Extreme event dynamics in methane ebullition fluxes from tropical reservoirs

Fernando M. Ramos,[1] Ivan B. T. Lima,[1,2] Reinaldo R. Rosa,[1] Edmar A. Mazzi,[2] João C. Carvalho,[1] Maria F. F. L. Rasera,[2] Jean P. H. B. Ometto,[2] Arcilan T. Assireu,[1] and José L. Stech[1]

[1] Tropical hydroelectric reservoirs generally constitute an appreciable source of CH_4 (methane), a potent greenhouse gas. In this letter, we investigate the statistical characteristics of methane ebullition fluxes in hydroelectric reservoirs. To this end, we use CH_4 flux measurements obtained in Manso (wet season, 2004) and Corumbá (dry and wet seasons, 2005) reservoirs, located respectively in Mato Grosso and Goiás, Brazil. Methane ebullition fluxes were measured using open dynamic chambers, connected to an infrared photo-acoustic trace gas analyzer (TGA). Our main result indicates that when properly rescaled, all methane ebullition data collapse into a single statistic well described by a Generalized Pareto distribution, with shape parameter well above zero. The approach presented here, which combines high-frequency CH_4 ebullition data and Extreme Value theory analytical tools, shows that, although bubbling patterns appear to be highly complex and unpredictable, they may still be described by a rather simple (but non trivial) dynamics. **Citation:** Ramos, F. M., I. B. T. Lima, R. R. Rosa, E. A. Mazzi, J. C. Carvalho, M. F. F. L. Rasera, J. P. H. B. Ometto, A. T. Assireu, and J. L. Stech (2006), Extreme event dynamics in methane ebullition fluxes from tropical reservoirs, *Geophys. Res. Lett.*, *33*, L21404, doi:10.1029/2006GL027943.

1. Introduction

[2] Tropical hydroelectric reservoirs may constitute an appreciable source of methane (CH_4) to the atmosphere [*Rudd et al.*, 1993; *Svensson and Ericsson*, 1993; *Novo and Tundisi*, 1994; *Duchemin et al.*, 2000; *Fearnside*, 2002; *Abril et al.*, 2005; *Lima*, 2005]. Methane is produced under anaerobic conditions in the sediment layer at the bottom of the reservoir; acetate and CO_2 reductions are the main methanogenic pathways [*Cicerone and Oremland*, 1988; *Whalen*, 2005]. Methane is exported from the sediment by ebullition or by diffusion. Diffusive export from anoxic sediment is largely depleted by methane-oxidizing bacteria in oxic sediment or water, while ebullition results in direct flux of methane bubbles from the sediment to the atmosphere, with limited methane oxidation in the water column. [*Bastviken et al.*, 2004; *Lima*, 2005]. Ebullition is quantitatively most important, accounting in average for 40–60% of the open water emissions, but ebullition is also highly variable, and more difficult to measure than other emission components [*Bastviken et al.*, 2004]. Moreover, in tropical reservoirs, bubbling fluxes are marred by either failure to comply with normality or insufficiency of data [*Soumis et al.*, 2005]. For these reasons, ebullition dynamics, mainly in tropical areas, remains poorly understood, a fact that represent a serious limitation for providing more robust regional and global estimates of CH_4 emissions.

[3] Considering the importance of CH_4 as a greenhouse gas, theoretical and empirical emission models have been proposed. Most are process-based models that relate *time-averaged* (i.e., integrated over several days or seasons) methane fluxes to climatic, geophysical, and biogeochemical factors. In this letter we follow a different path, directly inspired on the approach usually used in the study the of small-scale turbulence phenomenology [*Frisch*, 1995]. Here, we look for a probabilistic description of *quasi-instantaneous* methane fluxes from reservoirs. Although emission patterns appear to be highly complex and unpredictable, our goal is to advance the current knowledge about the following two fundamental questions: (1) Is there a *universal* (i.e., independent of local characteristics) statistical framework for describing CH_4 ebullition fluxes? (2) Is there a *simple* stochastic process that (possibly) underlies the dynamics of methane ebullition in tropical reservoirs, and that reproduces the statistical features observed empirically? Our general aim is to shed some light on this relevant and intricate pathway of carbon to the atmosphere. To this end, we combine experimental data from three field campaigns over a wide range of local conditions.

