# Monitoring oil contamination in vegetated areas with optical remote sensing: A comprehensive review

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ABSTRACT

The monitoring of soil contamination deriving from oil and gas industry remains difficult in vegetated areas. Over the last decade, optical remote sensing has proved helpful for this purpose. By tracking alterations in vegetation biochemistry through its optical properties, multi- and hyperspectral remote sensing allow detecting and quantifying crude oil and petroleum products leaked following accidental leakages or bad cessation practices. Recent advances in this field have led to the development of various methods that can be applied either in the field using portable spectroradiometers or at large scale on airborne and satellite images. Experiments carried out under controlled conditions have largely contributed to identifying the most important factors influencing the detection of oil (plant species, mixture composition, etc.). In a perspective of operational use, an important effort is still required to make optical remote sensing a reliable tool for oil and gas companies. The current methods used on imagery should extend their scope to a wide range of contexts and their application to upcoming satellite-embedded hyperspectral sensors should be considered in future studies.

MAIN ABBREVIATIONS

HM: Heavy Metal
LAD: Lead Angle Distribution
LAI: Leaf Area Index
LCC: Leaf Chlorophyll Content
LWC: Leaf Water Content
NIR: Near-Infrared
REP: Red-Edge Position
RTM: Radiative Transfer Model

SWIR: Short-Wave Infrared
TPH: Total Petroleum Hydrocarbons
UAV: Unmanned Aerial Vehicle
UV: Ultraviolet
VI: Vegetation Indices
VIS: Visible

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# 1. Introduction

Oil and gas industry currently holds a key role in the global energy mix [1–3]. Since the beginning of the 20th century, crude oil supply has continuously increased to satisfy a growing demand, reaching over 35 billion barrels (Gb) produced in 2017 [4–6]. Although a global peak of production – followed by a decline – is expected in the future, its timing remains largely unprecise as it depends on several factors, such as reserve estimates, and on the scenario that will frame the energy mix [7–10]. According to the International Energy Agency, oil production will become 8 million barrels per day greater in 2040 than today under the New Policy Scenario, which considers current government goals and policies. However, the increase of oil production

[11] goes together with a greater exposure of ecosystems to contamination, which remains a global ecological issue.

Once extracted from oil fields, crude oil is then refined to petroleum products [12–14]. At every step of the production process, oil spills and leakages may contaminate the soil and affect ecosystems. They result from facility failures, bad practices and storm events (Figure 1a-g). For example, extraction wells, pipelines, refineries and mud pits are common sources of contaminant leaked in the environment [15–20]. This includes crude oil, petroleum products, wastewaters and oil sludge [21–23]. All these contaminants cause severe ecological disturbances, such as landscape fragmentation and habitat loss or alteration, and affect human health [24–27]. Therefore, fast-detection is needed for assessing contamination and limiting its impacts. Lots of techniques have been developed for this purpose in response to major offshore oil spills [28]. However, the onshore domain – which stands for 70% of the global oil supply [29] – did not receive the same attention. Main advances have been achieved in pipeline leak detection, one of the most important source of oil contaminants in the environment [30–33]. Conversely, only little improvements have been made in assessing soil contamination deriving from extraction and refining activities or bad cessation management. Such operations are often made by field operators and do not guarantee an early detection of released contaminants, especially when it implies low and continuous quantities. They are time-consuming and lead to heavy ecological consequences when the contamination is not detected at early stage. Among promising alternatives, remote sensing could achieve fast detection of oil at large scale, fulfilling the needs of oil and gas companies. Encouraging perspectives of operational applications have emerged in this field, thanks to a growing interest over the last decades.


Figure 1. Principal sources of environmental contamination caused by oil activities. (a) Oil sludge pit [34], (b-c) vegetation and soil contaminated by crude oil leakage near a refining facility [35], (d) pipeline leakage [36], (e) crop contamination resulting from oil well blow out [37], (f) oil leakage from damaged storage tank following a storm [38] and (g) contaminated wastewater near a production site [39].

Active and passive remote sensing provide information about the composition of surfaces at large scale, by analyzing their radiometric properties in various domains of the electromagnetic spectrum [40,41]. Applications in onshore oil industry mainly rely on passive optical remote sensing, which exploits the [400:2500] nm reflective domain [42]. However, the real interest given to remote sensing by oil and gas companies started a few decades ago, with the emergence of passive hyperspectral sensors (Figure 2) [43]. Hyperspectral sensors provide reflectance data over multiple and contiguous wavelengths of the optical reflective domain [41]. They give access to the spectral signature of surfaces (*e.g.* waterbodies, soils, vegetation), which helps determining their composition (Figure 2). Hyperspectral imaging sensors include drone-/UAV-, airborne- and satellite-embedded sensors [44]. Some of them provide high to very high spatial resolution images (metric to centimetric), making possible to detect small targets. In complement, field portable spectroradiometers are usually used for collecting point reflectance data under controlled conditions or in the field [45]. The use of hyperspectral sensors for detecting apparent oil usually relies on exploiting the optical properties of petroleum hydrocarbons. For example, recent attempts succeeded in detecting contamination around industrial facilities using hyperspectral airborne and satellite imagery, by exploiting the spectral signature of soils [35,46]. From an operational point of view, hyperspectral imagery could thus provide a rapid diagnosis of oil-contaminated surfaces at large scale, but serious limits still compromise its use in vegetated regions.

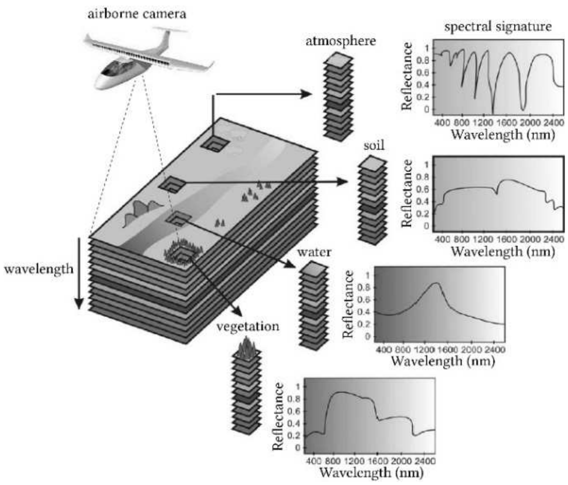


Figure 2. Principle of passive hyperspectral imagery (adapted from [47]). This technology provides the reflectance of surfaces over a continuous spectrum in the optical reflective domain (*i.e.* the spectral signature).

On sites covered by dense vegetation, optical remote sensing remains ineffective for detecting oil seepages and leakages directly, because light penetration is strongly limited by the foliage and the spectral signature of soils is thus not accessible. The only information about soil composition can be provided indirectly by vegetation through its optical properties [48–50]. This can be achieved because vegetation reflectance is closely linked to its biophysical and biochemical parameters (*e.g.* pigments), which are good indicators of environmental – especially stressful – conditions [51–53]. Consequently, unfavorable growing conditions in soils result in modifications of vegetation health and optical properties that can be tracked using hyperspectral remote sensing [23,54,55]. Therefore, since crude oil and petroleum products affect vegetation health, they can be detected and quantified indirectly using optical imagery [56–59]. To achieve this, several conditions must be fulfilled: (1) The contamination must affect the biophysical and biochemical parameters of vegetation, (2) alterations in these parameters must modify the spectral signature of vegetation and (3) the specifications of imaging sensors (e.g. the spatial and spectral resolutions) must make it possible to track these alterations. This implies good knowledge about the parameters of vegetation influencing its reflectance, as well as their response to oil contamination. Recent studies carried out under controlled and natural conditions have highlighted the need to develop methods specifically dedicated to this purpose, as well as the current pitfalls and limits to overcome [50,54,55,58]. Hence, an important effort still remains to make hyperspectral remote sensing an operational tool for monitoring oil contamination. Yet, no review has been proposed in that field. Previous review focused either on heavy metals contamination deriving from agriculture and mining [60,61] or on *soil contamination* in general [62,63]. However, recent studies emphasized that crude oil and petroleum products cannot be treated in the same way as other contaminants when assessing sol contamination from vegetation reflectance. Hence, they must be addressed separately.

The present review is intended to provide a comprehensive state-of-the-art of advances and challenges in the use of optical remote sensing for monitoring oil contamination in vegetated areas. It is addressed to non-specialists from a wide range of disciplines. This review is organized in accordance to the three points listed above. A first section summarizes the optical properties of vegetation in the reflective domain. Then, an overview of the effects induced by oil contamination on vegetation health is proposed. These two sections introduce key notions for non-specialists. Finally, the following sections go further into details of the topic. They focus on the consequences on these effects on vegetation reflectance and the methods developed to detect them under controlled and field conditions and using airborne and future satellite imagery.

## 2. Vegetation optical properties in the reflective domain (400 – 2500 nm)

Over the last 30 years, vegetation health assessment sparked an extensive attention by the remote sensing community. Then, the development of airborne- and satellite-embedded optical sensors opened the way to various applications in agriculture and ecology, thanks to a better comprehension of vegetation optical properties. The use of field portable spectroradiometer helped achieving this by providing reflectance data acquired at leaf or canopy scales. In the reflective domain, vegetation optical properties are driven by biophysical and biochemical parameters. They provide a singular shape to the spectral signature of healthy green vegetation, characterized by a peak of reflectance in the visible (VIS, 400 – 750 nm), a plateau in the near-infrared (NIR, 750-1300 nm) and two marked peaks in the short-wave-infrared (SWIR, 1300 –

2500 nm) (Figure 3). Leaf pigment and water contents and anatomy are the main parameters involved.

