5 Fungi and Industrial Pollutants

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I. Introduction

Fungi may be exposed to a wide variety of organic and inorganic pollutants in the environment. Since fungi play a major role in carbon, nitrogen, phosphorus and other biogeochemical cycles (Wainwright 1988a, b; Gadd 2006, 2007, 2008a, b, 2011), impairment of fungal activity could have important consequences for ecosystem function. It is obviously desirable that more is known about the impact of pollutants on these organisms. Unfortunately, while it is easy to speculate on the likely effects of pollutants on fungi, it is often far more difficult to demonstrate such effects. Studies on pollutant effects on fungal populations are difficult, largely because of the inadequacy of many of the techniques which are available to study fungi and the complexity of mixed microbial communities (Anders and Domsch 1975; States 1981; Doelman 1985; Gadd et al. 2007). However, an appreciation of the effects which pollutants can have on fungi can be obtained by a combination of the following measurements: (1) pollutant concentration, composition and distribution, (2) pollutant bioavailability, (3) pollutant concentrations that cause a toxic or physiological response in vitro, (4) effects of the pollutant on fungal population/community size and composition and (5) secondary changes resulting from pollution effects on fungal populations, e.g. impact on leaf litter decomposition. While pollutant concentration and composition may be determined using standard analytical techniques, with varying degrees of difficulty depending on the pollutant and the environmental matrix,

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the analysis of pollutant speciation and the bioavailability remain challenging problems.

The effect of pollutants on fungal population/community size and composition is particularly difficult to assess. Many earlier studies used the dilution plate count or similar approaches to assess changes in fungal community composition. The shortcomings of this technique have been criticised at length and are well known. To overcome problems relating to the use of plate counts, biomarkers such as phospholipid fatty acid (PLFA) composition and extraction and analysis of DNA are now routinely used, though no methods are exempt from problems (Gadd et al. 2007). Another problem is that it is unlikely that a meaningful picture of how fungi respond to pollutants in the environment can be gained from determining responses to pollutants added to solid or liquid growth media in laboratory experiments. The effects of toxic metals on soil fungi growing in vitro, for example, are markedly influenced by the composition of the medium used: metals are likely to be more toxic to fungi in low-carbon media than in carbon-rich media where the production of large amounts of extracellular polysaccharides and chemical interactions with the medium will tend to reduce metal availability. Medium components may also complex or precipitate metals out of the solution, making them unavailable (Gadd and Griffiths 1978; Hughes and Poole 1991; Gadd 1992). Finally, interactions between different pollutants and their breakdown products may have a major influence on the toxicity of a pollutant in the natural environment. This chapter will outline some of the main effects of organic and inorganic pollutants on fungi and will include the discussion of effects at cellular and community levels and their applied and environmental significance.

II. Predicted Effects of Pollutants on Fungal Populations

Environmental pollution might be expected to lead to both toxic (destructive) and enrichment disturbances on fungal populations (Wainwright 1988b). Although toxic disturbance is likely to predominate, instances will occur where both types of disturbance are found together. Toxic disturbance of fungal populations is likely to be particularly damaging to ecosystem function, while the rarer enrichment disturbance may occasionally produce beneficial effects on soil processes. Toxic disturbance is likely to lead to a reduction in fungal numbers and species diversity, as well as biomass and activity changes which may detrimentally influence fundamentally important processes such as litter decomposition (Freedman and Hutchinson 1980; Hiroki 1992; Fritze and Baath 1993). The resultant degree of toxic disturbance will depend upon both toxicant concentration and its availability to the fungal population, as well as to the susceptibility of the individuals involved. Toxicants may be selective and affect only a few species, or they may have a more generalised effect. Selective inhibition may have less of an impact on overall soil fungal activity than might be imagined, since susceptible species can be replaced by more resistant fungi, some of which may be more active in a given physiological process than the original population. While concentration effects are generally emphasised, it is surprising how often the question of toxicant bioavailability is avoided in studies on the effects of pollutants on microorganisms. In soils, for example, bioavailability of a pollutant will generally depend upon factors such as (1) adsorption to organic and inorganic matter, (2) chemical speciation, (3) microbial transformation and/or degradation and (4) leaching. Another factor of importance in relation to the effects of toxicants on soil fungi concerns nutrient availability. Fungi are generally thought to be already stressed by the low levels of available carbon present in most soils and other environments (Wainwright 1992). They will grow slowly, if at all, under these conditions and may be more susceptible to pollutants than when growing in high-nutrient conditions.

Fungal populations are unlikely to remain static when confronted with a toxic agent, and resistant populations are likely to develop which will be a major factor in determining population responses to the pollutant. On the other hand, a number of studies have shown that fungi isolated from metal-contaminated soils show less adaptation to toxic metals, such as copper, than might be expected (Yamamoto et al. 1985; Arnebrant et al. 1987). Mowll and Gadd (1985) also found no differences in the sensitivity of *Aureobasidium pullulans* to lead when isolates from either contaminated or uncontaminated phylloplanes were compared.

Enrichment disturbances may also be either selective or nonselective. Nonselective enrichment disturbance might theoretically result from the input into the ecosystem of a pollutant which is widely used as a nutrient source. Since such enrichment is rare, most examples of this form of disturbance will be selective. Reduced forms of sulphur are, for example, likely to enrich the soil for S-oxidising fungi, while phenolics and hydrocarbons may favour species capable of utilising these compounds.