2. Experimental Data

[4] Flux measurements were conducted at the hydroelectric reservoirs of Manso (wet season, March 2004) and Corumbá (wet and dry seasons, March and August 2005), both built over savanna (*Cerrado*) vegetation, respectively in Mato Grosso and Goiás, Brazil. In Corumbá (flooded in 1997; location: 17°45′S, 48°34′W), data were collected over clay-rich areas; in Manso (flooded in 2001; location: 14°57′S, 55°45′W), over sandy sediments.

[5] Gas fluxes were measured using open, floating dynamic chambers. A schematic illustration showing the basic experimental set-up is presented in Figure 1 (left). Open dynamic (or airflow) chambers (DCs) have been previously used in air-soil gas efflux measurements [*Carpi and Lindberg*, 1998; *Fang and Moncrieff*, 1998; *Subke et al.*, 2003]. Closed DCs were developed and deployed by

[1]National Institute for Space Research, São José dos Campos, Brazil.
[2]Laboratory of Isotope Ecology, Nuclear Energy Center for Agriculture, Piracicaba, Brazil.
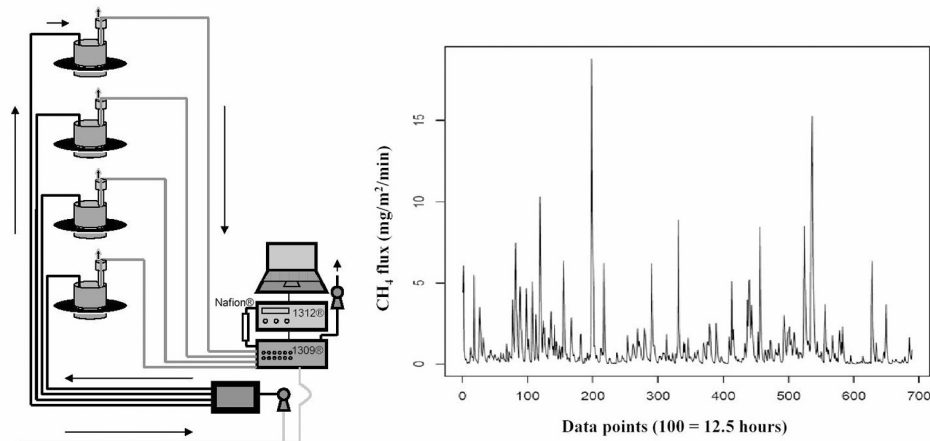
Figure 1. (left) Experimental set-up and (right) one of the data sets, measured in Corumbá (Aug. 2005; chamber 3), comprising 689 measurement points, or more than 86 hours of monitoring.

Sebacher and Harriss [1982] in the 1980s for studies of methane fluxes in wetlands. This approach was later used by *Crill et al.* [1988]. The use of open DCs connected to a photoacoustic gas analyzer for air-water flux measurements was first proposed by *Lima et al.* [2005b], although similar approaches are given by *Yamulki and Jarvis* [1999] and *Christensen et al.* [2003]. In an open DC, there is a continuous airflow within the chamber that allows a quasi-instantaneous flux sampling. The main advantage of this technique is the continuous monitoring during long periods, and the ability to capture the flux dynamics (for instance, intermittent ebullition events) at short time scales. The DCs were placed over water ranging from 0.4 to 11 m in depth. Each DC was equipped with a quick connector in the top plate to allow pumping of shoreline atmospheric air into the chamber. A chimney-like system permitted exit air to flow ashore to the measuring instrumentation. The design allowed continuous airflow inside the chamber, minimizing temperature fluctuations, by means of an external thermal insulation, and pressure variation effects, through an aperture to the atmosphere. Two Charles Austen Capex-V2 pumps connected to nylon tubes were used to drive shoreline atmospheric air into the chambers at a constant flow rate of ca. 0.3 L/min. A photoacoustic trace gas analyzer (TGA) Innova 1312 was used to determine trace gas concentrations. The instrument was calibrated, including a correction for water vapor (which was also measured) and appropriate cross interference calibrations. A multisampler Innova 1309 automatically switched the outlet (inlet) air from the chambers through nylon tubes to the TGA. The methane flux (mg/m^2/min) is calculated by $\Phi = f\,(C_o - C_i)/A$, where A corresponds to the water surface exchange area (m^2), f to the airflow (m^3/min) and C_o and C_i respectively to the outlet and inlet concentrations (mg/m^3). Temperature was assumed constant (25°C), while the multisampler corrected for air pressure changes. The sampling periods were approximately 5 min (March 2004, Manso), 5 min (March 2005, Corumbá), and 7.5 min (August 2005, Corumbá). The influence of water vapor at low methane concentrations was circumvented by dehumidifying equally the air enter-

