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- Influence of species and stand position on isotopic and molecular composition
- of leaf litter during degradation in an urban mangrove forest
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- 8 * corresponding author: sarah.robin@unc.nc
- **Abstract**

 Understanding the diagenetic processes of organic matter (OM) within mangrove forests is essential to grasp ecosystem dynamics and exchanges with adjacent ecosystems. This study investigated the influence of urban runoff on leaf litter degradation in a New Caledonian mangrove forest, subjected to urban rainwater for over 50 years. Focusing on *Avicennia marina* and *Rhizophora stylosa*, our objectives were to determine factors affecting leaf litter degradation, assess urban runoff effects on decay rates and element concentrations, and understand OM changes at the molecular level. Litterbags containing senescent leaves placed on the mangrove floor were collected after 7, 14, 28, 56, and 72 days. C and N along with their stable isotopes were evaluated during degradation as well as lignin and neutral carbohydrates contents. Despite lower initial N content, *R. stylosa* 19 exhibited faster degradation $(t_{1/2}$ of 36 ± 3 and 28 ± 2 days) than A. *marina* ($t_{1/2}$ of 43 ± 9 and 33 ± 4 days), emphasizing the critical role of species position within the mangrove forest regarding tidal immersion. Urban runoff, submerging the urban site, intensified leaf litter degradation, influencing both mass loss and molecular changes in OM. After 72 days of leaf litter degradation, the loss of rhamnose and glucose was more pronounced at the control site (13% and 75% for rhamnose and 46% and 53% for glucose for *A. marina* and *R. stylosa*, respectively) compared to the urban site. The study also exposed molecular tendencies during mangrove leaf litter degradation. The content 26 of ferulic acid in the leaf litter decreased at all stands after 72 days of degradation (between -25% and -58%), while total syringyl phenols increased (between +64% and +232%). This research exposed the global implications of urban runoff, indicating accelerated leaf litter degradation in

 mangrove forests, potentially disrupting C sequestration dynamics and threatening ecosystem services.

31 Keywords: mangrove, litterbag, stable isotopes, lignin, neutral carbohydrates

1. Introduction

 Mangrove forests are coastal ecosystems established in tropical and sub-tropical areas around the world, with some species present in temperate regions (e.g. Auckland, NZ). These forests have a very large organic carbon (OC) stock, much larger than any marine and terrestrial ecosystems within the same latitudes (Alongi, 2014). Most of this OC is stored in the soil, but about 15% is in the aboveground biomass (Alongi, 2020). 31% of the total net primary production of mangrove forests comes from the production of litter (Bouillon et al., 2008). Once this biomass turns into litter, it becomes a crucial part of the trophic chain of the mangrove forest and adjacent ecosystems. Litterfall degradation actively contributes to the energy and material flow in the forest and is considered an energy source for coastal productivity (Lugo and Snedaker, 1974; Twilley et al., 1986). The litterfall organic matter (OM) can be consumed in the forest floor by autochthonous fauna and microorganisms, dissolved during decomposition, and exported to adjacent ecosystems at ebb tide as debris, dissolved OM, or dissolved inorganic matter, which also has a key role in the trophic chain (Fleming and Lin, 1990; Rezende et al., 1990; Wafar et al., 1997; Kristensen et al., 2017; Kida et al., 2019).

 Mangrove leaves account for the major part of the litterfall (Twilley et al., 1986; Day et al., 1987), varying between 40 and 90% (Mackey and Smail, 1996). Fruits, flowers, and the woody tissues account for the remaining litterfall. Therefore, most studies on litterfall degradation focused on leaf litter, using the litterbag experiment for comparison with literature (Nordhaus et al., 2017; Yang et al., 2018; Vinh et al., 2020). Leaf litter degradation occurs in three main stages: 1) the initial leaching of soluble compounds, 2) the colonization by microorganisms (i.e., fungi, bacteria, and protozoa) and decomposition via litter breakdown (Fell et al., 1975; Cundell et al., 1979; Fell and Master, 1980), and 3) the slow refractory phase where the least labile molecules are consumed (Valiela et al., 1984; Wilson et al., 1986; Tam et al., 1990). The rate of degradation of the leaf litter depends on multiple parameters, with varying significance depending on the context. The initial chemical composition of the leaves, especially C/N ratio, tannin, and lignin content, is one of the key parameters influencing the decay rates (Robertson, 1988; Tam et al., 1990; Mfilinge et al., 2002; Vinh et al., 2020). The leaf-consuming fauna and microbial communities of the forest floor also impact degradation rates (Fell and Master, 1980; Robertson, 1986; Imgraben and Dittmann, 2008). Many abiotic factors can influence litterfall degradation such as particle size of the forest soils, redox conditions, temperature, available oxygen, and the degree and frequency of tidal inundation (Lugo and Snedaker, 1974; Steinke and Ward, 1987; Chale, 1993; Vinh et al., 2020).

 Leaf litter degradation in mangrove forests is a source of nutrients; therefore, the change in element contents such as C, N, macronutrients, and neutral carbohydrates during degradation is of interest. The capacity of elements to be mobilised from degrading litter depends on the concentrations of these elements in the soil and incoming water, as well as on their role for litter feeders and whether they form complexes with leachable or refractory compounds (Mfilinge et al., 2002; Hossain et al., 2014; Gautam et al., 2016; Nordhaus et al., 2017). Neutral carbohydrates and organic N-rich compounds are easily degraded from the plant material, while lignin-rich litter resists decay (Fell et al., 1975; Cundell et al., 1979; Twilley et al., 1986; Chale, 1993). The depletion of elements during leaf litter degradation indicates leaching to the surroundings, or breakdown and consumption by microorganisms (Fell and Master, 1980; Fourqurean and Schrlau, 2003; Gautam et al., 2016; Nordhaus et al., 2017). The enrichment of elements and macronutrients in leaf litter during the degradation process is attributed to the production of these elements from microorganisms during decomposition such as the polysaccharides exudates from bacteria (Fell et al., 1975; Robertson, 1988; Mfilinge et al., 2002; Yang et al., 2018), or inputs from the water column (Rice and Windom, 1982; Lacerda et al., 1988; Tam et al., 1990; Vinh et al., 2020). The study of these various elements and molecular compounds such as neutral carbohydrates and lignin give essential information on the litterfall degradation and preservations processes, which directly affect the soil 81 OM and exported OM quality.