III. Fungi and Xenobiotics

Some fungi have remarkable degradative properties, and lignin-degrading white rot fungi, such as *Phanerochaete chrysosporium*, can degrade several xenobiotics including aromatic hydrocarbons, chlorinated organics, polychlorinated biphenyls, nitrogen-containing aromatics, and many other pesticides, dyes, and xenobiotics (Prenafeta-Boldú et al. 2006; Pinedo-Rilla et al. 2009; Cerniglia and Sutherland 2010; Harms et al. 2011). Such activities are of bioremedial potential where ligninolytic fungi have been used to treat soil contaminated with pentachlorophenol (PCP) and polynuclear aromatic hydrocarbons (PAHs). In general, treatment involves inoculation of the contaminated soil followed by nutrient addition, irrigation and aeration and maintenance by general land farming procedures. Correct preparation of the fungal inoculum can be crucial: fungi may be grown on lignocellulosic substrates prior to introduction into the soil (Singleton 2001; Baldrian 2008). Treatment can take weeks to months or longer depending on the level of contamination and environmental factors. In many cases, xenobiotic-transforming fungi need additional utilisable carbon sources because although capable of degradation, they cannot utilise these substrates as an energy source for growth. Therefore inexpensive utilisable lignocellulosic wastes such as corn cobs, straw and sawdust can be used as nutrients for enhanced pollutant degradation (Reddy and Mathew 2001). Wood rotting and other fungi are also receiving attention for the decolorisation of dyes and industrial effluents and various agricultural wastes such as forestry, pulp and paper by-products, sugarcane bagasse, coffee pulp, sugar beet pulp, apple and tomato pulp and cyanide (Knapp et al. 2001; Barclay and Knowles 2001; Cohen and Hadar 2001).

Most pollutant degraders belong to the phyla *Ascomycota* and *Basidiomycota*, followed by the subphylum *Mucoromycotina* (Harms et al. 2011). Some genera with well-known degradative properties include species of *Cladophialophora*, *Exophiala*, *Aspergillus*, *Penicillium*, *Cordyceps*, *Fusarium*, *Pseudallescheria*, *Acremonium*, *Neurospora*, *Graphium* and *Phoma* with degradable substrates including aliphatic hydrocarbons, chlorophenols, polycyclic aromatic hydrocarbons (PAHs), pesticides, dyes, 2,4,6-trinitrotoluene (TNT), polychlorinated dibenzo-p-dioxins (PCDDs), Royal Demolition Explosive (RDX) and methyl tert-butyl ether (MTBE) (Chang 2008). Yeasts include degraders of n-alkanes, n-alkylbenzenes, crude oil, the endocrine-disrupting chemical (EDC) nonylphenol, PAHs and TNT, e.g. *Candida*, *Kluyveromyces*, *Pichia*, *Saccharomyces* and *Yarrowia* spp. (Harms et al. 2011). In the *Mucoromycotina*, *Cunninghamella*, *Mucor* and *Rhizopus* spp. (*Mucorales*) include degraders of PAHs, pesticides, textile dyes and TNT (Harms et al. 2011). Mycorrhizal fungi are also able to degrade various organic pollutants, e.g. chloroaromatics, PAHs, TNT, certain herbicides and atrazine (Meharg and Cairney 2000a, b; Volante et al. 2005; Harms et al. 2011). The low specificity of many fungal degradative enzymes means that producing organisms can co-metabolise many different compounds. *Phanerochaete chrysosporium*, for example, can degrade benzene, toluene, ethylbenzene and xylene (BTEX) compounds, nitroaromatic and N-heterocyclic explosives (TNT and RDX, respectively), organochlorines (chloroaliphatics, chlorolignols, chlorophenols, polychlorinated biphenyls and PCDDs), PAHs, pesticides, synthetic dyes and synthetic polymers (Asgher et al. 2008; Baldrian 2008). The range of oxidoreductases that can degrade organic compounds includes laccases, tyrosinases and peroxidases (Majeau et al. 2010). Other enzymes include mixed function cytochrome P450 oxidases, transferases, aromatic nitroreductases and quinone reductases (Harms et al. 2011).

Polycyclic aromatic hydrocarbons (PAHs) enter the environment via many routes, including fossil fuel combustion, vehicle exhaust emissions, gas and coal tar manufacture, wood preservation processes and waste incineration (Harvey 1997; Pozzoli et al. 2004). Many PAHs are toxic towards microorganisms, plants and animals, and PAHs of low molecular weight and high water solubility are the most toxic (Cerniglia and Sutherland 2006). PAHs disappear relatively slowly in the environment through physical, chemical and biological processes, some of which are mediated by bacteria and fungi. PAH recalcitrance in soils and sediments increases with molecular weight, but several other physicochemical and biological factors can contribute to this, e.g. lack of PAH-degrading microorganisms, nutrient deficiency, low bioavailability, preferential utilisation of more easily degradable substrates, the presence of other toxic pollutants or breakdown of products (Cerniglia and Sutherland 2006). Other related factors that affect PAH biodegradation in soil include soil type, pH, temperature, oxygen concentration, irradiation as well as the solubility, volatility, and sorption properties of the PAHs (Lehto et al. 2003; Huesemann et al. 2003; Rasmussen and Olsen 2004). Bioremediation by mixed communities may be enhanced by bacteria that produce degradative enzymes as well as biosurfactants (Straube et al. 1999; Cameotra and Bollag 2003). Aerobic biodegradation of PAHs by soil microorganisms uses monooxygenase, peroxidase and dioxygenase pathways; the first and third of these pathways are utilised by bacteria, while the first and second are found in fungi. The use of filamentous fungi may be advantageous when translocation of the pollutant through the mycelium is required for detoxification (Harms et al. 2011). Fungi have also been shown to stimulate organic pollutant degradation by bacteria in the soil when the hyphae act as continuous pathways for motile bacteria, bridging pore spaces and soil aggregates and thereby facilitating movement and pollutant degradation by the bacteria (Kohlmeier et al. 2005; Wick et al. 2007, 2010; Banitz et al. 2011).

Many fungi can metabolise PAHs (Cerniglia and Sutherland 2001, 2006, 2010; Sutherland 2004; Verdin et al. 2004). Since fungi cannot generally use PAHs as the sole carbon and energy source (Cerniglia and Sutherland 2001), they must be supplied with nutrients to allow co-metabolism. A small number of yeasts and filamentous fungi have been reported to use some PAHs, including anthracene, phenanthrene, pyrene and benzo[*a*]pyrene, as carbon and energy sources (Romero et al. 2002; Lahav et al. 2002; Saraswathy and Hallberg 2002; Veignie et al. 2004). Some fungi co-metabolise PAHs to *trans*-dihydrodiols, phenols, quinones, dihydrodiol epoxides and tetraols, but seldom degrade them completely to CO_2 (Casillas et al. 1996; Cajthaml et al. 2002; da Silva et al. 2003).

