Summary
The effects of global warming are becoming more and more noticeable every year. To try and prevent global warming from rising to dangerous levels, most countries have agreed to reduce their greenhouse gas (GHG) emissions. These countries annually report their GHG emissions based on inventories of known sources, but this method potentially contains (systematic) errors which can be as large as the reduction targets or higher.

The aim of this thesis was to determine the net annual surface fluxes of CH₄, N₂O and fossil fuel-derived CO₂ for the Netherlands, using an observationally based approach, and thereby to validate the national inventories in a fully independent way.

All ambient observations were performed at the atmospheric measurement station Lutjewad (6° 21’ E, 53° 24’ N, 1 m a.s.l.) at the north coast of the Netherlands which, for this purpose, was updated extensively by the Centre for Isotope Research (CIO) of the University of Groningen (RUG). Most notably, a new Gas Chromatograph (GC, chapter 3) and a ²²²Radon detector (chapter 2) were installed at Lutjewad.

Before the instalment of the GC at Lutjewad in May 2006, initially for the purpose of measuring the ambient mixing ratios of CO₂, CH₄, N₂O and SF₆ (sulphur hexafluoride), the GC was heavily modified (chapter 3). The GC was very much improved and extended with the measurement of the ambient mixing ratios of carbon monoxide (CO), which is an important tracer for fossil fuel originated CO₂. This was the first single device to measure in-situ and with high precision and accuracy the ambient mixing ratios of CO₂, CH₄, N₂O, CO and SF₆ simultaneously. The system is designed to operate autonomously, which is necessary at remote and unmanned stations, and is very cost-efficient. Together with a target cylinder for quality control, only two local reference cylinders are needed for daily routine. The system is very reliable, easy to operate, and is able to perform about 6 measurements of all compounds per hour. The GC has performed stable enough to deliver high quality measurements with only one calibration per year against international standards. Only a small amount of sample air is needed, which makes this system also
highly suitable for flask air measurements. This system is therefore an ideal solution for high precision measurements of CO$_2$, CH$_4$, N$_2$O, CO and SF$_6$ at remote and unmanned stations. The measurement precisions over a year of observations (including non-optimal conditions) were: ±0.06 ppm for CO$_2$, ±0.8 ppb for CH$_4$, ±1.7 ppb for CO, ±0.4 ppb for N$_2$O and ±0.10 ppt for SF$_6$. For a shorter but more optimal period we find 1 σ standard deviations of: ±0.04 ppm for CO$_2$, ±0.7 ppb for CH$_4$ and ±0.8 ppb for CO, ±0.3 ppb for N$_2$O and ±0.09 ppt for SF$_6$.

A $^{222}$Radon detector was already installed in September 2005 at Lutjewad and is, similar to the GC, sampling from top of the Lutjewad tower at 60 m height. Together with the GC it is used for estimating surface emissions from ambient mixing ratios. The radioactive noble gas $^{222}$Rn (its radioactive half-life is 3.825 days) is used as a reference tracer for atmospheric mixing and transport. $^{222}$Rn is produced at a constant rate from $^{226}$Radium which is relatively uniformly distributed in all soils. When released to the atmosphere, $^{222}$Rn experiences the same atmospheric circumstances (transport and mixing) as all other gases. The ratio of the $^{222}$Rn soil flux to the $^{222}$Rn mixing ratios at 60 m gives the transport- and dilution coefficient (to the free troposphere) for the air mass. If (e.g.) the mixing ratios of CH$_4$ are also sampled at 60 m, its surface flux can be calculated by multiplying it with this ratio. Using this approach, $^{222}$Rn is used in this thesis to translate the mixing ratios of CH$_4$, and N$_2$O (chapter 4) and fossil fuel-derived CO$_2$ (FFCO$_2$, chapter 5) into their surface emissions. This method provides an independent emission verification tool without the need for inverse modelling techniques, which are currently not suitable for estimating surface emissions for a small country or region. As $^{222}$Rn decays, a correction is needed based on the transit time of the air mass. In chapter 5 a small modification to the usually applied correction method is proposed which takes into account non-linearity of the radioactive decay.

In this thesis, the $^{222}$Rn flux method is customized for estimating surface emissions for the Netherlands using data from station Lutjewad. It was found that station Lutjewad is an ideal measurement location as it is situated in the upper north of the country and the prevailing wind direc-
tion is south-southwest (chapter 4). This implies that the bulk of the air masses sampled at Lutjewad are dominantly influenced by emission from the Netherlands. The methodology was based on selecting individual so-called $^{222}\text{Rn}$ events\textsuperscript{9} from which surface fluxes were calculated for each of them. The total duration of an event was assumed to indicate the total transport time from the source to the mast. The total distance covered (i.e. the area influencing the measurements) was determined with a back trajectory model\textsuperscript{10}. This way, a distinction could be made between emissions from the Netherlands and those from abroad based on their atmospheric trajectories.

