

## Chapter 14

### Smoke from Wildfires and Prescribed Burning in Australia: Effects on Human Health and Ecosystems

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#### Abstract

Much of Australia is seasonally hot and dry, and fuel beds can become very flammable. Biomass burning ranges from annual savanna fires in the north to sporadic but extensive forest fires in the south. In addition, prescribed burning (the controlled application of fire) is being used more frequently as a means of reducing fuel loads, for maintenance of plant and animal biodiversity and in forestry practices. Despite this and in comparison to the Northern Hemisphere, there are few Australian studies of the production or composition of smoke from biomass burning. There is also relatively minimal Australian literature detailing the effect of wildfire smoke on human health and flora and fauna. Most of the literature dealing with smoke and human health issues in Australia outline epidemiological studies that document the incidence of hospital visits and admissions during wildfire events. The causal link between smoke and respiratory illness is yet to be established. The bulk of the publications dealing with ecological effects of smoke are concerned with germination of seed, with little information available on the direct effects of components of smoke on the physiology and biochemistry of plants, animals, invertebrates, or microorganisms. We will outline the knowledge of emissions and effects of smoke from prescribed and wildland fire in Australia on human health and the environment and will indicate potential areas for future research. In addition, a large proportion of the vegetation of Australia is composed of forests dominated by native species of *Eucalyptus* and *Acacia*, while large expanses of plantations are dominated by

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single species of *Eucalyptus*, and the production of volatile organic compounds (VOCs) by such vegetation is substantial. Thus, we will also outline an emerging research area in which the links among the production of VOCs by native Australian species, environmental conditions, and VOCs found in smoke produced from burning native vegetation are explored.

#### 14.1. Introduction

Australia is a fire-prone continent primarily because of increased aridity during the Pleistocene (1.8 million to 10,000 years BP). As Australian ecosystems became more sclerophyllous, fire became more frequent and accelerated the change in biota (Barlow, 1981). With the onset of human occupation 50,000 years BP, a wave of anthropomorphic burning followed and played a major role in altering the distributions of sclerophyll forests and assuring the dominance of *Eucalyptus* and *Acacia* in southern Australia (Bowman, 1998). Today, wildfires or bushfires have become more frequent and may be started naturally, accidentally, or intentionally. Controlled burning for fuel-reduction or biodiversity outcomes has also increased. An average area of 46.8 million hectares has been burnt annually during the period 1997–2003, and this area includes both planned and unplanned fires (Ellis et al., 2004). The need for specific Australian research into the effect of smoke on human health and ecosystems from both these types of fires has been recognized with the recent formation of targeted projects within a federally funded cooperative research center. Firefighter health and safety is also of considerable importance in Australia and has been funded under the same research scheme. Other consequences of smoke such as impairment of visibility or contribution to regional haze, while important to understand, do not have such a high priority for national study and will only be briefly commented on in this review.

This chapter reviews the body of knowledge concerning smoke from vegetation fires in Australia. The current state of knowledge of the effects of smoke on human health in Australian communities will be discussed briefly before turning to the effects of smoke on biota. Particular attention will be given to the production and effect of volatile organic compounds (VOCs) in smoke, as this is the current research interest of our research group. The natural production of large amounts of VOCs by native Australian vegetation will be described and used as a basis for tailoring our future studies of smoke composition.

#### 14.2. The nature of smoke from vegetation fires

The production of smoke through the combustion of vegetation (also referred to here as biomass burning) is one of the most common of all chemical reactions, but it may well be the least understood (Radojevic, 2003). Smoke is a natural by-product of an integral natural process, but it is more often than not viewed and reported in a negative manner. Smoke, whether resulting from consumption of wood for energy, slash-and-burn agricultural practices, prescribed burning activities or wildfires, contains a complex mixture of the visible products of burning (particulates and water vapor), and primary and secondary gaseous products, many of which are air pollutants or greenhouse gases (Ward, 1999).

Components of smoke include gaseous aerosols, such as carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>), oxides of nitrogen (NO<sub>x</sub> as nitrous oxide [NO] and nitrogen dioxide [NO<sub>2</sub>]), sulfur dioxide (SO<sub>2</sub>), VOCs, and polycyclic aromatic (or polynuclear) hydrocarbons (PAHs; Crutzen & Andreae, 1990; McKenzie et al., 1994; Ward, 1999). Smoke also includes aerosols that are stable solid or liquid suspensions and may vary in concentration, composition, and size distribution. Aerosols may also be formed from gaseous precursors by a variety of oxidation pathways (Koutrakis & Sioutas, 1996). As an indication of the complexity of emissions in biomass smoke, McKenzie et al. (1994) identified 26 oxygenated organic compounds in the condensable fraction of smoke from smouldering sapwood of ponderosa pine (*Pinus ponderosa*), and over 70 different compounds were listed by Andreae and Merlet (2001) as being produced by burning of various types of vegetation.

The composition and quantity of smoke produced during vegetation burning will differ depending on the chemistry and moisture content of the fuel, the amount and arrangement of fuel layers, and on the behavior of the fire and weather conditions (Ward, 1990; Ward & Hardy, 1991). For example, fires of low intensity (low heat and light emissions) tend to produce more particulate emissions than fires of higher intensities (high heat and light emissions), while smouldering (flameless) combustion produces more CO, NH<sub>3</sub>, and particulates than flaming combustion (Ward, 1999). Different types and amounts of smoke can even be produced simultaneously within a single fire; for example, heading fires generally produce two to three times more emissions than backing fires (Ward, 1990). Fine fuels with a high moisture content will encourage smouldering, while drier fuels will produce flaming combustion (Lobert & Warnatz, 1993). Brushy vegetation with highly dissected leaves and branches produces more smoke per weight of fuel than non-brushy

