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Materials on Plant Leaf Surfaces are Deliquescent in a Variety of Environments

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Abstract

Many materials on plant leaf surfaces are hygroscopic, and they impact foliar applied agrochemicals, foliar water uptake, gas exchange and stomatal density. Few studies are available on the nature of these substances, and we quantify how hygroscopic these materials are. Water vapor sorption experiments on twelve leaf washes were conducted and analyzed with inductively coupled plasma-optical emission spectroscopy and X-ray diffraction. Oils were found in all *Eucalyptus* samples studied. The leaf materials can deliquesce and form an aqueous solution in a variety of environments where plants grow, including glasshouses and by the ocean. All plant materials studied were hygroscopic. For mangroves that excrete salt to the leaf surfaces, significant sorption occurred at high humidity of a total of 316 mg ($\sim$0.3 mL) over 6–10 leaves. These fitted a Guggenheim, Anderson, and de Böer isotherm; mostly due to sodium chloride, though other more hygroscopic materials were also present.

Keywords: foliar, water use, hygroscopic, point of deliquescence, sorption, plant leaf, aerosol, adsorption isotherm

1. Introduction

The deposition of aerosols onto plant leaves is a common occurrence in the environment, yet its ecophysiological impacts are poorly understood. The aerosols are highly variable in composition and size (1 nm to 100 μm[1]), and are transported around the globe in air streams[2]. Hygroscopic materials on plant leaves can impact many factors, both in experimental settings and field work in the environment. Areas of impact include gas exchange experiments, stomatal apertures and distribution[3, 4], foliar water uptake[5], and foliar-applied agrochemical penetration[6]. In the context of foliar-applied agrochemical spray penetration, the effect of additional hygroscopic materials on the surface is significant, including changing the point of deliquescence of the applied salt[7, 8], total droplet evaporation time, droplet contact angle and area, and total amount of chemical penetrated[6, 9, 10]. Ionic substances are often present on plant leaves (especially in saline environments, such as mangroves[5]), in atmospheric particles and in sprinkler irrigation[8, 11]. Hygroscopic materials can reduce the surface tension of droplets [12] and may allow stomatal penetration[2, 4, 13]. The deposition of calcium aerosols has increased over decades in western USA, due to mineral aerosols from dust storms, increased human activity upwind, increased aridity and wind transport[14]. The impact of aerosols deposited onto plant leaves requires further attention and few studies are available on the implications of deposited aerosols on plants in regards to plant-atmosphere relations, plant physiology and micrometeorology.

Whether hygroscopic materials exist on plant leaves across all locations in which plants grow, what these materials are composed of, how likely these materials are to deliquesce into an aqueous solution and how much water is present, has not yet been investigated in the literature. We aim to understand this distribution better, understand the material's composition better and determine how much water can form over a range of relative humidities. Our hypothesis is that salts can attract water, along with other substances collected from the surface of leaves, in a variety of environments, and in some cases with liquid water accumulating to form visible deliquescence. These considerations may be relevant even for plants grown in glasshouses and growth cabinets. The focus of this study is any substance present *in situ*, on the plant leaf surface, which is easily washed off, from deposited aerosols, soils and salts or from inside the leaf due to leaching or excreted salts and oils.

The average thickness of a liquid layer present on a leaf surface due to hygroscopic particles is estimated to be approximately 1 μm, which is two orders of magnitude thinner than morning dewfall[2]. Particulate matter present on leaf surfaces can reach a similar mass to that of leaf waxes (leaf waxes being around 50 μg cm^{-2})[2, 15]. The electrical conductance for a leaf and artificial leaf in a field is similar at night (leaf stomata closed), while during

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Figure 1: Naturally occurring salts visible *in situ* on the adaxial leaf surface of 'Cabinet mangrove' (grey/white mangrove *Avicennia marina*). The salts are present on the leaf due to glands that excrete salt. The leaf is visibly dry.

the day (leaf stomata open) the leaf is more conductive. Stomata opening during the day play an important role in controlling leaf moisture[2, 16].

Foliar water uptake may be important for the plant during drought, though the mechanisms of penetration are not yet fully defined. To date, the majority of plant species have been found to have a capacity for foliar water uptake, in a study of 135 species, 124 species were capable and 11 incapable [17]. Water may be present on the leaf surface from a variety of sources including rain, dew and high humidity. Fog suppresses water loss from leaves, for example ameliorating daily water stress in a coastal redwood. Older, well watered leaves take up the most water and have a diurnal rhythm[18]. Without fog, species with high foliar water uptake are more likely to lose turgor during seasonal droughts[19].

Many mangrove species have glands in their leaves that excrete salts to the leaf surface. This can be seen on a mangrove grown in a growth cabinet, as shown in Fig. 1, where sea spray is not a possibility. Mangroves are known to rely on non-saline water to maintain productivity, although several mangrove species persist in areas where non-saline water from rain and groundwater is limited. Foliar water uptake from fog and mist may be important in these cases. Three species of mangroves growing in arid and humid environments have been shown to have a contribution from foliar water uptake of 32% in *Avicennia germinans*, 26% in *Laguncularia racemosa* and 16% in *Rhizophora mangle*, and out of these only *Avicennia germinans* excretes salts onto the leaf surface. Within the same species, uptake was comparable across field and controlled environments, suggesting that uptake is not a plastic arid-zone adaptation but may be used as a supplemental water balance strategy in humid and arid neotropical mangroves[20]. Leaf water potential and reverse sap flow rate increase above the point of deliquescence (POD) (75%RH for sodium chloride, NaCl)[5], indicating that surface salts are an important consideration in foliar water uptake for mangroves. In these plants, trichomes have been shown to take up water[21] and achieving full leaf hydration requires the input of water from additional sources other than root water, such as atmospheric water [22]. Other plants living in halophilic environments, such as saltbush (*Atriplex halimus*)[23] excrete salt onto the leaf surface. Species with hygroscopic salts on the leaf surface will stay wet longer and may provide a convenient trap for aerosols. Species with more NaCl have very limited diversity of bacteria and fungi on the leaf surface as seen for example on saltbush (*Atriplex halimus*) and two mangroves (*Avicennia germinans, Laguncularia racemosa*)[23, 24], indicating that salt on plant leaves may be a defense mechanism. Thus the presence of salts on the leaves may yield multiple benefits, including improved water relations and bacterial control.

1.1. Hygroscopicity and Point of Deliquescence

Ionic substances can sorb water from the air, due to their strong attractive forces for highly polar water molecules. Calcium chloride can attract 14 times its dry weight in water at high relative humidity[25]. The ability to attract (adsorb or absorb) water molecules from the air is termed hygroscopicity. The point, in terms of relative humidity, at which a hygroscopic material can sorb sufficient quantities of water to dissolve and form an aqueous solution is called the point of deliquescence (POD) or deliquescent relative humidity (DRH). Most deliquescent materials are ionic salts and their POD can vary significantly at room temperature, from 32%RH for $CaCl_2$[26], 75%RH for NaCl, to 97%RH for K_2SO_4[28]. If the relative humidity is above the POD, solid crystals will sorb moisture from the air until the salt dissolves and remains in solution[25, 27, 29]. The solution will continue to sorb water from the air until an equilibrium is reached between the vapor pressure of the solution and the air. $CaCl_2$ has been found to increasingly sorb water over several hours [30]. For example, if the relative humidity of the air is 50%RH and is above the POD of $CaCl_2$ (32%RH), salt crystals or salt solution will attract water. If the relative humidity is below the POD, for example at 10%RH, the solution will continue to evaporate and eventually form crystals, with hysteresis possible. Additional to relative humidity, the rate of sorption by hygroscopic material depends on temperature, the

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surface area of the salt exposed to the air and the wind or air circulating over it[25]. NaCl crystals are seen under fluctuating relative humidities around the POD of NaCl on astomatous isolated tomato fruit cuticles, and pools of water form[31]. Small amounts of additives can significantly alter the POD of a solution, for example, surfactants, impurities and deposits on the leaf surface. Adding 1% of NaCl to an ammonium (NH_4^+) solution, lowers the POD of the solution by 17%RH (from 75%RH to 58% RH)[8].

A mechanistic model has been developed to account for droplet evaporation including hygroscopic water absorption, the POD of the material and the ability to change the POD when adjuvants were added to the formulation[6]. Droplet evaporation is especially relevant for foliar-applied ionic agrochemicals as penetration will cease when water has evaporated. Theoretical results indicate that a high POD could be severely limiting to penetration[6]. Hygroscopic wetting can prolong droplet evaporation and penetration. Experimental and theoretical results show that at 50-70%RH and 20°C, a 1μL droplet of pure water will evaporate in 0.5-0.7 hours on a leaf[6, 33], and with the inclusion of $CaCl_2$ in the droplet, the mechanistic model shows droplet evaporation is prolonged to 9.4 hours[6].

The POD of salts is well defined in the literature, though there is less known about the sorption of salt mixtures, and salt and oil mixtures. Plant materials such as the plant cuticle, seeds and cellulose are hygroscopic[10], but generally to a lesser extent than ionic salts. Sorption at high humidity, in terms of weight increase of moisture over the dry weight in cuticles is generally around 8%, cellulose 30%, polar polysaccharides isolated from cuticles 49%, clays (smectite) 21%, while $CaCl_2$ can sorb 1400% [10, 25, 34–37].

Heterogeneous stomatal pore area or patchy stomatal conductance may have substantial implications for photosynthetic efficiency. Plants grown in filtered or unfiltered air were compared and aerosols deposited onto the leaf from unfiltered air suppressed the heterogeneity of stomatal pore opening and response to vapor pressure deficit (VPD)[38] while increasing the minimum epidermal conductance[4], $g_{\min}$, which is a key factor of drought tolerance in plants[39]. Hygroscopic aerosols may contribute to the formation of a thin aqueous film across the leaf surface that can connect stomata to each other and the leaf interior [3, 38]. The deposited aerosols in the experiment above for unfiltered air, were deliquescent and formed an aqueous solution at 89%RH, visualized with an environmental scanning electron micrograph[3]. However, only one location was investigated and the hygroscopicity of the deposits was not quantified. Salts artificially sprayed onto leaves increased the minimum epidermal conductance[39], and the electrical conductance of the leaf in darkness responded to changes in relative humidity close to the point of deliquescence of the salt[40].

This paper aims to find if hygroscopic materials exists on plant leaves, across all locations that plants grow. We aim to determine the materials composition, how hygroscopic they are over a large range of relative humidities and whether they deliquesce and form an aqueous solution. We focus on any substance present on the plant leaf surface, which is easily washed off and dissolved in solution, from deposited aerosols, soils and salts or from inside the leaf due to leaching or excreted salts and oils. We utilize vapor sorption methods to analyze the leaf material sorption. We analyze the leaf wash composition using powder X-ray diffraction and inductively coupled plasma-optical emission spectroscopy (ICP-OES). We conduct vapor sorption on salt and oil mixture controls to compare our leaf wash materials to.

