrepresentation of the boundary layer development at Weybourne. Since Weybourne is located on the coast, boundary layer development is not as pronounced as it would be over land. Larger fluctuations in
boundary layer height would result in larger fluctuations in CO$_2$ concentration. This means that the underestimations in CO$_2$ fluctuations would be due to an underestimation of boundary layer development in the model. The average simulated boundary layer height fluctuates between about 600 m at night and 920 m during the day on average. Bannan et al. (2017) measured an average boundary layer height fluctuating between 300 m at night increasing to 1300 m in the morning up until 1800 m in the afternoon in March and April at Weybourne. Even though boundary layer development is expected to be smaller in October as compared to March/April, this comparison to literature does offer a potential explanation as to the underestimation in diurnal variation of the compound concentrations. Furthermore, it is important to note that the simulations in domain 2 are over a 12x12 km domain, whereas the observation data from Weybourne can be influenced by local processes. It could be that the averaging of concentrations over the 12x12 km grid cell smoothens out the simulated compound concentrations, resulting in lower fluctuations.
5 Simulating (fossil fuel) CO$_2$, fossil fuel O$_2$, and fossil fuel oxidative ratios

One of the main objectives of this research is to introduce atmospheric oxygen as a tracer for fossil fuel emissions in urban areas. The main processes influencing the oxygen concentration on short time scales are fossil fuel burning, the uptake and release of O$_2$ through respiration and photosynthesis, and O$_2$ exchange with the ocean. One of the advantages of modelling O$_2$ fluctuations as opposed to measuring O$_2$ concentrations, is that the different processes are introduced as separate tracers and can thus be separately analysed (as shown in Section 4.1). In order to investigate fossil fuel CO$_2$ sources, variation in O$_2$ concentrations due to fossil fuel burning (ffO$_2$) are of interest. The modelled CO$_2$ and fossil fuel CO$_2$ (ffCO$_2$) are first discussed. After a general overview of the (fossil fuel) CO$_2$ concentrations and CO$_2$ emission sources in the study areas is obtained, the fluctuations in ffO$_2$ are discussed, as well as the oxidative ratios (OR$_{ff}$) that follow from this. This is done for Rijnmond (Section 5.1), the north of Groningen (Section 5.2), and North Norfolk (Section 5.3). The applicability of OR$_{ff}$ values during specific emission events to identify ffCO$_2$ emission sources is explored in Section 5.4.

5.1 Fossil fuel CO$_2$, O$_2$, and OR$_{ff}$ at Rijnmond

5.1.1 CO$_2$ concentrations

CO$_2$ concentrations in Rijnmond vary between about 390 and 480 ppm during October 2014. Figure 24 shows the simulated CO$_2$ concentrations at Zweth. As depicted in Figure 24b, winds originate mostly from the south southwest. As the wind originates from the south, concentrations are in the higher range; generally above 420 ppm. This is due to the location of the industrial area Botlek situated south to southwest from Zweth, and the city of Rotterdam situated southeast from Zweth (as can be seen in Figure 5). On the occasion the wind originates from the north, concentrations are in the lower range; below 420 ppm.
In section 4.2.1, the average diurnal cycle of CO\textsubscript{2} concentrations at Zweth is discussed. From the time series of the total CO\textsubscript{2} concentration over the entire month in Figure 24a, the diurnal pattern is not easily distinguished. A few moments with exceptionally high atmospheric CO\textsubscript{2} concentrations can be distinguished as ‘high CO\textsubscript{2} events’ or ‘CO\textsubscript{2} peaks’. This is during the 3\textsuperscript{rd}, 15\textsuperscript{th}, and 30\textsuperscript{th} of October. These events will be further analysed in Section 5.4.

5.1.2 Dominant CO\textsubscript{2} emission sources

Most of the fluctuations in CO\textsubscript{2} concentrations at Zweth are due to fossil fuel emissions in the area. The various CO\textsubscript{2} emission sources distinguished in the model are described in Section 1.1.2 and Section 2.3.1. Not all anthropogenic emission sources are equally influential in Zweth, as depicted in Figure 25b. Overall, CO\textsubscript{2} emissions from industrial production processes (SNAP category 03/04) are the largest contributors to fossil fuel CO\textsubscript{2} at the surface. These emissions are on average responsible for more than 38% of the simulated anthropogenic CO\textsubscript{2} at Zweth in October 2014. Non-industrial processes, road transport, and power generation are other large emission sources, contributing to about 20%, 19%, and 12% of all anthropogenic CO\textsubscript{2} simulated at Zweth, respectively. It is expected that the relative importance of the emission sources varies with height, since emissions of certain production processes and power generation plants are stack emissions. The analysis in this chapter is however limited to surface concentrations only.
The CO$_2$ emission categories are linked to the uptake of O$_2$ through the average oxidative ratio (OR$_{\text{ff}}$) per category as described in Section 2.3.2 (Table 1). The average ffCO$_2$ and the consequential O$_2$ uptake (ffO$_2$) in Rijnmond are shown in Figure 26a and b. The maps are averages for October 2014 as simulated by WRF. It is apparent that ffO$_2$ uptake follows the patterns of ffCO$_2$ emissions. As expected, ffCO$_2$ is largest around the industrial area and the harbour, and is then transported by the southwesterly winds. From the ffCO$_2$ emissions and the additional ffO$_2$ uptake, a time-average OR$_{\text{ff}}$ can be calculated as shown in Figure 26c. This value is variable due to the processes of atmospheric transport and mixing, and thus not necessarily equal to the value assigned to the emissions in its particular grid cell. The OR$_{\text{ff}}$ shows spatial fluctuations over the area, ranging between -1.49 and -1.56. These values are, as expected, lower than the world average OR of -1.4 for fossil fuel burning due to the above average gas use in the Netherlands. OR$_{\text{ff}}$ values closer to -1 can be found in the same areas as the fossil fuel CO$_2$ plumes of the industrial area and harbour, suggesting that the usage of coal and oil are larger in those regions. In other areas, gas would be a relatively more important fuel source. This is however based on the average OR$_{\text{in}}$ per SNAP category in the Netherlands, and thus not specifically for Rijnmond. An attempt to improve on this is presented in Chapter 6.
O₂ uptake and release and ORs do not only show spatial variation, but also variation in time. In this study, the model run is limited to one month due to the required simulation time. Because of this, only variations on a relatively short time scale can be studied. Seasonal variations are thus not shown, although they are expected to be apparent as well, with a higher amount of net O₂ uptake in winter due to larger emissions and less biosphere release of O₂. Furthermore, certain fuel types might gain relative importance as the seasons change, resulting in a seasonal variation in OR_eff. For instance, increased heating might result in a lower OR_eff during wintertime. This seasonal fluctuation is expected to have an amplitude of 0.03 (I. Van Der Laan-Luijkx 2010) to 0.04 (Steinbach et al. 2011) on the northern hemisphere.

The average diurnal ffCO₂ concentration as simulated for October 2014 at Zweth shows the highest concentrations at night and in the morning, with a maximum at 8:00 LT and a minimum at 16:00 LT (Figure 27a). The increase in concentrations in the morning are due to the increased anthropogenic activity and the persistence of the nocturnal boundary layer in winter, trapping anthropogenic CO₂ emissions. This causes an increase in ffCO₂ of 4 ppm on average.
On a diurnal time scale, ffO\textsubscript{2} concentrations show a low in the morning hours, around 8:00 and 9:00 LT, in line with the increasing CO\textsubscript{2} emissions (Figure 27a). From that time on, the O\textsubscript{2} concentration increases again. This can be attributed to the decrease in CO\textsubscript{2} emissions in between commuting hours and the growth of the atmospheric boundary layer (ABL). As the ABL grows, mixing of the air and entrainment takes place. In the case of oxygen, this entrainment is with air containing higher O\textsubscript{2} concentrations (i.e. closer to the background value, in reality around 20.95\%).

The OR\textsubscript{ff} also shows variation in time. It should be noted that a larger OR\textsubscript{ff} is not necessarily related to larger CO\textsubscript{2} emissions or O\textsubscript{2} uptake or release. Instead, variations in OR\textsubscript{ff} are due to temporal factors influencing the relative importance of the different fuel mix types. For instance, during the morning and afternoon commuting hours, transport (SNAP category 07) will have a relatively large contribution to the CO\textsubscript{2} emissions. During these times, OR\textsubscript{ff} values are pulled more towards about -1.5 (Figure 27b). Other important emission sources in Rijnmond are production processes and energy production (SNAP categories 01 and 03/04). These processes do not have a clear diurnal variation, and are thus relatively more important when other emissions sources are smaller, causing lower than average OR\textsubscript{ff} values at night and around noon. It should be noted that the average diurnal variation in simulated OR\textsubscript{ff} is limited, with an average variation of 0.022.

![Figure 27: Average diurnal cycle of a) ffCO\textsubscript{2} and ffO\textsubscript{2} concentration, and b) OR\textsubscript{ff} in Zweth for October 2014.](image)
5.2 Fossil fuel CO$_2$, O$_2$, and OR$_f$ at the north of Groningen

5.2.1 CO$_2$ concentrations

As opposed to Rijnmond, the north of Groningen is a more rural area with less CO$_2$ emissions. As a consequence, the total CO$_2$ concentration is smaller, showing weaker variations. In Lutjewad total CO$_2$ concentrations vary between 397 and 441 ppm during October 2014 (Figure 28a), in line with measurements done by I. Van Der Laan-Luijkx (2010) at the site. Just as simulated at Zweth, winds at Lutjewad also generally originate from the south southwest. This means that the air at Lutjewad has traveled over land and is thus expected to be influenced by the biosphere and anthropogenic emissions (south) southwest, causing relatively high fluctuations in CO$_2$ concentration for a coastal station.

