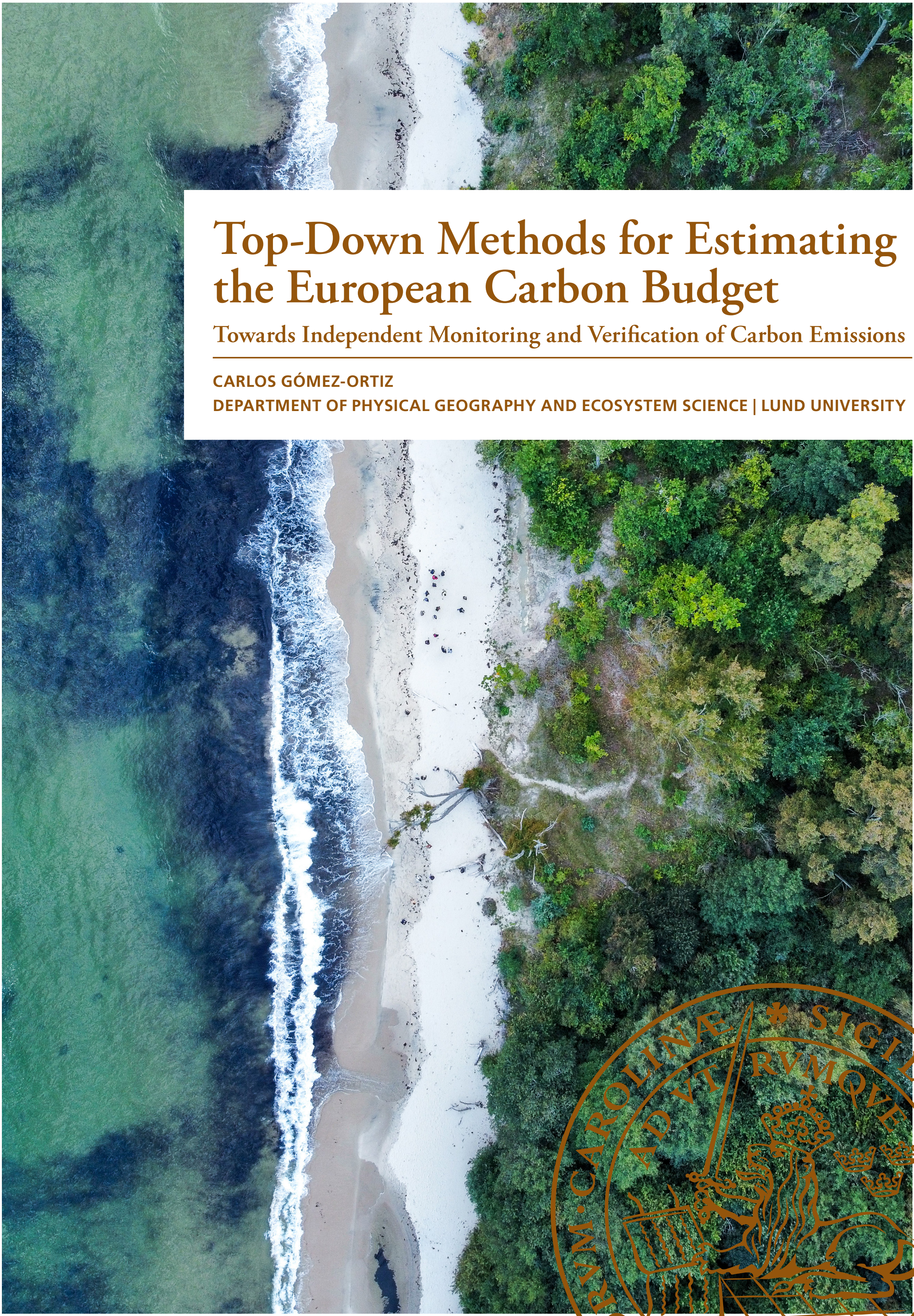
Top-Down Methods for Estimating the European Carbon Budget

Towards Independent Monitoring and Verification of Carbon Emissions

Gómez-Ortiz, Carlos



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DOCTORAL DISSERTATION

Doctoral dissertation for the degree of Doctor of Philosophy (PhD) at the Faculty of Science at Lund University to be publicly defended on 21st of February at 10.00 in Lundmarkssalen Hall, Astronomy Building, Sölvegatan 27, Lund

Faculty opponent
Dr. Carlos A. Sierra

Organization: LUND UNIVERSITY

Document name: Doctoral dissertation

Date of issue 2025-02-21

Author(s): Carlos Gómez-Ortiz

Sponsoring organization:

Title and subtitle: Top-Down Methods for Estimating the European Carbon Budget: Towards Independent Monitoring and Verification of Carbon Emissions

Abstract:
This thesis investigates the role of advanced atmospheric inversion techniques and $\Delta^{14}CO_2$ observations in improving the accuracy of regional CO_2 flux estimates across Europe. Accurate quantification of fossil fuel emissions and biospheric fluxes is essential for understanding regional carbon budgets and supporting climate policy. However, significant uncertainties persist due to limited observational coverage and discrepancies in bottom-up inventories. The research integrates dual-tracer, regional isotope budget, and CO_2 inversion methods with CO_2 and $\Delta^{14}CO_2$ measurements to enhance fossil fuel emission and Net Ecosystem Exchange (NEE) estimates. The results demonstrate that $\Delta^{14}CO_2$ serves as a critical tracer for distinguishing fossil fuel emissions from biospheric CO_2 fluxes, significantly reducing biases in NEE estimates caused by prior assumptions about fossil fuel emissions. These methods produced the most reliable results in regions with dense observational networks, such as Western and Central Europe, while revealing larger uncertainties in under-sampled areas like Southern and Eastern Europe. Using Italy as a case study, a southern European country with sparse observational coverage, the thesis evaluates the optimization of the Integrated Carbon Observation System (ICOS) network. Strategic placement of monitoring stations, particularly in Chieti and Lecce, significantly improved CO_2 flux estimates, while additional stations provided diminishing returns. These findings underscore the importance of targeted, cost-effective network expansion guided by inverse modeling frameworks. The research also examines sampling strategies to maximize the value of $\Delta^{14}CO_2$ observations, highlighting the importance of prioritizing high fossil CO_2 signal and minimizing nuclear radiocarbon contamination. A well-designed sampling strategy is critical for enhancing the signal-to-noise ratio in $\Delta^{14}CO_2$ measurements and improving flux estimates, especially in regions with complex emission dynamics. This thesis demonstrates the potential of integrating $\Delta^{14}CO_2$ data into inversion systems to provide independent and robust constraints on carbon fluxes. It also highlights the utility of inverse modeling as a decision-making tool for stakeholders involved in network design and sampling strategies. Additionally, the work explores the intercomparison of inversion approaches as complementary tools for validation, offering valuable insights for improving greenhouse gas monitoring systems, supporting climate policy, and advancing the understanding of regional carbon dynamics.

Key words: Inverse modeling, Atmospheric modeling, Bayesian statistics, Top-down estimation, Fossil fuels, CO_2 emissions, Radiocarbon, *In situ* measurements, Carbon budget

Classification system and/or index terms (if any)

Supplementary bibliographical information

Language English

Number of pages: 56

ISSN and key title:

ISBN: 978-91-89187-51-1 (print), 978-91-89187-52-8 (PDF)

Recipient's notes

Price

Security classification

Signature

Date 2025-01-13

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Printed in Sweden by Media-Tryck, Lund University
Lund 2025

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MADE IN SWEDEN

To my lovely little family

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Abstract

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Popular Summary

Understanding how much carbon dioxide (CO_2) we emit into the atmosphere is crucial for tackling climate change. CO_2, especially from burning fossil fuels like coal, oil, and gas, is one of the main drivers of global warming. But measuring these emissions accurately is not easy. Some methods rely on reported data from industries and governments, which can have gaps or inaccuracies. Others, called "top-down" methods, use observations of CO_2 in the atmosphere (top) to estimate emissions produced in the terrestrial surface (down). This thesis explores how combining these approaches with advanced techniques and unique tools, like measuring the amount of radiocarbon ($\Delta^{14}CO_2$) in the air, can improve our understanding of where and how much CO_2 is being emitted.

Radiocarbon ($\Delta^{14}CO_2$) is the radioactive form of carbon that is naturally found in the atmosphere but is absent in fossil fuels due to their age. By measuring $\Delta^{14}CO_2$ in the air, we can separate CO_2 emissions from burning fossil fuels from those naturally released by plants and soils. This research shows that using $\Delta^{14}CO_2$ measurements significantly improves the accuracy of emission estimates, particularly in regions with dense networks of monitoring stations, like western and central Europe. In areas with fewer stations, such as southern and eastern Europe, the uncertainties are higher, showing the need for better coverage.

Italy was used as a case study because its southern regions have relatively few monitoring stations. By running simulations, this thesis identified specific locations where new stations could make the biggest difference in improving CO_2 estimates. However, the study also found that adding too many stations doesn't always lead to big improvements, which highlights the importance of smart planning to use resources efficiently.

Another important part of this research focuses on how to choose the best times and places to collect air samples. Prioritizing areas with strong fossil fuel signals and avoiding contamination from other sources, like nuclear power plants, helps make the data more reliable. These strategies are key to improving how we measure emissions.

This work not only advances scientific methods but also helps policymakers and organizations responsible for tracking emissions. By improving how we measure and understand CO_2 emissions, we can make better decisions to meet climate goals, such as those in the Paris Agreement, and ensure a more sustainable future for the planet.

Resumen de divulgación científica

Entender cuánto dióxido de carbono (CO_2) emitimos a la atmósfera es crucial para abordar el cambio climático. El CO_2, especialmente el que proviene de la quema de combustibles fósiles como el carbón, el petróleo y el gas, es uno de los principales responsables del calentamiento global. Sin embargo, medir estas emisiones con precisión no es tarea fácil. Algunos métodos se basan en datos reportados por industrias y gobiernos, los cuales pueden tener vacíos o errores. Otros, conocidos como métodos "de arriba hacia abajo" (top-down), utilizan observaciones de CO_2 en la atmósfera (arriba) para estimar las emisiones que se producen en la superficie terrestre (abajo). Esta tesis explora cómo combinar estos enfoques con técnicas avanzadas y herramientas únicas, como la medición de radiocarbono ($\Delta^{14}CO_2$) en el aire, puede mejorar nuestra comprensión de dónde y cuánto CO_2 se está emitiendo.

El radiocarbono ($\Delta^{14}CO_2$) es una forma radiactiva del carbono que se encuentra de forma natural en la atmósfera, pero que está ausente en los combustibles fósiles debido a su antigüedad. Al medir $\Delta^{14}CO_2$ en el aire, podemos separar las emisiones de CO_2 provenientes de la quema de combustibles fósiles de las que se liberan naturalmente por plantas y suelos. Esta investigación muestra que el uso de mediciones de $\Delta^{14}CO_2$ mejora significativamente la precisión de las estimaciones de emisiones, especialmente en regiones con redes densas de estaciones de monitoreo, como Europa occidental y central. En áreas con menos estaciones, como el sur y el este de Europa, las incertidumbres son mayores, lo que demuestra la necesidad de una mejor cobertura.

Italia se utilizó como estudio de caso porque sus regiones del sur tienen relativamente pocas estaciones de monitoreo. Al realizar simulaciones, esta tesis identificó ubicaciones específicas donde nuevas estaciones podrían marcar una gran diferencia en la mejora de las estimaciones de CO_2. Sin embargo, el estudio también encontró que agregar demasiadas estaciones no siempre conduce a grandes mejoras, lo que resalta la importancia de una planificación inteligente para usar los recursos de manera eficiente.

