

Isoscapes

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Editors

Isoscapes

Understanding Movement, Pattern, and
Process on Earth Through Isotope Mapping

 Springer

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Cover illustration: Top right: A monarch butterfly. Top center: A Boreal landscape in northeastern Alberta, Canada. Oxbow lakes surrounding the Winifred River channel situated 4 km east of the Christina River confluence, looking north. Photo provided courtesy of Alberta Research Council (photo taken 13 September 2007). Bottom center: A leaf water isoscape provided courtesy of Jason West (see Chapter 8, this volume).

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Preface

Context and Background for the Topic and Book

Since the discovery of isotopes and the development of precise instrumentation capable of measuring small differences in isotope abundances, there has been an interest in quantifying and understanding the spatio-temporal distributions of isotope ratio variation in natural systems. The wealth of information about spatially-distributed Earth system processes potentially available in these records drives this interest and includes insights to such processes as the origins and mixing of meteoric, surface and ground water, human movement, carbon cycling between vegetation and the atmosphere, and tracking of atmospheric pollution (Friedman 1953; Clayton et al. 1966; Zimmermann and Cegla 1973; Adar and Neuman 1988; Martinelli et al. 1991; Rozanski et al. 1991; Farquhar et al. 1993). The recent and continuing development of analytical tools for isotope analysis, in particular continuous-flow isotope ratio mass spectrometry (CF-IRMS) methods, as well as other newer approaches such as laser spectroscopy (e.g., Metzger 1978; Preston and Owens 1983; Marshall and Whiteway 1985; Jensen 1991; Lis et al. 2008), have led to dramatic increases in the availability of light stable isotope data, while advances in the measurement of radioactive isotopes (Wöflfi 1987; Southon et al. 2004) and heavy stable, radiogenic isotopes (Capo et al. 1998; Barnett-Johnson et al. 2005) have also increased the availability of these data. In addition, an abundance of spatially-explicit datasets have emerged from a host of Earth-observing instruments (Justice et al. 1998; Njoku et al. 2003), and computer and software developments, especially in Geographic Information Systems (Goodchild 2003), continue to supply critical tools for exploring spatial variation in isotope ratios and its application to questions across a spectrum of scientific domains.

It was in this context that two of the editors of this book (West and Bowen) were engaged in research in the laboratories of Jim Ehleringer and Thure Cerling developing the capacity to reconstruct histories and origins of materials based on their isotopic composition. As we worked on these problems, including sampling the spatial isotopic variability of various systems, developing and evaluating models to describe and predict observations, constructing new approaches for mapping, and developing inferences and approaches to tackle unknowns, a common language and set of ideas

began to emerge that unified these efforts. An important element common to efforts to understand human movements over landscapes, the changing sources of water to cities, or the geographic origin of drugs or counterfeit money (taking some of our work as examples) is the development of maps of the spatial isotopic variation of the material(s) of interest. We have called these maps “isoscapes” from “isotope landscapes” and thought that, more than just a useful new term, this represented an opportunity to advance science by recognizing commonalities across disciplines through the expanding interest in isoscapes. Although perhaps not previously recognized as having a common ground, questions being addressed using isoscapes come from plant and animal ecology, geology, atmospheric sciences, anthropology, forensic science, and microbiology. We believed that there were significant and important commonalities in the ways questions were being asked, the models being developed and tested, the products derived from these modeling efforts and the conclusions drawn from them. It was these commonalities that promised to form the basis for new interactions and insights both within individual fields and across disciplines.

To foster these interactions, we envisioned a conference dedicated to isoscapes followed by publications highlighting advances across and between fields. This conference would assemble a diverse set of scientists and students interested in isoscapes and allow for synergistic interactions, generate new ideas and insights, and foster a kind of common arena for a community of scientists interested in isoscapes. The idea was strongly supported by the National Science Foundation-funded Research Coordination Network BASIN (Biogeosphere Atmosphere Stable Isotope Network), which provided significant financial and organizational support for the *Isoscapes 2008* meeting. An additional RCN that represented a key isoscapes “contingency” in the study of animal migration also provided financial support (MIGRATE). So, along with the other two editors of this book (Dawson and Tu), we designed a meeting that we believe accomplished our goals, bringing together individuals from a diverse set of disciplines (see Fig. 1) for substantive dialogs about isoscapes. The meeting was held in Santa Barbara, California in April 2008 and, in spite of the beautiful weather and very nearby beach, the sessions were well-attended and generated exciting dialogs about questions being asked, methodology, results, analytical approaches, and of course interpretations. Break-out discussions developed ideas that were incorporated in an article published in *Eos* (Bowen et al. 2009) and there were 81 contributions to poster sessions, some of which resulted in publications in a special issue of the *Journal of Geochemical Exploration*.