2. Methods

2.1. Leaf Wash Sample Preparation

Plant samples were taken at a range of distances from the ocean, with locations and species described in Table 1, and total dry weights in Table 4. The leaves were collected from the same individual plant at each location, and from the same unshaded part of the plant. All samples were collected after at least two weeks without rain and were from mature plants, unless otherwise stated. No spray applications or pre-treatments were used during the experiment. Leaves of around the same area (6 - 10 leaves washed in total, with a total leaf area including the 2 washed leaf surfaces of approximately 430 cm^2), enough to fill a glass container (125 mL) with a screw cap lid, were collected intact on their branch (so a small area of petiole was washed) and removed carefully from the plant. The leaves were placed in the bottle with 60 mL of de-ionized water, immediately after collection from the plant, and shaken lightly for 20 seconds[4], before the leaves were removed. The glass bottle was thoroughly cleaned beforehand, with detergent, then rinsed with de-ionized water and ethanol. The wash was centrifuged at 2,000 g for 15 minutes (Orbital 420, Clements, Australia). The centrifuging process was repeated if particles remained suspended. For each plant species and location, a total of two sample sets were collected from one individual plant, 120 mL in total; one for the vapor experiment and one for the ICP-OES experiment. The ICP-OES sample had the leaf matter removed, and was then centrifuged and dried from 60 mL to 5 mL. For the vapor experiment, each

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Table 1: Sample reference, plant species and location of leaf wash samples. 6–10 leaves were collected with similar leaf area. Mature plants were collected 2 weeks after rain unless otherwise specified. Locations are in the Australian Capital Territory (ACT) or New South Wales (NSW), Australia. Collection dates between February and July 2020. Growth cabinets were contained in a large air conditioned indoor facility with 210 micron mesh air filtration, rated to P2 standards for genetically modified organism (GMO) plants.

Reference	Common name	Scientific name	Location	Notes
Brackish mangrove	river mangrove	*Aegiceras corniculatum*	Currowan, NSW, Aust	10 km to ocean, submerged leaves at certain tides, excretes salt
Cabinet mangrove	grey/white mangrove	*Avicennia marina*	growth cabinet	excretes salt, not watered on leaves, 30°C day 20°C night, 60%RH day 70%RH night, 8 months old
Glasshouse chilli	birds eye or Thai chilli	*Capsicum annuum*	glasshouse	not watered on leaves, 28°C day 20°C night, around 2 years old
Ocean common reed	common reed	*Phragmites australis*	Surf Beach, NSW, Aust	20m from beach, unlikely to be submerged
Cabinet setaria	setaria green foxtail	*Setaria viridis*	growth cabinet	mature, 30°C day 25°C night, 60%RH day 70%RH night, not watered on leaves
Brackish euc	eucalyptus grey ironbark	*Eucalyptus paniculata*	same as brackish mangrove	less likely to be submerged
Indoor peace lily	white peace lily	*Spathiphyllum cochlearispathum*	indoors	not watered on leaves
Cabinet barley	barley	*Hordeum vulgare*	growth cabinet	as setaria
Town euc rain	eucalyptus torelliana	*Cadaghi corymbia torelliana*	Acton, ACT, Aust	6 hours after rain, rained for several days, leaves dry after rain, 200kms inland from coast
Town euc no rain	eucalyptus torelliana	*Cadaghi corymbia torelliana*	Acton, ACT, Aust	same plant as Town euc rain
Lake euc	long-leaved box eucalyptus	*Eucalyptus goniocalyx*	Acton, ACT, Aust	20m from lake
Euc farm	inland scribbly gum eucalyptus	*Eucalyptus rossii*	Monga, NSW, Aust	Near farms, 10m from dirt road, 100m from highway, halfway between town and ocean

60 mL sample was divided equally into 3. Samples were dried in an oven for 3 days at 50°C and until no liquid remained. To find the initial dry weights, three empty 1.5 mL polypropylene Eppendorf tubes were prepared by drying them in the oven prior to use and then weighed to determine the vessel dry weights, dw_v. The wash was dried down to a smaller volume, then placed in the dry Eppendorf tube and dried further to a solid. The total dry weight of the sample and vessel was recorded, dw_{v+s}. The wash was centrifuged but not filtered as we wanted to investigate the insoluble particles from the leaf surface as well. Sample mass was determined for all dry weight and sorption experiments using a Mettler AT21 Comparator, Mettler Toledo, Italy, d $= 1\ \mu$g, max $= 22$ g.

2.2. Static Vapor Gravimetric Sorption Experiment - Leaf Washes

The static vapor gravimetric sorption technique [41] was used to determine the sorption of water by the samples. Briefly, samples start out oven dry, then are successively placed in environments of increasing relative humidity to test their adsorption properties. To create a specific relative humidity, a range of salt solutions were used, being $MgCl_2$, $Ca(NO_3)_2$, NaCl, KCl, KNO_3, K_2SO_4, with the equilibrium RH being 33.4, 55.5, 75, 84, 93 and 97%RH, respectively. To create these saturated salt solutions, 50 mL of de-ionized water was placed in a large petri dish, next to the leaf sample with the cap open, inside an air-tight larger glass vessel. The larger vessel was then stored in a temperature controlled environment for 3 days (21.9°C $\pm$ 0.4°C). At the end of 3 days, samples were quickly taken out of the large vessel, re-capped and weighed in their Eppendorf tubes to provide the wet weight of the sample, ww_{v+s}. It was also noted if liquid was clearly visible without the need for special equipment. Triplicates were compared and averaged. Error bars produced are the standard error of the mean. The polypropylene Eppendorf tubes can also sorb moisture, and each sample was held in a different Eppendorf tube. The wet weight of the tubes was approximated from 6 empty tubes exposed to each humidity. We focused on isothermal experiments, in order to investigate the effect of humidity on plant leaves over a large range of locations though we note that sorption can vary with temperature.

2.3. Salt and Oil Controls - Water Sorption Experiment

We compare the sorption of the leaf washes for similar weights to controls based on salts and oils including mixtures. Salts and oils were weighed as shown in Table A6 and added to 1mL of de-ionized water. The samples were then mixed and dissolved where possible, and dried in the oven at 50°C for 3 days. The same procedure was then

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conducted for measuring water sorption as described in the previous section. The mangrove nutrient, *Eucalyptus* oil (100% pure) and tea tree oil (100% pure, *Melaleuca alternifolia*, Australia) were purchased. The mangrove nutrient comprising mainly of NaCl, 1295 ppm Mg, 430ppm Ca and 390 ppm K plus micronutrients.

2.4. X-ray Diffraction

Powder X-ray diffraction (XRD) analysis was carried out with a Malvern Panalytical Empyrean Series 3 diffractometer, equipped with Bragg-Brentano^{HD} divergent beam optic and a PIXcel^{3D} detector (1D scanning mode, 3.347° active length), using Co$K\alpha$ radiation. Two samples were analyzed with the leaf wash method (Table 2). Samples were analyzed with a broad beam (long-fine focus) over a range of 4–85° 2θ, with a step with of 0.0131303° and scan speeds ranging from 298–2598 seconds per step depending on sample requirements. Samples were rotated horizontally to increase sampling size. Two other methods were utilized with 6 plant species; by directly studying the leaf, and its scrapings. Samples were obtained by scraping materials off the leaves (Figs. A14,A15) with a scalpel and washing any residual sample into an agate mortar with ethanol, then grinding the material with an agate pestle by hand as finely as possible. The sample was then deposited with a Pasteur pipette onto a low-background sample holder (made of Si or quartz), dried and presented to the X-ray beam without the leaf substrate. The only possible contaminant of samples prepared this way is small amounts of epicuticular wax (paraffin). Leaf wash samples (see Section 2.1, Table 2 and Figs. A12,A13) were also prepared on such low background holders. The wash samples proved somewhat sub-optimal for XRD analysis because salts readily dissolve and precipitated as potentially different compounds. The suitability of each sample for yielding instructive powder XRD data varied, depending on the sample preparation (leaf wash, leaf scraping or direct analysis of the leaf surface), the amount of material on the leaf surface, the crystal sizes (1–10 μm ideal), and leaf shape (flat better than curled for direct leaf analysis), requiring individual optimization of analytical conditions and methods for each sample. Phase identification was carried out with the software DiffracPlus Eva 10[42] and ICDD PDF-2 database[43], and quantification with Siroquant V4[44].

2.5. ICP-OES - Inductively Coupled Plasma-optical Emission Spectroscopy

The quantification of 70 elements was carried out using an Agilent 5110 ICP-OES (Agilent Technologies, Australia), operating in Synchronous Vertical Dual View (SVDV) mode, allowing for the simultaneous detection of axial and radial emission signals. Only concentrations for Al, B, Ca, Cu, Fe, K, Mg, Na, P, Si, Sr and Zn were detected above the method detection limit of 0.1 μg/g. A double pass cyclonic spray chamber, a SeaSpray nebuliser, and a 2.4 mm quartz injector were used as the introduction system. Operating parameters for the ICP-OES analysis are tabulated in Table A8. All dilutions and sample preparation of samples for ICP-OES measurement were performed using ultrapure water (MilliQ, Merck), as well as sub-boiling distilled HNO_3. A custom multi-element calibration solution for the elements of interest was prepared from single element standard solutions (Inorganic Ventures) and diluted to concentrations ranging from 0.1 to 20 μg/mL. All samples were diluted and acidified to fall within the calibration curve and repeat analyses were carried out with multiple dilution steps for samples that initially exceeded the calibration range. Blank contribution was monitored by acidifying and analyzing the de-ionized water used for the wash.

2.6. Chloride and Sulphate Presence Test

To test for the presence of chloride (Cl^-) and sulphate ($SO_4{}^{2-}$), the most abundant anions in sea-water[45], 2 mL of liquid was removed from the 60 mL leaf sample washes destined for the sorption experiment. 1 mL aliquot of solution placed in clean 2 mL glass vials was used to identify chloride and sulphate non-quantitatively. For chloride, a few drops of dilute nitric acid followed by a few drops of silver nitrate ($AgNO_3$) in solution (2% (w/v)); were added to the 1 mL sample. A control solution of $CaCl_2$ was used for comparison. After 10 mins the presence of a white precipitate of AgCl was recorded. The silver nitrate test had the unexpected effect of turning some samples brown. If the solution changed color from clear to yellow or brown tinted, it indicated that oils were present such as *Eucalyptus* oil, producing silver nanoparticles. Ag^+ is known to react with halide ions and various other compounds such as lipopolysaccharides and amino acids[46]. For the sulphate test, the same procedure was conducted but a few drops of barium chloride solution (2% (w/v)) followed after 10 minutes by a few drops of dilute hydrochloric acid and a white precipitate of $BaSO_4$ was formed if sulphate was present.

