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OZONE AND PLANT LIFE: THE ITALIAN STATE-OF-THE-ART

Reflectance spectroscopy: a novel approach to better understand and monitor the impact of air pollution on Mediterranean plants

Lorenzo Cotrozzi[1] · Philip A. Townsend[2] · Elisa Pellegrini[1] · Cristina Nali[1] · John J. Couture[3]

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Abstract The Mediterranean basin can be considered a hot spot not only in terms of climate change (CC) but also for air quality. Assessing the impact of CC and air pollution on ecosystem functions is a challenging task, and adequate monitoring techniques are needed. This paper summarizes the present knowledge on the use of reflectance spectroscopy for the evaluation of the effects of air pollution on plants. First, the history of this technique is outlined. Next, we describe the vegetation reflectance spectrum, how it can be scaled from leaf to landscape levels, what information it contains, and how it can be exploited to understand plant and ecosystem functions. Finally, we review the literature concerning this topic, with special attention to Mediterranean air pollutants, showing the increasing interest in this technique. The ability of spectroscopy to detect the influence of air pollution on plant function of all major and minor Mediterranean pollutants has been evaluated, and ozone and its interaction with other gases (carbon dioxide, nitrogen oxides, and sulfur dioxide) have been the most studied. In the recent years, novel air pollutants, such as particulate matter, nitrogen deposition, and heavy metals, have drawn attention. Although various vegetation types have been studied, few of these species are representative of the Mediterranean environment. Thus, major emphasis should be placed on using vegetation spectroscopy for better understanding and monitoring the impact of air pollution on Mediterranean plants in the CC era.

Keywords Carbon dioxide · Heavy metals · Nitrogen deposition · Ozone · Particulate matter · Reflectance spectroscopy

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✉ John J. Couture
couture@purdue.edu

[1] Department of Agriculture, Food and Environment, University of Pisa, Via del Borghetto 80, 56124 Pisa, Italy

[2] Department of Forest and Wildlife Ecology, University of Wisconsin-Madison, 1630 Linden Dr., Madison, WI 53705, USA

[3] Departments of Entomology and Forestry and Natural Resources and Purdue Center for Plant Biology, Purdue University, 901 W. State St., West Lafayette, IN 47907, USA

Abbreviations

AIS	Airborne imaging spectrometer
ASD	Analytical Spectral Devices
AVIRIS	Airborne Visible/Infrared Imaging Spectrometer
CASI	Compact airborne spectral imager
CC	Climate change
Chl	Chlorophyll
chl.index	Total canopy chlorophyll content index
CF	Crude fiber
CI	Chlorophyll index
CO_2	Carbon dioxide
CP	Crude protein
DCI	Derivative chlorophyll index
DVI	Difference vegetation index
FLI	Fluorescence line imager
GER	Geophysical Environmental Resources Inc.
GIS	Geographic information system
H_2O	Water
LAI	Leaf area index
LAIDI	Leaf area index determining index
N	Nitrogen
NASA	National Aeronautics and Space Administration
NDNI	Normalized difference nitrogen index
NDVI	Normalized difference vegetation index
NDWI	Normalized difference water index

NH_4^+	Ammonium
NIR	Near-infrared
NIRS	Near-infrared spectroscopy
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NO_3^-	Nitrate
NO_x	Nitrogen oxides
O_2	Oxygen
O_3	Ozone
OII	Ozone injury index
OTCs	Open top chambers
PCR	Principal component regression
PLSR	Partial least squares regression
PM	Particulate matter
PRI	Photochemical reflectance index
REP	Red-edge position
RFI	Red fall index
RuBP	Ribulose-1,5-bisphosphate
RVI	Ratio vegetative index
RS	Remote sensing
SO_2	Sulfur dioxide
SMLR	Stepwise multiple linear regression
SWIR	Shortwave-infrared
TSPs	Total suspended particles
V_{cmax}	RuBP carboxylation
VIRIS	Visible infrared intelligent spectrometer
VIs	Vegetation indices
VIS	Visible
VNIR	Visible-near infrared
VSWIR	Visible-near infrared-shortwave infrared
WHO	World Health Organization

Introduction

Climate change and air pollution in the Mediterranean environment

Climate change (CC) is a scientific certainty as the effects of biotic and abiotic stresses on ecosystems are already detectable and will likely be more evident in the next years (IPCC 2014). The European Mediterranean region is considered an esthetically appealing area, containing a rich amount of biodiversity, unique combinations of landscapes due to the climate, relief, and soil conditions, and has had human occupation for centuries (de Jong et al. 2012). However, in this area, the impact of CC is particularly severe in comparison to the other areas worldwide as the Mediterranean basin, characterized by a unique climate regime with wet and mild winters, hot and dry summers, and an inconsistent inter-annual and inter-seasonal distribution of precipitation, is greatly sensitive to even minor changes in global atmospheric dynamics (Luterbacher et al. 2006). Here, CC manifests itself in two fundamentally different ways: increasing the yearly temperature and/or modifying the frequency and the intensity of extreme meteorological events, such as heat waves, rain pulses, and dust events (Rumukainen 2012; Gaetani and Pasqui 2014). Moreover, climatic models indicate that the Mediterranean basin will be one of the areas subjected to the most drastic reductions in precipitation and increases in warming globally, with a predicted reduction in precipitation of 25 to 30% by the end of the twenty-first century and an increase in air temperature between 2 and 3 °C by 2050 (Christensen et al. 2007). Furthermore, sustained human population growth, anthropogenic activities, and environmental alterations (Matesanz and Valladares 2014) strongly contribute to the substantial vulnerability of ecosystems in the Mediterranean under future predicted patterns of CC.

Atmospheric pollution is one of the most difficult environmental problems currently facing society. Airborne particles induce several negative impacts on human health (World Health Organization (WHO) 2013). Similarly, exposure to tropospheric ozone (O_3), nitrogen oxides (NO_x), sulfur dioxide (SO_2), or heavy metals can cause cardiovascular and lung disorders, premature deaths, and have carcinogenic effects. In addition, these air pollutants may also affect ecosystem functioning and agricultural productivity, having pronounced adverse effects on growth, development, and longevity of plants (Cerro et al. 2015; Pellegrini et al. 2017). Finally, air pollution will have a major effect on climate (IPCC 2014). Atmospheric pollution is stimulated by the South European climate and is likely to grow in the future due to rapid urbanization (Kanakidou et al. 2011). For these reasons, the Mediterranean basin can be considered a hot spot not only in terms of CC (Giorgi and Lionello 2008) but also for air quality (Cristofanelli et al. 2016).

The most widespread pollutant in the Mediterranean region is O_3 (Cristofanelli and Bonasoni 2009), which frequently exceeds the limit values established for the protection of natural vegetation and crops (EEA 2016). Despite efforts to control this pollutant over recent decades, the background mean concentrations in the Northern Hemisphere have more than doubled to 35–40 ppb since the industrial revolution, and daily peak concentrations continue to exceed the WHO guideline values of 50 ppb in many regions (Mills et al. 2016). Moreover, ground levels of O_3 are expected to increase in Mediterranean regions as a consequence of CC because its formation and accumulation in the atmosphere is connected to elevated solar radiation and high temperature and is favored by high-pressure conditions (Nali et al. 2001, 2006; Lorenzini et al. 2014; Pellegrini 2014). Elevated O_3 levels may contribute to increased rates of CC directly due to its status as an important greenhouse gas and, indirectly, due to its effect on rates of carbon dioxide (CO_2) uptake by terrestrial ecosystems.

Another main issue for Mediterranean ecosystems is increasing levels of atmospheric CO_2. Atmospheric CO_2 is the single most important greenhouse gas derived from human activity, predominately from the combustion of fossil fuels and changes in patterns of land use, and is responsible for 74% of global warming over the past decade (Canadell and Schulze 2014). In the last 200 years, global atmospheric CO_2 concentration has risen from the 280 ppm of the pre-industrial age to the present levels that can exceed 400 ppm, and models predict a further increase (potentially up 700 ppm) within this century (IPCC 2014). Especially in the Mediterranean environment, elevated CO_2 may play an important role in decreasing water use efficiency and altering plant growth and productivity in water-limited ecosystems. Simultaneously, increases in atmospheric CO_2 concentrations can have a positive effect on soil carbon accumulation. However, the influence of CO_2 on changes in climate include increased heat waves, redistribution of precipitation, and an increased susceptibility in plants to pathogen infection and herbivore damage—stress events which impair photosynthetic machinery, and therefore efficiency, and plant growth (Cramer et al. 2001; Couture et al. 2015) ultimately limiting benefits gained by plants under elevated CO_2 levels.

