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Analyzing Solar Pyrolysis Process of Walnut Shells: Thermal Biomaterial Behavioral Outcomes

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Abstract. This paper presents a new experimental method for the thermal analysis of solar pyrolysis of walnut shells. The method consists of two types of thermal experiments: (A) the pyrolysis of walnut shells, and (B) the heating-cooling of the biochar obtained during experiment A. Nutshells are a waste product from the pecan nut industry. The state of Sonora, Mexico, produces large volumes of walnuts and their residue. Likewise, this region has a considerable solar resource. The motivation of this study is to obtain biochar - a bi-product of high commercial value used for soil enhancement - using solar energy and agro-industrial waste. In this experiment, biomass pyrolysis of 50g of nutshells was carried out inside a stainless-steel reactor heated with concentrated radiation from a solar simulator. Three different heat fluxes were used: 234, 482, and 725 W. The maximum reaction temperatures were: 382, 498, and 674 °C respectively. The composition of the pyrolysis gases (H_2, CO, CO_2, and CH_4) was measured and the biochar obtained was characterized. Finally, the performance of the solar reactor allowed us to identify and differentiate between evaporation, pyrolysis of cellulosic material, and lignin degradation.

Keywords: Solar Pyrolysis, Concentrated Solar Energy, Biochar.

1. Introduction

Mexico is a significant producer of pecan nuts (*Carya illinoinensis*). The state of Sonora, located in the northwest of Mexico is the second national pecan producer with 18,326 Tons in 2016, [1]. The largest volume of pecans is sold as a shelled product, resulting in an equivalent amount of shell waste for every gram of nuts produced. Sonora also has a considerable solar resource with 7 kW hr/m^2 of direct irradiation [2]. Hence, it is reasonable to explore the development of an efficient and low-cost process that can harness this solar resource and transform nutshells and pecan tree pruning into a high-value commercial material – biochar and syngas. Concentrated Solar Energy (CSP) technology can be used as a heat source for biomass pyrolysis and gasification processes. At the National Laboratory of Concentration and Solar Chemistry in Mexico, we are dedicated to the development of a process that uses the renewable resources of the country to produce solar fuels and biochar.

The process studied here mainly consists of the solar pyrolysis of biomass, which is the thermal degradation of materials within an inert atmosphere to prevent combustion [3]. This process yields combustible gases and liquids, along with the production of biochar, which is a solid fuel. Remarkably, biochar can also be used for environmental purposes such as soil

remediation [4] and carbon capture [5]. In previous experiments, the determination of the physicochemical properties of the biochar was achieved [6].

In the specific context of solar biomass pyrolysis, the most studied and reported reactors are those utilizing a quartz window, allowing concentrated solar radiation to directly impact the biomass. This configuration is attractive due to its thermal efficiency [7]. Furthermore, there is scarce published information on reactors for indirect radiation solar pyrolysis; herein lies the significance of this paper, as the employed reactor is a windowless stainless-steel reactor, where heat transfer to the sample primarily occurs through conduction. Additionally, most biomass pyrolysis experiments are conducted at fixed heating rates. In contrast, in these experiments, power is held constant; whereas heating rates become a study variable rather than a controlled variable. In this research work, heating rates were analyzed, proving to be a useful tool to identify behavior patterns during pyrolysis reactions; this analysis was enhanced by the comparison of the heating of the biochar with the pyrolysis curves of the walnut shell.

2. Experimental Setup

The experimental setup for biomass pyrolysis employed in this study consists of four parts: i) the solar simulator, ii) the cylindrical stainless-steel reactor, iii) the gas cleaning system and iv) the gas chromatography unit (Figure 1). The raw material is placed within the reactor with one of its sides exposed to the heat generated by the solar simulator. The solar simulator features a 7 kWe Xenon lamp that concentrates radiation using an ellipsoidal mirror. The concentrated radiation hits one of the faces of the reactor that functions as a receiver, heats it and the absorbed thermal energy is transferred to the interior of the reactor mainly by conduction and convection processes. The reactor is a partially closed vessel. Thus, the heating of the biomass is carried out indirectly. One of the advantages of using a solar simulator is the control of radiative power and its constancy during the experimentation.

