Variation in the Oxidative Ratio of U.S. Agricultural Ecosystems from 1930 to 2010

ME Gallagher[1], CA Masiello[1], WC Hockaday[2], S Snapp[3,4], CP McSwiney[3], and JA Baldock[5]

Email: morgan.gallagher@rice.edu

[1]Dept. of Earth Science, Rice University; [2]Geology Dept., Baylor University; [3]W.K. Biological Station, Michigan State University; [4]Dept. of Crop & Soil Sciences, Michigan State University; [5]CSIRO Land and Water and The CRC for Greenhouse Accounting, Adelaide, Australia

Introduction

What is Oxidative Ratio?

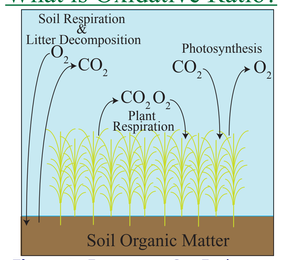

Figure 1. Ecosystem Gas Exchanges

Oxidative Ratio (OR) is the O_2/CO_2 ratio of an ecosystem and describes the net gas exchange between an ecosystem and the atmosphere.

$$OR = \frac{O_2\ [moles]}{CO_2\ [moles]}$$

The terrestrial biosphere exchanges O_2 and CO_2 with the atmosphere through a number of processes (Fig. 1) including:

- -soil respiration,
- -litter decomposition,
- -photosynthesis,
- -plant respiration,
- -fire.

Flux OR and Stock OR (Fig. 2)

Like C & N isotopes, there are OR values associated with bulk organic matter pools (plant biomass stocks, soil organic matter), & with gas fluxes (net primary production, soil respiration, decomposition, fire, etc.).

The OR of organic matter records the O_2/CO_2 ratio of previous ecosystem gas exchanges.

The OR of fluxes that transfer C from the atmosphere to the biosphere (e.g. net primary production) is known as OR_{ab}.

The OR of fluxes that return C from the biosphere to the atmosphere (e.g. decomposition) is known as OR_{ba}.

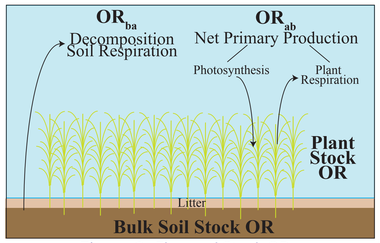

Figure 2. Flux and Stock OR

Why is Oxidative Ratio Important?

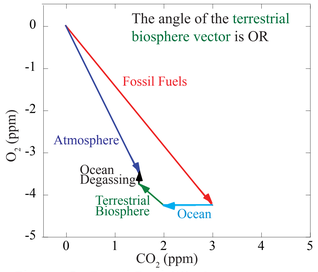

Figure 3. Fossil Fuel CO_2 Apportionment (Keeling et al. 1996; Randerson et al. 2006)

OR is the angle of the terrestrial biosphere vector in CO_2 apportionment calculations (Fig. 3), & determines the size of the terrestrial biosphere & ocean C sinks (Fig. 4).

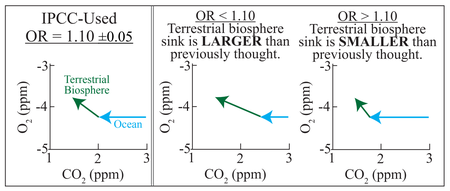

Figure 4. Small Errors in OR can Cause Large Shifts in the Size of the C Sinks (adapted from Keeling et al. 1996)

If OR off by ±0.01

0.1 Pg C/yr is misapportioned

(Randerson et al. 2006)

If OR is smaller than the value used by the IPCC, our view of the C cycle is skewed. We are estimating the terrestrial biosphere C sink to be smaller than it actually is.

How is Oxidative Ratio Measured?

OR can be measured directly from simultaneous O_2 & CO_2 measurements (Stephens et al. 2007; Seibt et al. 2004; Severinghaus 1995).

However, there are problems with this approach:

- -prone to error (Seibt et al. 2004; Severinghaus 1995);
- -provides no long term record of OR;
- -is not ideal for ecosystems undergoing fire or land use change.