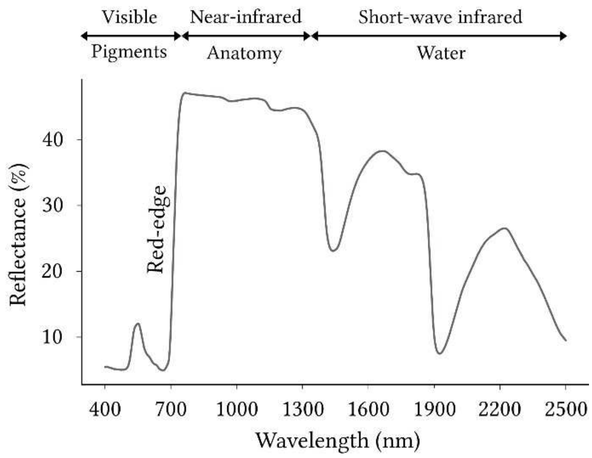


Figure 3. Typical spectral signature of healthy green leaf and most influential parameters in the different spectral regions.

### 2.1. Influence of leaf pigments in the visible region (400 – 750 nm)

A large diversity of pigments is present in plants [64–66]. Pigments are essential to the development of vegetation, because of their implications in photochemical reactions. They absorb light at various wavelengths in the ultraviolet (UV) and VIS regions, depending on their chemical properties. Consequently, the spectral signature of vegetation is strongly linked to leaf pigment content between 400 and 750 nm [64,67,68]. This makes possible to track changes in pigments using multi- and hyperspectral sensors.

Chlorophylls a and b are the main pigments present in leaves. They are good indicators of vegetation health [69–71], making them largely studied in remote sensing [72–74]. Chlorophyll concentration usually ranges from 0 to 80 $\mu g.cm^{-2}$ in crops [75], of which only 20% are represented by chlorophyll b in healthy green leaves [76]. These pigments show two light absorption peaks at 440-450 (blue) and 650-670 nm (red) [77,78]. Due to their important concentration in leaves, chlorophylls have a strong influence on the spectral signature, so they are likely to hide the effects of other pigments sharing common absorption wavelengths. More precisely, the weak light absorption of chlorophylls around 550 (green) and 700 nm (red-edge) results in high correlation with leaf reflectance in these regions [67,79]. Hence, remote sensing mostly exploits these wavelengths to quantify leaf chlorophyll content (LCC) [74]. A large diversity of approaches have been developed for tracking changes in LCC, such as simple or normalized reflectance ratios (vegetation indices (VI)) and Radiative Transfer Models (RTM) [52,64]. These approaches gave particular attention to the inflexion point of reflectance in the red-edge region – named the *Red-Edge Position* (REP), which is sensitive to little changes in LCC (Figure 3) [73,80,81].

Carotenoids are the other photosynthetic pigments found in plants [82]. They can be distinguished in two categories: carotenes and xanthophylls, which absorb light mainly in the blue region (400 – 500 nm). This common feature with chlorophylls explains their masking in healthy leaves, as their concentration rarely exceeds 25 $\mu g.cm^{-2}$ [75]. They are usually less influential on the spectral signature in the VIS and thus more difficult to quantify by remote sensing. However, the chlorophyll breakdown observed during leaf senescence increases the carotenoid-chlorophyll ratio [76,83]. Consequently, leaf reflectance rises between 500 and 750 nm (green – red), so carotenoids become more easily quantifiable (Figure 4).

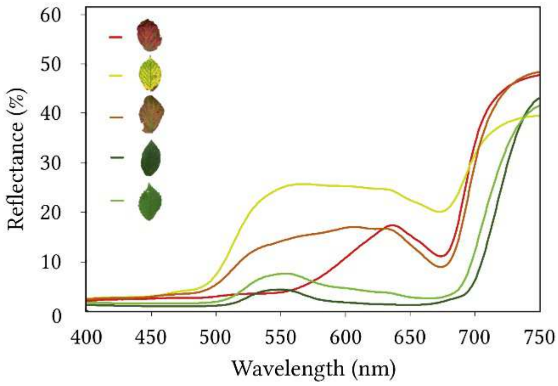


Figure 4. Spectral signatures of *Rubus fruticosus L.* in the visible region across different seasonal stages (unpublished data).

Frequently described as accessory pigments, carotenoids ensure essential photoprotective functions in plants [84,85]. They prevent leaf tissues from harmful effects of reactive oxygen species and photochemical stress that occur when absorbed light exceeds the photosynthetic capacity of leaves [82,83]. Therefore, the quantification of leaf carotenoid content is of great importance for monitoring vegetation health. Several VI have been designed for this purpose, such as the Photochemical Reflectance Index (PRI) [86,87]. The PRI exploits reflectance at 531 and 570 nm to track the epoxidation state of the xanthophyll cycle and can be used for assessing variations of photosynthetic activity across seasons [88,89].

Leaves also contain non-photosynthetic pigments that are responsible for color changes in autumn. Several plants turn red during senescence, because of the accumulation of anthocyanins in vacuoles. Anthocyanins are water-soluble flavonoids that absorb light in the ultraviolet (UV, 250 – 350 nm) and green (500 – 560 nm) regions [90,91]. They ensure a photoprotective function through UV screening, making them relevant indicators of vegetation health [92,93]. Other compounds such as tannins are also found in leaves, but their influence on leaf optical properties is restricted to the late senescence – or pre-abscission – period [83]. They are responsible for the browning of leaves.

### 2.2. Influence of leaf anatomy in the near-infrared region (750 – 1300 nm)

As pigments do in the VIS, leaf anatomy drives reflectance in the NIR region [53,94]. Leaves of Angiosperms are formed by successive cellular layers structured in parenchyma – also called mesophyll – and protected by a cuticle and an epidermis on abaxial (lower) and adaxial (upper) faces. This anatomy is at the origin of the plateau observed on leaf spectral signature in the NIR (Figure 3), ranging from 30 to 80% reflectance [53,95,96]. The upper cuticle and epidermis are the first barriers to the penetration of light. Incident light follows diffuse and specular reflection at leaf surface, but most radiations go through it and are transmitted to lower layers [97,98].

The internal anatomy of leaves greatly contribute to their optical properties in the NIR, but differs between mono- and dicotyledonous species [95,99,100]. In dicotyledonous leaves, cells are typically arranged in two distinct parenchyma. The upper one – known as palisade parenchyma – is made of well-structured elongated cells with high chloroplast concentration. Intercellular spaces are almost absent from this layer so light scattering remains limited. Conversely, the lower – spongy – parenchyma is characterized by irregularly-shaped and spaced cells with low chloroplast content. The spongy parenchyma has an important function in leaves, as it sends back a fraction of incident light to the palisade parenchyma, thus increasing the photosynthetic activity [101]. In monocotyledonous leaves, parenchyma are undifferentiated. Cells form a unique layer similar to the spongy parenchyma of dicotyledonous leaves, although this one is more compact so intercellular spaces are reduced. Several studies showed that the cuticle and parenchyma thickness, the proportion of intercellular spaces and the arrangement of chloroplasts greatly affect leaf reflectance in the NIR [53,94,95,102]. Leaf anatomy substantially varies among species, partly as a result of phylogeny and adaptation to light conditions [103–105]. Additional factors also influence leaf anatomy and NIR reflectance, such as nutrient and water availability or soil contamination.

While the anatomy of leaves determines their reflectance in the NIR, other biophysical parameters prevail when measuring reflectance at canopy scale. The Leaf Area Index (LAI) and the Leaf Angle Distribution (LAD) are the most influential ones [51,101,106]. Canopy reflectance is positively correlated to LAI in the NIR, because the influence of bare soil is reduced in this region as LAI increases (Figure 5) [107]. However, the reflectance reaches a plateau above very high LAI values (>6) [101]. LAD characterizes canopy architecture, *i.e.* the angular orientation of leaves. de Wit [108] proposed to classify species in the following six LAD types: Planophile, plagiophile, erectophile, extremophile, spherical and uniform. As leaf orientation is moving away from zero degrees (toward planophile LAD), canopy reflectance decreases in the NIR [51].

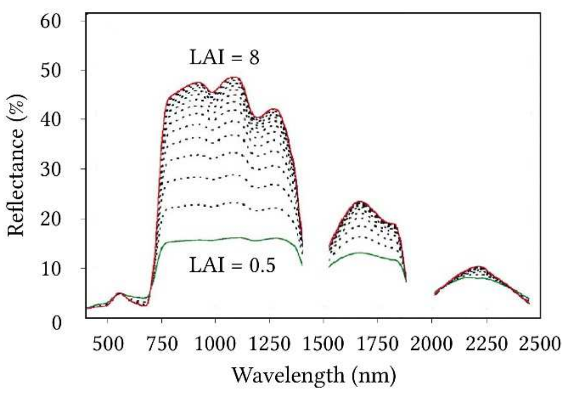


Figure 5. Influence of the Leaf Area Index (LAI) on canopy reflectance [51].

Because of its relationship with vegetation biophysical parameters, reflectance in the NIR can be used to describe leaf anatomy, canopy architecture and ground cover [53,109]. These parameters have in common to be directly or indirectly influenced by vegetation water status [96,110,111]. Water availability is a key parameter for understanding vegetation optical properties, as it drives many physiological mechanisms.

### 2.3. Influence of leaf water and dry matter contents in the near-infrared (750 – 1300 nm) and short-wave infrared (1300 – 2500 nm) regions

Vegetation optical properties are directly influenced by water contained in leaves, which absorbs light around 970, 1200, 1450, 1950 and 2450 nm [112–114]. These features are easily observed on the spectral signature of healthy plants and are affected by changes in leaf water content (Figure 6) [96]. Hence, they are reliable indicators of vegetation water status [115]. In addition, water is likely to affect reflectance indirectly in other spectral regions, as it is involved in many physiological mechanisms in plants, such as photosynthesis and leaf turgor. This is particularly marked for plants undergoing water-deficit stress [57,116]. Changes in leaf turgor and tissue destructuring induced by insufficient water uptake greatly affect light scattering and thus leaf reflectance in the whole NIR region [96]. These effects are also observed at canopy scale, as plant LAI and LAD are also modified by water-deficit stress [117].