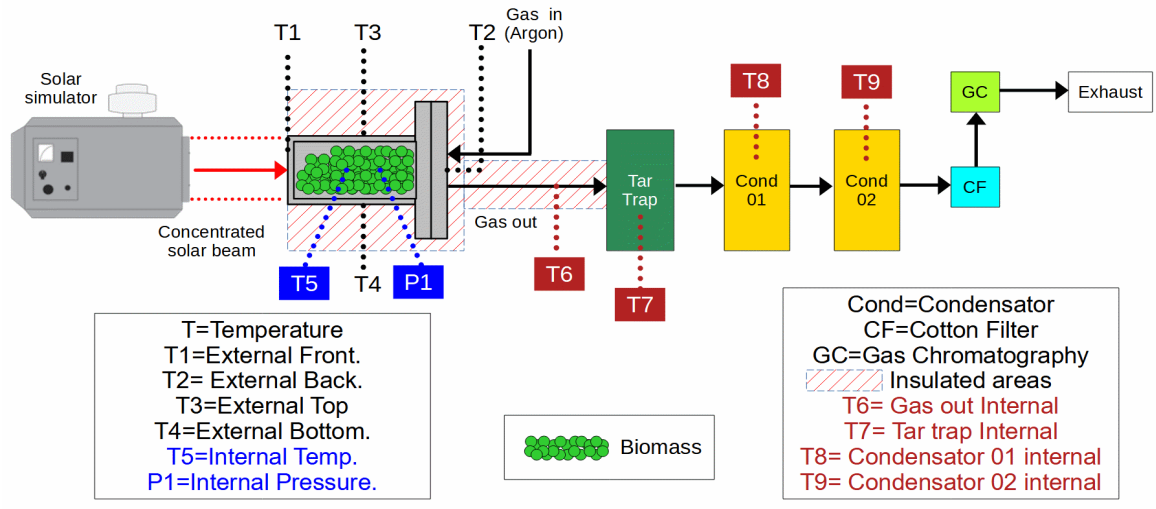

Figure 1. *Scheme of the experimental setup for biomass pyrolysis in stainless steel reactor with solar radiation.*

The system instrumentation includes sensors for temperature, pressure, and the chemical composition of the gases. Temperature sensors were categorized into two types: (1) peripheral thermocouples, which contact the external surfaces of the reactor, and (2) internal thermocouples, which encounter the biomass and gases. To determine the composition of the generated, a gas chromatography unit connected to the outlet of the system was used. Additionally, Figure 1 shows the process through a flow diagram with instrumentation. Thermocouples T1, T2, T3, and T4 correspond to the peripheral sensors, situated at the front, rear, top, and bottom of the reactor, respectively. T5 is an internal thermocouple in direct contact with the biomass. P1 is the reactor's internal pressure sensor. T6 measures the

temperature of the gases leaving the reactor. T7 measures the condensation temperature of the tar. The exhaust gases pass through a cleaning system that removes tars, so that the composition of the gases can be measured in a chromatograph (GC). The gas cleaning system consists of three condensers that cool the drag gas flow, with each condenser collecting a fraction of the liquids produced in the pyrolysis reaction. Furthermore, a cotton filter was placed for safety purposes to prevent damage to the GC; because pyrolysis liquids are corrosive.

3. Experimental design

Two types of experiments were conducted. The first type (type A) were pyrolysis experiments in which 50 g of crushed walnut shell (1mm to 4 mm particle size) were introduced into the reactor. After heating and cooling the pyrolysis products were obtained, in particular the biochar. The second type (type B) consisted of experiments in which the biochar produced in type A was reintroduced into the reactor and subjected to the same heating and cooling under the same conditions as in the previous pyrolysis experiments, but without chemical reactions - only heating and cooling were applied.

For the heating-cooling process in experiments A and B, three constant powers were used: 234, 482, and 725 W. Thus, there were six experimental runs, namely, three for type A and three for type B. In each experimental run, a constant flow of argon gas (inert gas) of 1 L/min was maintained as carryover gas.

During the pyrolysis process in type A runs, it was expected to observe the effect of the pyrolysis reaction on the installed sensors. The purpose of type B experiments was to determine the heating behavior of the inert material. By comparing these two behaviors (type A and B experiments), it was possible to identify the various pyrolysis stages and record the time and temperature at which each of them is manifested.