The transformation of PAHs by ligninolytic, wood-decaying fungi involves several different enzymes (Asgher et al. 2008). The enzymes produced by white-rot fungi that are involved in PAH degradation include lignin peroxidase, manganese peroxidase, laccase, cytochrome P450 and epoxide hydrolase (Haemmerli et al. 1986; Bezalel et al. 1996; Cerniglia and Sutherland 2006). Ligninolytic fungi metabolise PAHs via reactions involving reactive oxygen species to phenols and quinones (Pickard et al. 1999; Steffen et al. 2003), and these may be further degraded by ring-fission enzymes (Cerniglia and Sutherland 2006).

Several wood-decaying fungi, e.g. *Bjerkandera*, *Coriolopsis*, *Irpex*, *Phanerochaete*, *Pleurous* and *Trametes* spp., have been investigated for bioremediation of PAH-contaminated soils (Baldrian et al. 2000; Novotný et al. 2000; Cerniglia and Sutherland 2006; Baldrian 2008). Laboratory trials have demonstrated their ability to degrade complex mixtures of PAHs, such as those in creosote and coal tar, but actual bioremediation of contaminated soils using these fungi has met with varying success (Canet et al. 2001; Cerniglia and Sutherland 2001; Pointing 2001; Hestbjerg et al. 2003). Non-ligninolytic fungi, including *Cunninghamella*, *Mucor*, *Fusarium* and *Penicillium* spp., have also been considered for PAH bioremediation (Colombo et al. 1996; Pinto and Moore 2000; Ravelet et al. 2001; Saraswathy and Hallberg 2002).

Biodegradation may require the presence of mixed bacterial and fungal communities, although less is known about the pathways of PAH degradation by co-cultures (Juhasz and Naidu 2000). The evolution of $^{14}CO_2$ from ^{14}C-phenanthrene in soil was enhanced almost twofold (from 19.5 % to 37.7 %) when *P. chrysosporium* was added to the indigenous soil microflora (Brodkorb and Legge 1992). Boonchan et al. (2000) combined *Penicillium janthinellum* with either *Stenotrophomonas maltophilia* or an unidentified bacterial consortium. The fungus could partially degrade pyrene and benzo[*a*]pyrene but could not use either as a carbon source; *S. maltophilia* could use pyrene as a carbon source and cometabolise benzo[*a*]pyrene. The fungal–bacterial combinations grew on pyrene, chrysene, benz[*a*]anthracene, benzo[*a*]pyrene and dibenz[*ah*]anthracene, converting 25 % of the benzo[*a*]pyrene to CO_2 in 49 days. The white-rot fungus *P. ostreatus* and the brown-rot fungus *Antrodia vaillantii* enhanced the degradation of fluorene, phenanthrene, pyrene and benz[*a*]anthracene in artificially contaminated soils (Andersson et al. 2003). Unlike *P. ostreatus*, which inhibited the growth of indigenous soil microorganisms, *A. vaillantii* stimulated soil microbial activity.

Ligninolytic fungi partially oxidise PAHs by reactions involving extracellular free radicals (Majcherczyk and Johannes 2000), making the PAHs more water soluble so that they are able to serve as substrates for bacterial degradation (Meulenberg et al. 1997). Partial oxidation increases PAH bioavailability in most contaminated sites (Mueller et al. 1996; Meulenberg et al. 1997), and PAH-contaminated soils may contain large populations of PAH-transforming bacteria (Johnsen et al. 2002) and fungi (April et al. 2000; Saraswathy and Hallberg 2002). Combinations of several microorganisms are usually better able to degrade benzo[*a*]pyrene and other high-molecular-weight PAHs than pure cultures (Kanaly et al. 2000).

IV. Effects of Acid Rain and Airborne Pollutants on Fungal Populations

Although acid rain is generally regarded as a long-range pollution phenomenon, high concentrations of mineral acids will pollute ecosystems close to point source emissions (Helander et al. 1993). Acid rain effects will also impinge on the availability and effects of other pollutants such as toxic metals, which may accompany atmospheric dispersal and/or be released from soil components as a result of increased acidity (Wainwright et al. 1982; Tabatabai 1985; Francis 1986; Persson et al. 1989). Baath et al. (1984) showed that soil biological activity, as determined by respiration rate, was significantly reduced following treatment with simulated acid rain. Mycelial lengths (FDA active) were also reduced by the treatment, while plate counts showed no response. Fritze (1987), on the other hand, showed that urban air pollution had no effect on the total length of fungal hyphae in the surface horizons of soils supporting Norway spruce (*Picea abies*). Bewley and Parkinson (1985) showed that the contribution which fungi make to the total respiration of a soil was reduced by acid rain, while, in contrast, Roberts et al. (1980) concluded that the addition of acid rain to forest soils did not affect the normal 9:1 balance of fungal to bacterial respiration. These studies clearly illustrate how difficult it is to generalise about the effects of atmospheric pollutants on soil microorganisms. Among higher fungi, simulated acid rain has been shown to increase the dominance of some ectomycorrhizal fungi, while decreasing species diversity among saprophytic species (Sastad and Jensenn 1993). Shaw et al. (1992) also showed that fumigation with sulphur dioxide or ozone had no effect on mycorrhizal populations. Acid treatments have been shown to impair the decomposition of both deciduous leaves and conifer needles (Baath et al. 1984; Prescott and Parkinson 1985). Small-scale inhibitory effects were common, although stimulatory effects were also observed. Pollution in the form of alkaline dust from iron and steel works was shown to lead to a doubling of the total length of fungal hyphae (Fritze 1987, 1991).

The measurement of leaf litter and cellulose decomposition provides a means of assessing the impact of atmospheric pollutants on soils. However, in the absence of a means of partitioning the relative impact of the toxicants on fungi, bacteria and soil animals, such methods provide only a measure of the effects of the pollutants on the total soil community. Atmospheric pollutants from coking works can, for example, reduce populations of soil microarthropods, a response which retards the rate of litter decomposition in deciduous woodland soils (Killham and Wainwright 1981).

Few examples of the effects of enrichment disturbance by air pollutants on fungal populations can be found in the literature. However, some fungi have been reported to utilise atmospheric pollution deposits from coking works as a nutrient source, as well as being able to oxidise the reduced sulphur which these particles contain (Killham and Wainwright 1982, 1984).

