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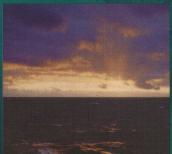
W. STEFFEN
A. SANDERSON
P. D. TYSON
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P. A. MATSON
B. MOORE III
F. OLDFIELD
K. RICHARDSON
H. J. SCHELLNHUBER
B. L. TURNER II
R. J. WASSON

## Global Change and the Earth System

A Planet Under Pressure











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# Global Change and the Earth System

**A Planet Under Pressure** 

With 258 Figures



#### **Authors**

Steffen, Will

IGBP Secretariat.

Royal Swedish Academy of Sciences, Stockholm

Sanderson, Angelina

IGBP Secretariat,

Royal Swedish Academy of Sciences, Stockholm

Tyson, Peter

Climatology Research Group,

University of the Witwatersrand, Johannesburg, South Africa

Jäger, Jill

Coordinator,

Initiative on Science and Technology for Sustainability

Matson, Pamela

School of Earth Sciences

Stanford University, CA, USA

Moore III, Berrien

Institute for the Study of Earth, Oceans and Space (EOS), University of New Hampshire, Durham, NH, USA

Oldfield, Frank

Department of Geography, University of Liverpool, UK

Richardson, Katherine

Department of Marine Ecology,

Århus University, Denmark

Schellnhuber, H. John

Tyndall Centre for Climate Change Research, University of East Anglia, Norwich, UK,

Potsdam Institute for Climate Impact Research, Germany

Turner, B. L. II

Graduate School of Geography & George Perkins Marsh Institute,

Clark University, MA, USA

Wasson, Robert J.

Centre for Resource and Environmental Studies The Australian National University, Canberra

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### Box 4.11. Emission of CO<sub>2</sub> from Riverine Systems

Jeffrey E. Richey

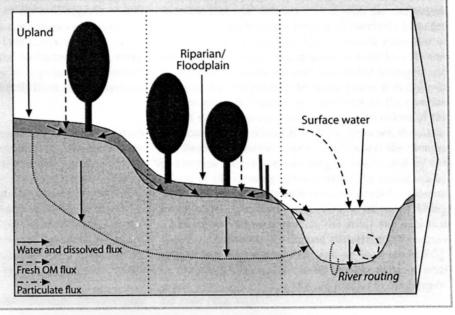
The partial pressure of carbon dioxide dissolved in river water  $(pCO_2)$  represents a deceptively simple expression of the coupling of the water and carbon cycles between terrestrial and fluvial environments. The distribution of  $pCO_2$  across a river basin is a function of a long sequence of complex biological and weathering processes and interactions, reflecting both internal carbon dynamics and external biogeochemical processes in upstream terrestrial ecosystems. The downstream expression of this coupling is the amount of organic matter and dissolved inorganic carbon mobilised to and through a river system, augmented by in-stream or riparian primary production and respiration. Perhaps the most evocative aspect of  $pCO_2$  is that it is almost always present at concentrations much greater than the atmosphere (that is, it is supersaturated). The question is why, and what are the implications?

What are the sources of pCO2, both direct and indirect (Fig. 4.32)? Total dissolved inorganic carbon (DIC) is produced via weathering, as the dissolution of primarily carbonate rocks. This process establishes the alkalinity and influences the pH of water, which governs the subsequent partitioning of DIC between pCO2, bicarbonate, and carbonate ions. The DIC in groundwater is enriched many-fold by the CO<sub>2</sub> produced by the decomposition of organic matter in soils (in productive environments, soil CO<sub>2</sub> may be hundreds of times supersaturated relative to the atmosphere). Hence the DIC entering a stream has both an inorganic weathering component, and an organically-produced respiration component. The land also exports organic matter as dissolved organic carbon (DOC) in groundwater. The DOC available for export to rivers represents a balance between production of fresh DOC via the solubilisation of soil organic matter and the adsorption to mineral particles. Particulate organic carbon (POC) enters rivers from the erosion of soils (typically older materials) and as leaf litter (typically newly-produced). Both DOC and POC may be mineralised within rivers, producing pCO2. These are all considered as external, or allochthonous, sources. The in situ (autochthonous) production and respiration of organic matter (by plankton and attached aquatic plants) can both consume and produce pCO2. The relative balance of autochthonous relative to allochthonous sources and sinks for pCO2 indicates what processes are dominant. The only way that pCO2 can exist at supersaturated conditions is if allochthonous sources dominate, and the waters are net heterotrophic, fueled by carbon from land.