Aerosols have both natural (e.g., sea salt, soil dust suspension) and anthropogenic (e.g., transport, industrial activities) sources and are either emitted directly into the atmosphere as primary aerosols or are chemically formed from precursors as secondary aerosols (Im et al. 2012). Both sources result in direct emission of particulate matter (PM) that it is probably the atmospheric component that best exemplifies the air quality-CC interaction. Observations over the last 30 years showed that annual averages of PM varied over an order of magnitude (from 5 to 54 $\mu g\ m^{-3}$; Nadal et al. 2015). Again, the highest levels of these pollutants were observed for urban sites in southern Europe (especially Italy, Spain, and Greece). Furthermore, in Europe, the predicted increase in overall aerosol concentrations will be by 20–40 $\mu g\ m^{-3}$ relative to the present-day values, and changes in climate (e.g., warming, shift in precipitation patterns, stagnant air events) are expected to further exacerbate the deleterious effect on human and plant health.

Increasing atmospheric concentrations of nitrogen (N)-containing compounds [both oxidized as nitrogen oxide (NO) and dioxide (NO_2) and reduced as nitrate (NO_3^-) and ammonium (NH_4^+)] have led to enhanced rates of N deposition, and there is growing concern throughout Europe that ecosystems formerly limited by the availability of N are being affected by N deposited from the atmosphere (Ochoa-Hueso et al. 2014). Anthropogenic N enrichment in the Mediterranean ecosystems is mainly due to dry N deposition, either as gases or as particles. The characteristic decoupling between the peaks of N availability derived from the solubilization of summer-deposited N with the onset of the autumnal rains and the peaks of nutrient demand by plants occur in the spring growing season. This makes communities from Mediterranean ecosystems also more vulnerable to indirect effects of N deposition than other ecosystem types due to alterations of soil processes, some of which are directly coupled with C storage (Ochoa-Hueso et al. 2013). However, Mediterranean ecosystems are among the less studied in terms of potential impacts of N as a pollutant (Ochoa-Hueso et al. 2014).

Although they are not the major pollutants in the Mediterranean environment, heavy metals, SO_2, and acid rain also negatively affect the Mediterranean basin. This pollution is mostly due to atmospheric fallout from several sources, the most important being industrial and traffic emissions (Bou Kheir et al. 2014). It is important to recognize that with heavy metals and metalloids, residual soil contamination can occur in combination with air pollution. SO_2 has been the most studied pollutant in terms of impact on plants, as this compound was the first to be designated as a phytotoxic air pollutant, as well as being together with NO_x a major component in acid rain (Legge and Krupa 2002). However, today SO_2 does not represent a great issue in Europe as it was the first pollutant regulated by legislation (Guerreiro et al. 2014), although it is still a major problem in many developing countries (Bell et al. 2011).

Assessing the impact of air pollution on Mediterranean plants in the climate change era

The science to accurately describe how air pollutants and other stress factors affect plants and ecosystems in a changing climate is of paramount importance to guide political decision making. Much focus in the Mediterranean region has recently been placed on environmental issues related to CC, such as air and water pollution (e.g., Cotrozzi et al. 2016a, b; Guidi et al. 2016). However, assessing the impact of air pollution and CC on ecosystems is still a challenging task, especially in an area so strongly affected and heterogeneous such as the Mediterranean. Adequate monitoring techniques are necessary for assessing vegetation status and evaluating the effectiveness of enacted policy (Cotrozzi et al. 2016c). Diagnoses of the impacts of air pollution on vegetation based on plant sampling and physiochemical analysis using traditional laboratory methods can be precise, but have a number of limitations as they are commonly time-consuming, destructive, and expensive. An alternative approach to monitoring ecosystem functions includes the development of new sensors, advancing computational capacity and improving methodological approaches to environmental monitoring.

Optical remote sensing (RS) provides a rapid assessment of ecosystem status and functioning and has the capability to be extended to larger spatial scales. In recent years, considerable progress has been made in the field of spectroscopy. In particular, the use of spectroscopy in RS represents an excellent candidate for biomonitoring natural vegetation responses to air pollution (Casale et al. 2015). The present paper summarizes the actual knowledge on the use of reflectance spectroscopy for the detection and evaluation of the effects of air pollution on plants. It first outlines the history, physical basis, instrumentation, and approaches of reflectance spectroscopy. It then describes the reflectance spectrum of vegetation, explains how it can be scaled from leaf to landscape levels, and outlines how the information it contains can be extrapolated to understand vegetation function. Finally, it reviews the literature concerning reflectance spectroscopy, with special attention to the air pollutants affecting Mediterranean plants. The reviewed literature (Table 1) was selected using the online versions of ScienceDirect, Scopus, and Google scholar, and searching for the terms "vegetation spectroscopy," "reflectance," "air pollution," "ozone," "carbon dioxide," "particulate matter," "nitrogen deposition," "nitrogen oxides," "nitrogen dioxide," "heavy metals," "sulfur dioxide," and "acid rain." The main aim of this work is to outline the utility of reflectance spectroscopy as an approach for better understanding and monitoring the impact of air pollution on Mediterranean plants in the CC era.

Vegetation spectroscopy

History, physical basis, instruments, and approaches

Spectroscopy—the branch of physics involved with the production, transmission, measurement, and interpretation of electromagnetic spectra (Kumar et al. 2001)—first emerged as a practicable technology to assess plant biochemistry related to physiological functions in the 1960s. Gates et al. (1965) provide one of the first comprehensive overviews of light interactions with leaves with respect to pigments and leaf structure, and cite some of the important early papers that provided the initial measurements of leaf absorption and reflectance (e.g., Shull 1929; McNicholas 1931; Rabideau et al. 1946; Clark 1946; Krinov 1953). Billings and Morris (1951) was one of the first papers to directly link leaf optical properties to ecological function, showing that visible and near-infrared reflectance of species growing in different environments were directly linked to strategies associated with thermoregulation. Gates et al. (1965) also note the potential of fluorescence spectrometry to detect leaf function.

Early studies used spectrophotometers with integrating spheres in benchtop laboratory settings. Starting in the 1970s, laboratories of "near-infrared spectroscopy" (NIRS) emerged as an efficient tool for nutritional analysis of grains. This work grew out of efforts by Karl Norris at the US Department of Agriculture to rapidly predict from spectroscopy the moisture, protein, fat, and carbohydrate content of food for both humans and livestock (Workman and Weyer 2012), with the landmark paper being Norris and Hart (1965), reprinted in Norris and Hart in (1997) (Davies 1998). Norris et al. (1976) and Shenk et al. (1981) are the most widely cited early papers providing comprehensive methodologies to estimate foliar quality from spectra using multiple linear regression. While the majority of work until the 1980s focused on agronomic applications of predictive spectroscopy, Wessman et al. (1988a) expanded the application to ecological applications in forest and grassland species. Most work prior to the 1990s focused on dried plant material, with Elvidge (1990) providing a comprehensive accounting of the spectral features between 400 and 2500 nm in dried plant material that enable detection of plant biochemistry from spectroscopy.

In 1980s, the Jet Propulsion Laboratory developed an airborne imaging spectrometer (AIS) (Vane and Goetz 1988), which was the precursor to Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) (Vane 1987). Wessman et al. (1988b, 1989) and Peterson et al. (1988) demonstrated the capacity to estimate canopy lignin and nitrogen content from AIS, which spurred interest in using spectrometers and imaging spectrometers to estimate foliar traits from live vegetation. Curran (1989) provided a comprehensive overview of how spectroscopy in the 400–2500 nm range could be used as an in situ RS tool rather than in the laboratory context. Curran's synthesis went beyond identification of wavelengths associated with absorption features in specific compounds (e.g., chlorophyll (Chl)), noting that the capacity of spectroscopy for vegetation studies in these wavelengths is a consequence of the harmonics and overtones resulting from bending and stretching vibrations of light interaction with molecular bonds of H with C, N, and O in organic compounds. Although strong absorption features due to pigments and water may dampen these features, it is widely recognized that relationships between spectral measurements and foliar biochemistry and biophysical traits depend more on numerous spectral features associated with the molecular bonds rather than specific wavelengths associated with specific compounds. Numerous studies have since suggested the potential to use such measurements as a basis to study nutrient use and cycling in natural ecosystems, work that culminated in a series of significant papers later in the 1990s and early 2000s from the laboratory of John Aber at the University of New Hampshire (e.g., Martin and Aber 1997; Ollinger and Smith 2005).