We have developed 3 methods (elemental analysis, bomb calorimetry, ^{13}C nuclear magnetic resonance spectroscopy; Masiello et al. 2008, Hockaday et al. 2009) to estimate OR directly from biomass through measuring carbon oxidation state (C_{ox}).

$$C_{ox} = \frac{2O - H + 3N}{C}$$

$$OR = 1 - \frac{C_{ox}}{4} + \frac{3N}{4C}$$

Biochemicals (e.g. carbohydrates, lignin, lipids, proteins) have unique C_{ox}/OR values (Fig. 5; Masiello et al. 2008), and variations in plant biochemistry drive changes plant OR.

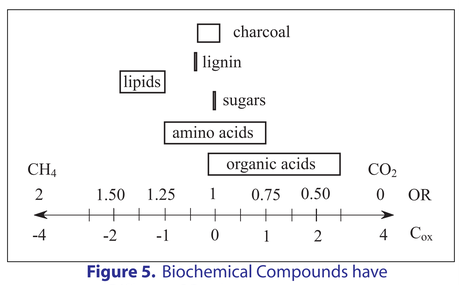

Figure 5. Biochemical Compounds have Different OR values (Masiello et al. 2008)

Abstract

Accurately and precisely constraining ecosystem oxidative ratio (OR) is necessary to assess the sizes of the terrestrial biosphere and ocean carbon (C) sinks, as well as the rate at which they are taking up anthropogenic carbon dioxide. The Intergovernmental Panel on Climate Change (IPPC)-used OR value used in apportionment calculations is 1.10 ± 0.05. Techniques currently used to estimate OR values are prone to error, which can lead to large errors in estimations of the sizes of carbon sinks: for example, an error of ±0.05 OR units is equivalent to an error of 0.5 Pg C/yr or 50 Pg C over 100 years (Randerson et al., 2006). We have developed several methods for estimating OR from biomass chemistry that are more accurate and precise. To better constrain biospheric OR, measurements need to be made across a range of ecosystems, and here we begin with 3 agricultural ecosystems. Here we analyze the top three crops in the United States (soybean, corn, and wheat) and show significant differences between the OR of legumes versus grass crops. Our preliminary estimate of the 2003-2005 average U.S. agriculture OR value of 1.06, an increase from 1.04 in the 1930s. This shift was driven by changes in cropland composition, with the major driver being the increase in soybean acreage between 1963 and the present.

Site Description

Figure 6. Kellogg Biological Station-LTER site (Michigan, USA)

SITE: W.K. Kellogg Biological Station-Long Term Ecological Research (LTER) site in southwest Michigan, USA (Fig. 6)

TREATMENTS: Conventional agriculture, 3-crop rotation
-Soybean (2003), Wheat (2004), & Corn (2005)

REPLICATES: 3 out of 6 replicates analyzed;
crops split into grain and stover organ fractions

http://lter.kbs.msu.edu/

Methods

%C and %N: Elemental Analysis

-Costech CHNSO 4010 Elemental Combustion System at Rice University

-Perkin-Elmer 2400 Series CHNS/O Elemental Analyzer at the University of California-Santa Barbara's Marine Science Institute

Carbon Oxidation State: ^{13}C Nuclear Magnetic Resonance (NMR) Spectroscopy

-Bruker 200 MHz NMR Spectrometer at Rice University

-4mm magic angle spinning (MAS) probe

Molecular Mixing Model (MMM)

-Developed by Nelson and Baldock (2005)

-Input sample C:N ratio and individual peak areas

-Determines sample biochemical composition and C_{ox}

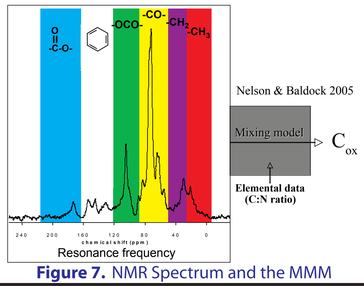

Figure 7. NMR Spectrum and the MMM

Results and Discussion

Crop Organs Can Have Different OR Values.