4. Results and discussion

The results of experiments type A (walnut shell pyrolysis) and type B (heating-cooling of biochar) carried out at a power of 725 W can be seen in Figure 2. Heating in both cases lasted 65 minutes. The red and black curves correspond to the temperature readings of thermocouple T5, which makes direct contact with the material inside the reactor, whether biomass or biochar. Both T5 temperature curves illustrate the heating and cooling processes.

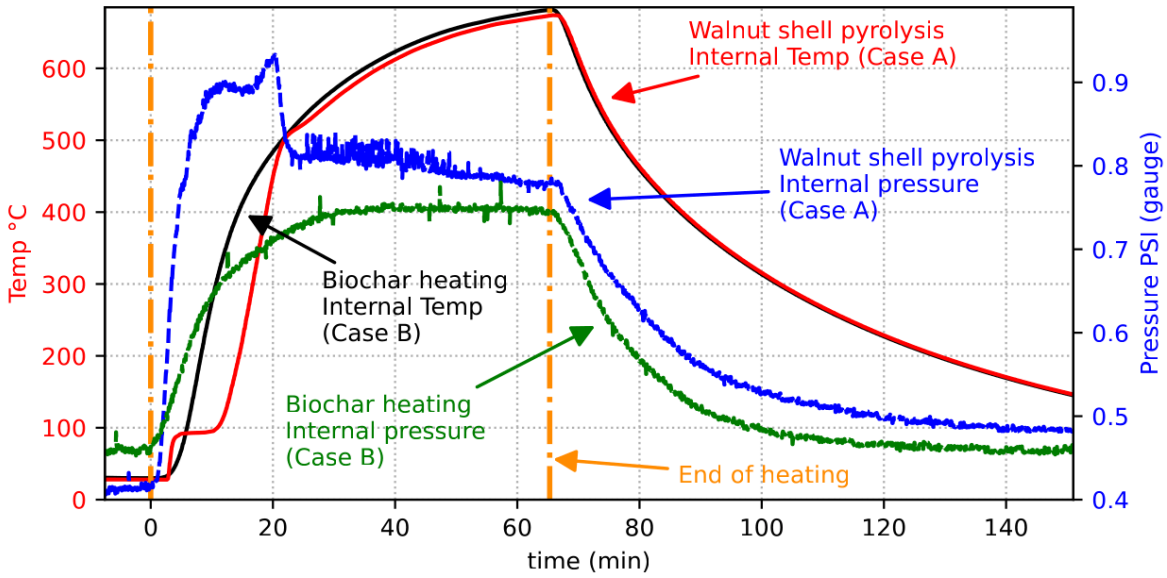

Figure 2. *Temperature and pressure histories inside the reactor for the biomass pyrolysis process (case A) and the heating-cooling of biochar (case B). Power: 725W.*

During the cooling phase, the curves closely align, indicating that the inertial thermal behavior of both materials is the same, this is, the biochar heated for type B and freshly produced for type A. Figures 3 and 4 further show the behavior of T5 and its derivatives for types A and B, respectively.

The temperature behavior of T5 during the heating for type B exhibits the typical pattern of heating of an inert solid, that is, a rapid initial increase followed by a gradual deceleration until it reaches the peak temperature, as shown in Figure 4.