In fact, pCO2 is present at elevated levels in most rivers of the world, from small streams to large rivers. Kempe (1982) called early attention to the elevated levels of pCO2 in many rivers, and that this was a sensitive indicator of the sources for river respiration. Jones and Mulholland (1998) analysed a time series of elevated pCO2 in a small temperate stream. Cole and Caraco (2001) computed that the average pCO2 concentration in 47 rivers averaged 3230 µatm, or nearly 10 times saturation. Similar conclusions can be drawn from a wide survey of the literature. There are two important consequences of this. The first is that by far the majority of this CO2 must be derived from the respiration of organic matter of terrestrial origin (allochthonous production). If the pCO<sub>2</sub> were derived from primary production within the water (autochthonous production), the pCO<sub>2</sub> would be near or below equilibrium (which certainly happens in localised environments). The second consequence is that according to the rules of gas exchange, this CO2 is outgassed (evaded) back to the atmosphere (that is, it becomes a source of CO2 to the atmosphere). In toto, the export of CO2 and organic matter from land to rivers constitutes a significant sink of terrestrial net ecosystem pro-

How large is the return flux (outgassing) of CO2 to the atmosphere? Telmer and Veizer (1999) computed that outgassing was about 30% of the DIC export in the Ottawa River. Applying that ratio to the global export of DIC to the ocean, they computed that the flux of CO2 to the atmosphere from rivers would be 0.13 Pg yr-1, or about an order of magnitude higher than early estimates (e.g., Kempe 1982). Cole and Caraco (2001), using a gas exchange coefficient from the Hudson River, 47-river average as representative of flowing waters in general, and assuming that rivers cover -0.5% of land surface area, computed a global outgassing of ~0.3 Pg C yr-1. More recently, Richey et al. (2002) computed that outgassing of CO2 from rivers and wetlands of the central Amazonian basin was about 1.2 Mg C ha-1 yr-1, an amount comparable to conservative estimates of carbon storage in the Amazon (i.e., an equivalent partitioning of net ecosystem production). Extrapolated across the entire basin, this would produce a flux of about 0.5 Pg yr<sup>-1</sup> from the Amazon alone. This is an order of magnitude greater than the fluvial export of organic carbon and DIC from the Amazon to the ocean. In contrast to other studies, this calculation emphasised the full drainage network, from first-order streams to the river

Fig. 4.32. Fluxes of carbon from terrestrial ecosystems and the atmosphere to riverine systems



mainstem and flood-plains, and was done for a specific region of the humid tropics. Assuming that the humid tropics behaves uniformly, then the total outgassing from the tropics would be about 0.9 Pg yr<sup>-1</sup>. If the estimates of the tropics are then added to the estimates for more temperate systems, total outgassing likely exceeds 1 Pg yr<sup>-1</sup>.

The outgassing of CO<sub>2</sub> is supported by extensive oxidation of organic matter of terrestrial origin within the river systems. This raises a very interesting question. The prevailing wisdom is that riverborne organic matter is already very refractory and not subject to oxidation (after centuries on land). There is evidence based on <sup>14</sup>C that the mix of dissolved and particulate organic matter in transport is of variable ages but often quite old, and that the production of CO<sub>2</sub> in rivers is supported by old carbon (Cole and Caraco 2001; Raymond and Bauer 2001). That is, organic C that had resided in soils for centuries to millennia without decomposing is then decomposed in a matter of a few weeks in the riverine environment. Thus, pre-aging and degradation may alter significantly the structure, distributions and quantities of terrestrial organic matter before its delivery to the oceans.

It is necessary to put the outgassing flux into context by relating it back to current views of the role of rivers in the global carbon cycle (Richey et al. 2003). As the main pathway for the ultimate preservation of terrigenous production in modern environments, the transfer of organic matter from the land to the oceans via fluvial systems is a key link in the global carbon cycle, hence the role is most typically expressed as the fluvial export of total organic and dissolved inorganic carbon to the ocean. These fluxes are in the range of 0.2-0.4 Pg yr<sup>-1</sup> for DOC, 0.2-0.5 Pg yr<sup>-1</sup> for POC, and 0.4 Pg yr<sup>-1</sup> for DIC. On the order of 0.2-1 Pg yr<sup>-1</sup> may be stored in reservoirs and as part of overall continental sedimentation. As a global aggregate, there would appear to be a net sink (between continental sedimentation and marine sedimentation and dissolution) of ~1 to 1.5 Pg yr<sup>-1</sup>. As bulk numbers, these sinks are partially compensated for by the outgassing. But it is likely that these processes are very geographically disperse, with the continental sedimentation occurring in northern temperate regions, and much of the marine sedimentation and outgassing occurring in more tropical regions.

Overall, this sequence of processes suggests that the organic carbon that is being respired is translocated in space and time from its points of origin, such that over long times and large spatial scales, the modern aquatic environment may be connected with the terrestrial conditions of another time (Richey et al. 2003). Linkages between land and water would be stronger than traditionally thought, with river corridors representing a significant downstream translocation of carbon originally fixed on land.