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2.7. Moisture Gain Calculations

To find the total mg and percentage increase in moisture gained for each relative humidity step over the dry weight of the sample, we need to consider the dry weight and the blank vessel water sorption. We consider

$$\text{moisture gain}(\%) = \frac{100\% \ (\text{wet weight} - \text{dry weight})}{\text{dry weight}}. \tag{1}$$

We formulate Δw (%), the weight increase of moisture adsorbed above the dry weight of the sample (sample being the salt taken from the leaf surface) scaled with the blank, as follows:

$$\Delta w = \frac{100\% \ [(ww_{v+s} - dw_v - dw_v \ b/(100\%)) - (dw_{v+s} - dw_v)]}{dw_{v+s} - dw_v}, \tag{2}$$

and simplifying, the final equation for Δw becomes:

$$\Delta w = \frac{100\% \ (ww_{v+s} - dw_{v+s}) - dw_v \ b}{dw_{v+s} - dw_v}, \tag{3}$$

and the total weight of the sample in mg including the initial dry weight of the sample is:

$$\text{Total mg} = ww_{v+s} - dw_v \, (1 + b/(100\%)), \tag{4}$$

where dw_v (mg) is the empty vessel/ Eppendorf tube dry weight, dw_{v+s} (mg) is the total vessel and sample dry weight, ww_{v+s} (mg) is the total wet weight of the vessel and sample together at a given RH, b (%) is the blank percentage moisture weight gain at a given RH and Total mg (mg) is the total weight of the sample including the sample dry weight. All parameters are direct weight measurements, except Δw, Total mg, and b, which are calculated. Dry weights were determined following oven drying. As Eppendorf tubes vary in weight, each tube is weighed dry and with the sample. To correct for water sorption by the polypropylene, 6 blank Eppendorf tubes were weighed with successive humidity steps, and averaged, to find b using Equation (1), producing sorption between 0.033% to 0.23%, at 33%RH to 97%RH. The initial dry weight is the weight of the sample from the oven. The data point (0,0) in plots of Δw, is calculated based on the dry weight, and is equivalent to $dw - dw = 0$, based on Equation (3). When processing the data, if a negative value for Δw was produced, the sample did not sorb much more than the blank, so the value for Δw was set to zero.

2.8. GAB isotherm

We consider the Guggenheim, Anderson, and de Böer (GAB) isotherm[47–50] for fitting a selection of samples. The GAB isotherm describes water adsorption as a monolayer that can form multilayers at high humidities. It is formulated by applying the Langmuir isotherm to each layer (evaporation and condensation can occur only from or on exposed surfaces) and is at equilibrium where the rate of adsorption equals the rate of desorption. The GAB isotherm is as follows:

$$\Delta w = \frac{w_S \ \beta \ k \ RH}{(1 - k \ RH)(1 + k \ (\beta - 1) \ RH)}, \tag{5}$$

where Δw is the percentage weight increase above dry weight at each relative humidity as a percentage, RH ($RH = a_w \times 100\% = p/p_0 \times 100\%$), w_S is the monolayer of water adsorbed per solid, β is the equilibrium parameter of adsorbed water or the interaction energy between water and solid and k represents the difference in free enthalpy of the water molecules in the monolayer and layers above the monolayer, where β and k depend on temperature with the Arrhenius equation and k is always less than 1. The fitting and analysis were performed using MATLAB® (Mathworks, U.S.A.).

3. Results

To investigate what materials are on the surface of plant leaves, we use a range of techniques, with the plant species and locations described in Table 1. We use the word “materials" due to the highly mixed nature of the surface deposits which may include salts, insoluble mineral grains, organic debris, insect eggs and material sloughed from the leaf itself. The total dry weights of the triplicates are shown in Table 4, and indicate that the brackish mangrove

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Table 2: XRD results for the two leaf wash samples that were expected to have the most and least amounts of materials present on the surface; 'Brackish mangrove' and 'Town euc rain'. An 'x' in the table indicates that significant amounts were present, 'trace' indicates presence in small quantities. The XRD profiles are shown in Figs. A12 and A13.

Minerals	Chemical composition	Brackish mangrove	Town euc rain
quartz	SiO_2		x
plagioclase	$(Ca,Na)_{1-2}(Si,Al)_{2-3}O_8$		x
K-feldspar	$KAlSi_3O_8$		trace
illite/muscovite	$KAlSi_3O_{10}(OH)_2$		x
kaolinite	$Al_2Si_2O_5(OH)_4$	x	trace
2:1 clay - chlorite, vermiculite or smectite			x
boehmite	AlOOH		x
halite	NaCl	x	
sylvite	KCl	x	trace
talc	$Mg_3(OH)_2Si_4O_{10}$		x
unidentified phase, possibly quartz		x	

had a large amount of material present on its leaves, 40 mg, the cabinet mangrove with appropriate scaling 41 mg, with the other sample having 3–8 mg. The total weight of dry material is relevant in this study as the total weight gain will be greater when the leaf coating is more hygroscopic, and our main interest is the total amount of water on the leaf. Our initial analysis was performed using XRD, as shown in Table 2 and Figs. A12 and A13, on the samples predicted to have the most and least hygroscopic materials. 'Brackish mangrove' contained significant amounts of ionic hygroscopic compounds such as NaCl and KCl, along with other minerals, while 'Town euc rain' contained trace amounts of KCl and mostly trace amounts of other minerals. These samples were dissolved in de-ionized water, and do therefore represent the compounds on the leaf but may not represent the original *in situ* configuration of the elements, for example NaCl and K_2SO_4 might become Na_2SO_4 and KCl. Tests were carried out to determine what the original compounds were on the leaf and the results were similar, as shown in Figs. A14 and A15. Scrapings from the leaves gave better results than viewing the leaf directly and significant portions of wax were also present on the leaves but not quantified. XRD is unable to detect and analyze materials without a repetitive or crystalline structure that occur in very small amounts (lower detection limits for XRD range from about 0.1 to 2 wt.% depending on compound). Therefore, ICP-OES analyses were carried out to examine the elemental composition of the samples, including trace elements.

The ICP-OES results are shown in Table 3 in $\mu g/g$ (ppm (parts per million)). The results indicate that the samples having significant amounts of hygroscopic salts are the 'Brackish mangrove', 'Cabinet mangrove', 'Brackish euc', 'Glasshouse chilli' and perhaps the 'Euc farm' and 'Ocean common reed', based on the determined concentration of Ca, Mg and Na. The 'Brackish mangrove' and 'Cabinet mangrove' have similarly large amounts of Na, and similar amounts of the other elements. The presence of Cl^- was tested using silver nitrate, indicating 'Brackish mangrove', 'Cabinet mangrove' and 'Brackish euc' contained significant amounts of Cl^-, consistent with the calculated Na values. The silver nitrate test changed all 5 *Eucalyptus* samples brown, related to *Eucalyptus* oil[46], as seen in Fig. A6. 'Town euc no rain' shows the darkest color, indicating the largest amount of oil. Testing for ${SO_4}^{2-}$ was also carried out on these samples, with no positive indications. The results of the water vapor sorption experiment with

Table 3: ICM-OES results in $\mu g/g$ (ppm) of similar leaf area for all leaf wash samples studied except Cabinet barley. The silver nitrate test for Cl^- is described in Section 2.6. A test for ${SO_4}^{2-}$ was also carried out, with no positive indications.

Sample	Al	B	Ca	Cu	Fe	K	Mg	Mn	Na	P	Si	Sr	Zn	Cl
Brackish mangrove	0.06	0.11	7.24	0.00	0.00	29.31	6.55	0.11	148.03	0.19	0.19	0.07	0.03	x
Cabinet mangrove	0.03	0.16	9.78	0.06	0.01	30.20	4.46	0.04	199.20	0.15	0.23	0.03	0.09	x
Glasshouse chilli	0.02	0.08	6.07	0.09	0.01	4.14	3.63	0.05	0.98	0.62	0.22	0.01	0.06	
Ocean common reed	0.03	0.07	3.20	0.04	0.01	5.88	3.09	0.09	3.02	0.05	0.27	0.05	0.17	
Cabinet setaria	0.01	0.09	3.91	0.06	0.00	13.65	1.30	0.03	0.55	0.91	0.02	0.01	0.03	
Brackish euc	0.02	0.05	22.76	0.03	0.01	6.60	14.22	0.02	24.69	0.08	0.06	0.26	0.09	x
Indoor peace lily	0.05	0.08	2.87	0.04	0.01	2.39	0.90	0.04	0.77	0.24	0.00	0.01	0.09	
Town euc rain	0.12	0.06	1.58	0.08	0.08	10.38	1.98	0.08	0.80	0.24	0.36	0.00	0.14	
Town euc no rain	0.06	0.02	1.06	0.00	0.00	5.30	0.88	0.05	0.86	0.58	0.14	0.00	0.08	
Lake euc	0.09	0.04	1.35	0.07	0.04	5.37	0.91	0.04	1.32	0.43	0.19	0.01	0.07	
Euc farm	0.13	0.05	1.99	0.04	0.04	54.90	1.12	0.33	2.25	0.25	0.17	0.01	0.22	

the leaf wash samples are shown with standard error bars in Fig. 2. The percentage weight increase of moisture sorbed above the dry weight, Δw, is plotted with relative humidity, RH, as calculated in Equation (3). Significant sorption occurs at high humidities at and above 75%RH with the 'Brackish mangrove' and 'Cabinet mangrove'. Less so but still significant sorption occurs with the 'Glasshouse chilli' and the 'Brackish euc'. All leaf washes appear to

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be somewhat hygroscopic. As the leaf sample washes are mixtures of different salts, minerals, oils, waxes and other materials, sorption behaves less predictably, with the exception of the mangroves with their high NaCl content. This is especially true above 84%RH and this is discussed further around Fig. 5 in relation to the oil controls. As our focus is total water on the leaves, we consider the same data, plotted as the total of the triplicates, as total weight (mg) with relative humidity in Fig. A7, calculated with Equation (4). We compare the strongly deliquescent leaf wash samples that produced a clearly visible aqueous solution, in Fig. 3. The 'Brackish mangrove' as expected, was the most hygroscopic and becomes visibly liquid at 75%RH, aided by its high initial dry weight. The 'Cabinet mangrove' also sorbed large amounts of water and became visibly wet at 75%RH, compatible with the dominance of NaCl in the coating. The 'Brackish euc' became visibly wet at 84%RH, and the 'Glasshouse chilli' and 'Ocean common reed' at 97%RH. If we compare these results to the ICP-OES data in Table 3 for the combined weight of Ca, Mg and Na in μg (that are postulated to be the most hygroscopic here) in Table 4, we see the five samples that visibly deliquesce in Fig. 3 correspond well to the five highest combined masses of these cations. The highest to lowest of the sum of Ca, Mg and Na also correspond reasonably well to the ranking of the maximum percentage weight increase over the dry weight, Δw - %, in Fig. 2, which suggests that hygroscopicity of the leaf wash material may be predicted from the combined mass of Ca, Mg and Na from the ICP-OES data. For the 'Brackish mangrove', the materials present significantly deliquesced, over the total sample (total of three repeats), at 97%RH, produced 316 mg, as shown in Figs. 3. This equates to 0.03–0.05 mL on one leaf (assuming uniformity over 6–10 leaves), with a thickness of liquid on one leaf of 7.3 μm (14.6 μm considering salt glands are mainly on the adaxial surface of the 'Brackish mangrove'), similar but higher to estimates of 1 μm using other methods with plants that do not excrete salt[2]. We note other samples were hygroscopic and could also be deliquescent but were not included in Fig. 3 as the water layer was not visible without the need for special equipment. Table 5 compares the dry weight and maximum sorption to the leaf area. The two mangrove samples produce a similar dry weight and maximum sorption.