V. Effects of Toxic Metals on Fungi

The ability of fungi to survive in the presence of potentially toxic metals depends on a number of biochemical and structural properties, including physiological and/or genetical adaptation, morphological changes and environmental modification of the metal in relation to the speciation, availability and toxicity (Fig. 5.1) (Gadd and Griffiths 1978; Turnau 1991; Gadd 1992, 2007). Terms such as resistance and tolerance are often used interchangeably in the literature, and may be arbitrarily based on the ability to grown on a certain metal concentration in laboratory media (Tatsuyama et al. 1975; Williams and Pugh 1975; Baath 1991; Gadd 1992). ‘Resistance’ is probably more appropriately defined as the ability of an organism to survive metal toxicity by means of a mechanism produced in direct response to the metal species concerned, the synthesis of metallothionein and γ-glutamyl peptides in response to Cu and Cd, respectively, providing perhaps the best examples (Mehra and Winge 1991). Metal tolerance may be defined as the ability of an organism to survive metal toxicity by means of intrinsic properties and/or environmental modification of toxicity (Gadd 1992). Intrinsic properties that can determine survival include possession of impermeable pigmented cell walls, extracellular polysaccharide and metabolite excretion, especially where this leads to detoxification of the metal species by binding or precipitation (Gadd 1993a). However such distinctions are often difficult to recognise because of the involvement in fungal survival in response to metal toxicity of several direct and indirect physicochemical and biological mechanisms. Biological mechanisms implicated in fungal survival (as distinct from environmental modification of toxicity) include extracellular precipitation; complexation and crystallisation; the transformation of metal species by, for example, oxidation, reduction, methylation and dealkylation; biosorption to cell walls, pigments and extracellular polysaccharide; decreased transport or impermeability and efflux; intracellular compartmentation; and finally precipitation and/or sequestration (Fig. 5.1) (Gadd and Griffiths 1978; Gadd 1990, 1992, 2007; Mehra and Winge 1991).

A. Effects of Metals on Fungal Populations

A range of fungi from all the major groups may be found in metal-polluted habitats (Gadd 1993a, 2007, 2011). In general terms, toxic metals may affect fungal populations by reducing abundance and species diversity and selecting for a resistant/tolerant population (Jordan and Lechevalier 1975; Babich and Stotzky 1985; Arnebrant et al. 1987). However, the effect of toxic metals on microbial abundance in natural habitats varies with the metal species and the organism present and also depends on a variety

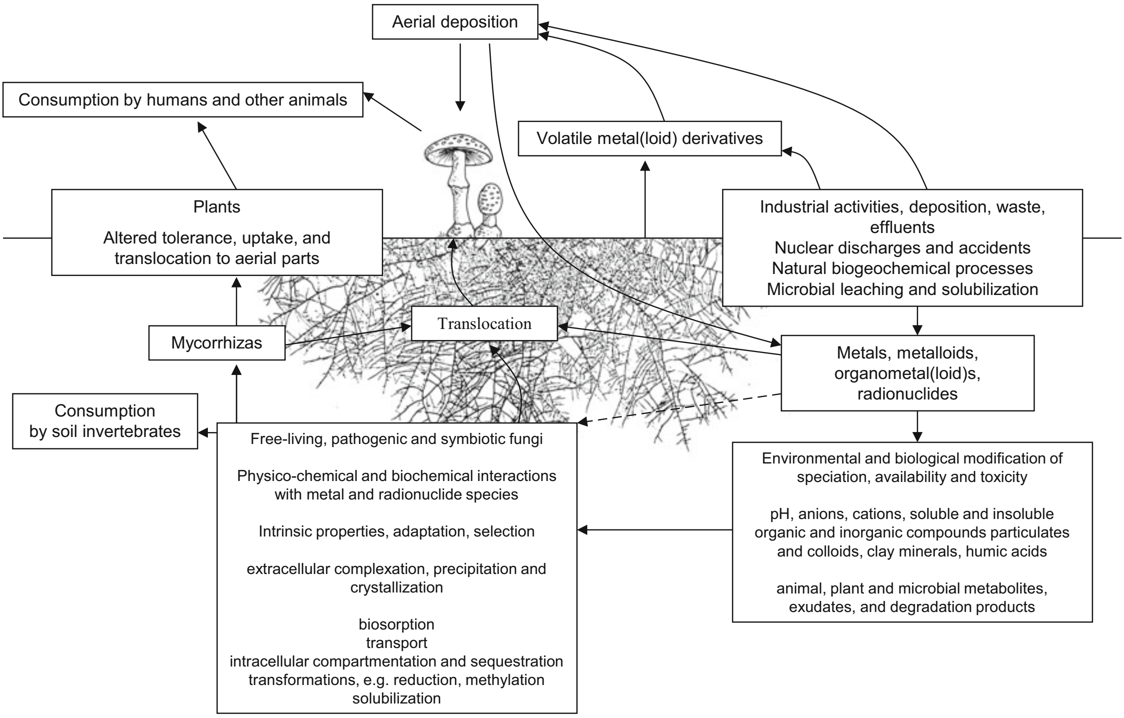

Fig. 5.1 Diagrammatic representation of the interactions of toxic metals and radionuclides with fungi in the terrestrial environment. The *dotted line* shows direct effects of metal species on fungi; this may sometimes occur and is more likely for metal species, such as Cs^+, which are highly mobile. The release of metal/radionuclide species from dead and decomposing animal and plant and microbial biomass is not shown but will be an important part of metal cycling. Fungal roles in metal solubilisation from naturally occurring substrates and/or industrial materials are indicated (see Burgstaller and Schinner 1993; Gadd 2007). For more detailed information regarding physiological and cellular interactions, see Gadd (1993a, 2007, 2010)

of environmental factors making generalisations difficult (Gadd and Griffiths 1978).