Otra parte importante de esta investigación se centra en cómo elegir los mejores momentos y lugares para recolectar muestras de aire. Priorizar áreas con señales fuertes de combustibles fósiles y evitar la contaminación de otras fuentes, como plantas nucleares, ayuda a que los datos sean más confiables. Estas estrategias son clave para mejorar la forma en que medimos las emisiones.

Este trabajo no solo avanza en los métodos científicos, sino que también ayuda a los responsables de formular políticas y a las organizaciones encargadas de monitorear las emisiones. Al mejorar la forma en que medimos y comprendemos las emisiones de CO_2, podemos tomar mejores decisiones para cumplir con los objetivos climáticos, como los establecidos en el Acuerdo de París, y garantizar un futuro más sostenible para el planeta.

List of papers

Paper I

Villalobos, Y., **Gómez-Ortiz, C.**, Scholze, M., Monteil, G., Karstens, U., Fiore, A., Brunner, D., Thanwerdas, J., Cristofanelli P., *Towards improving top-down national CO2 estimation in Europe: Potential from expanding the ICOS atmospheric network in Italy*. Manuscript under review at IOP Science Environmental Research Letters.

Paper II

Gómez-Ortiz, C., Monteil, G., Basu, S., Scholze, M. (2025), *A CO_2-$\Delta^{14}CO_2$ inversion setup for estimating European fossil CO_2 emissions*. Atmospheric Chemistry and Physics, 25, 397–424, https://doi.org/10.5194/ACP-25-397-2025, 2025.

Paper III

Gómez-Ortiz, C., Monteil, G., Karstens, U., Scholze, M., *Preparing for an extensive $\Delta^{14}CO_2$ flask sample monitoring campaign over Europe: Towards a better constrain of fossil CO_2 emissions*. Manuscript under review at Atmospheric Chemistry and Physics. Preprint: https://doi.org/10.5194/egusphere-2024-3013

Paper IV

Gómez-Ortiz, C., Monteil, G., Villalobos, Y., Karstens, U., Scholze, M., E*stimating fossil fuel CO_2 emissions over Europe from atmospheric CO_2 and $\Delta^{14}CO_2$ measurements*. Manuscript under preparation for submission PNAS: Proceedings of the National Academy of Sciences of the United States of America.

Author's contribution to the papers

Co-authors are abbreviated as follows:

Carlos Gómez-Ortiz (**CG**), Marko Scholze (MS), Guillaume Monteil (GM), Ute Karstens (UK), Sourish Basu (SB), Yohanna Villalobos (YV), Angela Fiore (AF), Dominik Brunner (DB), Joel Thanwerdas (JT), Paolo Cristofanelli (PC).

Paper I

Conceptualization was done by YV, **CG**, GM, UK, and MS. YV and **CG** performed the data collection, simulations, and data analysis. YV wrote the original draft with assistance of **CG**, and all co-authors contributed to the revisions of the manuscript.

Paper II

Conceptualization was done by **CG**, GM, MS, and SB. **CG** developed the multi-tracer features of LUMIA with guidance from GM and MS. SB provided radiocarbon data and assisted with data handling. **CG** set up the experiments and received advice from GM, SB, and MS. **CG** wrote the manuscript, with input and revisions from all authors.

Paper III

Conceptualization was done by **CG** and MS. **CG** collected the data with support from UK and GM. **CG** designed the experiments and sampling strategies with guidance from MS and UK. CG performed the simulations and data analysis with input from GM, MS, and UK. **CG** wrote the manuscript, with contributions and revisions from all co-authors.

Paper IV

Conceptualization and methodology were developed by **CG** and MS. UK provided key data and guidance for its integration. **CG** conducted the simulations and data analysis, with input from MS, UK, GM, and YV on analysis and interpretation. **CG** wrote the manuscript, with contributions and revisions from all co-authors.

Acknowledgements

This thesis would not have been possible without the support and collaboration of many people, whom I will mention below.

First, I would like to express my deepest gratitude to my supervisors. Marko, thank you so much for the trust and support you have given me throughout these PhD years. It was always a relief to know that in every meeting we had, I could count on your guidance to overcome any obstacle and that you would always see the positive side of things. Thank you for trusting me when I worked remotely from Iceland—it truly was one of the best moments of my PhD. I think we never really talked about it, but it will be one of those conversations we will have someday when we know each other more deeply. Guillaume, thank you for your patience and for the countless hours of meetings in which you tried to explain the model and the algorithms as clearly as possible, even when you knew I was not fully understanding. Watching you leave Lund was a moment of great uncertainty, but I also felt as though you had waited for the moment when I was ready to work on my own. Ute, thank you for always welcoming me into your office and for making time in your busy schedule to answer my sometimes confusing and absurd questions. You always found a way to make my life easier by providing the necessary tools and resources to move forward in my work.

Turning to my co-authors, I would especially like to thank Yohanna, who arrived at just the right moment to give me the push I needed to finish this PhD. Thank you for your incredible support during this last year, for listening, and for being my “rubber duck” whenever I had a problem with any of my results. I would also like to thank Sourish. Your visit to Lund was a turning point in my PhD. It was amazing to work with you, learn from your experience, and see the clarity with which someone who practically has the numbers in their head can explain things.

Next, I would like to thank all the people who provided data or made important comments at some stage of my thesis. First, Ida, Zhendong, and everyone at the ICOS Carbon Portal for facilitating data access. I would also like to thank Tobias and all the people at ICOS Sweden for the visits to Hyltemossa and for teaching me firsthand about the technical aspects of monitoring and collecting atmospheric data. My thanks also go to Sam Hammer and Ingeborg Levin from the ICOS Radiocarbon Laboratory, not only for providing essential data but also for their constant support and collaboration during my research.

I also wish to acknowledge Fortunat Joss at the University of Bern, Grégoire Broquet at LSCE, Hugo Denier van der Gon at TNO, Ingrid Luijkx at Wageningen University, Matt Rigby and Angelina Wenger at the University of Bristol, Michael Voßbeck and Thomas Kaminski at the Inversion Lab, and everyone from the CoCO2, CORSO, and Avengers projects who at some point listened to my presentations. Your curiosity helped me see my own results from a new perspective.

On a more personal note, I would like to thank Cheryl Sjöström and Ylva Van Meningen for their incredible dedication to ClimBECo, and for the effort they consistently put into all the activities of this research school. They always managed to push me out of my comfort zone and helped me adjust to life in Sweden.

To all my friends and colleagues at INES, both those who have already left and those who remain, thank you for all the moments we shared during this journey. In particular, I would like to thank Tristan and his family—María, Donna, and Artur—for their friendship, the outings, and all our shared experiences. I think you always believed we were doing you a favour by taking care of Donna, but you were actually the one doing us a favour. To Akash, it was great spending time with you. I would always choose you as a roommate. Tristan and Akash, Sundays just aren't the same without you, but I know you will always be present in my memories and the stories I share. I also want to thank Jalisha, our first friend upon arriving in Sweden, for giving Kim and me your unconditional support without even knowing us, and I will always be grateful for that. Thanks as well to Shubham, for all the dinners and shared moments; one day, you too will be writing acknowledgments like these.

I want to thank my Colombian friends in Sweden, those who became like family. I would particularly like to acknowledge Sergio and Juli for always keeping their doors open to us, for making us a part of their lives, and for bringing such joy to our time in Sweden. I also want to thank Daniel, Paula, and Luis for being like those relatives you rarely talk to but who are always there for life's important moments. To Juan José, for his incredible friendship and the endless conversations while waiting for the beer to brew—it's been amazing sharing this past year with you and navigating the final stages of our PhDs together. To Cata, for her friendship and el chisme. I know that you know what nobody else notices, even from across the room. Thank you also for giving me my only Swedish-born friend, Benji. Thank you both for all the shared moments, for being an important part of our lives, and for always taking good care of Pepper. We still don't know who's going to arrive first, but the little one already won with such loving and caring parents-to-be.

Gracias a mi papá, mi mamá y mi hermana por todo el apoyo que me han brindado durante estos años. A mis papás, por enseñarme que no hay mejor herencia que la educación y que los mejores frutos se recogen con esfuerzo y trabajo duro. Gracias a esto, hoy puedo decir que vivo de algo que me apasiona. A mi hermana, por las extensas charlas y por mantenerme informado de la actualidad familiar. Migrar nos ha acercado aún más, y espero que algún día podamos reunirnos de forma más permanente.

A mi segunda familia, Marthica y don Alonso, muchas gracias por recibirme con los brazos abiertos, por abrirme las puertas de su hogar y llenarme de su cariño. Su apoyo incondicional y sus sabios consejos han sido un pilar fundamental a lo largo de este proceso y me han hecho sentir parte de su familia desde el primer día.

A todos, los quiero mucho.

Last but not least, my lovely little family. Thank you, Pepper, for always being by my side and keeping me sane during this last year. Each walk and "talk" (monologue) has been the most therapeutic and rewarding experience—you are such a good girl. To Kim: you are the love of my life and my greatest companion. Thank you for being there from day one—when it was only a call for an interview—and for staying by my side through this roller coaster. You left behind so much of what you love to support my dream, and one lifetime won't be enough to repay you. Life is too short, but I will live for you. Thank you for your selfless and unconditional love, for being the most generous person, and for showing me that life can be amazing.

Motivation

Understanding the global carbon budget is crucial for addressing climate change, as it provides a comprehensive account of the sources and sinks of carbon dioxide (CO_2) in the atmosphere. This understanding helps to assess the effectiveness of mitigation efforts and track progress toward climate goals like those outlined in the Paris Agreement. Accurate quantification of the carbon budget requires precise estimates of both anthropogenic emissions and natural fluxes.

Among anthropogenic sources, CO_2 emissions from fossil fuels and cement production are the dominant contributors, driving significant increases in atmospheric CO_2 levels since the pre-industrial era. Despite advancements in emission reduction strategies, fossil fuel CO_2 remains a major driver of climate change, with global emissions rising by 46% since the turn of the century. While land and ocean sinks have absorbed large amounts of CO_2, their capacity is limited and is projected to decline as atmospheric CO_2 concentrations continue to rise.

Given these challenges, robust methods are needed to monitor and verify carbon fluxes. One key tool supporting these efforts is the Integrated Carbon Observation System (ICOS) Atmosphere network, which provides high-precision, long-term greenhouse gas measurements across Europe. By delivering essential data to constrain carbon budgets, ICOS forms the foundation for advanced analytical approaches.

Building on this foundation, top-down approaches such as atmospheric inverse modeling play a critical role. These methods integrate atmospheric measurements, such as those from ICOS, of CO_2 and tracers like radiocarbon ($\Delta^{14}CO_2$) with prior estimates of carbon fluxes to enhance our understanding of the carbon cycle. These systems are highly flexible, enabling the incorporation of diverse observational data to address a range of scientific and policy-related questions. They can be configured to distinguish between fossil and natural CO_2 sources, validate emission inventories, and refine estimates of anthropogenic and natural fluxes, making them invaluable for improving carbon budgets, assessing mitigation efforts, and guiding climate policy.

One such system is LUMIA (Lund University Modular Inversion Algorithm), a flexible and modular platform designed to perform atmospheric inversions at regional and national scales. Its modular design allows for customization to address specific research questions, from evaluating fossil fuel emissions to disentangling natural fluxes.

In my thesis, I combine the flexibility of LUMIA and the strategic design and measurement framework of the ICOS Atmosphere network to explore various aspects of inverse modeling, carbon monitoring, and carbon flux estimation. This work covers a range of applications, including the evaluation of network design, sampling strategies, and methodological approaches for estimating fossil and natural CO_2 fluxes. This investigation is compiled into four papers, each addressing a critical component of improving the accuracy and reliability of carbon budget assessments.

