

1 **Sensing the energetic status of plants and ecosystems**

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17 **Abstract**

18 The emerging consistency of the relationship between biochemical, optical and  
19 odorous signals emitted by plants and ecosystems offers promising prospects  
20 for continuous local and global monitoring of the energetic status of plants and  
21 ecosystems, and therefore of their processing of energy and matter.

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24 **NADPH/NADP as biochemical indicator of reducing power**

25 Photosynthesis converts solar energy into chemical energy in the form of  
26 reducing power (NADPH) which is essential for the primary metabolism. Plants  
27 very often generate more reducing power than is needed for their primary  
28 metabolism, for example under light saturation or stressful conditions. The  
29 NADPH/NADP ratio thus becomes an excellent biochemical indicator of this  
30 over-reduction of the photosynthetic electron-transport chain and thus of the  
31 cellular energetic status of plants. Indeed, this ratio has been used as a  
32 biochemical indicator of changes in the availability of reducing power linked to  
33 stressors such as drought [1], high light [2], salinity [3], nutrient deficiency [4] or  
34 pathogens [5].

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36 **Reflectance and fluorescence signals**

37 The rate of electron transport is down-regulated by various mechanisms to  
38 overcome the over-reduction of the photosynthetic electron-transport chain and  
39 to dissipate the excess energy signaled by high NADPH/NADP ratios. The  
40 dissipation of energy by non-photochemical quenching through the xanthophyll  
41 cycle is one of these mechanisms. It is especially interesting because it can

42 provide an indirect optical signal of excess reducing power, increased  
43 NADPH/NADP ratios and reduced light-use efficiency (LUE) through the  
44 associated changes in reflectance at the blue side of the green region of the  
45 spectrum. Increases in the concentration of zeaxanthin translate into decreases  
46 in reflectance at 531 nm, while reflectance at 570 nm is insensitive to short-term  
47 changes in zeaxanthin. The Photochemical Reflectance Index (PRI), defined as  
48  $[R_{531} - R_{570}] / [R_{531} + R_{570}]$  where R indicates reflectance and the numbers indicate  
49 wavelength in nanometers [6, 7], is thus used as a reflectance index for  
50 reducing power and LUE. The PRI also measures the relative reflectance on  
51 either side of the green reflectance "hump" (550 nm), i.e. the reflectance in the  
52 blue side of the green region of the spectrum (chlorophyll and carotenoid  
53 absorption) relative to the reflectance in the red side (chlorophyll absorption  
54 only). The PRI consequently also behaves as an index of the  
55 chlorophyll/carotenoid ratios and therefore of the energetic status and  
56 photosynthetic activities associated with changes in chlorophyll/carotenoid  
57 ratios throughout foliar development, aging or stress [8]. The PRI estimation of  
58 LUE and photosynthetic performance has been studied extensively at the leaf  
59 and canopy levels and is now also increasingly used at the ecosystem level [9].

60 In addition to changes in reflectance such as those monitored with the  
61 PRI, the shifts in energetic status translate into changes in fluorescence and  
62 temperature that may thus become relevant optical signals of different stresses.  
63 Two major fluorophore groups that dominate plant fluorescence emissions can  
64 potentially be sensed remotely. The first group of compounds, which includes  
65 NADPH itself, emits photons in the blue and green spectral regions under  
66 natural or artificial UV excitation, but it is Chlorophyll a (Chl a) the fluorophore

67 that contributes most to plant fluorescence. Chl a emits fluorescence in two  
68 broad bands with peaks at 684–695 and 730–740 nm. Various ratios of  
69 fluorescence intensity, combining the emissions at blue (F440), green (F520),  
70 red (F690) and far-red (F740) wavelengths, have been proposed for probing the  
71 status of vegetation vitality and stress responses, but the relationship between  
72 fluorescence and photochemistry is complex [10].

73 Further research is clearly warranted to understand better the temporal  
74 and spatial dynamics of these reflectance and fluorescence signals and their  
75 relationships with the energetic status, reducing power and LUE of plants and to  
76 resolve the problems that may still preclude the generalization of their use at  
77 ecosystemic and biospheric scales. In brief, these problems are related to the  
78 structural differences of canopies, to varying “background effects” (e.g. soil  
79 color, moisture, shadows or the presence of other non-green landscape  
80 components), to the effects of seasonality or to the signals derived from  
81 variations in illumination and viewing angles [10, 11]. The emerging consistency  
82 of the relationships among the PRI, sun-induced fluorescence (SIF), LUE and  
83 ecosystemic CO<sub>2</sub> uptake [9, 12], however, suggests a surprising degree of  
84 “functional convergence” of biochemical, physiological and structural  
85 components affecting ecosystemic carbon fluxes. In other words, ecosystems  
86 possess emergent properties that may allow us to effectively explore their  
87 seemingly complex photosynthetic-energetic behavior using surprisingly simple  
88 optical sampling methods based on energetic status, such as the measurement  
89 of the PRI or SIF. The enormous potential benefits are worth exploring.

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91 **Odorous signals**

92 Plants and ecosystems emit not only optical signals (reflectance and  
93 fluorescence) of their physiological status associated with the imbalance  
94 between supply and demand of reducing power; they also emit “scents” of such  
95 status. The excess reducing power and higher NADPH/NADP ratios generated  
96 when the NADPH sink in carboxylation decreases also increases the synthesis  
97 of highly reduced secondary metabolites, including volatile metabolites such as  
98 isoprenoids that are then emitted in significant amounts [13, 14]. The synthesis  
99 and emission of isoprenoids would be highest when the demand of carbon  
100 assimilation for reducing power is lowest [13, 14]. In fact, isoprene and  
101 monoterpene emissions increase when LUE decreases [15], which has driven  
102 the use of the PRI signal for estimating not only carbon fixation but also  
103 isoprenoid emissions themselves [15]. Isoprenoids are emitted at the nanomolar  
104 scale, but electron flux involved in the NADPH/NADP ratio is at the micromolar  
105 scale, so the emission is not a matter of mass balance of competing processes  
106 but of an enhancement under higher flow.

