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Effects of Relative Humidity on Temperature Dynamics in Natural Ecosystems: Comparison of Measured and Model-Predicted Data

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Abstract

Understanding the factors influencing temperature variations in natural ecosystems is crucial for processes such as species distribution, phenology, and carbon cycling. This article presents a theoretical framework that investigates the impact of relative humidity (*RH*) on these variations. Previous analyses based solely on environmental thermodynamics governed by radiation and the Stefan–Boltzmann law, named the *dry model*, revealed a nocturnal cooling rate of approximately 0.9 °C/h in low-relative-humidity conditions (<85%) using data of three distinct Brazilian forests within the Amazonian biome. However, this rate decreased significantly at higher *RH*, suggesting an additional heating effect, which is likely attributed to the coalescence of water molecules in the air. In this study, a novel *humid model* is developed, integrating terms proportional to *RH* and its time derivative. This model is based on the premise that clusters of water molecules and latent heat depend on the quantity of water molecules and intermolecular forces. The findings demonstrate a superior fit to the data using the proposed model, with R^2 values ranging from 0.7 to 0.95, effectively capturing both the nocturnal temperature decline and diurnal variations. This advancement is significant as it underscores the importance of considering water molecule clusters in developing a more precise model that improves upon the *dry model* methodology.

Keywords: water molecules; natural ecosystems; humidity; thermodynamic model; temperature dynamics



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1. Introduction

Understanding energy and matter transfer between the biosphere and atmosphere, crucial for studying ecosystem responses to environmental changes, relies on the principle of energy closure. This principle states that all incoming energy to an ecosystem is balanced by outgoing energy fluxes. However, achieving perfect energy closure in real-world measurements remains a challenge. One well-known issue is the lack of energy balance closure. When the energy fluxes are measured by the Eddy Covariance (EC) method, the sensible and latent heat fluxes are underestimated [1–3]. This underestimation has significant consequences for our understanding of ecosystem processes, such as evapotranspiration rates and CO₂ fluxes. Researchers have proposed several mechanisms to explain the persistent non-closure, attributing it to factors like: (i) turbulence dynamics: fluctuations in atmospheric conditions introduce uncertainties in energy budget closure assessments [4–6];

(ii) scale mismatch: when the measurement scale does not adequately capture the spatial variability of turbulent fluxes, it leads to underestimation [1]; (iii) EC method limitations: the frequency response of the EC system and data processing methods can introduce unavoidable biases, potentially underestimating energy fluxes [7].

In studying ecosystems, energy balance is estimated by measuring four energy fluxes: net radiation (R_n), sensible (H) and latent (Le) heat fluxes, and energy flux in the soil (G) [8]. However, these quantities are measured at different spatial scales: R_n is typically a point measurement in the top of a tower, G is measured within the soil, while H and Le represent a footprint covering a much larger surface area of thousands of square meters [9]. Much of the existing literature focuses on fluxes rather than the energy density of ecosystems, which would provide a more complete picture of energy distribution within an ecosystem at each point in space. Developing such approaches could help address the challenges associated with spatial mismatches in flux measurements.

Although the Eddy Covariance (EC) method is widely used for measuring turbulent fluxes, it has limitations, particularly in precisely measuring latent heat flux. This limitation arises due to several factors. The EC method relies on assumptions like stationarity (constant fluxes) and horizontality (constant wind direction with height), which can be violated in real-world scenarios with changing weather conditions.

A limitation of the Eddy Covariance (EC) method is its difficulty in accounting for spatial heterogeneity in water vapor distribution, especially in areas with mixed vegetation or surface types. If water vapor concentration (c_w) is uneven, EC may underestimate latent heat flux Le . The method estimates c_w using an infrared gas analyzer that measures absorption at a specific frequency and derives Le from the covariance between c_w and wind velocity [10]. However, EC assumes uniformly distributed single water molecules and does not account for molecular clusters. These clusters release or absorb latent heat during their formation or dissociation, respectively. The EC sensor might not detect the change from individual water molecules to molecular clusters because the infrared absorption coefficients of liquid water and vapor are not significantly different [11]. Consequently, the sensors may underestimate the variations in latent heat flux, particularly in situations where cluster formation is prevalent. Improving sensor sensitivity or developing alternative methods that capture this heterogeneity could enhance the accuracy of latent heat flux estimates.

Analytical models that describe the behavior of temperature in relation to relative humidity or other variables are not as common as models based on machine learning and neural networks, as cited in relevant studies [12–16]. Over-reliance on machine learning methods may sometimes limit our understanding of the fundamental physical processes governing climate. Our work contributes to the discussion and provides a less explored approach to the comparison of predictive climate models by utilizing analytical models, which offer greater transparency, allowing us to see how climatological variables like temperature and humidity influence climate behavior. Analytical models have shown great success in various areas of climatology and meteorology, offering conceptual clarity and computational efficiency. Notable examples include the Schwarzschild radiative transfer model [17], fundamental for understanding the greenhouse effect; the advection-diffusion equation, which describes the dispersion of substances in the atmosphere; and the Clausius–Clapeyron law, crucial for predicting changes in relative humidity as a function of temperature [18]. Additionally, the Monin–Obukhov similarity theory determines atmospheric profiles based on stability parameters and surfaces [19], while simplifications of the Navier–Stokes equations allow for the study of atmospheric fluid dynamics [20]. These models stand out not only for their practical applicability but also for providing a robust theoretical foundation that complements numerical and machine learning approaches.

In order to better understand the complex interactions within environmental systems, a more precise approach based on environmental non-equilibrium thermodynamics is fundamentally important. It allows us to study systems that are constantly exchanging energy and matter with their surroundings, which is a defining characteristic of most environmental systems. Through the application of information theory, prior research has indicated that temperature is the variable that holds the most information in environmental science, as it affects various processes, including plant growth, water cycles, and atmospheric dynamics [21]. Unfortunately, current methods for describing the hourly behavior of temperature often rely on empirical relations [22–28] that can miss the underlying physical processes governing how temperature changes in response to biosphere-atmosphere interaction.

In this framework, relative humidity is employed instead of water vapor concentration or partial pressure, overcoming the experimental limitations associated with point-based water vapor measurements and sensor sensitivity to molecular clusters.

2. Materials and Methods

2.1. Study Area and Experimental Data

Automated sensors were utilized to measure air temperature (T), net radiation (R), and relative humidity (RH) in three distinct Brazilian ecosystems: deep forest, border forest, and transitional forest, as shown in Figure 1. The employed sensors were the most commonly used in the micrometeorological research: NR-LITE, Kipp & Zonen, Bohemia, NY, USA, for net radiation, and psychrometer Campbell Scientific Inc.—HMP45AC for temperature and humidity measurements. The data were averaged every 30 min and stored using a solid-state data logger (CR5000, Campbell Scientific, Inc., Logan, UT, USA).

The deep forest measurements were conducted between January and December 2008 at a height of 60 m from a tower located in São Gabriel da Cachoeira (0.15° N; 66.45° W), an area that remains largely unaffected by human activities within the Amazon Forest. The average annual rainfall in this location ranges from 3000 to 3500 mm/y [29]. The border forest site, located in the Rebio-Rebio-Jaru Reserve (61.56° W; 10.46° S), is characterized by a mean canopy height of 33 m, where measurements were likewise conducted between January and December 2008. Despite being situated within the Amazon Forest, this site is close to agricultural zones (approximately 50 km away) with intensive agricultural activity. Consequently, the average annual rainfall in this location is considerably lower than that of the deep forest, at 2100 mm/y [30]. In the transitional forest, measurements were taken between January and December 2002, using a 40 m tower situated in an ecosystem that lies within a region between the Amazon Forest and Brazilian savannah (Cerrado) in a farm located in the municipality of Sinop (55.19° W; 11.25° S) [30]. The mean annual rainfall in this region is 2000 mm/y, with an approximately 28 m high canopy [31]. All three ecosystems have distinct dry (June–August) and rainy (December–March) seasons, although with markedly different precipitation rates. According to data from the Brazilian National Institute of Meteorology (INMET), the peak monthly precipitation during the rainy season and the minimum during the dry season are approximately 320 mm and 160 mm for São Gabriel da Cachoeira, 280 mm and 10 mm for Jaru, and 270 mm and 5 mm for Sinop, respectively [32].

The collected data include a range of variables such as air temperature, net radiation, and relative humidity. Air temperature and humidity measurements were taken using psychrometers (HMP 35, Vaisala, Inc., Helsinki, Finland), while radiation measurements were obtained using CNR1 net radiometers (Kipp & Zonen, Bohemia, NY, USA). The averages of the three variables were generated every 30 min and stored in data loggers. All sensors used in this study—namely, radiometers as well as temperature and humidity sensors—were initially calibrated by their respective manufacturers. Additionally, the

data are validated against other sensors at roughly annual intervals to ensure quality and consistency.

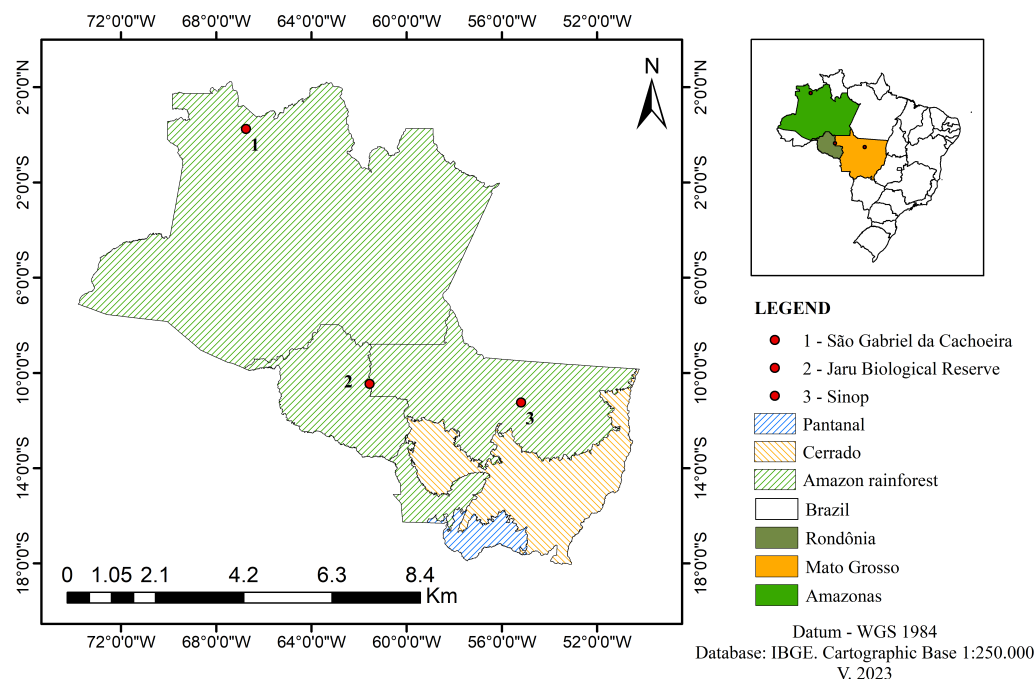


Figure 1. Research area showing the Brazilian states of Amazonas and Mato Grosso, where the study sites are located. These localities are situated within Amazon and Amazon-Cerrado transition biomes, allowing the proposed model to be tested under distinct environmental conditions. The Pantanal biome is also displayed on the map, as it occupies part of the state of Mato Grosso.