The results for the annual mean CH\textsubscript{4} and N\textsubscript{2}O emissions for the Netherlands are compared to the national inventories as reported to the UNFCCC. The measurement-based emissions for the period of May 2006–May 2009 (appendix 1, chapter 4) are calculated to be: (22.3±5.6) t km\textsuperscript{-2} a\textsuperscript{-1} for CH\textsubscript{4} and (14.8±3.7) 10\textsuperscript{-1} t km\textsuperscript{-2} a\textsuperscript{-1} for N\textsubscript{2}O. These measurement-based estimates are slightly higher than the inventory-based emissions (2006-2008 averages) of (18.3±3.3) t km\textsuperscript{-2} a\textsuperscript{-1} for CH\textsubscript{4} and (1.3±0.6) t km\textsuperscript{-2} a\textsuperscript{-1} for N\textsubscript{2}O and are comparable within the error margins. It is therefore concluded that national inventories are correct for CH\textsubscript{4} and N\textsubscript{2}O although the uncertainties are still relatively high.

To determine the Dutch emissions of FF\textsubscript{CO}\textsubscript{2}, a proxy FF\textsubscript{CO}\textsubscript{2}* record is constructed from $\Delta^{14}$C and mixing ratios of CO\textsubscript{2} and CO (chapter 5). Surface emissions are then calculated from FF\textsubscript{CO}\textsubscript{2}* and, similar to chapter 4, trajectories are analyzed to determine the emissions from the Netherlands. A further distinction was made, based on their trajectories, between observations from local sources and those which are more representative for the Netherlands by dividing the data in two different sectors. Furthermore, in chapter 5 an important improvement to the

\textsuperscript{9} Observed increases in $^{222}\text{Rn}$ mixing ratios under stable atmospheric conditions. Surface emissions are “trapped” in the lower part of the boundary layer when vertical mixing is low. An event typically lasts for about 10 hours.

\textsuperscript{10} For this study the HYbrid Single-Particle Lagrangian Integrated Trajectory model HYSPLIT 4 was used. Available at: http://www.ready.noaa.gov/ready/hysplit4.html
method is presented. It is shown that although the frequency distribution of the fluxes resembles a lognormal distribution, and similar studies have interpreted comparable distributions as statistical scatter around a "true value", the average flux over the "capture range" of all observations is represented best using the arithmetic mean. This data treatment is supported by results from using simulated mixing ratios from the regional atmospheric transport model REMO which was fed with EDGAR FFCO₂ emission data: the method returns what was put into the model for two defined sectors. It is therefore also concluded that, provided the area is sufficiently covered by the observations, a single monitoring station is capable of determining the FFCO₂ flux for an area at least the size of the Netherlands (36,000 km²). Station Lutjewad is an ideal location for estimating the Dutch surface emissions since most of the air masses have their trajectory over the country. Using this new approach, annually mean emissions for the Netherlands of (4.7±1.6) kt km⁻² a⁻¹ are estimated for FFCO₂ for the period of May 2006-June 2009, which is, similar to CH₄ and N₂O, in very good agreement with the Dutch FFCO₂ inventories of (4.5±0.2) kt km⁻² a⁻¹ (average of 2006-2008). Our results therefore suggest that the national inventories for the Netherlands are correct for these gases, at least within the uncertainty levels of our results.

As a side result, the ²²²Rn soil flux estimates of Szegvary et al. (2009) are found to be representative for the Netherlands. This is an important result since it is an important parameter in current atmospheric transport models. The ²²²Rn soil flux estimates for the Netherlands can further be improved using a new approach (chapter 6.2) based on a combination of the ²²²Rn soil flux method and Eddy Correlation (EC). In this proposal the EC system is applied to determine the atmospheric transport coefficient with which the mixing ratios of ²²²Rn can be converted to its regional soil flux. Since this method only requires two relatively simple devices, a mobile measurement system is feasible. This would greatly improve the existing knowledge about the spatial variation as well as

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¹¹ The dominant wind direction for the Netherlands is south-southwest (approx. 30-35%).
the temporal variation in the $^{222}$Rn soil flux and thereby significantly reducing the uncertainty in the observationally based emissions.

The combined uncertainties for the results in this thesis are estimated to be about 35% for FFCO$_2^*$ and 25% in the case of CH$_4$ and N$_2$O. The long-term trends can be determined with a higher level of confidence: about 25% for FFCO$_2^*$ and 20% for CH$_4$ and N$_2$O. It is thus concluded that this method is suitable for the verification of the Dutch reduction targets of 30% by the year 2020 compared to 1990 (expressed in CO$_2$-equivelents).

The method presented in this thesis will work equally well in other regions and for other stations. The maximum coverage for a station is dependent on the wind distribution field (direction and velocity), the orography of the region, and the time over which events are being collected. Similarly, the mean emission estimates for a given area will be dependent on how well the observations are homogeneously distributed both spatially and temporally.