Paper I investigates how the expansion of the ICOS atmospheric network in under-sampled regions can enhance the accuracy of national CO_2 flux estimates. The study identifies optimal locations for new stations, using Italy as case study, and demonstrates their potential to reduce uncertainties in carbon flux estimates. **Paper II** develops a CO_2-$\Delta^{14}CO_2$ inversion setup within LUMIA to estimate European fossil CO_2 emissions. The study evaluates the system's ability to separate fossil and natural CO_2 fluxes, demonstrating how integrating $\Delta^{14}CO_2$ observations improves the accuracy of fossil CO_2 emission estimates across Europe. **Paper III** explores the design of a $\Delta^{14}CO_2$ flask sampling strategy for ICOS to improve fossil CO_2 emission estimates across Europe using the setup developed in Paper II. The study evaluates different sampling approaches, emphasizing the importance of targeting high-emission areas and accounting for nuclear $^{14}CO_2$ contamination to enhance the accuracy and reliability of fossil CO_2 flux estimates. **Paper IV** estimates the fossil CO_2 emission and natural fluxes of Europe for the year 2021. The study evaluates the performance of the inversion setup developed in Paper II by comparing its results against widely used inverse modeling approaches that estimate fossil and natural fluxes independently such as the one used in Paper I. This comparison highlights the advantages and limitations of the different approaches in reducing biases and improving the accuracy of carbon flux estimates at the regional scale.

Together, these studies contribute to advancing top-down methods for estimating the European carbon budget, offering valuable insights toward the independent monitoring and verification of carbon emissions and their role in the broader carbon cycle.

Background

Carbon dioxide (CO_2) is a key greenhouse gas that significantly influences the Earth's radiative balance and contributes to climate change (Joos, 1996). Its atmospheric concentration has risen from approximately 277 ppm in pre-industrial times to over 420 ppm in 2024 (Lan et al., 2025) (see **Figure 1**), primarily due to anthropogenic activities such as fossil fuel combustion and cement production (Friedlingstein et al., 2023). This rapid increase has disrupted the natural balance between carbon sources and sinks, intensifying the need to understand the global carbon budget and its components. Accurate quantification of this budget requires the integration of various processes, including the exchange of CO_2 between the atmosphere, land, and oceans, as well as anthropogenic and natural emissions (Basu et al., 2016).

Radiocarbon (^{14}C), a radioactive isotope of carbon, serves as a crucial tracer for distinguishing fossil fuel emissions from natural sources due to its absence in fossil carbon. This isotopic tool provides unique insights into the sources and sinks of atmospheric CO_2, helping to refine global and regional carbon budgets (Levin & Hesshaimer, 2000). Modern monitoring efforts, such as those conducted by the Integrated Carbon Observation System (ICOS), have significantly advanced our ability to track CO_2 concentrations and isotopic composition across Europe. These observations, combined with atmospheric and inverse modeling techniques, enable researchers to better constrain CO_2 fluxes and improve the accuracy of carbon budget assessments (Levin et al., 2020a; Maier et al., 2023a).

This background section provides the necessary context to understand the processes and methodologies involved in estimating carbon fluxes. It begins with an exploration of the global CO_2 and $\Delta^{14}CO_2$ budgets, emphasizing the interplay of anthropogenic emissions, natural fluxes, and isotopic fluxes. Key processes influencing $\Delta^{14}CO_2$, such as isotopic disequilibrium, nuclear activities, and cosmogenic production, are also addressed. Finally, the section examines the tools and techniques used for monitoring and modeling CO_2 and $\Delta^{14}CO_2$, focusing on atmospheric and inverse modeling.

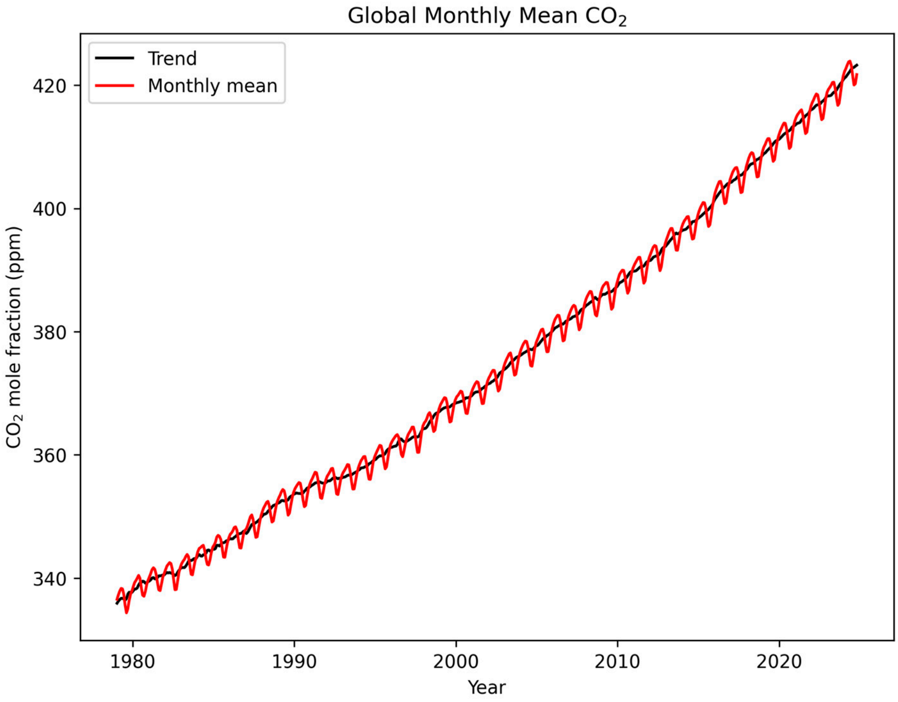

Figure 1. Global monthly mean CO_2
Global monthly mean carbon dioxide (CO_2) concentrations averaged over marine surface sites, as measured by the NOAA Global Monitoring Laboratory. The second graph displays all years since 1980. CO_2 concentrations are reported as dry air mole fractions in parts per million (ppm), calculated as the ratio of CO_2 molecules to total air molecules excluding water vapor. The red line represents unadjusted monthly mean values, while the black line shows these values corrected for the average seasonal cycle using a moving average over seven years (Lan et al., 2025).

The global CO_2 and $\Delta^{14}CO_2$ budgets

The global budgets of CO_2 and $\Delta^{14}CO_2$ provide a detailed understanding of the sources and sinks of atmospheric carbon dioxide, offering essential insights into the dynamics of the carbon cycle. These budgets integrate contributions from anthropogenic emissions, natural fluxes, and isotopic processes, highlighting the complex interplay between human activities and natural systems. The atmospheric CO_2 budget can be described as follows:

$$\frac{d}{dt}C = F_{\mathrm{bio}} + F_{\mathrm{oce}} + F_{\mathrm{ff}} \tag{1}$$

where C is the atmospheric CO_2 mixing ratio, F_{bio} represents the net exchange between the atmosphere and terrestrial ecosystems (net ecosystem exchange, NEE) including photosynthesis, respiration, and fires, F_{oce} represents the net exchange between the atmosphere and the oceans, and F_{ff} represents the fossil fuel and cement production emissions. On the other hand, the atmospheric $\Delta^{14}CO_2$ budget can be represented as:

$$\frac{d}{dt}(C\Delta_{\mathrm{atm}}) = \Delta_{\mathrm{atm}}(F_{\mathrm{bio}} + F_{\mathrm{oce}}) + (\Delta_{\mathrm{bio}} - \Delta_{\mathrm{atm}})F_{\mathrm{bio2atm}} + (\Delta_{\mathrm{oce}} - \Delta_{\mathrm{atm}})F_{\mathrm{oce2atm}} + \Delta_{\mathrm{ff}}F_{\mathrm{ff}} + \Delta_{\mathrm{nuc}}F_{\mathrm{nuc}} + \Delta_{\mathrm{cos}}F_{\mathrm{cos}} \qquad (2)$$

where the Δ terms correspond to the radiocarbon isotope signature of the reservoir or flux, corrected for mass-dependent fractionation between reservoirs and for radioactive decay between sampling and analysis making these quantities comparable (Stuiver & Polach, 1977). The multiplication of Δ values by CO_2 values (either mixing ratios or fluxes), make these quantities conservative and, therefore, additive (Tans et al., 1993). The terms $\Delta_{atm}F_{bio}$ and $\Delta_{atm}F_{oce}$ describe the exchange of "modern" ^{14}C between the atmosphere and terrestrial ecosystems or the ocean, where newly formed biomass and the ocean's surface layer exhibit ^{14}C levels similar to the atmosphere (Graven et al., 2020). The fluxes F_{biodis} and F_{ocedis} represent isotopic disequilibrium, reflecting differences in $\Delta^{14}C$ between the atmosphere and the biosphere or ocean. F_{biodis} involves the release of ^{14}C-enriched carbon from old organic matter via heterotrophic respiration, while F_{ocedis} results from ^{14}C-depleted carbon released by vertical oceanic mixing (Basu et al., 2016; Lehman et al., 2013). Δ_{ff} is set to -1000‰ because fossil fuels contain no radiocarbon, as it has completely decayed over millions of years. Lastly, F_{nuc} accounts for radiocarbon production from nuclear facilities, and Fcos is the natural production of ^{14}C in the stratosphere. Equations 1 and 2 can have slightly different representations depending on the author, with some examples explicitly including photosynthesis and respiration fluxes along with their respective radiocarbon signatures (Naegler & Levin, 2009; Turnbull et al., 2009). The version presented here is based on the studies by Miller et al. (2012) and Basu et al. (2016) and serve as the implementation used in **Papers II**, **III**, and **IV**.

Terrestrial and oceanic isotopic disequilibrium

The isotopic disequilibrium between the atmosphere and terrestrial or oceanic reservoirs arises from historical changes in atmospheric ^{14}C concentrations and the differing rates at which these reservoirs equilibrate with the atmosphere. This disequilibrium reflects the varying turnover rates of carbon within terrestrial ecosystems and oceanic compartments, introducing distinct isotopic signatures to carbon fluxes. This phenomenon introduces challenges in accurately estimating fossil fuel CO_2 emissions, as it influences the isotopic signature of CO_2 fluxes exchanged between these reservoirs and the atmosphere.

In terrestrial ecosystems, isotopic disequilibrium arises from the delayed turnover of carbon pools, such as soils and vegetation. The progressive uptake of bomb ^{14}C during the mid-20th century and subsequent changes in atmospheric ^{14}C levels have created a temporal mismatch between photosynthesis and respiration fluxes. Ciais et al. (1999) highlighted that the isotopic disequilibrium caused by heterotrophic respiration, releasing ^{14}C-enriched carbon from older soil pools, could lead to a "fake sink" effect, artificially increasing estimates of terrestrial carbon uptake by approximately 0.6 GtC yr^{-1}. This discrepancy is particularly pronounced in regions with slower carbon turnover, such as boreal and tropical forests. The terrestrial disequilibrium can also affect the estimation of the fossil CO_2 mole fraction leading to a consistent underestimation between 0.2 and 0.5 ppm, with a maximum in summer (Turnbull et al., 2009).

Oceanic isotopic disequilibrium reflects the delayed equilibration of dissolved inorganic carbon (DIC) with atmospheric CO_2. The isotopic composition of DIC varies with depth, as surface layers equilibrate with the atmosphere more rapidly than deeper waters. Galbraith et al. (2015) demonstrated that air-sea disequilibrium leads to underestimations of oceanic uptake of anthropogenic CO_2 when isotopic corrections are not applied. The slow ventilation of deep waters exacerbates this issue, as ^{14}C-depleted carbon from older oceanic reservoirs resurfaces, altering isotopic flux measurements.