The chapters here were developed by our invited speakers and their co-authors from ideas presented at the meeting. The book as a whole is intended to serve as a reference for the current state of the science and highlight some of the exciting avenues of future work envisioned by the chapter authors. It is organized into three thematic sections encompassing isoscapes in current research: (1) gathering and using spatially explicit isotope data, (2) isotope mapping: theory and methods, and (3) multidisciplinary applications of isoscapes. In the first section there are six chapters that address the development, advances, and future promise of spatially explicit isotope data. These chapters primarily focus on global and regional isotope data collection, including that of small groups of investigators, national and international organizations, and post hoc approaches to integrating data across multiple, individual

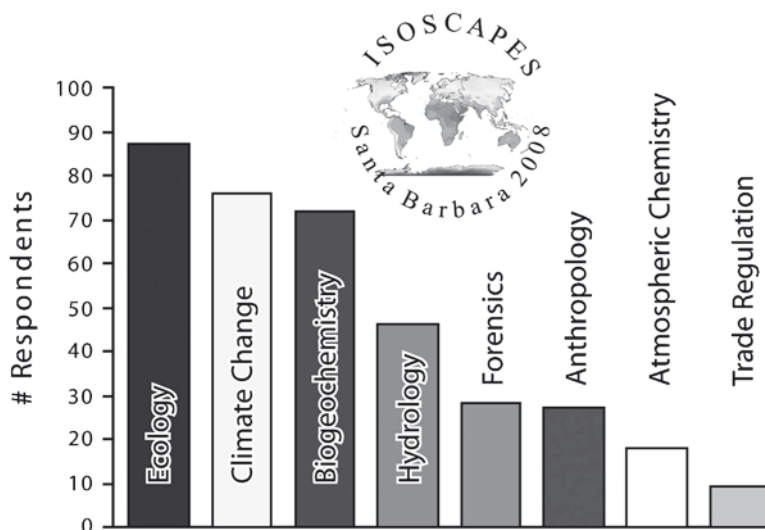


Fig. 1 Areas of research interest represented at the Isoscapes 2008 conference. Registrants ($N = 124$) were asked to indicate one or more primary areas of research interest

efforts. Atmospheric gases, precipitation and other surface waters are discussed, as are new approaches and methodologies for collecting isotope data using remote sensing instruments, laser spectroscopy, and plants as proxies. Section two is composed of chapters primarily on methodological and theoretical aspects of isoscapes modeling, including precipitation isoscapes at regional to global scales, plant carbon, hydrogen and oxygen isoscapes, nitrogen isoscapes of soils and plants and a discussion of statistical considerations important to inferring origins from these spatially explicit isotope predictions. Section three focuses on the wide array of questions addressed by researchers using isoscapes and highlights the diversity of insights that are possible. These include tracing the movements of animals across both terrestrial and aquatic environments in modern and paleoecological contexts, the information provided by isoscapes to archaeological investigations and modern forensic reconstruction efforts, improved understanding of large scale hydrologic systems, and the utility of plants as biomarkers of pollution. Together these sections offer case studies documenting the lifecycle of isoscapes, from the prerequisite and often fortuitous compilation of data, through quantitative, often multidisciplinary, data analysis, to application towards multiple problems in a range of scientific fields.

A Brief Isotope Primer

For those unfamiliar with isotope terminology and measurement approaches, we include here a very brief primer. Readers are also referred to books by Robert Criss (1999) and Zachary Sharp (2007) for more detailed information. Isotopes are elements

(or nuclides) with unique atomic masses – isotopes of a given element have the same number of protons, but have different numbers of neutrons. Stable isotopes are those that do not undergo radioactive decay, whereas radioactive isotopes are those that do decay with different half-lives and decay products. The light elements that are the primary focus of the book chapters presented here have more than one stable isotope. For example, carbon has two: ^{13}C and ^{12}C . The average abundances of the isotopes of elements discussed in this book are shown in Table 1.

Stable isotope abundances are expressed in a “difference” or delta (δ) notation relative to the rare to common isotope ratio of a standard:

$$\delta = \frac{R_{\text{sample}} - R_{\text{standard}}}{R_{\text{standard}}}, \quad (1)$$

where R is the molar ratio of the heavy (rare) to light (common) isotope of the sample and standard (e.g., the ratio of ^{13}C to ^{12}C). Delta values are quite small, and are usually reported in units of parts per thousand (per mil, ‰). Accepted standards used by the international community to allow traceability to internationally recognized scales

Table 1 Average abundances of stable isotopes and half-lives of radioactive isotopes important in an isoscapes context (Criss 1999; Fowler 1990). The *dashed line* separates the “light” isotopes from the “heavy” isotopes. Other “heavy” elements may also prove useful in the future as more efforts are directed at understanding their fractionations and abundances

Element	Isotope	Average abundance (atom fraction, %)	Half-life (years)
Hydrogen	^1H	99.985	
	^2H	0.015	
	^3H	–	12.3
Carbon	^{12}C	98.90	
	^{13}C	1.10	
	^{14}C	–	5,730
Nitrogen	^{15}N	99.63	
	^{14}N	0.37	
Oxygen	^{16}O	99.76	
	^{17}O	0.04	
	^{18}O	0.20	
Sulfur	^{32}S	95.02	
	^{33}S	0.75	
	^{34}S	4.21	
	^{36}S	0.02	

