Introduction

In December 2015, 195 member countries of the UN signed a declaration of intent that was called an historical event in the public. And – in fact for the first time – all of the world's governments except Syria and Nicaragua stated that they are:

> Recognizing the need for an effective and progressive response to the urgent threat of climate change on the basis of the best available scientific knowledge.

Consequently these nations agreed on adopting measures to achieve a limitation of the current temperature increase at "well below 2°C" above the pre-industrial level. The agreement encourages all parties to strengthen their efforts in scientific and technological progress to fulfil that goal . That goal, however, seems to be very ambitious as a later start in reducing of the global greenhouse gas (GHG) emissions means, that the rate of needed reduction, that have to be undertaken, will be more demanding. Figure shows modelled surface temperature changes for different emission scenarios, that range from a net negative emission in the middle of the century (blue lines) to the worst-case scenario with emissions increasing to more than 100GtCO_2/a and a corresponding temperature inrease of $3.2 - 5.4$°C (red lines). The black line in figure gives an impression of the rate of reduction of CO_2 equivalent GHGs the global community has to accomplish to not exceed the 2-degree goal at a 66% likelyhood. The emission pathways for individual nations or confederations following the intended national determined contributions (INDC) of the Paris agreement are shown in different colours. The emission pledges of the top-4 emitters leave no room for the rest of the world. This highlights once again how demanding the required GHG emission reductions are to stay below 2°C.

As shown in , the ten most populous nations span a wide range of emissions per capita. Beginning with the USA with 17 tons CO_2 equivalent per capita and year, EU and China with about 7 and India with 2. The world average amounts to 5 tons CO_2 per capita and year. Considering the 2°C goal and a growing world population that world average soon has to be reduced, since the remaining quota of CO_2 emissions amounts to 816Gt CO_2 and would be consumed within 25 years at the current emission rate 35Gt/a. Therefore we have to find a compromise between equity in the "right" to emit GHGs and making it possible for less wealthy countries to develop on a lower level of GHG emissions.

Europe's role in that situation could be not only to reduce it's own emission amount below these 5 tons CO_2 per capita and year but also to act as a model for emerging countries how to handle the will for prosperity of the population and the need to deal with climate change. In that setting there is a need to have tools to check the impact of the taken measures for reducing GHG emission in Europe independently, a need for that in 2008 the Integrated Carbon Observation System Research Infrastructure (ICOS RI) was founded.

The mission of ICOS RI is to enable research to understand GHG budgets and perturbations. ICOS provides a framework to perform and maintain long-term observations in order to understand the present state and predict future behaviour of the global carbon cycle and GHG emissions. In short it can be summarised in two objectives :

The 1st objective is to give access to a single and coherent data set to enable a multi-scale analysis of GHG emissions, sinks and underlying processes that determine them. ICOS aims to be a template of future similar integrated GHG observation networks

The 2nd objective is to provide reliable information for research and understanding of regional budgets of GHG sources and sinks, their drivers and their control mechanisms. The network shall give early warnings of negative changes and responses of natural fluxes to changes in climatic circumstances. Furthermore it permits to reduce uncertainties in earth system models.

The present thesis is dedicated to bring progress in fulfilling both objectives in the framework of ICOS. To improve our understanding of the impact of anthropogenic emissions to the climate system, we need to be able to measure the corresponding quantities in the atmosphere with sufficient precision.

The arrows in figure show the current yearly turnover rates between the three main carbon storage compartments on earth. The perturbation by human activities, mainly combustion of fossil fuels and change in land usage (e.g. deforestation) represents only a small proportion of the total fluxes between atmosphere and biosphere respectively ocean. However, the natural carbon fluxes between these reservoirs are in equilibrium, this is disturbed by anthropogenic emissions, which leads to a steady increase of most recently 6.3 ± 0.2Pg/a of carbon in the atmospheric reservoir of about 800Pg C . This increase in atmospheric CO_2 acts as the main driver in global warming , even though only 56% of the anthropologically caused CO_2 remained in the atmosphere in 2015. Averaged over the last 10 years, 44% of the anthropogenic emission lead to an increase in atmospheric CO_2 concentration, 30% was absorbed by the biosphere and 26% by the ocean.

The numbers above are determined by using national budgets and based on energy statistics and cement production data . That means the global budgets are calculated bottom-up, thus sensitive to systematic errors in these statistics and – in worst case – to manipulation by politics or the industry. In order to be able to validate emission reporting independently, it is inevitable to precisely measure a suitable tracer for fossil fuel CO_2 (ffCO_2) by atmospheric sampling.