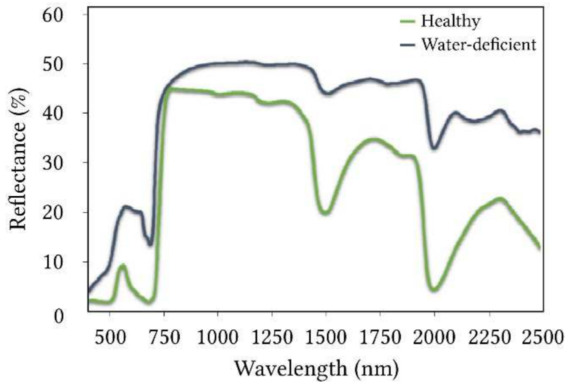


Figure 6. Spectral signatures of healthy and water-deficient plants.

Several studies demonstrated the effectiveness of the NIR and SWIR reflectance to assess vegetation water status by estimating Leaf Water Content (LWC) or Equivalent Water Thickness (EWT) [112,113,115]. VI and RTM have been widely used for this purpose [118–121]. Although water absorption bands previously cited may be appropriate [112,113], their utilization remains limited in airborne or satellite imagery, because of important noise due to atmospheric effects of water vapor. This limit can be however overcome by exploiting other water-dependent and atmospherically-resistant wavelengths in the NIR and SWIR regions [121–123].

As described in this section, vegetation optical properties are strongly linked in the NIR and SWIR regions, because of direct and indirect influence of water. According to Ceccato *et al.*[119], water stands for approximately 55 to 75% of healthy leaf fresh weight for temperate species. More than two thirds of the remaining part come from hemicelluloses, celluloses, lignins and proteins, which are often grouped in the “dry matter” term [124,125]. Celluloses are the most abundant organic compounds on earth and are found in all plants. Hemicelluloses and lignins are mostly represented in woody species [126,127]. These biochemical parameters share common light absorption features in the NIR and SWIR regions, at 1200, 1450 – 1490, 1540, 1760, 2100 and 2340 nm [128]. Proteins show quite different light absorption features, located at 1510 –

1520, 1730, 1980, 2060, 2165 – 2180 and 2300 nm. All these parameters remain difficult to estimate from vegetation reflectance, because their influence on reflectance in the NIR and SWIR regions is limited in comparison to water [124,128]. They become however more influential in dry leaves. Few VI have been designed for retrieving celluloses and lignins content in leaves or decomposing litter [129,130].

As outlined in this section, the biophysical and biochemical parameters driving vegetation optical properties differ according to the spectral region (VIS, NIR and SWIR). Modifications in these parameters are expressed as changes in the reflectance of leaves and canopies. This makes possible to detect oil-induced alterations in vegetation health using multi- and hyperspectral remote sensing. This purpose however requires identifying the most suitable (*i.e.* oil-sensitive) spectral regions. A good comprehension of the effects induced by crude oil and petroleum products on vegetation is mandatory for achieving it. These effects are described in the following section.

## 3. Effects of crude oil and petroleum products on vegetation health

Crude oil and petroleum products leaked from industrial facilities are likely to affect vegetation health and optical properties. Their particular nature and composition are greatly responsible for these effects.

### 3.1. Composition of crude oil and petroleum products

Crude oil refers to oil in its natural and extractible form, *i.e.* oil stored in geological formation and brought to the surface [12]. Petroleum products result from the refining of crude oil. They include fuels (diesel, gasoline, kerosene), lubricant, waxes and miscellaneous products used in various domains (*e.g.* transportation and industry) [131]. The term oil refers both to crude oil and petroleum products. Wastewaters and oil sludge are produced during the refining process [21,22]. Both crude oil and petroleum products are mixtures of volatile to dense hydrocarbons (called *Petroleum hydrocarbons*), heavy metals (HM, also termed *Trace Metal Elements*) and oxygen, sulfur and nitrogen compounds in various proportions [132–134]. Petroleum hydrocarbons include Mono- and Polycyclic Aromatic Hydrocarbons (BTEX and PAH, respectively), and saturated (alkanes or paraffins) and unsaturated (alkenes and alkynes) hydrocarbons [131]. *Total Petroleum Hydrocarbons* (TPH) is a generic term that encompasses all these compounds. Depending on the length of their carbon chain, petroleum hydrocarbons are refined to different petroleum products [135,136]. An illustration is given in Figure 7.

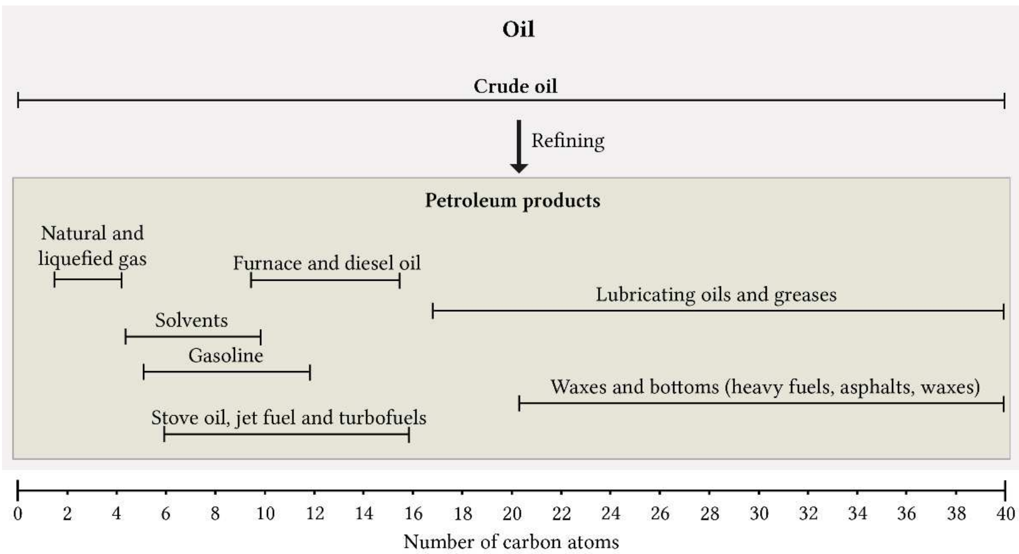


Figure 7. Crude oil and petroleum products according to petroleum carbon ranges (reproduced from [136]).

The composition of crude oil and petroleum products gives them a high toxicity towards vegetation [137]. When considered separately, each hydrocarbon and HM type is likely to affect vegetation health [138]. Since they are in mixture, it remains difficult to identify which of these compounds are responsible for the observed response. In addition, interactions can occur among hydrocarbons and HM and result in synergistic or antagonist effects on vegetation [57]. However, the influence of mixture composition is still misunderstood. Different mixtures such as crude oil, diesel or gasoline, lead to different responses of vegetation [57,58,139]. These responses result from indirect effects caused by modifications of soil physico-chemical and biological properties, and from direct effects through contact with plant and assimilation in tissues [140,141]. Both occur at root level and lead to anatomical and biochemical changes in leaves, so these direct and indirect effects remain difficult to differentiate [142–144]. They are described jointly here.

### 3.2. Effects on soil properties and on plant roots

The phytotoxicity of petroleum hydrocarbons and HM has been subject to numerous studies. However, no review has been proposed – for terrestrial plants – in this field for almost 50 years [137]. Since then, few studies have focused on the effects of petroleum hydrocarbons and HM in mixture [56,145,146]. This topic has been addressed recently and provided a better comprehension of how vegetation is affected by oil leakages.

Because of their particular nature and composition, crude oil and petroleum products induce important modifications of soil physico-chemical and biological properties [134,147,148]. Consequently, they impose selective growing conditions to plants [55]. Soil water regime is one of the most impacted properties. Because of hydrocarbons, crude oil and petroleum products are in liquid – highly hydrophobic – form [131]. When found in soils, they occupy a fraction of porosity that becomes unavailable to water. In addition, by interacting with soil materials (especially clay), oil forms a hydrophobic film at their surface, which forces water drainage toward deeper soil layers. These phenomena contribute to reducing the field capacity of soil and plant water supply [149–151]. It is amplified by HM, which affect soil water potential and water uptake by roots once transferred to the soil solution [152].

Petroleum hydrocarbons represent a considerable enrichment in organic material, leading to an increase of soil carbon content and carbon / nitrogen ratio (C/N) [134,151,153]. This stimulates the growth of microorganisms capable of degrading hydrocarbons, thus modifying organic matter mineralization cycles and reshaping microorganism communities [154–156]. The biodegradation of hydrocarbons is accompanied by an elevation of soil $CO_2$ concentration, especially in the presence of vegetation [157]. Some of the HM found in oil are essential to vegetation growth (*e.g.* Fe, Zn, Cu), but their occurrence at high concentrations along with other HM (*e.g.* Cd, Mg, Pb) also affect microorganisms [158]. They are not degradable and in the case of oil leakages, they concentrate in the first soil layers [159]. The nitrogen cycle is particularly impacted by carbon enrichment: the availability of inorganic nitrogen decreases so vegetation nitrogen status is highly altered [153]. Likewise, several studies revealed that petroleum hydrocarbons and HM reduce nutrient availability (P, K) and soil Cation Exchange Capacity (CEC) [150,151,160]. The latter is indeed closely linked to soil organic matter content, C/N ratio and pH; so many parameters affected by oil [132,134]. Through modifications of soil physico-chemical and biological properties, crude oil and petroleum products thus affect water and nutrient availability for plants [161]. These effects are called indirect effects. In addition, direct effects occur when oil is in contact with roots [162]. As they do with soil materials, petroleum hydrocarbons are able to coat plant roots by adsorbing at their surface. As well as HM, their assimilation inhibits root growth and causes a thickening of root epidermis, endodermis and cortex, and a reduction of root hair diameter and density [140,152,163,164]. These anatomical changes heavily alter water and nutrient uptake capacities of plants. For some species, they are partly compensated by a higher allocation of resources to roots.

As soon as water or nutrient supply is no longer sufficient to ensure essential physiological functions, stressful conditions arise so plant undergoes anatomical and biochemical modifications that affect its reflectance. These effects are amplified by the accumulation of certain hydrocarbons and HMs in leaves [138,141,142].