Rubidium	^{85}Rb	72	
	^{87}Rb	28	4.88×10^{10}
Strontium	^{84}Sr	0.6	
	^{86}Sr	10	
	^{87}Sr	7	
	^{88}Sr	83	

include (National Institutes of Standards and Technology-NIST) Vienna Standard Mean Ocean Water - VSMOW (NIST RM #8535) and Standard Light Antarctic Precipitation - SLAP (NIST RM #8537) for hydrogen and oxygen (SMOW scale), NBS 19 - limestone (NIST RM #8544) and L-SVEC - lithium carbonate (NIST RM #8545) for carbon (PDB scale), atmospheric air for nitrogen (on the AIR-N₂ scale), and IAEA-S-1 - silver sulfide (NIST RM #8554) for sulfur (on the VCDT scale). These materials can be obtained from the International Atomic Energy Agency (IAEA) or NIST and are used to calibrate laboratory reference materials that are then run with unknowns to allow data corrections (Werner and Brand 2001).

Changes in the isotopic composition of substances occurring as the result of a single process (e.g., evaporation), or sometimes, less satisfyingly, as the net result of a set of processes (e.g., cellulose formation), are expressed with fractionation factors. A fractionation factor is defined as:

$$\alpha_{A-B} = \frac{R_A}{R_B}, \quad (2)$$

where R_A and R_B are the isotope ratios of the two substances. Fractionations are also often expressed by simply subtracting the δ -value of one substance (e.g., that of the liquid) from the δ -value of its paired substance (e.g., that of the gas) as:

$$\Delta_{A-B} = \delta_A - \delta_B. \quad (3)$$

When the isotope ratio differences are small (e.g., <10‰) between substance A and substance B, then this so-called “big delta” is a reasonable approximation for α :

$$\Delta_{A-B} \approx 10^3 \ln \alpha_{A-B}. \quad (4)$$

Similarly, epsilon is defined as:

$$\varepsilon = (\alpha - 1)10^3, \quad (5)$$

is similar to Δ and also approximately equal to 10^3 . In α when the differences between A and B are relatively small. Sharp (2007) recommends against using ε since it has a different definition in radiogenic isotope geochemistry.

Radioactive carbon isotope abundances are expressed in a similar fashion, with reference to an Oxalic Acid standard (OX1) but also removing mass-dependent fractionation and accounting for the radioactive decay of the Oxalic Acid standard since 1950. Since the introduction of additional ¹⁴C into the atmosphere by atmospheric nuclear weapons testing, radioactive carbon isotopes can be expressed in the following manner:

$$\Delta^{14}\text{C} = \left[\frac{\left(\frac{^{14}\text{C}}{^{22}\text{C}} \right)_{\text{sample}(-25\%)}}{0.95 \times \left(\frac{^{14}\text{C}}{^{22}\text{C}} \right)_{\text{OX}_1, (-19\%, 1950)}} - 1 \right] \times 1000, \quad (6)$$

Most of the stable isotope ratio data discussed in this book will have come from analyses performed using isotope ratio mass spectrometers. These instruments are capable of measuring, at very high precision, the ratios of heavy to light isotopes in gases. They are often coupled to peripherals that generate and separate these gases from liquid and solid materials and then deliver these, using helium as a carrier gas, to the mass spectrometer (so-called continuous flow approaches; see Dawson and Brooks 2001 or Sharp 2007). The radioactive isotope of carbon (^{14}C) is often measured using accelerator mass spectrometers (AMS), with important offline preparation methodologies to ensure accurate measurements. The reader is referred to de Groot (2004, 2008) for extensive information on stable isotope methodology and Tuniz (2001) and references therein for additional information on accelerator mass spectrometry methodology.

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Part I
Gathering and Using Spatially
Explicit Isotope Data

Chapter 1

Global Network Measurements of Atmospheric Trace Gas Isotopes

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Christopher J. Still, Kenneth A. Masarie, and Jocelyn Turnbull**

1.1 Introduction

Human activities have been altering the environment in very visible ways for millennia, but only in the last century have we been able to detect significant changes in our global atmosphere. Numerous ice core records have documented the changing composition of the Earth's atmosphere, and the accompanying alterations in temperature and precipitation patterns (e.g., Indermühle et al. 1999; Flückiger et al. 2002; Spahni et al. 2005). Humans continue to play an ever-increasing role in driving environmental change, as documented by the four different assessments by the Intergovernmental Panel on Climate Change (IPCC). The 2007 IPCC assessment stated that continued greenhouse gas (GHG) emissions at or above current rates would cause further global warming, and induce many changes in the global climate system during the twenty-first century that would *very likely* be larger than those observed during the twentieth century (Solomon et al. 2007). Atmospheric monitoring programs with long-term direct measurements of GHGs and their isotopes in the lower troposphere provide critical observations that constrain global

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climate models to improve our understanding of biosphere/ocean processes that drive atmospheric changes. In this chapter we highlight several global measurement programs and outline critical elements necessary to operate these observational networks. Current consensus objectives and criteria for intercomparison and linking of atmospheric isotopic data sets from the global measurement community are presented along with some recent data products and results for isotopic models.