2.2. Beyond the Global Energy Balance Model

In the point of view of statistical thermodynamics, the formation of small clusters of water should not be impossible. Boltzmann statistics, a foundational concept in statistical thermodynamics, provides a framework to understand the probability of microscopic configurations in a system. One application is calculating the probability of small molecule clusters forming. According to the energy equipartition theorem, the average energy an individual molecule possesses is proportional to the temperature. This thermal energy can be distributed across various degrees of freedom, including translation, vibration, and rotation. Taking into account the energy equipartition theorem, the probability of constituting two water molecules bound together as a cluster can be estimated using the following equation [33]:

$$p \approx 1 - e^{-E/3kT}. \quad (1)$$

Here, E represents the energy required to break the bond between the two water molecules, k is the Boltzmann constant and T is the absolute temperature of the environment. The term $3kT$ accounts for the thermal energy available per molecule across its various degrees of freedom. For a typical environmental temperature of $T = 300$ K, the value of $3kT$ is around $1.2 \cdot 10^{-20}$ J. However, the value of E is not known with precision and is very difficult to be directly measured. Several research efforts have provided approximate estimates. For example, it is reported that $E \approx 4.8$ kcal/mol, which is equivalent to $3.3 \cdot 10^{-20}$ J [34]. By using the Lennard-Jones potential to describe the Hydrogen bond, $E \approx 4.9 \cdot 10^{-21}$ J [35]. The key takeaway here is that these estimations are comparable to the average thermal energy ($3kT$) of water molecules at typical environmental temperatures. This means that the energy bond of small clusters of water molecules is comparable with the kinetic energy of the molecules of water vapor at ordinary conditions. As predicted by

Equation (1), of finding two water molecules bound together in a cluster is, respectively, 94% and 33%. It means that the formation of small clusters of water molecules is expected. This highlights the impact of ϵ on the calculated probability. Furthermore, the exponential term in the equation amplifies the effect of temperature changes. A decrease in temperature will lead to a significant increase in the probability of cluster formation. It suggests that cluster formation might be more favorable at night when temperatures are lower.

The recent study by [36] investigates water clusters and density fluctuations in liquid water using extended hierarchical clustering methods. The study employs simulations at room temperature for various cluster sizes, estimating both their geometric shapes and the binding energy between molecules. An interesting finding from this research is that small clusters exhibit optimal shapes. This suggests a subtle balance between hydrogen bond enthalpies and the structural distortions. The study also found that the energy of water clusters, defined as the sum of interaction energy between molecules, is directly proportional to the cluster size. These findings on cluster shapes and energies provide valuable insights for understanding how temperature might influence cluster formation at the molecular level in our research. Another interesting result from [36] is that as the number of molecules decreases, the number of clusters increases. Additionally, heating can disrupt large, low-energy clusters into small, high-energy ones due to increasing defects in the topological structures [36,37]. This finding is particularly relevant to our discussion about nighttime favoring cluster formation. Since cooler temperatures at night would lead to less thermal disruption, larger clusters might be more prevalent during these periods.

Another study by [38] reports an average energy of hydrogen bonds between H_2O molecules cluster formation to be around 0.1067 eV, which is roughly equivalent to $1.7 \cdot 10^{-20}$ J. This study also suggests that as the energy of hydrogen bonds increases up to -0.14 eV, the cluster becomes unstable and breaks apart. This concept aligns with the idea of a threshold for cluster stability. Clusters with a bond energy exceeding this threshold are less likely to exist due to the increased energy disrupting the cluster's structure. The ordering of water molecules into cluster associates corresponds to a decrease in entropy, a thermodynamic property that signifies the level of disorder in a system. As the water molecules become more organized within a cluster, the system becomes less random, leading to a decrease in entropy. This decrease in entropy is often accompanied by a release of energy, which can contribute to a negative value for the Gibbs free energy. The Gibbs free energy considers both enthalpy and entropy, and a negative value indicates a spontaneous process, in this case, the formation of stable water clusters. Temperature is another important factor influencing cluster stability. Higher temperatures provide more thermal energy to the molecules, increasing the likelihood of exceeding the stability threshold and breaking cluster bonds.

During the day, substantially lower values of cluster formation might be expected compared to nighttime. This is because photon absorption from sunlight can excite water molecules, increasing their energy and potentially leading to the dissociation of existing clusters.

One way to try to evaluate the latent heat flux more correctly, considering the formation of small clusters of water molecules, is through mathematical modeling of temperature behavior in environmental systems. Latent heat flux refers to the exchange of energy between the Earth's surface and the atmosphere associated with phase changes of water (evaporation and condensation). Accurately accounting for cluster formation becomes important because these clusters can influence various processes that affect latent heat flux, such as heat transfer and vapor pressure. From a thermodynamic point of view, temperature is a critical variable that is sensitive to energy flows and is one of the variables that holds the most information about the thermodynamics in natural systems [21].

The approach adopted in this work starts from a basic model—the global energy balance model [39]:

$$\rho c_p \frac{dT}{dt} = \alpha R - \gamma \sigma T^4, \quad (2)$$

where R (W/m^2) is the net radiation flux, T (K) is the air temperature, t (s) is the time, ρ and c_p are the air density (kg/m^3) and specific heat ($\text{J}/\text{kg}^\circ\text{C}$), $\sigma = 5.6710^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ is the Stefan–Boltzmann constant and α and γ are two parameters with units of m^{-1} adjusted based on the *dry model* [39]. This equation describes the change in temperature (dT/dt) of a unit mass of air (represented by density, ρ) with specific heat c_p over time t . The terms on the right side of the equation represent the net energy fluxes affecting the temperature. αR represents the incoming solar radiation absorbed by the Earth's surface, while $\gamma \sigma T^4$ accounts for the outgoing longwave radiation emitted by the Earth. To account for the influence of water molecule clusters, we can add a term, ζ , to the equation:

$$\rho c_p \frac{dT}{dt} = \alpha R - \gamma \sigma T^4 + \zeta. \quad (3)$$

The term ζ represents the net energy exchange due to the formation or dissociation of water molecule clusters. A positive value of ζ would indicate energy release during cluster formation, while a negative value would indicate energy absorption during cluster dissociation. While the basic global energy balance model provides a starting point, it has limitations in capturing the complexities of real-world systems. Our research aims to address these limitations by incorporating more sophisticated models for cluster formation and its effects on various energy transfer processes.

It is important to note that Equations (2) and (3) do not directly represent energy fluxes. These equations express the change in energy density at a specific point within the air ($\text{Jm}^{-3}\text{s}^{-1}$). We can connect this concept of point-based energy changes to the concept of energy fluxes using the equation of balance of energy fluxes [4]:

$$H + Le = R_n - G \quad (4)$$

where H and Le are the sensible and latent heatfluxes, respectively, R_n is the net radiation and G is the energy flux in the soil ($\text{Jm}^{-2}\text{s}^{-1}$, or W/m^2). It is important to understand that Equation (4) represents average values of fluxes over a vertical column in the atmosphere with a unit horizontal area, not a single point in space, because some terms like G are only relevant at the ground surface. The continuity equation provides a crucial link between the point-based temperature changes and the energy fluxes we are interested in,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot \Gamma \quad (5)$$

where Γ is the energy density and $\nabla \cdot \Gamma$ the energy flux. This equation relates the change in energy density (left term, similar to Equation (3)) to the divergence of the energy flux (right term). The divergence represents the net flow of energy in or out of a specific volume. Therefore, even though Equation (3) describes changes at a single point, it can provide valuable information about energy fluxes, particularly when combined with the continuity equation and under specific conditions (e.g., good temperature modeling and negligible horizontal variations). This information becomes valuable, especially when independent measurements of fluxes (e.g., from infrared sensors) might be unavailable.

The method is not quite equivalent to the Bowen ratio technique [40]. The Bowen Ratio is a well-established method for calculating the ratio of sensible heat flux to latent heat flux, but it has limitations, such as requiring specific assumptions about the surface and atmospheric conditions. In contrast, this approach aims to extract information about

both sensible and latent heat fluxes by analyzing temporal series of temperature data. This is achieved by establishing a theoretical relationship between the rate of temperature change $\partial T / \partial t$ and the energy fluxes involved. To fulfill this purpose, it is necessary to compose a theoretical model for temperature variation.

2.3. The Model

A previous analysis [39] of time series of temperature and relative humidity measured during nighttime periods in five different Brazilian ecosystems pointed out a significant impact of atmospheric moisture on the cooling rate of these systems. The study found that lower relative humidity ($RH < 85\%$) is associated with a cooling rate close to $0.9\text{ }^{\circ}\text{C/h}$. This observation aligns with the predictions of the global energy balance model, Equation (2), which considers radiative cooling due to infrared emission. However, the study also found that the cooling rate decreases significantly at high humidity (above 85%). For conditions near 100% RH , the cooling rate is reduced by several orders of magnitude compared to lower humidity conditions. This suggests that at high relative humidity, water vapor in the air contributes a heating effect that counteracts the cooling due to infrared radiation emission, i.e., the heat liberation due to the coalescence (formation of clusters) of water molecules might be a factor in this reduced cooling rate at high relative humidity [39].