 One of the major worldwide threats to mangrove ecosystems is the urbanization of the littoral zone. Almost half of the world's mangrove forests are located in only 4 countries: Indonesia (28.4%), Brazil (9.4%), Malaysia (5.8%), and Papua New Guinea (5.1%) (Hamilton and Casey, 2016). On average, a third of the population of these countries lives on the coastline (CIESIN, 2012). Consequently, there is competition for space between mangrove ecosystems and economic and urban development. Urbanization can inhibit mangrove landward migration, prevent the water flow 88 into the mangrove forest, and be a source of urban water runoffs, which may contain contaminants (Friess et al., 2019). The inputs of urban runoff can modify the immersion conditions of the mangrove trees, change the physico-chemical parameters of the mangrove soil such as pH, redox conditions, and salinity, and be a source of dissolved nutrients, OM, and multiple contaminants (Cavalcante et al., 2009; Bastakoti et al., 2019; Robin et al., 2022; Fiard et al., 2022). Therefore, urban runoff in mangrove forests may influence the decay rates of the litterfall on the soil surface as well as the quality of this litterfall during degradation. To our knowledge, only one study looked at the effect of anthropogenic sewage on mangrove litterfall degradation and concluded that the discharge had no effect on the degradation processes (Tam et al., 1998). It is therefore essential to collect data and gain knowledge on which mangrove characteristic changes driven by the urbanization of the coasts influence the litterfall degradation processes.

 New Caledonia is a French archipelago located in the South Pacific Ocean between 20°S and 23°S. Semi-arid mangrove forests cover 80% of the West coast of the main island, which has semi-diurnal tidal cycles (Douillet, 2001). 24 mangrove species develop mainly in monospecific stands, but two are dominant, *Rhizophora* spp., which are present on the seaward side of the forests and represent more than 50% of mangrove plants, and *Avicennia marina*, which are established at higher elevation and on saltier soil, representing about 15% of mangrove plants in the archipelago (Deborde et al., 2015). The population density in New Caledonia is low (16 people per km²), but 60% of the population is concentrated in the capital and the four cities nearby, that are all located on the littoral zone where mangrove forests develop (Insee, 2020). Urbanization in New Caledonia has caused the destruction of mangrove forests, but only few studies have been conducted on the influence of urbanization on mangrove forests dynamics (Robin et al., 2022).

 The study of change in element concentrations during litterfall degradation in a mangrove forest is crucial to understand the OM diagenetic and preservation processes within the forest and exchanges with adjacent ecosystems. The aim of this paper is to evaluate leaf litter degradation dynamics in an urban semi-arid mangrove forest (New Caledonia), receiving urban rainwater for more than 50 years. The objectives of this study are 1) to determine factors influencing the differences in leaf litter degradation between mangrove species (i.e., initial composition of the leaves or position of the stand in the mangrove forest), 2) to assess the effects of urban rainwater runoff on leaf litter decay rates and leaf litter changes in element concentrations, and 3) to understand OM litterfall changes with degradation at the molecular level (neutral carbohydrates and lignin content). 119 We hypothesize that the main factors affecting leaf litter decay rates are the stands position in the intertidal zone and the urban rainwater runoff as higher stands immersion times enhance leaching and urban runoff modifies microbial communities. We also hypothesize that the change in composition of leaf litter during degradation will be mainly influenced by the initial composition of the litter and the redox conditions, both factors dependent on the mangrove species and the urban runoff. To this aim, a litterbag experiment has been undertaken for 72 days in a control and an urban mangrove forest for the two main mangrove species present in New Caledonia, *Avicennia marina* and *Rhizophora stylosa*. Decay rates have been calculated from the mass loss, while total C, total N, and their stable isotopes have been determined for each sample, as well as their neutral carbohydrates and lignin contents.

2. Materials and Methods

2.1. Study sites

 One of the main cities of New Caledonia, Dumbea, has seen its population increase by 33% this last decade resulting in the development of urban infrastructures in the littoral zone (Insee, 2020). Two mangrove forests in Dumbea have been chosen as study sites in order to compare forests that share a common geological unit as the source of their watersheds and the same vegetation type. The first site is the control mangrove forest (22°12'08"S, 166°26'20"E), located in the Apogoti Bay. Even though housing lots have developed recently around the mangrove, no direct anthropogenic inputs are discharged in the mangrove forest. The second site is the urban mangrove forest (22°12'39"S, 166°27'19"E). Urban rainwater runoff from the upper allotment (mainly housing lots for 10 000 inhabitants) flows into the mangrove forest and has done so for more than 50 years (Fig. 1). At both sites, the two main mangrove species observed, developing in monospecific stands, are *R. stylosa* and *A. marina*. Visible impacts of urban runoff in the urban mangrove forest are the position of *R. stylosa* stand landward of *A. marina* at the entrance of the runoff, with much higher *R. stylosa* trees (about 8-10 m high compared to 2 m high at the control site).

2.2. Sampling and processing

 Yellow senescent leaves about to fall on *A. marina* and *R. stylosa* trees were collected at the control site. To limit factors other than the urban runoff, potentially affecting leaf litter degradation 147 such as the senescent leaves initial composition, it was chosen to use the same senescent leaves samples at both sites. This is why senescent leaves were only collected at the control site. Fresh 149 green leaves were also collected from the trees in triplicates, but at both sites, to determine whether the composition of the leaves change significantly between the fresh and senescing stage. One sample of fresh leaves correspond to 30 leaves picked from 5 different adjacent trees. The leaves were carefully washed and air-dried for 24h at the laboratory. Three random samples of about 50 g of whole senescent leaves per species were frozen, freeze-dried, and ground with a cutting mill, corresponding to the samples at t0 "senescent leaves". Samples of about 6 g of dried *A. marina* whole leaves and 15 g of dried *R. stylosa* whole leaves were prepared and precisely weighed. Each samples were placed into individual nylon litterbags (2 mm mesh size) for the litterbag experiment. The 2 mm mesh size allowed for soil contact enabling bacterial activity while limiting the physical actions of large detritivores such as crabs. A total of 90 bags were attached to the roots of the corresponding tree species, on the surface of the soil, and in three different spots within the same species stand in both the control and urban mangrove sites. Triplicates of litterbags were collected at the three spots, for each species, after 7, 14, 28, 56, and 72 days (a total of 36 bags per day of collection). The experiment was stopped after 72 days because the degradation was already very advanced, and samples further degraded would be too hard to analyse properly. The litterbags were immediately opened at the laboratory, the leaves were carefully washed and air-dried for 24h prior to weighing. Samples were then frozen, freeze-dried, and ground with a cutting mill. Fresh green leaves were also collected immediately from the trees at both sites in triplicates, washed, freeze-dried, and ground.