The awareness of these hugely consequential changes in our atmosphere began in part with the visionary and insightful work of Charles Keeling and his colleagues, who initiated measurements of atmospheric carbon dioxide, at Mauna Loa, Hawaii in 1958 (Keeling et al. 1976). His pioneering efforts uncovered both the steady increase in concentration and the seasonal cycle in CO₂, beginning the record on which we base much of our present understanding of the carbon cycle. Continuing to monitor the changing composition of the atmosphere on a global scale will become even more crucial as the climate continues to adjust in response to increases in population, energy consumption and fossil fuel emissions, as well as land cover changes.

Greenhouse gases, along with solar input and albedo, are key elements in the Earth's energy balance that drives the climate system. Therefore the Earth's response to climate forcing from relatively short-term perturbations in greenhouse gases is important. However the mean lifetime of anthropogenic CO₂ can be complex to assess accurately (Siegenthaler and Joos 1992), any peak is also accompanied by a long tail associated with the role of ocean sequestration of CO₂ into carbonates through deep-water formation (Stouffer and Manabe 2003). Estimates of lifetimes of atmospheric CO₂ range from a few hundred years to a much longer estimate of 30–35 kyr for the entire process, depending upon the model (Archer 2005). Given the potential for long lifetimes of fossil fuel carbon releases, it follows that the anthropogenic climate perturbation will likely interact with ice sheets, methane clathrate deposits, and alter normal glacial/interglacial climate dynamics (Siegenthaler and Joos 1992; Archer 2005; Caldeira and Wickett 2005). And, the carbon cycle will likely take a long time to completely stabilize and sequester the current fluxes of anthropogenic CO₂. Because of these consequences, global measurements of GHGs are crucial to our ability to understand, quantify, and predict the planet's response to the perturbation of the composition of our atmosphere. And because isotopes are ubiquitous indicators, integrators and recorders, they will undoubtedly continue to inform our understanding of environmental processes and global change.

Isotopes of atmospheric constituents contain a wealth of information about biosphere–atmosphere and ocean–atmosphere interactions, particularly when examined in combination with trace gas mixing ratios. For example, the isotopes of carbon ($\delta^{13}\text{C}$) in atmospheric CO₂ track changes in key parts of the terrestrial carbon cycle, including photosynthesis, respiration, and organic matter decomposition, as well as interaction with oceans during air–sea gas exchange. The isotopes of oxygen ($\delta^{18}\text{O}$) of CO₂ reflect many complex processes including linkages between terrestrial carbon and water cycles through H₂O/CO₂ oxygen isotope exchanges in leaf water and soil water. Small-scale studies that link direct isotopic measurements with models have shown progress in understanding mechanisms at the ecosystem level (Bowling et al. 2002; McDowell et al. 2008; Schaeffer et al. 2008). Large-

scale isotopic measurement networks record regional to meso-scale processes that may ultimately affect global-scale climate change. Global observations also constrain top-down models that suggest flux mechanisms, quantify sources and sinks of critical greenhouse gases, and partition them between terrestrial biosphere and oceanic model fluxes (e.g., Ciais et al. 1995; Fung et al. 1997; Rayner et al. 1999; Randerson et al. 1999, 2002a, b; Battle et al. 2000). Currently, the stable isotopes of atmospheric CO₂ and CH₄ make up the majority of isotope measurements. Lessons learned from maintaining these atmospheric observing networks and the challenges in assessing comparability among measurements made using independent methods, can be directly applied to ecosystem monitoring networks at any scale.

1.2 Isotopic Measurement Programs

Today there are numerous international atmospheric programs making valuable measurements of gas concentrations that continue to expand our understanding of the dynamic nature of the troposphere (Fig. 1.1). Most atmospheric isotope measurement networks currently in operation have utilized the infrastructure of these existing trace gas programs. Following the work initiated by Keeling in 1958,