vegetation or dense wood (Lobert & Warnatz, 1993; Ward & Hardy, 1991). Fires in grassy savannah ecosystems may result in most of the vegetation being consumed in the flaming process, while in ecosystems with large amounts of peat, rotten logs, and deep duff, the majority of the biomass is burnt during smouldering combustion when the moisture content is low (Ward, 1999). Moisture content controls the amount of fuel consumed in a fire and has been used as a means of managing smoke production from larger logs and duff (Hardy et al., 2001). Carbon monoxide, methyl chloride, methyl bromide, and methyl iodide, together with amines and nitriles are formed predominantly in the smouldering stage of a fire, while  $\text{NO}_x$  and molecular  $\text{N}_2$  are released during flaming combustion (Shirai et al., 2003). Volatile organic hydrocarbons are vaporized from fuels early in the combustion process and at later stages, as lignin and cellulose are decomposed through pyrolysis (Ward & Hardy, 1991). Smouldering combustion produces greater levels of VOCs than flaming combustion (Miranda et al., 2005). Ward (1990) and Lobert and Warnatz (1993) both describe the combustion process in relation to the smoke produced, and Gao et al. (2003) provide an excellent description of the basic chemistry involved.

Visibility is impaired when particulate matter (PM) and gases in the atmosphere absorb and scatter incoming radiation and reflect light (Garcia-Nieto, 2002; Malm, 1999). PM less than  $2.5\ \mu\text{m}$  in diameter has the greatest effect on visibility and radiation transfer and can act as condensation nuclei for fog formation (Ward & Hardy, 1991). Smoke from wildfires and prescribed burns and annual agricultural or forestry burning can produce a haze that may last for several days or months (Legg & Laumonier, 1999; Nichol, 1997; Robock, 1991). In much of Australia, prevailing winds are often unpredictable and capital cities and larger towns are occasionally covered in a haze of smoke (Packham & Vines, 1978; Vines et al., 1971). For example, smoke from the extensive wildfires in 1939 was observed in New Zealand several days later as it was blown eastward (Vines et al., 1971), and this was certainly the case during bushfires in New South Wales and the ACT in 2001–2002 and in Victoria in 2003.

Much of the early information relating to the general composition of smoke comes from studies of industrial emissions, tobacco smoke, residential combustion, and burning of biomass under controlled laboratory conditions. However, an increasing number of investigations of smoke emissions from wildfires and other types of vegetation fires have been published in recent years. Much of this research has been conducted in southern Africa where annual burning of large quantities of biomass from tropical and savannah ecosystems is common practice

(Scholes et al., 1996). Many more examples are from the United States where a great deal of federal funding has been provided for fire research, particularly in response to a recent increase in the number of wildfires and greater use of prescribed burning. In comparison, investigation of the smoke from biomass burning in Australia has received only moderate research attention. Regardless of location, most of the studies relating to composition of smoke from biomass burning have been concerned with the measurement of CO<sub>2</sub> and CO, as well as NO<sub>x</sub>, O<sub>3</sub>, and trace gases. Much less research attention has been paid to measurement of H<sub>2</sub>, sulfides, VOCs, and PAHs. The literature suggests that continued and more comprehensive analyses of the compounds found in smoke from biomass burning is needed to advance the predictive capacity of smoke behavior and to determine the impacts of smoke (Sandberg et al., 2002).

### 14.3. Estimates of wildfire smoke emissions

Estimates of gaseous emissions from vegetation fires are largely constrained to the last 25 years with evidence emerging for long-range transport of smoke from large-scale slash burning and wildfires (Andreae & Merlet, 2001; Delmas et al., 1995). Severe air pollution caused by fires in Indonesia, the Philippines, and Brazil in 1997–1998 (bin Abas et al., 2004; Heil & Goldammer, 2001) and more recently in Australia have added to this increased profile (Simmonds et al., 2005). The demand for such information is increasing due to the following:

- Accountability by governments and companies for greenhouse gas emissions
- Increased capability for modelling of biogeochemistry, atmospheric processes, and global climate change
- Identification by health authorities of sources of air pollution affecting human health (Global Emissions Inventory Activity, 2002)
- Increased regional haze and impairment of visibility.

A number of large-scale, coordinated biomass burning experiments has allowed characterization of emissions from a range of vegetation types around the world (Andreae & Merlet, 2001; Delmas et al., 1995). Methods adopted in campaigns such as these and in other experimental work, were reviewed extensively by Ward and Radke (1993) and Delmas et al. (1995). Models of emissions from biomass burning using remote sensing data were recently reviewed by Palacios-Orueta et al. (2005).

Radke (1989) estimated that the worldwide total of biomass consumed by burning each year is 100,000 Tg (Teragram = 10<sup>12</sup>g).

Table 14.1. Total annual worldwide emissions from all sources compared to emissions from burning biomass<sup>a</sup>

	Species	Worldwide (Tg) <sup>b</sup>	Biomass burning (Tg)
Gases	CO	600–1300 C	120–510 C
	CH <sub>4</sub>	400–600 C	11–53 C
	NO	25–60 N	2.1–5.5 N
	HCN, CH <sub>3</sub> CN	> 0.4 N	0.5–1.7 N
	H <sub>2</sub>	~ 36	5–16
	CH <sub>3</sub> Cl	~ 2	0.5–2
	COS	0.6–1.5 S	0.04–0.20 S
Particulates	Organic C	~ 180	24–102
	Elemental C	20–30	6.4–28

<sup>a</sup>Data from Crutzen and Carmichael 1993.

<sup>b</sup>Teragram = 10<sup>12</sup> g.