2.3. Mass loss and half-life

169 The percentage mass loss or percentage mass remaining after 7, 14, 28, 56, and 72 days of 170 degradation were obtained with the initial mass (±0.001 g) of the air-dried leaves prior to placing in 171 the litterbags and the mass of the same air-dried leaves after collection (±0.001 g) in the mangrove 172 site. For comparison with literature, single exponential trends were plotted for each species:

$$
W_t = W_0 e^{-kt} \tag{1}
$$

174 with W_t the mean mass remaining in g, W₀ the initial mass in g, k the exponential factor, and t the 175 time in days. The half-lives $(t_{1/2})$ in days were obtained with the following equation and the 176 uncertainties calculated with R from the decay rates and their standard deviations:

177 $t_{1/2} = \ln(2)/k$ (2)

178 *2.4. Carbon, nitrogen, and stable isotopes analysis*

179 Total C, total N, and their stable isotopes were measured on an isotope ratio mass 180 spectrometer Sercon Integra 2 at the LAMA laboratory of the Institute of Research and Development 181 of New Caledonia. About 30 mg of samples were weighed in tin cups and folded into tightly closed 182 spheres. The samples were transported in a combustion column with helium gas where they were 183 heated at 1 000 °C and oxidized with Cu and Cr oxides, while silver wool trapped sulphur and 184 halogens. The samples were then transferred to the reduction column at 600 °C where the Cu 185 interacts with excess oxygen so that the NOx is reduced to N₂. The water in the samples was trapped 186 with $Mg(CIO₄)₂$ and N₂ and CO₂ of the samples were separated by gas chromatography. The 187 separated molecules were quantified by mass spectrometry in positive ESI mode. The mass 188 spectrometer measures the relative abundances of isotopes in the sample gas. For carbon, it 189 measures the ratio of ¹³C to ¹²C (expressed as δ¹³C), while for nitrogen, it measures the ratio of ¹⁵N 190 to ¹⁴N (expressed as δ¹⁵N). To calculate the δ values, the measured isotopic ratio is compared to a 191 known standard. The standard used is the Vienna Pee Dee Belemnite (VPDB) standard for C, and 192 the atmospheric nitrogen standard for N. For quality control, duplicate of samples were passed 193 through the spectrometer (1 every 10 samples) (Table S1).

194 *2.5. Neutral carbohydrates*

195 Neutral carbohydrates were analysed at the Earth Sciences Institute of Orleans (ISTO). 196 About 50 mg of samples were hydrolysed 4h at 105 °C in pyrex tubes with 5 mL of 4M of 197 trifluoroacetic acid (TFA). After cooling in an ice bath, 500 µL of internal standard (2-deoxyglucose 198 at 8 mg L⁻¹) were added and the sample was centrifuged for 30 min at 5 600 rpm. The extract was 199 evaporated, and the dried samples were kept frozen. Prior to analysis, neutral carbohydrates were 200 derivatized with the addition of 500 µL of ethoxy ammonium chloride solution in pyridine (40 mg mL⁻ 201 ¹) heated for 1h at 70 °C. 250 μ L of BSTFA were added and the sample was once again heated at 202 70 °C for 1h. After evaporation, the residue was dissolved in 2 mL of heptane, and the solution 203 passed through a 45 µm filter prior to injection in the GC-MS. The GC is a Trace 1 300 (Thermo 204 Scientific) coupled to a MS ISQ7000 (Thermo Scientific). The GC is equipped with at Restek Rxi-205 5Sil MS column (60 m x 0.25 mm, 0.25 µm diameter) with 5 m of pre-column. Helium gas is used 206 as vector and the analysis is carried out at constant 1 mL min⁻¹ flow rate. The injector was heated 207 at 280 °C and the transfer line at 300 °C. 1 μ L of sample was injected in splitless mode and passed 208 through the column with a temperature program (Table S2). For the MS analysis the source was 209 heated at 240 °C and the ions obtained via electronic impact (70 eV). The spectra were obtained 210 between 50 and 750 Da with a scan time of 0.4 s scan⁻¹. Quality control consisted of duplicate 211 technical samples (≤11% standard deviation) and measurement of the internal standard (Table S3).

212 *2.6. Lignin-derived phenols*

213 200 mg of samples were hydrolysed for 3 h at 170 °C in 8 mL of 2N NaOH with 100 mg of 214 Fe(NH₄)₂(SO₄)₂ under N₂. After cooling, the extract was collected once the sample was centrifuged 215 at 3 000 rpm for 10 min. The extract was acidified at pH 1 with HCl and lignin-derived phenols were 216 extracted twice with 3 mL of anhydrous diethyl ether. After complete evaporation, lignin-derived 217 phenols were diluted in 1 mL of 50:50 methanol: H₂O, filtered at 45 µm and analysed via UPLC-MS. 218 Chromatographic separation was achieved using a Vanquish Flex system (Thermo Fisher Scientific, 219 France) consisting of a binary pump, an autosampler and a heated column compartment. Samples 220 were separated on a Hypersil GOLD column (1.9 µm particle size), 50 x 2.1 mm (Thermo Scientific). 221 For elution, a binary gradient program was used (Table S4), the mobile phase was a mixture of 222 ultrapure water containing 0.1% of formic acid (Carlo Erba) (eluent A) and methanol OPTIMA LC/MS

223 (Fischer) with 0.1% of formic acid (eluent B). The flow rate was set to 0.5 mL min⁻¹ and injection (2 224 µL) was made automatically by the autosampler. UV detection was carried out at 280 nm. MS detection was performed using an Orbitrap Exploris 120 (Thermo Fisher Scientific, France) and operated with the heated electrospray ionization source in negative ion mode with a vaporizer 227 temperature of 300 °C. Scan modes were both full MS – ddMS² and SRM. The full MS mode had a resolution of 30 000 and a scan range of 50 – 250 m/z with HCD Collision energies specified for each molecule. The SRM mode had a resolution of 120 000 at 20% HCD collision energy. The full UPLC-MS optimized parameters are displayed in Table S4. The quantification was performed with an external calibration curve (Table S5) and laboratory reference materials spiked with the analytes. For quality control, a blank solution was passed at the beginning and end of every series in the same conditions as the samples and values were all below detection limits (Table S6). A quality control solution (QC) consisting of a point of the calibration curve was passed every 10 samples in the same conditions as the samples and the values obtained were all below 15% difference with the expected value (Table S6).