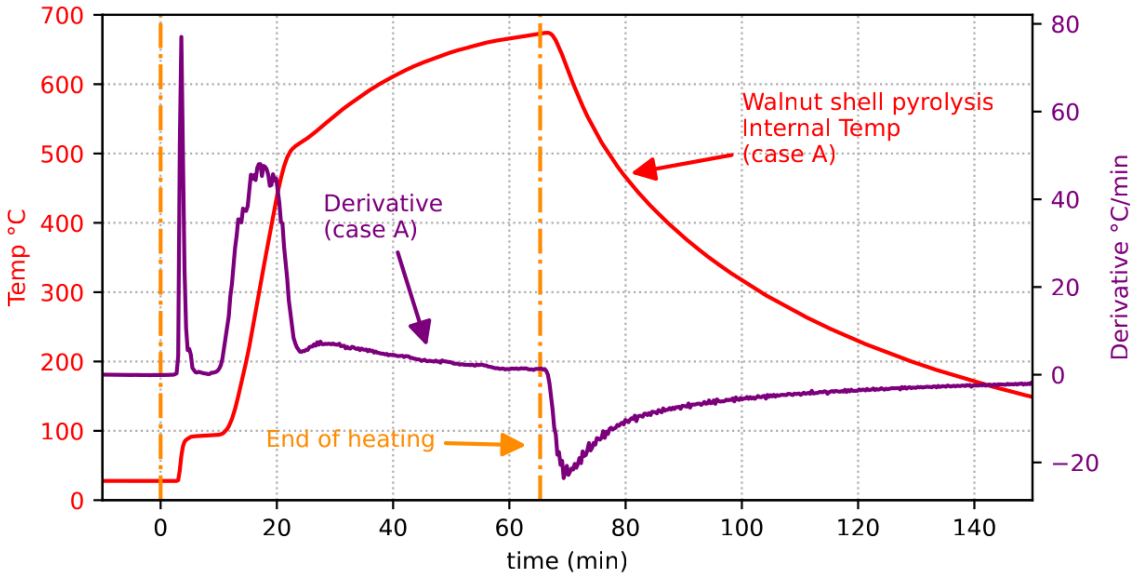

Figure 3. *History of the biomass temperature variation inside the reactor for the pyrolysis process (case A) and its derivative.*

In contrast, the temperature behavior of T5 during heating for type A differs, the temperature rises and levels off in a small plateau in the range of 5 to 10 minutes, possibly indicating a drying process due to the temperatures reached during this period. Then it rises abruptly until 20 minutes, where a change in slope occurs, softening and already having a similar behavior to that of biochar until reaching the peak, as depicted in Figure 3. The divergence in T5 behavior between types A and B provides valuable insight into the pyrolysis process.

In Figure 2, the behavior of the inside pressure for both cases are also shown. The blue and green curves correspond to the cases A and B, respectively.

The volume percentage (% v/v) of the main gaseous compounds produced during the pyrolysis experiment, including H_2, CO_2, CO, and CH_4 is shown in Figure 5. Likewise, the behavior of the internal pressure as a function of time is shown. With the information presented it is possible to interpret that different phenomena were observed at specific times. For instance, it suggests that the drying of the biomass occurred between 5 to 15 minutes, as evidenced by a temperature plateau around 100°C in Figures 2 and 3. Furthermore, the derivative of the temperature T5 is zero during the phase change from water to steam.

Following the drying phase, it is interpreted that thermal degradation of cellulose and hemicellulose took place. In Figure 5, the peak of the maximum pressure of the process is observed, signifying the point of the maximum degradation of cellulosic material.

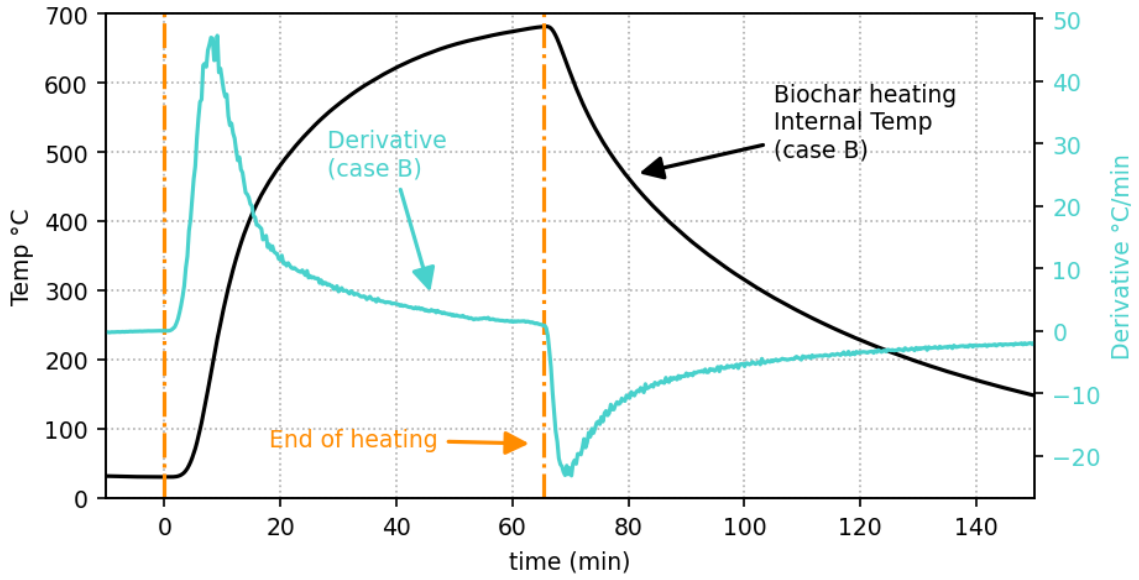

Figure 4. *History of the biochar temperature variation inside the reactor for the heating-cooling process (case B) and its derivative*

