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18 **Abstract**

19 Terrestrial ecosystem dynamics are strongly modified by stresses associated with climate
20 change, impacting plant growth and development, mortality, and ecological succession. Here we
21 highlight the potential role of plant cell wall esters to link changes in cell wall structure/function
22 with biosphere-atmosphere fluxes of methanol, acetic acid, carbon dioxide, and water.

23

24 **Main text**

25 Terrestrial ecosystem dynamics, including carbon stocks and biosphere-atmosphere fluxes of
26 carbon dioxide (CO_2), water (H_2O), and volatile organic compounds (VOCs) are dramatically
27 changing in response to climate factors such as trends in surface warming and a higher frequency
28 and intensity of large-scale droughts and associated insect infestation epidemics [1].
29 Understanding the mechanisms that drive forest responses to climate change is vital for predicting

30 how the structure and function of natural and managed ecosystems will react to environmental
31 change including alterations in carbon and H_2O cycling, and the ecosystem services and products
32 provided. Therefore, understanding the underlying biochemical, physiological, and ecological
33 processes including plant growth and development, abiotic and biotic stress responses, mortality,
34 and ecological succession and forest recovery are critical for accurately predicting the future of
35 forest structure and function.

36 Increased abiotic and biotic disturbances threaten the ability of terrestrial ecosystems to maintain
37 a net carbon sink and consequently mitigate anthropogenic climate effects in the atmosphere. For
38 example, reductions in net primary productivity (NPP), decreases in biomass gains, increased
39 vegetation mortality, and shortening of carbon residence times have been linked to drought and
40 warming anomalies across numerous ecosystems [1]. However, mortality-linked generation of
41 forest gaps can lead to the release of suppressed understory trees and increased rates of early
42 successional species recruitment. Thus, forest regrowth can counterbalance carbon losses and
43 contribute to accelerated forest dynamics with the majority of tree biomass being in the form of
44 **plant cell walls** (80-95%; see glossary). Here, we highlight cell wall-derived emissions of
45 methanol and acetic acid, along with associated changes in cell wall structure and function as a
46 common thread among the processes that underlie ecosystem responses to climate change (**Fig.
47 1**).

48 Methanol is the most abundant non-methane volatile in the atmosphere with emissions from
49 terrestrial vegetation the largest global source. High methanol emissions, often dominating
50 ecosystem release of VOCs, have been reported from agricultural crops and temperate, boreal,
51 and tropical forests. Methanol emissions are closely associated with plant growth, stress, and
52 senescence processes attributed to physicochemical changes in cell walls [2]. While field
53 observations are rare, acetic acid is also an important volatile emitted by terrestrial ecosystems
54 [3] and like methanol was recently suggested to derive primarily from cell walls [4]. Methanol
55 emissions tightly correlate with leaf expansion rates and young expanding leaves emit
56 substantially higher amounts of both methanol and acetic acid than mature leaves. Moreover, leaf
57 methanol emissions more than double for each 10 ºC increase in leaf temperature [5].
58 Furthermore, leaves undergoing age-related senescence show elevated emissions of methanol
59 and acetic acid [6], while detached leaves undergoing desiccation release large pulses of
60 methanol and acetic acid [4]. These findings suggest that methanol and acetic acid emissions
61 increase together with NPP during forest growth and recovery processes, but diverge during high
62 temperature and drought stress with stimulated emissions of methanol and acetic acid and
63 suppressed NPP. Thus, if terrestrial forests are becoming more dynamic, gap-phase processes
64 play a critical role in determining carbon stocks, residence times and biosphere-atmosphere
65 fluxes of VOCs, CO_2, and H_2O.