Work with imaging spectrometers led to the need to better develop methods to estimate leaf status and biochemistry from fresh, green leaves (Curran et al. 1992). In particular, there was also the need to develop portable field spectrometers to support rapid measurement of leaves, as many chemical compounds are highly labile and degrade rapidly following leaf excision. Specifically, for work in remote areas, alternatives were needed than the widely used benchtop instruments from Cary, Perkin Elmer, and Foss. In the 1990s, a number of portable spectroradiometers were introduced to the commercial market and enabled the growth of physiological spectroscopy. John Gamon, who introduced the photochemical reflectance

Table 1 Vegetation spectroscopy applications on Mediterranean air pollutant stress detection

Air pollutant	Species	Scale	Spectral range (nm)	Approach	Aim(s)	Reference
Air pollution	Conifer stands (spruce/fir)	C	400–2500	SC	Remote detection of forest damage due to air pollution	Rock et al. (1986)
Air pollution	*Picea rubens*, *Picea abies*	L, C	400–2500	SC	Compare in situ and airborne spectral measurements of forest decline due to air pollution	Rock et al. (1988)
Air pollution	*Picea pungens*, *Picea abies*	L	350–2500	SC, VIs	Compare two spruce species in a polluted mountainous region	Soukupová et al. (2001)
Air pollution	*Picea abies*	L, C	450–900	SC, VIs	Remote detection of initial damage in forest canopies	Entcheva Campbell et al. (2004)
O_3	*Phaseolus vulgaris*	L	500–700	SC	Assessment of chronic O_3 injury to leaves	Runeckles and Resh (1975)[a]
O_3 (and SO_2)	*Lycopersicon esculentum*	L	475–725	SC	Identification of injury resulting from atmospheric pollutants	Schutt et al. (1984)[a]
O_3	*Glycine max*	C	350–720	SC	Investigate reflectance changes induced by O_3 and how they might be related to yield	Cure et al. (1988)[a]
O_3	*Pinus jeffreyi*, *Sequoiadendron giganteum*	L	350–720	SC, REP	Evaluate the roles of leaf anatomy, moisture, and pigment content on spectral reflectance	Westman and Price (1988)[a]
O_3	*Pinus ponderosa*	C	450–900	SC, REP	Explain reflectance changes in terms of pigment concentrations and stress due to air pollution	Curtiss and Ustin (1989)[a]
O_3	*Pseudotsuga menziesii*, *Pinus ponderosa*, *Pinus contorta*	C	400–750	SC, REP	Assess the spectral characteristics of O_3-treated conifers	Ustin and Curtiss (1990)[a]
O_3	*Pinus taeda*	L	400–2500	SC	Response of leaf spectral reflectance to increased atmospheric O_3 and precipitation acidity	Carter et al. (1992)[a]
O_3	*Picea abies*	C	400–110	SC, REP	Assess the impact of O_3 and acid mist on the spectral reflectance	Essery and Morse (1992)[a]
O_3 (and SO_2 and NO_2)	*Trifolium repens*	C	500–1750	SC	Evaluate spectral changes due to gaseous pollutants and acid mist	Williams and Ashenden (1992)[a]
O_3	*Pinus taeda*	L	400–2500	SC	Response of leaf spectral reflectance to increased atmospheric O_3	Carter (1993, 1994)[a]
O_3	*Pinus halepensis*	L	390–1100	SC, VIs, REP	Assess the potential of VIs to identify O_3-induced morphological and physiological changes	Peñuelas et al. (1995)[a]
O_3	*Triticum aestivum*, *Trifolium repens*, *Zea mays*	L	450–950	SC, VIs	Find out which of the VIs is suitable to detect and quantify O_3 effects on different crop species	Kraft et al. (1996)[a]
O_3	*Populus deltoides* × *maximowiczii*	L	325–1075	VIs	Early assessment of O_3 injuries by passive fluorescence and VIs	Meroni et al. (2008a)[a]
O_3	*Trifolium repens*	C	350–1050	VIs	Investigate the feasibility of detecting stress in its early phase using Fs and VIs at the canopy level	Meroni et al. (2008b)[a]

Table 1 (continued)

Air pollutant	Species	Scale	Spectral range (nm)	Approach	Aim(s)	Reference
O_3	–	–	–	–	Review on optical remote sensing techniques to track the development of O_3-induced stress	Meroni et al. (2009)
O_3	*Pinus jeffreyi*, *Pinus ponderosa*	L, C	400–800	SC, VIs	Spectral identification of O_3-damaged pine needles	Di Vittorio and Biging (2009)
O_3	*Pinus jeffreyi*, *Pinus ponderosa*, *Pinus uncinata*	C	400–2500, 400–900	VIS, IS, SMLR	Using topographic and remotely sensed variables to assess ozone injury to conifers	Kefauver et al. (2013)
O_3	*Glycine max*	L	500–2400	VIs, PLSR	Detect ozone effects on photosynthetic capacity and foliar biochemistry of 11 genotypes of soybean	Ainsworth et al. (2014)
O_3	*Triticum aestivum*	C	300–1100	SC, VIs	Find sensitive indictors for real-time detection of O_3 effects on four wheat cultivars	Chi et al. (2016)
CO_2	*Lolium perenne*, *Trifolium repens*	L	1100–2500	MPLS	Assess the effects of elevated CO_2 on yield, mineral content, and the nutritive value of blended turfs	Schenk et al. (1997)
$O_3 \times CO_2$	*Triticum aestivum*, *Glycine max*	C	400–1100	SC, REP	Remote sensing of crop responses to O_3 and CO_2 treatments	Leblanc et al. (1996)[a]
$O_3 \times CO_2$	*Triticum aestivum*, *Zea mays*	C	450–900	SC, VIs	Evaluate canopy reflectance under elevated O_3 and CO_2	Rudorff et al. (1996)[a]
$O_3 \times CO_2$	*Pinus sylvestris*	L	320–1050	SC, REP	Assess reflectance changes under elevated O_3 and CO_2	Meinander et al. (1996)[a]
$O_3 \times CO_2$	*Glycine max*	L	400–800	SC, VIs	Evaluate the capabilities of spectral reflectance and fluorescence for the detection of vegetation stress	Campbell et al. (2007)
$O_3 \times CO_2$	*Glycine max*	C	300–1100	VIs	Establish VIs to detect the effects of CO_2 and O_3 on leaf area, Chl content, and photosynthesis	Gray et al. (2010)
$O_3 \times CO_2$	*Populus tremuloides*, *Betula papyrifera*	L	Unspecified	PLSR	Assess the foliar quality of host species under CO_2 and O_3 and the performance of an invasive insect	Couture and Lindroth (2012)
PM	*Citrus* sp.	L	350–2500	SC	Characterize the particulate layer accumulating on surfaces	Saaroni et al. (2010)
PM	*Bougainvillea spectabilis*	L	345–1047	VIs, PLSR, IS	Utilize spectral reflectance and VIs in monitoring particulate air pollution in metro Manila	Olpenda and Paringit (2011)
N deposition	*Calluna vulgaris*	C	800–2400	SMLR	Estimate total foliar N heathland plants in different locations affected by increased abundance of N	Kalaitzidis et al. (2008)
N deposition	*Calluna vulgaris*	C	800–2400	SMLR	Estimate total foliar N heathland plants in different locations affected by increased abundance of N	Kalaitzidis et al. (2008)

Table 1 (continued)

Air pollutant	Species	Scale	Spectral range (nm)	Approach	Aim(s)	Reference
N deposition	Temperate and boreal tree species	L	500–2500	PLSR	Develop a set of accurate and precise spectroscopic calibration for determination of N and isotopic N content	Serbin et al. (2014)
N deposition	Temperate and boreal tree species	C	400–2500	PLSR, IS	Estimate N and isotopic N through space and time using NASA's AVIRIS	Singh et al. (2015)
Heavy metals (Zn)	*Paspalum notatum*	C	450–750	VIs, IS	Compare two hyperspectral imaging and two laser-induced fluorescence instruments for the detection of Zn stress	Schuerger et al. (2003)
Heavy metals	*Salicornia virginica*	C	450–1700	SC	Determine the potential to remotely characterize and monitor pollution	Rosso et al. (2005)
Heavy metals (Hg)	*Brassica rapa*	L	350–2500	SC, VIs, REP, SMLR	Establish spectral characteristics from which changes due to Hg stress can be distinguished	Dunagan et al. (2007)
Heavy metals (Pb)	*Oryza sativa*	C	350–2500	SC, REP	Hyperspectral remote sensing to monitor vegetation stress due to Pb	Ren et al. (2008)
Heavy metals (Pb)	*Ficus microcarpa*	L	350–2500	SC, VIs	Study the spectral features of polluted leaf surface of *Ficus microcarpa*	Wang et al. (2008)
Heavy metals	*Rubus* sp., *Acacia* sp., *Castanea* sp., *Ficus* sp., *Genista* sp., *Juglans* sp., *Quercus* sp., *Olea* sp.	C	350–2500	SC, VIs, REP	Assessment of environmental pollution in a geothermal site of Mt. Amiata (Italy)	Manzo et al. (2013)
SO_2	*Pinus massoniana*, *Schima superba*, *Castanopsis fissa*, *Acmena acuminatissima*, *Cryptocarya concinna*	L	400–800	SC, VIs	Evaluate the changes in leaf reflectance of several subtropical woody plants under simulated SO_2 treatment	Liu et al. (2006)
Acid rain	*Pinus massoniana*	L	450–750	VIs	Detect the spectral change caused by acidic stress to a native forest type of China	Song et al. (2008)
Acid rain	–	–	–	–	Review on spectroradiometers to detect acid rain stress effect on plants	Kolhe and Deshmukh (2016)

C canopy, *CO_2* carbon dioxide, *L* leaf, *NO_2* nitrogen dioxide, *O_3* ozone, *REP* red-edge position, *SCs* spectral profile changes, *SO_2* sulfur dioxide, *VIs* vegetation indices

[a] Reviewed by Meroni et al. (2009)

index (PRI; Gamon et al. 1997) as a method to characterize photosynthetic function, commented in 1992 that "The advent of portable radiometers with high spectral resolution offers new possibilities for examining dynamic physiological processes occurring on fine temporal and spectral scales" (Gamon et al. 1992, p. 36). Field portable instruments that captured the visible-near infrared (VNIR; 400–1000 nm) using silicon detector arrays included devices from Spectron Engineering, LiCor, and later PP Systems (UniSpec).