2.7. Statistical analyses

 Statistical analyses were performed using R studio software (version 1.2.5001). For comparison between species or study sites the Mann-Whitney test was performed. All other statistical analyses with more than two variables were tested with a Kruskal-Wallis test followed by 241 a Wilcoxon test. All tests were performed with a 95% confidence interval and $n \ge 3$. Kendall correlation analysis was performed to obtain correlation matrices.

3. Results

3.1. Sources characteristics

 All measured variables for the fresh and senescent leaves of *A. marina* and *R. stylosa* at 246 both sites are displayed in Table 1. The fresh leaves of both species have significantly higher $\delta^{15}N$ 247 values (p< 0.01) and lower δ¹³C values (p< 0.05) at the urban site (5.8‰ and -27.7‰, and 2.6‰ and -30.7‰, for *A. marina* and *R. stylosa*, respectively) than those collected at the control site (1.1‰ and -25.8‰, and -1.3‰ and -27.5‰, for *A. marina* and *R. stylosa*, respectively). At the control site,

 fresh leaves are more enriched in ¹³C than senescent leaves for both species, but for *R. stylosa* they are less enriched in ¹⁵N (-1.3‰ vs -0.2‰). Both fresh and senescent leaves of *A. marina* have significantly higher N contents (p< 0.01), δ ¹³C (p< 0.05), and δ ¹⁵N values (p< 0.05) than *R. stylosa* but lower C/N ratios (p< 0.01) (39 for *A. marina* and 166 for *R. stylosa*).

 In Table 1 it is shown that the total lignin contents (Σ11 phenols) of the fresh and senescent leaves of *A. marina* are significantly higher than those of *R. stylosa* (p< 0.05), which is also the case for the 4 phenol groups (p-hydroxyl or P, vanillyl or V, syringyl or S, and cinnamyl or C). The senescent leaves at the control site have significantly higher total lignin concentrations than the fresh leaves (p< 0.01) by a factor of 10 for *A. marina* and a factor of 6 for *R. stylosa* due to higher 259 vanillyl and cinnamyl contents. Therefore, the ratios P/(V+S), P/V, and S/V are much lower in the senescent leaves than in the fresh leaves for both species. The acid over aldehyde ratios (Ad/Al) in senescent leaves are also much higher than in the fresh leaves (Table 1).

 Fresh leaves of *A. marina* are more enriched in neutral carbohydrates than *R. stylosa* but the leaves of *R. stylosa* have higher concentrations of hexoses (mannose and galactose) and deoxy sugars (fucose and rhamnose), especially fucose and galactose than *A. marina* (Table 1). Total carbohydrates content is significantly higher in the senescent leaves than the fresh leaves at the control site (p< 0.05) (Table 1). Neutral carbohydrates represent 45.2% and 49.9% of the total mass for the senescent leaves of *A. marina* and *R. stylosa*, respectively (Table 1). Xylose, arabinose, and glucose are the most concentrated neutral carbohydrates measured representing up to 33%, 34%, and 42 % of the total neutral carbohydrates, respectively. Ribose and fucose are the least concentrated neutral carbohydrates measured in both fresh and senescent leaves with values as 271 low as 0.48 mg g^{-1} , and 0.71 mg g^{-1} , respectively (Table 1).

3.2. Decay rates

 The decay rates of *A. marina* and *R. stylosa* leaf litter degradation at both sites are displayed in Figure 2. The calculated half-lives are 43±9 days and 36±3 days for *A. marina* and *R. stylosa* at 275 the control site, respectively, and 33±4 days and 28±2 days at the urban site, respectively. At both sites, in the first 7 days, *A. marina* leaves lost 41% of their initial mass and *R. stylosa* leaves lost

 61% of their initial mass. After 72 days, on average, 26% and 19% of the initial mass of *A. marina* leaves remained at the control and urban sites, respectively, while 17% and 11% were remaining for *R. stylosa,* respectively.

 Leaf litter mass loss is significantly more important after 56 and 72 days at the urban site than at the control site (p< 0.01). Through the entire degradation experiment, the leaf litter mass loss of *R. stylosa* is more important than that of *A. marina* (p< 0.001).

3.3. Carbon and nitrogen content, and respective stable isotope composition

 The C and N content generally increased at both sites over time and for both species. At the control site, the C content for both species and N content for *A. marina* increased the first 28 days, and after 56 days. The N content of *R. stylosa* continuously increased during the 72 days of degradation. At the urban site, the *R. stylosa* litterfall constantly increased in N and C contents. C and N contents increased for *A. marina* until day 56 and 28, respectively, prior to a loss (Fig. 3A & B). The C/N ratios for *A. marina* were stable the whole 72 days of degradation, while *R. stylosa* C/N ratios continuously decreased with time (Fig. 3C).

291 The stable isotope ratios showed an initial enrichment for 7 days for $\delta^{15}N$ and 14 days for ¹³C at both sites and for both species. Overall, after 72 days of degradation, the δ¹⁵N of the litterfall significantly decreased compared to the initial values (p< 0.05) except for *A. marina* at the urban site where it increased (Fig. 3D). The δ ¹³C values significantly decreased for *R. stylosa* (p< 0.001) while they were similar for *A. marina* at both sites after 72 days of degradation (Fig. 3E).

3.4. Molecular analyses

3.4.1. Neutral carbohydrates

 After 72 days of litterfall degradation, total neutral carbohydrates content decreased from 299 452 to 380 mg g⁻¹ (-16%) and to 385 mg g⁻¹ (-15%) for *A. marina* at the control and urban sites, respectively, and from 498 to 250 mg g -1 (-50%) and to 388 mg g -1 (-22%) for *R. stylosa* at the control and urban sites, respectively (Fig. 4A). The most labile neutral carbohydrates after 72 days of degradation were arabinose, rhamnose, galactose, and glucose with loss ranges of 23% to 80%,

 2% to 76%, 31% to 50%, and 33% to 53%, respectively (Table 2). Xylose, ribose, fucose, and mannose all increased their concentrations in the leaf litter after 72 days of degradation for most 305 stands reaching up to 152 mg g⁻¹, 1.2 mg g⁻¹, 10 mg g⁻¹, and 16 mg g⁻¹, respectively (Table 2).