ing and exiting the chamber by means of a Nafion (trademark) dryer (see Figure 1).

3.   Results and Discussions

[6]   Figure 1 (right) shows one of the data sets collected at Corumbá (Aug. 2005; chamber 3), comprising 689 measurement points, or more than 86 hours of monitoring. The series of spikes are characteristic of ebullition events. Figure 2 shows empirical histogram log-log plots for all measurements (comprising 14 data sets), after properly rescaling the data by $(x - \langle x \rangle)/s_2$, where $\langle x \rangle$ and s_2 are, respectively, the mean and the standard deviation of each time-series. The subtraction of the mean flux from the original signal permits to extract the relative contribution of ebullition, here defined as large episodic events of CH$_4$ emission. This procedure is similar to the one proposed by *Christensen et al.* [2003] to quantify bubbling fluxes. The relative contribution of ebullition varied across data sets but was on general above 50%. Although the measurements were made under different local
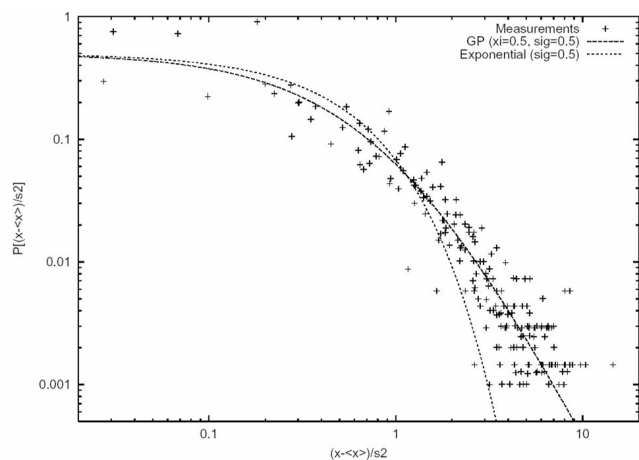

Figure 2. Empirical histogram log-log plots for all measurements, after properly rescaling the data. Generalized Pareto ($\xi = 0.5$, $\sigma = 0.5$) and exponential ($\sigma = 0.5$) distributions.
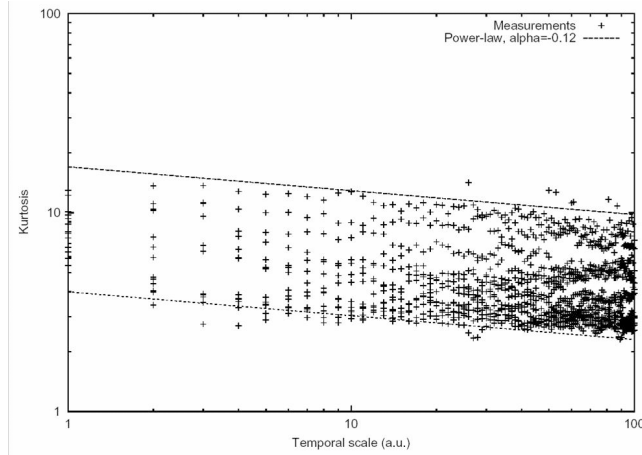
Figure 3. Log-log plot of the kurtosis $K(\Delta t) \equiv \langle\Delta\Phi^4\rangle/\langle\Delta\Phi^2\rangle^2$ of CH$_4$ flux differences $\Delta\Phi = \Phi(t + \Delta t) - \Phi(t)$ against the time lag Δt.