Table 4: Total dry weight of each leaf wash sample wash (sum of the three repeats) after oven drying. The maximum sorption weight percentage increase over the dry weight Δw, is compared with the combined weight in μg of the Ca, Mg and Na ICP-OES data. The list is ordered by this combined weight: samples above the line visibly deliquesced. The combined μg of Ca, Mg and Na has a positive correlation with visible deliquescence and maximum sorption. The dry weight may include some moisture that is not easily driven off. This will increase the dry weight but not appear in the ICP analyses. Note the cabinet mangrove sample comprised only 3 leaves so the dry weight should be scaled accordingly for comparison with the other samples (as shown in brackets).

Sample	Total dw leaf wash - mg	Max sorption - Δw - %	Ca, Mg, Na - μg
Cabinet mangrove	12 (41)	782	1067
Brackish mangrove	40	694	809
Brackish euc	4	340	308
Glasshouse chilli	5	159	53
Ocean common reed	5	100	47
Cabinet setaria	3	124	29
Euc farm	4	92	27
Indoor peace lily	5	46	23
Town euc rain	5	56	22
Lake euc	4	105	18
Town euc no rain	8	28	14

Control experiments for salt and oil sorption were conducted, for comparison to the leaf washes, to better understand whether the results were similar when salts and oils were present, as shown in Figs. A8–A11. All the controls deliquesced and formed an aqueous solution that was visible to the naked eye, except the two pure oils - *Eucalyptus* and tea tree. The salts and mixtures with $CaCl_2$ generally formed liquid at 32%RH, the POD for that $CaCl_2$. Similarly mixtures with NaCl deliquesce at its POD of 75%. The mangrove nutrient is dominantly NaCl, but contains other salts with a lower POD. When comparing NaCl with *Eucalyptus* oil to the large pure NaCl sample, the POD is similar, however the change in weight is less, indicating the oil was able to prevent some level of sorption but did not prevent deliquescence. When applying this outcome to the leaf wash results, it could be relevant for the 'Brackish euc', which was able to form an aqueous solution, despite the presence of some oils but to a lesser extent than the mangroves. We note that the small NaCl sample has higher than expected sorption at 33%RH and this might be corrected with additional repeats.

The experimental data in Fig. 4, for the 'Brackish' and 'Cabinet mangrove', compared to the mangrove nutrient and NaCl control, is modeled with the GAB isotherm shown in Equation (5). Fig. 4 shows that the percentage moisture gain is similar for both mangroves, the GAB isotherm has a similar trend and the percentage sorption

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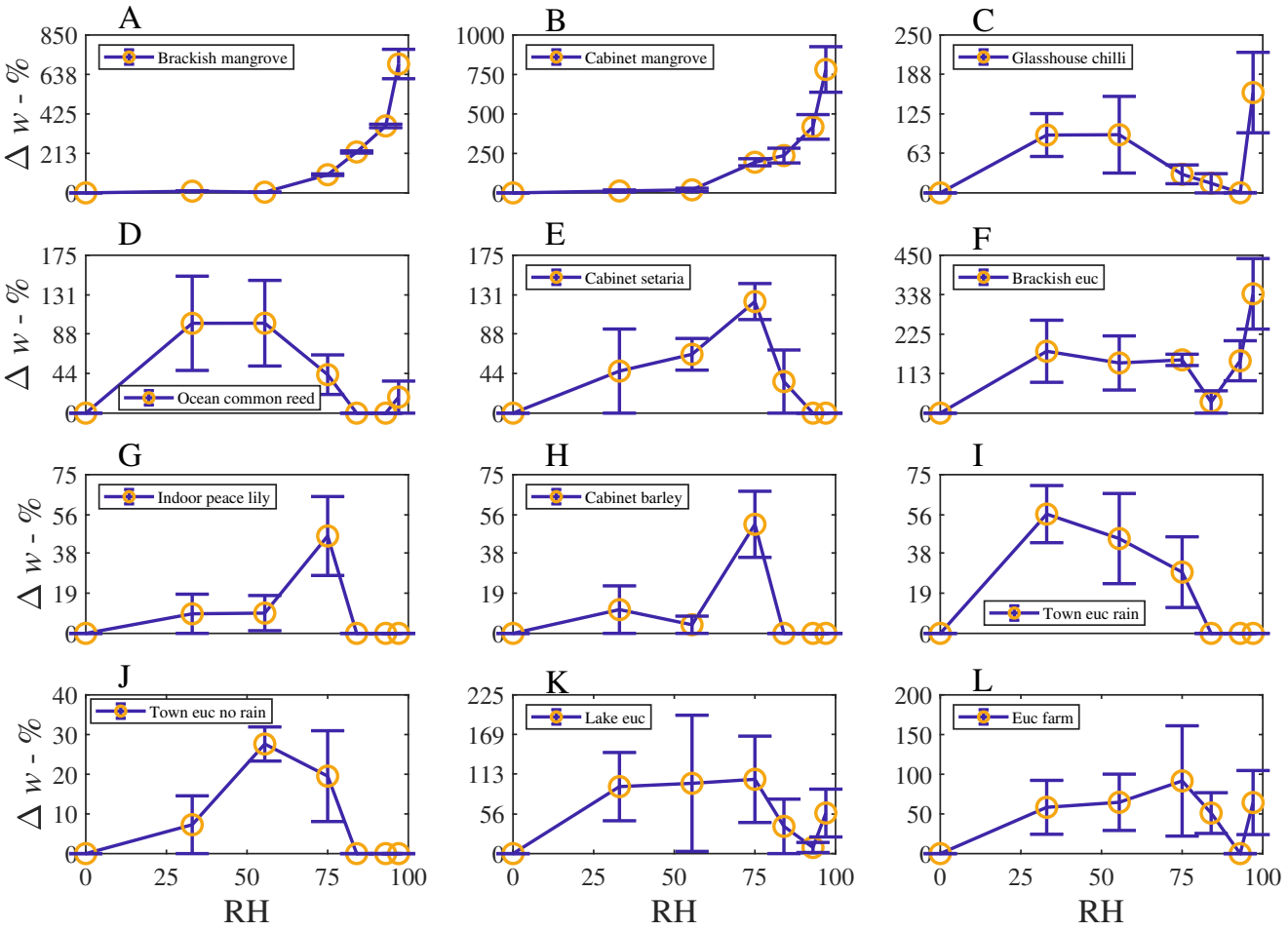

Figure 2: The percentage weight increase of moisture adsorbed above the dry weight of the leaf wash samples, Δw - %, vs relative humidity, RH - %, plotted with standard error bars. Note the x-axis range is always the same but the y-axis range changes for each subfigure.

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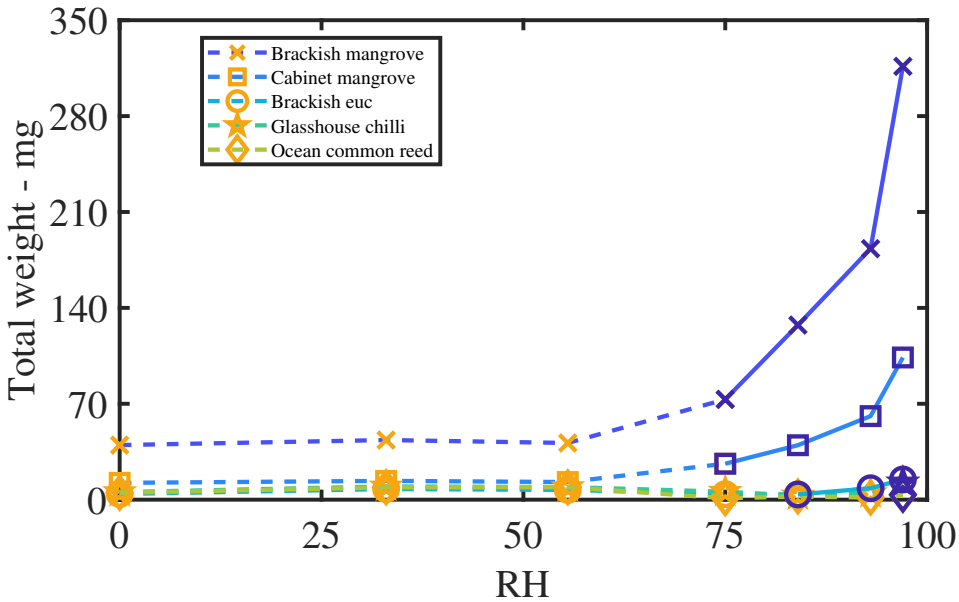

Figure 3: Samples that deliquesce visibly to the naked eye. Total weight (of three repeats with the dry weight, scaled with the blank) vs humidity (%). The orange symbols and dashed lines indicate water is not yet visible (but may have hygroscopic growth), and the blue symbols and solid lines indicate where an aqueous solution was clearly visible. Note the significant weight of the brackish mangrove sample at 97%RH of 316 mg. It is possible that other leaf samples were deliquescent, though the water was not visible to the naked eye and so were not included in this plot.

Table 5: Dry weight per leaf area and maximum wet weight per leaf area, in μg cm^{-2} . The cabinet mangrove sample comprised only 3 leaves so the value in brackets from Table 4 has been utilized. The salt glands of the two mangrove species are located on the adaxial surface and as such for comparison could be scaled by 2 (as shown in brackets).

Sample	dw per leaf area μg cm^{-2}	Max sorption per leaf area μg cm^{-2}
Cabinet mangrove	95 (190)	805 (1609)
Brackish mangrove	93 (185)	736 (1471)
Brackish euc	10	34
Glasshouse chilli	13	29
Ocean common reed	12	21
Cabinet setaria	6	10
Euc farm	9	23
Indoor peace lily	12	12
Town euc rain	12	19
Lake euc	9	14
Town euc no rain	18	23

is very similar at nearly all humidities. The mangroves compare well to the mangrove nutrient and NaCl, and therefore the sorption is driven by hygroscopic particles of NaCl and the mangrove nutrient. The 'Brackish' and 'Cabinet mangrove' sorption at humidities between 75–100%RH, is somewhat greater than the mangrove nutrient and NaCl, which indicates that other compounds are present, which are moderately hygroscopic. When comparing the percentage moisture gain to the total weight in Fig. 3, the 'Brackish mangrove' has a much greater total weight at 97%RH but also started out with a heavier dry weight. When scaled with the dry weight, the percentage moisture gains of both mangrove samples are similar. The GAB constants have physical meaning and the values of k for the four isotherms are similar, so the interaction energy between the multiple layers of water is similar. The values for w_s are higher for the two controls, indicating that they have a larger monolayer saturation value but possibly less multilayers than the two leaf washes. In summary, the two mangroves studied from a cabinet and near brackish water, both excrete salt through the leaves, have sorption properties similar to, but greater than, NaCl and the mangrove nutrient, suggesting a dominance of NaCl but also with other, more hygroscopic materials.