Figure 28: a) Time series of total CO$_2$ concentration and b) wind rose showing the origin of the CO$_2$ concentrations, simulated at Lutjewad.

The segregation of emission peaks or high CO$_2$ events from the time series in Figure 28 is more difficult than for Zweth. This is because the CO$_2$ peaks are lower, and the signal is relatively more influenced by the biosphere. However, based on the modelled ffCO$_2$ signal (as shown in Section 4.2), three emission events are selected which will be further analysed in Section 5.4.
5.2.2 Dominant CO\textsubscript{2} emission sources

As mentioned in Section 5.2.1, air at Lutjewad is influenced by anthropogenic CO\textsubscript{2} emissions due to the prevailing wind direction during October 2014. Figure 29\textsuperscript{a} shows the average CO\textsubscript{2} emissions as modelled for the model domain in which Lutjewad is located. It can again be seen that emissions in the area around Lutjewad are smaller than those in Rijnmond. Nearby cities Leeuwarden and Groningen can be distinguished from this figure (further described in Section 2.1). Considering the south southwesterly winds during October 2014, air at Lutjewad can be expected to be influenced by emissions from Leeuwarden.

The relative importance of emissions from the city is also portrayed in Figure 29\textsuperscript{b}, as road transport (SNAP category 07) is on average the most important emission source at Lutjewad. Industrial production processes (SNAP category 03/04) are however almost equally influential, responsible for an average of about 23\% of all CO\textsubscript{2} emissions. Overall, CO\textsubscript{2} emissions at Lutjewad find their origin in a mix of SNAP categories, all (with the exception of category 05/06/09) of significant importance at the site.

![Figure 29: a) Map of the average ffCO\textsubscript{2} emissions in kmol/hr in the Netherlands and b) the relative importance of various CO\textsubscript{2} emission sources (per SNAP category) in Lutjewad (after transport) for October 2014.](image)

5.2.3 Fossil fuel O\textsubscript{2} and OR\textsubscript{(ff)}

Maps of the average ffCO\textsubscript{2} and consequential ffO\textsubscript{2} over the Netherlands are shown in Figure 30\textsuperscript{a} and b. The location of study sites Zweth and Lutjewad are indicated in the figures. Again,
it can be seen that $\text{ffO}_2$ is lowest where $\text{ffCO}_2$ is highest. Some cities can be identified, and transport of the emissions towards the northeast is visible. The average fossil fuel oxidative ratio ($\text{OR}_\text{ff}$) that follows from Figure 30a and b is shown in Figure 30c. It can be seen that $\text{OR}_\text{ff}$ in Groningen is lower than $\text{OR}_\text{ff}$ in Rijnmond. This suggests a larger amount of gas use in Groningen as opposed to Rijnmond. Figure 30c shows the $\text{OR}_\text{ff}$ values after transport. It can be seen that relatively high $\text{OR}_\text{ff}$ values originating in Belgium are transported and still visible over the southern part of the Netherlands. The Ruhr area in Germany shows interesting results. $\text{ffCO}_2$ concentrations are the highest around this area over the entire domain. As a result, $O_2$ uptake is also largest. The calculated $\text{OR}_\text{ff}$ shows a relatively strong spatial fluctuation over this area, with the highest $\text{OR}_\text{ff}$ value in the domain north of Düsseldorf, and the lowest $\text{OR}_\text{ff}$ in the domain south of Düsseldorf. With a difference in $\text{OR}_\text{ff}$ of almost 0.1, the variation in dominant emission categories are evident. The values for $\text{OR}_\text{in}$ are based on the average $\text{OR}_\text{in}$ per emission category, resulting in a mix of fuel types. If the actual fuel type used at certain locations were to be implemented into the model, these kind of differentiation in emission sources is likely to become even more evident.
The average diurnal cycle of ffCO₂ is shown in red in Figure 31. It can be seen that the ffCO₂ concentrations are generally highest at midnight, decrease about 2.5 ppm until 8:00 LT, and then increase again. This is not the diurnal trend which may be expected. The low ffCO₂ at 8:00 LT suggests relatively clean air. Around this time, the standard deviation is also smallest, showing a relatively constant concentration around this time. After 8:00 LT ffCO₂ concentrations increase due to emissions. On the one hand, the increase is limited due to ABL growth during the day. The relatively large fluctuation in average ffCO₂ in Lutjewad compared
to Zweth considering its remote location could be attributed to its limited ABL growth due Lutjewad’s location at the coast, causing accumulation of the emissions that do occur or are transported toward the location.

The average diurnal cycle of ffO₂ as shown in Figure 31a follows the inverse trend of ffCO₂: Concentrations are highest around 8:00 LT, when the air is less influenced by human activity, after which ffO₂ decreases about 6 ppm until it reaches its low around midnight. The average values for OR₀ff are shown in Figure 31b. An average OR₀ff of -1.551 is simulated, with an average variation of 0.017 (0.005 smaller than at Zweth).

![Figure 31: Average diurnal cycle of a) ffCO₂ and ffO₂ concentration, and b) OR₀ff in Lutjewad for October 2014.](image)

### 5.3 Fossil fuel CO₂, O₂, and OR₀ff at North Norfolk

#### 5.3.1 CO₂ concentrations

As is apparent in the site descriptions in Section 2.1, North Norfolk is less urbanised than Rijnmond. This results in less CO₂ emissions and consequently smaller total CO₂ concentrations. At Weybourne, CO₂ concentrations vary between about 390 and 430 ppm during October 2014 (Figure 32). Weybourne is a background station. However, due to the prevailing wind direction, CO₂ concentrations still show relatively large fluctuations as compared to concentrations observed at sea in this region by Pickers et al. (2016). These measurements show concentrations more constant around 390 ppm (for September 2014). Figure 32 shows winds originating mainly from the southwest. The largest concentrations originate from the south, potentially from the city of Norwich.
The time series for October 2014 in Weybourne shows numerous peaks with higher than average CO$_2$ concentrations. Even though ffCO$_2$ emissions are relatively small in Weybourne, some peaks in Figure 23a do coincide with anthropogenic CO$_2$ emissions in the area. It should be noted that the peaks are of a smaller magnitude than those identified in simulations for Zweth, however, they are still easily identified in the time series. The events of the 7th, 15th, 28th, and 30th are further analysed in Section 5.4.

5.3.2 Dominant CO$_2$ emission sources

The origin of the emissions at Weybourne differs from those at Rijnmond: Where in Rijnmond most of the fossil fuel CO$_2$ came from industrial production processes and power generation, in Weybourne the largest fossil fuel CO$_2$ source is road transport, similar to Lutjewad (SNAP category 07). Next to road transport, non-industrial processes, power generation, and industrial production processes, are large fossil fuel sources, responsible for about 23%, 18%, and 16% of anthropogenic CO$_2$ in Weybourne, respectively. The relatively large importance of road transport in Weybourne is very likely attributed to the city of Norwich, which is located about 40 km south.
5.3.3 $O_2$ fluctuations and OR

Average $ffCO_2$ concentrations, $ffO_2$, and $OR_{ff}$ values are plotted for domain 2 (containing North Norfolk and Weybourne). These maps, shown in Figure 34, identify large cities as CO$_2$ emitting areas, and consequently the places where $ffO_2$ uptake is the largest. The average $OR_{ff}$ varies over the domain, ranging between -1.50 and -1.60. Some differences in average $OR_{ff}$ between cities can be identified. For instance, Paris the Ruhr area seem to be two of the largest emitters of fossil fuel CO$_2$ within the domain. The $OR_{ff}$ around Paris is however higher than in the Ruhr area. This suggests that coal and oil are more important in the fuel mix in Paris than in the Ruhr area. It should however be noted that the values for $OR_{in}$ used in the model are based on the average fuel mix used per SNAP category in the Netherlands. Considering these values, this thus means that power generation is a larger CO$_2$ source in the Ruhr area compared to Paris. The $OR_{ff}$ may change if more information is known about the actual fuel mix used within the various regions over Europe. Since many of the power plants in the Ruhr area are coal-based power plants (RWE 2016), the actual $OR_{ff}$ is expected to be considerably larger.
Figure 34: Maps of a) the average ffCO₂, b) average ffO₂, and c) average ORff over Europe for October 2014 as simulated by WRF. d) shows the OR according to the COFFEE dataset by Steinbach et al. (2011). The location of the measurement station in Weybourne is indicated on the maps.

Figure 34c shows the average ORff that follows from this study for October 2014 after transport of the compounds. As mentioned, to calculate this, average ORin values per SNAP category are used. In reality however, locations may be more dominated by the use of a specific fuel type. This would result in more spatial variation in ORin and consequently more spatial variation in ORff over the domain. An example of this is shown in Figure 34d. This figure shows an OR as calculated by the O₂/CO₂ emissions per grid cell according to the CO₂ release and Oxygen uptake from the Fossil Fuel Emissions Estimate (COFFEE) dataset (Steinbach et al., 2011). In COFFEE, CO₂ emissions from the Emission Database for Global Atmospheric Research (EDGAR) at a 1x1° scale were combined with oxidative ratios at the national level. It contains spatial, as well as temporal variation. For more details and information about the
COFFEE dataset, please refer to Steinbach et al. (2011). Figure 34d shows the time-average OR for October 2014 according to this dataset. It can be seen that the spatial variation in OR over the domain is larger, and can vary significantly within relatively small distances. This figure however does not include transport of the emissions over the domain, which would smoothen out some of the strong regional variations in ORff. A database like COFFEE is likely to offer a more accurate input for ORin compared to the Dutch average ORs per SNAP category to calculate ffo2 on this (i.e. continental) scale. In the current study, this database was not used with the scale of one of the main objectives in mind; investigating fossil fuel sources in urban areas (i.e. Rijnmond). The 1x1° resolution of COFFEE is thus not appropriate to model O2 on this regional scale. However, the database may be useful to model ffo2 in the outer domains in the future.