conditions (i.e., different reservoirs, climate and water depths), all rescaled data points collapse into a similar pattern, which is well approximated by a Generalized Pareto (GP) distribution, with shape parameter $\xi = 0.5$, and scale parameter $\sigma = 0.5$. GP distributions typically arise in the analysis of extreme events. Extreme events are those phenomena described by the tails of the probability distribution [*Coles*, 2001; *Katz et al.*, 2002, 2005]. One of the main analytical results of Extreme Value theory states that the statistics of exceedances over a sufficiently high threshold of an independent, identically distributed random variable converge to a GP distribution [*Coles*, 2001]. The GP distribution has a cumulative distribution function given by $H(x; \xi, \sigma) = 1 - (1 + \xi x/\sigma)^{-1/\xi}$, for $\xi \neq 0$. For $\xi = 0$, an exponential distribution is recovered with $H(x; \xi, \sigma) = 1 - e^{-x/\sigma}$. Positive shape parameters, like the one estimated for our data ($\xi = 0.5$), corresponds to a heavy-tailed distribution, indicating the presence of rare, intense events, which in the present context corresponds to the arrival of large bubbles of CH$_4$ at the surface. The exponential distribution ($\xi = 0$) with same scale parameter σ as the GP, decreases too steeply to model properly the events in the low-probability extremes of the empirical histograms. In practice, this result is particularly relevant because natural systems which exhibit extreme event dynamics are not well described by central values and typical fluctuations [*Sornette*, 2006]. In this class of systems, the largest values dominate their long term trends as much as the largest terms dominate a sum of random variables with a power-law probability distribution function (provided its tails decay slow enough).

[7] A positive ξ also indicates the presence of long-range correlations or memory in the data being modeled. Indeed, although at longer time scales ebullition events are uncorrelated, we found that, in several data sets, the high-frequency end of the power spectra (not shown) follows a scaling similar to the one typically obtained from turbulence data [*Frisch*, 1995]. Ebullition fluxes are primarily related to the net production rate in the sediments and the hydrostatic pressure which has to be overcome for the bubbles to leave the sediment [*Bastviken et al.*, 2004]. However, it is well known that exchanges of physical and chemical

properties in lakes and reservoirs are driven by wind- and heat flux-induced turbulence [*Crill et al.*, 1988; *Engle and Melack*, 2000; *MacIntyre et al.*, 2001; *Lima et al.*, 2005a; *Lorenzzetti et al.*, 2005]. Hence, it is somewhat natural to find fingerprints of a turbulence-like process, with some sort of cascade phenomenology underlying it, in the dynamics of methane ebullition. Figure 3 shows the log-log plot of kurtosis $K(\Delta t) \equiv \langle\Delta\Phi^4\rangle/\langle\Delta\Phi^2\rangle^2$ of CH$_4$ flux differences $\Delta\Phi = \Phi(t + \Delta t) - \Phi(t)$ against the time lag Δt. The kurtosis of all data sets follow approximately a similar power-law trend $K(\Delta t) \sim \Delta t^\alpha$. For comparison, we also plot straight lines corresponding to an exponent $\alpha = -0.12$, which is close to the kurtosis scaling found theoretically and experimentally in fully-developed turbulence [*She and Leveque*, 1994; *Benzi et al.*, 1995].