Nuclear facilities

Activities of the nuclear power industry are an important influence in the atmospheric content of radiocarbon. Nuclear power and spent fuel reprocessing sites release ^{14}C in gaseous and liquid effluents, enriching ^{14}C content of CO_2 in the atmosphere, biomass, and water in the surrounding areas of nuclear sites by 4 – 20000‰ (Graven & Gruber, 2011). This ^{14}C is produced mainly through reactions of nitrogen impurities and oxygen in uranium oxide fuel or coolant water of nuclear reactors, but also in structural material, in the graphite of graphite-moderated reactors and the cooling gas of gas-cooled reactors (Yim & Caron, 2006). Nearly all ^{14}C from nuclear facilities is released in the form of $^{14}CO_2$, except in Pressurized Water Reactors (PWRs) where ^{14}C is mainly released as $^{14}CH_4$ (Eisma et al., 1995). On the other hand, spent nuclear fuel during reprocessing plants are significant sources of ^{14}C, which is released in gaseous effluents as $^{14}CO_2$ (Koarashi et al., 2005).

Radiocarbon emissions from nuclear activities can significantly influence ^{14}C-based estimates of fossil fuel CO_2 emissions, posing challenges for accurate quantification at both local and continental scales. Vogel et al. (2013) and Turnbull et al. (2009) found that nuclear power plant ^{14}C emissions can significantly mask the depletion of atmospheric $^{14}CO_2$ caused by fossil fuel CO_2, potentially leading to inaccurate estimates of fossil fuel CO_2 concentrations in regions with high nuclear activity. Similarly, Graven & Gruber (2011) found that nuclear influences could offset up to 20% of the fossil fuel dilution signal in ^{14}C across large regions, including Europe, North America, and East Asia, where nuclear facilities are prevalent. These studies underscore the necessity of incorporating nuclear ^{14}C contributions into inversion models to avoid misattributing nuclear emissions to biospheric or fossil fuel sources. Additionally, Graven et al. (2018) proposed that expanding the observational network to include sites less affected by nuclear influences could improve the accuracy of ^{14}C -based flux estimates.

These findings emphasize the importance of a dual strategy: (1) enhancing the resolution of atmospheric sampling networks to capture ^{14}C gradients more effectively and (2) integrating detailed ^{14}C nuclear emission inventories with high-resolution atmospheric models. Such approaches are critical to disentangle fossil fuel contributions from nuclear ^{14}C signals and to ensure the reliability of radiocarbon as a tracer for fossil fuel CO_2 emissions in regional and global carbon budget assessments.

Cosmogenic production of radiocarbon

Cosmogenic production of radiocarbon occurs naturally in the atmosphere through interactions between cosmic rays and nitrogen atoms, predominantly in the stratosphere. This process results in the formation of $^{14}CO_2$, which subsequently mixes throughout the atmosphere. The rate of production is influenced by the Earth's magnetic field and solar activity, leading to variations in ^{14}C production rates with latitude and over time (Kanu et al., 2016).

The majority of ^{14}C production occurs at higher altitudes, with maximum rates near the poles and a minimum near the equator. Masarik & Beer (1999) provided a detailed model of the spatial and temporal distribution of cosmogenic ^{14}C, emphasizing the strong vertical gradient between the stratosphere and the troposphere. This gradient affects regional ^{14}C levels and must be accounted for in carbon cycle studies. Despite these complexities, the overall contribution of cosmogenic ^{14}C to global atmospheric $^{14}CO_2$ is relatively small compared to other sources, such as anthropogenic emissions and natural fluxes.

In carbon budget assessments, the cosmogenic ^{14}C contribution is typically treated as part of the background atmospheric signal. Turnbull et al. (2009) demonstrated that while stratospheric-tropospheric exchange affects ^{14}C distribution, its impact on fossil fuel CO_2 estimates is minor when compared to more localized sources like nuclear power plants. Nevertheless, accurate modeling of cosmogenic ^{14}C production and its atmospheric transport remains critical for refining the use of ^{14}C as a tracer in regional and global carbon cycle studies.

Monitoring CO_2 and $\Delta^{14}CO_2$

Monitoring atmospheric CO_2 and its radiocarbon isotopic signature ($\Delta^{14}CO_2$) is critical for understanding carbon fluxes and improving carbon budget assessments. The Integrated Carbon Observation System (ICOS) is a European research infrastructure that plays a central role in this effort. ICOS operates a network of over 30 atmospheric stations across Europe, measuring CO_2 and other greenhouse gases with high precision. Among these, 17 stations also perform periodic sampling to analyze $\Delta^{14}CO_2$, a tracer essential for distinguishing fossil fuel emissions from natural fluxes (Levin et al., 2020a).

$\Delta^{14}CO_2$ measurements at ICOS stations are conducted using two-week integrated samples and, at some locations, higher-frequency flask sampling to capture temporal variations in emissions. The ICOS Central Radiocarbon Laboratory ensures precise analysis of these samples, following rigorous calibration and quality control protocols.

The ICOS network is designed to represent large spatial areas, with stations located at tall towers, mountain tops, and coastal sites. This strategic placement allows the network to capture signals from both local and distant sources and sinks, ensuring comprehensive spatial coverage of carbon flux dynamics (Storm et al., 2023). Furthermore, ICOS integrates its CO_2 and $\Delta^{14}CO_2$ observations with atmospheric modeling tools, enabling researchers to refine carbon budget estimates and reduce uncertainties in flux attribution (Karstens, 2023).

By combining state-of-the-art instrumentation, rigorous sampling strategies, and advanced modeling techniques, ICOS significantly enhances our ability to monitor and verify CO_2 emissions and removals. Its contribution to global and regional carbon cycle studies is indispensable for understanding the impacts of anthropogenic activities and guiding effective climate policies.

Modeling CO_2 and $\Delta^{14}CO_2$

Modeling CO_2 and $\Delta^{14}CO_2$ is essential for interpreting atmospheric observations and understanding the movement, mixing, and sources of these gases. Atmospheric transport models simulate the processes governing the distribution of CO_2 and its isotopic components, while carbon cycle models provide insights into fluxes and isotopic disequilibrium in terrestrial and oceanic reservoirs. These models enable researchers to link observations with flux estimates, accounting for the complexities of transport dynamics and source variability at global, regional, and local scales. By combining model outputs with observational data, it becomes possible to refine our understanding of carbon budgets and to improve the attribution of anthropogenic emissions and natural fluxes. In this section, I will focus on the atmospheric modeling and its use in inverse modeling to estimate the carbon budget.

Atmospheric modeling

Atmospheric modeling plays a fundamental role in understanding the movement and distribution of CO_2 and its isotopic component $\Delta^{14}CO_2$ in the atmosphere. Models simulate the transport, mixing, and interactions of atmospheric gases, providing insights into carbon sources, sinks, and fluxes on global and regional scales. Over time, atmospheric modeling has evolved from simplified conceptual box models to complex chemical transport models (CTMs), each with varying levels of resolution, complexity, and application.

Early atmospheric box models divided the atmosphere into a limited number of compartments or "boxes" to simulate the latitudinal and vertical distribution of CO_2 and $\Delta^{14}CO_2$. These models provided initial insights into global carbon dynamics, particularly the exchange between the atmosphere, oceans, and terrestrial reservoirs. Despite their simplicity, box models remain useful for large-scale and long-term studies due to their computational efficiency and ability to approximate observed latitudinal gradients of $\Delta^{14}CO_2$ (Levin et al., 2010; Naegler & Levin, 2006).

More advanced chemical transport models (CTMs) have been developed to overcome the limitations of box models. These models divide the Earth's surface into grids with high spatial and temporal resolution, allowing them to simulate the fine-scale processes that influence CO_2 and $\Delta^{14}CO_2$ distributions. CTMs incorporate meteorological data, detailed parameterizations of processes like convection and diffusion, and high-frequency input of flux data. For instance, the TM5 model has been widely used in carbon cycle studies to simulate atmospheric transport and quantify uncertainties in CO_2 flux estimates (Krol et al., 2005).

In addition to Eulerian CTMs like TM5, Lagrangian transport models, such as FLEXPART (Pisso et al., 2019) and STILT (Lin et al., 2003), offer alternative approaches to simulate atmospheric transport. These models track the trajectories of individual air parcels backward or forward in time, making them particularly useful for regional studies and source-receptor analyses. FLEXPART has been employed in conjunction with inverse modeling frameworks to estimate CO_2 fluxes and identify regional contributions to observed atmospheric concentrations (Maksyutov et al., 2021; Monteil & Scholze, 2021; Munassar et al., 2023). Similarly, STILT has been widely utilized to assess the sensitivity of atmospheric observations to surface fluxes, enabling detailed source attribution for regional CO_2 emissions (Levin et al., 2020b; Maier et al., 2022, 2023a).

Inverse modeling

Inverse modeling is a powerful approach for estimating carbon fluxes by integrating prior knowledge, observational data, and atmospheric transport models within a Bayesian framework. It enables researchers to quantify and attribute sources and sinks of CO_2 and $\Delta^{14}CO_2$, providing critical insights into the carbon cycle. The method relies on three key components: prior estimates, observations, and an observation operator.

Prior estimates ($\boldsymbol{x}_\mathrm{b}$) represent initial knowledge of carbon fluxes, typically derived from emission inventories for anthropogenic sources and ecosystem models for natural fluxes. Observations ($\boldsymbol{y}_\mathrm{o}$) are atmospheric measurements of CO_2 and $\Delta^{14}CO_2$, often collected by monitoring networks such as ICOS. These measurements serve as constraints that guide the optimization process. The observation operator ($\mathbf{H}$) links fluxes to observed concentrations by simulating atmospheric transport and mixing, frequently using transport models like TM5 (Maksyutov et al., 2021) or FLEXPART (Pisso et al., 2019).

The relationship between fluxes and observations is described mathematically as:

$$\boldsymbol{y} = \mathbf{H}(\boldsymbol{x}) + \boldsymbol{\epsilon} \tag{3}$$

where $\boldsymbol{\epsilon}$ represents the model and observational errors. Within the Bayesian framework, prior knowledge is updated with observational data to produce posterior flux estimates that better represent the actual fluxes. The optimization process balances the influence of prior uncertainties ($\mathbf{B}$) and observational uncertainties ($\mathbf{R}$), which determine the relative weight of these inputs.

Two primary approaches are used to solve the inverse problem: variational and filtering methods.

The variational approach is commonly employed in systems like LUMIA (Monteil & Scholze, 2021) and TM5-4DVar (Meirink et al., 2008) and focuses on minimizing a cost function derived from Bayesian theory:

$$J(\boldsymbol{x}) = \frac{1}{2}(\boldsymbol{x} - \boldsymbol{x}_\mathrm{b})^\mathrm{T}\mathbf{B}^{-1}(\boldsymbol{x} - \boldsymbol{x}_\mathrm{b}) + \frac{1}{2}(\mathbf{H}\boldsymbol{x} - \boldsymbol{y})^\mathrm{T}\mathbf{R}^{-1}(\mathbf{H}\boldsymbol{x} - \boldsymbol{y}) \tag{4}$$

where $J(\boldsymbol{x})$ represents the misfit between model predictions ($\mathbf{H}(\boldsymbol{x})$) and observations ($\boldsymbol{y}$), while incorporating prior knowledge ($\boldsymbol{x}_\mathrm{b}$) and uncertainties. Iterative minimization of this cost function generates a set of optimized fluxes ($\boldsymbol{x}$) that reconcile prior estimates with observations. This method is particularly flexible, enabling the incorporation of complex fluxes and uncertainties (Rayner et al., 2019).

Filtering approaches, such as the Kalman filter, take a different path by iteratively updating flux estimates in response to new observations. These methods rely on ensembles of simulations to track and update uncertainties, making them well-suited for real-time applications and non-linear systems. However, their high computational cost can limit their use in large-scale studies (Chatterjee & Michalak, 2013).