The average diurnal cycle of ffCO2 concentrations in Weybourne does not show a lot of variation. Concentrations increase during the day and decrease again at night, with an amplitude of only 0.4 ppm. As a consequence, ffo2 in Weybourne also shows limited diurnal variation, with only slightly increased ffCO2 concentrations on an average day. The average diurnal ORff does show a pattern, with an average of -1.550 and an amplitude of 0.01. ORff is relatively low during the night and relatively high during daytime. Road transport is an important emission source at Weybourne. The amount of road transport during the night is however expected to be limited. This would explain the ORff closer to -1.5 during the day. At night, energy production is a relatively more important source causing a decrease in ORff.

Figure 35: Average diurnal cycle of a) ffCO2 and ffo2 concentration, and b) ORff in Weybourne for October 2014.
5.4 CO₂ emission events

As found in Sections 5.1 to 5.3, when looking at a time series of CO₂ concentrations of October 2014, a number of moments with above average CO₂ concentrations can be distinguished. As these peaks are generally due to CO₂ emissions that follow from fossil fuel burning, they are often also accompanied by relatively low O₂ concentrations. From this information, not only average ORff values can be calculated (as previously done in this chapter), but also ORff values per specific event. This means that per event, based on the calculated ORff, suggestions can be done about the main fuel type responsible for and the origins of the high CO₂ concentrations.

5.4.1 CO₂ events at Zweth

The strongest CO₂ peaks simulated at Zweth are identified on the 3rd, 15th, and 30th of October. Information about the minimum and maximum fffCO₂ and fffO₂, along with the prevailing wind direction per event, are given in Table 9. The ORff that follows from this information is also included in this table. It is found that, for the main events at Zweth, the ORff is in the range between -1.49 and -1.56. This is within the range of the average ORff of -1.51 in Zweth. The values suggest the usage of a mix of fuel types, and thus no clear top contributor or source as to the CO₂ emission events can be derived from this without considering meteorological circumstances.

The ORff calculated for the 3rd of October, indicates relatively small contribution of power generation, and larger contribution of (industrial and non-industrial) production processes. Wind during this period generally originates from the south, confirming that the CO₂ simulated at Zweth on this day originates for the industrial area Botlek. The fffCO₂ peak simulated on the 15th has an ORff closer to -2. During this day, winds originate from the southwest, suggesting that the main contributor of the CO₂ concentration measured at Zweth is again Botlek. However, the contribution of a certain CO₂ plume coming from Botlek is more important during this event. This wind direction-ORff combination could thus be an indication of CO₂ originating from a power plant in the Botlek. The high CO₂ concentration on the 30th of October is marked by an ORff of -1.50, close to but slightly lower than the event on the 3rd. During the 30th, however, winds were freeing from north to south via the east. This means CO₂ concentrations on this day in Zweth originate mainly from outside Rijnmond. The only influential CO₂ source
from within Rijnmond is Rotterdam city. The wind direction during this event results in a mix of CO₂ sources and consequently a rather average value for OR₉ff.

**Table 9:** Minimum and maximum ffCO₂ and ffO₂, the corresponding OR₉ff, and prevailing wind direction per CO₂ event at Zweth.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>45</td>
<td>6</td>
<td>39</td>
<td>67</td>
<td>9</td>
<td>58</td>
<td>-1.49</td>
<td>south</td>
</tr>
<tr>
<td>15</td>
<td>31</td>
<td>6</td>
<td>25</td>
<td>47</td>
<td>8</td>
<td>39</td>
<td>-1.56</td>
<td>southwest</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>6</td>
<td>34</td>
<td>59</td>
<td>8</td>
<td>51</td>
<td>-1.50</td>
<td>freeing from north to south</td>
</tr>
</tbody>
</table>

5.4.2 CO₂ events at Lutjewad

For Lutjewad, the emission events of the 3rd, 7th, 15th, and 30th of October are chosen to be analysed. The minimum and maximum ffCO₂ and ffO₂, along with the OR₉ff and prevailing wind direction per event are given in Table 10. In general it is more difficult to assign certain sources to the ffCO₂ concentrations measured and simulated at Lutjewad. This is because the CO₂ signals found for this location are weaker due to the smaller amount of ffCO₂ emissions in the area. Furthermore, the site is located in a remote area, meaning that the ffCO₂ emissions that do find their way to Lutjewad are more diluted and mixed with ffCO₂ from other sources.

In Lutjewad, more variation in OR₉ff between the various emission events is found. The average OR₉ff at the location is -1.55. During the event of the 3rd, the OR₉ff is relatively close to -1. This suggests strong influences from (non-)industrial production processes (SNAP category 03/04) with origins in the south. During the 15th, the OR₉ff is closer to the average, with a value of -1.52. The same SNAP categories are however still relatively important, pulling the OR₉ff towards -1. This time however, the peak is stronger, and the wind direction suggests the source to be located more southeast of Lutjewad. The event on the 15th has a below average OR₉ff of -1.57. This suggests that power generation (SNAP category 01) is relatively more influential during this emission event. Winds during this event are coming from the southwest. Finally, the event on the 30th has a similar OR₉ff as the event on the 15th. This suggests similar source types between the two events. The wind at this time is variable, freeing from north to south within a few hours. This increases the difficulty of assigning a source to this emission event.
Table 10: Minimum and maximum ffCO$_2$ and ffO$_2$, the corresponding OR$_{ff}$, and prevailing wind direction per CO$_2$ event at Lutjewad.

<table>
<thead>
<tr>
<th>Peak date (day in October)</th>
<th>max ffCO$_2$ [ppm]</th>
<th>min ffCO$_2$ [ppm]</th>
<th>∆ffCO$_2$ [ppm]</th>
<th>max ffO$_2$ [ppm]</th>
<th>min ffO$_2$ [ppm]</th>
<th>∆ffO$_2$ [ppm]</th>
<th>OR$_{ff}$</th>
<th>wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>4.3</td>
<td>1.1</td>
<td>3.3</td>
<td>6.7</td>
<td>1.8</td>
<td>4.9</td>
<td>-1.48</td>
<td>south</td>
</tr>
<tr>
<td>7</td>
<td>10.3</td>
<td>1.0</td>
<td>9.3</td>
<td>15.7</td>
<td>1.6</td>
<td>14.1</td>
<td>-1.52</td>
<td>southeast</td>
</tr>
<tr>
<td>15</td>
<td>9.8</td>
<td>0.5</td>
<td>9.3</td>
<td>15.2</td>
<td>0.6</td>
<td>14.6</td>
<td>-1.57</td>
<td>southwest</td>
</tr>
<tr>
<td>30</td>
<td>30.4</td>
<td>0.1</td>
<td>30.3</td>
<td>47.8</td>
<td>0.2</td>
<td>47.6</td>
<td>-1.57</td>
<td>freeing from north to south</td>
</tr>
</tbody>
</table>

5.4.3 CO$_2$ events at Weybourne

The events of the 7th, 15th, 28th, and 30th are investigated for Weybourne. Details per event are shown in Table 11. Just as is the case for Lutjewad, identification of the sources responsible for the emission events at Weybourne are more difficult than at Zweth due to its remote location. Furthermore, the concentrations during the events have a smaller magnitude than those analysed for Zweth, again due to the more remote location. The values for OR$_{ff}$ calculated for the events at Weybourne are an indication of a fuel mix, where SNAP categories 02, 03/04, and 07 are important source types. These are substantial emission categories in this region, cumulatively responsible for almost 68% of all CO$_2$ emissions in Weybourne during the simulation period. Values of OR$_{ff}$ below -1.53 are not found, giving a weaker indication to the importance of SNAP category 01 during the events.

Table 11: Minimum and maximum ffCO$_2$ and ffO$_2$, the corresponding OR$_{ff}$, and the prevailing wind direction per CO$_2$ event at Weybourne.