However, while many researchers focused on the VNIR and its sensitivity to pigments and overall vegetation health, the sensitivity to longer wavelengths provided by InGaAs detectors enhanced the ability to detect a range of plant traits associated with nitrogen and ligno-cellulose compounds also important to plant function but not readily directly detectable at shorter wavelengths. In the 1990s, Analytical Spectral Devices (ASD, Boulder, CO, USA) developed a rugged hand-held spectroradiometer covering the full visible-near infrared-shortwave infrared (VSWIR; 400–2500 nm) whose successors (the FieldSpec series) became widely used for field vegetation research, with a number of companies such as Geophysical and Environmental Research Corporation and later Spectral Evolution and SpectraVista developing instruments with similar capabilities. The ability to measure across the full 400–2500-nm range is a major benefit of many of the portable instruments now available to researchers. A range of instruments are also now available from manufacturers such as Ocean Optics that can be deployed in numerous configurations, including tuning to very narrow wavelengths necessary to detect solar induced fluorescence.

Vegetation reflectance

Because of the information it contains regarding plant biochemistry and physiology, the portion of the electromagnetic radiation in which plant biologists are mainly interested is that of the solar spectrum (about 250–2500 nm; Fig. 1). Part of this radiation is absorbed by the atmosphere especially in the so called "atmospheric absorption bands" which are basically due to O_3, oxygen (O_2), water (H_2O), and CO_2. Then, radiation reaching the surface of vegetation (as well as of other materials) may be reflected (diffuse, specular), transmitted (with refraction), or absorbed. The interaction of radiation with the surface is dependent on both the properties of the radiation as well as those of the material (e.g., foliage). Therefore, to be able to compare spectra of vegetation collected on different days or in various illumination circumstances, a measure that is independent from illumination change or can somehow be calibrated for illumination variation is needed. A commonly used measure is reflectance, which is independent from the amount of radiation reaching the vegetation as it is the dimensionless ratio of radiation reflected from a surface to the radiation hitting that surface. Spectral reflectance of leaves can be determined from the measurement of the leaf radiance divided by the radiance of a 99.9% reflectance white standard panel, and it can be easily expressed as a percentage (Kumar et al. 2001).

The nature and amount of reflection (as well as absorption and transmission) is the result of wavelength and angle of incidence of radiation, surface roughness, and the differences in the optical and biochemical properties of the leaves. The typical reflectance spectrum of a green leaf is composed of three main regions (Fig. 2). Firstly, the visible (VIS) region extends from 400 to 700 nm and is characterized by low reflectance due to the strong absorption by foliar pigments (absorption peaks are shown around 420, 490, and 660 nm; Kumar et al. 2001). Before moving to the infrared, the red-edge has to be mentioned; it is a characteristic feature of the vegetation reflectance spectrum as plants have a sharp order-of-magnitude increase in leaf reflectance between approximately 700- and 750-nm wavelength. The red-edge has been the basis of a number of studies and can be quantified with a single value, so that this value can be compared with that of other species (e.g., Seager et al. 2005). Numerous studies have indicated that the shape of the red-edge is dependent on chlorophyll content (Horler et al. 1983; Rock et al. 1988; Filella and Peñuelas 1994), and changes in the ratio of relative heights of maxima in the first derivatives (the first derivative spectra method is largely used in spectroscopy; it is the result of applying a derivative transform to the data of the original spectrum) of red-edge have been revealed when chlorophyll content varied (Clevers et al. 2004; Smith et al. 2004; Zarco-Tejada et al. 2004). Furthermore, variation in the red-edge position (REP) is considered an indication of stress. The reduction of REP shows an increase in stress condition (Dawson and Curran 1998; Clevers et al. 2004; Smith et al. 2004; Mutanga and Skidmore 2007). The near-infrared (NIR) region ranges from 700 to 1300 nm where plants have generally a high reflectance mainly dependent on the leaf cell structural composition. Here, in contrast to light in the VIS, the energy levels are not great enough for photochemical reactions, and so are not absorbed by chloroplasts and other pigments. Finally, the shortwave-infrared (SWIR) spans from 1300 to 2500 nm and is characterized by strong water absorption and minor absorption features due to other biochemical metabolites. The reflectance in the SWIR region is much lower compared to the NIR as incident radiation is lower (Fig. 1), and several leaf biochemical, such as lignin, starch, cellulose, proteins, N, and phenolics absorb in the SWIR region. Low reflectance in the SWIR results in low signal-to-noise ratio, which combined with the overlapping of narrow spectral features, can potentially cause difficulty in exploiting this spectral region (Kumar et al. 2001).

Figure 3 summarizes the key points of vegetation spectroscopy; differences in plant physiognomy, biochemical composition, physiological capability, and water content lend themselves to producing different reflectance profiles in green

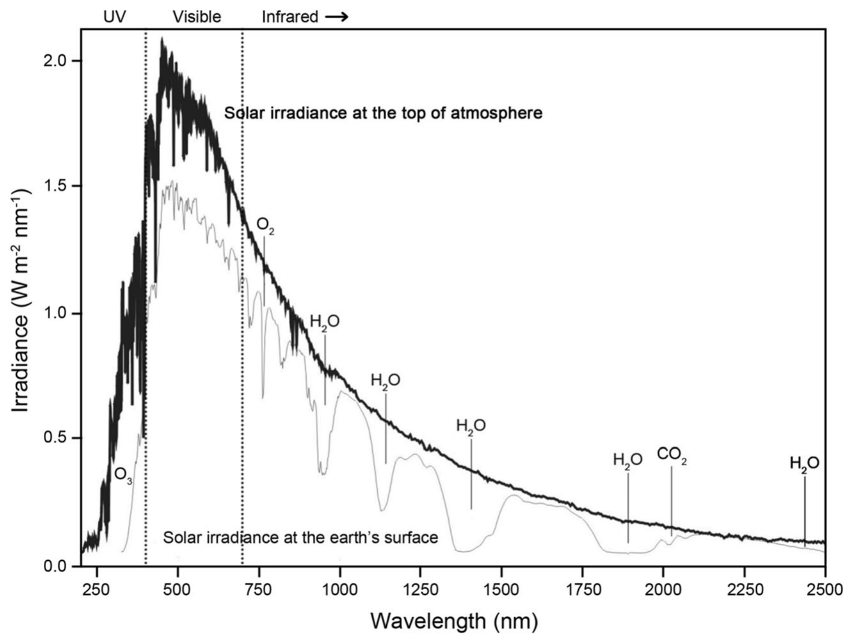

Fig. 1 Solar spectrum with indicated the main atmospheric absorption bands (modified from Kumar et al. 2001)

vegetation, resulting in the concept of optical type (sensu Ustin and Gamon 2010). Variation in plant optical types can be exploited for a wide variety of purposes, including mapping plant functional traits, species occurrence, and biodiversity, and monitoring responses to environmental variation and resource availability (Ustin and Gamon 2010; Cavender-Bares et al. 2016). A cornerstone of vegetation spectroscopy is to capture the diversity of plant traits through spectral fingerprints. The spectral reflectance of plants is itself a key trait that can be exploited to monitor plant and ecosystem response to stress factors (e.g., air pollution), and can be used as a basis to understand fundamental plant biology.

Importantly, measurements of leaf optical properties differ from standard biochemical analyses; they are (1) rapid, taking only a few seconds; (2) non-destructive, allowing for repeated measurements on the same tissue; and (3) relatively inexpensive if compared with the need to continuously pre-form multiple assays for chemical quantification. Therefore, spectra can be collected in the field on a large number of individual plants, dramatically increasing the complexity and robustness of ecological experiments (Couture et al. 2013). Furthermore, another benefit of spectroscopy is that it allows for the upscaling of vegetation functions and plant traits from leaf to landscape levels (Ainsworth et al. 2014).