General reductions in fungal 'numbers' (as assessed by the dilution plate count in many earlier studies) have often been noted in soils polluted with Cu, Cd, Pb, As and Zn (Bewley and Stotzky 1983; Babich and Stotzky 1985). However, numerical estimates alone may provide little meaningful information unless possible changes in fungal groups and species are considered, and the problems associated with plate counting are in any case well known. Frostegard et al. (1993) analysed the phospholipid fatty acid (PLFA) composition of soil in order to detect changes in the overall composition of the microbial community and provide more reliable information on fungal populations than can be produced using plate counts. Two soils were amended with Cd, Cu, Ni, Pb and Zn and analysed after 6 months. PLFA 18:2ω6 is regarded as an indicator of fungal biomass, and this increased with increasing metal contamination for all metals except Cu, possibly reflecting the well-known mycotoxicity of Cu. However, in forest soils, such an increase in PLFA 18:2ω6 was not observed because of masking by identical PLFAs derived from plant material (Frostegard et al. 1993).

Several studies have shown that microbial population responses to toxic metals are characterised by shift from bacteria, including streptomycetes, to fungi (Mineev et al. 1999; Khan and Scullion 2002; Chander et al. 2001a, b; Kostov and Van Cleemput 2001; Olayinka and Babalola 2001). However, other studies have shown a higher metal sensitivity of the fungal component of the microbial biomass (Pennanen et al. 1996). What seems clear is that all nutritional groups of fungi (saprotrophs, biotrophs and necrotrophs) can be affected by toxic metals. Ruhling et al. (1984) found that the soil respiration rate, fluorescein diacetate (FDA) active mycelium and mycelial standing crop were all reduced with increasing copper concentration in soils proximal to a brass mill. Nordgren et al. (1983, 1985) also showed that fungal biomass and soil respiration decreased by ~75 % along an increasing concentration gradient of metal pollution. A relative decrease in an indicator fatty acid for arbuscular mycorrhizal fungi and an increase for other fungi have been reported for zinc-polluted soil (Kelly et al. 1999). Toxic metals (Cd, Cr, Cu, Ni, Pb and Zn) led to a decrease in the number of arbuscular mycorrhizal fungi and low colonisation of plant roots and, as a result, changes in mycorrhizal species diversity (Del Val et al. 1999; Mozafar et al. 2002; Moynahan et al. 2002). Toxic metals also reduce plant root colonisation by ectomycorrhizal fungi and ectomycorrhizal species composition (Hartley et al. 1999; Markkola et al. 2002). The most frequent soil saprotrophic microfungi isolated from heavily metal-polluted habitats in Argentina, the Czech Republic and Ukraine were reported to be species of *Penicillium*, *Aspergillus*, *Trichoderma*, *Fusarium*, *Rhizopus* and *Mucor*, as well as *Paecilomyces lilacinus*, *Nectria invertum*, *Cladosporium cladosporioides*, *Alternaria alternata* and *Phoma fimeti* (Kubatova et al. 2002; Massaccesi et al. 2002; Fomina, Manichev, Kadoshnikov and Nakonechnaya, unpublished). Melanised fungi, such as *Cladosporium* sp., *Alternaria alternata* and *Aureobasidium pullulans*, were often isolated from soil containing high concentrations of copper and mercury (Zhdanova et al. 1986) and can be dominant members of the mycoflora of metal-contaminated phylloplanes (Mowll and Gadd 1985). Dark septate endophytes were found to be dominant fungi among isolates from roots of *Erica herbacea* L. in Pb-, Cd-, and Zn-polluted soil (Cevnik et al. 2000).

Metal pollution of plant surfaces is widespread, but many filamentous and polymorphic fungi appear to be little affected (Smith 1977; Bewley 1979, 1980; Bewley and Campbell 1980; Mowll and Gadd 1985). On polluted oak leaves, *Aureobasidium pullulans* and *Cladosporium* species were the most numerous organisms (Bewley 1980). In fact, numbers of *A. pullulans* showed a good positive correlation with lead, whether derived from industrial or vehicular sources, and this fungus was frequently the dominant microorganism present (Bewley and Campbell 1980; Mowll and Gadd 1985).

In conclusion, elevated concentrations of toxic metals can affect both the qualitative and quantitative compositions of fungal populations although it is often extremely difficult to separate their effects from those of other environmental pollutants. It is apparent that certain fungi can exhibit considerable tolerance towards toxic metals and can become dominant microorganisms in some polluted habitats. However, while species diversity may be reduced in certain cases, resistance/tolerance can be exhibited by fungi from both polluted and nonpolluted habitats. Physicochemical properties of the environment, including changes associated with the metal pollution, may also influence metal toxicity and thereby affect species composition (Gadd 1984, 1992, 1993a; Baath 1989).

B. Morphological and Growth Responses to Toxic Metals

Effects of toxic metals on fungal growth have shown intra- and interspecific variability and dependence on the metal species present (Gadd 1993a; Plaza et al. 1998). For *T. virens* and *Clonostachys rosea* colonising spatially discrete toxic metal-containing domains, colonisation distance, hyphal extension rates and the efficacy of carbon substrate utilisation decreased with increasing concentrations of copper and cadmium (Fomina et al. 2003). A decrease in metal toxicity may be correlated with an increase in available carbon source (Ramsay et al. 1999; Fomina et al. 2003).

Several toxic metals can induce or accelerate melanin production in fungi, leading to blackening of colonies and chlamydospore development (Gadd and Griffiths 1980). Chlamydospores and other melanised forms have high biosorption capacities for metals, the majority of metal remaining within the wall

(Gadd 1984, 2009; Gadd and Mowll 1985; Gadd et al. 1987; Gadd and de Rome 1988). In rhizomorphs of an *Armillaria* sp., the highest concentrations of metals were located on the melanised outer surface (Rizzo et al. 1992).

Fungal morphology can be altered by toxic metals, and changes in mycelial density and morphology can occur (Darlington and Rauser 1988; Lilly et al. 1992; Jones and Muehlchen 1994; Gabriel et al. 1996; Baldrian and Gabriel 1997; Gardea-Torresdey et al. 1997; Ramsay et al. 1999; Fomina et al. 2000, 2005b). Biomass distribution within *Trichoderma viride* colonies was altered by toxic metals, with biomass concentrated in the periphery of the colonies in the presence of Cu and towards the interior of the colonies in the presence of Cd (Ramsay et al. 1999; Gadd et al. 2001).