<table>
<thead>
<tr>
<th>Peak date (day in October)</th>
<th>max ffCO$_2$ [ppm]</th>
<th>min ffCO$_2$ [ppm]</th>
<th>∆ffCO$_2$ [ppm]</th>
<th>max ffO$_2$ [ppm]</th>
<th>min ffO$_2$ [ppm]</th>
<th>∆ffO$_2$ [ppm]</th>
<th>OR$_{ff}$</th>
<th>wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>9.2</td>
<td>1.5</td>
<td>7.7</td>
<td>14</td>
<td>2.3</td>
<td>11.7</td>
<td>-1.52</td>
<td>southwest</td>
</tr>
<tr>
<td>15</td>
<td>3.4</td>
<td>0.5</td>
<td>2.9</td>
<td>5.1</td>
<td>0.8</td>
<td>4.3</td>
<td>-1.48</td>
<td>southwest</td>
</tr>
<tr>
<td>28</td>
<td>5.3</td>
<td>0.0</td>
<td>5.3</td>
<td>8.1</td>
<td>0.0</td>
<td>8.1</td>
<td>-1.53</td>
<td>south southwest</td>
</tr>
<tr>
<td>30</td>
<td>7.3</td>
<td>0.2</td>
<td>7.1</td>
<td>11.0</td>
<td>0.5</td>
<td>10.5</td>
<td>-1.48</td>
<td>south southeast</td>
</tr>
</tbody>
</table>

The values for OR$_{ff}$ per event do not vary much between the different dates. This could be due to mixing and dilution of the concentrations before the site is reached. However the 12x12 km grid size on which the values are simulated are also likely to contribute to this lack in variation. This averages out local affects that emission sources might have on the OR$_{ff}$. The wind directions are similar in all cases, with winds direction generally varying between 180
and 250° during the events on the 7th, 15th, and 28th of October. The last event stands out, with winds originating from the south southeast, where the city of Norwich is located. This is expected to decrease the OR$_{ff}$ due to the relatively large amount of road traffic (SNAP categories 07). This is however not shown through the calculated OR$_{ff}$, which could again be due to mixing of concentrations. It should however also be mentioned that the OR$_{ff}$ calculated for the events are less accurate due to the lower peaks and lows in CO$_2$ and O$_2$ respectively, leading to a larger relative error in the identification in the minimum and maximum concentrations.
6 Source specific OR\textsubscript{in}

Of some CO\textsubscript{2} point sources in Rijnmond, the exact fuel type that is used is known. This information is used to calculate a more accurate OR\textsubscript{in} value which can be assigned to the grid cells containing these point sources. The results of this method are shown in Figure 36 and further discussed in Section 6.1. In Section 6.2, the CO\textsubscript{2} emission events at Zweth discussed in Section 5.4 are again analysed and compared to earlier results.

Figure 36: Map of source specific OR\textsubscript{in} values as model input over Rijnmond.

6.1 O\textsubscript{2} fluctuations and OR\textsubscript{ff}

The CO\textsubscript{2} point sources in Rijnmond consist of coal, oil, and gas burning industries. The amount of coal and oil usage in Rijnmond are however larger than they are on average over the Netherlands. This results in values for OR\textsubscript{in} closer to -1 in the study area using this method. This is especially the case around the industrial area, as can be seen in Figure 36. On the borders of the domain, OR\textsubscript{in} values are generally closer to -2, however, large areas within the domain do not have a distinct fuel type assigned to them and are thus assigned the average SNAP category values of around -1.5 (shown in Table 1). The OR\textsubscript{in} closer to -1 around the industrial area in Rijnmond results in smaller fluctuations in f\textsubscript{fO\textsubscript{2}} concentration, and lower values for average OR\textsubscript{ff} over the entire domain, as can be seen in Figure 37a and b, respectively. OR\textsubscript{ff} values in Rijnmond fluctuate spatially between -1.37 and -1.51 on average, compared to OR\textsubscript{ff} varying spatially between -1.49 and -1.56 in the analysis in Chapter 5. This is due to the increased
importance of coal (and oil) as fuel sources in Rijnmond in this method. ORff values are lowest around the industrial area in both cases. The values are however pulled more towards -1 compared to the surrounding areas when fuel types of point sources are specifically identified: The areas closer to the harbour and industry undergo a change in ORff of 0.12, whereas the area south of the industries undergo a change in ORff of 0.04.

![Figure 37: Map of a) average ffO2 and b) average ORff in Rijnmond for October 2014, calculated using the source specific ORin.](image)

The average diurnal ffCO2 is not influenced by the introduction of the source specific ORin, and is thus the same as the discussed in Chapter 5. The ffO2 at Zweth that follows from this does however deviate slightly through the introduction of the source specific ORin. On average, ffO2 concentrations are slightly higher, with an average of -8.7 ppm compared to -9.6 ppm, and an average diurnal variation of 4.4 ppm compared to 4.9 ppm when using the source specific ORin compared to the average ORin per SNAP category. The shape of the diurnal cycle in ffO2 is not affected when switching between the two methods.

The average diurnal ORff shows some notable deviations from the diurnal cycle shown in Chapter 5. When the source specific ORin is used to simulate O2 concentrations, the average diurnal ORff is closer to -1, more variable, and shows peaks and lows at different times of the day. The average ORff in Zweth is -1.452, with a variation of 0.033 (compared to the average of -1.524 with a variation of 0.022 using the SNAP average ORin). Using the current method, ORff in Zweth is lowest around 8:00 and 17:00 LT, and in the (late) evening. The ORff is around -1.47 during commuting times, and increases around noon and in the late night. The increased ORff at these times could be due to the relative importance of the point sources burning coal and oil. Many of the point sources included in this method are power generation plants and oil refineries.
SNAP category 01) which actually decreased the OR\textsubscript{ff} calculated in Chapter 5. These changes in OR\textsubscript{in} are the main contributor to the differences in average diurnal OR\textsubscript{ff} between the two methods. The simulated oxygen in Rijnmond cannot yet be validated due to the current lack of observations in this area. However, the method described in this Chapter is more in agreement with earlier research done by Steinbach et al. (2011). In this research, a similar diurnal cycle in OR\textsubscript{ff} is found, with variations of 0.04.

![Figure 38: Average diurnal cycle of a) f\textsubscript{CO2} and f\textsubscript{O2} concentration, and b) OR\textsubscript{ff} in Zweth for October 2014 simulated using source specific OR\textsubscript{in}.

Whether the simulated f\textsubscript{O2} concentrations and the values for OR\textsubscript{ff} that follow from the method using the source specific OR\textsubscript{in} values are more accurate than those calculated using the method using the SNAP average OR\textsubscript{in} cannot be validated, since measurements of atmospheric O\textsubscript{2} concentrations are not yet being conducted at Zweth at this moment. It is expected that the source specific OR\textsubscript{in} values are closer to reality and will therefore yield more accurate results. However, the actual amount of emission sources for which a specific fuel type is known is still limited. This method could therefore only be applied to Rijnmond at this moment. Furthermore, it is found in Chapter 4 that the largest discrepancy in the simulation of atmospheric O\textsubscript{2} concentrations is also found in the simulated CO\textsubscript{2} concentration. The modelled O\textsubscript{2} concentrations depends on the (negative) O\textsubscript{2} emissions, which are linked to CO\textsubscript{2} emissions. From this it follows that the errors are due to the simulation of the wind direction, rather than the values for OR\textsubscript{in} that are used. Some recommendations on how the modelling of O\textsubscript{2} can be further improved will be discussed in Chapter 7.
6.2 CO\textsubscript{2} emission events

The emission events in Zweth described in Section 5.4 are again analysed, this time simulated using the source specific OR\textsubscript{fm}. Information about the minimum and maximum fffCO\textsubscript{2} and fffO\textsubscript{2}, along with OR\textsubscript{ff} per event are given in Table 12. The values for OR\textsubscript{ff} found are closer to -1 than those found in Section 5.4, again indicating the relative importance of coal and oil as a fuel source in Rijnmond. The OR\textsubscript{ff} found for the events vary around the average of -1.45, ranging between -1.50 and -1.32. The deviation from the average is the largest for the event on the 15\textsuperscript{th}.

Table 12: Minimum and maximum fffCO\textsubscript{2} and fffO\textsubscript{2}, corresponding ΔfffCO\textsubscript{2} and ΔfffO\textsubscript{2}, and the corresponding OR\textsubscript{ff} per CO\textsubscript{2} emission event at Zweth, simulated using the source specific OR\textsubscript{fm}.

<table>
<thead>
<tr>
<th>Peak date (day in October)</th>
<th>max fffCO\textsubscript{2} [ppm]</th>
<th>min fffCO\textsubscript{2} [ppm]</th>
<th>ΔfffCO\textsubscript{2} [ppm]</th>
<th>max fffO\textsubscript{2} [ppm]</th>
<th>min fffO\textsubscript{2} [ppm]</th>
<th>ΔfffO\textsubscript{2} [ppm]</th>
<th>OR\textsubscript{ff}</th>
<th>wind direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>45</td>
<td>39</td>
<td>6</td>
<td>64</td>
<td>8</td>
<td>56</td>
<td>-1.43</td>
<td>south</td>
</tr>
<tr>
<td>15</td>
<td>31</td>
<td>25</td>
<td>6</td>
<td>40</td>
<td>7</td>
<td>33</td>
<td>-1.32</td>
<td>southwest</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>34</td>
<td>6</td>
<td>57</td>
<td>6</td>
<td>51</td>
<td>-1.50</td>
<td>freeing from north to south</td>
</tr>
</tbody>
</table>

On October 3\textsuperscript{rd}, a fffCO\textsubscript{2} peak is simulated with a OR\textsubscript{ff} of -1.43. During this time, winds originate from the south. This means air is coming from the industrial area Botlek and the city of Rotterdam. The OR\textsubscript{ff} suggests relatively strong influences of coal and oil burning. During this event, Zweth is not directly affected by the major point sources in Rijnmond as indicated in Figure 25a. The fffO\textsubscript{2}:fffCO\textsubscript{2} signal is thus expected to be a result of the mixing of various emission sources with their origin mainly in Botlek. The method described in Section 5.4 resulted in an OR\textsubscript{ff} of -1.49 during this event. This shows the influence of the higher OR\textsubscript{fm} as a result of the relatively large amount of coal and oil use in Botlek.