Gaseous emissions from burning of this vegetation represent only a small fraction of total emissions from all sources (Table 14.1). Other estimates indicate that 3800–4300 Tg of carbon (C) is released annually to the atmosphere from vegetation fires (Andreae, 1991; Andreae & Merlet, 2001), including 20,000–33,000 Tg of C as CO<sub>2</sub> (Seiler & Crutzen, 1980). In Australia, estimates of gross release of C from vegetation fires range from 80 to 250 Tg based on estimates of the area burnt that range from 40 to 130 × 10<sup>6</sup> ha (Cheney et al., 1980). In a low fire year (1992) in the Northern Territory, almost 30 Tg of biomass was burnt resulting in emission of 11.3 Tg of CO<sub>2</sub>, 1.0 Tg of CO, 5.2 × 10<sup>-3</sup> Tg of PM, and 26.1 × 10<sup>-3</sup> Tg of NO<sub>x</sub> (Beringer et al., 1995). According to the Darwin Air Emission Inventory (2001), wildfires in the same area caused 94% of annual emissions of PM, and some 83% of that of benzene, 78% of CO, and 46% of VOCs. In contrast, in southern Western Australia, wildfires caused only 3% of annual emissions of PM, no gaseous benzene, 39% of CO and only 3% of VOCs (Department of Environmental Protection, 2003). Differences among topography, climate, burning patterns, and fuel types make a significant difference to gaseous and particulate emissions from vegetation fires in Australia.

#### 14.4. Smoke from vegetation fires and effects on human health

Smoke from any source is known to have significant deleterious effects on human health, particularly in children and the elderly and people with poor respiratory function (World Health Organisation, 1999). Much of the current knowledge about the impact of smoke on human health is

derived from studies of tobacco smoke from cigarettes, smoke from wood fires and ovens (“indoor biomass smoke”) and industrial smoke in densely populated cities (Larson & Koenig, 1994; World Health Organisation, 1999), rather than smoke from vegetation fires. In these studies, exposure to smoke is generally investigated at known concentrations and for a specified duration. In contrast, wildfires and prescribed burning expose humans to high levels of smoke episodically and only for short periods of time (Breysse, 1984; Pinto & Grant, 1999). In Australia, it has been recognized that emissions from both woodsmoke and smoke from bushfires or fuel-reduction burns are generally unknown and need to be monitored and assessed (Lewis & Corbett, 2002; Manins et al., 2001; Sim, 2002).

Smoke contains toxic compounds of both a gaseous and particulate nature, and while the effects of gas phase toxicants are of concern, most of the deleterious effects on human health are from the inhaled particulate phase (Schollnberger et al., 2002; Spengler & Wilson, 1996). Determining the effects of particulates is not straightforward, since it is the gaseous compounds, particularly VOCs and PAHs adsorbed onto the surfaces of PM that have the greatest effect on respiratory health (Dost, 1991). The composition of chemicals on the surface of PM will depend on the conditions under which they are generated (Hueglin et al., 1997; Malilay, 1999).

PM is generally classified by aerodynamic diameter, since this parameter governs the transport and gravitational settling of particles from the air and the deposition within the respiratory system. Smaller particles are deposited further into the lungs; therefore, in health studies a description of particle size is particularly important in determining exposure and human dose. Most of the PM produced by biomass burning has diameters less than  $0.1\ \mu\text{m}$  or between  $0.1$  and  $2.5\ \mu\text{m}$  (Phuleria et al., 2005; Schollnberger et al., 2002); however, ambient air quality standards were originally set to quantify PM with aerodynamic diameter equal to or less than  $10\ \mu\text{m}$  ( $\text{PM}_{10}$ ; e.g., Pope et al., 1991). Annual average exposure to  $\text{PM}_{10}$  in the United States is recommended to be less than  $50\ \mu\text{m m}^{-3}$  with a maximum 24-hour standard period set at  $150\ \mu\text{m m}^{-3}$  (United States Environment Protection Agency, 1999). It is only relatively recently (July 1997) that guidelines determining exposure to finer PM ( $\text{PM}_{2.5}$ ) have been established (Brauer, 1999), with an annual average limit of  $15\ \mu\text{m m}^{-3}$  and a maximum 24-hour standard period set at  $65\ \mu\text{m m}^{-3}$ .

In Australia, health guidelines have taken even longer to be formulated, with air quality standards for  $\text{PM}_{10}$  only endorsed in June 1998. The Australian limits of exposure to  $\text{PM}_{10}$  are lower ( $50\ \mu\text{m m}^{-3}$

within a 24-hour period) than that in the United States; however, there is an allowance for exceeding this limit for up to 5 days per year to allow for smoke emissions from bushfires (Australian National Environment Protection Council, 1998). The national Australian guidelines for exposure to PM<sub>2.5</sub> have recently been amended (July 2003), with data collection taking place until 2005 to facilitate a review of the Advisory Reporting Standards (Australian National Environment Protection Council, 2003). Maximum limits of exposure to PM<sub>2.5</sub> have been set at 25  $\mu\text{m m}^{-3}$  within a 24-hour period and 8  $\mu\text{m m}^{-3}$  over the course of a year.

Gaseous components of vegetation smoke such as SO<sub>2</sub>, CO, NO<sub>x</sub>, O<sub>3</sub>, formaldehyde, acrolein (C<sub>3</sub>H<sub>4</sub>O), and benzene also cause health problems in humans. For example, SO<sub>2</sub> is a colorless gas that is readily soluble in water vapor forming sulfuric acid. Long-term exposure of animals to SO<sub>2</sub> produces damage to airways similar to chronic bronchitis in humans and the effects may be enhanced by simultaneous exposure to ultra-fine particles (World Health Organisation, 2000). Prolonged exposure results in a reduction in lung volume and capacity for gaseous diffusion. Another example is formic acid, which is one of the most abundant VOCs emitted from burning biomass and is produced when formaldehyde is oxidized in a moist environment or when low concentrations of oxygen are coupled with high concentrations of formaldehyde (Ciccioli et al., 2001). Formaldehyde is normally present in the atmosphere at concentrations of between 4 and 20  $\mu\text{g m}^{-3}$  depending on location of sampling and proximity to urban sources. Dost (1991) has reviewed the formation and toxicology of formic acid in detail. It can cause irritation to the nose, eyes and throat at concentrations of 100–3000  $\mu\text{g m}^{-3}$ , with damage to cells occurring through exposure at this concentration for longer periods of time or at greater concentrations (10,000–20,000  $\mu\text{g m}^{-3}$ ). The threshold concentration of formic acid for irritation is unknown but is thought to be higher than for formaldehyde. Acrolein is a more potent irritant than formaldehyde and can effect respiratory function at concentrations as low as 100  $\mu\text{g m}^{-3}$  (Ward, 1999) but is released in woodsmoke in much smaller quantities (Dost, 1991).