### 3.3. Effects on plant biochemical and biophysical parameters

The biophysical and biochemical parameters affected by exposure to crude oil and petroleum products are involved in vegetation optical properties. A review of these effects is proposed in Table 1. The alteration of leaf pigment content is the most frequently described response of plant to crude oil and petroleum products [58,142,165]. This alteration is induced by that of plant water and nitrogen status described above [149]. It can be visually observed through symptoms of leaf discoloration, which vary among species and according to mixture composition [57,59,163] (Figure 8a-d). The discoloration is caused by a reduction of LCC and indicates a decrease in photosynthetic activity [139]. This response is very common for water-deficient plants [37,111]. Although they are naturally present at lower concentrations in leaves, carotenoids and anthocyanins are also affected [58]. HM accumulation amplifies this effect [152,166].

Alterations of biophysical parameters can be observed at different scales. At leaf scale, they are expressed as a reduction in the number and size of cells and an increase of intercellular spaces in parenchyma [142,144]. The accumulation of certain hydrocarbons and HMs –

especially Cd and Mg – also causes tissue destructuring [137,138]. Consequently, important modifications of leaf spectral signature are expected in the NIR region. At canopy scale, water and nutrient deficiency leads to a limited development (*i.e.* a reduction of leaf and stem length and density), reducing aboveground biomass and LAI. In addition, changes in leaf anatomy and water content affect plant habit and consequently LAD.

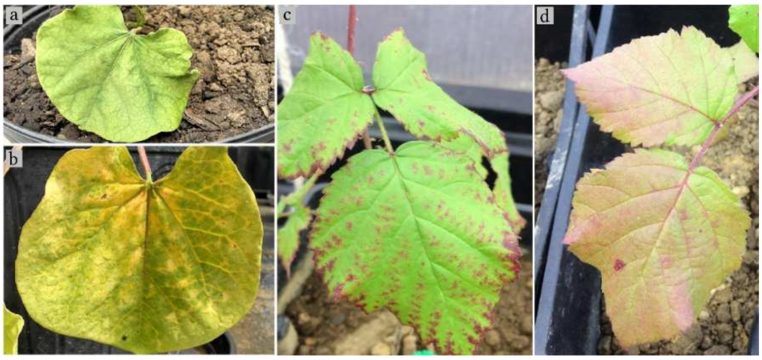


Figure 8. Visible stress symptoms commonly observed on leaves under exposure to crude oil and petroleum products. These symptoms are associated to alteration in pigment content. (a-b) *Canavalia ensiformis* (L.) DC grown on diesel-contaminated soil [163]. (c-d) *Rubus fruticosus* L. grown on (c) mud pit- and (d) crude oil-contaminated soils [57].

### 3.4. Sources of variability

The severity of the effects described in section 3.3 highly varies according to the context as described in Table 1, because these effects are influenced by many factors. The sensitivity of the species is a determining one [49,167,168]. Since all species do not share similar ecological requirements, their tolerance to stressful conditions differs. Consequently, a decrease in soil water and nutrient availability caused by crude oil and petroleum products will not affect all species in the same way [169]. Moreover, some species are capable of detoxifying hydrocarbons and HMs accumulated in leaves through mechanisms of sequestration, transportation and excretion [145,170]. This prevents biochemical alterations and tissue destructuring. Few species are even stimulated by the enrichment of soil organic matter provided by crude oil and petroleum products, but this response remains uncommon [171,172]. This variability in species' sensitivity has strong implications under natural conditions. For example, only few species are established around natural oil seepages [55]. Their presence is explained by a high tolerance to chronic crude oil exposure, so these species undergo no or little alterations. Mud pits contaminated by oil production residues (*e.g.* oil sludge) are similar cases [16,49,56,57,161]. Conversely, crude oil and petroleum products leaked from drilling well, storage tank and pipeline leakages consist in a rapid exposure of oil-intolerant species. In those conditions, severe alterations and sometimes plant death are observed [26,58,165].

Petroleum hydrocarbon and HM availability for plants strongly varies according to their chemical properties. For example, low-carbon PAHs and As are easily accumulated in leaves [138]. Therefore, mixture composition influences plant response, so different crude oils or petroleum products (*e.g.* diesel, gasoline) do not affect leaf biophysical and biochemical parameters of a single species in the same extent [57,137,141]. Apart from mixture composition, these effects are also conditioned by the level and time of exposure to oil [58,149,168]. More precisely, the amplitude of pigment and water content alteration in leaves is positively correlated to the overall TPH concentration [49]. Above a threshold concentration that depends on species' sensitivity (generally in $g.kg^{-1}$), plant death can be observed after only few days [142,167]. In contrast, several weeks of exposure might be required to induce biophysical and biochemical alterations at low concentrations ($\mu g$ to $mg.kg^{-1}$) [163,172].

Although the effects of petroleum hydrocarbons and HM mixtures on vegetation are well documented in the literature, they cannot be generalized to all contexts of oil leakages because their severity depends on many factors. Species' sensitivity, mixture composition and concentration and exposure time have been identified as the most influential ones. These factors have critical implications in remote sensing, since they determine the amplitude of reflectance changes in vegetation and thus hydrocarbon detectability using airborne and satellite-embedded sensors.

Table 1. Effects induced by crude oil and petroleum products on vegetation biophysical and biochemical parameters. (⇑ and ⇓ denotes increase and decrease in the measured parameter, respectively; * indicates dose-dependent effects; n.a.: not available or not measured.)

| Species | Crude oil Petroleum product | TPH | Total time of exposure | Anatomy / Development | Pigments / Photosynthesis | Water status | Ref. |
|---|---|---|---|---|---|---|---|
| *Ailanthus altissima Mill.* | Oil sludge | 10-40% | 240 days | ⇓ Shoot length and biomass* | ⇓ Photosynthesis* | ⇓ Stomatal conductance*<br>⇓ Leaf transpiration* | [173] |
| *Allophylus edulis* | Crude oil | 13.65 $g.kg^{-1}$ | 30-60 days | ⇑ Shoot length and biomass unchanged | n.a. | n.a. | [162] |
| *Amorpha fruticosa* | Crude oil | 5-20 $g.kg^{-1}$ | 6 months | ⇓ Shoot biomass* | ⇓ Leaf chlorophyll content* | ⇓ Leaf water content<br>⇓ Stomatal conductance and transpiration rate* | [174] |
| *Canavalia ensiformis* | Diesel | 22,219 $mg.kg^{-1}$ | 30 days | ⇓ Palisade and spongy parenchyma thickness<br>⇓ Stem and leaf length and biomass | Leaf discoloration and necrosis<br>⇓ Leaf chlorophyll content<br>⇓ Leaf carotenoid content | n.a. | [163] |
| *Capsicum annum* | Lubricating oil | 1-5% | 84 days | ⇓ Shoot length*<br>⇓ Leaf area* | n.a. | n.a. | [167] |
| *Cedrela odorata* | Crude oil | 18-47.10 $g.kg^{-1}$ | 245 days | ⇓ Shoot length and biomass | n.a. | n.a. | [168] |
| *Corchorus olitorius* | Engine oil | 0.2-3% | 6 weeks | ⇓ Shoot length*<br>⇓ Leaf area* | ⇓ Leaf chlorophyll content* | ⇓ Leaf water content* | [175] |
| *Cyperus brevifolius* | Crude oil | 10-50 $g.kg^{-1}$ | 6 months | ⇑ Cuticle thickness*<br>⇓ parenchymatous cell length and diameter*<br>⇓ intercellular spaces length and diameter*<br>⇓ Shoot biomass* | Light to very dark leaves<br>⇓ Leaf chlorophyll content* | n.a. | [142] |
| *Deschampsia caespitosa* | Petroleum cokes | n.a | 3 months | ⇓ Shoot length | ⇓ Leaf chlorophyll content<br>⇓ Leaf carotenoid content | ⇓ Transpiration rate and stomatal conductance | [176] |
| *Fraxinus rotundifolia Mill.* | Oil sludge | 10-40% | 240 days | ⇓ Shoot length and biomass* | ⇓ Photosynthesis* | ⇑ Stomatal conductance until day 80*<br>⇓ Stomatal conductance after day 80*<br>⇓ Leaf transpiration* | [173] |
| *Glycine hyspida* | Crude oil | 1.3-3.1 $g.kg^{-1}$ | >6 months | ⇓ Shoot biomass* | n.a. | n.a. | [134] |
| | Crude oil (spill) | 1.1-3.8 $g.kg^{-1}$ | >6 months | ⇓ Shoot biomass* | n.a. | n.a. | |
| | Drilling fluids | 1.6-76.1 $g.kg^{-1}$ | >6 months | ⇓ Shoot biomass* | n.a. | n.a. | |
| *Haematoxylum campechianum* | Crude oil | 18-47.10 $g.kg^{-1}$ | 245 days | ⇓ Shoot length and biomass | n.a. | n.a. | [168] |
| *Hordeum vulgare* | Crude oil | 1.3-3.1 $g.kg^{-1}$ | >6 months | ⇓ Shoot biomass | n.a. | n.a. | [134] |
| | Crude oil (spill) | 1.1-3.8 $g.kg^{-1}$ | >6 months | Shoot biomass unchanged | n.a. | n.a. | |
| | Drilling fluids | 1.6-76.1 $g.kg^{-1}$ | >6 months | ⇓ Shoot biomass* | n.a. | n.a. | |
| *Lycopersicon esculentum* | Lubricating oil | 1-5% | 84 days | ⇓ Shoot length*<br>⇓ Leaf area* | n.a. | n.a. | [167] |

