

Computing Methane Solubility in Reservoir Waters Using Remote Sensing Data

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Abstract. There have been many experimental investigations on the methane solubility in pure and impure water. However, these investigations cover only limited temperature-pressure domains that are inconvenient for some special environments as tropical hydroelectric reservoirs. In this paper we show that due to the complex temperature variation and water composition, measured in Brazilian tropical reservoirs as *Serra da Mesa* and *Manso*, expressive secular variation on the traditional solubility constants (concentration of a species in the aqueous phase by the partial pressure of that species in the gas phase) can change in a rate of approximately 15% in 10 decades. This estimation comes from a computational analysis of temperature variation measured during 6 months in *Serra da Mesa* and *Manso* reservoirs taking into account a simulated density and molar mass variation of the aqueous composition in these environments. As an important global change issue from this preliminary analysis, we discuss its role in the current estimations on the concentration, emission rates, mitigation and recovery of gas emissions from hydroelectric dams, mainly considering secular scales greater than 60 years which justifies developing satellite observational missions dedicated to monitoring water volatility as a function of the biomass in reservoir environments.

Palavras-chave: water reservoirs, Henry's law, water temperature, methane, remote sensing.

1. Introduction

Atmospheric greenhouse gases (GHG) concentration has increased during the past centuries basically due to biogenic and pyrogenic anthropogenic emissions (Ferretti et al., 2005). Recent investigations have shown that gas emission (methane as an important example) from Tropical Hydroelectric Reservoirs (THR) may comprise a considerable fraction of the total anthropogenic bulk. In THR, water intakes are generally located well below the surface where CH₄ concentrations are greater than 6 mg/l (Abril et al. 2005). Much of the dissolved gas is quickly degassed when the pressure drops as the water passes through the turbines. In order to evaluate the concentration of gases of potential importance in environmental chemistry, the solubility of such gases have been collected and converted into a uniform format using the Henry's law, which states that the solubility of a gas in a liquid is directly proportional to its partial pressure. However, the Henry's law can be derived as a function of temperature, density, molar mixing ratio in the aqueous phase and molar mass of water (Sander, 2006). One of the main limnological variables, the water temperature, in the context of determining the Henry's

constant, can be measured through the Brazilian automated system for environmental monitoring.

The automated *System for Environmental Monitoring* (SIMA) was developed in partnership between the Vale do Paraíba University (UNIVAP) and the National Institute of Space Research (INPE). It is a set of hardware and software designed for data acquisition and real time monitoring of hydrological systems (Stevenson et al. 1993; Stech et al. 2006). It is formed by an anchored buoy, in which sensors, data storage systems, battery and the transmission antenna are fixed (Fig. 1a). The data are collected in preprogrammed time intervals and are transmitted by satellite in quasi-real time for any user in a range of 2500 km from the acquisition point.

As shown in Figure 1b, three stations were placed in hydroelectric reservoirs: Tucuruí and Serra da Mesa in the Araguaia-Tocantins basin (region of tropical forest and savanna, respectively), and APM-Manso in north of Paraguai basin (region of savanna and tropical forest). These stations serve as models of environments modified by anthropic action and subject to pressures of public development policies. The last one was installed in Lake Curuai, located in the low Amazon River floodplain (tropical forest) and represents an almost pristine area where human activities exert negligible environmental impact.

Water temperature time series collected by the SIMA stations present hourly values at 2-m depth. In Figure 1c is shown the corresponding time series measured in Manso reservoir from 19 January to 23 March 2004. Despite the parameters being observed at a single point, which is a drawback for spatial application, the continuous data acquisition generates a high resolution temporal accompaniment of the water temperature variation whose average, in secular scales, can act on the determination of the THR water quality. Thus, it is important to know the influence of secular water temperature variation on the traditional solubility constants as given by the Henry's law.

2. Gas Solubility in Reservoir Waters

In the Amazon region, diffusive methane fluxes at the reservoir surface are smaller in deeper water because they have a higher probability of being oxidized before reaching the water-air interface (Lima et al. 2005). The water bulk is thermally stratified, with a thermocline usually at roughly 10m below the surface, which prevents water mixing and diffusion between deep and shallow waters. This complex scenario favors a CH₄ concentration profile that increases rapidly with depth towards the methanogenic sediments. Besides, thermal inhomogeneity in the water composition is far from pure water due to the presence of solutes and suspended particles. However, GHG concentrations in THR have been calculated based on the solubility of high quality water whose temperature standard deviation is taken as very low. Recent accurate model for calculating methane solubility and gas phase composition of methane-bearing aqueous fluids have been performed (Duan and Mao, 2006). In this context, is considered, implicitly, the Henry's law which states that the solubility of a gas in a liquid is directly proportional to its partial pressure. Actually, there are several ways of describing the solubility of a gas in water. Usually the Henry's law constant k_H is defined as $k_H \equiv c_a / p_g$ where c_a is the concentration of a species in the aqueous phase and p_g is the partial pressure of that species in the gas phase. In standard conditions is assumed a constant