Worldwide, wildfires are becoming more prevalent and prescribed burning is being used more frequently as a means of reducing fuel loads. In addition, air quality regulations are becoming stricter, more people are living in the interface between urban and rural areas, and the general public is becoming less tolerant of air contamination (Sandberg et al., 2002). Despite this, the effects of smoke from biomass burning on human health at regional or global scales are unknown (Ward, 1999). There is a relatively large pool of information regarding the effect of smoke on

firefighter health and safety (e.g., Brandt-Rauf et al., 1988; Mustajbegovic et al., 2001; Reinhardt & Ottmar, 1997; Slaughter et al., 2004), but little long-term health effects studies have been done in regard to firefighter exposure (Booze et al., 2004). There is a distinct lack of studies concerning the production of smoke at the “ground level” and the impact this smoke may have on localized human populations. Brauer (1999) highlights this inadequacy by recommending further studies on health impacts of large-scale fire-related episodes of air pollution by using standardized study protocols and over a range of locations.

The association between respiratory impairment and exposure of the general public to smoke from wildfires or prescribed burning has been noted in a number of epidemiological studies, but a causal link is yet to be established. For example, smoke from the 1997–1998 fires in Indonesia affected air quality (Aditama, 2000) and resulted in a significant increase in the number of people requiring clinic visits or hospital admission for smoke-related illnesses, and this has been reported as such in some studies (Phonboon et al., 1999), but not in others (Emmanuel, 2000). In the United States, smoke from large forest fires resulted in increased hospital visits in at least two studies (Duclos et al., 1990; Mott et al., 2002). Similarly, increased levels of particulates (PM<sub>10</sub>) in smoke from biomass burning in northern Australia caused an increase in hospital visits or use of medication for asthma (Chen et al., 2006; Johnston et al., 2002) but not after a large wildfire event in New South Wales (Smith et al., 1996). A fourth Australian study did not find any reduction in lung function in symptomatic children during the same fires (Jalaludin et al., 2000). In comparison, exposure to high levels of particulates in anthropogenic air pollution is more strongly linked to respiratory illness and reduced lung function (Vedal et al., 1998), and exposure to smoke in indoor air generated from cooking and heating has been linked to respiratory disease and poor lung function (Brauer, 1999; Eisner et al., 2002; Larson & Koenig, 1994). These studies relate to exposure to particulates at very high levels (1000–2000  $\mu\text{g m}^{-3}$ ) for long periods of time (20 years or more) so comparisons with exposure to smoke from wildfires or prescribed burns are neither straightforward nor particularly valid.

#### **14.5. Effects of smoke on Australian ecosystems**

There is a small body of literature relating smoke from biomass burning to plant functioning and even less dealing with fauna (see Whelan, 1995). The literature concerning fauna reports of survival of mice in burrows with adequate ventilation or death of animals due to suffocation from

smoke. There are no studies on the toxicology of smoke from biomass burning on any form of native fauna. The bulk of Australian publications are concerned with the effect of smoke on germination of seed, with little information available on the direct effects of smoke from biomass burning on plant or animal physiology or biochemistry. In contrast, the effect of air pollution (as opposed to vegetation smoke) on whole ecosystems, particularly vegetation, has long been noted and is a major topic of research worldwide. Thus, there are many books and review articles dealing with the effects of air pollution, and this topic is the subject of regular international symposia. Because many of the reactive chemicals found in air pollution are also common in smoke from vegetation fires, the literature dealing with air pollution is a potential source of information. However, several failings can be levelled at the majority of these pollution studies when considered in the context of the effects of smoke. These inadequacies are discussed below.

The first, a more general criticism, is that plant responses to air pollution are generally measured using seedlings and saplings of target species, with only a few extrapolations to mature field-grown trees (Bytnerowicz, 1996). Another general criticism is that many of the pollution studies are done in the laboratory under carefully controlled conditions, whereas pollutants in the free atmosphere (including those in smoke) are dynamic and can vary in concentration over a great range of time scales (Cape & Unsworth, 1988). A third failing is that many of the pollution studies have been from mesophytic or tropical environments and are therefore generally inappropriate for predicting the response of sclerophyllous vegetation from xerophytic communities (Wilson, 1995). A useful exception is the body of air pollution literature relating to *Pinus ponderosa*, *P. radiata*, and *P. halepensis*, species which are typically associated with fire-prone mediterranean climates (e.g., Momen et al., 2002; Takemoto et al., 2001).

A final inadequacy we might note is that air pollution studies are mostly concerned with long-term exposure to air pollution (months) whereas exposure to smoke from biomass burning is episodic and transitory (hours to days, occasionally weeks). In addition, the effects of the gaseous and particulate components of air pollution on plant growth and development are investigated at concentrations two to three times ambient, whereas this is generally not a realistic situation for vegetation fires. Despite these problems, the synthesis presented here draws heavily on studies of air pollution, as these often provide the only guide to what might be expected from exposure of flora and fauna to smoke from biomass burning. Similarly, the chemico-physical influences of smoke, such as high temperatures, low light and high vapor pressure

deficit, are poorly studied, and information must be obtained from related fields.