During growth of fungi in metal-containing agar tiles simulating a spatially heterogeneous distribution of metal concentrations and available nutritional resources, a range of morphological changes and growth responses occurred including negative chemotropism, cessation of growth, swelling and lysis of hyphal tips (Fomina et al. 2003). Penetration of hyphae into metal-containing domains was often followed by the formation of very dense mycelia or mycelial ‘bushes’ (Fomina et al. 2003). Such hyphal aggregation could facilitate substrate colonisation and the production of high local concentrations of extracellular metabolites such as complexing agents (e.g. organic acids, siderophores, polyphenolic compounds), metal precipitating agents (e.g. oxalate) and polysaccharides and pigments with metal-binding abilities (Gadd 1993a; Dutton and Evans 1996; Baldrian 2003). Under poor nutritional conditions, fungi often produced long sparsely branched or branchless hyphae in toxic metal-containing domains representing an explorative growth strategy (Fomina et al. 2003). Some fungi also exhibited multiple repeated ‘phase shifts’ with a mixture of mycelial ‘bushes’ and long branchless explorative hyphae (Fomina et al. 2003). Further, microfungi-penetrating metal-contaminated domains may form mycelial cords and synnema which may be atypical for these fungi under normal conditions. The production of synnema results in a wider separation between the conidia and the substrate than in non-synnematal colonies, and this may aid dispersal as well as ensuring conidia formation away from the substrate toxicants (Newby and Gadd 1987).

C. Mycorrhizal Responses Towards Toxic Metals

Mycorrhizal fungi are involved in phosphate solubilisation, proton-promoted and ligand-promoted metal mobilisation from mineral sources, metal immobilisation within biomass and extracellular precipitation of mycogenic metal oxalates (Fomina et al. 2004, 2005a; Finlay et al. 2009; Gadd 2007, 2010, 2011). Plant symbiotic mycorrhizal fungi can therefore accumulate metals from soil components, and this may have consequences for metal nutrition of the symbiosis as well as increased or decreased toxicity (Brown and Wilkins 1985a, b; Jones and Hutchinson 1986, 1988a, b). Since plants growing on metalliferous soils are generally mycorrhizal, an important ecological role for the fungus has frequently been postulated although such a role, e.g. phytoprotection, is often difficult to confirm (Meharg and Cairney 2000a, b). Ericaceous plants appear to be entirely dependent on the presence of ericoid mycorrhizas for protection against copper, the fungus preventing metal translocation to plant shoots (Bradley et al. 1981, 1982). Arbuscular mycorrhizas (AMs) from metal-contaminated sites are often more metal tolerant to, for example, Cd and Zn, than other isolates, suggesting a benefit to the plant via increased metal resistance, nutrient uptake, etc., though in some instances, AM plants do not necessarily require fungal colonisation for survival (Griffioen 1994). It is often postulated that mycorrhizas provide a barrier to the uptake of potentially toxic metals (Bradley et al. 1981, 1982; Wilkins 1991; Hetrick et al. 1994; Wilkinson and Dickinson 1995; Leyval et al. 1997; Meharg and Cairney 2000a, b) though this has not been confirmed in every case. Further, in some instances, AM may mediate enhanced accumulation of essential metals, which, unless regulated, may lead to phytotoxicity (Killham and

Firestone 1983). It is generally concluded that local conditions in metal-contaminated sites may determine the nature of the relationship between the plant and the AM fungus, since detrimental, neutral or beneficial interactions have all been documented (Meharg and Cairney 2000a, b). For ericaceous mycorrhizas, clear host protection is observed for host plants, e.g. *Calluna* sp., *Erica* sp. and *Vaccinium* sp., growing on polluted and/or naturally metalliferous soils (Bradley et al. 1981, 1982). Further, ericaceous plants are generally found on nutrient-deficient soils, and it is likely the mycorrhiza additionally benefits the plants by enhanced nutrient uptake (Smith and Read 1997). A protective metal-binding effect of ectomycorrhizal fungi (EcM) has been postulated frequently (Denny and Wilkins 1987; Leyval et al. 1997; Dixon and Buschena 1988; Colpaert and Van Assche 1987, 1993). During growth, mycorrhizal fungi often excrete low-molecular-weight carboxylic acids and siderophores (Martino et al. 2003; Fomina et al. 2004). Ericoid mycorrhizal and ectomycorrhizal fungi can dissolve a variety of cadmium, copper, zinc and lead-bearing minerals including metal phosphates (Leyval and Joner 2001; Martino et al. 2003; Fomina et al. 2004, 2005b).

D. Metal and Metalloid Transformations by Fungi

Fungi can transform metals, metalloids (elements with properties intermediate between those of metals and non-metals: the group includes arsenic, selenium and tellurium) and organometallic compounds by reduction, methylation and dealkylation (Gadd 1993b, 2007). These are all processes of environmental importance since the transformation of a metal or metalloid may modify its mobility and toxicity. For example, methylated selenium derivatives are volatile and less toxic than inorganic forms, while the reduction of metalloid oxyanions, such as selenite or tellurite to amorphous elemental selenium or tellurium, respectively, results in immobilisation and detoxification (Thompson-Eagle and Frankenberger 1992; Morley et al. 1996). The mechanisms by which fungi (and other microorganisms) effect changes in metal speciation and mobility are important survival determinants as well as components of biogeochemical cycles for metals and many other elements including carbon, nitrogen, sulphur and phosphorus (Gadd 1999, 2004b, 2007, 2008c).