water temperature of 298.15 K. A simple way to describe Henry's law as a function of temperature is (Sander, 2006):

$$k_H(T) = k_H^* \exp\left[\frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T^*}\right)\right], \quad (1)$$

where $\Delta H/R$ is the rate between the solution enthalpy and the gas constant, and k_H^* is the value of Henry's constant when $T^* = 298.15$ K. Here, T is the average temperature that can be calculated from the annual temperature variation measured by our SIMA. Recent estimates of the climate sensitivity lead to global average surface warming by 2100 of between 2°C and 6°C (Annan and Hargreaves, 2006). According to the global heating change in our approach one can expect an extreme secular temperature water variation following a linear annual rule as $T(i+1)=T(i)+0.06$, where i represents a year resolution. Taking into account the methane gas and calculating the mean of water temperature measured by SIMA in Manso and Serra da Mesa, our algorithm can be written as:

$$k_{H,T}(i+1) = 1.4 \times 10^{-3} \exp\left[-1.700 \left(\frac{1}{T(i)+0.06} - \frac{1}{298.15}\right)\right]. \quad (2)$$

$$T_0 = 299.65 \text{ K},$$

where T_0 is the average estimated from the SIMA measures collected from January 2004 to January 2006.

3. Results and Interpretation

The algorithm above express a secular variation on the traditional solubility constants (concentration of a species in the aqueous phase by the partial pressure of that species in the gas phase), values that can change in a rate of approximately 15% in 10 decades (See Table 1). This estimation comes from a computational analysis of temperature variation measured during 24 months in Serra da Mesa and Manso reservoirs. Preliminary results are also considered taking into account a simulated density and molar mass variation of the aqueous composition in these environments. As an important global change issue from this preliminary analysis, we stress the importance of this approach in the current estimations on the concentration, emission rates, mitigation and recovery of gas emissions from hydroelectric dams, mainly considering secular scales greater than 50 years.

Note that one can also estimate the volatility instead of solubility. In this case the volatility will be a function of the molar mixing ratio of the aqueous phase, density of water and molar mass of water, all depending on the solutes and suspended material produced in the THR environment. However, such characteristics can be observed in detail when high resolution spatio-temporal data are provided. This image information demand justifies developing satellite observational missions dedicated to monitoring water reservoir environments.