 For *A. marina*, the concentrations of pentoses (xylose + arabinose) and deoxy sugars 307 (rhamnose + fucose) in the senescent leaves (212 and 54 mg g⁻¹, respectively) are similar to the concentrations in the 72 days-degraded leaves. For *R. stylosa*, the concentrations in the degraded 309 leaves are lower by 9% to 67% than the senescent leaves (235 mg g⁻¹ of pentoses and 66 mg g⁻¹ of deoxy sugars). After 72 days of degradation, the concentrations of hexoses (mannose + galactose) significantly decreased (p< 0.001) for the four stands by a range of 20% to 39% (Table 2).

3.4.2. Lignin-derived phenols

 During the whole decay process, the sum of the lignin-derived phenols is significantly larger in the *A. marina* litter than in *R. stylosa* litter (p< 0.01), whatever the site (Fig. 4B). This is also the case for the four phenol groups (Table 3). After 7 days of degradation, the lignin content increased for *R. stylosa* but decreased for *A. marina*. The total lignin content after 72 days of degradation also increased for *R. stylosa* and decreased for *A. marina* compared to the lignin content in the senescent leaves (Fig. 4B). This is only the case for the vanillyl phenols, while after 72 days of degradation the syringyl phenols increased all between 71% and 231% (Table 3). In contrast to the total lignin content, the ratios p-hydroxyl/vanillyl (P/V), syringyl/vanillyl (S/V), and cinnamyl/vanillyl (C/V) increased after 7 and 72 days of degradation for *A. marina,* but decreased for *R. stylosa,* and followed similar patterns with degradation at the two sites (Table 3). In the first days of degradation, 323 there was a decrease in the p-hydroxybenzoic acid/p-hydroxybenzaldehyde ratio $((Ad/Al)_p)$ at both 324 sites and a decrease in the vanillic acid/vanillin ratio ((Ad/Al)_v) at the urban site only. After 72 days of degradation, the three acid/aldehyde ratios (Ad/Al) decreased at both sites and for both species (Table 3).

4. Discussion

328 4.1. Variability of organic matter quality of the fresh and senescent leaves of A. marina and R. stylosa

 Our investigation into the OM quality of leaves from *A. marina* and *R. stylosa* in urban and control sites presented findings that connect with broader scientific contexts. Fresh leaves from the 331 Urban site revealed high N and $\delta^{15}N$ values, aligning with expectations given the anthropogenic 332 influence in urban runoff. This is consistent with previous studies indicating elevated δ^{15} N values in urban environments (Rumolo et al., 2011). Our study expanded upon this understanding by 334 demonstrating the species-specific nature of ¹⁵N discrimination during N uptake, evident in the greater δ ¹⁵N values observed in *A. marina* compared to *R. stylosa*, which was previously observed for the same two genus in other studies (Herbon and Nordhaus, 2013; Regina Hershey et al., 2021).

337 The isotopic values, particularly δ^{13} C mean values of fresh leaves, provided valuable insights into the adaptive responses of mangrove trees. Coastal plants, including mangrove trees, often 339 exhibit enhanced water-use efficiency under salinity stress. Our findings, showing lower δ¹³C values in the urban site and in *R. stylosa*, contributed to the understanding of these adaptive mechanisms 341 (Medina and Francisco, 1997). Plants have a decarboxylating enzyme that discriminates ${}^{13}CO_2$ 342 when assimilating atmospheric $CO₂$ (O'Leary, 1981). The salinity of the soil and the position of the mangrove stand in the mangrove forest may impact the mangrove species efficiency to assimilate CO² or discriminate ¹³CO² (Farquhar et al., 1982; Lin and Sternberg, 1992). In New Caledonia, *A. marina* grows on saltier soil than *R. stylosa* (26 and 37 psu, respectively at the control site) (Robin 346 et al., 2022) and therefore, has less $^{13}CO_2$ discrimination and higher δ^{13} C values. Moreover, the upper soil at the urban site had a salinity of 0 psu for the first 10 cm (Robin et al., 2022), which may explain the lower values measured.

 As we explore the changes from fresh to senescent leaves at the control site we observed a decline in N content, δ ¹³C values, and a notable rise in C/N ratios, especially in *R. stylosa* (up to 150%). These senescence-related shifts are connected with biochemical changes before leaf falling, linking to established knowledge in mangrove ecology (Garten and Taylor, 1992; Rao et al., 1994; Nordhaus et al., 2011). Prior to leaf falling, the mangrove trees can relocate the N from the leaves to other tissues of the plant to limit N loss explaining the decline in N content. A general decrease in C content during senescing can be expected due to the loss of photosynthetic activity, but the relative increase in carbohydrates as a signal for senescing may induce the increase in C content in some mangrove species as observed in this study for *A. marina* (Wingler et al., 2006).

 Examining lignin-derived phenols and neutral carbohydrates content, our study contextualized findings within the existing literature on mangrove leaf composition and degradation dynamics (Marchand et al., 2005; Lallier-Vergès et al., 2008; Bala Krishna Prasad and Ramanathan, 2009). Higher lignin and neutral carbohydrate content in the fresh leaves of *A. marina* compared to *R. stylosa* agree with previous studies (Dittmar and Lara, 2001). However, the higher proportions of hexoses and deoxy sugars in the leaves of *R. stylosa*, especially fucose and galactose, underscored the need for a comprehensive insight of initial leaf compositions. The production or loss of neutral carbohydrates and lignin-derived phenols during senescence contribute to our knowledge of the intricate senescence process in mangrove leaves (Benner et al., 1990b; Opsahl and Benner, 1995, 1999).