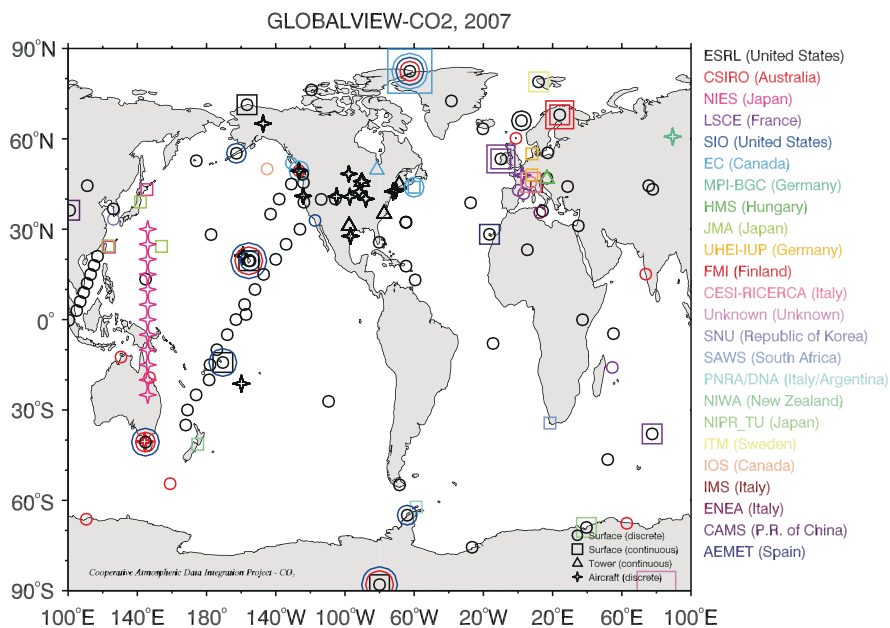


Fig. 1.1 Map of sampling sites for multiple laboratories that measure trace gas concentrations and contribute to GLOBALVIEW. A smaller subset of these labs also measure stable isotopes. Fig. 1.1, see Appendix 1, Color Section

researchers from Scripps Institute of Oceanography (SIO) joined with Willem Mook at the Centrum voor Isotopen Onderzoek (CIO) at the University of Groningen, The Netherlands, to make some of the first large-scale measurements of carbon and oxygen isotopes of atmospheric CO_2 in 1977. The network began with 10 sampling stations, along a rough latitudinal transect of the Pacific Ocean (Keeling et al. 1979; Keeling and Whorf 2005). This measurement program continues today with other sites around the globe.

The Commonwealth Scientific and Industrial Research Organization (CSIRO), Australia maintains an atmospheric monitoring network that began in 1976 with sampling at Cape Grim Australia, and at present data are available for four atmospheric trace gases at nine stationary sites and one moving platform (aircraft sampling over Cape Grim, Tasmania, and Bass Strait, during flights between the Australian continent and Tasmania). Measurements of $\delta^{13}\text{C}$ from CO_2 are made at each site, along with trace gas mixing ratios for CO_2 , CH_4 , CO , and H_2 .

European researchers have been active participants in campaigns to measure trace gases and their isotopes. The CarboEurope program emerged as a group of European projects in the late 1990s, collaborating to understand and quantify the terrestrial carbon balance of Europe and the associated uncertainty at local, regional and continental scales. Since then, it has consolidated an interdisciplinary research community focused on ecosystems, the atmosphere, measurements, and models into the CarboEurope-IP, which expands on these earlier projects and allows for consistent gathering of data and integration of space and time scales (Sturm et al. 2005). In January 2004, over 60 research centers from 17 European countries joined forces for a 5-year European Union-funded continuation of CarboEurope-IP which addresses carbon cycle issues, and helps support a European network of measurement sites including 24 lower troposphere sites, seven tall tower sites, and four aircraft profile sites. It is a multi-scale and multi-method exercise, which goes beyond basic atmospheric measurements, and requires both methodological as well as technical integration. The new European Union Integrated Carbon Observation System (ICOS) will build on the CarboEurope framework with a longer-term vision and additional measurements. Measurements from these programs, including trace gases, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, and $\Delta^{14}\text{C}$ of CO_2 , are rigorously intercompared, and the data will be available from a common website.

Perhaps the most extensive observing network for monitoring atmospheric trace gases, is the U.S. program operated by the United States National Oceanic and Atmospheric Administration (NOAA), Earth System Research Laboratory (ESRL), Global Monitoring Division (GMD) Carbon Cycle Greenhouse Gas (CCGG) cooperative air sampling network. This program, which began in 1967 at Niwot Ridge, Colorado today includes regular discrete samples from the four NOAA baseline observatories (Barrow, Alaska; Mauna Loa, Hawaii; American Samoa; South Pole, Antarctica), plus a network of over 50 cooperative fixed sites, several commercial ships, as well as a growing network of aircraft sampling programs and tall tower sampling sites in the United States. Air samples are collected approximately weekly from the globally distributed network of sites, and are analyzed in Boulder, Colorado by CCGG for mixing ratios of: CO_2 , CH_4 , CO , H_2 , N_2O , and SF_6 ; these

same air samples are analyzed for the stable isotopes $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 , $\delta^{13}\text{C}$ and δD of CH_4 , and $\Delta^{14}\text{C}$ of CO_2 by the Institute of Arctic and Alpine Research, (INSTAAR) at the University of Colorado. Both the concentration and isotopic data are used to identify long-term trends, seasonal variability, and spatial distribution of carbon cycle gases. From this program, the largest of its kind, we can learn much about the organization, methodology, and analyses required of a global network to function successfully, and will be revisited in subsequent sections.