107

### 108 **Monitoring of the energetic status**

109 We thus propose that the energetic status of plants (and ecosystems) resulting  
110 from the balance between the supply and demand of reducing power can be  
111 assessed biochemically by the cellular NADPH/NADP ratio, optically by using  
112 reflectance and fluorescence as indicators of the dissipation of excess energy,  
113 and odorously by the emission of volatile organic compounds such as  
114 isoprenoids, as indicators of an excess of reducing equivalents. These signals  
115 can provide information on the energetic status, the associated health status

116 and the functioning of plants and ecosystems. The integration of these three  
117 ways of assessing the excess of reducing power in different species and  
118 ecosystems with different ecophysiological traits will provide further knowledge  
119 of the links among the three signals and the strategies of the different species to  
120 deal with excess of energy. These signals and their integration are thus of  
121 academic interest, but may also have multiple applications for environmental  
122 and agricultural monitoring, e.g. by extending the spatial coverage of carbon-  
123 flux observations to most places and times, or/and for improving the process-  
124 based modeling of carbon fixation and isoprenoid emissions from terrestrial  
125 vegetation at ecosystemic and global scales. Significant benefits can thus be  
126 expected if we are able to solve the considerable challenges that remain for a  
127 wide-scale and routinary implementation of these biochemical, optical and  
128 odorous signals for ecosystemic and/or agronomic monitoring, a key issue in  
129 global ecology, agricultural applications, the global carbon cycle and Earth  
130 science.

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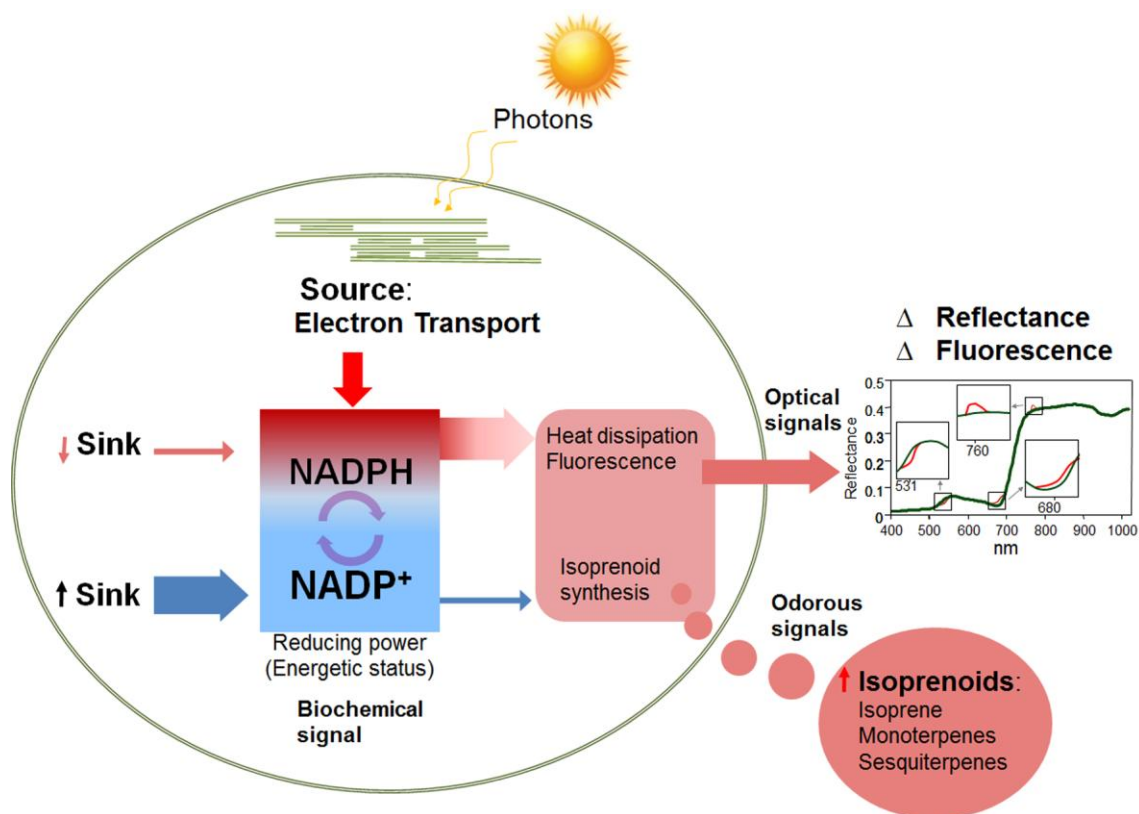


186 **Figure caption**

187 Figure 1. Overview of the biochemical, optical and odorous signals in response to  
188 changes in the reducing power of plants. The energetic status of plants (and  
189 ecosystems) resulting from the balance between the supply and demand of  
190 reducing power can be assessed by the resulting biochemical changes in the  
191 cellular NADPH/NADP ratio, optical changes in the foliar reflectance and  
192 fluorescence, and changes in production and emission of odorous volatile  
193 organic compounds such as isoprenoids.

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