In this way, a model for temperature was developed in this work, considering a dependence with radiation and relative humidity. Relative humidity was chosen instead of the concentration of water vapor molecules due to two reasons. First, as mentioned earlier, gas sensors currently have limitations in distinguishing between independent water vapor molecules and small clusters. Second, RH is a variable that is already closely connected to the transfer of thermal energy in the environment.

The dependence of the nocturnal cooling rate on RH , described above, suggests that any theoretical approach aimed at modeling nocturnal temperature in Amazonian ecosystems must consider a positive term that reflects the observation that a higher RH is associated with a lower cooling rate. In this work, the proposed model incorporates an additional term in the *dry model* that is linear in RH . This addition accounts for the influence of RH on nocturnal cooling. Measured time series of temperature reveal another type of dependence on RH that must also be considered in the new model: its time derivative. When dRH/dt is higher (during an abrupt increase in RH , for example), an additional term linear in dRH/dt that contributes to cooling alongside the Stefan–Boltzmann term (which represents radiative cooling due to infrared radiation emission).

Figure 2 plots time series of nocturnal temperature for three nights in the Amazonian ecosystems when RH exhibited an intensive increase. The empirical behavior demonstrated in these figures provides the foundation for justifying the inclusion of RH and its rate of change (dRH/dt) as dependencies in the temperature dynamics model. The data show the actual temperature variations during these nights compared to the linear cooling rate of $0.9\text{ }^{\circ}\text{C/h}$ (represented by a black line), predicted by the existing model for low-humidity conditions [39].

Note that in all graphs of Figure 2, RH is initially lower than 85% —close to this value in Sinop and around 40% in Rebio-Jaru. The first two graphs for Sinop show temperatures dropping below those predicted by the linear model, unlike the third graph for Rebio-Jaru, where it decreases at approximately $0.9\text{ }^{\circ}\text{C/h}$. Although RH reaches values above 90% in Sinop and below 55% in Rebio-Jaru within the first 2 h, the difference in the behavior during this initial period can be attributed to the more rapid rate of humidity increase observed in Sinop (about 15% within the first 2 h) compared to Rebio-Jaru (around 10%). This highlights the importance of considering not only the absolute value of RH but also its rate of change in the temperature model.

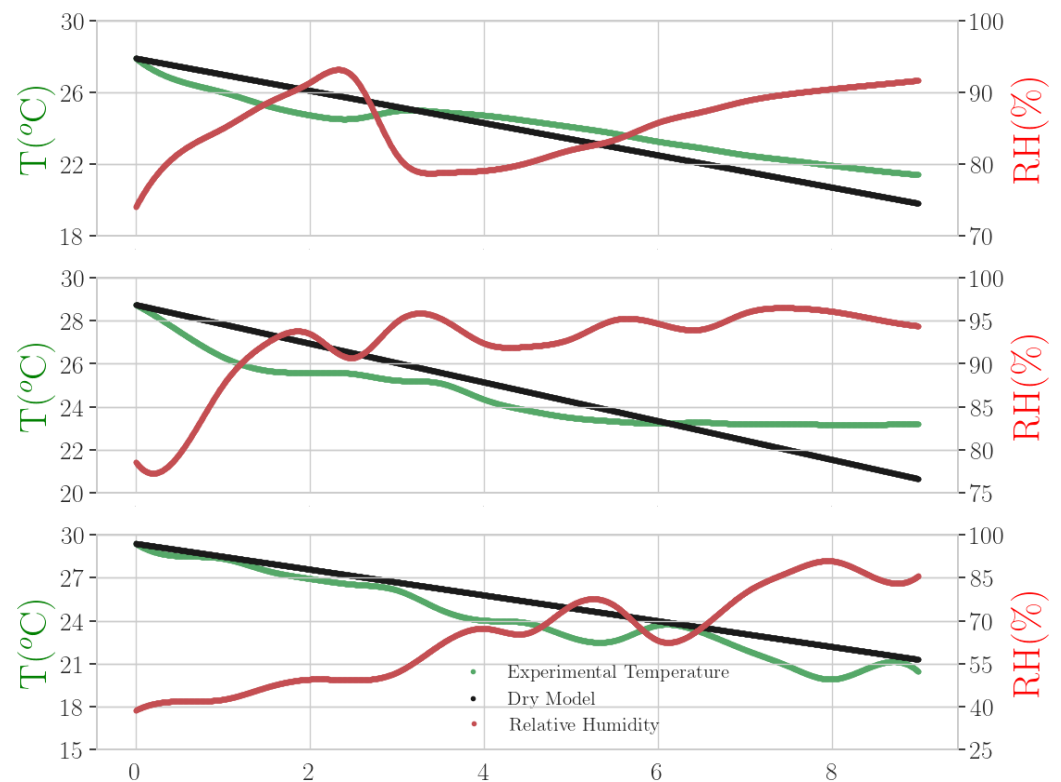


Figure 2. Nocturnal temperature feature in conditions of high increase of relative humidity in the Sinop transition forest in a night of June-2002 (**top**), October-2002 (**middle**) and Rebio-Rebio-Jaru Forest in August-2008 (**bottom**). The linear approximation of temperature corresponds to the rate of $0.9\text{ }^{\circ}\text{C/h}$ [39].

Furthermore, in the following hour of the first graph, there is a sudden decrease in RH , resulting in a positive rate of temperature change, contrasting with the previous abrupt increase. This emphasizes the sensitivity of temperature dynamics to rapid fluctuations in RH . Throughout the remainder of the period, RH changes more gradually, maintaining high values and resulting in a slower cooling of the air temperature compared to what the *dry model* predicts.

The second graph shows RH fluctuating between 90–95% after the initial 2 h, with no significant variation. Due to this persistently high RH , the cooling rate remains consistently slower than $0.9\text{ }^{\circ}\text{C/h}$, approaching zero (constant temperature) by the end of the analyzed period. Finally, in the third graph, numerous abrupt changes in RH occur after the third hour (at least $\pm 15\%$ per hour). They cause the temperature rate to vary significantly, according to the explanations provided earlier. This behavior further emphasizes the need to incorporate dRH/dt into the model for a more accurate representation of nocturnal temperature dynamics in the Amazonian ecosystem.

Therefore, based on this detailed analysis of the influence of RH and its rate of change on nocturnal cooling rates, the following model is proposed to describe temperature dynamics:

$$\rho c_p \frac{dT}{dt} = \alpha R - \gamma \sigma T^4 + \beta RH - \delta \frac{dRH}{dt} \quad (6)$$

where $\rho = 1.184\text{ kg/m}^3$, $c_p = 1012\text{ J/kg}^{\circ}\text{C}$ and α , γ , β and δ are adjustable parameters to be determined. They quantify the influence of RH and dRH/dt on temperature variations.

The term on the left side of the equation represents the variation in sensible heat, while the first two terms on the right side correspond to the effect of radiation. Hence, the parameters α and γ represent the extinction coefficients of radiation in the air. To

estimate the values of α and γ for the Brazilian ecosystems, data from a single ecosystem at intermediate latitude (Sinop) was used [39].

The last two terms on the right side of the equation can be interpreted physically based on the hypothesis of clusters with few water molecules. The latent heat critically depends on the number of water molecules that are bound together, which is determined by the binding energy that is proportional to the number of molecules. From the physical point of view, the terms depending on RH should be related with the intermolecular force between water molecules. Commonly it is described by the Lennard-Jones potential [35]:

$$V_{ij} = A \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (7)$$

where r_{ij} is the distance between the two interacting molecules and σ and A are constants. This expression can be rewritten as:

$$V_{ij} = A(\xi_{ij}^2 - \xi_{ij}) \quad (8)$$

where $\xi_{ij} = (\sigma/r_{ij})^6$, or:

$$V_{ij} = A \left(\chi - \frac{k}{2} \frac{\partial \chi}{\partial r} \right) = A \left(\chi - \frac{k}{2v} \frac{\partial \chi}{\partial t} \right) \quad (9)$$

where $\chi = \xi^2$, $k = (\partial \xi / \partial r)^{-1}$ and considering a dynamical process of coalition/dissociation characterized by a mean velocity v . This mathematical estimative points out that, if the interaction of the water molecules in the air is characterized by the Lennard-Jones potential, it is expected that the transference of energy due to latent heat is a process dependent of a couple of terms in which one is proportional to the variation rate of the other. In this way, the last two terms are directly connected to the intermolecular force between water molecules in the air. To obtain a more complete description, it is interesting to consider incorporating a factor related to the probability (P) of two water molecules meeting in the air, as this probability is influenced by the overall number of water molecules (dependent on RH). Therefore, we will modify the model by introducing P in the terms related to the influence of relative humidity:

$$\rho c_p \frac{dT}{dt} = \alpha R - \gamma \sigma T^4 + P \left(\beta RH - \delta \frac{dRH}{dt} \right). \quad (10)$$

As evidenced by a previous study [39], the *dry model* is capable of accurately reproducing the behavior of nighttime temperature when relative humidity is equal to or greater than 85%. This indicates that, for humidity values below this threshold, the presence of water in the air likely has a minimal impact on local thermodynamics. Therefore, in this study, P is incorporated using a Heaviside-type function:

$$P = [1 + e^{-(RH-80)/(100-RH)}]^{-1}. \quad (11)$$

The Heaviside function acts like a switch, turning P on (close to 1) for high relative humidity (above 80% in this case) and off for low relative humidity. The performance of the models with and without P , Equations (6) and (10), will be compared in the analysis of time series of temperature data to assess the impact of considering the interaction probability on the model's accuracy.

2.4. Computational Fitting

Prior to analysis, the raw measurements undergo filtering to remove outliers and physically unrealistic values. Interpolation is then applied to generate additional data points at a finer temporal resolution than the original measurement interval, facilitating subsequent modeling and analysis.

To find the best possible values for the coefficients in Equation (6), a technique called curve fitting is employed. Curve fitting essentially finds an optimal set of parameters for a mathematical function that best matches a given set of data points. It requires defining the functional form of the mapping function that maps examples of inputs to outputs, then searching for the parameters to the function that result in the minimum error. This provides the flexibility and control to define the form of the curve, where an optimization process is used to find the specific optimal parameters of the function. Once fit, one can use the mapping function to interpolate or extrapolate new points in the domain.