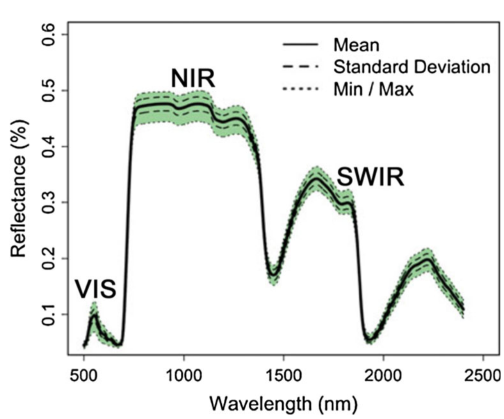

Fig. 2 Leaf reflectance spectra of soybean collected with a high spectral resolution ASD FieldSpec full-range spectroradiometer (Analytical Spectral Devices, Boulder, CO, USA; from Ainsworth et al. 2014)

Scale-up vegetation functions and plant traits (remote sensing)

Scaling of foliar traits from leaf to broader spatial scales can utilize allometric scaling or physical models. Allometric relationships upscale leaf-level measurements (whether derived from spectra or traditional assays) to a plot or a RS pixel by

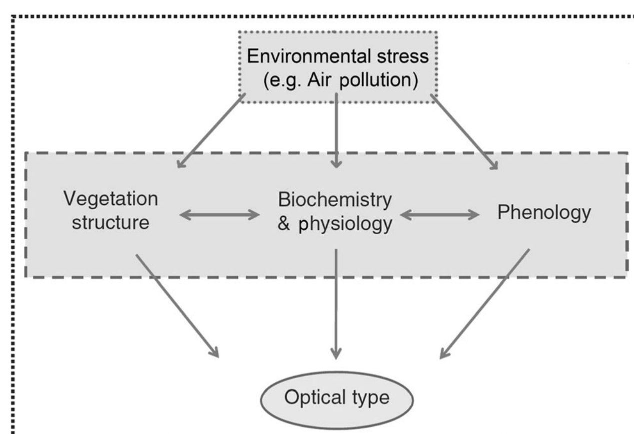

Fig. 3 Proposed concept of "optical type" based on the assessment of vegetation structure, physiology and biochemistry, and phenology—three variables historically contributing to ecological definition of "plant functional type," as well as of stress conditions (e.g., due to air pollution; modified from Ustin and Gamon 2010)

the relative proportion of the ecosystem that the species or functional type occupies at a location (Smith and Martin 2001). Scaling can be performed using any relative measure of the abundance of different species, such as percent cover, leaf area index (LAI), foliar biomass, or basal area (in forests) by species calculated from an inventory. Each of these metrics has trade-offs, since the allometric scaling factors essentially assume equal prominence among species, whereas in reality, any one of these may not accurately represent the importance of a species in an ecosystem. Specifically, LAI, cover, and biomass do not correlate perfectly, and in fact, differences in LAI/biomass scaling are important to explaining functional differences among species or sites. As well, scaling to RS imagery can be a challenge, in which understory species may be important functionally but do not contribute to the signal detected by an airborne or spaceborne sensor. Scaling from the canopy to the landscape then uses relationships between a value from a pixel (which has been scaled from individual leaf measurements) and pixel spectra to predict and map from the imagery (e.g., Singh et al. 2015; Asner et al. 2015). The risk in any of these endeavors is that the leaf measurements made on site are not appropriate for scaling more broadly; e.g., the wrong species are sampled, the species or particular leaf samples are not representative of the site, or trait variability within a location (pixel) is such that it is difficult to correctly characterize a canopy. For example, some traits vary within species and by position in the canopy (e.g., sunlit vs. shaded leaves) and sampling or scaling that does not consider these issues may lead to erroneous or inaccurate interpretations. An alternative approach to scaling is the use of a radiative transfer model (Asner and Martin 2008; Jacquemoud et al. 2009) either to characterize canopy reflectance from leaf measurements or invert leaf reflectance from canopy characteristics. The appropriate models can then be used to estimate foliar traits. Such approaches are hampered by increasing model complexity to attain realism in traits that are retrieved, and often work best to inform or compare to empirical approaches.

Exploitation of reflectance spectra

Simple spectral reflectance vegetation indices (VIs) based on the ratio of reflected light at different wavelengths have been developed to predict foliar variables concerning the structure of vegetation [e.g., normalized difference vegetation index (NDVI; Rouse et al. 1973) and leaf area index determining index (LAIDI; Delalieux et al. 2008)], as well as biochemistry [e.g., chlorophyll index (CI; Gitelson and Merzlyak 1994), derivative chlorophyll index (DCI; Zarco-Tejada et al. 2002), and normalized difference nitrogen index (NDNI; Serrano et al. 2002)] or to evaluate plant physiology or stress conditions [e.g., PRI (Gamon et al. 1992), normalized difference water index (NDWI; Gao 1996), D_{725}/D_{702} ratio (Smith et al. 2004), D_{725} and D_{702} mean, the first derivative of reflectance at 725 and 702 nm, respectively]. A list of the most common vegetation indices has been reported by Pu and Gong (2011). However, the accuracy of the estimations by these indices can lack of robustness because these relationships do not take into account aspects as the anatomical structural differences between leaves or other factors of variability (Ainsworth et al. 2014).

A number of statistical approaches have been utilized to exploit reflectance data, with the main goals of retrieving biochemical or physiological information. Two potential problems arise with utilizing variation in hyperspectral data: (i) the number of predictors (i.e., spectra) often outweighs the responses and (ii) the spectra themselves are highly intercorrelated. In these cases, often associated with hyperspectral information, the use of traditional regression techniques produces unreliable coefficients and error estimates (Grossman et al. 1996; Couture et al. 2013), thus prompting the need to reduce the number and collinearity of predictor variables. To date, the majority of approaches combining physical and spectral data have used three approaches: stepwise multiple linear regression (SMLR), principal component regression (PCR), and partial least squares regression (PLSR).

SMLR (forward and backward) has been utilized to select a small number of bands in hyperspectral data that explain a large proportion of the variation in the physical reference data. Yet, a comprehensive analysis on specific utilizations of this approach revealed inconsistencies in the bands selected across data sets, spectral transformations, and physical expression of chemical data (i.e., content vs. concentration; Grossman et al. 1996). Moreover, the same study found that artificial data sets, randomizing the associations between chemical and spectral data, found reasonably strong statistical relationships between chemical and spectral data (Grossman et al. 1996), indicating the likelihood of a purely statistical relationship. PCR deals with the problem of multicollinearity by generating uncorrelated vectors that explain variability in the data matrix. In addition, by excluding some of the low-variance principal components in the regression step and utilizing on only a subset of all the principal components generated, PCR can result in dimension reduction through substantially lowering the effective number of parameters characterizing the underlying model (Martens 2001). PLSR (Wold et al. 2001) has become the current standard of chemometric modeling (Asner and Martin 2008; Serbin et al. 2014; Couture et al. 2016). The strength of PLSR is its ability to reduce a number of highly correlated variables in few, uncorrelated latent variables. Once a number of latent variables are selected, they are transformed into a linear equation for the response variable. A number of approaches have been suggested independent of or in combination with SMLR and PLSR to reduce the number of wavelengths selecting into model building, including genetic algorithm and successive projection algorithm techniques (Araújo et al. 2001; Niazi and Leardi 2012).

The potential to produce models of a purely statistical nature is possible given the highly dimensional nature of hyperspectral data; thus, care should be taken in deciding on which regions of the spectrum should be included in modeling response variables. While an approach utilizing known absorption features for a specific chemical compound is most intuitive, the considerable overlap in biochemical features, including base structures and functional groups, among closely related chemical compounds may prohibit producing reasonable models (Grossman et al. 1996). Approaches for determining spectral features from single wavelengths (e.g., Kokaly and Skidmore 2015) provide evidence for physical validity of biochemical retrievals, but lack the ability to predict the diversity of compounds within a specific chemical class because of an assumed linear relationship with the compounds of interest. A priori incorporation of multiple wavelengths in regions with known absorption features enables models to potentially capture the variation in functional groups and other biochemical features of closely related chemical species.

Additionally, an emerging approach is to utilize the entire spectral profile as a vector of information and examine variation in the profile as an indicator of genetic identity or responses to stress (e.g., Arens et al. 2017). A number of different multivariate approaches aimed at classifying plants as a product of spectral profiles, including linear discrimination, partial least squares discrimination, and numerous classification techniques utilizing support vector machine learning. The integration of biochemical and mathematical techniques with spectroscopy will provide a powerful tool for addressing a number of global challenges.