| Species | Crude oil Petroleum product | TPH | Total time of exposure | Anatomy / Development | Pigments / Photosynthesis | Water status | Ref. |
|---|---|---|---|---|---|---|---|
| *Medicago sativa* | Oil sludge | 4-5% | 9 weeks | ⇓ Shoot length and biomass unchanged | n.a. | n.a. | [161] |
| *Melia azedarach L.* | Oil sludge | 10-40% | 240 days | ⇓ Shoot length and biomass*<br>⇓ Leaf area | ⇓ Photosynthesis* | ⇓ Stomatal conductance*<br>⇓ Leaf transpiration* | [173] |
| *Phragmites australis* | Crude oil | 2-12 $g.kg^{-1}$ | 2 months | ⇓ Shoot biomass* | n.a. | n.a. | [153] |
| *Robinia pseudoacacia L.* | Oil sludge | 10-40% | 240 days | ⇓ Shoot length and biomass*<br>⇓ Leaf area | ⇓ Photosynthesis | ⇓ Stomatal conductance | [173] |
| *Swietenia macrophyll* | Crude oil | 18-47.10 $g.kg^{-1}$ | 245 days | ⇓ Shoot length and biomass | n.a. | n.a. | [168] |
| *Tabebuia rosea* | Crude oil | 18-47.10 $g.kg^{-1}$ | 245 days | ⇓ Shoot length and biomass | n.a. | n.a. | [168] |
| *Terminalia catappa* | Crude oil (spill) | n.a | 3 weeks | ⇑ Cuticle thickness<br>⇑ Epidermal cell diameter<br>⇑ Palisade and ⇓ spongy parenchyma thickness | n.a. | n.a. | [144] |
| *Triticum aestivum* | Crude oil<br>Crude oil (spill)<br>Drilling fluids | 1.3-3.1 $g.kg^{-1}$<br>1.1-3.8 $g.kg^{-1}$<br>1.6-76.1 $g.kg^{-1}$ | >6 months<br>>6 months<br>>6 months | ⇓ Shoot biomass<br>⇓ Shoot biomass*<br>⇓ Shoot biomass* | n.a.<br>n.a.<br>n.a. | n.a.<br>n.a.<br>n.a. | [134] |
| *Triticum aestivum* | Petroleum cokes | n.a | 2 months | ⇓ Shoot length<br>⇓ Leaf area | ⇓ Leaf chlorophyll content<br>⇓ Leaf carotenoid content | ⇓ Transpiration rate and stomatal conductance | [176] |
| *Vicia faba* | Crude oil | 1.56-50% | 30 days | ⇓ Shoot biomass | ⇓ Leaf chlorophyll content<br>Leaf carotenoid content unchanged | ⇓ Leaf water content | [177] |
| *Vicia faba* | Crude oil<br>Diesel<br>Engine oil | 9-18 $g.kg^{-1}$<br>9-18 $g.kg^{-1}$<br>9-18 $g.kg^{-1}$ | 5 weeks<br>5 weeks<br>5 weeks | ⇓ Shoot length and biomass*<br>⇓ Shoot length and biomass*<br>⇓ Shoot length and biomass* | n.a.<br>n.a.<br>n.a. | n.a.<br>n.a.<br>n.a. | [141] |
| *Zea mays* | Crude oil | 0.28-0.66% | 6 weeks | ⇓ Shoot biomass | ⇓ Leaf chlorophyll content | ⇓ Leaf water, osmotic and turgor potentials | [149] |

## 4. Detection of crude oil and petroleum products using vegetation optical properties

The previous introductory sections provided key elements to understand how the biophysical and biochemical parameters of vegetation drives its reflectance, and how these parameters are affected by oil contamination. It is therefore expected that these biophysical and biochemical alterations will modify the reflectance of vegetation, at leaf and plant scales, making possible to detect oil contamination indirectly. This section summarizes the modifications of vegetation reflectance induced by crude oil and petroleum products, and the existing methods developed to track these modifications, under controlled and field conditions.

Vegetation optical properties have been extensively used for tracking alterations in pigment or water content caused by biotic and abiotic factors [178–182]. Conversely, their exploitation in oil leakage detection has been initiated more recently [57,59,165]. Major progress has been made in this field by taking advantage of multi- and hyperspectral methods developed for assessing vegetation health in other contexts, such as crop and ecosystem monitoring. Some of these methods – especially VI and RTM – proved efficient for tracking oil-induced alterations in vegetation reflectance under controlled and field conditions, from spectroradiometer-acquired reflectance data [57,59,172,183].

### 4.1. Effects of crude oil and petroleum products on vegetation reflectance

As described in section 3, crude oil and petroleum products affect the main biophysical and biochemical parameters driving vegetation optical properties. These effects result in modifications in the spectral signature at leaf and canopy scales, which have been studied under greenhouse or field conditions. They are summarized in Table 2. The VIS has been mostly exploited for tracking the effects of crude oil and petroleum products from the spectral signature of vegetation, because of its strong link with pigments [59,139,165,183]. The alteration of chlorophyll content described in the previous section immediately leads to an increase of reflectance in this region, at leaf and canopy scales (Figure 9) [57,58].

This increase is essentially located in the green-red wavelengths (500 – 670 nm), where it can reach 20%, and is expressed as a shift of the REP toward shorter wavelengths around 700 nm. In comparison, the blue wavelengths (400 – 500 nm) are weakly affected. This response is observed after few days of exposure – even at low concentration – and becomes more pronounced in time, making crude oil and petroleum products more easily detectable. Once again, it is difficult to identify the most contributing hydrocarbons and HMs, since a single of these compounds is able to induce a similar response [146,184,185].

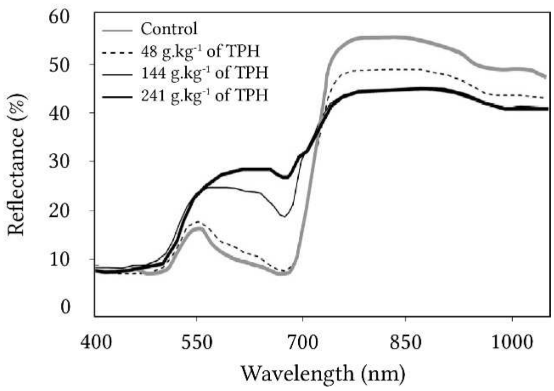


Figure 9. Spectral signatures of leaves of *Zea mays* L. grown for 14 days on engine oil-contaminated (48 – 214 g.kg$^{-1}$) or uncontaminated soils (modified from [59]).

Although the increase of green-red reflectance and the shift of the REP are frequent, an absence of reflectance change has been sometimes observed in studies (Table 2) [16,139,186]. In addition, some oil-tolerant species exhibit modifications of reflectance in the first stages of exposure to oil, and then recover reflectance values similar than those of healthy plants [57].

Other species are even stimulated by low TPH concentrations, inducing a decrease in reflectance [172]. This underlines the variability of vegetation response to crude oil and petroleum products discussed in section 3.4. Of the mentioned studies, some clearly linked the level of pigment content alteration to that of reflectance in the VIS [49,57,183]. They focused on leaf chlorophyll content, because of its major influence on reflectance in the 500 – 670 nm wavelengths [183]. Sanches *et al.* [58,165] conducted an experiment on four oil-sensitive species exposed to gasoline and diesel and concluded that carotenoid content had only few contribution to reflectance changes in the VIS. Conversely, these pigments were highly involved in the reponse of oil-tolerant species in other studies [57,172].

As described in section 2.2, reflectance in the NIR is highly dependent on the species – especially mono- and dicotyledonous – and on the acquisition scale (leaf, canopy). The same factors, as well as mixture composition, lead to contrasted response of vegetation in this region (Table 2). Whether they result from an increase or a decrease of reflectance, differences between healthy and affected vegetation can exceed 20% in the NIR [58]. A decrease in reflectance is more likely to be observed at canopy scale, since plant development – and thus LAI – is strongly limited by hydrocarbons and HMs. However, several exceptions have been noticed in the literature. As pointed out by three studies [57,58,139], a single species can undergo opposite reflectance changes in the NIR, depending on the crude oil or petroleum product to which it is exposed. Likewise, two species exposed to a similar concentration of the same petroleum product can exhibit contrasted responses in this region [187]. This causes serious detection limits in regions with high species diversity. Similar observations have been made at leaf scale, where reflectance in the NIR mainly depends on anatomy. However, no study demonstrated the relationship between alterations of parenchyma and reflectance changes in this region.

Because of modifications in vegetation water status, the SWIR is largely impacted by exposure to crude oil and petroleum products. As well as in the NIR, the response of vegetation in the SWIR varies among studies (Table 2). In the case where a decrease of reflectance is observed on exposed vegetation, it remains rarely lower than 10% [188]. Conversely, an increase of reflectance, which is more consistent with the reduction of leaf water content and canopy LAI, can exceed 20% for the most oil-sensitive species. In both cases, the response appears later than in the VIS and is thus a good indicator of a long-term exposure. As expected, the most affected wavelengths are located in water absorption features [183]. Because of low atmospheric transmission, these features are however unusable at canopy – and image – scale, but other ones (*e.g.* 1600 and 2200 nm) proved to be good alternatives [57,58]. Vegetation reflectance in the SWIR also depends on celluloses, hemicelluloses, lignins and proteins, which have already been reported as slightly sensitive to petroleum products in one study [58]. Because of the strong influence of LWC in this region, it is unlikely that alterations in these biochemical compounds have major contribution to the modifications of reflectance described here.