Error is calculated by using the observations from the domain and passing the inputs to the candidate mapping function and calculating the output, then comparing the calculated output to the observed output. In our case, we used the least squares method of Levenberg–Marquardt (LM) [41,42], a powerful iterative optimization algorithm specifically designed for non-linear problems. LM works by starting with an initial guess for the coefficients and then iteratively refining those guesses. Unlike simpler methods, LM considers both the direction of steepest descent and a trust-region approach to ensure efficient convergence towards a minimum of the error function. This makes it a well-suited choice for finding the optimal parameters of the temperature model (Equation (10)).

The primary application of the Levenberg–Marquardt algorithm is in the least-squares curve fitting problem: given the empirical pairs (x_i, y_i) of independent and dependent variables, one needs to find the parameters w of the model curve $f(x, w)$ so that the sum of the squares of the deviations $S(w)$ is minimized:

$$S(w) = \min_i \sum [y_i - f(x_i, w)]^2. \quad (12)$$

The function `curve_fit()` of the SciPy open source library of Python version 3.13.5 was used for curve fitting. The mapping function in this case will be

$$f(T, R, U, \alpha, \gamma, \beta, \delta) = \rho c_p \frac{dT}{dt} - \alpha R + \gamma \sigma T^4 - P \left(\beta RH - \delta \frac{dRH}{dt} \right) \quad (13)$$

where (T, R, RH) corresponds to the experimental input data and $(\alpha, \gamma, \beta, \delta)$ to the remaining coefficients that must be optimized by a nonlinear least squares optimization process.

Further important considerations arise regarding the negative value of the model term involving the parameter δ . This term was originally introduced based on the experimental observation that temperature decreases significantly during the nighttime when relative humidity increases rapidly [39]. This contrasts with scenarios of high but slowly varying humidity, which involve a release of thermal energy that prevents temperature from falling at rates as high as 0.9 °C per hour—a phenomenon accounted for by the term involving β [39].

From a microscopic perspective, the justification for including the delta term lies in the nature of intermolecular binding forces, which comprise both attractive and repulsive components. Macroscopically, this dual nature may manifest as follows: a rapid increase in relative humidity can lead to a correspondingly rapid growth in water molecule cluster size. Should a cluster exceed a critical size, the repulsive component of the binding force may become dominant. This would cause clusters to dissociate more rapidly than they form, resulting in a net consumption, rather than release, of latent heat.

3. Results and Discussion

To test the model, time series of high quality temperature data corresponding to a month (approximately 1500 data points) were selected, which correspond to periods when the equipment was continuously operating. The chosen month was June for all three considered ecosystems.

The time evolution of temperature, humidity and radiation in the chosen time series is shown in Figure 3 for Sinop, Rebio-Jaru and São Gabriel. The data in the first two locations is relatively stable, while in the third location it appears to have more measurement instability and fluctuations, which can be related to the presence of clouds inhibiting the radiation incidence and to the amount of rainfall in the area, which affects the measurements taken by the sensors.

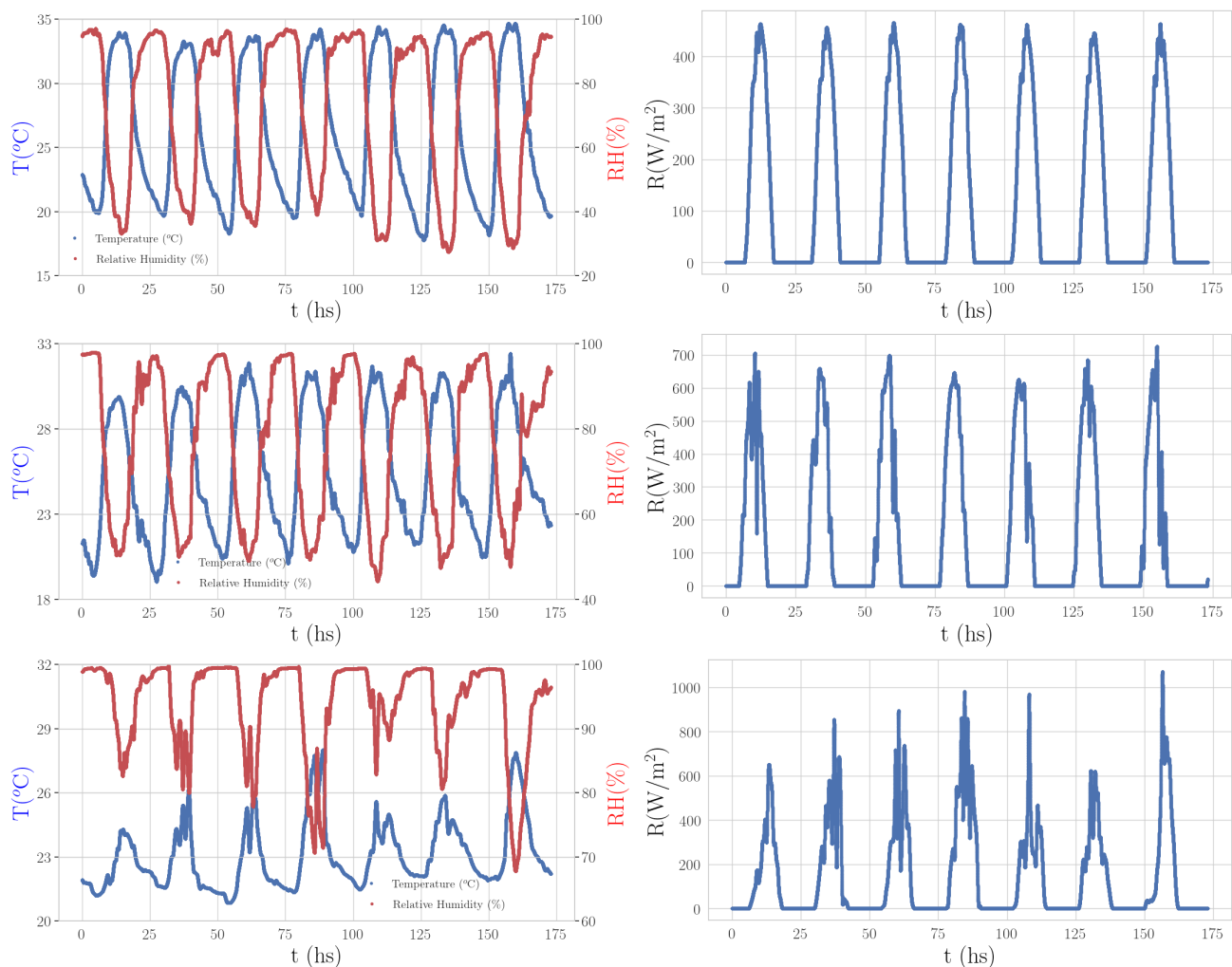


Figure 3. Experimental temperature, humidity and net radiation measured in Sinop (top), Rebio-Jaru (middle) and São Gabriel (bottom) in June.

First, the *dry model*, Equation (2), was tested on the temperature data for the three locations shown in Figure 3, yielding the results depicted in red in Figure 4. It is noticeable that the model's behavior is consistently linear, increasing during the day and decreasing at night, as noted in [39]. This model is unable to capture the curvature of the temperature profile, especially at night, where the temperature generally drops more rapidly initially and more slowly later. Such behavior stems from the fact that the Stephan–Boltzmann constant, although proportional to the fourth power of temperature, is expressed in absolute scale (Kelvin), which has an almost linear behavior in the range of variation between 0

and 40 °C. Despite being a simple model, it closely matches the measured maximums and minimums for Sinop and Rebio-Jaru. However, for São Gabriel, which has more unstable data, the model diverges significantly from the observations, confirming that the *dry model* is not adequate.

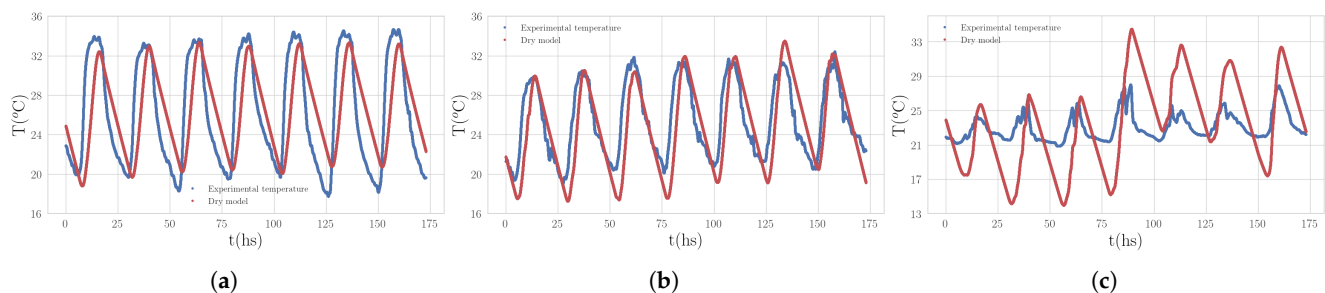


Figure 4. Experimental temperature and the fittings using the *dry model* for Sinop (a), Rebio-Jaru (b) and São Gabriel (c) in June.

Next, an attempt to improve this model, the values of $\alpha = 2.7 \cdot 10^{-3}$ and $\gamma = 6.5 \cdot 10^{-4}$ from the *dry model* were applied to the *humid model*, but they did not result in satisfactory curve fittings. As γ is connected to the emissivity and should not vary considerably, the effort to improve the fitting was focused on finding better values for α . Using the optimal values of α , the curve fitting was performed again to determine the values of β and δ . The comparison of these fittings with the experimental data is presented in Figure 5. The model fitting in the first two forests showed a satisfactory approximation to the data, although it could not accurately reproduce the minimum temperatures. The third region experienced some instability, as described above, but the model still managed to capture the general behavior of the data well.

In contrast to the *dry model*, the *humid model* is capable of reproducing the correct curvature of the hourly variation of temperature, in which the second temporal derivative is negative during the day and positive during the night. This validates the hypothesis of energy released by the clusters, which acts as a warming term. However, the model fails to reproduce the daily minimum temperature values. As mentioned above, the model must take into account not only the intensity of intermolecular forces but also the probability P of two water molecules encountering each other in the air.