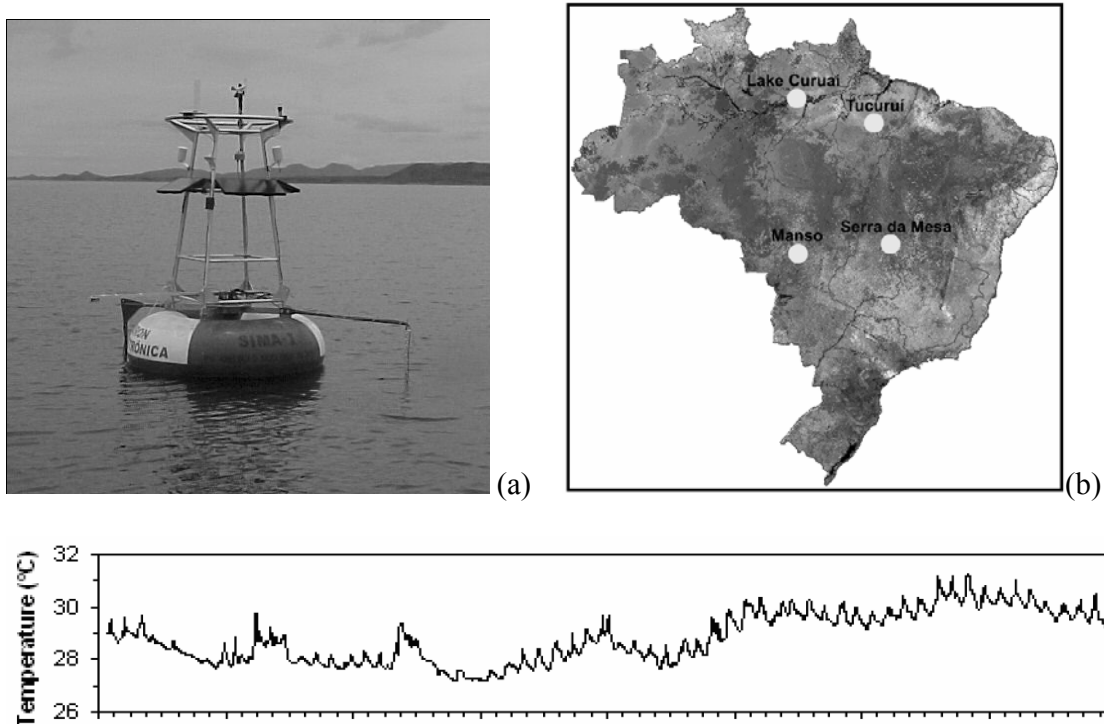


Figure 1. (a) Photo of the SIMA installed at *Manso* Reservoir. (b) Location of *Curuai* lake, *Serra da Mesa*, *Manso* and *Tucuruí* reservoirs. (c) An example of water temperature profile at 2-m depth collected from SIMA at *Manso* reservoir (1512, 1h time resolution, measurements from jan 19 to march 23, 2004).

Year	$\langle T \rangle (^{\circ}K)$	k_H
2005	299.65	0.001441
2055	302.65	0.001524
2105	305.95	0.001619

Table 1. Some representative output values from the computation given by equation 2.

4. The Role of Satellite Observations

Remotely sensed data obtained from satellites could provide secular estimates of water microbiomass composition and temperature distribution within high accuracy. As an example, shown in Figure 2, Color composite of Landsat TM bands 3, 4 and 5 at the scale 1:250.000 have been used to evaluate the biomass evolution in the Amazon reservoirs with great accuracy (Lima et al. 2002).

Based on remote sensing technology, especially that applied to the oceanographic research, new specific satellite applications should be developed in order to provide spatio-temporal measures for water composition and water temperature in THR. In this sense, changes in high frequency water quality and other environmental variables measured by the SIMA coupled with satellite data can be used to better understand the connections between GHG emissions from aquatic ecosystems as THR and oceanic surface (Hoppe et al. 2002).

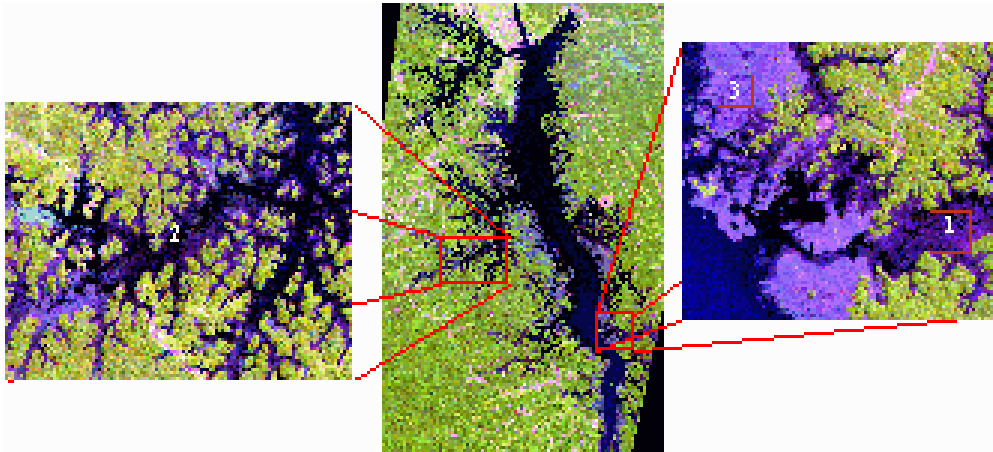


Figure 2. Landsat-TM high resolution image from *Tucuruí* reservoir, from where some quality water details, as macrophyte distribution on the water, that is direct product from the biomass amount, can be characterized by color contrast.

5. Concluding Remarks

In summary, we have shown that the secular variation of water solubility (or volatility) in a particular THR should be explicitly dependent of both water temperature and water composition. In this sense, automatic monitoring system of limnological variables supported by spatially high resolution radar orbital images could provide a more comprehensive assessment of the role of the THR as source of GHG. Thus, the investigation of different time and space processes of water reservoir requires sequenced and synoptic data, which can be better provided by the integration of remote sensing technology. Once long term environmental time series of continuously collected data are fundamental to performing the identification and classification of pulses and determining its role in aquatic systems, particularly in the variability of greenhouse gas emissions (Fernside, 1995; Rosa and Schaeffer, 1995; Ramos et al., 2006), this approach is essential for addressing the main issues of the 21st century environmental agenda, which focus on global change and sustainable development.

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