Table 2. Effects induced by crude oil and petroleum products on vegetation reflectance in the different spectral regions, at leaf and canopy scales. This review includes studies carried out under experimental or field conditions and implying point reflectance measurements using a spectroradiometer. (VIS: Visible, NIR: Near Infra-Red, SWIR: Short-Wave InfraRed, ⇑ and ⇓ denotes reflectance increase and decrease, respectively; FC: Field capacity; * indicates dose-dependent effects; n.a.: not available; n.s.: non-significant effect.)

| Species | Conditions | Crude oil petroleum product | TPH | Total time of exposure | Reflectance - Leaf scale | | | Reflectance - Plant / Canopy scale | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | VIS | NIR | SWIR | VIS | NIR | SWIR | |
| *Brachiaria brizantha* | Field | Diesel | 12.7 $L.m^{-3}$ | 30 days | ⇑* | ⇑* | ⇑* | ⇑* | ⇑* | ⇑* | [58] |
| | Field | Gasoline | 12.7 $L.m^{-3}$ | 30 days | ⇑* | ⇓* | ⇑* | ⇑* | ⇓* | ⇑* | |
| *Buddleja davidii* Franch. | Field | Mud pit | 16-77 $g.kg^{-1}$ | n.a.[a] | n.s. | n.s. | n.s. | n.a. | n.a. | n.a. | [49] |
| *Cenchrus alopecuroides* (L.) | Experimental | Mud pit | 14 $g.kg^{-1}$ | 60 days | | | | ⇑ | ⇓ | ⇑ | [56] |
| *Cenchrus alopecuroides* (L.) | Experimental | Mud pit | 1-19 $g.kg^{-1}$ | 42 days | ⇑* | ⇑* | ⇑* | ⇑* | ⇑* | ⇑* | [172] |
| *Cornus sanguinea* L. | Field | Mud pit | 16-77 $g.kg^{-1}$ | n.a.[a] | ⇑* | ⇑* | ⇑* | n.a. | n.a. | n.a. | [49] |
| *Forsythia suspensa* | Experimental | Engine oil | 20-60 % soil FC | 28 days | ⇑* | ⇑ | n.a. | | | | [187] |
| *Neonotonia wightii* | Field | Diesel | 6.25 $L.m^{-3}$ | 184 days | ⇑* | ⇓* | ⇓* | ⇑* | ⇓* | ⇓* | [188] |
| | Field | Gasoline | 6.25 $L.m^{-3}$ | 184 days | ⇑* | ⇓* | ⇓* | ⇑* | ⇓* | ⇓* | |
| *Panicum virgatum* L. | Experimental | Mud pit | 14 $g.kg^{-1}$ | 60 days | n.a. | n.a. | n.a. | ⇑ | ⇓ | ⇑ | [56] |
| *Pennisetum alopecuroides* | Experimental | Engine oil | 20-60 % soil FC | 28 days | ⇑* | ⇓* | n.a. | n.a. | n.a. | n.a. | [187] |
| *Phragmistes australis* | Field | Oil well leak | 9.45-652 $mg.kg^{-1}$ | n.a.[a] | n.a. | n.a. | n.a. | ⇑* | ⇓* | n.a. | [189] |
| *Populus x canadensis* Moench. | Field | Mud pit | 16-77 $g.kg^{-1}$ | n.a.[a] | ⇑* | ⇑* | ⇑* | n.a. | n.a. | n.a. | [49] |
| *Quercus pubescens* Wild. | Field | Mud pit | 16-77 $g.kg^{-1}$ | n.a.[a] | ⇑* | ⇑* | ⇑* | n.a. | n.a. | n.a. | [49] |
| *Rubus fruticosus* L. | Experimental | Mud pit | 4-40 $g.kg^{-1}$ | 100 days | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | [16] |
| *Rubus fruticosus L.* | Experimental | Mud pit | 36 $g.kg^{-1}$ | 60 days | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | ⇑ | [56] |
| *Rubus fruticosus L.* | Experimental | Mud pit | 6-25 $g.kg^{-1}$ | 32 days | ⇑ or n.s.* | ⇑ or ⇓* | ⇑ or ⇓* | ⇑ or n.s.* | ⇓* | ⇑ or ⇓* | [57] |
| | Experimental | Crude oil | 25 $g.kg^{-1}$ | 32 days | ⇑ | ⇑ | ⇑ | ⇓ | ⇓ | ⇑ | |
| *Rubus fruticosus* L. | Field | Mud pit | 16-77 $g.kg^{-1}$ | n.a.[a] | ⇑* | ⇑* | ⇑* | n.a. | n.a. | n.a. | [49] |
| *Salicorna virginica* | Experimental | Alba' crude oil | 7.7-9.1 % | 32 days | n.s. | ⇑ | n.a. | n.a. | n.a. | n.a. | [139] |

[a] Naturally-established vegetation

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Experimental | Escravos' crude oil | 0.7-1.4 % | 32 days | ⇓ | ⇓ | n.a. | n.a. | n.a. | n.a. | |

| Species | Conditions | Crude oil petroleum product | TPH | Total time of exposure | Reflectance - Leaf scale | | | Reflectance - Plant / Canopy scale | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | VIS | NIR | SWIR | VIS | NIR | SWIR | |
| *Triticum sp.* | Experimental | Gasoline | 10-100 ml.kg$^{-1}$ | 106 days | n.s. | n.s. | n.s. | n.a. | n.a. | n.a. | [186] |
| *Zea mays* | Field | Diesel | 6.25 L.m$^{-3}$ | 184 days | ⇑* | ⇓* | ⇓* | n.a. | n.a. | n.a. | [188] |
| | Field | Gasoline | 6.25 L.m$^{-3}$ | 184 days | ⇑* | ⇓* | ⇓* | n.a. | n.a. | n.a. | |
| *Zea mays* | Experimental | Engine oil | 48-241 g.kg$^{-1}$ | 14 days | ⇑* | ⇓* | n.a. | n.a. | n.a. | n.a. | [59] |
| *Zea mays* | Experimental | Mud pit | 4-40 g.kg$^{-1}$ | 100 days | n.s. | ⇓ | ⇑ | n.a. | n.a. | n.a. | [16] |
| *Zea mays* | Field | Gasoline | 8.33 L.m$^{-3}$ | 203 days | ⇑* | ⇓* | ⇓* | n.a. | n.a. | n.a. | [188] |
| | Field | Diesel | 8.33 L.m$^{-3}$ | 203 days | ⇑* | ⇓* | ⇓* | n.a. | n.a. | n.a. | |
| *Zea mays* | Experimental | Engine oil | 96 g.kg$^{-1}$ | 20 days | ⇑ | ⇑ | ⇑ | n.a. | n.a. | n.a. | [116] |

### 4.2. Methods developed for detecting crude oil and petroleum products under controlled and field conditions

The studies carried out to characterize the spectral response of vegetation to crude oil and petroleum products gave rise to various methods for detecting and quantifying TPH. These methods are based on exploiting the modifications of reflectance described in section 4.1, under controlled or field conditions. Most of existing methods rely on visual or statistical comparisons of spectral signatures between healthy and oil-exposed vegetation [16,139]. These methods are however limited for application beyond the context studied. Other authors exploited reflectance at particular wavelengths by using VI, REP and spectrum transformations, and converged on the critical importance of VIS wavelengths [58,59,183]. Gürtler *et al.*[188] compared these methods for discriminating among healthy and gasoline- or diesel-exposed vegetation, at leaf and canopy scales, and concluded that their performance depends on the species. In a single experiment, Sanches *et al.* [58] combined first derivative and *continuum* removal spectra transformation to Principal Component Analysis (PCA) for similar purpose and identified the red-edge region as a good indicator of soil contamination. However, none of the above-mentioned methods aimed to predict whether vegetation is – or has been – exposed to crude oil or petroleum products from its spectral signature. This represents an important issue for detecting contamination under natural conditions without *a priori* knowledge about their presence.

VI, REP and spectrum transformations have been used for assessing stress-induced alterations in vegetation health in a wide range of contexts. Filella & Peñuelas [81] used reflectance derived in the red-edge for tracking changes in LCC and LAI of *Capsicum annuum* and *Phaseolus vulgaris* resulting from nitrogen deficiencies. Likewise, VI exploiting the NIR and SWIR regions succeeded in tracking water-stress caused by insufficient irrigation or pests [120,190]. When used in classification or simple and multiple regression methods, these reflectance data allow predicting stressed vegetation and quantifying biophysical and biochemical parameters automatically [191–194]. Therefore, they are great candidates for detecting crude oil and petroleum products and quantifying TPH indirectly.

Classification relies on the combination of several discrete or continuous variables (*e.g.* reflectance data, VI) to predict a categorical response variable (*e.g.* “healthy” or “stressed”) through a mathematical function [195]. Here, we only consider supervised classification. In most cases, these methods are first calibrated on a set of data with known categories, called the *training set*, and tested on an independent set – the *test set* - by predicting categories and comparing them to the true ones [196]. Numerous classification methods have been proposed in the literature [197–199]. When dealing with hyperspectral data, several constraints yet arise. Since reflectance is measured over multiple and contiguous wavelengths, it is not rare to have more variables than observations (*i.e.* reflectance wavelengths > sample size). This phenomenon, known as the Hughes’ effect [200], leads to overfitting of the training set, which negatively affects classification accuracy. This effect can be partly avoided by reducing the dimensionality of the variables using, for example, Principal Component Analysis (PCA). Focusing on vegetation studies, Linear Discriminant Analysis (LDA), Support Vector Machines (SVM), Random Forest (RF) and Spectral-Angle-Mapper-based classification (SAM) revealed to be particularly efficient for discriminating healthy and stressed categories while avoiding overfitting [192,194,201,202]. However, an exhaustive review proposed by Lowe *et al.* [179] stated that no consensus is made in the choice of the method, since their performance highly depends on the purpose of the classification. Few methods allow identifying the most important (*i.e.* discriminant) variables through weighting or stepwise selection criteria [201,203]. Stepwise

Forward LDA [204] has been specifically designed for this purpose, but remains poorly adapted to hyperspectral data because of high multicollinearity. In a spectral region, multicollinearity occurs when reflectance data are linear combination of each other [205]. For example, correlation coefficients (*r*) among reflectance data from different red wavelengths can easily exceed 0.8, which indicates high redundancy. Variable selection becomes very difficult in this case. To achieve it, penalized methods have been developed, such as the Elastic net [206], but remain underexploited in vegetation studies.