Taking into account Equations (10) and (11), a new fit was performed for the same data. The results are shown in Figure 5. It is worth emphasizing how the model fitting closely follows the temperature decay during nighttime, in contrast to the *dry model*, which resulted in a practically linear decay. This demonstrates the crucial role that relative humidity plays in determining nighttime temperature behavior. Figure 5 also compares the model's performance with and without the inclusion of the P term. It is noticeable that the inclusion of P tends to help the model better estimate the minimum temperatures. However, the maximum temperatures tend to be slightly overestimated. This term was originally introduced into the model based on experimental observations that, for relative humidity values below 80%, the influence of humidity on temperature behavior was not significant [39]. However, as shown in Figure 5, the fit of the model to the experimental data did not demonstrate any relevant contribution from the P factor, suggesting that it may be omitted from the model.

To quantify the performance of the models, the R^2 , RMSE, Willmott, Spearman, and Pearson metrics were calculated for the cases presented in Figures 4 and 5 (*dry* and *humid model* in June), as well as for other months (August, October, and December), see Appendix A. The results in Table 1 clearly demonstrate that the *dry model* performs the worst; in most cases, the R^2 values are not even acceptable, with the best case achieving an

R^2 value close to 0.58. The performance of the *humid model* significantly exceeded that of the *dry model*, especially without P . Despite the improvement in estimating lower temperatures, as observed in Figure 5, the likely overestimation of the maximum temperatures resulted in R^2 values for the *humid model* with P being around or below those of the *humid model* without P , whose lowest value was 0.87.

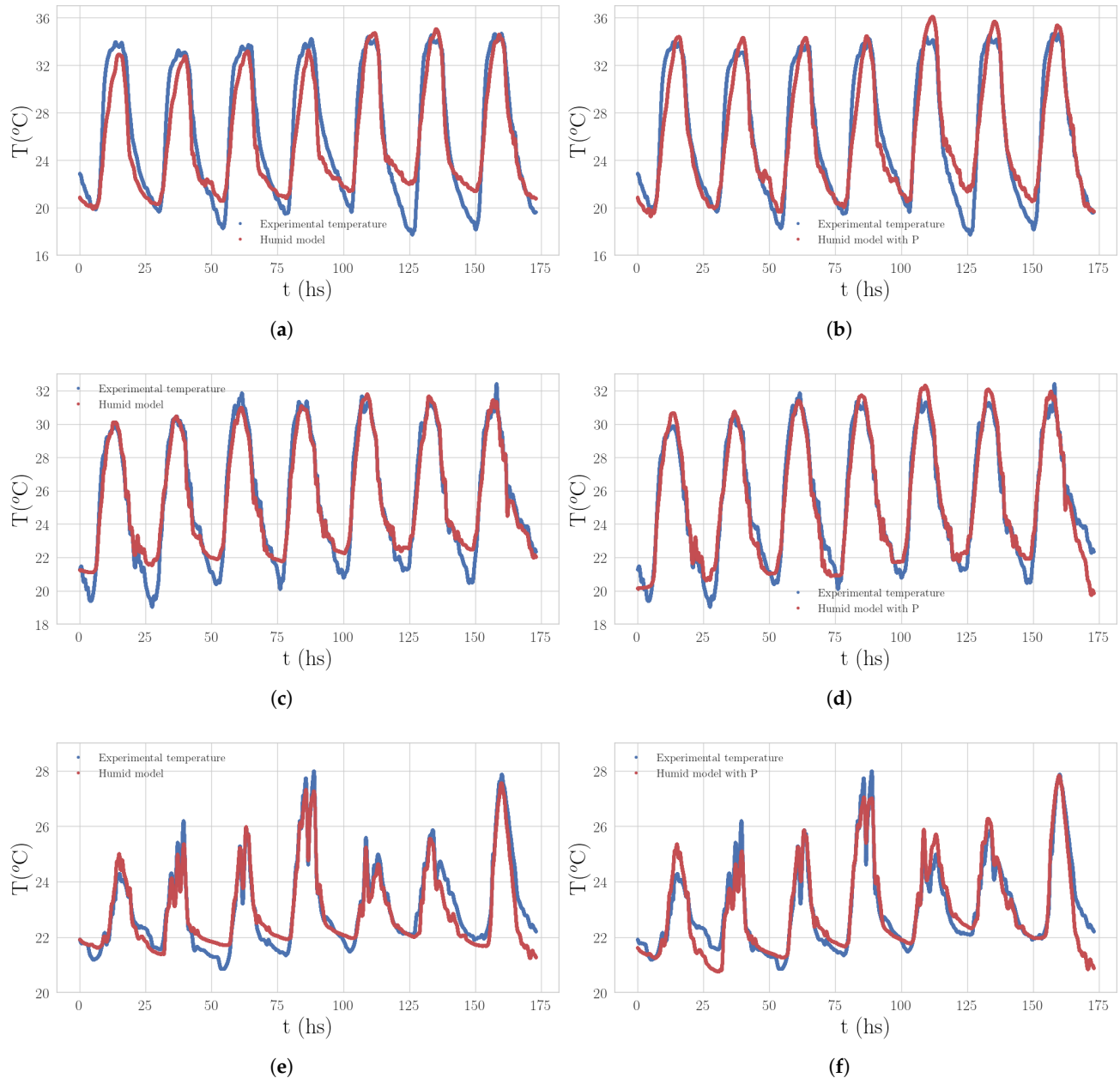


Figure 5. Experimental temperature and the fittings using the *humid model*. For the probability $P = 1$ of water molecules interaction (left), the coefficients obtained are $\alpha = 1.05 \cdot 10^{-3}$, $\beta = 2.4 \cdot 10^{-3}$ and $\delta = 179$ for Sinop (a), $\alpha = 0.55 \cdot 10^{-3}$, $\beta = 2.7 \cdot 10^{-3}$ and $\delta = 154$ for Rebio-Jaru (c) and $\alpha = 0.2 \cdot 10^{-3}$, $\beta = 2.7 \cdot 10^{-3}$ and $\delta = 191$ for São Gabriel (e). Considering the probability P of water molecules interaction (right), the coefficients obtained are $\alpha = 1.55 \cdot 10^{-3}$, $\beta = 2.3 \cdot 10^{-3}$ and $\delta = 385$ for Sinop (b), $\alpha = 0.9 \cdot 10^{-3}$, $\beta = 3.0 \cdot 10^{-3}$ and $\delta = 273$ for Rebio-Jaru (d) and $\alpha = 0.4 \cdot 10^{-3}$, $\beta = 2.7 \cdot 10^{-3}$ and $\delta = 248$ for São Gabriel (f); $\gamma = 6.5 \cdot 10^{-4}$ was kept the same from the *dry model*.

Table 1. Performance metrics— R^2 , RMSE, Willmott (W), Spearman (S), and Pearson (P)—obtained with the *dry* and *humi* model without/with *P* for Sinop, Rebio-Jaru, and São Gabriel data over different periods.

	Period	Dry Model					Humid Model				
		R^2	RMSE	W	S	P	R^2	RMSE	W	S	P
Sinop	Jun	0.37	4.41	0.77	0.66	0.62	0.88/0.91	1.94/1.67	0.96/0.97	0.94/0.95	0.95/0.96
	Oct	0.38	3.18	0.84	0.71	0.71	0.87/0.87	1.32/1.44	0.97/0.97	0.95/0.93	0.96/0.93
	Dec	−0.21	4.12	0.77	0.67	0.64	0.89/0.90	1.24/1.20	0.97/0.97	0.94/0.94	0.96/0.95
Rebio-Jaru	Jun	0.44	2.80	0.88	0.80	0.79	0.95/0.95	0.82/0.85	0.99/0.99	0.98/0.97	0.98/0.98
	Aug	0.58	2.96	0.88	0.79	0.78	0.88/0.84	1.52/1.83	0.97/0.96	0.96/0.92	0.96/0.92
	Oct	−0.14	3.99	0.74	0.56	0.55	0.88/0.7	1.27/2.08	0.97/0.93	0.93/0.87	0.94/0.87
São Gabriel	Jun	−6.71	4.38	0.53	0.62	0.59	0.90/0.88	0.49/0.54	0.97/0.97	0.87/0.89	0.95/0.94
	Aug	−1.82	4.79	0.65	0.60	0.57	0.91/0.79	0.86/1.32	0.98/0.95	0.93/0.88	0.95/0.92
	Dec	−2.76	5.23	0.58	0.48	0.49	0.91/0.83	0.83/1.10	0.98/0.96	0.92/0.88	0.96/0.92

As shown in Figure 4 and Table 1, the model's fit is less accurate for data from São Gabriel da Cachoeira, which represents a more humid ecosystem. This indicates the complexity of the processes governing energy transfer between the air and water molecules. It is worth noting that this specific factor is not comprehensively accounted for in the most widely used models in micrometeorology [43–45], which typically adopt a simplified macroscopic approach to energy partitioning in the air.

The fundamental hypotheses of this study are that relative humidity encodes information about the influence of water availability in ecosystems on the temporal variation of temperature, and that this influence can be represented by a term proportional to *RH*, together with another term involving its time derivative. Given the quality of the fit between the experimental data and the model—particularly when compared to the results of the *dry* model—it can be inferred that these hypotheses are consistent.

To better illustrate the comparison between the model and experimental data during the night, selected cases are presented in Figures 6 and 7. These cases were chosen specifically to highlight instances where the relative humidity reaches more than 85% or experiences significant fluctuations, in order to demonstrate the impact of the derivative term. The proposed model demonstrates an excellent fit with the temperature data, as evidenced by the close correlation in the plotted data in Figures 6 and 7. This supports the effectiveness of the model in describing the temperature behavior during the night.

A key feature of the model proposed in this study is its parsimonious representation of the diurnal temperature cycle, relying on only a few locally measured microclimatological variables. This represents a clear departure from existing approaches, such as NOAA-MP [45] and SiB4 [43]. These comprehensive, general-purpose models were not specifically designed for temperature simulation and require non-local data inputs, including satellite-derived products [44]. From a statistical standpoint, models driven by heterogeneous, non-local data sources are more prone to uncertainties arising from error propagation. Therefore, our model provides a simplified yet robust framework that yields valuable complementary insights to those offered by the more complex models found in the literature.