The event on the 15\textsuperscript{th} of October occurs during southwesterly winds. During this time, Zweth is downwind of two of the strong point sources in Rijnmond. These point sources are easily distinguished in the map showing the average fffCO\textsubscript{2} emissions over Rijnmond in Figure 25a. The point sources are a power generation plant (SNAP category 01), and a manufacturing/production process factory (SNAP category 03/04). These two point sources use coal and oil as a power source, respectively. This is indeed reflected in the relatively low OR\textsubscript{ff}, suggesting a mix of mainly coal and oil during the event. Furthermore, the OR\textsubscript{ff} of -1.56 as calculated in Section 5.4 can be assigned to the importance of power generation plant using coal. In this
method the OR\textsubscript{in} as modelled for this plant is set to -1.762 (1).

The wind directions during the emission event on the 30\textsuperscript{th} already suggest that the ffCO\textsubscript{2} concentrations during this event do not originate from within Rijnmond to the same extent as they do during the other emission events. This is also reflected in the OR\textsubscript{ff}, which is 0.05 below the average of -1.45. This means that gas and oil usage are more important during this emission event. The wind originates largely from outside the domain, where the OR\textsubscript{in} is again more influenced by the average OR\textsubscript{in} per SNAP category for the Netherlands. The only main source within the range upwind of Zweth during this emission event is Rotterdam city, from which emissions are expected to find their origin mainly in oil and gas, resulting in a relatively low OR\textsubscript{ff} after transport at Zweth. As a result of the wind originating from outside of the industrial area, the OR\textsubscript{ff} as modelled here and in Section 5.4 shows no difference.
7 Discussion

Oxygen was introduced into the regional model WRF-chem in order to study the importance of the various fossil fuel types (i.e. coal, oil, and gas) and improve fossil fuel carbon dioxide estimates in urban areas. Until now, O\textsubscript{2} had not been included in WRF-chem or similar, regional models. This means that this ‘new’ compound had to be introduced from scratch. Therefore, along with the time restraints of this research, there is still a considerable amount of research that can be done to improve the model results. Likewise, an extension of the analysis on the current results is recommended to fully reach the objectives posed in this research. In the following sections, some important modelling methods and results are discussed in order to give insight in potential points of improvement in the currently used methods. Based on this, recommendations are done in order to improve on modelling of O\textsubscript{2} and answer the posed research questions with more certainty.

7.1 Model uncertainties and recommendations

O\textsubscript{2} is modelled based on uptake through fossil fuel burning, exchange with the land biosphere, and exchange with the ocean. Considering the general aim of this research, O\textsubscript{2} fluctuations due to fossil fuel burning are most important. However, in order to complete the modelling and compare the model outcome to measurements, land biosphere and ocean exchange are also implemented.

7.1.1 Ocean exchange

O\textsubscript{2} exchange from the ocean is introduced in the model based on the Atmospheric Potential Oxygen (APO) inversion modelling as done by Rödenbeck et al. (2008). This is however a global model with a coarse resolution as compared to the WRF-chem regional model resolutions. There is thus some uncertainty in the precision of the ocean O\textsubscript{2} exchange as implemented on this regional scale. The ocean exchange is found to have a relatively small influence on the O\textsubscript{2} concentration on the time scales as studied in this research, especially in urban areas. The potential for improvement of the overall O\textsubscript{2} fluctuation modelling is thus relatively small here.
7.1.2 Biosphere exchange

The fossil fuel and land biosphere exchange is based on the exchange of CO$_2$ from these components, and the Oxidative Ratio (OR) coupled to the process. The OR used as model input (OR$_{in}$) for the land biosphere is set to -1.1. This value is debated in literature, and is found to vary within different vegetation and soil types (Worrall et al. 2013; Masiello et al. 2008; Hockaday et al. 2009). According to this literature, the OR$_{in}$ for the land biosphere can range from -0.96 to -1.22, which could considerably alter the modelled O$_2$ fluctuations resulting from this biosphere exchange, especially in more rural areas where the biosphere tends to dominate as an O$_2$ source or sink.

7.1.3 Fossil fuel burning

The OR$_{in}$ used for fossil fuel burning may be a larger factor in model uncertainty, especially in urban areas. At first instance, OR$_{in}$ is based on the average OR per SNAP category in the Netherlands (see Section 2.3.2 and Table 1). This is done because of the implementation of CO$_2$ emissions according to the same SNAP categories in the model setup. The averaging of the fuel mix within the categories results in a small amount of spatial variation in OR$_{in}$ over the domains, and make the modelling of O$_2$ in theory strictly applicable to the Netherlands only. This is shown in the OR according to the COFFEE dataset in Figure 34d as developed by Steinbach et al. (2011). Steinbach et al. (2011) find more variation in OR$_{in}$, however, due to the coarse spatial resolution of COFFEE, the dataset is not useful for modelling in urban areas. The OR as presented by Steinbach et al. (2011) could however be useful as model input for the outer domains. The use of source specific information (i.e. what fuel types are used in a certain process at a specific location) is expected to be more reliable model input for OR$_{in}$. An attempt to implement this is shown in Chapter 6. This method requires very detailed and high resolution information. This makes it challenging to apply, especially on a large scale.

7.1.4 Uncertainties in advection

As mentioned, the modelling of fossil fuel and land biosphere exchange of O$_2$ is based on CO$_2$ and OR$_{in}$. In the comparison of the model results to observations, it is found that the majority of the errors in modelled O$_2$ fluctuations are also found in the modelled CO$_2$ con-
centrations. Therefore, improvement in the modelling of compound concentrations in general yield the largest potential for improvement in the modelled $O_2$ concentrations as well. Statistical measures found in this study for the modelling of $CO_2$ concentrations are similar to those found by Super et al. (2017). They found that these discrepancies are largely due to faults in the simulation of the wind direction in the model. This is further elaborated on in Chapter 3 of this research. The wind field - and therefore compound concentrations - simulation in the urban areas may be improved on by the introduction of a plume model, as done by Super et al. (2017).

### 7.1.5 Initial conditions, boundary conditions, and entrainment

The initial and boundary conditions as currently modelled only include ocean $O_2$ exchange (as following from Rödenbeck et al. (2008), see Section 2.3.3). $O_2$ exchange though fossil fuel burning and land biosphere processes are thus not included. $O_2$ fluctuations at the edge of the outer domain may be simulated more accurately, either by integrating atmospheric $O_2/N_2$ data from Rödenbeck et al. (2008), or by converting $CO_2$ fluctuations into $O_2$ fluctuations using a world average value for OR. These are however fluctuations that in the end would not directly contribute to the objective of identifying fossil fuel emission sources in certain urban areas.

The amount of entrainment involved in the $O_2$ modelling depends on the difference in $O_2$ concentration between the air within the boundary layer and the air in the free troposphere. Fitting of $O_2$ data from a forest in the Netherlands to an idealised model resulted in an $O_2$ jump of 19ppm (Bindels 2018). This is in the same range as the fluctuations from the background concentration found at the currently researched study areas. The $O_2$ concentration in the free troposphere in first instance depends on the initial and boundary conditions set in the model, which only include ocean exchange. The concentration difference between the air within the boundary layer and the free troposphere is therefore equal to the $O_2$ fluctuation modelled within the boundary layer at that time, minus fluctuations due to the ocean exchange at the top of the boundary layer.

Research done on the effect of $O_2$ exchange from the three sources and sinks on the $O_2$ concentration at various heights and in the free troposphere is limited. Popa (2008) found that the amplitude of the diurnal cycle in $O_2$ concentration diminished with height, and even becomes
indistinguishable during wintertime. This is based on measurements done over a rural area in Poland, which reached a maximum height of 300 m. Evidence of a diurnal cycle in the free troposphere is thus not found based on this. A seasonal variation in O\textsubscript{2} concentration was more clearly found in the study by Popa (2008). The amplitude again decreases with height. The oceanic contribution of this variation, however, increases with height. This result agrees with research by Van Der Laan et al. (2014), who found a decreased seasonal O\textsubscript{2} cycle at 3000 m height compared to the cycle at 100 m height, with increased importance of the oceanic component with height. At 300 m height, Popa (2008) found the ocean to be responsible for 32 \% of the of the seasonal variation, whereas at 3000 m height, Van Der Laan et al. (2014) found the ocean to be responsible for 30 \% of the seasonal variation. Based on this, the boundary conditions as in WRF-chem are assumed to cover about 30-32 \% of the seasonal variation in O\textsubscript{2} in the free troposphere. The seasonal variation due to other sources and sinks are thus not yet implemented in the model. Even though the lack of sophistication in the modelled initial and boundary conditions - and therefore entrained concentrations - is not expected to have a large influence on the (diurnal) time scale modelled and analysed in this study, it is part of the model that may be improved for future use.