Measurements utilizing aircraft have helped define vertical profiles of trace gases in the atmosphere, potentially alleviating problems in interpreting surface observations, such as the rectifier effect, whereby daily and seasonal variability in vertical mixing is correlated with daily and seasonal variability in (for example) CO_2 fluxes, so that annual budgets based solely on surface measurements may be biased. These aircraft programs can help identify distinct air mass plumes, boundary layers, and large gradients over large distances. Programs that utilize commercial aircraft are growing both in technology and scope. Since December 2004, a consortium of eleven partners from seven European countries have supporting the efforts of the CARIBIC (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container) system, that involves the monthly deployment of an automated atmospheric chemistry observatory inside an air-freight-container onboard a Lufthansa Airlines Airbus A340–600 (Brenninkmeijer et al. 2007). Measurements of over 25 different atmospheric parameters are made either in-flight or in the lab, including isotopes of CO , CH_4 and CO_2 .

The Japanese have also initiated a program to measure CO_2 from commercial aircraft that has yielded broad, long-range transects of tropospheric measurements never before obtained (Machida et al. 2007). Stable carbon isotopes are also being measured for CO_2 and CH_4 , but have not yet been published.

The French MOZAIC (Measurements of OZone, water vapour, carbon monoxide and nitrogen oxides by in-service AIRbus aircraft, <http://mozaic.aero.obs-mip.fr/web/>) program has been funded by the European Commission from 1994 to February 2004 to use commercial aircraft for measuring vertical profiles of ozone and water vapor (Gierens et al. 1997; Clark et al. 2007). Currently, stable isotopes are not measured, but MOZAIC has established itself as a long-term sustainable European research infrastructure with potential to expand its measurement capabilities. Since 2006, it has transformed into the European initiative IAGOS-ERI (In-service Aircraft for a Global Observing System – European Research Infrastructure) adding more measurements.

There are also organizations, both national and international that serve to promote, facilitate, and orchestrate atmospheric isotope measurement efforts, including Ameriflux, BASIN, Euroflux, and others. In the United States, the North American Carbon Program is a recently formed overarching organization that is supported by multiple U.S. Federal agencies (i.e. NOAA, NIST, NASA, NSF, DOE, EPA, USDA) in an effort to enhance scientific understanding of North America's carbon cycling through measurements of carbon dioxide, methane, and carbon monoxide across North America and over adjacent ocean regions. A major thrust of the program is to make measurements from atop tall (~100–400 m) towers that

may otherwise be used for television or radio broadcasting. These towers allow for analyses of the vertical dimension to local sources and sinks over short timescales. Another NOAA program, MAGNETT (Measurements of Anthropogenic Gases and Natural Emissions from Tall Towers) began in 1992 and utilizes existing tall (>400 m) towers as sampling platforms for in-situ and flask sample analyses of atmospheric trace gases.

All of these ongoing, long-term observational networks and programs are essential to understanding atmospheric composition and how it relates to the dynamics of global climate change. Unfortunately, these programs struggle with obtaining long-term funding, necessary for projects that take the long view. Typically, funding is for a set of specific short term scientific objectives that address questions relevant to government agencies. Monitoring does not fit neatly within this structure. Another problem is the relatively short funding cycles that agencies operate within, usually one to a few years. Monitoring generally requires a longer-term commitment to yield the required information. As a result, there are limited global networks that are maintained at the levels necessary to capture large-scale, long-term signals in atmospheric dynamics, or that are able to insure their political survival for scientific funding.

An international community of CO₂ measurement experts have been working together for more than 25 years to improve measurement techniques and develop network comparison methods designed to better assess the comparability of measurements made by different laboratories. Every two years, the World Meteorological Organization (WMO) Global Atmospheric Watch (GAW), and the International Atomic Energy Agency (IAEA) bring this community together with the purpose of sharing information and results; evaluating measurement practices and programs; facilitating interaction and collaborations; and recommending procedures and actions to the entire atmospheric carbon cycle measurement community. They have made explicit recommendations regarding the level of network comparability for many trace species and isotopes required to meet current research topics and have developed several intercomparison activities designed to meet these recommendations. We will refer to the most recent set of recommendations from the WMO/IAEA CO₂ Experts meeting in Helsinki, September 2007, throughout this chapter in the appropriate sections. In addition, the WMO/GAW World Data Center for Greenhouse Gases (WDCGG) serves as a data archive center for atmospheric carbon cycle measurements, a topic that will be addressed in detail later.