Inverse modeling is the central tool of this thesis, providing the foundation for exploring various applications in carbon flux estimation. Throughout my research, I apply inverse modeling techniques to assess the impact of network design, sampling strategies, and methodological approaches on the estimation of fossil fuel CO_2 emissions and natural fluxes. By integrating observational data, such as those provided by the ICOS network, with a flexible inverse modeling system, such as LUMIA, I aim to reduce uncertainties and improve our understanding of the European carbon budget. This work demonstrates the versatility and significance of inverse modeling in addressing key challenges in carbon cycle research and supporting robust climate policy frameworks.

Methods

In this thesis, I use different inverse modeling approaches to estimate the net ecosystem exchange (**Papers I** and **IV**) and the fossil fuel CO_2 emissions (**Papers II**, **III**, and **IV**) over Europe, all of them implemented in the Lund University Modular Inversion Algorithm (LUMIA). **Papers I**, **II**, and **III**, use observing system simulation experiments (OSSEs) to evaluate the impact of different factors in the posterior estimates, such as network configuration (**Paper I**), simultaneous assimilation of CO_2 and $\Delta^{14}CO_2$ observations and prior estimates (**Paper II**), and the sampling strategy of flask $\Delta^{14}CO_2$ measurements (**Paper III**). In **Paper IV**, I perform inversions using real observations and study the impact of different prior estimates of fossil CO_2 emissions on different inversion approaches.

The four papers share common methodological aspects such as the regional transport model (FLEXPART) and the inversion framework (LUMIA), and different assumptions in terms of boundary conditions, mass balance equations and optimized flux categories that I summarize in this section.

The LUMIA inverse modeling framework

The Lund University Modular Inversion Algorithm (LUMIA) is a Python-based framework developed for atmospheric inverse modeling, with a focus on adaptability and modularity. It is designed to estimate greenhouse gas (GHG) fluxes, such as fossil CO_2 emissions and natural fluxes, by assimilating atmospheric observations within regional domains (Monteil & Scholze, 2021). The framework is versatile and supports both synthetic experiments and inversions based on real observations, making it a powerful tool for various research applications.

LUMIA employs a Bayesian statistical approach to optimize a cost function that balances the fit between modeled and observed data against deviations from prior flux estimates. The framework originally incorporated the two-step atmospheric inversion scheme proposed by Rödenbeck et al. (2009) for the calculation of an optimized boundary condition based on a global-scale inversion using TM5-4DVar. However, alternative applications and methodologies has been used in this thesis for the estimation of the background contribution. **Paper III** follows the two-step scheme for both CO_2 and $\Delta^{14}CO_2$, while **Papers II** and **IV** extract the background

CO_2 from global inversions (CAMS and Jena CarboScope, respectively) using the final particle position of Lagrangian footprints.

A key strength of LUMIA is its modular design, which allows researchers to replace or upgrade individual components, such as transport models or inversion techniques, without affecting the overall system. This flexibility enables experimentation with different configurations and supports the continuous adaptation of the framework for future developments. Some applications of LUMIA include the coupling of FLEXPART for regional applications with the TM5-4DVar global model for background fluxes (Monteil & Scholze, 2021) and STILT with TM3 (Munassar et al., 2023) for the same purposes. Its modularity extends to multi-tracer inversions, presents in this thesis, enabling the simultaneous assimilation of CO_2 and $\Delta^{14}CO_2$ atmospheric observations and the optimization of fossil and natural fluxes (**Papers II-IV**).

Net ecosystem exchange inversions

In NEE inversions, only the F_{bio} term in **Equation 1** is optimized (i.e., is part of the control vector $\boldsymbol{x}_{\mathrm{b}}$ in the cost function), while fossil emissions and ocean fluxes of CO_2 are prescribed. Additionally, only CO_2 observations are assimilated. This approach represents the most conventional CO_2 inversion scheme and forms the original implementation of LUMIA. Net ecosystem exchange inversions were conducted in **Papers I** and **IV**.

LUMIA has been widely applied in regional and European-scale studies to estimate the net ecosystem exchange. Its application includes observing system simulation experiments (OSSEs) to evaluate the performance of atmospheric networks and the ability to reconstruct known fluxes from synthetic observations (Monteil & Scholze, 2021). It has also been employed in real observation inversions, utilizing data from ICOS tall towers and other European networks to estimate fluxes with high temporal and spatial resolution (Monteil et al., 2020; Munassar et al., 2023; Thompson et al., 2020).

Dual-tracer inversion framework

In the dual-tracer inversion framework, fossil fuel (F_{ff}), biospheric (F_{bio}), and terrestrial disequilibrium (F_{biodis}) fluxes in **Equations 1** and **2** are optimized simultaneously by assimilating atmospheric measurements of both CO_2 and $\Delta^{14}CO_2$, using the radiocarbon signal to separate fossil fuel emissions from natural fluxes. This inversion framework was first described by Basu et al. (2016) and it was developed with the aim of reducing the carry-over bias in the net ecosystem exchange produced by the assumption of well-known fossil fuel CO_2 fluxes in NEE inversions.

The dual-tracer inversion framework was first implemented in LUMIA in **Paper II**, and further developed and applied in **Papers III** and **IV**. Additionally, **Paper IV** compares net ecosystem exchange estimates from dual-tracer and NEE inversions. Ocean fluxes were prescribed in this thesis, as their $\Delta^{14}CO_2$ signal is relatively minor compared to terrestrial and fossil fuel contributions.

Regional isotope budget approach

The regional isotope budget approach is a method used to estimate recently added CO_2 from fossil fuel combustion and cement production by analyzing the radiocarbon signature ($\Delta^{14}CO_2$) of atmospheric CO_2 (Levin et al., 2003). This approach determines the excess fossil fuel CO_2 (C_{ff}) concentration at a monitoring site (C_{obs}, Δ_{obs}) relative to a background site (Δ_{bg}) that ideally captures unaffected air masses. The calculations are based on a mass balance that combines contributions from fossil fuels, biosphere respiration, and photosynthesis, with their respective isotopic signatures:

$$C_{\mathrm{ff}} = C_{\mathrm{obs}} \frac{\Delta_{\mathrm{bg}} - \Delta_{\mathrm{obs}}}{\Delta_{\mathrm{bg}} + 1000‰} + \beta \tag{5}$$

The method assumes that the background station integrates contributions from external sources, including oceanic and stratospheric inputs, making it suitable for regions dominated by continental signals (Maier et al., 2023b). However, contamination from nearby sources, such as nuclear facilities, must be corrected (β). These corrections are typically modeled using atmospheric transport simulations, ensuring accurate representation of local conditions. The unique property of fossil fuels being devoid of radiocarbon ($\Delta^{14}CO_2$ = -1000 ‰) allows this method to directly isolate the fossil fuel component of observed CO_2.

This approach is particularly effective in areas with significant $\Delta^{14}CO_2$ depletion caused by high fossil fuel emissions. It provides robust estimates of fossil fuel contributions and serves as a foundation for further applications, such as integrating fossil CO_2 mole fraction into inverse modeling frameworks for regional emission optimization. This approach is implemented in **Paper IV** to estimate fossil CO_2 emissions by assimilating the pre-computed fossil CO_2 mole fraction within LUMIA.

Regional transport model (FLEXPART)

The FLEXPART Lagrangian particle dispersion model (version 10.4) (Pisso et al., 2019) is the regional transport model used in **Papers I-IV**. FLEXPART is used to calculate observation footprints representing the sensitivity of atmospheric observations to surface fluxes and are pre-computed for use in the inversion system LUMIA. FLEXPART simulations were driven by meteorological data from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA5 reanalysis, utilizing a spatial resolution of 0.25° × 0.25° and a temporal resolution of 1 hour. The simulation domain spanned from 25°W, 23°N to 45°E, 83°N, covering the regional extent of the studies.

For each observation, FLEXPART tracked the movement of 10,000 particles per hour of the integration time, and backward in time over 14 days, aggregating their residence time in surface grid cells below 100 meters above ground level to compute the footprints. Instantaneous footprints were used to simulate continuous CO_2 (**Papers I-IV**) and flask $\Delta^{14}CO_2$ observations (**Paper III**), while integrated footprints were calculated for Δ^{14}CO2 integrated samples with integration times of up to three weeks (**Papers II-IV**).

The footprints generated by FLEXPART were also used to calculate background CO_2 mixing ratios in **Paper I**. For this, the final particle positions (latitude, longitude, time, and height) were interpolated against CO_2 fields provided by the Copernicus Atmosphere Monitoring Service (CAMS).

Observing system simulation experiments (OSSEs)

Observing System Simulation Experiments (OSSEs) are used to evaluate the performance of inversion systems and the impact of observing networks on estimating CO_2 and $\Delta^{14}CO_2$ fluxes in **Papers I-III**. In OSSEs, synthetic observations are generated using "true" fluxes derived from realistic assumptions. These observations are then used to test the system's ability to reconstruct the true fluxes with alternative prior fluxes.

Perfect transport OSSEs assume the same atmospheric transport model and background conditions for generating synthetic observations and performing the inversion. While this idealized setup ignores systematic errors, it allows for robust testing of the inversion framework, including its sensitivity to network configurations and sampling strategies.

By comparing reconstructed fluxes with the "true" fluxes, OSSEs assess the system's accuracy and quantify uncertainty reductions. This approach is particularly useful for optimizing network designs and refining inversion methods, such as dual-tracer inversions using CO_2 and $\Delta^{14}CO_2$, under controlled conditions.

The observation networks

In all papers, I use sampling stations located inside the EUROCOM regional domain (Monteil et al., 2020), ranging from 15°W, 33°N to 35°E, 73°N, as shown in Figure 2.

The 37 ICOS and non-ICOS (stations that are not part of ICOS) stations in the European ObsPack CO_2 dataset (ICOS RI et al., 2023) located within the regional domain and reporting observations for the year 2018 were used in **Paper I**. Additionally, the locations of 23 potential future atmospheric stations in Italy were evaluated, including 15 current ICOS ecosystem stations, 5 non-ICOS atmospheric stations, and 3 proposed future stations (see Figure 2, **Paper I**). In **Paper II**, 33 ICOS stations were used, with 18 measuring only CO_2, and 15 measuring both CO_2 and $\Delta^{14}CO_2$ (Figure 2, **Paper II**, crosses and diamonds, respectively). In Paper **III**, 32 ICOS stations and 3 non-ICOS stations were used. This study was made in the context of the intensive $\Delta^{14}CO_2$ flask sampling campaign developed in the CO2MVS Research on Supplementary Observations (CORSO) project in 2024. As part of this campaing, 12 stations were selected to measure flask samples every 3 days (10 per month, ~120 per year), while 3 additional stations were designated as background sites, measuring 2-weekly integrated samples (only Mace Head was included in the regional domain) (Figure 2, **Paper III**). Finally, in **Paper IV**, all the ICOS sites measuring $\Delta^{14}CO_2$ in 2021 were selected, with the exemption of Jungfraujoch. Additionally, Mace Head was included as background station (Figure 2, **Paper IV**).