7.2 Recommendations for future analysis

Apart from the potential points of improvement in the modelling of O\textsubscript{2} fluctuations discussed above, there is analysis still to be done on the results that follow from the model as it is. First of, study area Rijnmond was chosen to contribute to the RINGO project (ICOS n.d.) and improve fossil fuel CO\textsubscript{2} estimates. O\textsubscript{2} measurements are planned to start at Zweth (located in Rijnmond) related this project. These measurements are currently not yet being conducted, however, the data that follows from this will be useful to validate the model. Observations at Zweth will not only give insight in the O\textsubscript{2} modelling in the finest horizontal resolution (1x1 km), but will also give insight in the modelling of O\textsubscript{2} in an urban area as opposed to the more rural (coastal) locations which are currently used to validate the model. Furthermore, the O\textsubscript{2} fluctuations that follow from the method using the average OR\textsubscript{m} per SNAP category (Chapters 4 and 5) and the method using the source specific OR\textsubscript{m} (Chapter 6) can be compared to measurement values.
O₂ fluctuations as analysed and discussed in this study are limited to surface concentrations only. Super et al. (2017) modelled CO₂ emissions at the surface, as well as stack emissions. Due to variability of the importance of various emission sources with height, the O₂ concentration is also expected to have a vertical gradient subject to these emissions. The O₂ gradients that follow from this are however not shown in the results or further analysed. It was decided not to do this based on the time limit of this research, the fact that there are no O₂ measurements at various heights within the finer domains, and the uncertainties in the entrainment discussed in Section 8.1.5. The latter has an increased influence on modelled concentrations with height.
8 Conclusion

Oxygen is implemented in the regional model WRF-chem, in order to use as a tracer for fossil fuel CO₂ emission sources. Fluctuations in atmospheric O₂ concentration are modelled based on O₂ exchange with the ocean, the land biosphere, and fossil fuel burning. The partitioning of O₂ from these three components shows that fossil fuel burning and exchange with the biosphere are the dominant O₂ sinks during autumn and wintertime (in this case October). The ocean is relatively neglectable in the total O₂ fluctuations on a diurnal time scale as modelled here.

The total O₂ fluctuations are validated using measurements conducted at coastal stations Weybourne in North Norfolk (UK) and Lutjewad in the north of Groningen (NL). The modelled fluctuations at Weybourne follow the trend of the observations well, resulting in a statistical index of agreement of 0.75. The index of agreement at Lutjewad is slightly lower, with a value of 0.71. For Lutjewad, the modelled fluctuations deviate from the observations at times. The cause of this is however uncertain, due to unreliability in the O₂ measurements conducted at this station. Overall, errors in the modelled O₂ fluctuations are also found in the modelled CO₂ concentration to which the O₂ fluctuations are linked. It is found that errors in modelled compound concentrations can be largely attributed to misrepresentation of the wind direction.

Fluctuations in O₂ concentration due to fossil fuel burning (ffO₂) are further analysed for the study areas North Norfolk, the north of Groningen, and Rijnmond. The OR that follows from the ffO₂ and ffCO₂ yields information about the source of the ffCO₂, which varies spatially as well as temporally. ffO₂ uptake is mainly found in areas with large amounts of ffCO₂ emittance. Through the analysis of the corresponding fossil fuel oxidative ratio (ORff), distinct ffCO₂ sources can be distinguished within these areas. Moreover, the diurnal cycle in ORff shows the relative importance of emission sources during the day. The ORff can also yield information about dominant emission sources during specific moments with high CO₂ concentrations (i.e. emission events).

The distinction of actual fuel types (i.e. coal, oil, and gas) are only recognised if the ORin is modelled using source specific information. However, this method requires high resolution information, making the actual implementation challenging on larger scales. Values for source specific ORin are implemented for point sources in Rijnmond. Though this method cannot yet
be validated, it is expected to produce more accurate fO2 concentrations with more spatial and temporal variation.

Overall, the modelling of O2 proofs to contribute to the fossil fuel CO2 estimate. There is still room for improvement in the modelling of O2, though the largest potential for improvement is found in the representation of meteorological circumstances and wind direction, affecting all compound concentrations. There is also analysis still to be done on the current model outcomes, mainly in validating the model results in urban areas. O2 observations at measurement site Zweth (Rijnmond) in the near future will allow for this.
9 Research outlook

This study on modelling oxygen can serve as a contribution to the Readiness of Integrated Carbon Observation (ICOS) for the Necessities of Integrated Global Observations (RINGO) project. The aim of RINGO is to develop ICOS readiness to provide information on fossil fuel emissions. Amongst others, this is attempted through emission estimates for anthropogenic CO$_2$ and co-emitted tracers, such as CO and NO$_2$, and independent $^{14}$CO$_2$-based fossil fuel CO$_2$ emission estimates. Therefore, $^{14}$CO$_2$ and other tracers are sampled in test regions Rijnmond, the Rhine Valley, and Paris (Hammer and Levin 2017). In addition, O$_2$ can be used as a consumed tracer to increase the temporal resolution of the fossil fuel CO$_2$ estimates. Solid understanding of tracer-to-fossil fuel CO$_2$ ratios are key to derive reliable fossil fuel CO$_2$ estimates. The addition of information from emission models such as presented in this study can contribute to the project and provide a framework to interpret the measurements that are to be conducted in the study areas.
References


Bindels, Michelle (2018). To entrain or not to entrain - Modelling forest carbon and oxygen exchange in CLASS.

Bozhanova, D. et al. (2014). “Simulating the integrated summertime δ14CO2 signature from anthropogenic emissions over Western Europe”. In: Atmospheric Chemistry and Physics 14.14, pp. 7273–7290. ISSN: 16807324. DOI: 10.5194/acp-14-7273-2014

Bullock, O. Russell et al. (2014). “An observation-based investigation of nudging in WRF for downscaling surface climate information to 12-km grid spacing”. In: Journal of Applied Meteorology and Climatology 53.1, pp. 20–33. ISSN: 15588424. DOI: 10.1175/JAMC-D-13-030.1

Carvalho, David et al. (2012). “A sensitivity study of the WRF model in wind simulation for an area of high wind energy”. In: Environmental Modelling and Software 33, pp. 23–34. ISSN: 13648152. DOI: 10.1016/j.envsoft.2012.01.019 URL: http://dx.doi.org/10.1016/j.envsoft.2012.01.019


Cook, J. et al. (2013). “Quantifying the consensus on anthropogenic global warming in the scientific literature”. In: Environmental Research Letters 8.

Daniels, Emma et al. (2016). Relative impacts of land use and climate change on summer precipitation in the Netherlands. DOI: 10.5194/hess-20-4129-2016


Huszar, P., M. Belda, and T. Halenka (2016). “On the long-term impact of emissions from central European cities on regional air quality”. In: *Atmospheric Chemistry and Physics* 16.3, pp. 1331–1352. ISSN: 16807324. DOI: [10.5194/acp-16-1331-2016](https://doi.org/10.5194/acp-16-1331-2016)

ICOS. *READINESS OF ICOS FOR NECESSITIES OF INTEGRATED GLOBAL OBSERVATIONS*. URL: [https://www.icos-ri.eu/ringo](https://www.icos-ri.eu/ringo)


Jimenez, Pedro A. and Jimy Dudhia (2013). “On the ability of the WRF model to reproduce the surface wind direction over complex terrain”. In: *Journal of Applied Meteorology and Climatology* 52.7, pp. 1610–1617. ISSN: 15588424. DOI: [10.1175/JAMC-D-12-0266.1](https://doi.org/10.1175/JAMC-D-12-0266.1)


---

83


Laan, S. van der et al. (2014). “Atmospheric CO2, δ(O2/N2), APO and oxidative ratios from aircraft flask samples over Fyodorovskoye, Western Russia”. In: *Atmospheric Environment* 97, pp. 174–181. ISSN: 18732844. DOI:10.1016/j.atmosenv.2014.08.022


Li, Xiangshang et al. (2016). “The impact of observation nudging on simulated meteorology and ozone concentrations during DISCOVER-AQ 2013 Texas campaign”. In: *Atmospheric Chemistry and Physics* 16.5, pp. 3127–3144. ISSN: 16807324. DOI:10.5194/acp-16-3127-2016


Lopez, M. et al. (2013). “CO, NOx<sup>13</sup>CO<inf>2</inf> as tracers for fossil fuel CO<inf>2</inf>: Results from a pilot study in Paris during winter 2010”. In: *Atmospheric Chemistry and Physics* 13.15. ISSN: 16807316 16807324. DOI:10.5194/acp-13-7343-2013


Mlawer, Eli J. et al. (1997). “Radiative transfer for inhomogeneous atmospheres: RRTM, a validated correlated-k model for the longwave”. In: *Journal of Geophysical Research: At-
*Department of Commerce: NCEP FNL Operational Model Global Tropospheric Analyses, continuing from July 1999, updated daily.* In, *Research Data Archive at the National Center for Atmospheric Research, Computational and Information Systems Laboratory.*


ONS (2016). *Local Authority District population 2016.* URL: https://www.ons.gov.uk/peoplepopulationandcommunity/populationandmigration/populationestimates


Pickers, Penelope (2016). “New applications of continuous atmospheric O2 measurements: meridional transects across the Atlantic Ocean, and improved quantification of fossil fuel-derived CO2”. In: *School of Environmental Sciences.*


UCAR (2014). NCEP ADP Global Surface Observational Weather Data. URL: https://rda.ucar.edu/datasets/ds461.0/index.html


Van Der Laan-Luijkx, I. T. et al. (2010). “CO2, δO2/N2 and APO: Observations from the Lutjewad, Mace Head and F3 platform flask sampling network”. In: Atmospheric Chemistry and Physics 10.21, pp. 10691–10704. ISSN: 16807316. DOI:10.5194/acp-10-10691-2010

Van Der Laan-Luijkx, I.T. (2010). “Atmospheric oxygen and the global carbon cycle. Observations from the new F3 North Sea platform monitoring station and 6 additional locations in Europe and Siberia Groningen: s.n.” In:


Vickers, Dean, Larry Mahrt, and Edgar L. Andreas (2015). “Formulation of the sea surface friction velocity in terms of the mean wind and bulk stability”. In: Journal of Applied Meteorology and Climatology 54.3, pp. 691–703. ISSN: 15588432. DOI:10.1175/JAMC-D-14-0099.1


Wilson, Philip (2012). “Insight into the Carbon Cycle from Continuous Measurements of Oxygen and Carbon Dioxide at Weybourne Atmospheric Observatory, UK”. In: October.