Atmospheric $\Delta^{14}CO_2$ has proven to be an efficient tracer to separate anthropogenic from ecosystem fluxes . It is constantly produced in the upper atmosphere by cosmic-ray induced interaction of atmospheric nitrogen with neutrons. So, in in the undisturbed carbon cycle, balance is reached between cosmic production and radioactive decay of ^{14}C. With the start of the industrialisation the first major anthropogenic disturbance of the ^{14}C balance began. Fossil energy carrier are free from radioactive carbon through their long storage time in comparison to the 5730 years half life of ^{14}C. Hence, with the invention of the steam machine and the combustion of fossil coal humanity begun to dilute the $^{14}C/C$ ratio in the more rapidly exchanged carbon reservoirs on earth, namely biosphere, the top of the ocean and especially the atmosphere. That effect was described 1955 by Hans Suess and is therefore called Suess effect . The second large disturbance was caused by extensive testing of nuclear weapons from 1956 until the signature of the Nuclear Test Ban Treaty by the Soviet Union and the USA in 1963. Production of ^{14}C by released neutrons doubled the inventory of $^{14}CO_2$ in the atmosphere. The intake of that ^{14}C into slower reservoirs superposed the decline caused by the Suess effect for several decades. Recently the larger perturbation is once again the emission of $ffCO_2$. Figure shows the long term trend in atmospheric $\Delta^{14}C$ in the northern hemisphere. In section a short introduction in radiocarbon units and calculations used in that thesis will be given.

As mentioned above, radiocarbon observations are – due to the properties of $^{14}CO_2$ – essential to separate the fossil part of the atmospheric CO_2. This can be done by using a regional $\Delta^{14}C$ offset from a background value. But, since only one in 10^{12} atmospheric carbon atoms is a ^{14}C atom and disturbance signals are narrow to the the background signal, it is challenging to measure $\Delta^{14}C$ sufficiently precise in a reproducible way.

The WMO (World Metereological Organisation) recommends to achieve a reproducibility of $30 - 50\%$ for individual measurements of the regional $\Delta^{14}C$ offset. **Beispiel fuer regional offste 14C!!! + Compatbilitaetsziel 0.5Prom**

Therefore, coming now back to the first of the ICOS objectives, the main part of this work was the set-up a new extraction and graphitisation line (EGL) at the the Central Radiocarbon Laboratory (CRL) in Heidelberg.

The CRL offers its expertise built upon decades of monitoring $^{14}CO_2$ in Heidelberg to analyse various types of atmospheric samples for their $^{14}CO_2$ content. In that framework, we built up a new extraction and graphitisation line (EGL), which provides a preprocessing capacity of 1500 atmospheric $^{14}CO_2$ samples for accelerator mass spectrometry (AMS) analysis per year. It combines three preprocessing steps, which had to be performed separately until now; namely extraction from whole air samples, determination of $\delta^{13}C$ and graphitisation. A flexible and disturbance tolerant control software has been developed to provide a high degree of automation and standardisation that we expect to lead to **!!!erfuellung der compatibiltaetsziele??**. Furthermore in-line determination of the sample's $\delta^{13}C$ facilitates fractionation correction to its true value and avoidance of the $\delta^{13}C$-Suess effect, which causes a slight $\Delta^{14}C$ offset, and allows the calculation of a $\delta^{14}C$ value . Extensive tests of measurement stability and reaction parameters have been conducted to ensure a process fraction of less than $0.1‰$ in $\delta^{13}C$ and a spread of the standards for the AMS measurement of ???. A detailed description of the technical details, the software architecture and the results of the performed tests is given in chapter .

Finally, chapter addresses the understanding of regional $ffCO_2$ sources and budgets and, hence, the second of the two objectives of ICOS. Even though we are now able to measure 1500 whole-air samples for $\Delta^{14}C$ per year that is far from being able to perform continuous $\Delta^{14}C$ in the ICOS network. Moreover, most stations are located far from $ffCO_2$ emission hotspots, therefore providing weak $\Delta^{14}C$ signals. Thus, new sampling strategies for atmospheric $^{14}CO_2$ have been tested in that work on a model basis, that address the problem to resolve weak signals in few samples by triggering sampling by anticipating air mass trajectories passing emission hotspots. On the basis of STILT model data for different ICOS stations, the increase of sensitivity of the $ffCO_2$ signal for a defined target region has been examined. This includes estimates of large-scale station-specific $ffCO_2$ background, which needs to be subtracted from the total signal. !!!Hier schon Ergebnisse?