Spectroscopy for the understanding of stress responses of Mediterranean plants

A technique able to monitor the impact of air pollution on vegetation

The capability of spectroscopy to monitor the impact of air pollution on vegetation is not a recent discovery. Already more than 30 years ago, reflectance spectroscopy was used in extensive field experiments at spruce/fir sites in order to assess and monitor rapid forest decline suspected of being due to various forms of air pollution (Rock et al. 1986, 1988). Rock et al. (1986) suggested that developing a tool of detecting and quantifying the impact of air pollution on forest decline from orbital and/or airborne RS platforms provided scientists with the opportunity to track this phenomenon on a global scale. As reported by Rock et al. (1988), in situ Visible Infrared Intelligent Spectrometer (VIRIS) (Geophysical Environmental Resources Inc. (GER), 400–2500 nm) reflectance data showed similar characteristic features corresponding with visual forest decline damage in red spruce of Vermont (*Picea rubens*) and Norway spruce of Baden-Württemberg (*Picea abies*). Spectra of both species from high-damage sites showed a blue shift (a 5-nm shift of the red-edge inflection point to the shorter wavelengths) and a reduction in the reflectance of the NIR plateau (750–1300 nm) indicating that spectroscopy was able to detect stressed plants. Moreover, similar features came out from spectral data at canopy level collected with the airborne fluorescence line imager (FLI): a blue shift of the Chl absorbance minimum, a decrease in the reflectance in the NIR plateau, and an increase in reflectance in the VIS red. Although a blue shift of the red-edge was seen in normalized FLI spectral data, it was not supported by statistical analysis.

Similarly, Soukupová et al. (2001) evaluated the sensitivity to air pollution and variable climatic conditions of Colorado blue spruce (*Picea pungens*) and Norway spruce from the Krušné Hory Mountains of Czech Republic. By means of a GER 2600 spectroradiometer (350–2500 nm), they determined in situ reflectance signatures of first-, second-, and third-year needles. Then, they calculated spectral indices indicating pigment and water contents, as well as the position of the red-edge inflection point (Vogelmann et al. 1993), to compare both species. Additionally, they used the ratios R_{1680}/R_{1454} and R_{1680}/R_{1983} (R_{1680}, R_{1454}, and R_{1983} mean the reflectance at 1680, 1454, and 1983 nm, respectively) to determine the tannin and lignin contents. For both species, they concluded that the red-edge inflection point, as well as stress indices and reflectance ratios, indicated an age-dependent extension in needle damage. Similar outcomes were reported later by Entcheva Campbell et al. (2004) in an investigation aimed to evaluate the potential of hyperspectral data for detecting initial stages of forest damage at the canopy level in the Norway spruce from the same study area. Canopy hyperspectral data, obtained by the Airborne Solid-state Array Spectroradiometer (410–1032 nm), were able to separate healthy from initially damaged canopies (the 673–724-nm region showed maximum sensitivity to this scope). Further, the authors selected nine spectral indices having the highest potential as indicators of the initial impairment.

Using reflectance spectroscopy to detect the effects of the major Mediterranean air pollutants on vegetation

Ozone

The review paper by Meroni et al. (2009) reported that studies on the effects of O_3 on vegetation reflectance have been conducted since late 1970 (Runeckles and Resh 1975). Using the stress concept advanced by Levitt (1980) and extended by Lichtenthaler (1998) which identified two consecutive phases, strain and damage, for stress development, Meroni et al. (2009) showed that most of the reviewed papers addressed only the second (i.e., damage) phase. Leaf and canopy reflectance spectra were collected using both broadband and high-resolution spectroradiometers. Generally, the VIS spectral region showed greater sensitivity to O_3, increasing reflectance in both leaf and canopy of conifers and crop species, a result probably due to chlorosis related to leaf pigment degradation from premature senescence. The interpretations of changes in the NIR were more debatable and mainly associated to modifications of water content and internal structure leaves. The initial stage of senescence, that could be characterized by leaf dehydration, resulted formerly in a slight raise of NIR spectrum; then, the loss of integrity in mesophyll structure causes a decrease in NIR reflectance shown in the majority of the experiments.

Several VIs have been demonstrated to have a great potential to detect the impact of O_3 exposure on plant physiology through changes in reflectance. Regarding the strain phase of O_3-stress development, the works by Meroni et al. (2008a, b) were reported as the first to assess the capability of solar-induced steady-state fluorescence and PRI to assess plant O_3 stress under natural environmental conditions both at leaf and canopy level. Regarding leaf-level measurements, Meroni et al. (2008a) conducted four measurement campaigns on poplar clone plants (*Populus deltoides* × *maximowiczii* Eridano, O_3 sensitive) treated with 80 ppb of O_3 for 5 h d^{-1} for 26 consecutive days. At canopy level, Meroni et al. (2008b) performed six measurement campaigns on potted small closed canopies of white clover (*Trifolium repens* L. cv. Regal clone NC-S, O_3 sensitive) treated with 100 ppb of O_3 for 5 h d^{-1} for 21 consecutive days. Both experiments showed that the remotely sensed excess energy dissipation trends tracked the decrease in net CO_2 assimilation due to O_3 stress, demonstrating the feasibility of detecting the strain phase of O_3-stress development using spectroscopy, providing an early detection tool. Furthermore, the practicability of this technique in revealing the damage phase was confirmed by the widely used NDVI that decreased in treated plants at the end of the treatment in both the experiments when visible injury already occurred.

Similarly, Di Vittorio and Biging (2009) classified pine needles damaged by O_3 using spectral data. In particular, they collected samples from Jeffrey and Ponderosa pine trees from three areas of the Sierra Nevada, grouping them following five live needle conditions (green, winter fleck, sucking insect, scale insect, and O_3 damage). The authors collected reflectance and transmittance measurements of leaf abaxial and adaxial surfaces using an USB2000 spectrometer (Ocean Optics, Dunedin, FL, USA, using the 400–800-nm range), and combined them with AVIRIS (400–2500 nm) data. At both resolutions, O_3-damaged needles harvested from Jeffrey pine trees at one site had significantly different abaxial surface spectral slope signatures from needles of other sites. Furthermore, they showed different spectra (with different slopes) also from needles from the same site but belonging to green and winter fleck groups. In addition, the authors provided a new red fall index (RFI) with a high classification accuracy for O_3-damaged and non-O_3-damaged pine needles.

A paper by Kefauver et al. (2013) presented two case studies of an integrative approach combining terrain-driven geographic information system (GIS) analyses and imaging spectroscopy for landscape-scale analyses of the effects of O_3 on the health of a forest bioindicator species in California, USA, and Catalonia, Spain. Using an ozone injury index (OII), the authors found that species classifications of AVIRIS in California and Compact Airborne Spectral Imager (CASI; Cartographic Institute of Catalonia, 400–900 nm) in Spain hyperspectral imagery all approached 80% overall accuracy for the selected bioindicator species (*Pinus ponderosa* and *Pinus jeffrey* in the USA; *Pinus uncinata* in Spain). Furthermore, stepwise regression models of O_3 injury developed combining RS indices with topographic variables were significant for OII in California and in Catalonia, whereas multiple regression ones were significant both with imaging spectroscopy indices alone and with terrain-derived GIS variables added in Catalonia.

Recently, vegetation spectroscopy has proved also to be an efficacious tool for screening of genotypes with different degrees of O_3 tolerance. Ainsworth et al. (2014) explored the potential to use near-surface reflectance spectroscopy (500–2400 nm) to assess the effects of O_3 on photosynthetic capacity of 11 soybean (*Glycine max* Merr.) genotypes exposed to ambient (44 ppb) and elevated O_3 (~80 ppb target) concentrations. Reflectance properties of leaves were analyzed using an ASD FieldSpec FR spectroradiometer (350–2500 nm). The author's objective was to calibrate a spectral PLSR model for the estimation of the maximum rates of ribulose-1,5-bisphosphate (RuBP) carboxylation (V_{cmax}) using two genotypes (Pana and Dwight). They utilized variation in V_{cmax} observed across the ambient plots, O_3 treatments, and genotypes to generate a PLSR model that was able to estimate V_{cmax} with high accuracy and precision. However, they did not detect an effect of O_3 on this parameter, and they speculated that this was due to the fact that the season-long average O_3 concentration in the ambient air exceeded the threshold for damage in soybean. In contrast, across all genotypes, leaf N concentration, total Chl content (determined using Richardson et al. 2002), and PRI (determined using Letts et al. 2008) significantly decreased due to elevated O_3 concentrations. Furthermore, in this study, leaf N content, total Chl content, and PRI were significantly correlated to soybean yield and yield loss to O_3, supporting the use of leaf reflectance measurements for screening for O_3 tolerance in a larger collection of soybean genotypes.