4.2. Factors influencing leaf litter degradation between mangrove species

 The leaf litter of *R. stylosa* was degraded more rapidly on the soil surface than the leaf litter of *A. marina* at both sites; a trend opposite to conventional findings where species with higher initial 371 N content, and consequently lower C/N ratios, typically undergo faster degradation (Mfilinge et al., 2002; Yang et al., 2018; Vinh et al., 2020). Notably, *A. marina*, initially possessed five times more N in its senescent leaves than *R. stylosa*. The higher N content in plant material is known to attract leaf-degrading organisms due to the nutritional value of N compounds (Wafar et al., 1997; Nordhaus et al., 2011). We propose that the species' position within the mangrove forest is a crucial determinant of litterfall decay rates. Generally, species the most submerged experience faster degradation rates (Twilley et al., 1986; Steinke and Ward, 1987; Silva et al., 1998; Bosire et al., 2005). The physical impact of tides facilitates plant material breakdown (Vinh et al., 2020), and submersion by seawater or runoff promotes microbial development and leaching of soluble compounds from litterfall (Robertson, 1988; Tam et al., 1990; Ashton et al., 1999). In the mangrove forests of New Caledonia, *R. stylosa* is found on the seaward side of the mangrove forest, while *A. marina* is present at higher elevations with higher soil salinity (Deborde et al., 2015). However, in the urban mangrove forest, continuous runoff from urban rainwater altered soil physico-chemical

 parameters, particularly pH and salinity (0 psu in the upper 10 cm) (Robin et al., 2022). Consequently, *R. stylosa* trees are established on the landside and at the entrance of the runoff in the mangrove, providing a subtidal context unique to the urban site. Therefore, submersion of the *R. stylosa* stand by seawater at the control site and submersion by the urban runoff at the urban site may contribute to enhanced litterfall degradation for *R. stylosa*, by favoring leaching and microbial development on the leaf litter compared to *A. marina* (Robertson, 1988; Molnar et al., 2014).

 Despite the unexpected degradation trend observed in the leaf litter of *R. stylosa* compared to *A. marina*, further insights into the isotopic dynamics shed light on unique microbial processes driving the decomposition of litterfall of *R. stylosa*. The statistically significant decrease in δ ¹⁵N values with leaf litter degradation was only observed for *R. stylosa*. Bacteria dominating 394 decomposition processes have low δ^{15} N values as bacteria favour the immobilization of 15 N-depleted nitrate (Bragazza et al., 2010; Nordhaus et al., 2011). The results therefore suggest that microbial development beneath the *R. stylosa* stands at both sites was enhanced, possibly due to their position compared to the water sources, and can therefore ultimately lead to the lowering of 398 degrading leaf litter δ¹⁵N values (Leopold et al., 2013; Molnar et al., 2014).

 Leaf litter composition changes during degradation, specifically the N content, C/N ratio, and isotopic values (δ¹³C and δ ¹⁵N), were investigated. Degradation of the leaf litter of *R. stylosa* resulted in a decrease in the C/N ratio not observed for the leaf litter of *A. marina*. The decreasing ratio for *R. stylosa* may be associated with the immobilization of N by bacteria as observed in a variety of tropical environments (Gotto and Taylor, 1976; Rice and Tenore, 1981; Twilley et al., 1986; Benner et al., 1990a). As suggested in the previous paragraph, the decreasing ratio may only be observed for *R. stylosa* as microbial development beneath the *R. stylosa* stands at both sites was possibly enhanced. The decrease in the C/N ratio may also be partly linked to the degradation of hydrolysable components, particularly neutral sugars, rather than refractory N-rich components like lignin (Chale, 1993; Yang et al., 2018). Indeed, the neutral carbohydrate content of the leaf litter of *R. stylosa* decreased during degradation by 22% and 50% at the urban and control sites, respectively, while the lignin content increased after 7 and 72 days of degradation. Therefore, bulk leaf decayed more rapidly than lignin, as reported in the literature for anaerobic and sulphate reducing environments (Benner et al., 1984, 1991; Dittmar and Lara, 2001). Conversely, the lignin content decreased in the leaf litter of *A. marina*. The upper soil beneath *A. marina* was less reducing than *R. stylosa* (Robin et al., 2022), which can favour lignin degradation (Benner et al., 1991; Opsahl and Benner, 1995). *A. marina* also had a higher percentage of lignin content in its senescent leaves than *R. stylosa*, suggesting that the initial molecular composition of the leaves influenced the lability of the molecules during degradation. Higher lignin content may enhance lignin degradation by favouring microbial access to lignin polymers. This phenomenon, where the concentrations of the molecules in senescent leaves influence their decays, aligns with findings in terrestrial plants (Talbot et al., 2012).

4.3. Urban runoff effects on leaf litter degradation

 Urban runoff and associated modified conditions at the urban site seemed to affect leaf litter degradation rates as the mass loss was faster in the urban mangrove forest compared to the control mangrove forest. This discrepancy in mass loss can be attributed to the continuous flooding of the forest floor by urban rainwater runoff, which could enhance the early leaching process of the leaf litter. While previous studies have reported faster mass loss in subtidal stands compared to intertidal stands (Robertson et al., 1992), our findings reveal that, after 7 days of degradation, there is no significant difference in leaf litter mass loss between the urban and control sites. However, it is after 428 56 days of leaf litter degradation that statistical differences in mass loss emerge between the urban and control sites. This suggests that the second phase of degradation, involving the breakdown of 430 litter by microorganisms, becomes more prominent at the urban site. Therefore, we suggest that urban runoff likely favors microbial activity on the soil surface, leading to the observed divergence 432 in mass loss between the two sites during the later stages of leaf litter degradation. The runoff gives a more stable, nutritious, and humid environment for microbial development (Robertson, 1988; Leopold et al., 2013; Molnar et al., 2014). Mineralization of OC in coastal wetland soils is significantly influenced by temperature and soil water content, which regulate microbial metabolism (Marchand et al., 2022a). Additionally, it is impacted by the rate of electron acceptor renewal, varying with immersion. As the duration of immersion increases, the mineralization process may be enhanced or reduced, depending on soil permeability (Marchand et al., 2022b).

 The influence of urban runoff on leaf litter degradation was also evident in the larger increase in N content during degradation at the urban site than the control site. Urban rainwater runoff may have acted as an additional source of N to the forest floor and litter (Tam et al., 1998). Nitrogen can also be produced by microorganisms during leaf litter degradation (Tam et al., 1990; Mfilinge et al., 2002). The higher degradation rates associated with the higher enrichment of fucose and ribose at the urban site, characteristic of microbial production (Cowie and Hedges, 1984), indicated stronger microbial activity on the soil surface at the urban site.