The influence of air pollution on plants is a complex subject and dependent on the interactions of concentrations and types of pollutants involved and on biochemical and physiological properties of the vegetation (Fig. 14.1; Bytnerowicz, 1996). By extrapolation, the effect of smoke from biomass burning on vegetation must be equally complex. Unfortunately, much of the biochemistry involved in the interaction of plant tissues with pollution is not yet fully elucidated (Bytnerowicz, 2002; Polle, 1998), and little, if anything, is known about the biochemical reactions of smoke emissions in plant tissues. Effects of air pollution (and therefore smoke) on vegetation can be at cellular, whole plant, species, and ecosystem levels and can have both positive and negative effects on cells (Fig. 14.1; Bytnerowicz, 1996; Heck, 1973; Kozłowski, 1980).

As with general air pollution, smoke may impinge on plant organs (leaves, stems, trunks) and on soil surfaces. There is equal opportunity for smoke to promote cell growth as there is for it to be detrimental by causing cell injury or death (Fig. 14.1). Growth of plants would certainly be promoted if nutrients such as ammonium and nitrate were deposited or washed from a smoky atmosphere to soil surfaces in the course of a wildfire. However, reduced light conditions and lower vapor pressure deficit may temporarily alter the capacity for photosynthesis (environmental level effects, Fig. 14.1). However, unlike air pollution, separation of the effects of heat from fire from the effects of the smoke produced is a difficult task. As suggested earlier, air pollution is relatively long-lasting, whereas smoke from biomass burning is fairly transitory, and the effects of smoke from vegetation fires are likely to be short. Biotic factors such as mycorrhizas, pathogens, insects, competition, N<sub>2</sub>-fixation, and genetic variability, and abiotic factors such as humidity, temperature, radiation (light and UV-B), wind, CO<sub>2</sub>, water and nutrient availability, and soil type and condition can also interact with vegetation to modify physiological responses (Bytnerowicz, 1996; Krupa & Manning, 1988). The interaction of smoke from vegetation fires with this list of factors remains unclear.

#### **14.6. Types of deposition**

Air pollutants, including those from biomass burning, can reach plant and soil surfaces as PM and can enter through cuticular surfaces or stomata as gases (both often referred to as dry deposition) or dissolved in rain, snow, hail or fog (wet deposition; Bytnerowicz & Grulke, 1992;

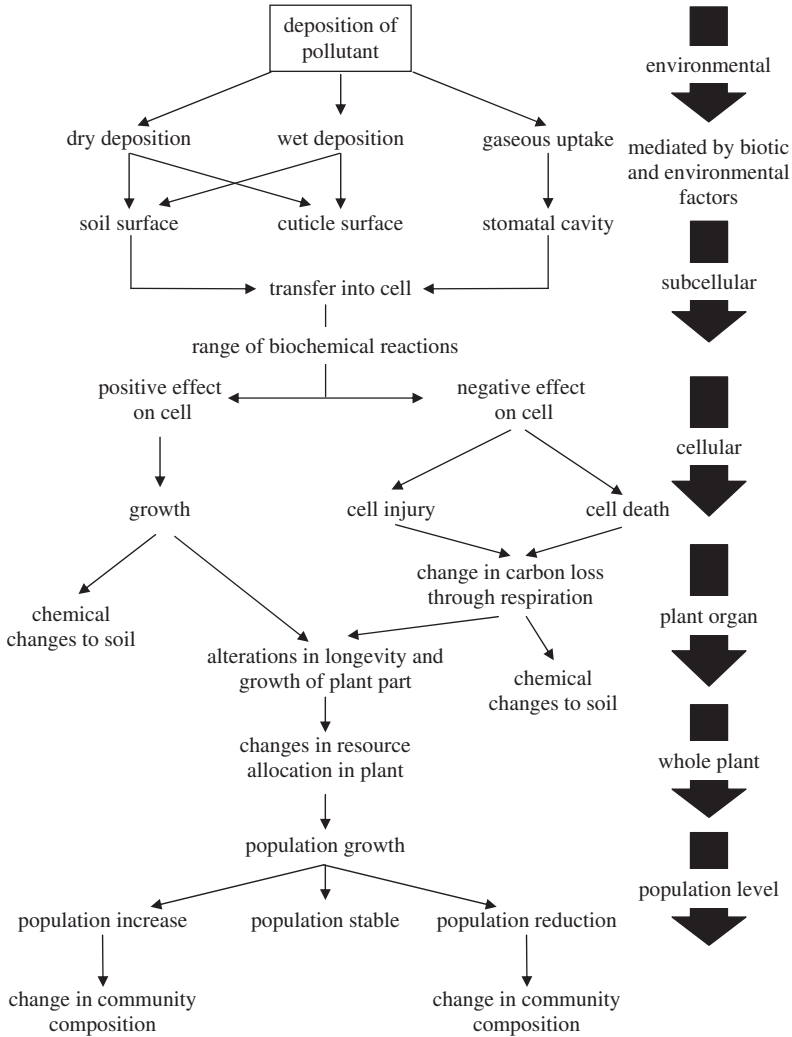


Figure 14.1. Deposition of air pollutants and the effects on plants at the ecosystem, individual, and cellular organizational levels. The range of biochemical reactions includes effects on enzymes, changes to metabolic pathways and cellular constituents, and alterations in the genetic code by transcription and translation. (Redrawn from Bytnerowicz, 1996; Heck, 1973; Kozlowski, 1980.)