We found a significant presence of lipophilic compounds, possibly oils or waxes. The presence of *Eucalyptus* oils

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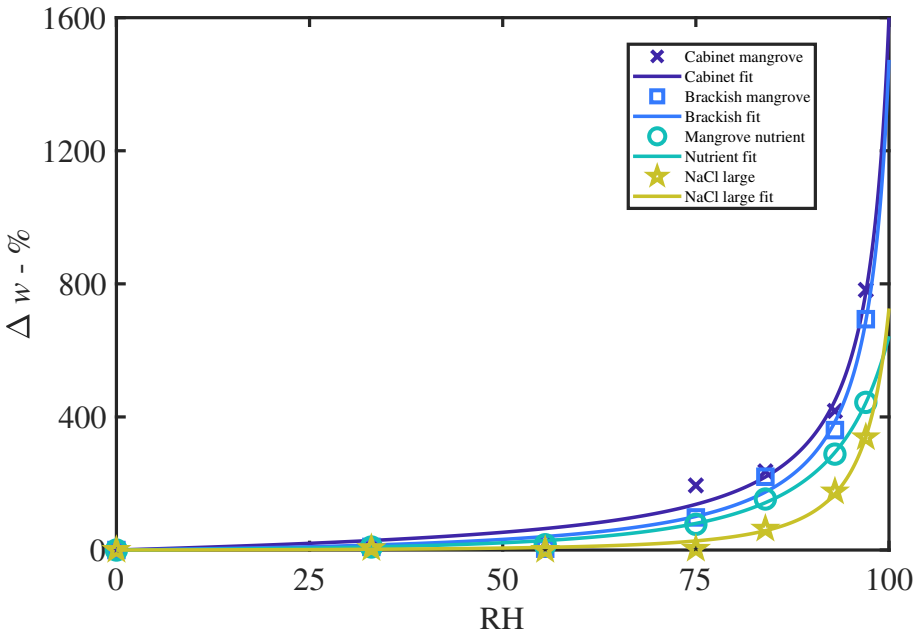

Figure 4: A selection of adsorption isotherms including cabinet and brackish mangroves, along with the controls of the mangrove nutrient and NaCl with a large sample size. The plot is percentage moisture gain over the dry weight vs relative humidity. The data are fitted with the GAB isotherm, as described in Equation (5). The controls were formulated with a similar dry weight to the leaf wash samples. The parameters are described in Table A7 and R^2 values are greater than 98.6%.

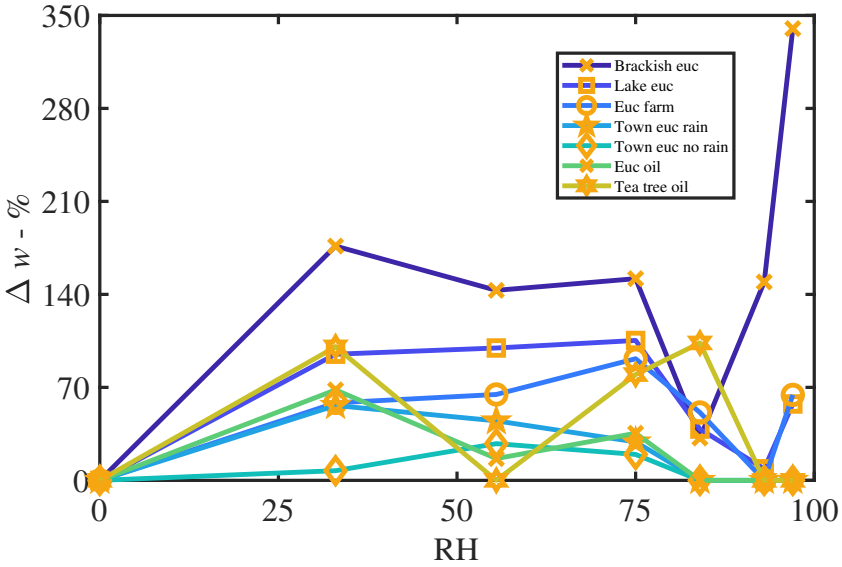

Figure 5: Percentage weight gain of moisture vs relative humidity of all *Eucalyptus* leaf wash samples, along with two oil controls for comparison. The oils contributed to the increasing sorption at low humidity then decrease in sorption between 33%RH and 84%RH, while the other hygroscopic ionic compounds present in the sample contributed to weight gain at high humidities such as shown by 'Brackish euc'. The oil controls follow a similar trend to the leaf washes.

in some leaf wash samples is indicated by the silver nitrate study, shown in Fig. A6, and waxes were found with the XRD. In Fig. 5, as leaf washes are mixtures of salts and lipophilic compounds, the hygroscopicity of the samples is less predictable than in the controls. By comparing the *Eucalyptus* leaf wash samples to the *Eucalyptus* and tea tree oil controls, we can see that the presence of oils results in an increase of weight gain due to moisture followed by a decrease at increasingly high humidity. It is hypothesized that crystals of salts are carrying oils, which dominate the signature at low relative humidity ($\leq$75%RH). Once higher relative humidities are reached ($\geq$75%RH), then

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the salts start to dissociate in the liquid and dominate the observed sorption behavior. This behavior can be seen mimicked by several samples in Fig. 2. One difference to this in Fig. 5 is 'Brackish euc', where at high humidities high sorption is possible to the point of visibly deliquescing. We observe that for this sample, the significant presence of salts as well as oils, results in the hygroscopic properties of the salts overcoming the oil after a critical mass of water is reached, the salts dissociate and high sorption occurs. The 'NaCl with euc oil' control sample experiment in Fig. A8 (J), indicates that this was also possible at high humidities if the amount of salt present is large enough to mask the oil effect, and the effect of the *Eucalyptus* oil on NaCl was that the maximum Δw was reduced, compared to NaCl alone, in Fig. A8 (B).

4. Discussion and Conclusions

Materials on leaf surfaces substantially impact on the interaction between the leaf surface and atmospheric moisture, even for plants grown in relatively clean environments. Our results, in line with other recent work[3, 38], show that water forming on the leaf surface can influence the stomatal function and anatomy, producing not only microscopic water but relatively large volumes of water visible to the naked eye. These results suggest that some experimental designs may require the incorporation of tests, to determine if leaf washing/misting and air filtration are necessary and if a range of relative humidities is required instead of a single humidity, depending on the research question. These considerations may be particularly important when comparing crops/field work to glasshouse/cabinet studies, agrochemical penetration experiments with foliar sprays and certain gas exchange experiments. We note the case of the experimental data where the material from 'Glasshouse chilli' was able to form water visible at 97%RH. This plant was 2 years old, did not experience any leaf washing from rain and was not watered or rinsed on the leaves. It is demonstrably possible that plants grown in a range of locations from glasshouses to growth cabinets may experience this phenomenon, if washing of their leaves does not occur over prolonged periods. This should be considered when growing plants.

The ICP-OES results in Table 3 show 'Brackish euc' has a larger than expected amount of Ca (though an indication for Cl was found), unexpected as the sorption is less than other samples, and $CaCl_2$ is quite hygroscopic (Fig. A8 (D)). Perhaps the oils hinder sorption. However, when we consider Table 4, the totals of Ca, Mg and Na correspond well to the rankings for maximum sorption. The results in Table 4 implies that a balance is needed and suggests that hygroscopicity of the leaf wash material may be predicted from the combined mass of Ca, Mg and Na from the ICP-OES data. The 'Euc farm' sample in Table 3 also has excess K that did not correspond to large sorption, perhaps reduced due to the effect of oils. The excess K may be related to agrochemical spray drift or particles from the nearby highway.

Hygroscopic materials on the plant leaf surface will be affected by the adjacent/local humidity. Due to the boundary layer[2], temperature and the action of stomata releasing water vapor from the interior of the leaf, the humidity on the leaf surface may be higher than the relative humidity in the air. Going from air to leaf surface humidity, an increase of 35%RH above the daytime humidity has been found[51]. If the leaf surface humidity is greater than the air humidity, for example if the environment has a relative humidity of 41% and the leaf surface humidity is at 77%, then NaCl (POD 75%RH) on the leaf surface will be able to sorb moisture, while on a passive surface, such as rock, the humidity would be below the POD of NaCl and closer to the air humidity (of 41%). When applying the boundary layer effect to sorption of salts when *in situ* on the plant leaf, salts will sorb moisture from the local environment even though the humidity is less than the salts POD. Therefore salts on plant leaves due to this boundary layer may form an aqueous solution at a much larger range of environment humdities, further increasing the significance of this study. The boundary layer is relevant to plant leaves in their natural environment, but may have less importance in artificial settings, for example the cuvette of a photosynthesis system (for example Li-6400 or Li-6800) where a high fan speed is used to minimize the boundary layer thickness. In an environmental scanning electron microscope (ESEM) the vacuum conditions would minimize the boundary layer, therefore results of salts on leaves viewed with ESEM may not be influenced by this boundary layer effect seen in other studies[3, 31].

From observations during the salt control experiments, 1 g of solid $CaCl_2$ can adsorb significant proportions of water and visibly deliquesce very quickly, in a matter of 5–10 mins in relatively low humidities, while it may take days to reach adsorption equilibrium, or completely dry out again in the oven (desorption). We note that in the context of hygroscopic materials on plant leaves in the environment, these adsorption and desorption timescales are very relevant as the temperature and humidity change through the day. For example, if the air humidity increases, water may be quickly adsorbed by these materials, or if the air temperature increases in the morning leading to a decrease in air humidity, hygroscopic particles on the leaf surface will extend evaporation times of residual water, and keep the leaf wet longer. These adsorption and desorption timescales for hygroscopic particles *in situ* on the plant leaf require further research.

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The results from the current work of sorption of materials on leaves, Δw, can be utilized in a mechanistic model[6] for droplet evaporation, along with additional data for the concentration of the solution at a given RH. If considering evaporation where the RH is changing significantly with time, over the evaporation timescale, it may be necessary to consider additional mechanisms [32] including desorption hysteresis (involving crystallization or the point of efflorescence, for example NaCl[28]) of the material on the plant leaf.

Future work could include desorption, sorption data measured with time increments over a time span of longer than 3 days, conducting a similar study but looking more specifically at one location including many plant species, and individuals/biological replicates within that species. Water vapor sorption experiments could be performed on the leaf wash pellet left behind after centrifugation. This is especially relevant for the brackish mangrove sample, where the leaves had a larger amount of dried mineral dust present. The pellets were tested via XRD for the same species as in Figs. A12–A13 but no NaCl or other salts were found, and were not investigated further. It is however likely that some minerals, such as layered clays, sorb quite substantial quantities of water.