 The modified soil conditions created by the submerging urban runoff may also have influenced molecular degradation processes of the leaf litter. After 72 days of degradation rhamnose and glucose loss was more important at the control site than at the urban site. With a lower soil surface salinity (Robin et al., 2022), the urban mangrove forest was a less suitable environment for the secretion of some enzymes such as cellulases, which enhance cellulose and hemicellulose hydrolysis (Arfi et al., 2013; Ivaldi et al., 2021). Also, the more anoxic environment of the urban forest's upper soil (Robin et al., 2022) limited the hydrolysis of neutral carbohydrates including rhamnose and glucose. The more reducing conditions may also have favoured lignin conservation over bulk OC during the early phase of degradation (Benner et al., 1984, 1991), explaining the higher relative lignin enrichment in the leaf litter of *R. stylosa* at the urban site than at the control site after 7 days of degradation.

4.4. Leaf litter molecular composition during degradation

 The molecular-level changes of OM during leaf litter degradation revealed species-specific and site-dependent influences on the stability of some molecules. In this study, we observed that the most abundant sugars, that is glucose, arabinose, galactose, and rhamnose, were the most labile, and the least abundant, that is sugars fucose, ribose, and mannose, were the most refractory ones. Trends like this one were observed in neutral carbohydrates and lignin-derived phenols during degradation, suggesting a potential end for compositional uniformity (Opsahl and Benner, 1999). The hypothesis of compositional uniformity suggests that the most abundant sugars would be more labile than the least abundant in order to end up with a uniform composition of neutral carbohydrates in the most degraded leaves (Opsahl and Benner, 1999). Except for xylose in this study, results

 seem to agree with this hypothesis. We suggest that xylose may be associated to more refractory components of the litter such as lignin, which enhanced protection from enzymatic degradation (Opsahl and Benner, 1999), as suggested by the correlation between xylose and p-hydroxyl phenols $(r = 0.61)$ and cinnamyl phenols $(r = 0.50)$ (Table S7).

 The order of lability of the 11 lignin-derived phenols differed between mangrove species and 472 sites but observations agreed with previous work. In the literature, syringyl phenols were classified as the most stable phenols and ferulic acid the least (Benner et al., 1990b). In the present study, ferulic acid content per g of TOC decreased in the leaf litter at the four stands after 72 days of degradation (Table S8), while total syringyl phenols increased. The hypothesis of compositional uniformity may also work here as for both species, the most abundant phenol group in the senescent leaves was also the most labile during degradation; that is vanillyl phenols for *A. marina* and cinnamyl phenols for *R. stylosa.*

4.5. Limitations of the experiment and models

 The litterbag experiment was conducted using senescent leaves from the control site only for both species. This design of experiment aimed to evaluate the changes in leaf litter mass and composition over 72 days of degradation with a focus on the influence of urban runoff on these changes. The choice of having the same senescent leaves at both sites enabled to limit the factors potentially affecting these changes other than runoff such as initial senescent leaves composition. The influence of initial composition was evaluated between species but not between sites. This experiment design was therefore not a limitation regarding the general processes investigated in this study. However, it is not possible from this experiment to quantify the elements or molecules released, stored, or gained by the leaf litter at the urban site. Furthermore, the experiment ended after 72 days of degradation as the mass remaining was the lower limit to conduct all the analyses. A longer experiment could have given further information relative to the refractory degradation stage.

 In this study, single exponential models were computed on the mass loss of the leaf litter with degradation. Single exponential models were used to calculate the half-lives of the litter and are frequently used in similar works using the litterbag experiment (Flores-Verdugo et al., 1987;

 Ashton et al., 1999; Bosire et al., 2005; Nordhaus et al., 2017; Vinh et al., 2020). However, double exponential models seemed more suitable for the degradation rate in this study as shown by the regression coefficients (R²) of the exponential regression lines (Figure S1), as previously suggested in the literature (Wider and Lang, 1982). Two phases of degradation stood out in the double exponential model with a first stage from 0 to 14 days for *R. stylosa* or to 28 days for *A. marina*, and a second to 72 days (Figure S1). The double exponential model indicated that the mass loss of the leaf litter was faster for the four stands during the first days of degradation as soluble compounds were leached. Still, the use of the single exponential model is preferential as comparison with literature is possible and the differences between species and sites were noticeable as much as with the double exponential model.

5. Summary and conclusions

 In this study, changes in mangrove leaf litter OM quality during degradation was analysed in relation to mangrove species (*A. marina* and *R. stylosa*) and to mangrove forests (urban and control) with a focus on the potential influence of urban runoff. Considering mangrove species, we were surprised to observe that despite lower initial N content, degradation of *R. stylosa* leaf litter was faster than the one of *A. marina* at both sites. We suggest that species position in the intertidal zone is crucial and that length of immersion, either tidal or runoff, are key factors controlling degradation rates. The immersion not only influences the leaching but also enhances the microbial development, 512 as evidenced by δ¹⁵N values variations beneath both *R. stylosa* stands. Regarding mangrove forests, the urban runoff submerging the mangrove soil amplified leaf litter degradation as shown by the lower half-lives (about ten days) for both species compared to the control site. We suggest that the runoff enhanced both leaching and microbial activity. Further experiments in mesocosms with controlled parameters should be undertaken to better understand the decay processes generated by the runoff. The physico-chemical conditions (more reducing, lower salinity, …) at the urban site not only influenced mass loss but also shaped the molecular composition of the OM during leaf litter degradation. The lower soil surface salinity may have limited enzyme secretion and hydrolysis of neutral carbohydrates. While urban runoff and site conditions impact leaf litter degradation, this study highlights that the initial molecular composition of the litter also plays a crucial role in controlling its molecular evolution during degradation. The observed leaf litter composition in neutral carbohydrates and lignin-derived phenols during degradation underscored the intricate interplay between environmental factors and OM stability in mangrove ecosystems.

 These findings have broader implications for understanding the global impacts of urban runoff on mangrove ecosystems, including potential reductions in carbon sequestration capacity and threats to ecosystem services such as habitat provision, fisheries support, and coastal erosion mitigation.

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Data Availability

Data are available through Mendeley Data, V2 at https://doi:10.17632/hh48m5g37v.2.

Appendix A. Supplementary Material

- Supplementary data referred in the text are available as supplementary material. Information on the
- instrument methods and quality control is available (GC-MS and UPLC-MS).