Crutzen & Andreae, 1990; Grantz et al., 2003). These pathways are indicated in Fig. 14.1. Occult deposition is intermediate between wet and dry deposition and refers to deposition of small water droplets in fog or interception of cloud water at high altitudes (Cape & Unsworth, 1988). Logically, dry deposition of pollutants on vegetation and soil surfaces dominates in low rainfall regions, particularly during dry periods, and wet deposition dominates in more humid and mountainous regions (Cape & Unsworth, 1988; Crutzen & Andreae, 1990).

The type and location of deposition of pollutants on plants will cause different types and extent of interactions (Bytnerowicz & Grulke, 1992). For example, stomata might be expected to be the main point of entry for gaseous pollutants (Fig. 14.1), so regulation of the opening and closing of stomata will play a key role in determining plant sensitivity (Darrall, 1989). The molecular weight and permeability of a gas will determine how well it penetrates into plant tissue (Lendzian & Kerstiens, 1991). At the leaf surface there is generally little active uptake or exclusion of substances, including pollutants, but passive movement of solutes will be dependent on the physical and chemical nature of the leaf surface (Cape & Unsworth, 1988). Once water droplets are in contact with the leaf surface, organic and inorganic ions may diffuse from solution into the leaf (e.g.,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) or are leached from within cells (e.g.,  $\text{SO}_4^{2-}$ ). The presence of epicuticular wax, trichomes, and hairs provide a barrier for water adhesion and wet deposition and consequently for solute transfer. Consequently, the morphological and anatomical adaptations of fire-prone, sclerophyllous vegetation are likely to confer different protection to airborne pollutants than that of mesophytic vegetation.

Plants generally respond differently to air pollution at different stages of their life cycle (Reiling & Davison, 1994). Young expanding leaves are likely to be more sensitive than older leaves, and seedlings may be more sensitive than established plants (Kozłowski, 1980). However, it is still a matter of dispute if seedlings are more susceptible than adult plants to pollution and most of the differences between seedlings and older plants, as well as between young and old foliage, can be attributed to differences in rates of uptake. Since much of the prescribed burning in Australia takes place during periods of active growth and flowering, there may be greater implication for response to components of combustion than at other times of the year. As Robinson et al. (1998) point out, a small disturbance in stomatal control during periods of stress may have considerable consequences for plant survival. Given that wildfires in Australia are most common in the hot dry months (i.e., periods of water-stress), vegetation may well be vulnerable to additional stress induced by the effects of smoke, albeit for a relatively short period of time.

The position of leaves within plant canopies largely determines the extent of their exposure to wet and dry deposition (Grantz et al., 2003). Modelling of large-scale deposition suggests that most aerosols are deposited on upper and outer surfaces of forests with exponentially lower transfer downwards into the canopy (Shaw et al., 1994). The canopy thus acts as a filter for tree seedlings and understory vegetation. Several studies have sampled leaves from outer edges and well within the canopy and herbaceous layer to try to quantify exposure to air pollution (Kozłowski, 1980; Steubing et al., 1989). This line of evidence suggests that understory vegetation in Australia in open woodlands with less crown cover is more likely to be exposed to smoke from prescribed burns and wildfires than the understorey in closed canopy forests.

Leaves of vegetation in unburnt areas surrounding a fire are likely to be coated in a layer of PM. Smoke from wildfires contains particulates that may range in size from 0.5 to 43  $\mu\text{m}$  (Ward & Hardy, 1991), the smallest of which may have long residence times in the atmosphere and can be carried hundreds of kilometers in drifting smoke plumes (Crutzen & Andreae, 1990). Hirano et al. (1995) found that dust applied to leaves of cucumber and kidney bean decreased stomatal conductance under well-lit conditions, decreased photosynthetic rate by shading the leaf surface, and increased leaf temperature by greater absorption of incident radiation. Such physiological changes are likely to be similar for plants coated with fine ash from biomass burning. In addition, it seems likely that prevailing warm and dry conditions, that produce water and heat stress in plants and that are associated with the lack of rainfall for washing leaf surfaces, could well exacerbate the leaf-coating effects of fire-produced ash and particulates. Given that the variety of effects of PM on vegetation, soils, and whole ecosystems has been thoroughly reviewed by Grantz et al. (2003), investigation into the load and effect of PM on surrounding unburnt vegetation after prescribed burning and wildfires is clearly warranted.

It is obvious that plant responses to long-term exposure to gaseous pollutants are not always indicative of responses to short-term exposure. For example, in one of the few publications dealing directly with the effect of smoke on plants, Gilbert and Ripley (2002) found exposure to smoke for only 1 minute was enough to reduce stomatal conductance and intercellular levels and rates of assimilation of  $\text{CO}_2$  of *Chrysanthemoides monilifera* for up to 5 h. Normal stomatal functioning was re-established after 24 h. Following a similar pattern, all populations of *Plantago major* showed reduced stomatal conductance within hours of coming in contact with high levels of  $\text{O}_3$ , but more sensitive populations showed different stomatal responses to that of less sensitive populations over the following

4 days of exposure (Reiling & Davison, 1995). Stomata of *Vicia faba* responded within 15 min of exposure to SO<sub>2</sub> regardless of the concentration of the pollutant, and the effect remained for several days after exposure (Black & Unsworth, 1980). Stomatal response to low concentrations of gaseous pollutants (particularly ozone) often includes loss of stomatal control so that stomata remain open under dry conditions, rendering plants more susceptible to drought and presumably, the effect of pollutants. This may be a more realistic scenario for short-term exposure to vegetation smoke during summer wildfires and should be investigated further.

#### 14.7. Effects of smoke on soil, roots, and microorganisms

Along with the obvious effects of airborne pollutants on aboveground vegetation there may be indirect effect via the soil (Fig. 14.1). Several authors have concluded that induced changes in soil chemistry will have a greater impact than will direct action of pollution on foliage (Cape & Unsworth, 1988; Grantz et al., 2003). As an example, elevated CO<sub>2</sub> has also been shown to alter soil properties by promoting greater accumulation of carbon and nutrients in vegetation and soil horizons (Johnson et al., 2003). The impact of smoke from biomass burning on soil has yet to be considered.