It is highly likely that the peak pressure is more associated with tar production than with the production of non-condensable gases because the GC did not register peaks in gas concentration. Additionally, it is noteworthy that after this peak pressure, stabilization is observed. Furthermore, the onset of the pressure curve plateau coincides with the second peak of maximum CO_2 and CO production, whose values show a progressive decrease over time.

This relatively stable pressure can also be attributed to the thermal degradation of lignin. In other words, after minute 25, the pyrolysis reaction continues, with only lignin reacting, as cellulose and hemicellulose have been completely consumed. This can be inferred because the typical temperature ranges for degradation reported are 220-315°C for hemicellulose, 300-400°C for cellulose, and 150-900°C for lignin [8]. Consequently, the GC indicates that pyrolysis gases continue to be produced but to a lesser extent. The heating curves and their respective derivatives obtained in the low (234 W) and medium (482 W) power experiments were found to be very similar to those presented in Figures 2, 3, and 4. The difference between each of the experiments lay in that the maximum temperature is directly proportional to the power. On the other hand, the time taken for the drying and pyrolysis stages to manifest was inversely proportional to the power; however, they exhibited behavior patterns that allowed differentiation between sample drying, cellulose material pyrolysis, and lignin pyrolysis for all three cases.

4.1 Mass balance

At the end of the experiments, the mass of tar and biochar recovered was measured with an analytical balance. The mass of the gases produced was calculated with the area under the curve of the data returned by the GC. Table 1 shows the mass percentages (wt%) of each of the products. It was observed that the amount of gas produced is directly proportional to the power. Conversely, the production of biochar exhibited the opposite trend, being inversely proportional to the power. Additionally, tar production showed a maximum yield at medium power (482 W).

Table 1. *Experimental conditions and products yield (wt%)*

Power (W)	Max Reaction Temp (T5) (°C)	Char (%)	Tar (%)	Gas (%)
234	382	41.61	41.67	9.02
482	498	32.90	49.91	9.49
725	674	28.17	45.59	18.54

Before running the experiments with the solar simulator, a TGA (Thermogravimetric Analysis) characterization of the walnut shell was carried out. These TGA curves served as a reference to compare the maximum reaction temperature observed in the thermogram.