Appendix I

Table A1: Overview of the model parameterisation settings.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid resolution</td>
<td>48 x 48, 12x12, 4x4, 1x1 km</td>
</tr>
<tr>
<td>Boundary-Layer scheme</td>
<td>1: YSU scheme</td>
</tr>
<tr>
<td>Surface Layer scheme</td>
<td>1: MM5 Monin-Obukov scheme</td>
</tr>
<tr>
<td>Land surface scheme</td>
<td>2: Unified Noah land surface model</td>
</tr>
<tr>
<td>Cumulus scheme</td>
<td>3: Grell-Feitas ensemble scheme</td>
</tr>
<tr>
<td>Microphysics</td>
<td>4: WSM 5-class scheme</td>
</tr>
<tr>
<td>Shortwave radiation</td>
<td>1: Dudhia scheme</td>
</tr>
<tr>
<td>Longwave radiation</td>
<td>1: RRTM scheme</td>
</tr>
<tr>
<td>Chemical option</td>
<td>15: Ensemble tracer option using individual tracers and an ensemble tracer array</td>
</tr>
<tr>
<td>Emission option</td>
<td>15: Emissions analogue to chemical option 15</td>
</tr>
</tbody>
</table>

Table A2: Statistical analysis of wind speed for WRF version 3.2.1 at Rotterdam. The inclusion of all values are compared to daytime average values only as calculated by Super et al. (2017). Terms N, b, d, and R2 are dimensionless, the remaining terms have unit m/s.

<table>
<thead>
<tr>
<th>Wind speed</th>
<th>$\bar{\omega}$</th>
<th>$\omega$</th>
<th>sd,$\bar{\omega}$</th>
<th>sd,$\omega$</th>
<th>N</th>
<th>a</th>
<th>b</th>
<th>MAE</th>
<th>RMSE</th>
<th>RMSE$_s$</th>
<th>d</th>
<th>R2</th>
</tr>
</thead>
<tbody>
<tr>
<td>All values</td>
<td>4.7</td>
<td>4.5</td>
<td>2.2</td>
<td>2.0</td>
<td>697</td>
<td>0.84</td>
<td>0.85</td>
<td>0.63</td>
<td>1.5</td>
<td>0.18</td>
<td>1.5</td>
<td>0.87</td>
</tr>
<tr>
<td>Daytime averages by</td>
<td>0.8</td>
<td>0.7</td>
<td>0.72</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Super et al. (2017)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure A1: Differences between the modelled and observed wind direction against wind speed for WRF version 3.2.1 at Rotterdam airport. It can be seen that most of the largest discrepancies are simulated along with relatively low wind speeds.
Table A3: Most important quantitative measures of wind direction model performance for the various model versions with and without updates, locations, horizontal resolutions, and nudging as described in Chapter 3. The default settings are WRF-chem version 3.2.1 at Rotterdam with a horizontal resolution of 4x4 km, without nudging applied. Terms $d$ and $R^2$ are dimensionless, the remaining terms have unit $^\circ$.

<table>
<thead>
<tr>
<th>version/location/horizontal resolution/nudging applied</th>
<th>$\overline{O}$</th>
<th>$\overline{P}$</th>
<th>sd($O$)</th>
<th>sd($P$)</th>
<th>N</th>
<th>a</th>
<th>b</th>
<th>MAE</th>
<th>RMSE</th>
<th>RMSE$_a$</th>
<th>RMSE$_u$</th>
<th>d</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Model version comparison</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.1</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>697</td>
<td>92.3</td>
<td>0.471</td>
<td>32.2</td>
<td>66.3</td>
<td>7.14</td>
<td>65.9</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>3.9.1</td>
<td>190</td>
<td>206</td>
<td>62.3</td>
<td>55.7</td>
<td>721</td>
<td>57.2</td>
<td>0.642</td>
<td>25.2</td>
<td>57.3</td>
<td>7.06</td>
<td>56.9</td>
<td>0.762</td>
<td>0.329</td>
</tr>
<tr>
<td>3.9.1 – update</td>
<td>190</td>
<td>202</td>
<td>62.3</td>
<td>51.4</td>
<td>721</td>
<td>61.8</td>
<td>0.632</td>
<td>28.1</td>
<td>57.9</td>
<td>7.06</td>
<td>57.4</td>
<td>0.730</td>
<td>0.271</td>
</tr>
<tr>
<td>3.2.1 (u&gt;3 m/s)</td>
<td>197</td>
<td>212</td>
<td>50.6</td>
<td>46.2</td>
<td>526</td>
<td>68.2</td>
<td>0.607</td>
<td>23.0</td>
<td>48.4</td>
<td>8.60</td>
<td>47.5</td>
<td>0.752</td>
<td>0.307</td>
</tr>
<tr>
<td>3.9.1 (u&gt;3 m/s)</td>
<td>202</td>
<td>212</td>
<td>50.6</td>
<td>48.4</td>
<td>562</td>
<td>51.0</td>
<td>0.709</td>
<td>17.0</td>
<td>41.2</td>
<td>8.50</td>
<td>40.3</td>
<td>0.827</td>
<td>0.459</td>
</tr>
<tr>
<td>3.9.1 – update (u&gt;3 m/s)</td>
<td>205</td>
<td>215</td>
<td>54.2</td>
<td>46.4</td>
<td>416</td>
<td>43.4</td>
<td>0.748</td>
<td>19.9</td>
<td>44.6</td>
<td>10.0</td>
<td>43.4</td>
<td>0.804</td>
<td>0.411</td>
</tr>
<tr>
<td><strong>Location comparison</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rotterdam</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>697</td>
<td>92.3</td>
<td>0.471</td>
<td>32.2</td>
<td>66.3</td>
<td>7.14</td>
<td>65.9</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>Eindhoven</td>
<td>187</td>
<td>212</td>
<td>58.7</td>
<td>48.4</td>
<td>697</td>
<td>65.2</td>
<td>0.575</td>
<td>36.0</td>
<td>61.1</td>
<td>7.94</td>
<td>60.8</td>
<td>0.673</td>
<td>0.224</td>
</tr>
<tr>
<td>Lauwersoog</td>
<td>190</td>
<td>198</td>
<td>63.6</td>
<td>58.1</td>
<td>697</td>
<td>44.8</td>
<td>0.733</td>
<td>26.6</td>
<td>50.4</td>
<td>7.18</td>
<td>49.8</td>
<td>0.820</td>
<td>0.448</td>
</tr>
<tr>
<td>Rotterdam</td>
<td>197</td>
<td>212</td>
<td>50.6</td>
<td>46.2</td>
<td>526</td>
<td>68.2</td>
<td>0.607</td>
<td>23.0</td>
<td>48.4</td>
<td>8.60</td>
<td>47.5</td>
<td>0.752</td>
<td>0.307</td>
</tr>
<tr>
<td>(u&gt;3 m/s)</td>
<td>190</td>
<td>210</td>
<td>49.3</td>
<td>43.6</td>
<td>612</td>
<td>36.6</td>
<td>0.775</td>
<td>27.6</td>
<td>42.7</td>
<td>7.68</td>
<td>43.9</td>
<td>0.792</td>
<td>0.469</td>
</tr>
<tr>
<td>Eindhoven</td>
<td>190</td>
<td>197</td>
<td>62.3</td>
<td>56.5</td>
<td>681</td>
<td>41.7</td>
<td>0.752</td>
<td>25.5</td>
<td>48.1</td>
<td>7.29</td>
<td>47.5</td>
<td>0.827</td>
<td>0.467</td>
</tr>
<tr>
<td>Lauwersoog</td>
<td>190</td>
<td>197</td>
<td>62.3</td>
<td>56.5</td>
<td>681</td>
<td>41.7</td>
<td>0.752</td>
<td>25.5</td>
<td>48.1</td>
<td>7.29</td>
<td>47.5</td>
<td>0.827</td>
<td>0.467</td>
</tr>
<tr>
<td><strong>Horizontal resolution comparison</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4x4 km</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>697</td>
<td>92.3</td>
<td>0.471</td>
<td>32.2</td>
<td>66.3</td>
<td>7.14</td>
<td>65.9</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>1x1 km</td>
<td>189</td>
<td>204</td>
<td>57.2</td>
<td>57.2</td>
<td>697</td>
<td>92.3</td>
<td>0.471</td>
<td>32.2</td>
<td>66.3</td>
<td>7.14</td>
<td>65.9</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>4x4 km (u&gt;3 m/s)</td>
<td>197</td>
<td>212</td>
<td>50.6</td>
<td>46.2</td>
<td>526</td>
<td>68.2</td>
<td>0.607</td>
<td>23.0</td>
<td>48.4</td>
<td>8.60</td>
<td>47.5</td>
<td>0.752</td>
<td>0.307</td>
</tr>
<tr>
<td>1x1 km (u&gt;3 m/s)</td>
<td>197</td>
<td>212</td>
<td>24.5</td>
<td>46.5</td>
<td>548</td>
<td>166</td>
<td>0.200</td>
<td>28.2</td>
<td>43.6</td>
<td>8.92</td>
<td>42.7</td>
<td>0.560</td>
<td>0.145</td>
</tr>
<tr>
<td><strong>Nudging option comparison</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nudging</td>
<td>190</td>
<td>210</td>
<td>57.5</td>
<td>52.3</td>
<td>673</td>
<td>61.3</td>
<td>0.612</td>
<td>28.5</td>
<td>55.6</td>
<td>8.67</td>
<td>43.0</td>
<td>0.739</td>
<td>0.310</td>
</tr>
<tr>
<td>Nudging (u&gt;3 m/s)</td>
<td>198</td>
<td>214</td>
<td>51.4</td>
<td>46.2</td>
<td>576</td>
<td>68.1</td>
<td>0.604</td>
<td>26.1</td>
<td>49.8</td>
<td>37.3</td>
<td>31.5</td>
<td>0.739</td>
<td>0.295</td>
</tr>
</tbody>
</table>
Figure A2: Relation between the simulated and the observed wind direction for WRF model version 3.2.1 at Rotterdam (a) and Lauwersoog (b). Wind directions simulated at wind speeds below 3 m/s are shown in red and directions simulated at wind speeds above 3 m/s are shown in blue. An ideal regression line is shown in black.