Root growth can be used as an indirect yet sensitive indicator of the physiology of plant shoots, and changes in shoot–root ratios are often used as an indicator of changes in nutritional status of plants and reduced translocation of photosynthate (Ormrod, 1982). Using the milieu of pollution studies, root biomass of mature trees in natural stands of *Pinus ponderosa* was up to 16 times greater in unpolluted sites than polluted sites (Grulke et al., 1998). At a different scale, root initiation in mung bean (*Vigna radiata*) and tomato (*Lycopersicon esculentum*) can be promoted by application of aqueous extracts of smoke (Taylor & van Staden, 1996, 1998), but this research has yet to be extended to woody plants or natural environments. The interaction of coal-smoke and root-knot nematode infection on okra and eggplant suggests greater susceptibility for infection and reduced productivity in areas of high air pollution (Khan & Khan, 1994a, 1994b). This type of response is from plants with relatively long-term exposure to coal-smoke (3 months) and may or may not be translatable to the effect of smoke from vegetation fires. Changes in the availability of nutrients to vegetation and soil microorganisms may cause disruptions in ecosystem functioning, particularly in Australian ecosystems where balanced nutrient cycling is

commonplace. Losses and additions of nutrients in soil during burning have been well-studied for Australian ecosystems (see [Raison, 1979](#)), but nutrient alterations via smoke from vegetation fires is yet to be fully elucidated.

Smoke has been shown to have variable impacts on microorganisms. In early studies, traditional preservative applications of smoke to fungal species produced a range of responses, with critical exposure time of spores and mycelium ranging from seconds to minutes ([Parmeter & Uhrenholdt, 1975a, b](#); [Zagory & Parmeter, 1984](#)). At the other extreme, liquid condensates of smoke from beech wood killed spores of several common mold fungi ([Wolkowskaja & Lapszin, 1962](#)). Despite the well-known use of smoke as a sterilizing agent, there has been little research into smoke effects on soil microbes in natural ecosystems.

In a broader context, functional groups of fungi have been used as bioindicators of environmental pollution (e.g., [Arnolds, 1991](#); [Fellner, 1993](#); [Lagana et al., 1999](#); [Wallenda & Kottke, 1998](#)). Similarly, lichens have been used as indicators of air quality (e.g., [Conti & Cecchetti, 2001](#); [Seaward, 2004](#)). Decreases in the ratio of mycorrhizal to saprophytic fungi have been used to indicate forest decline due to anthropogenic contamination ([Fellner, 1993](#); [Rühling & Tyler, 1991](#)), while nitrogen deposition appears to affect formation of fruiting bodies more readily than belowground structures ([Wallenda & Kottke, 1998](#)). [Steubing et al. \(1989\)](#) found the ratio of soil bacteria to fungi was depressed when exposed to SO<sub>2</sub>, NO<sub>2</sub>, and O<sub>3</sub> applied separately and in combination. Infection by mycorrhizal fungi is generally reduced with increased additions of nitrogen ([Caporn et al., 1995](#)), and simulation of long-term atmospheric deposition of nitrogen by [Lee and Caporn \(1998\)](#) demonstrated its potential to radically change above- and belowground processes. Microbial and fungal activities are essential to the efficient and healthy functioning of all ecosystems, and knowledge of how smoke affects their ecological processes would be productive.

#### **14.8. Effects of smoke on seed germination and other processes**

By far the most intensively studied effect of smoke on plants is the ability of combustion compounds from burnt vegetation to stimulate germination of seed. This research has been reviewed extensively by [Brown \(1993\)](#), [Brown and van Staden \(1997\)](#), and [Vigilante et al. \(1998\)](#) and will not be elaborated here. However, since the publication of these three major reviews, research has focussed on extending the range and type of species tested (e.g., [Tang et al., 2003](#); [Wills & Read, 2002](#)).

Other recent research has concentrated on the interaction of smoke-promoted germination with other germination cues such as temperature, irradiance, hormones, mechanical and chemical scarification, seed burial and nitrogenous compounds. Smoke not only enhances seed germination but has also been found to stimulate flowering (Keeley, 1993; LeMaitre & Brown, 1992) and release of bulbs from dormancy (Tompsett, 1985).

#### 14.9. Effects of volatile organic compounds on ecosystems

VOCs are a diverse group of compounds and include isoprene, terpenes, alkanes, alkenes, alcohols, esters, carbonyls, and acids (Ciccioli et al., 2001; Kesselmeier & Staudt, 1999; Owen et al., 2001). Acetic and formic acids are the most abundant VOCs emitted from burning biomass (Ciccioli et al., 2001), whereas isoprene and monoterpene constitute more than 50% of VOCs in natural plant emissions (Kesselmeier & Staudt, 1999). Detailed identification and chemical analysis of functional groups of particulates such as VOCs have the potential to be used as markers compounds, which could then be used to distinguish smoke from biomass burning from other sources (Brauer, 1999). This information would aid in tracing smoke plumes in both time and space and could be used to distinguish biomass smoke from other sources of pollution, thus improving emission quantifications (Sandberg et al., 2002).

There are limited studies on the effects of VOCs as primary pollutants on plants (Cape, 2003; Cape et al., 2003a). Several of these studies have suggested that plants may absorb and metabolize VOCs under different circumstances, but the effects on the plant, toxic or otherwise, is largely unknown (e.g., Binnie et al., 2002; Collins et al., 2000; Cornejo et al., 1999). The research that is available is generally concerned with the effects of ethylene as a plant hormone (Cape et al., 2003b) or the effect of VOCs as components of air pollution, such as in vehicle exhaust gases (e.g., Viskari et al., 2000). Responses to VOCs are variable; for example, exposure of herbaceous plants to a mixture of six VOCs caused changes (both reductions and increases) in seed production, leaf water content and photosynthetic efficiency in some species (Cape et al., 2003a). These and other relevant studies involve relatively short-term exposure (hours and days rather than months or years, see Cape, 2003), which, unlike most air pollution studies, can provide realistic comparisons for exposure of plants to VOCs in smoke from vegetation fires.