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- **Tables**
- 735 Table 1. Fresh and senescent leaves characteristics (mean value ±SD).

 11 phenols = p-hydroxybenzoic acid, p-hydroxybenzaldehyde, p-hydroxyacetophenone, vanillic acid, vanillin, acetovanillone, syringic acid, syringaldehyde, acetosyringone, coumaric acid, and ferulic acid; p-hydroxyl = p- hydroxybenzoic acid, p-hydroxybenzaldehyde, and p-hydroxyacetophenone; vanillyl = vanillic acid, vanillin, and acetovanillone; syringyl = syringic acid, syringaldehyde, and acetosyringone; cinnamyl = coumaric acid and ferulic acid; 740 P/V = ratio of p-hydroxyl over vanillyl; S/V = ratio of syringyl over vanillyl; $P/(V+S)$ = ratio of p-hydroxyl over the sum of 741 vanillyl and syringyl; (Ad/Al) = acid/aldehyde. vanillyl and syringyl; (Ad/Al) = acid/aldehyde.

742 Table 2. Mean neutral carbohydrate concentrations (\pm SD) in mg g⁻¹ in leaf litter with degradation at 743 the control and urban sites for both *A. marina* and *R. stylosa*.

745 Table 3. Lignin-derived phenols parameters in leaf litter with degradation at the control and urban 746 sites for both *A. marina* and *R. stylosa* (mean values ± SD).

Control A. marina	senescent	7 days	$\overline{14}$ days	28 days	56 days	72 days
p-hydroxyl (mg g-1)	0.27 ± 0.03	0.15 ± 0.03	0.20 ± 0.02	0.22 ± 0.04	0.26 ± 0.07	0.26 ± 0.04
Vanillyl (mg g ⁻¹)	$33 + 10$	$18 + 14$	15±2	$10 + 2$	4.4 ± 0.9	14 ± 3
Syringyl (mg g-1)	0.22 ± 0.001	0.14 ± 0.05	0.31 ± 0.21	0.42 ± 0.10	$0.47 + 0.26$	$0.50 + 0.05$
Cinnamyl (mg g ⁻¹)	$9.2 + 1.1$	$6.8 + 0.7$	$6.8 + 0.5$	11±2	$12 + 2$	$12 + 2$
$P/(V+S)$	0.029	0.022	0.028	0.020	0.021	0.022
P/V	0.008	0.008	0.013	0.021	0.058	0.019
S/N	0.007	0.008	0.021	0.041	0.106	0.037
C/V	0.27	0.38	0.45	1.00	2.68	0.86
(Ad/Al)p	2.57	2.01	1.50	0.54	0.49	0.52
(Ad/Al)v	10.98	11.62	5.57	0.89	0.70	1.10
$(Ad/Al)_s$	2.99	2.53	0.52	0.39	0.45	0.47
Control R. stylosa	senescent	7 days	$\overline{14}$ days	28 days	56 days	72 days
p-hydroxyl (mg g^{-1})	0.15 ± 0.001	0.12 ± 0.02	0.13 ± 0.01	0.11 ± 0.004	0.14 ± 0.01	0.13 ± 0.004
Vanillyl (mg g^{-1})	$0.90+0.17$	$5.7 + 4.1$	$2.6 + 1.5$	2.2 ± 0.9	$3.3 + 1.2$	3.4 ± 0.4
Syringyl (mg g-1)	0.14 ± 0.06	0.12 ± 0.01	0.14 ± 0.03	0.16 ± 0.04	0.20 ± 0.03	0.24 ± 0.02
Cinnamyl (mg g ⁻¹)	5.4 ± 2.3	4.2 ± 0.5	$3.8 + 0.3$	$3.0 + 0.3$	4.7 ± 0.9	$4.9 + 0.7$
$P/(V+S)$	0.026	0.027	0.034	0.033	0.029	0.025
P/V	0.160	0.021	0.051	0.048	0.042	0.039
S/N	0.152	0.021	0.054	0.073	0.061	0.073
C/V	5.99	0.75	1.45	1.36	1.42	1.45
(Ad/Al)p	4.58	3.71	2.32	2.38	1.82	1.78
(Ad/Al)v	20.88	19.53	34.32	26.32	19.50	13.59
$(Ad/Al)_s$	1.36	1.08	1.12	1.38	1.40	1.10
Urban A. marina	senescent	7 days	$\overline{1}4$ days	$\overline{28}$ days	56 days	72 days
p-hydroxyl (mg g-1)	0.27 ± 0.03	0.23 ± 0.005	0.23 ± 0.08	0.21 ± 0.02	$0.28 + 0.03$	$0.30 + 0.16$
Vanillyl (mg g-1)	$33 + 10$	$7.5 + 6.0$	15±9	11±5	16 ± 6	$23 + 16$
Syringyl (mg g ⁻¹)	0.22 ± 0.001	$0.39 + 0.01$	$0.68 + 0.22$	$0.53 + 0.19$	$0.61 + 0.15$	$0.73 + 0.35$

747 $P = p$ -hydroxyl, $V =$ Vanillyl, S = Syringyl, C = cinnamyl, Ad = acid, Al = aldehyde.

748 **Figure captions**

749 Figure 1. Control mangrove forest and urban mangrove forest in Dumbea city in New Caledonia with 750 delimitation of the new allotments and the old allotment and the entrance of the urban rainwater 751 runoff.

 Figure 2. Decay rates of leaf litter degradation represented by the mean mass remaining of the leaf litter in the litterbags during degradation at the control site for (A) *A. marina* and (B) *R. stylosa* and at the urban site for (C) *A. marina* and (D) *R. stylosa*. The error bars represent the standard deviations.

756 Figure 3. Mean values (±SD) of (A) C in g kg⁻¹, (B) N in g kg⁻¹, (C) C/N ratio, (D) δ¹⁵N (‰vsAir) and 757 (E) δ ¹³C (‰vsVPDB) during leaf litter degradation for *A. marina* and *R. stylosa* at the control and 758 urban sites.

759 Figure 4. (A) Mean (\pm SD) total neutral carbohydrate content in mg g⁻¹ in leaf litter with degradation 760 at the control and urban sites and for *A. marina* and *R. stylosa* and (B) mean (±SD) sum of the 11 761 lignin-derived phenols in mg g⁻¹.

762 **Figures**