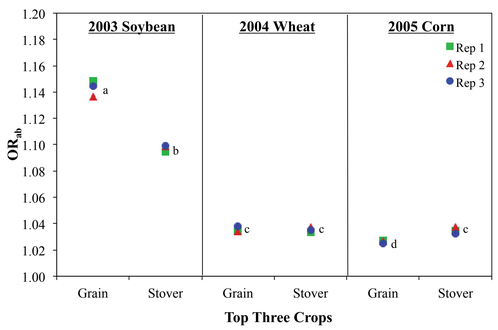

Figure 8. Crop Organ OR Can Vary

Different plant organs have different biochemical compositions (carbohydrate, protein, lignin, & lipid; Gallagher et al. in press), which affects organ OR.

Soybean grain has a higher OR than soybean stover due to higher protein concentrations, while corn stover has a higher OR than corn grain due to higher lignin concentrations (Fig 5; Fig. 8).

OR Varies with Crop Species.

$$\text{Crop OR} = \frac{NPP_{Stover} * OR_{Stover} + NPP_{Grain} * OR_{Grain}}{NPP_{Stover} + NPP_{Grain}}$$

Soybean:	1.112±0.003
Wheat:	1.035±0.001
Corn:	1.030±0.002

All 3 crops have significantly different OR values, with the N-fixing crop (soybean) having a higher OR value compared to the 2 grass crops (Fig. 9).

Wheat & corn have significantly lower OR values compared to the IPCC-used value (1.10±0.05).

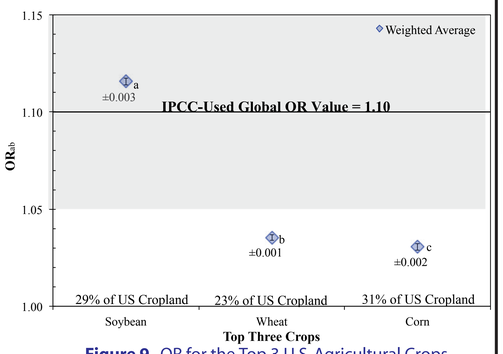

Figure 9. OR for the Top 3 U.S. Agricultural Crops

Results and Discussion (Cont.)

Estimating U.S. Agricultural OR.

We estimated a preliminary U.S. agricultural OR value for 2003-2005 (Fig. 10) by calculating a weighted average using crop OR values for soybean, corn, and wheat (Fig. 9; which make up 83% of U.S. Croplands), and planted acreage data (Fig. 11).

$$\text{U.S. Agricultural OR} = \frac{OR_{Soy} \cdot Acreage_{Soy} + OR_{Corn} \cdot Acreage_{Corn} + OR_{Wheat} \cdot Acreage_{Wheat}}{Acreage_{Soy} + Acreage_{Corn} + Acreage_{Wheat}}$$

U.S. Agricultural OR = 1.060±0.003

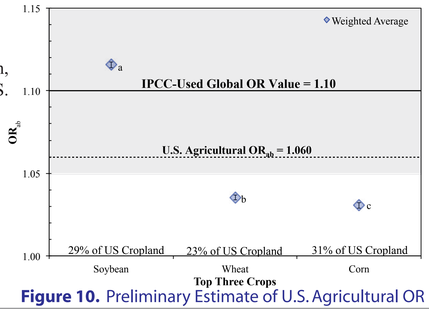

Figure 10. Preliminary Estimate of U.S. Agricultural OR

U.S. Agricultural OR Has Increased Over the Past 80 Years.

Using this approach we estimated the U.S. agricultural OR for each year (Fig. 12) from 1930-2010 using:

-U.S. Planted Acreage data (Fig. 11)

-Crop OR values for the top 3 crops

-ASSUMPTION: Crop OR has not change over time

OR for Top 3 Crops (by acreage):

-1963-2010:

- -Soybean: 1.112
- -Wheat: 1.035
- -Corn: 1.030

-1930-1962:

- -Wheat: 1.035
- -Corn: 1.030
- -Oat: 1.081

(Estimated from biochemical composition data; Nelson & Baldock 2005)

Decadal Averages (Fig. 12)	
1930s: 1.042±0.000	1970s: 1.054±0.002
1940s: 1.043±0.000	1980s: 1.056±0.001
1950s: 1.043±0.001	1990s: 1.056±0.002
1960s: 1.047±0.004	2000s: 1.059±0.001