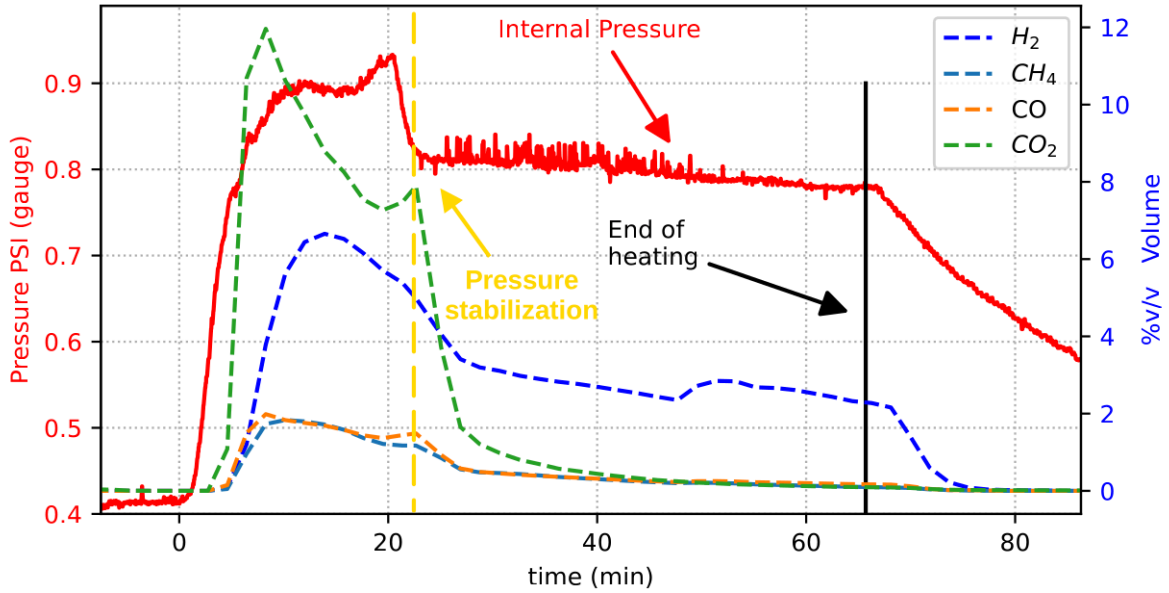

Figure 5. *Main gases produced during nutshells pyrolysis and internal pressure.*

Furthermore, it was noted that the mass percentages obtained in the experiments align with the yields indicated by the thermogram at corresponding temperatures. These yields indicate the absence of combustion during heating or cooling phases, as lower biochar percentages would have been expected if combustion had occurred. Likewise, this result indicates that the internal thermocouple (T5) has good contact with the biomass; therefore, the T5 curve is a reliable indicator of the reaction temperature.

Table 2 presents the elemental analysis of unpyrolyzed walnut shell and biochar at their respective temperatures, with results reported in mass percentage (wt%). The table shows that the percentage of carbon increases as a function of the reaction temperature, while the oxygen percentage decreases. To facilitate the description of the solid products, a column of suggested applications has been included.

For soil remediation applications, the presence of functional groups in biochar is required. The percentage of oxygen is an indicator of the presence of these compounds; therefore, biochar produced at 234 and 482 W have the potential for soil remediation. Biochar produced with a power of 482 W and above is suitable for gasification because a temperature above 500 °C leads to the complete removal of the tar produced in pyrolysis.

Table 2. *Biochar's elemental analysis. H=Heating by combustion. SR= Soil remediation. G=Gasification. Cstor=Carbon Storage.*

Power (W)	Max Reaction Temp (T5) (°C)	C (%)	H (%)	O (%)	N (%)	S (%)	Application
-	Nutshell (Raw Material)	47.97	5.41	45.92	0.61	0.09	-
234	382	73.70	3.18	22.43	0.69	0.00	H/SR
482	498	77.88	3.15	18.02	0.95	0.00	G/SR
725	674	82.84	2.26	14.22	0.68	0.00	G/Cstor

For solar gasification and carbon storage applications, tar-free biochar with minimal oxygen content as possible is required. It has been reported in the literature that biochar produced below 400 °C is considerably less stable than that produced at higher temperatures [9]. Therefore, this solar reactor is capable of producing biochar suitable for carbon storage when operating with a heat flux of 725 W.

5. Conclusions

The experiments aimed to understand the thermal behavior of organic matter during the pyrolytic decomposition process have been presented. The experimental setup and the methodology followed to conduct the experimentation were described.

Two types of experiments were conducted: A) the pyrolysis of the walnut shell and B) the heating-cooling of the biochar obtained in experiment A.

The comparison made between the experiments A and B allowed us to understand when the processes of moisture evaporation, the decomposition of cellulose and semi-cellulose, as well as the heating of lignite occur.

The behavior of the pressure and the production of the gases H_2, CO, CO_2 and CH_4 allowed us to determine the completion of the degradation of cellulose and hemicellulose.

The comparative methodology used in this study has enhanced our understating of the pyrolysis process of walnut shells.

Data availability statement

Raw data were generated at the Institute for Renewable Energy of the National University of Mexico. Derived data supporting the findings of this study are available from the corresponding author C.A. Estrada on request.

Author contributions

A. Aspiazu-Méndez: Methodology, Experimental Set Up, Formal Analysis, Experimental Component Manufacturing & Construction, Writing – Original Draft, Writing – Review and Editing, Visualization. **N. Aracely Cisneros-Cárdenas:** Formal Analysis, Writing – Review and Editing. **Carlos A. Pérez-Rábago:** Methodology, Conceptualization, Experimental Set Up, Experimental Analysis, Supervision. **Aurora M Pat-Espadas**: Methodology, Formal

Analysis. **Fabio Manzini-Poli**: Methodology, Formal Analysis. **C.A. Estrada:** Conceptualization, Methodology, Formal Analysis, Writing - Review and Editing, Visualization, Supervision, Resources.

Competing interests

The authors declare no competing interests.

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