Initial tests were conducted to refine the leaf wash method, and several plant species were deemed unsuitable and were not used for the experiment. In particular, spongy tobacco leaves (native tobacco (*Nicotiana benthamiana*)) that were 6 weeks of age. When shaken, tobacco stained the water green, likely with chlorophyll leaching from ruptured cells, so were discarded and not used in the experiment.

We designed the weights of our salt and oil mixture controls to be similar to the dry weights of materials washed from leaves. If experiments were conducted with a much larger dry weight, the sorption curves may be different. For the control experiments, we dissolved the salts in de-ionized water and then dried them in the oven, to be consistent with the method used for the leaf wash samples. For mixture control samples involving oils, there was significant weight loss upon oven drying and the dry sample did not sorb a large amount of additional water at high relative humidities. We note that it is uncommon for sorption isotherms of oils to be studied, and when they are studied, stabilizers are often included. Sorption experiments on oils can reach equilibrium after 1–2 weeks[52].

Hygroscopic salts on leaves assist in maintaining leaf surface wetness when stomata are open during the day even at low humidity, maintain stomatal function and development, assist with foliar water uptake and extend the droplet evaporation time of dewfall. In terms of foliar applied agrochemicals, hygroscopic salts on the leaf either *in situ* or in the applied droplet formulation, can impact agrochemical penetration by altering the formulation's effectiveness at a given relative humidity, rate of droplet evaporation, penetration effectiveness of active ingredients and surface tension. Salts can also impact the experimental setup and design, and if leaves are regularly washed with water or not, especially when comparing field and glasshouse grown plants.

This work has demonstrated our aim of showing that the materials on plant leaves are hygroscopic and that an aqueous solution can form over small amounts of particles on the plant leaf surface grown in a range of environments. Five leaf washes attracted water to the point of visibly deliquescing, even in a glasshouse plant. Mangroves that excrete salt are covered with a layer that can form up to a total of 0.3 mL of liquid (for 6–10 leaves or 30μL on one leaf) at high humidities. This salt is mostly NaCl, but also contains other, more hygroscopic particles. An unexpected outcome of our study was the higher than expected levels of oils on the surface that created nanoparticles with a silver nitrate test, for all *Eucalyptus* samples studied.

As the surface properties of leaves vary a great deal, as do environmental properties, no single study can be specifically applicable to other plants and areas. Despite that the general cases explored here have wide-reaching implications in ecological, physiological and agricultural studies.

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Author contributions

ET is responsible for project motivation, experimental design, conducting vapor sorption experiments, analysis, model fitting, results and article writing, editing and revision. HS is responsible for the experimental and biological consultation, article editing and revision. TE is responsible for conducting ICP-OES experiments and methodology, article editing and revision.

Conflict of interest statement

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Appendix

Table A6: Salt and oil control mixtures. Samples were dissolved/suspended in de-ionized water and oven dried. The percentage mix is found by weighing the salts before creating the solution. For all the oils, approximately 100 mg was the wet weight before oven drying, most of the oil evaporated in the oven. The mangrove nutrient is mainly NaCl, along with 1295 ppm Mg, 430ppm Ca and 390 ppm K.

Compound	Total dry weight - mg	Percentage mix - %
Mangrove nutrient	21.6	
NaCl + $CaCl_2$	60.0	41 NaCl, 59 $CaCl_2$
NaCl + $CaCl_2$ + KCl	172.5	12 NaCl, 71 $CaCl_2$, 17 KCl
$CaCl_2$ + KCl + NaCl + $Ca(NO_3)_2$	96.5	37 $CaCl_2$, 11 KCl, 17 NaCl, 35 $Ca(NO_3)_2$
$Ca(NO_3)_2$ +KCl	105.3	11 $Ca(NO_3)_2$, 89 KCl
NaCl + euc oil	49.0	96 NaCl, 4 euc oil
NaCl large	24.4	100
NaCl small	1.1	100
$CaCl_2$ large	35.8	100
$CaCl_2$ small	2.1	100
Euc oil	2.7	100
Tea tree oil	0.9	100

Table A7: GAB parameters for Figure 4, fitted with Equation (5)

Sample	w_S	β	$k \times 10^{-3}$	R^2 - %
Cabinet mangrove	46.5	1.5	9.71	98.6
Brackish mangrove	43.4	0.64	9.72	99.0
Mangrove nutrient	162.2	0.098	8.88	99.8
NaCl large	424.4	0.0081	9.36	99.3

Table A8: Operating parameters for ICP-OES measurements.

Parameter	Value
Read time	20 s
Replicates	3
Sample uptake delay	25 s
Rinse time	30 $\times$ 2 s (0.5 M HNO_3 & MQ)
Stabilization time	10 s
Pump speed	12 rpm
Fast pump	ON
RF power	1.5 kW
Aux flow	1.0 L min^{-1}
Plasma flow	12.0 L min^{-1}
Nebulizer flow	0.7 L min^{-1}
Viewing mode	SVDV
Viewing height	5 mm
Background correction	FACT
Number of pixels	2
Quality control	1 $\mu g\ g^{-1}$ multi element
Analytes	Al (396.152 nm); B (249.772 nm); Ca (422.673 nm); Cu (327.395 nm); Fe (238.204 nm); K (766.491 nm); Mg (279.553 nm); Mn (257.610 nm); Na (589.592 nm); P (213.618 nm); Si (251.611 nm); Sr (407.771 nm); Zn (213.857 nm)
Drift correction	C (193.027 nm); Ar (565.070 nm, 645.918 nm, 675.283 nm, 699.217 nm, 704.096 nm)

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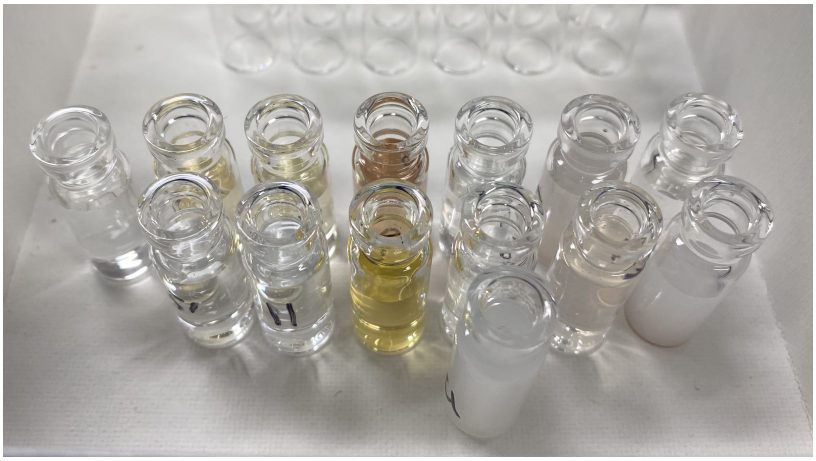

Figure A6: Silver nitrate test for the presence of Cl^-. Samples that reacted formed a milky white precipitate of AgCl. These were Brackish mangrove, Brackish Eucalyptus and Cabinet mangrove. This test also showed the presence of nanoparticles related to Eucalyptus oils with a change in colour from clear of milky to yellow to brown. All 5 Eucalyptus samples changed colour. The darkest colour (copper brown) was Town euc no rain, the second was Town euc rain (dark yellow).

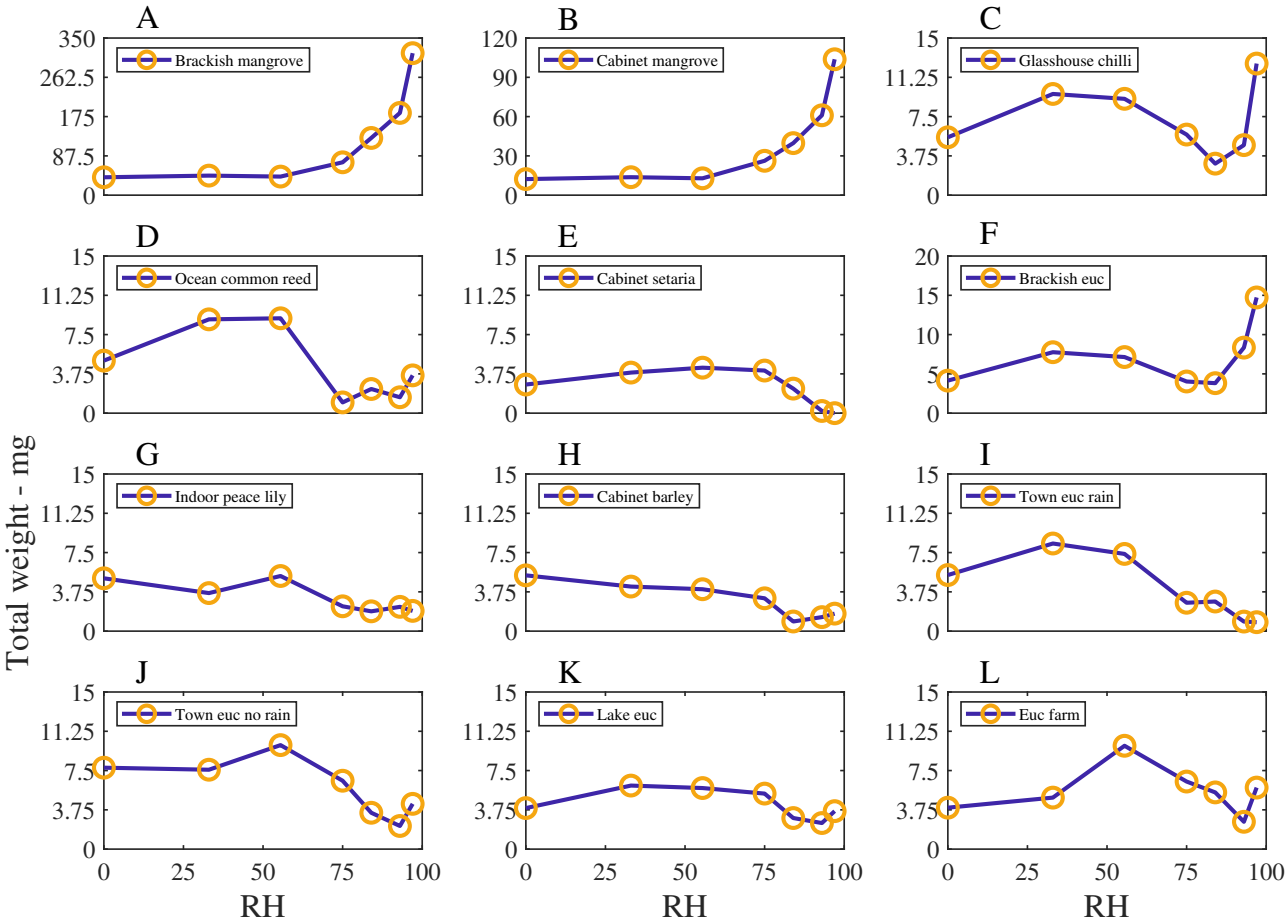

Figure A7: The Total weight (mg) of moisture adsorbed for the leaf wash samples, with relative humidity, RH (%). Total weight includes the dry weight and is scaled with the blank. Note that the y-axis range changes for each subfigure.