It is important to emphasize that the experimental data are collected in open, dynamic systems with a spectrum of interactions that are responsible for maintaining their self-organization and stability. Therefore, they are real and complex systems. Interactions of various orders, occasionally with abrupt disturbances, may be reflected in the data, causing fluctuations in relation to the model. This is to be anticipated when dealing with open systems far from equilibrium. Even so, the model presented in this work, which considers the influence of humidity, succeeds in capturing the behavior of daily and

nightly temperatures, characterized by a negative second-order temporal derivative during daytime heating and a positive one during nighttime cooling.

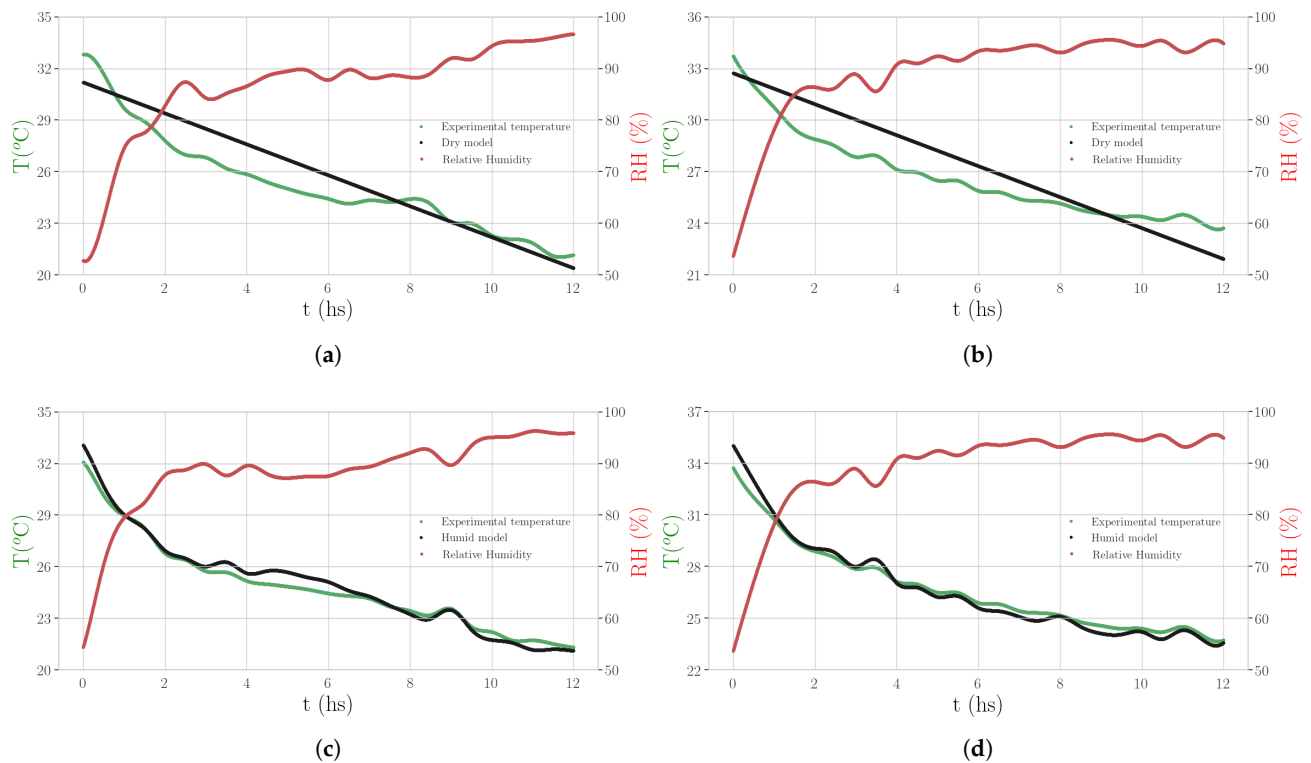


Figure 6. The fittings of the nocturnal variation of temperature using the *dry* (top) and *humid models* (bottom) in June (a,c) and October (b,d) in Sinop with $\beta = 2.3 \cdot 10^{-3}$ and $\delta = 385$.

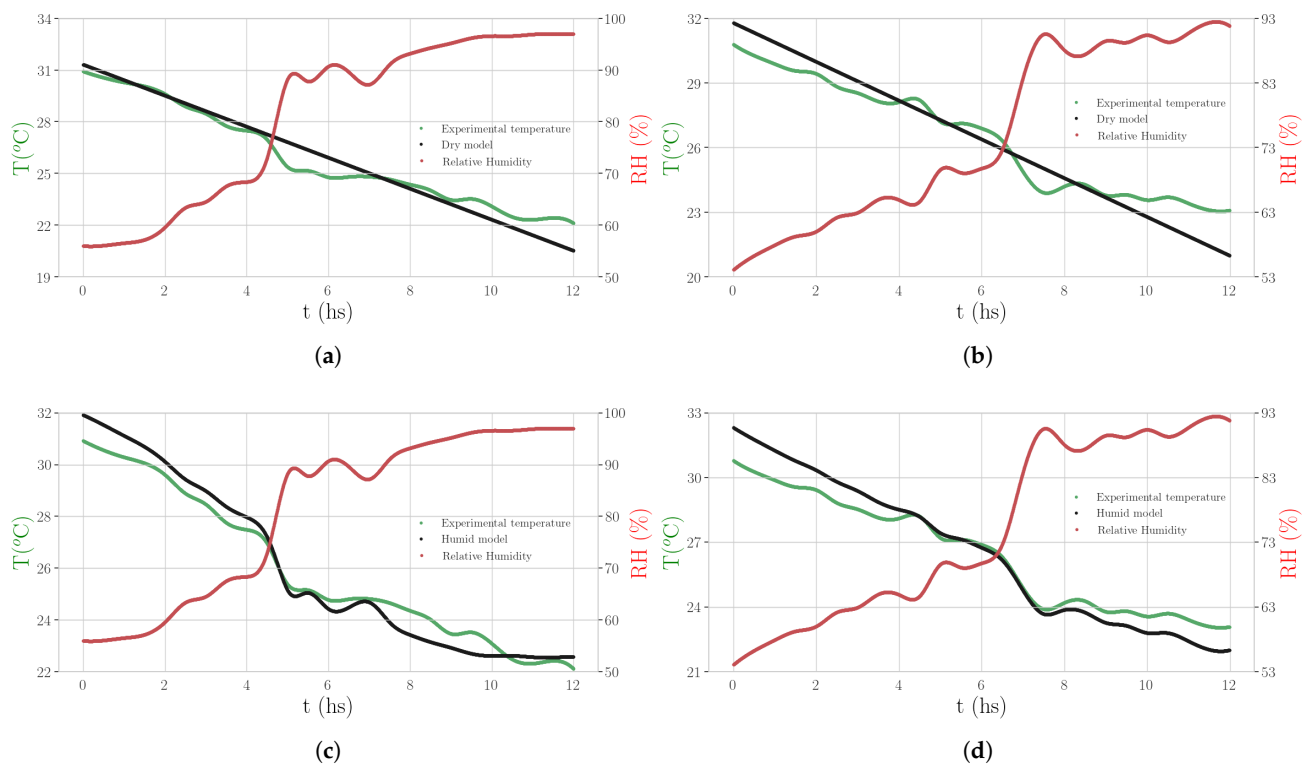


Figure 7. The fittings of the nocturnal variation of temperature using the *dry* (top) and *humid models* (bottom) in August with $\beta = 3.0 \cdot 10^{-3}$ and $\delta = 273$ in Rebio-Jaru (a,c) and $\beta = 2.7 \cdot 10^{-3}$ and $\delta = 248$ in São Gabriel (b,d).

Finally, it must be noted that the model presented in this work is based on point-based measurements. This represents an advance over models that combine local measurements with footprint-wide averages, as is common in flux measurements using the eddy covariance method. However, it is important to consider that point-based measurements are limited in heterogeneous ecosystems, necessitating measurements at multiple locations.

The proposed model represents a significant advancement, as it accurately reproduces the hourly temperature variation profile during both daytime and nighttime periods. However, its primary limitation lies in the assumption that the extinction coefficients (α , β , γ , and δ) are fully independent of atmospheric humidity and aerosol concentration—factors known to influence radiative interactions within a given air volume. This dependence may explain why the calibrated coefficient values vary across different ecosystems, a phenomenon that warrants further investigation in future studies.

However, the model exhibits certain limitations, such as not precisely reproducing the daily maximum and minimum temperature values. It is not surprising, however, that the model's best performance in replicating temperature behavior occurs during periods other than these extremes, since maximum and minimum values correspond to moments in the day when a transition in the thermodynamic process takes place. During these transitions, the factors favoring a temperature increase give way to those promoting its decrease, and vice-versa. As is known from complex systems theory [46], transitions between thermodynamic processes correspond to periods of lower stability. Consistent with this assertion, extensive temperature measurements in natural ecosystems indicate that daily maximum and minimum values are highly variable [47].

4. Conclusions

This study proposed a new analytical model to describe the temporal dynamics of air temperature based on principles of non-equilibrium thermodynamics. Unlike empirical or purely statistical approaches, the model explicitly incorporates the influence of radiation, relative humidity, and its rate of change—variables directly linked to energy and matter exchange between the biosphere and the atmosphere.

By extending the global energy balance equation with terms proportional to relative humidity (RH) and its temporal derivative (dRH/dt), the model captures key physical mechanisms underlying nocturnal temperature variations in humid tropical ecosystems. The inclusion of these terms is consistent with the hypothesis that molecular interactions between water molecules—specifically the formation and dissociation of small clusters—affect the local energy balance through the release or absorption of latent heat.

The results obtained from observational data in three distinct Brazilian ecosystems demonstrate that the proposed model successfully represents the observed reduction in nocturnal cooling rates under high-humidity conditions. This agreement reinforces the importance of considering microphysical processes, such as cluster formation, when interpreting energy exchanges derived from field measurements. Furthermore, the framework introduced here bridges microscale thermodynamic interactions with macroscale temperature variability, offering a physically grounded alternative to empirical formulations.

Future work could focus on incorporating the spatial dependence of the adjustable parameters in the model, allowing for more regionalized application. Additionally, upcoming efforts may explore how to integrate the dependence of relative humidity on incoming radiation for a more comprehensive understanding of these coupled processes in the Amazonian ecosystem. Despite these remaining limitations, the model effectively captured the observed nighttime temperature decay, demonstrating its potential for studying nocturnal cooling processes.