66 The **primary cell wall**, which surrounds all plant cells, provides shape, strength and flexibility. It
67 consists of a complex structure composed of **hemicellulose** and cellulose microfibrils embedded
68 in a gel-like matrix composed of **pectin**. In addition to providing structure, the cell wall is dynamic,
69 facilitating numerous interactions within the extracellular matrix including cell adhesion, migration,
70 and growth, and exchange of macromolecules, nutrients, metabolites and hormones. Such
71 dynamic responses are facilitated by chemical modifications that can significantly alter

72 physicochemical, mechanical, and biological properties. The cell wall is the first line of defense
73 against many stresses, and cell wall remodeling is a common stress response. While cell wall
74 structure and function are controlled to a large extent by the polysaccharide composition, which
75 varies with tissue type, developmental stage, and plant species, more rapid secondary chemical
76 modifications can occur in response to environmental or developmental cues. For example, non-
77 cellulosic cell wall polysaccharides can be extensively modified with methyl and/or *O*-acetyl esters
78 [7],[8]. The removal of esters via enzymatic hydrolysis leads to rapid physicochemical changes in
79 the cell wall and the release of methanol and acetic acid, which can then be transported in the
80 transpiration stream and emitted to the atmosphere as a VOC or feed into central carbon and
81 energy metabolism (**Fig. 2**).   Changes in cell wall esters during stress induce signaling via
82 damage-associated molecular patterns, which in turn activate immunity responses [9]. This
83 suggests that cell wall-derived methanol and acetic acid are involved in signaling and immune
84 responses as an essential component of plant monitoring systems.

85 Once released from the cell wall, acetic acid and methanol may be efficiently integrated into
86 central carbon and energy metabolism[10]. Following activation to acetyl-CoA, acetic acid can
87 participate in numerous catabolic and anabolic processes whereas methanol initiates the C_1
88 pathway integrating into photosynthesis/photorespiration via formaldehyde/formate/CO_2 and the
89 universal C_1 donor **5,10-CH$_2$-THF**. Given that high temperature and drought stress suppresses
90 stomatal conductance and photosynthesis and accelerates photorespiration, enhanced release
91 of cell wall-derived methanol and acetic acid may play important roles in thermal tolerance by **1)**
92 providing an alternative carbon source for glycine methylation in photorespiration thereby
93 potentially reducing glycine decarboxylation, **2)** enhancing CO_2 concentrations within chloroplasts
94 for photosynthesis, and **3)** producing key C_2 intermediates (e.g., acetyl-CoA) used in lipid and
95 secondary metabolite biosynthesis, energy generation during mitochondrial respiration, and
96 regulation of biopolymer function via acetylation. However, little is known about the quantitative
97 significance of cell wall ester metabolism to plant carbon and energy requirements during stress.

98 Although many hemicellulose and pectin polysaccharides can be heavily *O*-acetylated, only pectin
99 is thought to be substantially methyl esterified. Pectin provides both mechanical and adhesive
100 properties within the cell wall, properties which can be dramatically altered through de-
101 esterification. Newly synthesized pectin is exported to the cell wall in a highly methyl and *O*-acetyl
102 esterified state. Once positioned in the cell wall, pectin methyl and acetyl esterases can selectively
103 hydrolyze these esters. For example, following de-methylation, the generation of carboxylate
104 anion side chains can bind Ca^{+2} cations in an **egg-box structure**, increasing cell wall rigidity.
105 Alternatively, the de-methylated pectin can be targeted for degradation by polygalacturonases.
106 De-methylated pectin is suggested to be an essential component of plant response to heat stress
107 through its role in controlling cell wall mechanical properties [11] and is deemed vital for stomatal
108 function [7]. Enriched levels of methyl esterified pectin in stomatal guard cell walls lead to a
109 reduced dynamic range of conductance which in turn impacts transpiration and evaporative
110 cooling as well as photosynthesis and growth.

111 Recently it has been reported that acetyl groups on **xylan**, a major component of the **secondary**
112 **cell wall**, are essential for proper xylem structure and function through facilitation of xylan-
113 cellulose interactions [12]. Consequently, mutations in several genes associated with acetylation

114   of xylose residues during xylan biosynthesis lead to the collapse of xylem vessels and
115   dramatically reduced transpiration rates [8]. Additionally, *O*-acetylation of pectins and
116   hemicelluloses is essential for maintaining the structural integrity of leaf epidermis [13].
117   Additionally, a global stress response was activated, including a marked upregulation in **ROS**
118   detoxification. These findings support an emerging view of the interacting roles of cell wall esters
119   and ROS in sensing and signaling pathways involved in cell wall remodeling in response to stress
120   [14].