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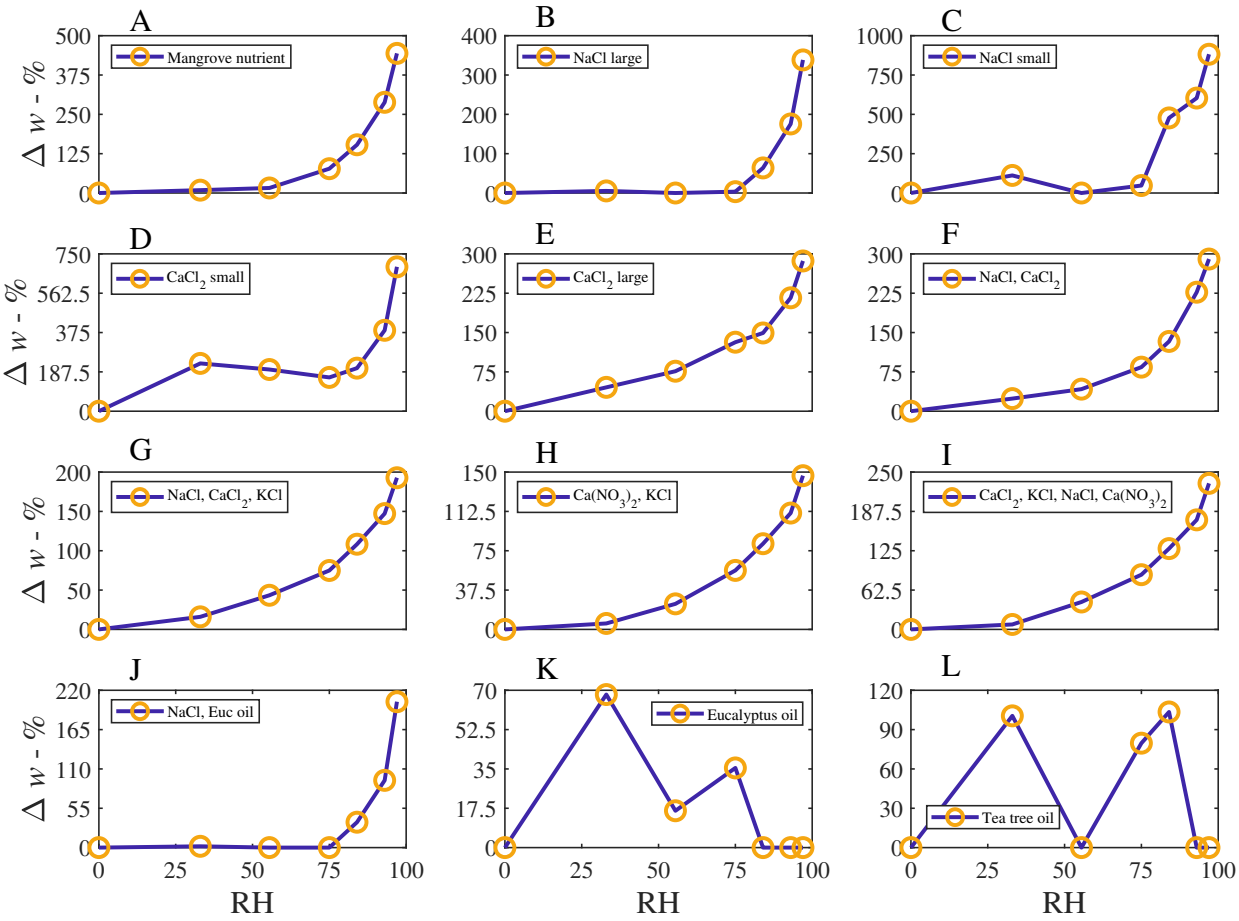

Figure A8: The percentage weight increase of moisture adsorbed above the dry weight of the controls, Δw - %, with relative humidity, RH - %. The y-axis range changes for each subfigure.

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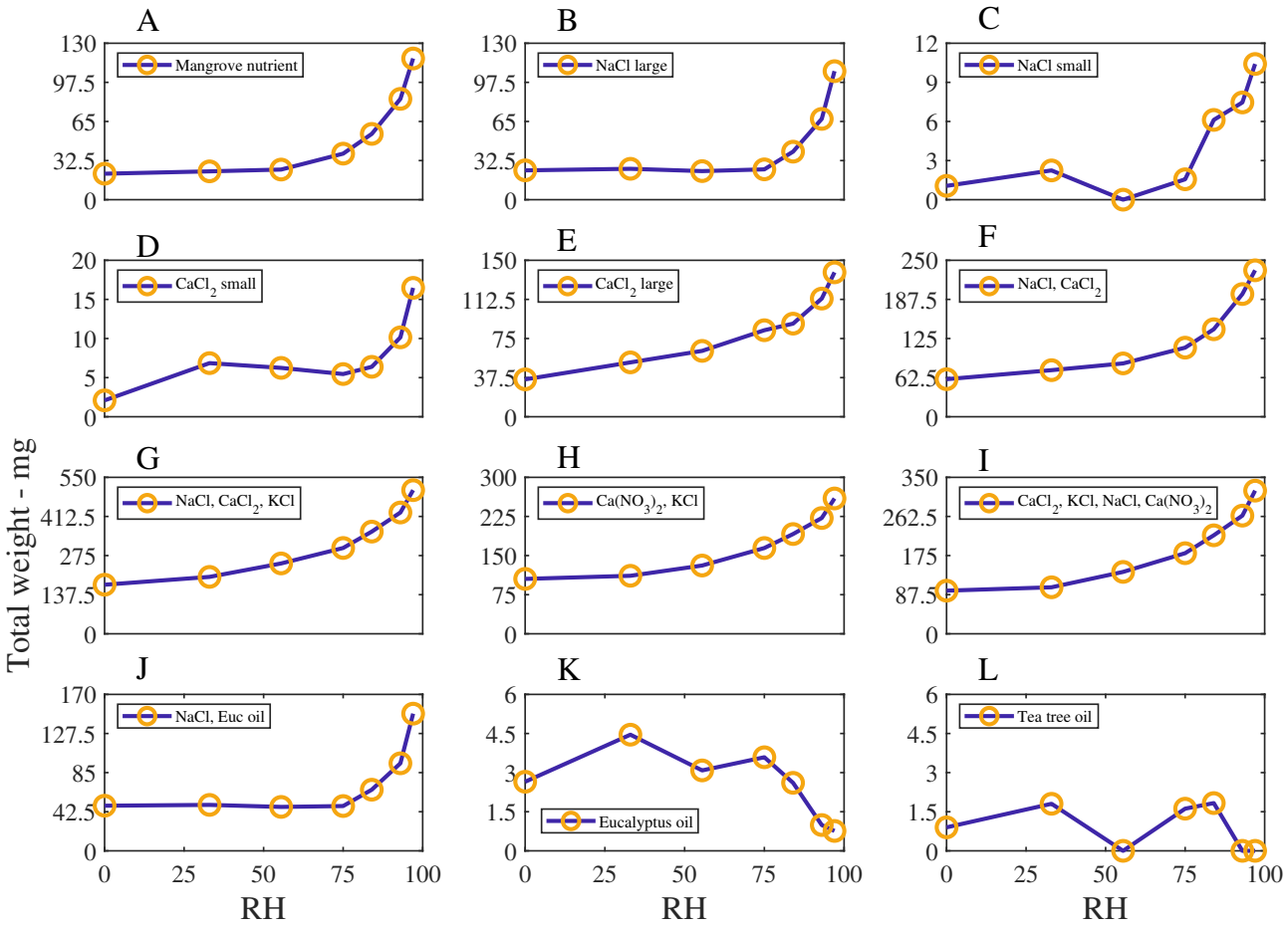

Figure A9: The Total weight (mg) of moisture adsorbed for the controls, with relative humidity, RH (%). The total weight includes the dry weight and is scaled with the blank. The y-axis range changes for each subfigure.

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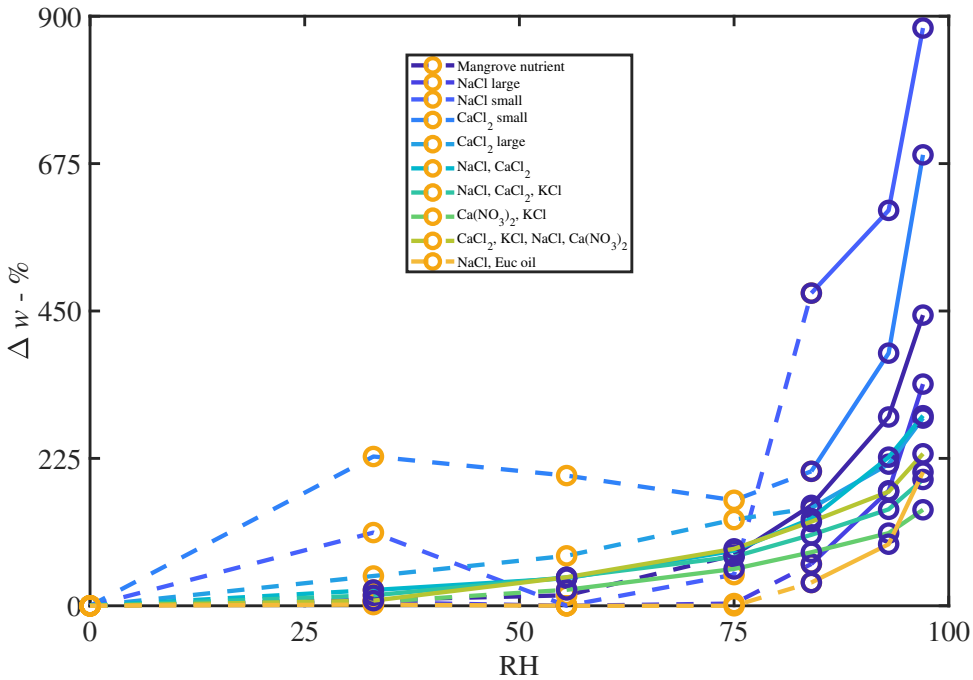

Figure A10: Control samples that have developed a coating of liquid water that is visible without the need for special equipment. The percentage weight increase of moisture adsorbed above the dry weight of the controls, Δw - %, with relative humidity, RH - %, is shown. The orange circles and dashed lines indicate water is not yet visible, and the blue circles and solid lines indicates where liquid water is visible.