Table A4: Most important quantitative measures of O₂, CO₂, and wind direction model performance for the Zweth (Rijnmond), Lutjewad (the north of Groningen), and Weybourne (North Norfolk). Terms d and R² are dimensionless, the remaining terms have unit ppm for O₂ and CO₂ and unit ° for wind direction.

<table>
<thead>
<tr>
<th></th>
<th>θ̄</th>
<th>θ</th>
<th>sd(θ)</th>
<th>sd(θ)</th>
<th>N</th>
<th>a</th>
<th>b</th>
<th>MAE</th>
<th>RMSE</th>
<th>RMSE_u</th>
<th>RMSE_v</th>
<th>d</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zweth, Rijnmond</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>418</td>
<td>410</td>
<td>15.2</td>
<td>11.4</td>
<td>697</td>
<td>2.32</td>
<td>0.841</td>
<td>5.921</td>
<td>13.5</td>
<td>2.61</td>
<td>12.9</td>
<td>0.697</td>
<td>0.283</td>
</tr>
<tr>
<td>CO₂</td>
<td>189</td>
<td>204</td>
<td>63.0</td>
<td>57.0</td>
<td>697</td>
<td>92.3</td>
<td>0.471</td>
<td>32.2</td>
<td>66.3</td>
<td>7.14</td>
<td>65.9</td>
<td>0.685</td>
<td>0.182</td>
</tr>
<tr>
<td>Wind direction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lutjewad, north of Groningen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>-16.4</td>
<td>-11.0</td>
<td>14.5</td>
<td>11.3</td>
<td>574</td>
<td>1.94</td>
<td>0.881</td>
<td>6.23</td>
<td>13.5</td>
<td>2.82</td>
<td>13.1</td>
<td>0.714</td>
<td>0.301</td>
</tr>
<tr>
<td>CO₂</td>
<td>412</td>
<td>407</td>
<td>12.2</td>
<td>9.42</td>
<td>697</td>
<td>1.63</td>
<td>0.891</td>
<td>5.33</td>
<td>11.5</td>
<td>2.53</td>
<td>10.9</td>
<td>0.712</td>
<td>0.303</td>
</tr>
<tr>
<td>Wind direction</td>
<td>190</td>
<td>198</td>
<td>63.6</td>
<td>58.1</td>
<td>697</td>
<td>44.8</td>
<td>0.733</td>
<td>26.6</td>
<td>50.4</td>
<td>7.18</td>
<td>49.8</td>
<td>0.820</td>
<td>0.448</td>
</tr>
<tr>
<td>Weybourne, North Norfolk</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>-11.3</td>
<td>-8.3</td>
<td>7.72</td>
<td>6.43</td>
<td>697</td>
<td>1.01</td>
<td>0.913</td>
<td>2.92</td>
<td>6.70</td>
<td>3.03</td>
<td>5.92</td>
<td>0.752</td>
<td>0.344</td>
</tr>
<tr>
<td>CO₂</td>
<td>404</td>
<td>405</td>
<td>6.83</td>
<td>6.01</td>
<td>697</td>
<td>0.834</td>
<td>0.943</td>
<td>2.23</td>
<td>5.63</td>
<td>2.12</td>
<td>4.18</td>
<td>0.778</td>
<td>0.381</td>
</tr>
<tr>
<td>Wind direction</td>
<td>214</td>
<td>219</td>
<td>58.2</td>
<td>60.3</td>
<td>697</td>
<td>61.8</td>
<td>0.632</td>
<td>28.1</td>
<td>77.8</td>
<td>7.06</td>
<td>74.4</td>
<td>0.471</td>
<td>0.019</td>
</tr>
</tbody>
</table>
Appendix II: WRF-chem \( \text{O}_2 \) manual

This manual contains information about the changes made to the files and scripts needed to run WRF-chem in order to implement oxygen. An overview of the model runs conducted in this research and the adapted files and scripts corresponding to those runs is given in Table A5.

Table A5: Overview of the files and scripts that were adapted and used in the model runs for method 1 and method 2.

<table>
<thead>
<tr>
<th>( \text{O}<em>2 ) - average ( \text{OR}</em>{\text{in}} )</th>
<th>( \text{O}<em>2 ) - source specific ( \text{OR}</em>{\text{in}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>registry.chem.O2</td>
<td>registry.chem.OR2</td>
</tr>
<tr>
<td>emissions_driver.O2.F</td>
<td>emissions_driver.OR2.F</td>
</tr>
<tr>
<td>wrf_ibcs_O2_1000ppm.py</td>
<td>wrf_ibcsO21000ppm_OR.py</td>
</tr>
<tr>
<td>ibc_O2.ipynb</td>
<td>ibc_O2.ipynb</td>
</tr>
<tr>
<td>apo97_v1.5_mix_2014.nc</td>
<td>apo97_v1.5_mix_2014.nc</td>
</tr>
<tr>
<td>Chemi_Rijnm.py</td>
<td>Chemi_Rijnm.OR.py</td>
</tr>
<tr>
<td>Rijnmond_EI.txt</td>
<td>Rijnmond_EI.OR.txt</td>
</tr>
<tr>
<td>MACC_chemi.py</td>
<td>MACC_chemi.OR.py</td>
</tr>
</tbody>
</table>

The runs conducted in this research are based on the WRF-chem model setup as created by Super et al. (2017), covering four domains that zoom in on Rijnmond, the Netherlands. \( \text{O}_2 \) is added to this setup, resulting in the use of two different methods. In the first method \( \text{O}_2 \) is calculated based on the average oxidative ratio (\( \text{OR}_{\text{in}} \)) per emission category and the \( \text{CO}_2 \) emissions from that emission category. In the second method, \( \text{O}_2 \) is calculated based on the \( \text{OR}_{\text{in}} \) of the actual fuel type used at the emission source and the corresponding \( \text{CO}_2 \) emissions from that source. More information about the two different methods is given in Section 2.3.

The differentiation between the two methods resulted in the following main model runs:

1. \( \text{O}_2 \) - average \( \text{OR}_{\text{in}} \)

2. \( \text{O}_2 \) - source specific \( \text{OR}_{\text{in}} \)

In both runs \( \text{O}_2 \) is added as separate tracers per emission category in registry.chem as follows:

\[
\text{state real e_tracer_xx i+jf emis_ant 1 - i5 "E_O2yyy" "NEG EMISSIONS O2_yyy" "mol km^{-2} hr^{-1}"}, \text{in which xx is the number of the tracer variable and yyy a number corresponding to a certain emission category. The added tracers are then added to: package etracer_ens emiss_opt==15.}
\]

Once the tracers are added to the registry.chem file, \( \text{O}_2 \) concentrations are calculated in the
emissions_driver.F file. In method 1, this is done as such: chem(i,k,j,p_tracer_xx) = chem(i,k,j,p_tracer_xx) + emis_ant(i,k,j,p_e_tracer_zz) * conv * OR_in * RME1(MNTH) * RWE1(DAYW) * RDE1(HR). In this, zz is the number of the CO_2 tracer corresponding to the same emission category as the O_2 tracer_xx. OR_in can be replaced by the value for the average OR_in corresponding to the emission category to which tracer_xx corresponds. The value for OR_in is negative, however, this would result in a negative value for tracer_xx as well. Negative concentrations cannot however not be modelled in WRF-chem. Therefore, the separate O_2 tracers are modelled as positive which are subtracted in the final calculation of the total O_2. The background concentration of the total O_2 is then set to a value of 1000 ppm. This is done in the wrf_ibcs.py script, which writes the initial and boundary conditions for the tracers in the wrfinput and wrfbdy files. Other tracers are set to 0 ppm, whereas O_2 is set to 1000 ppm. This value is later subtracted in analysis. In order to model ocean exchange, APO data by Rödenbeck et al. (2008) is added to the initial and boundary conditions. The data is imported from the apo97_v1.5_mix_2014.nc file, and is used in both model runs. In method 2, the values for OR_in are added as an extra tracer in the registry.chem file: state real e_tracer_OR i+jf emis_ant 1 - i5 "OR" "oxidative ratio" "O2/CO2 [-]". Again, this tracer is also added to package etracer_ens emiss_opt==15. In the emissions_driver.F file, concentrations per tracer are now calculated as: chem(i,k,j,p_tracer_xx) = chem(i,k,j,p_tracer_xx) + emis_ant(i,k,j,p_e_tracer_zz) * conv * (emis_ant(i,k,j,p_e_tracer_OR)) * RME1(MNTH) * RWE1(DAYW) * RDE1(HR). The actual values for OR_in are added to Rijnmond_EI.txt, and loaded to the wrf_chemi files for domain 4 using Chemi_Rijnm.py.