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Conclusions

123   While little is known about the functions of cell wall ester modifications in trees, evidence from
124   model plant systems like *Arabidopsis thaliana* suggests that they may be highly dynamic, playing
125   central roles in cell growth, tissue development and function, participating in sensing and signaling
126   pathways involved in cell wall remodeling in response to stress, and integrate into primary C_{1-3}
127   metabolism. Although the reservoirs and fluxes of carbon through acetylated and methylated cell
128   wall polysaccharides are potentially large, they remain poorly characterized. Methanol and acetic
129   acid products of cell wall de-esterification may be transported over large distances within the plant
130   and enter central metabolism in distant tissues or be emitted into the atmosphere as gases, but
131   plant and ecosystem emissions studies investigating this are rare. Thus, interdisciplinary studies
132   linking cell wall biochemistry and metabolism with plant physiology and biosphere-atmosphere
133   gas exchange will lead to better predictive understanding of the mechanisms through which cell
134   wall esters facilitate forest response to climate extremes. Of particular interest are high latitude
135   forests responding to rapid warming through expansion of deciduous broadleaf trees and
136   commensurate declines in evergreen conifer trees [15]. These distinct plant functional types vary
137   in their leaf phenological cycles and cell wall composition, with deciduous trees undergoing
138   seasonal leaf emergence and senescence while conifer trees retain their needles over the winter
139   months. This may impact the timing, spatial distribution, and magnitude of biosphere-atmosphere
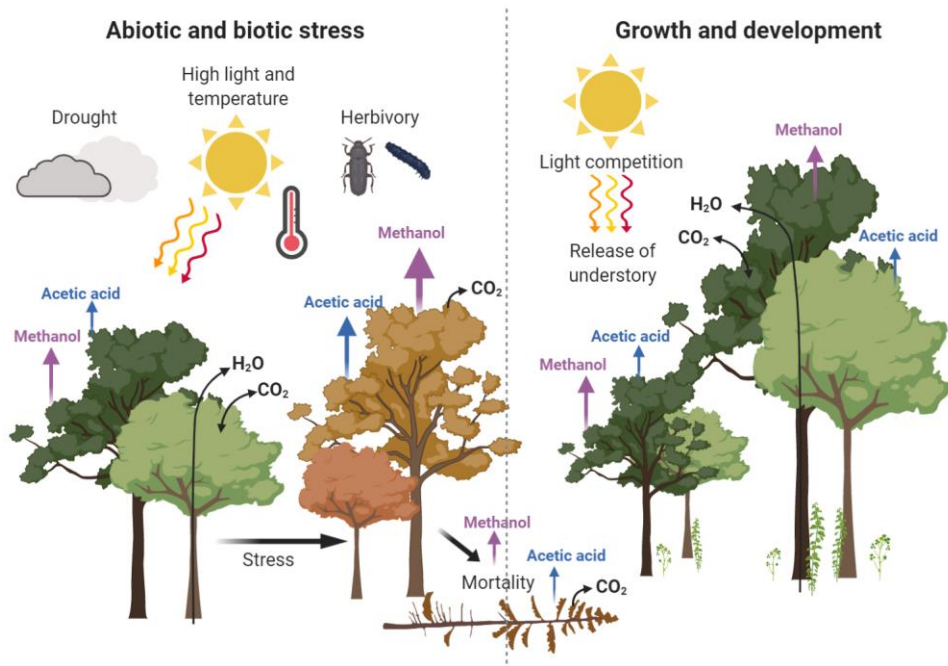140   fluxes of VOCs, CO_2, and H_2O in such changing forests in the future.

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Figure 1: Acceleration of forest dynamics and biosphere-atmosphere interactions associated with cell wall-derived methanol and acetic acid emissions under future predictions in surface warming, droughts, and biotic stress. The size of the arrows representing emissions of methanol and acetic acid are indicative of the relative strength of these emissions. Methanol is emitted in greater quantities than acetic acid, and emissions of both increase under stress. Figure created using Biorender.com.