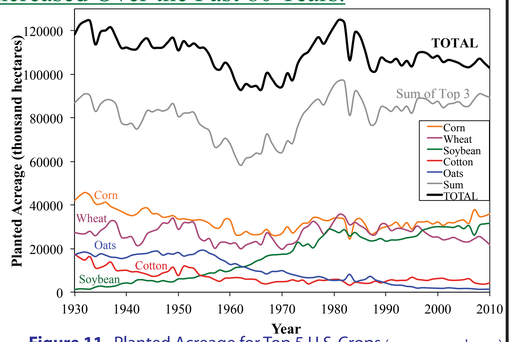

Figure 11. Planted Acreage for Top 5 U.S. Crops (www.nass.usda.gov)

U.S. Agricultural OR shifts from 1.04 in 1930 to 1.06 in 2010.

Shifts in crop acreage (e.g. increase soybean acreage) has led to the increase in agricultural OR with time.

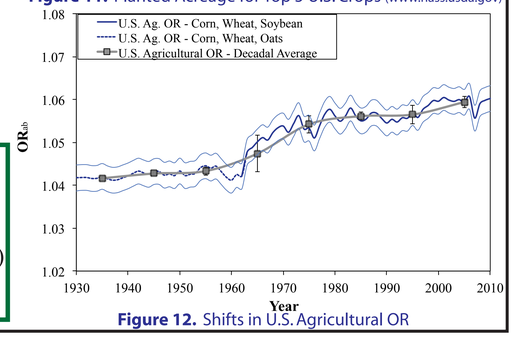

Figure 12. Shifts in U.S. Agricultural OR

Conclusion

Shifting demand for crops can lead to significant changes in U.S. agricultural OR through land use change.

Using an OR value that is too high (1.10 compared to 1.06), can lead to underestimating and overestimating the sizes of the terrestrial biosphere and ocean C sinks, respectively.

Future Work

In order to better constrain the sizes of the terrestrial biosphere and ocean C sinks, we need to better constrain the terrestrial biosphere's OR. OR data for other major ecosystems, including tropical forests, boreal forests, peatlands, and temperate forests need to be collected to estimate a true global terrestrial biosphere OR.

Ecosystem or Plant Type	OR
Soybean	1.112
Coniferous Forest Leaf Litter	1.060
Poplar Tree Bole	1.056
Weeds Mixture	1.036
Wheat	1.035
Deciduous Forest Leaf Litter	1.034
Goldenrod	1.034
Corn	1.030
Red Clover	1.021
Timothy	1.013

Acknowledgements

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References

Gallagher M.E. et al. (In Press). "Biochemical Suitability of Crop Residues for Cellulosic Ethanol: Disincentives to Nitrogen Fertilization in Corn Agriculture." Environmental Science & Technology.

Hockaday, W.C., et al. (2009). "Measurement of soil carbon oxidation state and oxidative ratio via ^{13}C nuclear magnetic resonance." JGR-Biogeosciences. 114.

Keeling, R.F., et al. (1996). "Global and Hemispheric CO_2 Sinks Deduced from Changes in Atmospheric O_2 Concentration." Nature. 381: 218-221.

Masiello, C.A., M.E. Gallagher, et al. (2008). "Evaluating 2 experimental approaches for measuring ecosystem carbon oxidation state &oxidative ratio." JGR-Biogeosciences. 113.

Nelson, P.N. and J.A. Baldock. (2005). "Estimating the Molecular Composition of a Diverse Range of Natural Organic Materials from Solid-State ^{13}C NMR & Elemental Analyses." Biogeochemistry. 72: 1-34.

Randerson, J.T., et al. (2006). "Is Carbon within the Global Terrestrial Biosphere Becoming More Oxidized? Implications for Trends in Atmospheric O_2." Global Change Biology. 12(2): 260-271.

Seibt, U., et al. (2004). "Observations of O_2:CO_2 Exchange Ratios During Ecosystem Gas Exchange." Global Biogeochemical Cycles. 18.

Severinghaus, J.P. (1995). Studies of the Terrestrial O_2 and Carbon Cycles in Sand Dune Gases and in Biosphere 2, Columbia University. Doctor of Philosophy.

Stephens, B.B., et al. (2007). "Application of a differential fuel-cell analyzer for measuring atmospheric O_2 variations." Journal Of Atmospheric &Oceanic Technology. 24, 82-94.