Regression methods are used to predict a continuous response variable from one (simple regression) or several (multiple regression) continuous input variables [207]. In practice, these methods follow the same calibration – test procedure than for classification. Simple regression relies on the calibration of univariate models (*e.g.* polynomial, exponential, etc.). It has been especially used for predicting LCC from single VI in previous studies [64,67,81]. Multiple regression regroups a wide range of methods that do not substantially differ from classification ones, and are constrained by the same overfitting and multicollinearity issues. Regarding vegetation studies, it has been shown that Stepwise LDA, Partial Least Square Regression (PLSR) and Support Vector Regression (SVR) are well-suited for retrieving biophysical and biochemical parameters from hyperspectral data [191,193,208]. Once again, there is no best method since the performance varies according to the context. Since both classification and regression methods perform well for detecting and quantifying stress-induced changes in vegetation health, they are promising for monitoring oil contamination from vegetation reflectance. Studies listed in Table 2 showed that the mixture composition and the overall TPH concentration strongly influence the amplitude of reflectance modifications observed in the whole spectral signature. Based on these observations, predictive methods combining VI and either classification and regression approaches have been recently proposed to detect and characterize oil (*i.e.* to identify the type of crude oil or petroleum product) and to quantify TPH concentration in temperate and tropical regions [57,172]. These methods rely on tracking subtle changes in chlorophyll or various carotenoid contents induced by oil contamination by exploiting reflectance at multiple wavelengths in the VIS. They proved suitable for use both under controlled conditions and in the field.

Other methods based on a different approach have been developed for similar purposes. Those based on RTM are of great interest. RTM are physically-based models aiming to simulate vegetation optical properties. They are typically classified in four categories: plate models, N-flux models, stochastic models and ray tracing models [98,209]. Focusing at leaf scale, the plate model PROSPECT is probably the most widespread [52,72]. In its direct mode, PROSPECT allows simulating leaf optical properties (reflectance and transmittance) in the optical reflective domain from its biophysical and biochemical parameters (structure and pigment, water and dry matter contents). Inversion of the model allows retrieving these parameters from reflectance and transmittance measurements performed on leaves [125]. PROSPECT has been used in many studies dealing with environmental monitoring purposes [72,210]. While LCC and LWC remain the most targeted parameters in vegetation stress assessment [119,211], recent improvements of the model allow separating chlorophylls, carotenoids and anthocyanins with good precision [68,92]. In a recent study, Arellano *et al.* [48] inverted the model to compare LCC of various tropical plant families among uncontaminated and oil-spill sites, and found significant alterations for some of them. More recently, *Lassalle et al.* [49] inverted PROSPECT to retrieve oil-induced chlorophyll alterations in leaves from reflectance data, making possible to quantify TPH concentrations in soils (Figure 10). These two studies also highlighted the importance of taking the species' sensitivity to oil and the development stage into account, which both determine the detection and quantification accuracy.

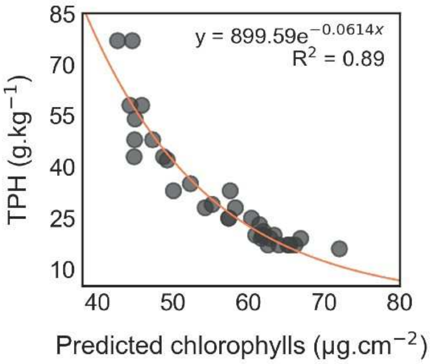


Figure 10. Relationship between Leaf Chlorophyll Content (LCC) retrieved from the spectral signature of *Rubus fruticosus* L. by inverting the PROSPECT model, and the concentration of Total Petroleum Hydrocarbons (TPH) in mud pit soils [49].

Hence, the methods developed for monitoring oil contamination from vegetation reflectance are largely inspired from those of other fields (agronomy, ecology). In a perspective of application at large scale – using airborne or satellite imagery, an upscaling of these methods is necessary. This represents a difficult step to cross toward operational applications over industrial facilities.

# 5. Application in contamination monitoring using airborne and satellite imagery

## 5.1. Synthesis based on previous studies

Few attempts have been made in detecting oil leakages and contaminated mud pits in vegetated areas using optical remote sensing in the past (Table 3). In most cases, studies aimed to assess the impact of crude oil and petroleum products on the environment using multi- (Landsat) or hyperspectral (Hyperion) satellite imagery at 30-m spatial resolution [23,212–214]. More rarely, the goal was to detect natural oil seepages (Figure 11a-b) [55]. A limited number of authors have used airborne hyperspectral images, and those who did have rarely exploited the entire spectral signature of vegetation. Almost all the mentioned studies used REP or VI to detect changes in vegetation health induced by crude oil or petroleum products. As for experiments carried out under controlled conditions, these methods rely on mean comparison between sites with healthy and oil-exposed vegetation [54,212,215]. They proved to be efficient for identifying vegetation stress on seepage or leakage sites, but suffered from serious limits when applied outside the study area (Figure 11a-b).

Table 3. Studies aiming to detect and quantify crude oil and petroleum products using multi- and hyperspectral airborne and satellite images. (Refl.: Reflectance; VI: Vegetation Indices; CR: *Continuum* Removal; RF: Random Forest; REP: Red-Edge Position; comp.: Comparison; RTM: Radiative Transfer Model.)

| **Vegetation type** | **Target** | **Sensor name** | **Sensor type (spatial resolution)** | **Bands (spectral domain)** | **Method** | **Ref.** |
|---|---|---|---|---|---|---|
| | | **Multispectral** | | | | |
| Mangrove | Crude oil leakage | Landsat-8 | Satellite (30 m) | 9 (435 - 2294 nm) | VI + Mean comp. | [212] |
| Crops, grassland & trees | Crude oil leakage | Landsat-8 | Satellite (30 m) | 9 (435 - 2294 nm) | VI + RF classification | [213] |
| Mangrove | Crude oil leakage | Landsat-5 & -7 | Satellite (30 m) | 6 (450 - 2350 nm) | VI + Simple regression | [216] |
| Mangrove | Crude oil leakage | Landsat-5 & -7 | Satellite (30 m) | 6 (450 - 2350 nm) | VI + Mean comp. | [216] |
| | | **Hyperspectral** | | | | |
| Wetland | Crude oil leakage | AISA | Airborne (1.5 m) | 286 (400 - 2400 nm) | Reflectance + Classification | [217] |
| Crops | Benzene pipeline leak | HyMap | Airborne (4 m) | 128 (436 - 2485 nm) | REP & VI + Spatial filter | [23] |
| Temperate shrubs | Mud pit | HySpex | Airborne (1 m) | 409 (400 – 2500) | VI + Classification<br>RTM + Regression | [50] |
| Mediterranean grassland | Crude oil microseepage | Probe-1 | Airborne (8 m) | 128 (436 - 2480 nm) | REP & VI + Spatial filter | [55] |
| Tropical forest | Crude oil leakage | Hyperion | Satellite (30 m) | 242 (400 - 2500 nm) | VI + Threshold | [54] |
| Plain & rainforest | Crude oil leakage | Hyperion | Satellite (30 m) | 242 (400 - 2500 nm) | CR + Mean comp. | [215] |
| Plain & rainforest | Crude oil leakage | Hyperion | Satellite (30 m) | 242 (400 - 2500 nm) | Refl. & VI + Mean comp. | [215] |

In contrast to experimental studies, REP and VI have already been exploited in classification or anomaly detection methods on multi- and hyperspectral images. However, the performance of these methods has been rarely quantified. Their evaluation mostly relied on visual interpretation of detection mapping with lacking ground validation data, which are often difficult to obtain. Among notable examples, Ozigis *et al.* [213] combined 10 VI in random forest on 30-m resolution Landsat-8 images for detecting oil leakages and obtained an overall accuracy of maximum 70% on selected sites. Conversely, Arellano *et al.* [54] applied successive vegetation index thresholds to map oil-induced stress near production facilities using 30-m resolution Hyperion images. These methods were first calibrated on a study area, and then applied to the entire image. In all cases, they led to the apparition of false alarms, especially false positives (*i.e.* vegetation stress not induced by petroleum hydrocarbons and HMs) (Figure 11b). This phenomenon is observed under various contexts (*e.g.* temperate, tropical) and results from multiple factors. First, in most studies, the spatial resolution of the images was not adapted to the size of the target. In addition, as described in section 3.4, certain species are particularly tolerant to crude oil and petroleum products and undergo only little changes in their spectral signature, which make them difficult to discriminate from healthy vegetation. In that situation, high spectral resolution and signal-to-noise ratio are needed to catch these changes in reflectance, so hyperspectral sensors are required. In addition, natural differences in optical properties among species and individuals – as well as in sensitivity to oil – make the detection particularly challenging in areas with high species diversity. For instance, a species exposed to crude oil or petroleum products may exhibit a similar spectral signature than that of another unexposed species [49]. This becomes a serious issue at decametric spatial resolution, where species are highly mixed inside pixels. A similar issue arises when exposed species are mixed with bare soil. Very high spatial resolution (1 – 2 m) is thus needed to overcome these limits.

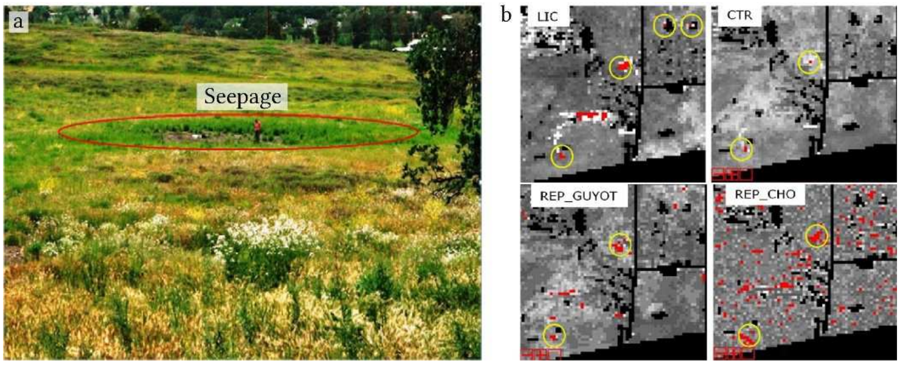


Figure 11. (a) Crude oil seepage in vegetated area. The seepage is surrounded by a particular vegetation distribution pattern, which allows being detected (b) from hyperspectral airborne images using various vegetation indices (see [55] for the description of indices). However, false alarms (red pixels outside yellow circles) cannot be avoided. Similar observations have been depicted for accidental oil leakages [54,216].