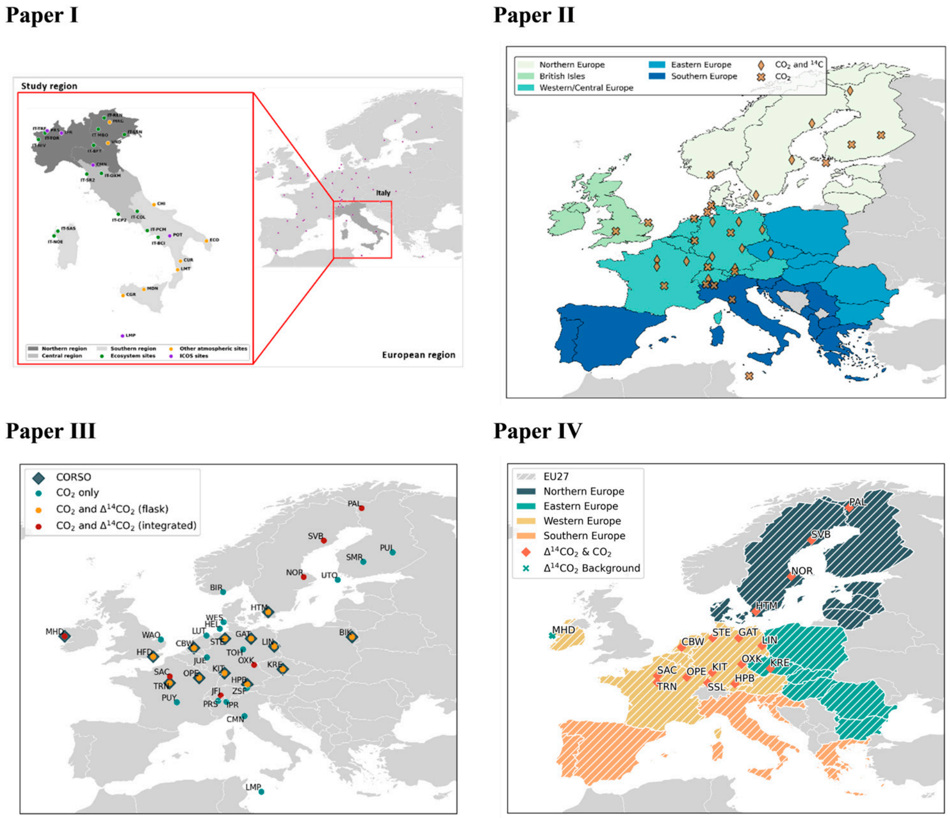

Figure 2. Observation networks used in Papers I-IV
Paper I Locations of current ICOS ecosystem and atmospheric stations in Italy, non-ICOS stations, and potential future atmospheric stations evaluated for the network expansion (zoomed inset of Italy). **Paper II** Spatial distribution of the 33 ICOS stations used, categorized by those measuring only CO_2 and those measuring both CO_2 and $\Delta^{14}CO_2$ (crosses and diamonds, respectively). Regions mentioned in the results are color-coded. **Paper III** Network of 12 stations participating in the CORSO $\Delta^{14}CO_2$ flask sampling campaign, including CO_2-only stations, $\Delta^{14}CO_2$ flask sampling stations, and integrated sampling background stations (Mace Head as the regional background site). Additional ICOS sites measuring CO_2 only were included. **Paper IV** The network of ICOS stations measuring $\Delta^{14}CO_2$ in 2021, with Mace Head included as a background site and Jungfraujoch excluded. Regional domains (EU27, Northern, Eastern, Western, and Southern Europe) are color-coded for clarity.

Observations and flux products

As mentioned at the beginning of this section, the methodology used in **Papers I–III** involves observing system simulation experiments (OSSEs). In this approach, synthetic observations are generated by transporting a set of assumed true fluxes to evaluate the ability of the inversion setup to recover them using a different set of fluxes (priors). The synthetic observations can be created at arbitrary observation times or locations, depending on the study's objectives. **Table 1** summarizes the types of observations used in each paper and the information derived from real observations.

Papers I and **II** utilized the observation times from their respective datasets. This approach accounts for the gap periods commonly observed in atmospheric station operations and the sampling frequency of $\Delta^{14}CO_2$ (**Paper II**). In **Paper I**, continuous time series without gaps were used for the proposed future stations. A similar approach was applied in **Paper III**, as the study was conducted prior to the conclusion and reporting of the sampling campaign. In **Paper IV**, real observation values and times were used to perform the inversions.

Table 1. Summary of the observation types and data sources used in Papers I-IV.

Paper	CO_2	$\Delta^{14}CO_2$	From real observations
I	Yes	N/A	Obs. times 2018 (ICOS RI et al., 2024)
II	Yes	Integrated	Obs. times 2018 (ICOS RI et al., 2023)
III	Yes	Integrated and flask	None
IV	Yes	Integrated	Observations 2021 (ICOS RI et al., 2024)

Diverse flux products were used in the simulations performed in **Papers I-IV**. Table 2 summarizes the main products by tracer (CO_2 and $\Delta^{14}CO_2$), flux category, their use in each paper, and references either to the flux product directly or to the study from which it was derived. A randomized version of the terrestrial disequilibrium product from Basu et al. (2020) was created for **Paper II** to be used as prior, due to the lack of an alternative product at the time. The nuclear emissions product by Storm et al. (2024) is mainly derived from emission factors from Graven & Gruber (2011) and energy production statistics from the Power Reactor Information System (PRIS) developed by the International Atomic Energy Agency (IAEA). Such data is only available as annual totals. An alternative product assigning an arbitrary time distribution was created for **Paper II** to study the impact of using a constant nuclear release in the estimation of fossil emissions.

Table 2. Summary of flux products, their use and references from Papers I-IV.

Tracer	Flux category	Product	Used as	Papers	Reference
CO_2	Fossil fuel CO2	EDGAR-BP	Truth, prior	I-IV	Koch & Gerbig (2023)
		ODIAC	Prior	I, III, IV	Oda & Maksyutov (2023)
		CTE-HR	Prior	IV	van der Woude et al. (2022)
	Biosphere (NEE)	LPJ-GUESS	Truth, prior	I-III	Wu (2023)
		VPRM	Prior	I-III	Gerbig & Koch (2021)
		LPJ	Prior	IV	Paper IV
	Fires	GFAS	Truth	I	Di Giuseppe et al. (2018)
	Ocean	Jena CarboScope	Truth	II-IV	Rödenbeck et al. (2013)
		Mercator	Truth	I	Lellouche et al. (2018)
$\Delta^{14}CO_2$	Terrestrial disequilibrium	Basu et al. (2020)	Truth, prior	II, III	Basu et al. (2020)
		LPJ	Prior	IV	Paper IV
	Ocean disequilibrium	Basu et al. (2020)	Truth	II, III	Basu et al. (2020)
	Nuclear production	Storm et al. (2024)	Truth	II-IV	Storm et al. (2024)
	Cosmogenic production	Basu et al. (2020)	Truth	II, III	Basu et al. (2020)

Results and Discussion

Inverse modeling as a network design tool

The Integrated Carbon Observation System (ICOS) plays a critical role in providing high-precision, continuous greenhouse gas (GHG) data for regional atmospheric CO_2 inversion systems in Europe. Despite its extensive reach, the spatial distribution of stations is uneven, with most stations located in western and central Europe. Italy's atmospheric ICOS network currently includes only five stations: Plateau Rosa, Ispra, Monte Cimone, Lampedusa, and Potenza, with three located in the north and one in the Mediterranean Sea. The recent addition of the Potenza station has addressed a key gap in the south, but central and southern Italy remain under-sampled, posing challenges for inverse modeling and the accurate estimation of CO_2 fluxes.

Expanding the Italian Integrated Carbon Observation System (ICOS) network significantly enhances the accuracy of carbon flux estimates, particularly in the southern region, as demonstrated in this study. The existing network already reduces biases in the south by 20%, but adding the Chieti (CHI) and Lecce (ECO) stations improves this to an 82% reduction in weekly seasonal biases. **Figure 3** illustrates the impact of incorporating these stations into the existing network.

Strategic placement of stations is critical for maximizing the performance of the Italian ICOS network. While adding stations generally improves accuracy, the gains diminish as the network expands. For example, including a third or fourth station provides only marginal additional error reduction compared to the significant improvement achieved by adding CHI and ECO. **Figure 4** visually represents the percentage reduction in posterior flux uncertainties compared to prior flux uncertainties for the whole of Italy and specifically for Northern, Central, and Southern Italy.

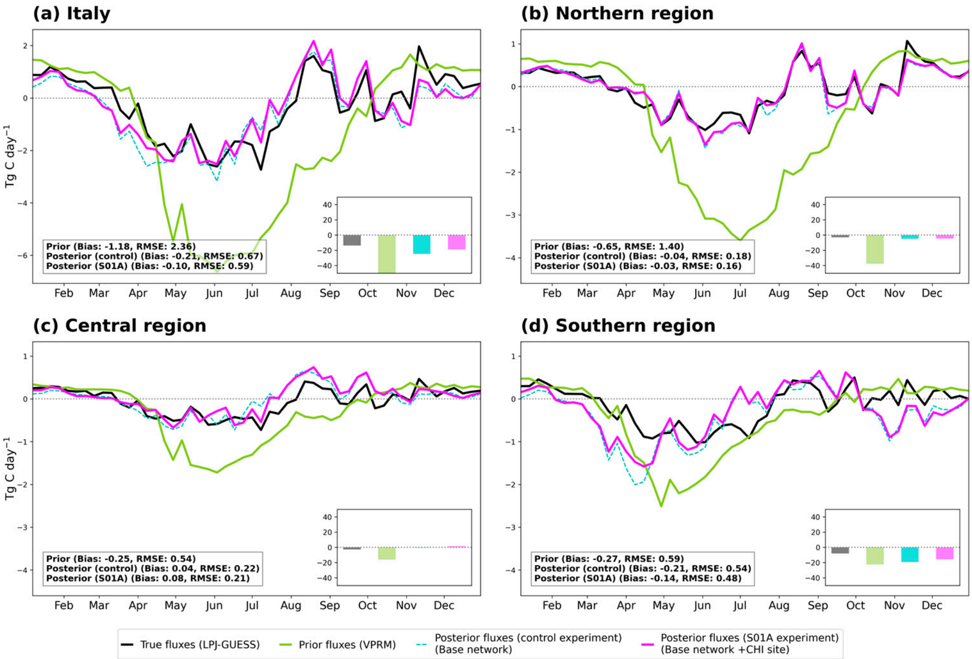

Figure 3. Impact of network expansion on CO_2 flux estimates in Italy
Seasonal cycle of weekly CO_2 fluxes for 2018, aggregated across all of Italy and divided into three sub-regions: Northern, Central, and Southern areas of the country. Inset bar plots in the lower right corner of each panel represent the annual CO_2 fluxes aggregated for 2018.

The selection of station locations in the Italian ICOS network is influenced by the configuration and assumptions of LUMIA. The inversion system's accuracy is affected by factors such as the resolution of the atmospheric transport model, the choice of correlation length scales for uncertainties, and the spatial distribution of existing stations. In this study, a 500 km spatial correlation for the prior fluxes was selected as the best option, consistent with other inversion studies. This relatively long correlation length is considered reasonable due to the sparse atmospheric network in Europe, including Italy.

These results emphasize the importance of strategic network design for carbon monitoring, particularly in underrepresented regions like southern Italy where achieving optimal flux constraints at a national scale is essential. This network design approach for Italy can be transferred to any other national monitoring network. This research has implications for greenhouse gas inventory reporting agencies and policymakers across Europe, as it provides valuable insights for the strategic selection of stations that could receive financial support as potential future atmospheric monitoring sites.