In order to determine hyperspectral markers capable of real-time assessment of O_3 effects, Chi et al. (2016) analyzed four cultivars of wheat (*Triticum aestivum*) with different degrees of O_3 sensitivity grown under a high O_3 concentration (60 ppb 9 h d^{-1}) in open-air field conditions. Elevated O_3 level decreased leaf thickness and pigment concentrations, resulting in a variation of canopy in leaf reflectance (measured with a Unispec, PP Systems, Haverhill, MA, USA, sprectroradiometer; 300–1100 nm). The effects of O_3 on both physiological and reflectance traits were cultivar-specific, with a stronger and earlier O_3 effect shown by the O_3-sensitive cultivars compared to the tolerant one. Spectral indices were tested, and high correlations were found between Chl content and three spectral parameters: ND_{705} [$(R_{750} - R_{705})/(R_{750} + R_{705})$ (Gitelson and Merzlyak 1994)], mND_{705} [$(R_{750} - R_{705})/(R_{750} + R_{705} - 2R_{445})$ (Sims and Gamon 2002)], and R_{550} (Lichtenthaler et al. 1996). Moreover, O_3-induced variations in these optical parameters followed the leaf Chl responses. Thus, the authors concluded that (i) the VIs could help to support the diagnosis and real-time monitoring of O_3-induced damage in wheat and (ii) to estimate the wheat yield accurately using the selected VIs, the filling stage was found to be the best time for measuring canopy reflectance.

Carbon dioxide

By reflectance measurements, Schenk et al. (1997) estimated the effects of high atmospheric CO_2 concentrations on yield, nutritive value, and mineral content of blended turfs of perennial ryegrass (*Lolium perenne*) and white clover (*Trifolium repens*) grown as monocultures and as different mixtures and exposed season-long to ambient (380 ppm) and elevated (670 ppm) CO_2 concentrations in open top chambers (OTCs). In addition to the measurements of S, P, K, Mg, Na, and Ca contents, the authors determined crude fiber (CF) and crude protein (CP) contents using NIR reflectance spectroscopy. Spectra were obtained by diffuse reflectance measurements of ground plant material in the 1100–2500-nm region using a NIR spectrometer with autocup sampler (6500 Perstorp Analytical, Rodgau, Germany). CF and CP were predicted by equations that correlated NIR spectra of calibration subsets with their CF and CP content determined by chemical analysis, and validation subsets revealed highly significant correlations of chemical and spectral analyses. The authors found that CF content was lowered by elevated CO_2 concentrations, whereas CP decreased at the beginning of the growing period and increased in later harvests.

Ozone and carbon dioxide together

It is known that the impacts of multiple stressors cannot be appropriately evaluated using additive unifactorial responses (Guidi et al. 2016). In this paragraph, we report reflectance spectroscopy capability in assessing the effects on vegetation of the combination of two of the major Mediterranean abiotic stressors (CO_2 and O_3) on vegetation. To establish a generalized spectral approach for plant stress assessment, Campbell et al. (2007) compared the capacity of reflectance and fluorescence leaf measurements to detect vegetation changes associated with CO_2 and O_3 that are related to plant growth and productivity. The effects of these stressors on leaf spectral properties were evaluated on two varieties of soybean, Manokin (O_3 sensitive) and KS4694 (CO_2 sensitive), which were planted within the same OTCs. Over the growing season, four treatments were provided with different CO_2 and O_3 concentrations. Focusing on the range of 400–800 nm, reflectance measurements were acquired contemporaneously with the fluorescence analyses using a Li-Cor 1800 integrating sphere coupled via a 100-mm-long, single-mode, 5-mm-diameter fiber optic probe to an ASD FieldSpec Pro FR spectroradiometer, and on the same foliar samples used for photosynthetic pigments, carbon, and N content analyses. Although both reflectance and fluorescence techniques were successful in detecting plant stress responses, only a few of the reflectance and fluorescence variables performed rigorously, including the D_{715}/D_{705} (where D means the first derivative variable) reflectance ratio and the green/far-red (F_{530}/F_{740}) fluorescence ratio. Narrow-band reflectance indices performed best; strongly correlated to pigment, C, and N contents and to the C/N ratio; and successfully discriminated among treatments. However, they could not determine the unstressed plant condition within a stress gradient, as was shown for the fluorescence data. Consequently, the authors concluded that the two compared techniques provided complementary information.

Gray et al. (2010) sought to determine if VIs could detect the independent and interactive effects of elevated CO_2 and O_3 on leaf area, photosynthetic capacity, and Chl content of soybean canopies grown under field conditions. They exposed large plots of soybean to ambient air (~380 ppm CO_2), elevated CO_2 (~550 ppm), elevated O_3 (1.2× ambient), and combined elevated CO_2 and O_3 at the SoyFACE facility (University of Illinois). Canopy reflectance was assessed weekly with a portable spectroradiometer (UniSpec Spectral Analysis System, PP Systems, Haverhill, MA, USA; 330–1100 nm), and four reflectance indices were calculated [NIR/red (R_{801}/R_{670}) (Daughtry et al. 2000), NDVI (Gamon et al. 1995), PRI (Gamon et al. 1997), and total canopy Chl content index (chl.index) (Gitelson et al. 2005)] in conjunction with traditional LAI measurements. This study confirmed the capability of NIR/red and PRI and chl.index to detect variations in LAI, photosynthetic carbon assimilation, and canopy Chl content, respectively, when soybean was exposed to high CO_2 and O_3 concentrations. Furthermore, the effects of these stressors on LAI and photosynthetic carbon assimilation reported by VIs were in accordance with previous studies where LAI and gas exchange were measured directly at SoyFACE.

Couture and Lindroth (2012) used NIR reflectance spectroscopy to examine the independent and interactive effects of CO_2 and O_3 on plants focusing on the foliar quality of two host species and performance of an invasive folivorous insect. In particular, they measured the effects of these stressors on trembling aspen (*Populus tremuloides*) and paper birch (*Betula papyrifera*) phytochemistry and on the growth, development time, survivorship, and fecundity of the gypsy moth (*Lymantria dispar*). Their results show that NIRS successfully predicted most chemical constituents of aspen and birch foliage; models built by PLSR predicting aspen and birch N, C/N ratios, and condensed tannins, as well as aspen salicinoids, performed well. However, models developed for sugar values performed only marginally well as predictors of absolute concentrations. Moreover, an innovative aspect of the work by Couture and Lindroth (2012) is that PLSR analysis was also used with success to evaluate the influence of foliar quality variables on gypsy moth performance (in terms of survivorship and development time).

Particulate matter

The title "Reflectance spectroscopy is an effective tool for monitoring soot pollution in an urban suburb" (Saaroni et al. 2010) is a good description of the capability of this technique to evaluate the effects of PM on vegetation. Saaroni et al. (2010) used an ASD FieldSpec Pro spectroradiometer (350–2500 nm) to detect and monitor environmental changes caused by a nearby power plant station converting its fossil fuel usage from oil to gas. The sampling (accumulated PM on tree leaves and paper bags) was conducted in the northern suburbs of Tel Aviv (Israel, in a Mediterranean climate) in a green residential neighborhood situated downwind of the power station, before (2004) and after (2006) the conversion. Their results validate that reflectance spectra serve as effective tools to detect environmental changes. Before the conversion of the power plant, the spectra of all samples (both paper bags and leaves) exhibit a distinctly concave slope between 400 and 1400 nm, indicating the presence of soot matter. In contrast, the spectra derived from samples collected during the second period exhibited a slightly convex slope, indicating the presence of dust of mineral origin, as sampled surfaces were coated with less soot matter due to lower PM pollution.

The study of Olpenda and Paringit (2011) confirms that VIS-NIR-SWIR spectroscopy is a useful tool for characterizing the PM accumulating on sampled surfaces. Specifically, *Bougainvillea spectabilis* leaves were utilized as indicators of air quality. Leaf spectra of potted bougainvilleas placed on three stations in Metro Manila, Philippines, were obtained at three levels (top, middle, and bottom) using a field spectroradiometer (Ocean Optics USB4000, 345–1047 nm). Simultaneously, ambient air quality (PM_{10}, PM_7, $PM_{2.5}$, PM_1, and total suspended particles (TSPs)) was also determined by a handheld monitoring instrument. Three VIs [ratio vegetation index (RVI; Jordan 1969), NDVI (Rouse et al. 1974), and difference vegetation index (DVI; Tucker 1979)] were computed from the measurements taken on field. Additionally, REP was calculated (Baret and Guyot 1991). The specimen in the least polluted station consistently maintained the highest average values for all indices throughout the sampling period (1 month). On the other hand, the station which recorded the highest TSP data had the lowest values of the indices quantified. The estimation model that was applied to WorldView-2 remotely sensed images produced maps that illustrated detailed and justifiable scenarios including low particulate air pollution levels on residential areas, parks, and along rivers while high concentrations can be seen on major thoroughfares.