Author Contributions: D.d.O.M. and J.G.d.S. developed the computational codes, with D.d.O.M. generating the results. S.R.d.P. and I.J.C.d.P. provided the data and developed the theoretical background. J.G.d.S. created the figures. D.d.O.M. and S.R.d.P. wrote the main manuscript text. All authors critically reviewed and contributed to the manuscript. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data and materials supporting the findings of this study are available upon reasonable request.

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Appendix A. Extra Fittings

The graphs depicting the experimental data for temperature, humidity, and net radiation measured in Sinop, Rebio-Jaru, and São Gabriel are shown for the months of August, October, and December, alongside the corresponding fits using both the *dry* and *humid models*. These graphs aim to complement the results already presented in the main text for the month of June, showcasing results that are equally satisfactory to those in the main text.

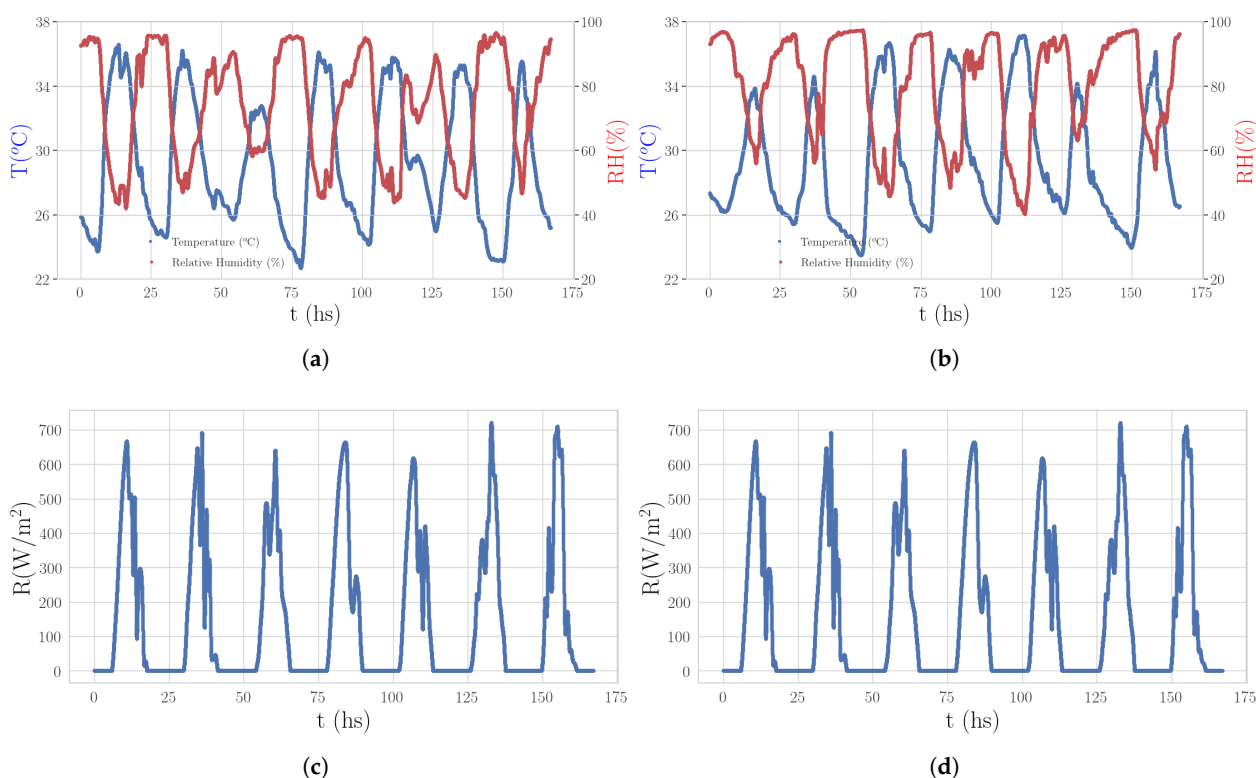


Figure A1. Cont.

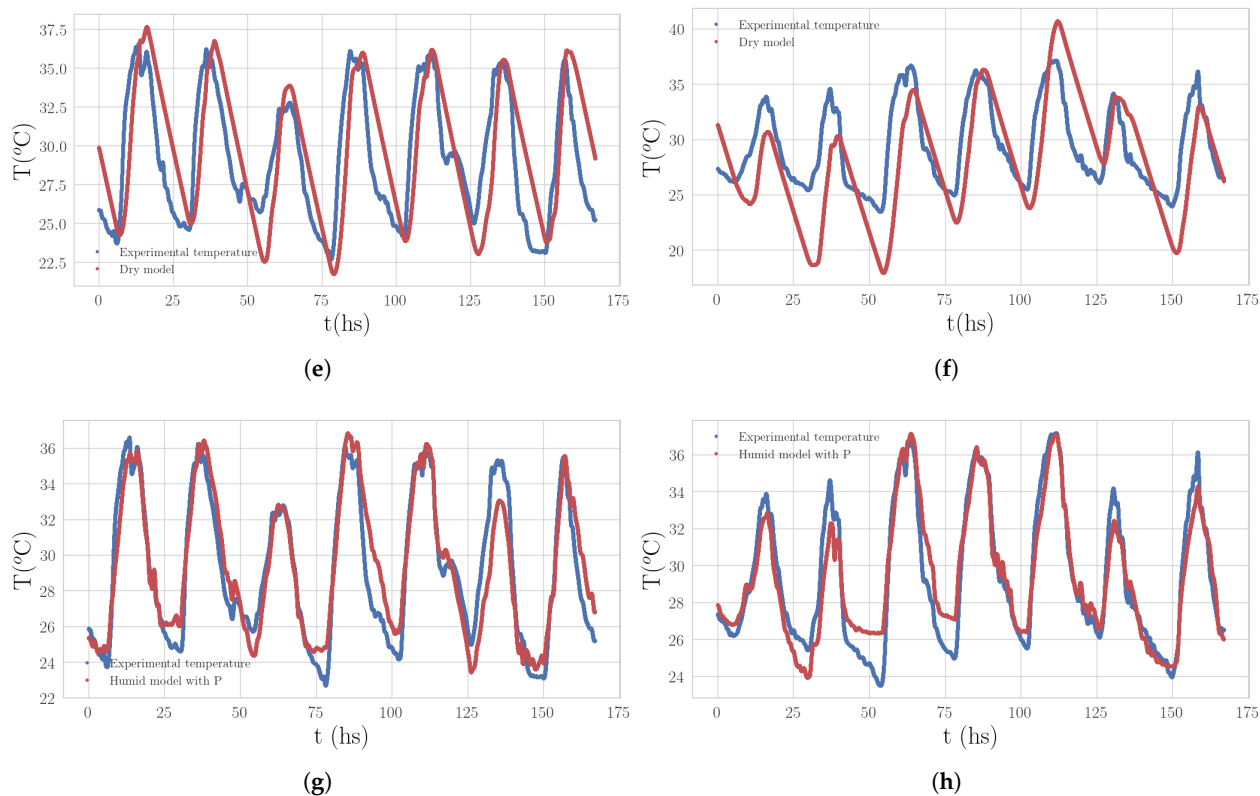


Figure A1. (a–d) Experimental temperature, humidity, and net radiation measured in Sinop in October (left) and December (right) 2002, along with the fitting using the *dry* (e,f) and *humid* models (g,h).

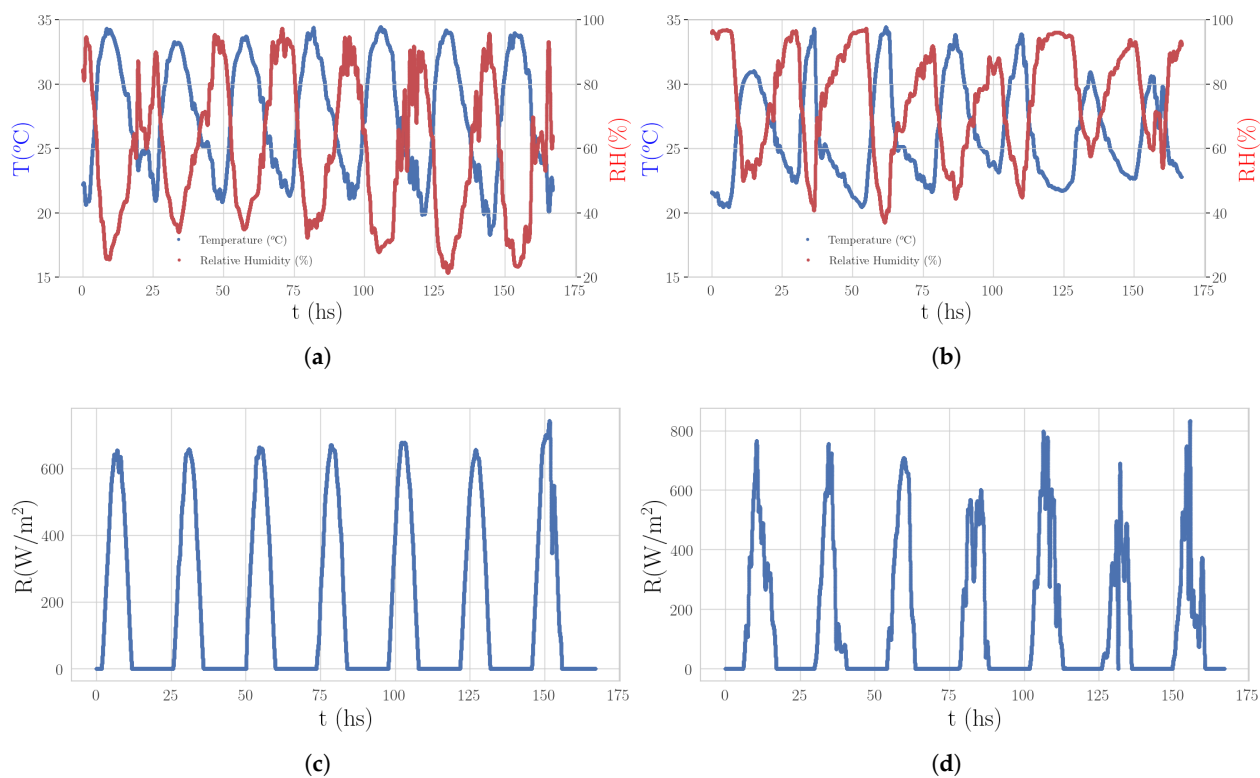


Figure A2. Cont.