1.3 Instrumentation

Traditionally, isotope ratio mass spectrometers have been the instrument used for measuring isotopic ratios in trace gases, but occasionally even the precision of these instruments can seem like a blunt tool for the task at hand. The current global growth rate and seasonal isotopic variations of atmospheric CO₂ are small and can

approach the detection limit of modern analytical techniques. Calculating fluxes with small uncertainty requires precise determinations of both the CO₂ mole fraction (ppm) and the δ¹³C concentration. For example, fossil fuel emissions during the 1990s are estimated at 6.4 Gt C per year and increased to ~7.4 Gt C per year in 2000–2005, resulting in a yearly change of the CO₂ mixing ratio in the atmosphere during 1995–2005 of approximately 1.9 ppm per year and a δ¹³C change of about –0.025‰ per year (Solomon et al. 2007). While CO₂ mixing ratio analyses typically can be made with a precision of 0.1 ppm or better, δ¹³C precision for IRMS methods is near ±0.01‰ (1 std dev) at best (Trolier et al. 1996; Vaughn et al. 2004; Ghosh et al. 2005). High precision measurements have been predominantly performed using dual inlet mass spectrometry that requires relatively large whole air sample sizes of approximately 500 cc (Vaughn et al. 2004, describe the typical method in detail). However, continuous flow mass spectrometry methods that utilize a carrier gas to introduce a single peak for the sample integration have steadily progressed in the 1990s and early 2000s, and precision for these measurements is approaching that of the dual inlet technique, while consuming considerably less gas (Allison and Francey 1995). Because these are laboratory instruments, neither IRMS method realistically lends itself (yet) to in situ measurements, forcing measurement programs to focus on sample collection by means of large (1–3 L) glass flasks that are collected and stored for subsequent laboratory analyses. Flasks have the advantage that a number of other laboratory intensive measurements can be made on that same aliquot of air. The disadvantage is that they are limited in time to discrete event sampling.

More recently, advances have been made in alternatives to mass spectrometry, including a variety of laser-based methods that exploit the radiation absorption qualities of trace gases or specific isotopic species at various wavelengths. Tunable diode laser absorption spectroscopy (TDLAS) for stable isotope applications is becoming more common, particularly for field experiments, where isotopic signals can be large (Becker et al. 1992; Durry and Megie 1999; Bowling et al. 2003; McDowell et al. 2008). Likewise, cavity ring down spectroscopy (CRDS) has shown promise since its development in the 1980s (O’Keefe and Deacon 1988), and continues to improve in both its precision and application (Wheeler et al. 1998; Crosson et al. 2002). Instruments have been developed that can analyze δ¹³C of CO₂ and CH₄, as well as δ¹⁸O and δD of water vapor (Crosson et al. 2002; Lee et al. 2005). Advances have also been made in Fourier transform infrared (FTIR) spectroscopy to measure isotopes of atmospheric N₂O, and atmospheric CO₂ (e.g. Esler et al. 2000; Griffith et al. 2002). So far, laser-based isotope techniques for δ¹³C fall short of the <0.01‰ precision goal of traditional mass spectrometry that is often required for long term atmospheric monitoring objectives, and hover in the ±0.3‰ range at best. But this number is probably far from static, and is bound to change in the future, as the technology continues to improve. Data from laboratory studies generally fare better than field studies, and in one study comparing flask-based IRMS to in situ laser-based measurements yielded reproducibility nearly ten times worse for laser measurements (Schaeffer et al. 2008). However, there are many field experiments and campaigns with large isotopic signals where laser-based

instruments offer the advantages of in situ capability, and since advances are still being made in the techniques, they remain an exciting prospect for the future development of the isotope measurement field.

Measuring the $\Delta^{14}\text{C}$ of CO_2 may be one of the best methods for quantifying fossil fuel CO_2 emissions (Levin et al. 2003a; Turnbull et al. 2006; Hsueh et al. 2007). Due to the very low abundance of ^{14}C (~ 1 in 10^{12} carbon atoms), current measurement precision is at best 2‰, but this is sufficient to detect recently added fossil fuel CO_2 concentrations of less than 1 ppm. Two distinct measurement methods are used. In the first method, conventional radioactive decay counting of ^{14}C is used. This method requires very large samples (the equivalent of 15 m^3 of whole air) to obtain sufficient precision, and to avoid collection and transportation of such large air samples, samples are collected by absorbing the CO_2 from air into sodium hydroxide over a period from days to weeks. The CO_2 is desorbed from the NaOH in the laboratory prior to ^{14}C analysis. In the second method, accelerator mass spectrometry (AMS) is used for the ^{14}C analysis, requiring vastly smaller sample sizes, currently as small as 2 L of whole air, and obtaining precision that is comparable to the decay counting method. The AMS method allows analysis of $^{14}\text{CO}_2$ in flask samples collected in many of the existing greenhouse gas sampling networks. Current research is focused on further improving the measurement precision and lowering the required sample size.