Nitrogen deposition

In addition to the work of Williams and Ashenden (1992), reviewed by Meroni et al. 2009, where the interactive effects on white clover of O_3, SO_2, and NO_x were evaluated, vegetation spectroscopy has been used to develop methods to monitor the N status of vegetation at landscape scales, and potentially for ecological changes due to atmospheric N deposition (Kalaitzidis et al. 2008; Serbin et al. 2014; Singh et al. 2015). Kalaitzidis et al. (2008) took canopy reflectance measurements from two heathland field sites and heather (*Calluna vulgaris*) plants grown in a greenhouse and exposed to experimental treatments of N. Canopy reflectance data were acquired with the use of a portable ASD FieldSpec Pro spectroradiometer (350–2500 nm; only the region between 800 and 2400 nm was reported). The N concentration was determined through destructive sampling and chemical analysis. SMLR analysis was used to identify the wavebands most associated with N concentration, and despite high variation in the selected wavebands between the three datasets, most of these wavebands were associated with N and protein absorption features within the spectral region 1990–2170 nm. In particular, the narrow 2140–2160-nm range was consistently selected in the regression at all three sites. Authors concluded that the results highlighted the potential of RS as a biomonitoring technique to estimate the response of native plants to N deposition.

Similarly, Serbin et al. (2014) developed a set of spectroscopic (500–2500 nm) calibrations, using PLSR, for determination of total N content and isotopic N concentration of temperate and boreal tree species using spectra of dried and ground leaf material. Singh et al. (2015) then illustrated a general approach for estimating key foliar chemical and morphological traits through space and time using National Aeronautics and Space Administration (NASA)'s AVIRIS-Classic. The authors applied PLSR to data from 327 field plots within 51 images acquired between 2008 and 2011 and generated spatially explicit maps of seven traits, including nitrogen content and isotopic N concentration. The spatial patterns of foliar isotopic N concentrations reported were associated with elevated external inputs such as N deposition and logging disturbance.

Minor Mediterranean air pollutants

Heavy metals

Reflectance spectroscopy has also shown the ability to assess the effects of heavy metals on vegetation in several works. While only Manzo et al. (2013) performed on-site spectral analyses studying the environmental impact of geothermal activities in the Mt. Amiata area (Italy) on vegetation and lichen communities located both near and far from geothermal areas and potential pollution sources (e.g., power plants), numerous experiments have been performed in control conditions. Schuerger et al. (2003) conducted a study to determine the accuracy and precision of two hyperspectral imagers and two laser-induced fluorescence instruments in detecting stress symptoms induced in bahia grass (*Paspalum notatum*) by deficient or toxic levels of the heavy metal Zn; Rosso et al. (2005) aimed to determine the potential to remotely characterize and monitor pollution (applications of different concentrations of Cd and V) on *Salicornia virginica*, a major component of wetland communities in California; Dunagan et al. (2007) measured spectra of Mustard spinach (*Brassica rapa perviridis*) plants grown in Hg-contaminated soil in the laboratory over an entire growth cycle to establish baseline spectral characteristics from which changes due to Hg stress can be distinguished; Ren et al. (2008) explored the possibility of hyperspectral reflectance spectroscopy in the detection of differences in Pb concentration in rice plants at an appropriate growth stage; and, finally, Wang et al. (2008) performed a study analyzing the leaf reflectance features of *Ficus microcarpa* exposed to air pollutants (S, Cd, Cu, Hg, Pb, XCl, XF) in order to examine the possibility of using leaf reflectance spectra of vegetation as a rapid method to simultaneously assess pollutant in the atmosphere of the Guangzhou area, China. These results highlight the potential of spectroscopy as a biomonitoring technique to estimate the response of native plants to heavy metals.

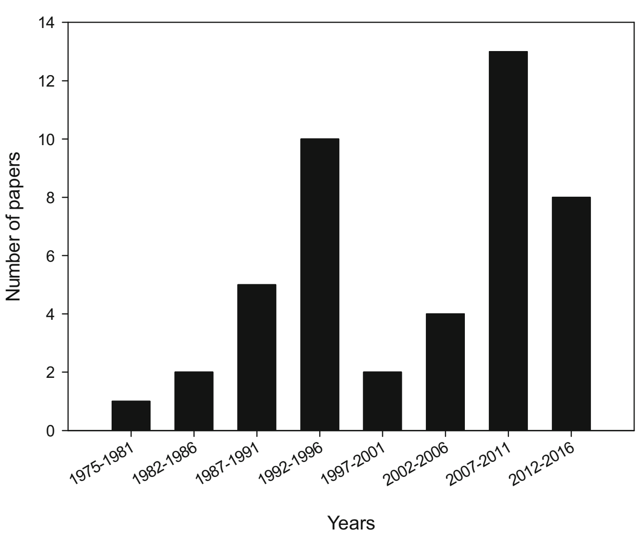

Fig. 4 Distribution of the years of publication of the studies (n = 45) concerning the use of reflectance spectroscopy for the evaluation of the effects of air pollution on plants, and selected using the online versions of ScienceDirect, Scopus, and Google scholar, and searching for the terms "vegetation spectroscopy," "reflectance," "air pollution," "ozone," "carbon dioxide," "particulate matter," "nitrogen deposition," "nitrogen oxides," "nitrogen dioxide," "heavy metals," "sulfur dioxide," and "acid rain"

Sulfur dioxide and acid rain

In addition to the already mentioned papers by Schutt et al. (1984) and Williams and Ashenden (1992) [reviewed by Meroni et al. (2009)], the effects of simulated SO_2 treatment on five subtropical forest plants (*Pinus massoniana*, *Schima superba*, *Castanopsis fissa*, *Acmena acuminatissima*, and *Cryptocarya concinna*) were investigated by Liu et al. (2006). Furthermore, several works from China emerged recently using reflectance spectroscopy to evaluate the impact on vegetation of acid rain (mainly caused by SO_2 and NO_x). For example, Song et al. (2008) discuss the ability of hyperspectral data to detect acidic stress in forests in the Three Gorges region. A review by Kolhe and Deshmukh (2016) discusses using spectroscopy to detect the influence of acid rain stress on vegetative status.

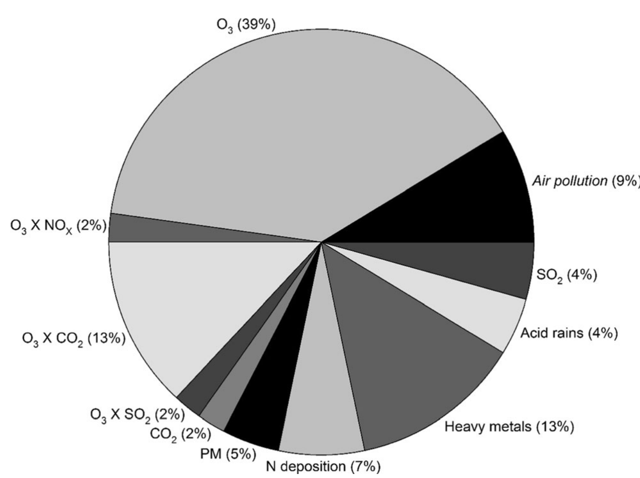

Fig. 5 Frequency distribution of the Mediterranean air pollutants of which the impact on plants was assessed in the studies reviewed

Conclusions

This review highlights the potential of reflectance spectroscopy as a novel approach for evaluating the impact of air pollution on vegetation status. The reviewed literature shows that the interest in using this technique to evaluate Mediterranean atmospheric pollutant-plant interactions is increasing. After a peak of research published from 1992 to 1996, a drop in published research occurred likely due to a lack of accessibility to instrumentation. However, the last 10 years have been the most productive ever, especially the years from 2007 to 2011 (Fig. 4). All the current major and minor Mediterranean pollutants have been evaluated in the last 40 years, and O_3 and its interaction with other gases (especially CO_2, but also NO_2 and SO_2) has been the most studied (55% of all studies we report); however, in recent years, novel air pollutants have drawn the attention of the scientific community (PM, 5%; N deposition, 7%; heavy metals, 13%; Fig. 5). Furthermore, reflectance spectroscopy has been used worthwhile to assess the responses to air pollution of various vegetation types. The most studied have been herbaceous species and gymnosperm trees (41 and 38%, respectively), although also, angiosperm trees have been largely evaluated. Only 4% of the reviewed works were performed on shrubs. Although the extent in the studied species, few of these plants are typical of the Mediterranean environment, the most affected by CC in comparison to the other areas worldwide and a hot spot for air quality. We thus suggest that a major emphasis should be placed on the use of vegetation spectroscopy to monitor the impacts of air pollution on Mediterranean plants in the CC era.

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