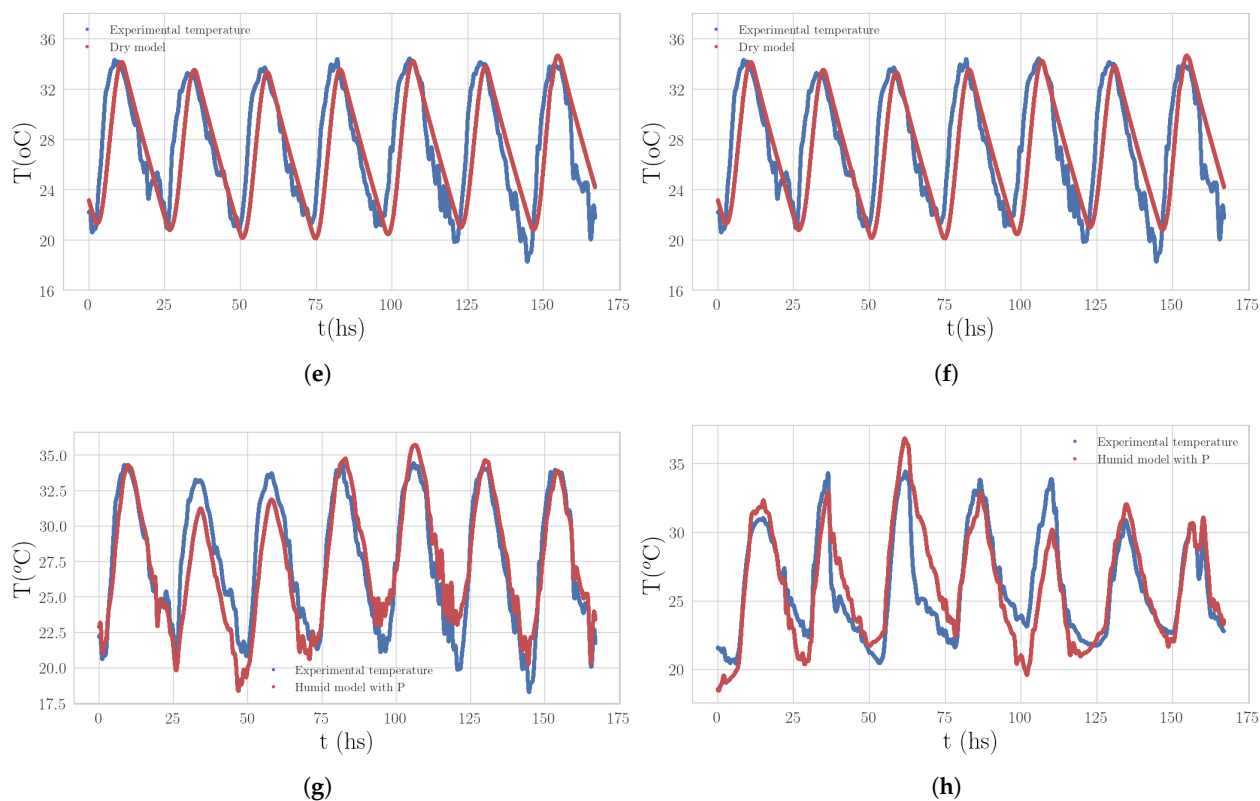


Figure A2. (a–d) Experimental temperature, humidity, and net radiation measured in Rebio-Jaru in August (left) and October (right) 2008, along with the fitting using the *dry* (e,f) and *humid* models (g,h).

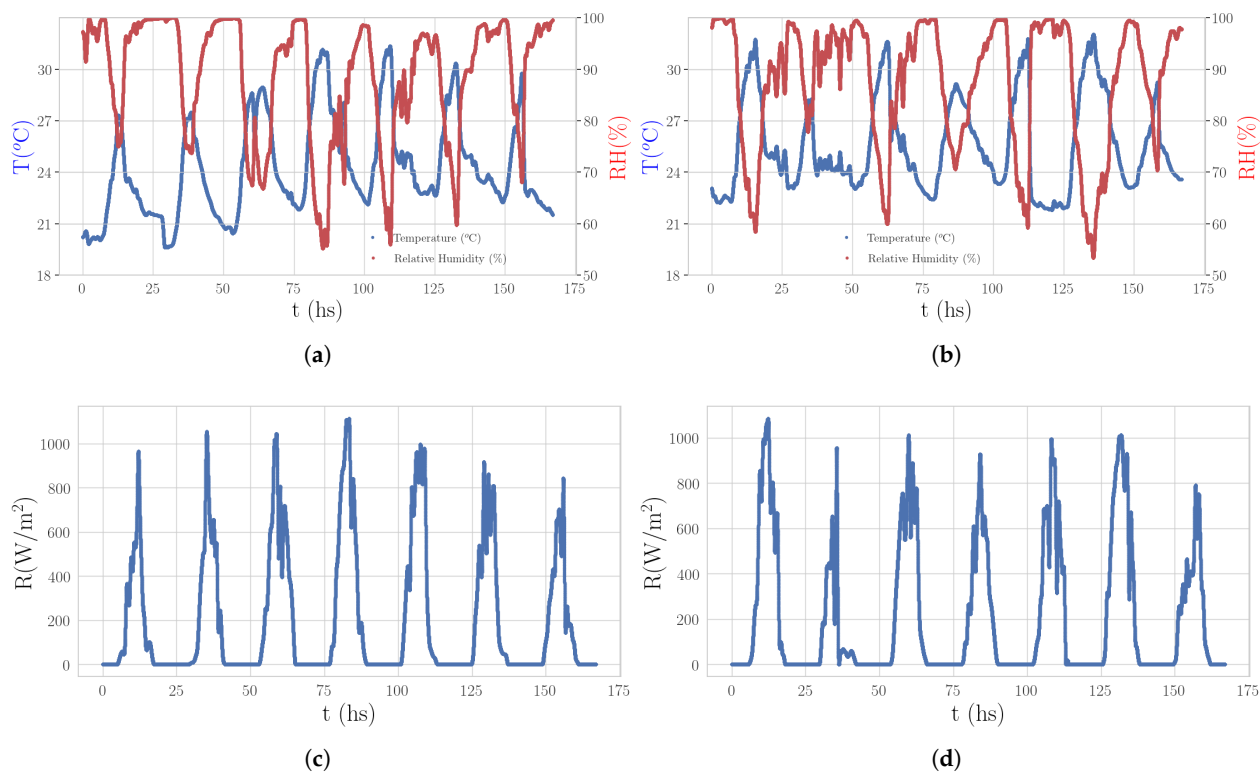


Figure A3. *Cont.*

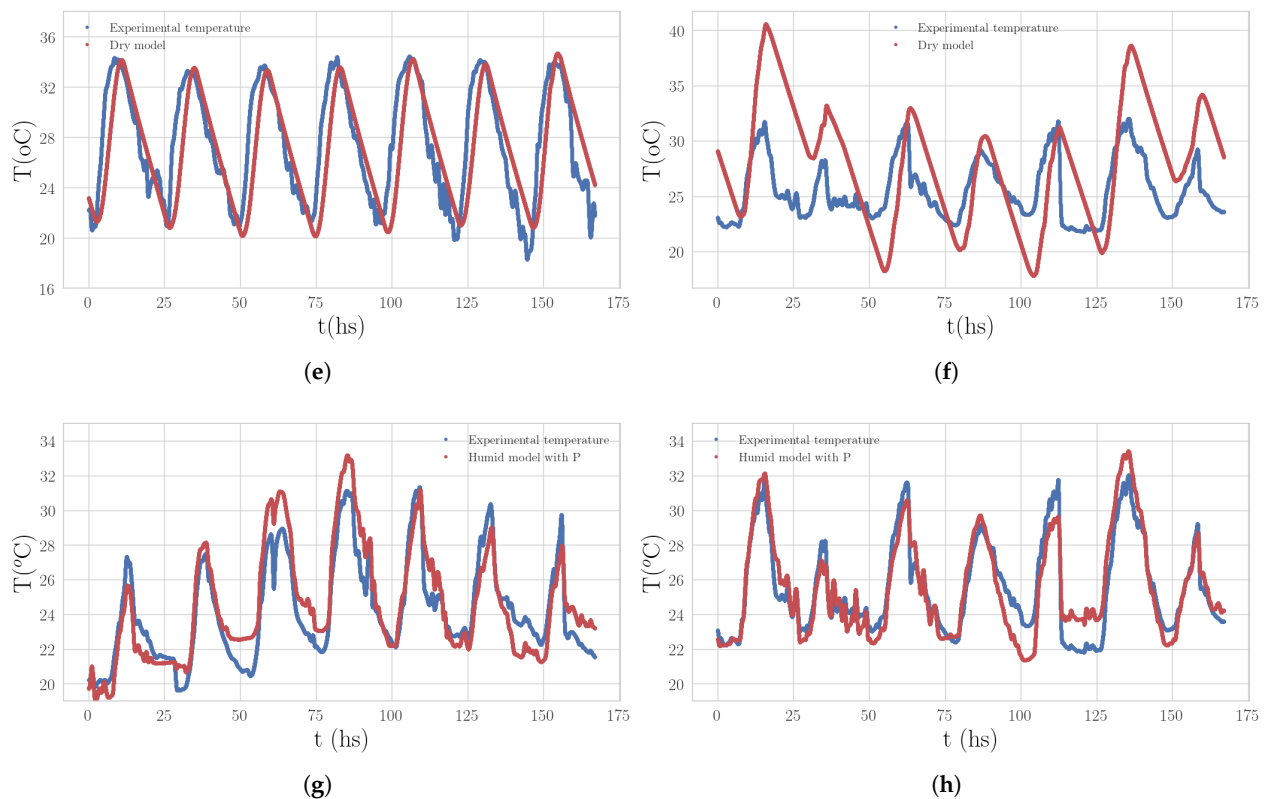


Figure A3. (a–d) Experimental temperature, humidity, and net radiation measured in São Gabriel in August (left) and December (right) 2008, along with the fitting using the *dry* (e,f) and *humid* models (g,h).

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