#### 14.10. Biogenic production of volatile organic compounds

More often than not, research has been initiated to determine VOC emissions from plants rather than absorption from the atmosphere (see reviews by Cape, 2003; Penuelas & Llusia, 2001). Along with isoprene and monoterpene (Guenther et al., 1995), other VOCs emitted from plants included aromatic hydrocarbons such as toluene, xylenes, ethyl-, methyl- and propyl-benzenes and naphthalene (e.g., Viskari et al., 2000). Actual rates of VOC emission can equate to more than 10% of the carbon gained through photosynthesis (Holzinger et al., 2000). Plants can be categorised according to major VOC compounds produced and emitted (Harley et al., 1999; Lerdau & Gray, 2003; Owen et al., 2001). For example, the composition and concentration of terpenoids in plant tissue has been used to taxonomically separate certain species (Adams, 1994; Benjamin et al., 1996). Along similar lines, recent unpublished research by one of the authors has focused on environmental conditions associated with production and emission of VOCs in eucalypts. Intercepted radiation has a strong influence on emissions of isoprene but not monoterpenes or carbonyl compounds. Temperature strongly influenced emissions of all classes of terpenes but again had less influence over carbonyl compounds. Instead, factors such as atmospheric concentration and concentrations of the precursor compounds within tree sap appear to be better predictors for these compounds.

Many studies have identified and quantified monoterpenoids in plants, but only one study has made the link between this group of phytochemicals, seasonal conditions, and plant flammability (Owens et al., 1998; and see Bond & Midgley, 1995; Zedler, 1995). Most studies of plant flammability only concentrate on heat and ash content, temperature of ignition, and physical properties such as surface area-to-volume ratio and fuel particle density (e.g., Dimitrakopoulos, 2001; Mak, 1988; Papio & Trabaud, 1990). The line of study involving phytochemistry and flammability of plants may be useful in conjunction with distribution patterns of species and to predict the composition and production of VOCs.

Plant roots and other microorganisms in the rhizosphere also produce VOCs but in different patterns and responses from aboveground vegetation (Steeghs et al., 2004). Such exudates can have a wide variety of effects on the rhizosphere and soil microbial community, including changing chemical and physical properties of the soil, chemical communication, and inhibiting growth of competing organisms. For example, the effect of VOCs produced by soil bacteria on fungal growth and enzyme activity varied widely and depended on the species of fungi

and bacteria involved and on the environment in which they interacted (Mackie & Wheatley, 1999). How these metabolic emissions may be affected by changes in simple parameters such as temperature and moisture is unknown, and information about more complex interactions such as the effect of smoke from biomass burning is yet to be acquired. Further studies investigating aspects of physiological responses of ecosystems to smoke including VOCs are needed in both practical (e.g., effect of smoke from prescribed fires on grape and soft fruit quality) and land management contexts (e.g., losses and gains of nutrients in smoke).

Eucalypts grow widely in the Australian landscape and are cultivated in large numbers in plantations here and around the world. In Australia, there are over 160 million hectares of native forests dominated by species of *Eucalyptus* and *Acacia* and 740,000 ha of plantations of *Eucalyptus globulus* (National Forest Inventory, 2007). The production of VOCs by such vegetation is estimated to be up to 60% of total VOC emissions (National Environmental Protection Council, 1997). For example, the characteristic blue haze in the Dandenong Ranges in Victoria and the Blue Mountains in New South Wales is associated with emissions of VOCs from eucalypts. Rates of emissions of monoterpene range from 0 to  $5.4 \mu\text{g g}^{-1} \text{h}^{-1}$  and from 5.3 to  $69.0 \mu\text{g g}^{-1} \text{h}^{-1}$  for isoprene (He et al., 2000). In this study, *E. globulus* was the greatest emitter of both VOCs. There is emerging evidence that emissions vary with changes in temperature and water availability (Guenther, 2001; Guenther et al., 1999) and may be exacerbated under extreme conditions of heat or drought (Llusia et al., 2006). Biogenic emissions from eucalypts are species-specific in both rates of production and composition (He et al., 2000; Maleknia et al., 2006). The age of the leaf is also important, with young eucalypt leaves often containing more oil than mature leaves (Silvestre et al., 1997) and with higher emission rates (Street et al., 1997). With eucalypts dominating the forested vegetation of Australia and increasing establishment of eucalypt plantations worldwide, it is important to understand the background emissions of VOCs from living trees and the potential for increased emissions with changes in environmental condition, particularly during fire events.

#### 14.11. Summary

Advancing our knowledge of the composition of smoke—including its unique, hazardous, or reactive compounds—would have a number of advantages. First, detailed identification and chemical analysis of

functional groups on particulates (e.g., VOCs) could be used to determine markers compounds that could then be used to distinguish smoke from biomass burning from other sources and aid in increasing the accuracy of quantification of worldwide emissions. Second, the quantification of hazardous compounds in smoke from biomass burning could be used in risk analysis of health and safety of firefighters and the general public during wildfire and prescribed burning activities and allow decision-making processes to be better informed. Third, studies involving phytochemistry and flammability of ecosystems may provide the potential to use distribution patterns of groups of species to predict the composition and production of VOCs and other important components in smoke. Knowledge of all aspects of smoke from biomass burning has developed steadily over the past 25 years and will continue to progress as governments, land management and health agencies, and researchers and the general community become more aware of the potential impacts of this source of air pollution on their surrounding environment.

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