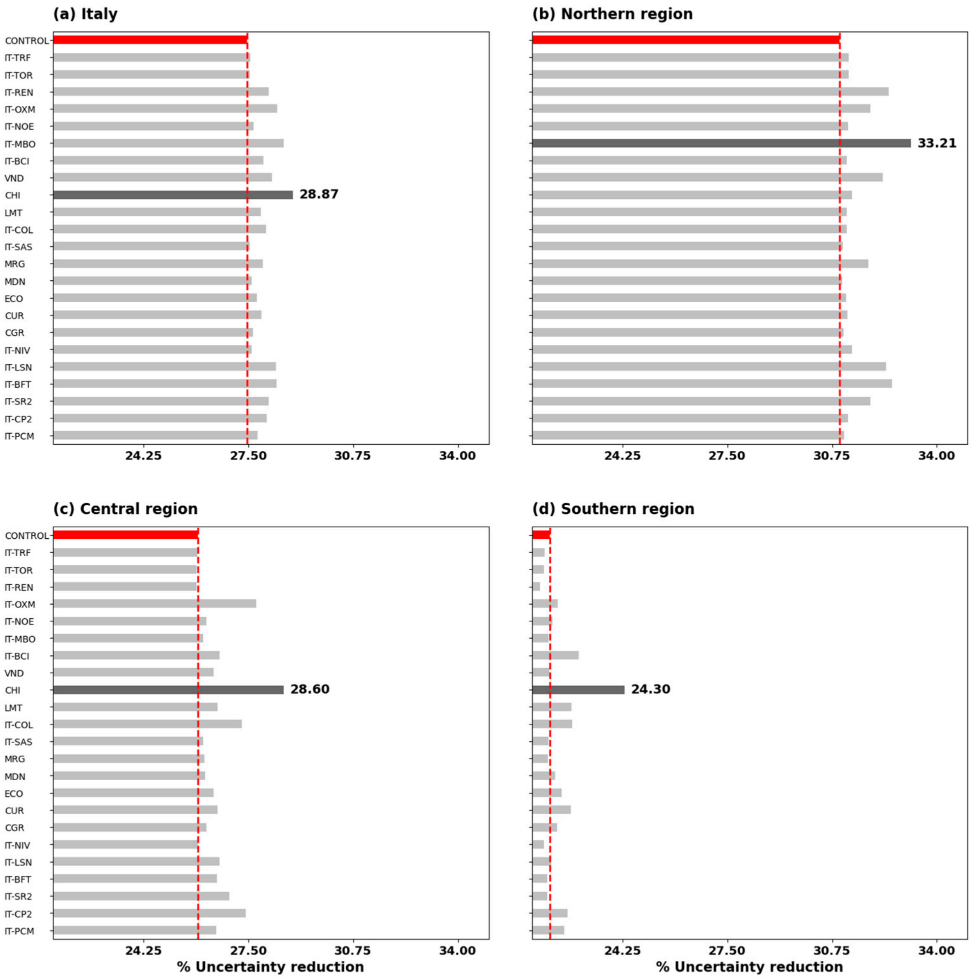

Figure 4. Impact of network expansion on uncertainty reduction in CO_2 flux estimates
Percentage reduction in posterior flux uncertainties compared to prior flux uncertainties for (a) the whole of Italy, and specifically for (b) Northern Italy, (c) Central Italy, and (d) Southern Italy.

Setting up a dual-tracer inversion framework

Paper II describes the development and evaluation of a new inversion system that uses atmospheric CO_2 and $\Delta^{14}CO_2$ measurements to estimate fossil fuel and biosphere CO_2 fluxes over Europe. The system is based on the Lund University Modular Inversion Algorithm (LUMIA) and incorporates radiocarbon data to distinguish between fossil fuel and biospheric CO_2 fluxes. The study uses Observing System Simulation Experiments (OSSEs) to evaluate the system's performance under different scenarios, including varying levels of sampling density and prior uncertainty.

Incorporating radiocarbon measurements ($\Delta^{14}CO_2$) is crucial for accurately estimating fossil CO_2 emissions, as demonstrated through the ZBASE and ZCO2Only experiments. These experiments, which set prior fossil CO_2 and biosphere fluxes to zero, revealed that adding $\Delta^{14}CO_2$ observations (ZBASE) significantly enhances the accuracy of fossil CO_2 emission estimates in regions with dense sampling networks, such as western and central Europe, in compared to ZCO2Only, which only assimilates CO_2 measurements. This improvement is evident in the lower root mean square error (RMSE) of ZBASE relative to ZCO2Only.

For example, in western/central Europe, ZBASE achieved a remarkable recovery of the true fossil CO_2 budget, capturing 95% of the actual values. In comparison, ZCO2Only recovered only 32% of the true budget in the same region (**Figure 5**). This highlights the substantial benefits of incorporating $\Delta^{14}CO_2$ observations into the inversion system, significantly improving the precision and reliability of fossil CO_2 emission estimates.

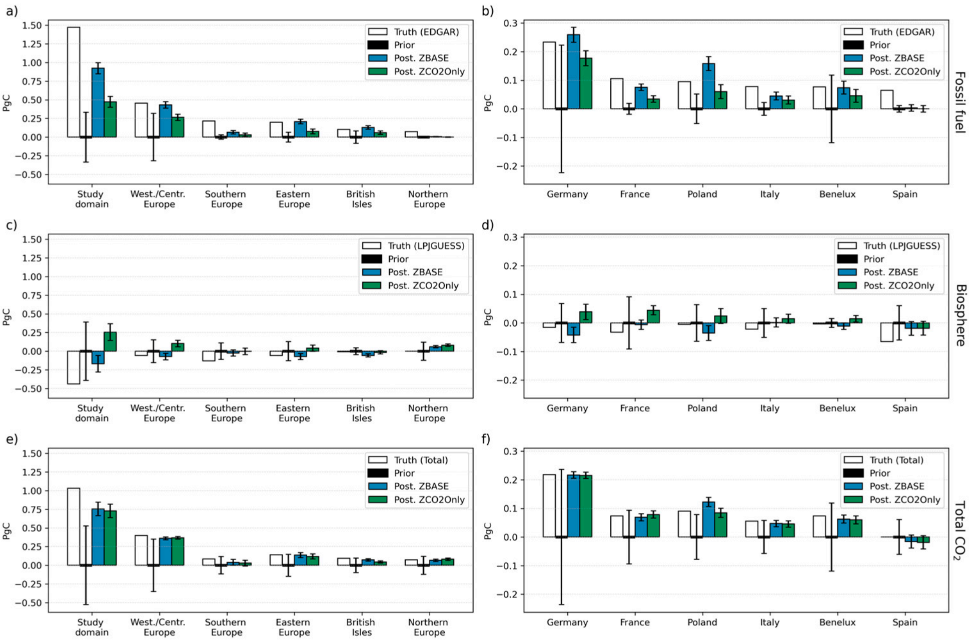

Figure 5. True, prior, and posterior annual budgets of fossil, biosphere, and total CO_2
Annual budgets of fossil (a-b), biosphere (c-d), and total CO_2 (e-f) for the study domain, sub-regions (right), and some of the largest European countries by area (left). The white bars show the true annual budgets based on EDGAR and LPJ-GUESS flux products. The black bars represent the prior value, 0 PgC. The blue and green bars show the posterior budgets of ZBASE and ZCO2Only, respectively. Error bars represent the prior and posterior uncertainty calculated with a Monte Carlo ensemble of 100 members.

The accuracy of the prior terrestrial isotopic disequilibrium product (F_{biodis}) significantly influences the estimated fossil CO_2 emissions. It is important to use a reliable F_{biodis} product to prevent additional noise from being introduced into the posterior fossil CO_2 flux estimates. To illustrate this impact, experiments were conducted using a deliberately incorrect prior F_{biodis} product. The results revealed that the maximum difference between the prior and the true F_{biodis} is of a similar magnitude in western/central (2.1 TgC day^{-1}) and eastern Europe (1.3 TgC day^{-1}) during July (**Figure 6**). However, for the fossil fuel flux, the difference between the prior and true values is approximately one order of magnitude larger in western/central Europe compared to eastern Europe (0.03 vs. 0.005 TgC day^{-1}).

This larger discrepancy in eastern Europe causes a stronger dilution of the fossil emissions, effectively reducing the signal-to-noise ratio of the $\Delta^{14}CO_2$ measurements. Combined with the lower network coverage in eastern Europe compared to western/Central Europe, this results in a weaker constraint on fossil CO_2 emissions, particularly during the summer months when the fossil CO_2 signal is further masked by substantial biospheric uptake.

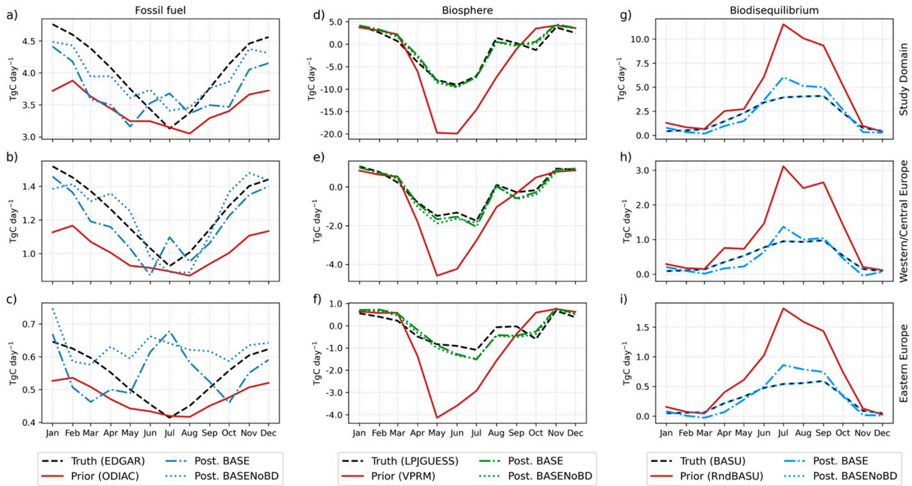

Figure 6. Impact of terrestrial isotopic disequilibrium on fossil CO_2 emission estimates
Monthly time series of fossil fuel CO_2 emissions (a to c), biosphere fluxes (d to f), and biospheric disequilibrium (g to i) for the study domain, western/central Europe, and eastern Europe. The truth is represented by black dashed lines, prior by red solid lines, posterior fluxes from BASE0.1 by blue dashed-dotted lines, and BASENOBD by blue dotted lines.

Optimizing $\Delta^{14}CO_2$ flask sampling strategies using inverse modeling

Paper III investigated the impact of combining intensive sampling with regular integrated sampling for estimating fossil CO_2 emissions on a subregional and subannual scale. The study employed the multi-tracer enabled version of LUMIA and performed a series of perfect transport OSSEs. The research focused on evaluating the added value of intensive $\Delta^{14}CO_2$ sampling compared to current sampling methods, assessing the benefits of selecting $\Delta^{14}CO_2$ flask samples based on their fossil contribution, and determining if further selection based on nuclear contamination provided additional benefits when estimating fossil CO_2 emissions.

A higher sampling density during periods of low fossil fuel activity, such as summer, can lead to a more accurate estimation of fossil CO_2 emissions by capturing subtle variations and trends that might otherwise be missed. For instance, in western/central Europe and Germany, the CORSO experiment, which includes additional flask samples, led to a substantial reduction in uncertainty, consistently exceeding 90% in both regions. This observation is supported by **Figure 7**, which illustrates that the CORSO experiment, incorporating additional flask samples, resulted in a better agreement with the true emissions throughout the year, particularly during the summer months (June and July). The study concludes that a well-distributed and frequent sampling strategy, such as the one employed in the CORSO experiment, is crucial for obtaining reliable estimates of fossil CO_2 emissions.

Selecting $\Delta^{14}CO_2$ flask samples based on nuclear contamination can be particularly important in regions with high nuclear activity, where emissions from nuclear facilities can potentially mask the fossil fuel signal, leading to inaccurate estimations. The CORSO_ffCO2_nuc14C experiment, in which samples with low nuclear contamination are selected, consistently shows lower uncertainty throughout the year compared to the CORSO_ffCO2_nuc14Cmax experiment, which selects samples with high nuclear contamination.

For example, in Western/Central Europe, the uncertainty in the posterior fossil CO2 emissions for the CORSO_ffCO2_nuc14C experiment ranges from 12% to 44%, while for the CORSO_ffCO2_nuc14Cmax experiment, it ranges from 42% to 118%. This difference highlights the importance of minimizing nuclear contamination in the selected samples to improve the accuracy of emission estimates.