Metals and their compounds interact with fungi in various ways depending on the metal species, organism and environment, while fungal metabolism also influences metal speciation and mobility. Many metals are essential, e.g. Na, K, Cu, Zn, Co, Ca, Mg, Mn and Fe, but all can exert toxicity when present above certain threshold concentrations (Gadd 1993a, b). Other metals, e.g. Cs, Al, Cd, Hg and Pb, have no known biological function, but all can be accumulated by fungi (Gadd 1993b, 2001a, b). Metal toxicity is greatly affected by environmental conditions and the chemical behaviour of the particular metal species in question. Despite apparent toxicity, many fungi survive, grow and flourish in apparently metal-polluted locations, and a variety of mechanisms, both active and incidental, contribute to tolerance. Fungi have many properties which influence metal toxicity including the production of metal-binding peptides, organic and inorganic precipitation, active transport and intracellular compartmentalisation, while fungal cell walls have significant metal-binding abilities (Gadd and Griffiths 1978; Gadd 1993b, 2007; Fomina and Gadd 2002). All the mechanisms by which fungi (and other microorganisms) effect changes in metal speciation and mobility are survival determinants but also components of biogeochemical cycles for metals and many other associated elements including carbon, nitrogen, sulphur and phosphorus (Gadd 2004a, b, 2006, 2007, 2008a; Gadd et al. 2005, 2007). These may be simply considered in terms of metal mobilisation or immobilisation mechanisms.

1. Metal Mobilisation

Metal mobilisation from solids, e.g. rocks, minerals, soil, ash, mine spoil and other substrates, can be achieved by chelation by excreted metabolites and siderophores and methylation which can result in volatilisation.

Fungi can solubilise minerals by means of proton efflux and the production of Fe(III)-binding siderophores and as a result of respiratory carbon dioxide accumulation. In addition, other excreted metabolites with metal-complexing properties, e.g. amino acids, phenolic compounds and organic acids, may also be involved. Fungal-derived carboxylic acids provide a source of protons for solubilisation and metal-complexing anions (Gadd 1999, 2001a, 2010; Burgstaller and Schinner 1993; Gadd and Sayer 2000). Many metal citrates are highly mobile and not readily degraded. Oxalic acid can act as a leaching agent for those metals that form soluble oxalate complexes, including Al and Fe (Strasser et al. 1994). Solubilisation phenomena can have consequences for mobilisation of metals from toxic metal-containing minerals, e.g. pyromorphite ($Pb_5(PO_4)_3Cl$), contaminated soil and other solid wastes (Sayer et al. 1999). Fungi can also mobilise metals and attack mineral surfaces by redox processes. Fe(III) and Mn(IV) solubility is increased by reduction to Fe(II) and Mn(II), respectively. Reduction of Hg(II) to volatile elemental Hg(0) can also be mediated by fungi (Gadd 1993a, b).

The removal of metals from industrial wastes and by-products, contaminated soil, low-grade ores and metal-bearing minerals by fungal 'heterotrophic leaching' is relevant to metal recovery and recycling and/or bioremediation of contaminated solid wastes and perhaps the removal of unwanted phosphates (Gadd 2007, 2010). The ability of fungi, along with bacteria, to transform metalloids has also been utilised successfully in the bioremediation of contaminated land and water. Selenium methylation results in volatilisation, a process which has been used to remove selenium from the San Joaquin Valley and Kesterson Reservoir, California, using evaporation pond management and primary pond operation (Thompson-Eagle et al. 1989; Thompson-Eagle and Frankenberger 1992).

2. Metal Immobilisation

Fungal biomass provides a metal sink, either by sorption to biomass (cell walls, pigments and extracellular polysaccharides), intracellular accumulation and sequestration, or precipitation of metal compounds onto and/or around hyphae. Fungi are effective biosorbents for a variety of metals including Ni, Zn, Ag, Cu, Cd and Pb (Gadd 1990, 1993b, 2009), and this can be an important passive process in both living and dead biomass (Gadd 1990, 1993b; Sterflinger 2000). The presence of chitin, and pigments like melanin, strongly influences the ability of fungi to act as biosorbents (Gadd and Mowll 1985; Manoli et al. 1997; Fomina and Gadd 2002; Gadd 2009). In a biotechnological context, fungi and their by-products have received considerable attention as biosorbents for metals and radionuclides (Gadd and White 1992; Gadd 2002). However, attempts to commercialise biosorption have been limited, primarily due to competition with commercially produced ion exchange media of high specificity (Gadd 2009).

Fungi can precipitate a number of inorganic and organic compounds, e.g. oxalates, oxides, phosphates and carbonates (Grote and Krumbein 1992; Arnott 1995; Verrecchia 2000; Gadd 1999; Gharieb and Gadd 1999), and this can lead to the formation of biogenic minerals (mycogenic precipitates). Precipitation, including crystallisation, will immobilise metals but also leads to the release of nutrients like sulphate and phosphate (Gadd 1999). Fungi can produce a variety of metal oxalates with a variety of different metals and metal-bearing minerals, e.g. Cd, Co, Cu, Mn, Sr, Zn and Ni (Gadd 1999), which may provide a mechanism whereby fungi can tolerate toxic metal-containing environments. Fungi produce other metal oxalates besides calcium on interacting with a variety of different metals and metal-bearing minerals, including those of Ca, Cd, Co, Cu, Mg, Mn, Sr, Zn, Ni and Pb (Sayer and Gadd 1997; Gadd 1999, 2007; Sayer et al. 1999; Adeyemi and Gadd 2005; Fomina et al. 2007a, b; Wei et al. 2013). The formation of toxic metal oxalates may contribute to fungal metal tolerance (Gadd 1993a; Clausen et al. 2000; Jarosz-Wilkołazka and Gadd 2003; Green and Clausen 2003). Mycogenic oxalate minerals produced by free-living fungi include glushinskite ($MgC_2O_4{\cdot}2H_2O$) (Burford et al. 2003a, b; Kolo and Claeys 2005; Kolo et al. 2007; Gadd 2007), moolooite ($Cu(C_2O_4)\cdot 0.4H_2O$) (Fomina et al. 2005a, 2007b) and lindbergite ($MnC_2O_4\cdot 2H_2O$) (Wei et al. 2012). A similar mechanism occurs in lichens growing on copper–sulphide-bearing rocks, where precipitation of copper oxalate occurs within the thallus (Purvis 1996). Oxalate production by *Aspergillus niger* and *Serpula himantioides* has been shown to induce the dissolution and conversion of both rhodochrosite and Mn oxides to Mn oxalate minerals (Sayer et al. 1997; Wei et al. 2012). Oxalate can act as a reductant of Mn(IV) oxides, and this can result in mobilisation of Mn(II), which can then precipitate. Both *A. niger* and *S. himantioides* were capable of solubilising the insoluble manganese oxides MnO_2 and Mn_2O_3, mycogenic manganese oxide (MnO_x) and birnessite $[(Na_{0.3}Ca_{0.1}K_{0.1})(Mn^{4+},Mn^{3+})_2O_4\cdot 1.5H_2O]$. Precipitation of insoluble manganese oxalate occurred and manganese oxalate trihydrate was detected after growth of *S. himantioides* with birnessite which subsequently was transformed to manganese oxalate dihydrate (Wei et al. 2012). Several free-living and mycorrhizal fungi can attack and transform pyromorphite ($Pb_5(PO_4)_3Cl$) to lead oxalate (Sayer et al. 1999; Fomina et al. 2004, 2005b). It has also been shown that certain fungi (e.g. *Paecilomyces javanicus*, *Metarhizium anisopliae*) were able to mediate transformation of metallic lead into pyromorphite, representing biomineralisation of mobile lead species into a very stable form (Rhee et al. 2012, 2014a, b). This might be an important process occurring in lead-containing environments and of relevance to proposed bioremedial treatments (Rhee et al. 2012). It is likely that acidolysis and complexation involving excreted organic acids play an important role in mediating precipitation of pyromorphite (Rhee et al. 2012, 2014a, b) and other metal phosphates (Fomina et al. 2007c, 2008). Fungal activity can also play an important role in the biocorrosion and transformation of lead metal into pyromorphite in the aquatic environment. The ability of fungi to immobilise mobile lead species in an insoluble form provides a further approach for the removal and detoxification of lead from aqueous solution by bioprecipitation. The principles of such a process could also be applied to other metals and insoluble biominerals for bioremediation or biorecovery of valuable elements (Rhee et al. 2014a, b). Another research has demonstrated that fungi can solubilise uranium oxides and depleted uranium and reprecipitate secondary uranium phosphate minerals of the meta-autunite group, uramphite and/or chernikovite, which can encrust fungal hyphae to high accumulation values of 300–400 mg U g dry wt^{-1} (Fomina et al. 2007c, 2008). Such minerals appear capable of long-term U retention (Fomina et al. 2008). The phosphate may arise from inorganic sources in the environment or from phosphatase-mediated hydrolysis of organic P sources, with the hyphal matrix serving to localise the resultant uranium minerals (Liang et al. 2015).