Ozigis *et al.* [213] pointed out several sources of confusion that contribute to increasing false positives. The presence of crude oil and petroleum products is not the only factor affecting vegetation health and optical properties under natural conditions. Some biotic or abiotic factors are likely to induce similar effects, thus introducing confusion. As described in section 3.2, crude oil and petroleum products reduce water availability for plants and can induce a water-deficit stress. Under natural conditions, this effect can be easily confused with that of a “natural” water-deficit (*i.e.* resulting from insufficient precipitation and/or highly drained soils). Although it seems possible to discriminate these stressors for highly oil-sensitive species under controlled conditions [59,183], it is more difficult for oil-tolerant species and using airborne or satellite hyperspectral images. Stress confusion has been identified as one of the most important cause of misclassification in previous studies. It is therefore necessary to account for these sources of confusion in each context, when applying detection methods over an entire region. Once again, very high spatial and spectral resolutions are needed to achieve efficient discrimination of oil and other stressors. Although no current satellite-embedded sensor offers such resolutions simultaneously at the moment, airborne imagery represents a good alternative [217].

As concluded from the above-mentioned studies, it is not the best option to develop methods for detecting and quantifying oil using only airborne or satellite images, especially without solid knowledge about the context (species' sensitivity, hydrocarbon and HM mixture, other potential stressors). Experiments carried out under controlled conditions are a necessary first step, since they help determining the response of vegetation specifically induced by crude oil and petroleum products. These experiments must be representative of realistic field conditions (*i.e.* species, TPH concentrations) and serve as basis for developing classification or regression methods that are suitable for use on images. The upscaling of methods is the most important difficulty in this approach, so it is crucial to address it progressively; for example, from leaf to canopy scales and finally on images. The validation of the methods in the field is an intermediate – and critical – step prior to imagery application. Then, the methods should be progressively applied to imagery; first, on selected sites with known species' sensitivities, and thereafter at large scale. This multiscale approach proved efficient in recent studies. For example, Lassalle *et al.* [49,50,57] developed methods for detecting and quantifying TPH based on bramble reflectance under controlled and field conditions and succeeded in applying them on airborne hyperspectral images over contaminated mud pits (accuracy > 90%).

The studies listed in Table 3 demonstrated the feasibility of assessing oil contamination using optical remote sensing. However, the methods described in these studies were validated locally, in a specific context. As a perspective, they are intended to be applied operationally in a broader range of situations encountered in oil contamination monitoring (pipeline leakage, mud pits, storage tanks failure, etc.), in various regions (temperate, tropical, etc.). This implies extending the scope of these methods and overcoming their current limits regarding operating and future satellite-embedded sensors.

### 5.2. Perspectives toward operational applications in oil and gas industry

In an operational context, remote sensing should provide accurate mapping of oil over large industrial facility sites colonized by vegetation. At this stages, the methods developed for this purpose remain rarely effective – or often unassessed – outside a given study site [54,55,213], which limits their operational use. Most of them are adapted to a given species or vegetation type (mangroves, shrubs, etc.) with known location, so these methods can be applied for identifying new contaminated sites, provided they are colonized by the same species or vegetation type. This remains very restrictive, because oil can be mapped only locally and to pre-selected vegetated sites. Therefore, in an operational perspective, it is essential to extend the scope of the methods to other contexts (in terms of species and contamination type and level). Likewise, they should be applicable to entire images, in order to assess oil contamination at large scale. To achieve this, it is not conceivable to use airborne hyperspectral imagery – especially for daily monitoring, because it implies an important economic cost. Conversely, satellite imagery is already used operationally by oil and gas companies for mineralogical mapping and marine oil spill tracking [218,219]. Satellite-embedded sensors can provide images over industrial facilities on a daily – or weekly – basis, allowing continuous monitoring of oil contamination. To date, the best spatial resolution provided by operating and planned hyperspectral satellite-embedded sensors is 8 m, with less than 300 spectral bands in the reflective domain (Table 4). In contrast, the best methods developed for assessing oil contamination were developed using high to very high spatial and spectral resolutions [23,50,217]. Using satellite imagery, their performance would be impacted by the degradation of resolutions. Therefore, two conditions are required for applying these methods in an operational way, namely: extending their scope to a wide range of contexts and adapting them to future satellite-embedded hyperspectral sensors (Table 4).

Table 4. Specifications of operational and future satellite-embedded hyperspectral sensors. The name and specifications of future sensors may be modified until their operating (n.a.: not available).

| Sensor name | Spectral domain (nm) | Bands | Spatial resolution (m) | Launch date |
|---|---|---|---|---|
| CHRIS | 415 - 1050 | 19-63 | 18-36 | operational |
| EnMAP | 420 - 2450 | 244 | 30 | 2020 |
| HISUI | 400 - 2500 | 185 | 30 | 2020 |
| HJ-1A | 450 - 950 | 115 | 100 | operational |
| Hyperion | 357 - 2576 | 220 | 30 | operational |
| HypXim | 400 - 2500 | 210 | 8 | 2020-2022 |
| HySI | 400 - 950 | 64 | 550 | operational |
| HyspIRI VSWIR | 380 - 2500 | 212 | 30 | n.a. |
| PRISMA | 400 - 2505 | 249 | 30 | operational |
| SHALOM | 400 - 2500 | 275 | 10 | 2020 |
| TianGong-1 | 400 - 2500 | 128 | 10-20 | operational |

At this stage, the application of the methods at large scale is limited by the necessity to know the location of the species – or vegetation type – on images. In an operational frame, an automatic mapping of this species would be helpful. Without this preliminary step, the methods would lead to false-detection alarms and inaccurate quantification of TPH if applied to other species and vegetation types, which differ in optical properties and sensitivity to oil [50,55,220]. The mapping could be achieved quite easily for homogenous and dense covers, but would become harder in regions with high species richness. It is particularly true when using satellite imagery, as “pure” pixels of dense vegetation (*i.e.* including a single species or vegetation type and no bare soil) become even rarer with increasing spatial resolution. Spectral unmixing might help overcoming this issue [47]. Unmixing aims at identifying the different species or vegetation types inside pixels using, for example, spectral libraries. Lots of unmixing methods have been proposed in previous studies [47,221–223]. Focusing on vegetation studies, unmixing methods have been developed for two main purposes: mapping a single target species or vegetation type and discriminating among various ones. Thus, unmixing could be used for mapping the species or vegetation types of interest before applying the methods of oil detection and quantification. Toward operational monitoring, future studies should focus on applying unmixing methods prior to detecting and quantifying TPH at satellite spatial resolution. However, it might be interesting not to limit to the species or vegetation types on which the methods were developed. Various species might serve for detecting and quantifying oil, which would extend the scope of the methods and fulfill operational needs.

Once the target species or vegetation types have been mapped, it is important to note that the accuracy of the detection and quantification of oil will depend on the level of contamination. For example, the exact range of effectiveness of the methods proposed for quantifying TPH remains unknown [49,50,189]. This information is essential for operational applications, because oil contamination can extend to a wide range of concentrations. Further studies should focus on determining the exact limits of detection and quantification of existing methods, especially since they may vary among species. Depending on their sensitivity to oil, all species do not allow detecting and quantifying contamination in the same range. Species with different sensitivities could be complementary for quantifying TPH over a wide range of concentrations [49,189,220]. High spatial resolution is also needed, as TPH concentrations may vary locally. 8- or 30-m pixels may include different species exposed to different levels of contamination, making oil very difficult to detect and quantify accurately. Hence, an important effort remains to identify the species suitable for monitoring oil contamination and to define their respective range of effectiveness at the spatial resolution of satellite-embedded sensors.

At this stage, the scope of the methods developed for detecting and quantifying TPH is restricted to assessing huge oil leakages (e.g. major oil spills and large, contaminated mud pits). Toward operational applications, it should extend to other scenarios. Chronic crude oil or petroleum product leaks deriving from pipeline or storage tank failures are priority, because they represent one of the main sources of contaminant release from oil industry [15,18]. From the perspective of satellite imagery application, one possible limit to applying the methods may arise at the spatial resolution of satellite images for small contaminated areas. More precisely, pipeline and storage tank leaks can spread on a few square meters [35,43], making their detection challenging at satellite spatial resolution, because pixels would not only include oil-exposed vegetation. Therefore, the required spatial resolution depends on the contamination event to detect (mud pit, pipeline leak, etc.).

## 6. Conclusion

This review aimed at summarizing the advances and challenges in using optical remote sensing for assessing oil contamination in vegetated areas. Although the optical properties of vegetation have been well documented, their use in oil and gas industry is still recent. By exploiting modifications in these properties caused by pigment and water alteration in leaves, previous studies have shown that it is possible to detect and quantify TPH in soils under controlled and field conditions. However, at this stage, several limits discussed in this review prevent from applying the same methods in an operational way at large scale, using hyperspectral imagery. Hence, the work summarized in this review should continue in further research, in order to extend the scope of the methods and to assess their operational maturity. More precisely, future studies should first focus on identifying more relevant plant species and, for each of them, the types of oil (*i.e.* crude oil and petroleum products) and the range of concentrations that can be detected or quantified. This would be helpful for remote sensing operators of oil and gas companies, as the methods could be used for a wide range of purposes in oil exploration and contamination monitoring. Prior to operational applications, the methods should be evaluated at the spatial and spectral resolutions of future satellite-embedded hyperspectral sensors, along with species unmixing.

On the long term, oil and gas companies may spark growing interest in UAV-embedded hyperspectral sensors. Although they are still under development, they represent a promising complement or alternative to satellite imagery. UAV-embedded sensors allow multitemporal, localized, monitoring, while providing very high spatial (up to cm scale) and spectral resolutions [224,225], therefore overcoming some of the above-mentioned limits. In addition, active remote sensing could be used to improve oil detection and quantification, by providing complementary information about vegetation. For example, radar and LiDAR imagery are useful for estimating canopy height and biomass [226], which are affected by oil. Radar remote sensing is light-independent and atmospherically-resistant, which is a considerable advantage in wet tropical regions [227,228]. By combining various technologies (active and passive) and sensor platforms (satellite, drone), remote sensing will undoubtedly become an indispensable support to oil contamination monitoring in vegetated areas in the coming decades.

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