Furthermore, the spatial analysis presented in **Figure 8** demonstrates that the CORSO_ffCO2_nuc14C experiment achieves substantial uncertainty reductions across most of Europe, particularly in regions with high prior uncertainty. This emphasizes the effectiveness of strategically selecting samples with low nuclear contamination in enhancing the reliability of fossil fuel emission estimates.

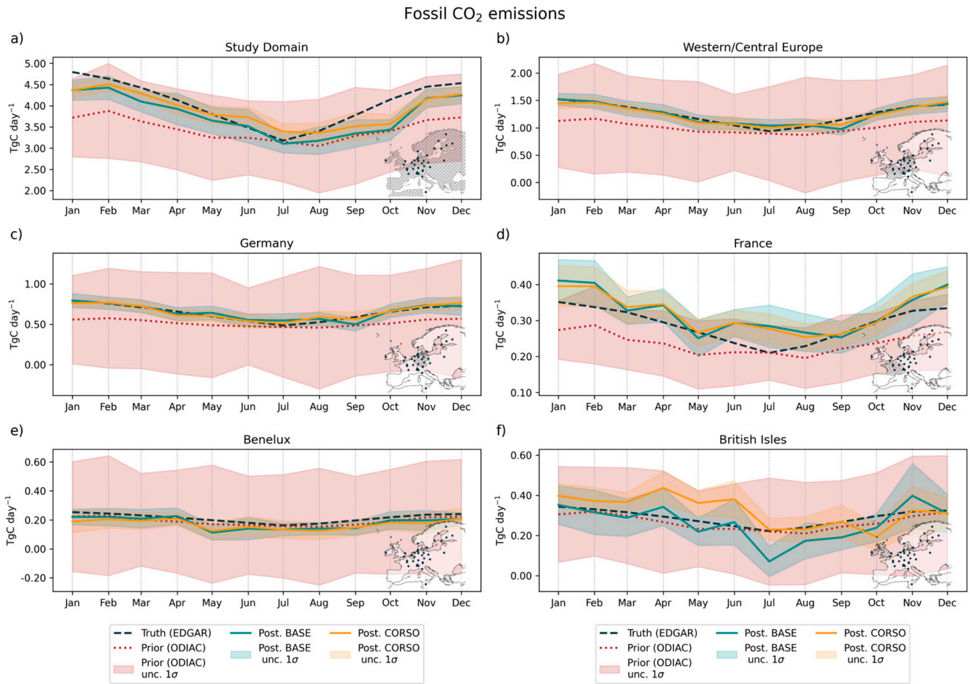

Figure 7. Monthly fossil CO_2 emissions comparing the current and proposed sampling
Monthly fossil CO_2 emissions for the study domain and five subregions: Western/Central Europe, Germany, France, Benelux, and the British Isles. The black dashed lines represent the assumed true emissions derived from EDGAR, while the red dotted lines represent the prior estimates from ODIAC. The solid lines show the posterior estimates from the BASE (teal) and CORSO (yellow) experiments. The shaded areas represent the uncertainty (1σ) calculated using a Monte Carlo ensemble of 25 members.

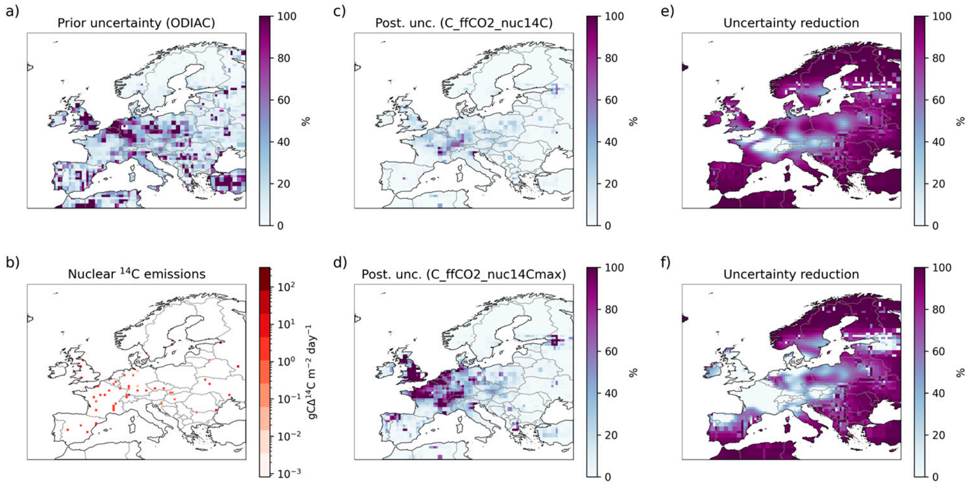

Figure 8. Spatial distribution of prior and posterior uncertainties, and the corresponding uncertainty reduction

Spatial distribution of the annual prior fossil CO_2 emission uncertainty (a), nuclear radiocarbon emissions (b), posterior uncertainties of the CORSO_ffCO2_nuc14C (c) and CORSO_ffCO2_nuc14Cmax (d) experiments, and their respective uncertainty reductions (e and f).

Comparison of inverse modeling approaches

Paper IV explores the complementary strengths of dual-tracer, regional isotope budget, and NEE inversion approaches for estimating fossil fuel CO_2 emissions and net ecosystem exchange (NEE) in Europe. The dual-tracer inversion estimates EU27 fossil fuel CO_2 emissions at 709.1 TgC yr^{-1}, slightly higher than the regional isotope budget's estimate of 692.4 TgC yr^{-1}. Despite these differences, both methods highlight the value of incorporating $\Delta^{14}CO_2$ observations in reducing dependence on prior estimates and enhancing the accuracy of emission estimates.

The optimization of NEE through the dual-tracer inversion also highlights its utility in minimizing biases caused by inaccurate fossil fuel priors. At the EU27 level, the dual-tracer inversion estimates NEE at -172.6 TgC yr^{-1}, less negative than the -255.7 TgC yr^{-1} estimated by NEE-only inversions. This difference reflects the dual-tracer method's ability to disentangle fossil fuel emissions from biospheric fluxes. Northern Europe exhibits the strongest biospheric sink, with NEE values of -68.83 TgC yr^{-1} (dual-tracer) and -89.77 TgC yr^{-1} (NEE-only). In Western Europe, where fossil fuel emissions are high and spatially variable, the use of a single-station $\Delta^{14}CO_2$ baseline in the dual-tracer approach may introduce biases, emphasizing the need for improved spatial representation of background $\Delta^{14}CO_2$ values.

The findings underscore the importance of expanding $\Delta^{14}CO_2$ observational networks in under-constrained regions, such as southern and eastern Europe, to reduce uncertainties and capture regional variations in carbon fluxes. Current limitations in observational coverage in these regions result in larger uncertainties, as seen in southern Europe's fossil fuel CO_2 emission estimates, which exhibit a prior spread of 62.34 TgC yr^{-1} for the dual-tracer inversion. Additionally, the study highlights the need to refine bottom-up inventories to better reflect shifts in energy use, technological advancements, and renewable energy adoption. Improved alignment of bottom-up and top-down methodologies will enhance the robustness of emission estimates, supporting efforts to achieve climate targets and improve the transparency of emissions reporting.

Suggestions for future research

This thesis highlights the potential of integrating $\Delta^{14}CO_2$ observations and advanced atmospheric inversion methods to refine fossil fuel CO_2 emission and biospheric flux estimates. However, several potential directions for future research could enhance the robustness and applicability of these approaches. Expanding and optimizing $\Delta^{14}CO_2$ observational networks is a critical priority, particularly in under-constrained regions such as southern and eastern Europe, where current data limitations lead to larger uncertainties in flux estimates. Establishing additional monitoring stations in these areas would improve the spatial coverage and enable more precise attribution of regional emissions.

Further development of bottom-up inventories is equally important. Current inventories often fail to account for regional variability in energy use, technological advancements, and the adoption of renewable energy sources. Future work should focus on incorporating high-resolution data on these factors, along with sector-specific emission patterns, to enhance the accuracy and relevance of bottom-up estimates. Collaboration between inventory developers and researchers utilizing top-down methods could also help harmonize methodologies and reduce systematic biases.

Advancing the representation of key processes in inversion systems is another essential step. Incorporating higher-resolution atmospheric transport models, such as those capable of simulating mesoscale dynamics, could improve the accuracy of flux reconstructions in complex terrain and urban areas. Integrating complementary datasets, such as satellite-based CO_2 measurements and independent tracers like carbon monoxide or APO (atmospheric potential oxygen), could provide additional constraints on fossil fuel emissions and biospheric fluxes.

Finally, further exploration of the interplay between fossil fuel emissions, biospheric processes, and terrestrial isotopic disequilibrium is needed. While this study demonstrates the effectiveness of dual-tracer and regional isotope budget methods, refining the assumptions underlying these approaches, such as the use of single-station $\Delta^{14}CO_2$ boundary condition, would address potential biases in flux attribution. Incorporating dynamic background $\Delta^{14}CO_2$ fields or employing ensemble-based methods could help improve confidence in regional flux estimates.

Future research should also explore the implications of these methodological advancements for climate policy and reporting frameworks. As governments and international bodies increasingly rely on top-down approaches to verify greenhouse gas inventories, ensuring the robustness, transparency, and accessibility of these methods will be essential for fostering trust and guiding effective mitigation strategies. By addressing these challenges, future studies can build on the foundation established here, further advancing the understanding of regional carbon dynamics and supporting the global effort to mitigate climate change.

Conclusions

This thesis integrates insights from four research papers to advance the understanding of top-down CO_2 flux estimation in Europe, with a focus on the interplay between fossil fuel emissions, biospheric fluxes, and methodological advancements in atmospheric inversion frameworks. The findings collectively emphasize the critical role of high-quality observations, such as $\Delta^{14}CO_2$ measurements, in improving estimation of the carbon budget, which is fundamental for supporting climate policy and mitigation efforts.

The first major conclusion of this work is the demonstrated potential of $\Delta^{14}CO_2$ observations to enhance the estimation of fossil fuel CO_2 emission. Incorporating $\Delta^{14}CO_2$ as a direct tracer in dual-tracer and regional isotope budget inversion methods effectively separates fossil fuel contributions from biospheric fluxes and isotopic disequilibrium. These approaches consistently reduce prior biases and uncertainties, particularly in regions with dense monitoring networks, such as western and central Europe.

The second key finding highlights the importance of strategic expansion of observational networks, particularly in under-constrained regions like southern and eastern Europe. Simulation experiments demonstrate that adding monitoring stations in critical locations, such as Chieti and Lecce in Italy, significantly improves the spatial distribution of CO_2 flux estimates. Beyond these key sites, further network expansion provides only marginal improvements, highlighting the importance of using inverse modeling frameworks to guide targeted and cost-effective network optimization. These findings are particularly relevant for Integrated Carbon Observation System (ICOS) network planning, both in Italy and across Europe.

A third conclusion relates to the interplay between bottom-up inventories and top-down inversion results. Across the studies, posterior estimates derived from atmospheric constraints consistently showed lower fossil fuel CO_2 emissions compared to broadly used prior estimates such as EDGAR and ODIAC. This discrepancy underscores the need to refine bottom-up methodologies, incorporating high-resolution data on energy transitions, sector-specific emissions, and regional variations. Aligning these inventories with observational data is critical to reducing systematic biases and improving the credibility of national and regional greenhouse gas inventories.

Finally, this research highlights the broader policy and scientific implications of integrating atmospheric observations into carbon monitoring frameworks. The dual-tracer and isotope budget methods provide independent, robust constraints on carbon fluxes, reducing reliance on prior assumptions and enhancing the reliability of emission estimates. These advancements support international climate commitments, such as those under the Paris Agreement, by enabling more accurate tracking of progress toward emission reduction targets.

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ISBN 978-91-89187-51-1