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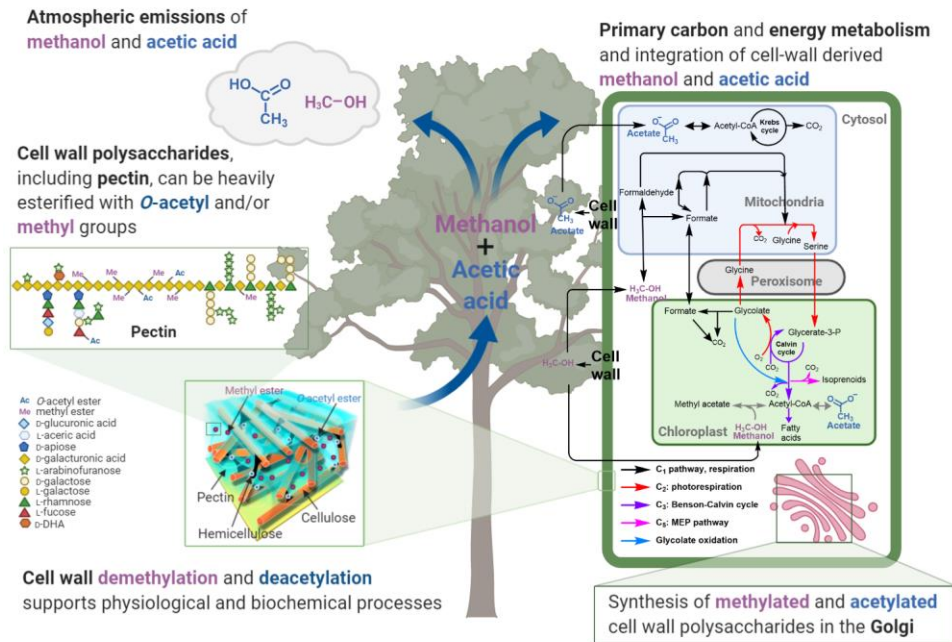
Figure 2: Integration of cell wall methyl and O-acetyl esters with atmospheric emissions and primary carbon metabolism. Created using Biorender.com and FigShare (*https://doi.org/10.6084/m9.figshare.7398800.v1*)

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Glossary box

5,10-CH$_2$-THF: 5,10-Methylenetetrahydrofolate, the universal one carbon (C_1) donor.

Egg-box structure: Calcium-induced association of two parallel pectic galacturonan chains with a pattern of specific de-esterified galacturonic acid monomers ionically bound via Ca^{2+} ions.

Hemicellulose: Plant polysaccharides that contain a β-(1→4) linked backbone, traditionally characterized by alkaline extraction. Hemicelluloses include xylan, arabinoxylan, xyloglucan, glucomannan, and mannan.

Pectin: A component of the plant primary cell wall. Pectic polysaccharides are characterized by a galacturonic acid-enriched backbone. There are four major pectic domains: homogalacturonan, xylogalacturonan, rhamnogalacturonan I and rhamnogalacturonan II.

Plant cell wall: Plant cells are surrounded by a cell wall which provides shape and strength. Cell walls consist of polysaccharides, including cellulose, hemicellulose, and pectin, proteins, and lignin.

Primary cell wall: A thin cell wall that surrounds all cells. It consists of cellulose, hemicellulose and pectin. It provides structure while retaining the flexibility and extensibility necessary to allow cell expansion.

ROS: Reactive oxygen species such as hydrogen peroxide, singlet oxygen, superoxide anion, and the hydroxyl radical.

Secondary cell wall: The secondary cell wall is deposited after the cell stops growing, and provides more strength and rigidity. The secondary cell wall contains mainly cellulose, lignin and hemicellulose. The secondary cell wall accounts for the majority of plant biomass.

Xylan: A hemicellulosic component of the cell wall, it is a polysaccharide with a β-1,4 linked xylose backbone, which carries various chemical substitutions.

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