1.4 Data Reporting, Corrections and Standards

Because of the need for high precision, advances in the various corrections used for the mass spectrometric determinations are important, and have continued to evolve in the last several decades. The ^{17}O correction is a good example. This accounts for the well-established phenomenon that the ion current on the mass 45 Faraday cup is comprised of $^{13}\text{C}^{16}\text{O}_2^+$ as well as $^{12}\text{C}^{17}\text{O}^{16}\text{O}^+$, where the latter isobaric interference amounts to about 7% of the total ion current. If the oxygen isotopic signature between the sample and the reference gas is different, traditionally, the ^{17}O contribution to the m/z 45 ion current can be corrected for by measuring the $\delta^{18}\text{O}$ signature on m/z 46 and assume a constant law for the fractionation of ^{17}O and ^{18}O . Although this does not strictly apply, this is the standard procedure first used by Harmon Craig (1957), and is usually referred to as the ‘Craig’ correction. A number of improvements or alterations have been proposed in the literature, including the set of absolute ratios for the reference materials and the exponent of the fractionation law (Craig and Keeling 1963; Santrock et al. 1985; Mook and Jongsma 1987; Merritt and Hayes 1994; Brenninkmeijer and Röckmann 1998; Assonov and Brenninkmeijer 2003, 2006). Clearly, a consensus regarding the ^{17}O correction is needed for improving the accuracy of air- CO_2 $\delta^{13}\text{C}$ data, because the choice of a particular ^{17}O correction can produce a significant $\delta^{13}\text{C}$ shift of about 0.03‰ when, for example, moving from Craig /Allison to the Assonov correction. In 2005, the 13th WMO/IAEA meeting of CO_2 experts recommended adopting the Assonov and Brenninkmeijer (2003) parameter set and

to discontinue the use of any others. However, Kaiser (2008) critically re-evaluated many of the historic and recent isotope ratio corrections in detail, and suggested that to achieve the highest accuracy in the $^{13}\text{C}/^{12}\text{C}$ ratio, independent triple oxygen isotope measurements are required. Consensus in the measurement community is an ever-evolving process, and this debate will no doubt continue. The ISO lab at the Max Planck Institute, Jena has compiled a good summation of some of the methods, and offers different correction techniques and algorithms in a spreadsheet file (http://www.bgc-jena.mpg.de/service/iso_gas_lab/activities/index.shtml).

Another even larger adjustment to isotope ratio measurements is the N_2O correction. For isotopic analyses, CO_2 is typically extracted from atmospheric samples using cryogenic (liquid nitrogen) methods that also condense N_2O . When ionized in the mass spectrometer, the N_2O will contribute to the same m/z values as the CO_2 (masses 44, 45 and 46). Therefore to determine the correct $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 , the raw isotopic data must be corrected for the N_2O contribution, which is typically about 0.22‰ and 0.33‰ for each isotope, respectively (Mook and van der Hoek 1983). However, though different techniques have been suggested, (Craig and Keeling 1963; Mook and van der Hoek 1983; Mook and Jongsma 1987; Ghosh and Brand 2004; Sirignano et al. 2004; and Assonov and Brenninkmeijer 2006), lack of awareness or consensus on methodology in the measurement community may be one of the reasons that laboratory intercomparisons remain difficult. Continuous flow methods for mass spectrometry typically isolate the CO_2 using chromatography, and are therefore free of N_2O , which offers a distinct advantage over cryogenic extraction methods, as there is no need for the N_2O correction.

Determinations of isotopic values for unknowns can be made with high confidence *relative* to another material; however, determining absolute isotopic concentrations is far more difficult. Different attempts have been made to tightly link the whole air- CO_2 carbon and oxygen isotopic scales to Vienna Pee Dee Belemnite (VPDB). The VPDB scale replaced the PDB scale in 1987 where VPDB was defined by assigning $\delta^{13}\text{C}$ VPDB = +1.95 and $\delta^{18}\text{O}$ VPDB = 2.2 (exactly) to the reference material NBS 19 (Coplen 1994, 1995, 1996). However, measurements of $\delta^{13}\text{C}$ of CO_2 extracted from whole air have much better long term reproducibility than measurements of $\delta^{13}\text{C}$ of CO_2 evolved from the reaction carbonate and 100% orthophosphoric acid (Ghosh et al. 2005). Laboratory intercomparison activities have helped illuminate this problem, and solutions to this issue are discussed below in the section on intercomparison activities.

Many of the issues described above, including scale and precision, are also true for $\delta^{13}\text{C}$ of methane. Issues of scale and laboratory intercomparison are more pronounced since far fewer measurements have been made and fewer labs are involved. Modern ambient concentrations are quite light ($\sim -47\text{‰}$ relative to VPDB), so a second standard that is lighter than VPDB is used, the IAEA reference material LSVEC. LSVEC is a lithium carbonate with a value set to -46.6‰ relative to VPDB (Coplen et al. 2006). In the case of ^{14}C , results are usually reported as $\Delta^{14}\text{C}$, which is analogous to $\delta^{13}\text{C}$, except that it is normalized to a standard $\delta^{13}\text{C}$ value, corrected for radioactive decay of ^{14}C between the time of collection and measurement, and reported according to the conventions described by Stuiver and Polach (1977).