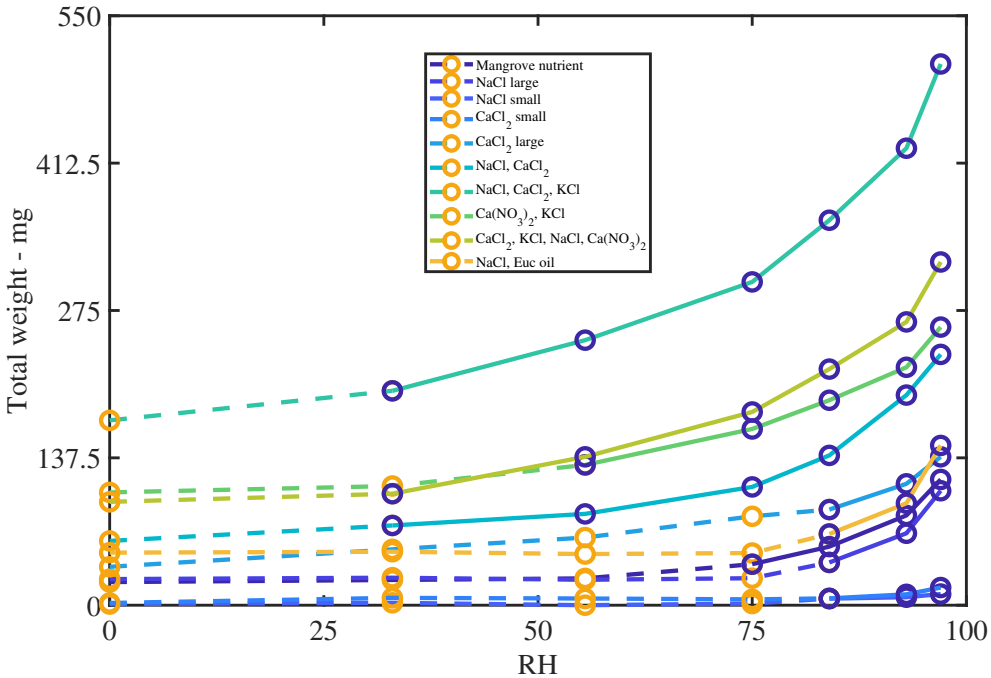

Figure A11: Control samples that have developed a coating of liquid water that is visible without the need for special equipment. The Total weight (mg) of moisture adsorbed for the controls, with relative humidity, RH (%), is shown. The orange circles and dashed lines indicate water is not yet visible, and the blue circles and solid lines indicates where liquid water is visible. Noteworthy is the significant weight of the NaCl + $CaCl_2$ + KCl sample at 97%RH of 500 mg or 0.5 mL, although this sample started with the largest dry weight.

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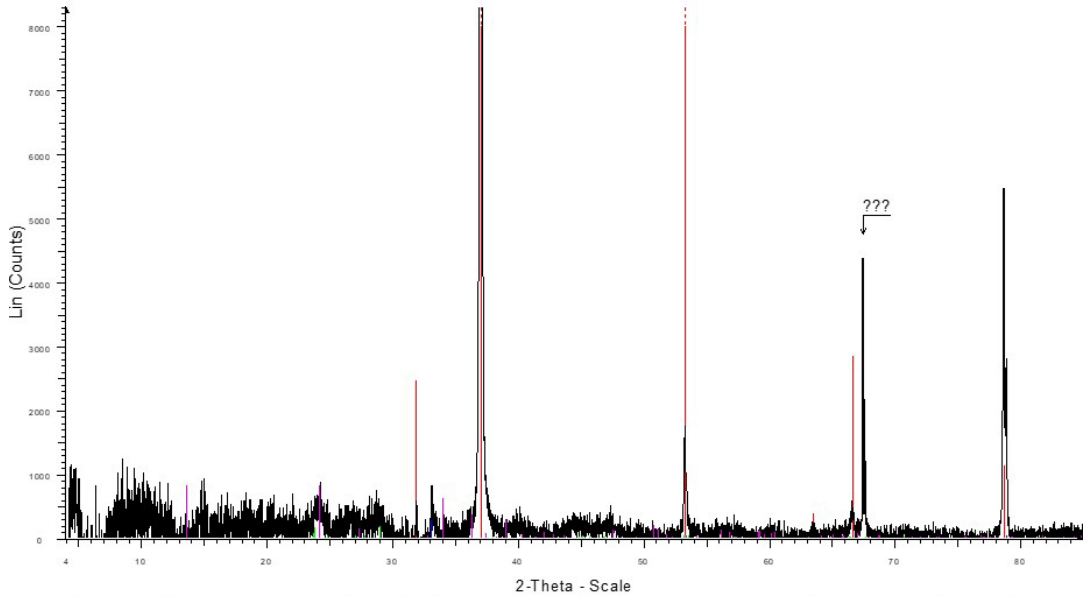

Figure A12: XRD results for Brackish mangrove leaf wash from the liquid wash, and corresponding results are shown in Table 2, with intensity (counts) vs angle (deg 2theta). Red is halite NaCl, blue is sylvite KCl, green is kaolinite $Al_2Si_2O_5(OH)_4$ and magenta is gypsum $CaSO_4$.

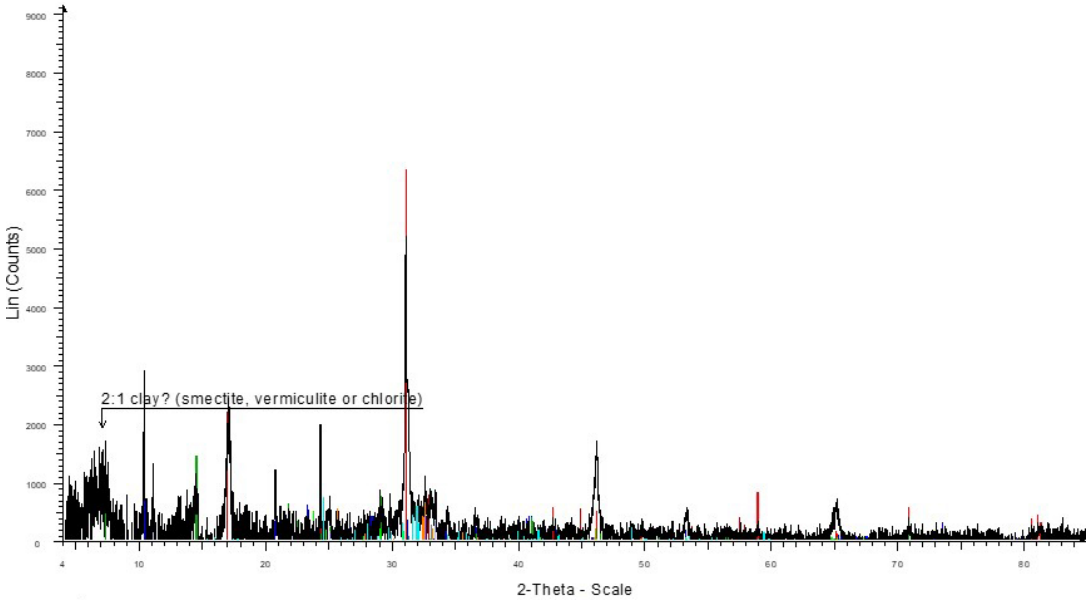

Figure A13: XRD results for Town euc rain leaf wash from the liquid wash, and corresponding results are shown in Table 2, with intensity (counts) vs angle (deg 2theta). Red is quartz SiO_2, blue muscovite, light green is kaolinite $Al_2Si_2O_5(OH)_4$, dark green is chlorite, orange is plagioclase $(Ca,Na)_{1-2}(Si,Al)_{2-3}O_8$, turquoise is K-feldspar $KAlSi_3O_8$, lilac is talc $Mg_3(OH)_2Si_4O_{10}$, grey is sylvite KCl and dark red is boehmite AlOOH.

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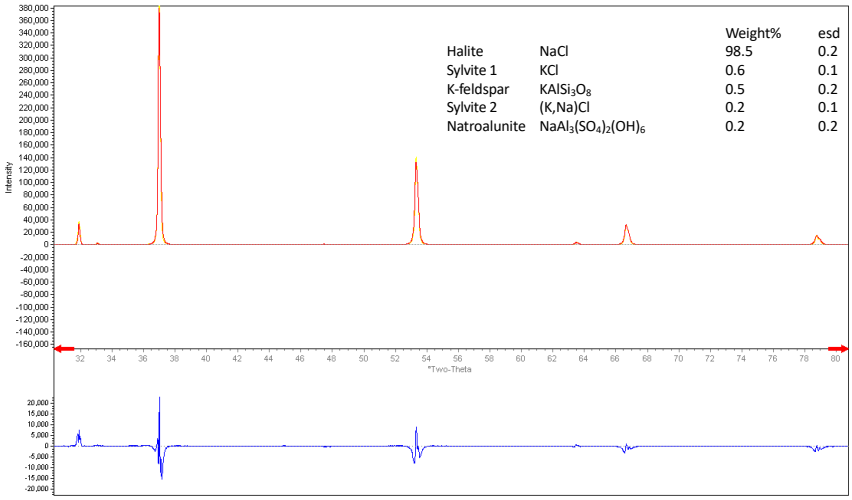

Figure A14: XRD results for a glasshouse mangrove, with intensity (counts) vs angle (deg 2theta). The sample for the XRD was collected by scraping the particles on the bottom of the leaf directly. Note this is the same plant species but a different individual as the Cabinet mangrove sample, and collected at a later date and grown in a glasshouse. No washing of the leaves occurred while the plant was growing.

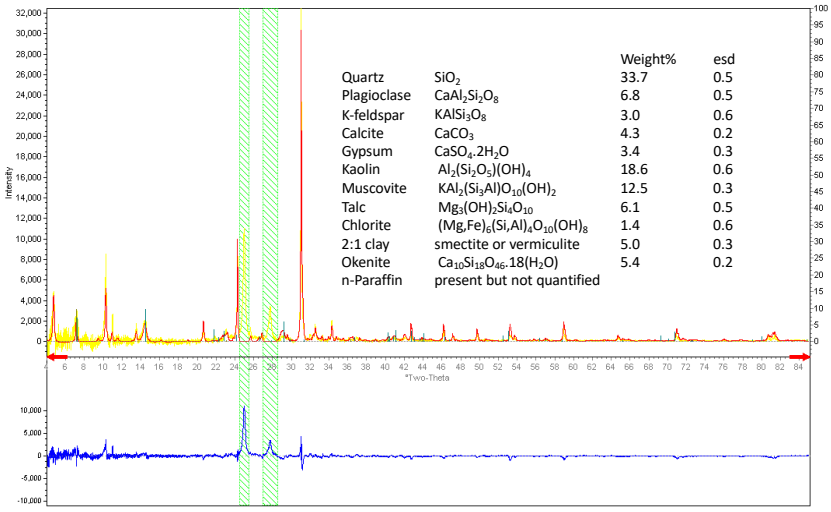

Figure A15: XRD results of Queensland kauri pine (*Agathis robusta* (syn. *A. palmerstonii)*), located indoors, with intensity (counts) vs angle (deg 2theta). This species was not included in the original sample set but was located in the same space as the Indoor peace lily. The plant was mature and had very waxy leaves that had a whitish sheen. Several waxes were seen but not quantified (n-Paraffin). The sample for the XRD was collected by scraping the top of the leaf. The bottom scraping shows similar results to the top, and similar to directly onto the leaf, however scraping showed the best results. Analysis was also conducted on the Town euc no rain and lambs ear (*Stachys byzantina*) with very hairy leaves located next to the town euc, and the results are similar to those shown here.