[8] An exponent $\alpha \neq 0$ implies that the scaling exponents ζ_n of structure functions $\langle\Delta\Phi^n\rangle \sim \Delta t^{\zeta_n}$ depend nonlinearly on n, meaning that $\Delta\Phi$ statistics are *not* self-similar, which is consistent with a multifractal description of CH$_4$ ebullition variability [*Paladin and Vulpiani*, 1987]. Multifractality generates signals that are intrinsically more complex and inhomogeneous than monofractals, and is a characteristic of nonlinear systems operating far from equilibrium [*Goldberger et al.*, 2002]. In order to independently check this result, we built a stochastic process which also displays multifractal properties. A simple way for obtaining multifractal measures is to construct a random multiplicative cascade (RMC) model of the type $\varepsilon_n = \varepsilon\, W_1 W_2 \ldots W_n$, with $W \geq 0$, $\langle W\rangle = 1$, $\langle W^q\rangle < \infty$ for any $q > 0$, where W_n is the n-th independent realization of a random variable W [*Meneveau and Sreenivasan*, 1991; *Frisch*, 1995]. Multiplication cascades, as defined above, are a well-known path to generate extreme fluctuations of the type we observed in the data. In turbulence, the cascade model is formulated in terms of random fluctuations of the energy dissipation ε. In the present context, the cascade picture may represent a random sequence of events that, say, a bubble of methane is subject before arriving at the water/air interface (eventually measured as a concentration signal by our instrumentation). We implemented a RMC model with 15 steps and W log-normally distributed ($\langle W^2\rangle = 0.35$). As shown in Figure 4, the RMC model results correlate with the experimental data. Other RMC models (log-Poisson, for example)
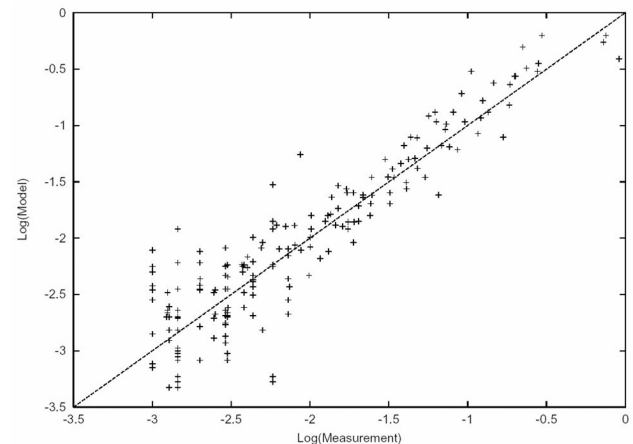

Figure 4. Random multiplicative cascade model results against the corresponding experimental data.

may yield equally good results but only larger data sets (i.e., measured with a shorter sampling period) will allow us to properly compare the performance of different RMC models. Since methane ebullition data is scarce and difficult to obtain, an immediate application of such a model is to generate synthetic bubbling fluxes with well defined statistical properties (for interpolation of missing data, for example). Moreover, if the kind of universality observed here is assumed, predictions for different locations or even different reservoirs can be made, only measuring the two characteristic parameters (necessarily local) of the GP distribution. In practice, the most popular method for measuring the parameters of the GP distribution is through maximum likelihood estimation [*Coles*, 2001].

4. Conclusion

[9] In summary, our main result indicates that when properly rescaled, methane ebullition data, gathered under different local conditions, collapse into a single statistic, described by a Generalized Pareto distribution, with shape parameter well above zero. The dynamics underlying this statistical behavior, which shows evidences of being modulated by turbulence intensity at the water-sediment interface, is well modeled by a multifractal, multiplicative random cascade. The approach presented here, which combines high-frequency CH$_4$ ebullition data and Extreme Value theory analytical tools, shows that, although bubbling patterns appear to be highly complex and unpredictable, they may still be described by a rather simple (but not trivial) dynamics.

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A. T. Assireu, J. C. Carvalho, I. B. T. Lima, F. M. Ramos, R. R. Rosa, and J. L. Stech, INPE, Avenida dos Astronautas 1758, 12227-010 São José dos Campos SP, Brazil. (fernando@lac.inpe.br)

E. A. Mazzi, J. P. H. B. Ometto, and M. F. F. L. Rasera, Laboratory of Isotope Ecology, CENA, Avenida Centenário 303, 13416-000 Piracicaba SP, Brazil.