Many fungi precipitate reduced forms of metals and metalloids in and around fungal hyphae, e.g. Ag(I) can be reduced to elemental silver Ag(0), selenate [Se(VI)] and selenite [Se (IV)] to elemental selenium and tellurite [Te (IV)] to elemental tellurium [Te(0)] (Gharieb et al. 1995, 1999).

3. Organometal(loid)s

Organometals (compounds with at least one metal–carbon bond) can be attacked by fungi with the organic moieties being degraded and the metal compound undergoing changes in speciation. Degradation of organometallic compounds can be carried out by fungi, either by direct biotic action (enzymes) or by facilitating abiotic degradation, for instance, by alteration of pH and excretion of metabolites. Organotins, such as tributyltin oxide and tributyltin naphthenate, may be degraded to mono- and dibutyltins by fungal action, inorganic Sn(II) being the final degradation product. Organomercury compounds may be detoxified by conversion to Hg(II) by fungal organomercury lyase, the Hg(II) being subsequently reduced to Hg(0) by mercuric reductase, a system analogous to that found in mercury-resistant bacteria (Gadd 1993b).

E. Accumulation of Metals and Radionuclides by Macrofungi

Elevated concentrations of toxic metals and radionuclides can occur in the fruiting bodies of higher fungi sampled from polluted environments. This phenomenon is of significance in relation to the use of macrofungi as bioindicators of metal pollution and because of human toxicity resulting from the consumption of wild fungi. In general, levels of Pb, Cd, Zn and Hg found in macrofungi from urban or industrial areas are higher than from corresponding rural areas, although there are wide differences in uptake abilities between different species and different metals (Tyler 1980; Bressa et al. 1988; Lepsova and Mejstrik 1989). Cadmium is accumulated to quite high levels in macrofungi, averaging around 5 mg (kg dry wt)$^{-1}$ although levels of up to 40 mg (kg dry wt)$^{-1}$ have also been recorded (Byrne et al. 1976). *Laccaria amethystina* caps exhibited total As concentrations of 100–200 mg (kg dry wt)$^{-1}$ (Stijve and Porette 1990; Byrne et al. 1991). Accumulation of ^{110}Ag and ^{203}Hg was studied in *Agaricus bisporus*, and concentration factors (metal concentration in mushroom, metal concentration in substrate) were found to be up to 40 and 3.7, respectively, with the highest Ag and Hg contents recorded being 167 and 75 mg (kg dry wt)$^{-1}$, respectively (Byrne and Tusek-Znidaric 1990). As well as fruiting bodies, rhizomorphs (e.g. of *Armillaria* species) can concentrate metals up to 100 times the level found in soil. Concentrations of Al, Zn, Cu and Pb in rhizomorphs were 3440, 1930, 15 and 680 mg (kg dry wt)$^{-1}$, respectively, with the metals primarily located in extracellular portions (Rizzo et al. 1992).

F. Accumulation of Radiocaesium by Macrofungi

Following the Chernobyl accident in 1986, there were several studies on radiocaesium (mainly ^{137}Cs) accumulation by fungi. Free-living and mycorrhizal basidiomycetes can accumulate radiocaesium (Haselwandter 1978; Elstener et al. 1987; Byrne 1988; Dighton and Horrill 1988; Haselwandter et al. 1988; Clint et al. 1991; Dighton et al. 1991; Muramatsu et al. 1991; Heinrich 1992); these organisms appear to have a slow turnover rate for Cs and comprise a major pool of radiocaesium in soil (Clint et al. 1991). Mean activities of 25 Ukrainian, 6 Swedish and 10 North American collections were 4660, 9750 and 205 Bq (kg dry wt)$^{-1}$, respectively (Smith et al. 1993). Deviations in the ^{137}Cs:^{134}Cs ratios attributable to Chernobyl have revealed considerable accumulation of pre-Chernobyl Cs in macrofungi, probably as the result of weapon testing (Byrne 1988; Dighton and Horrill 1988). It appeared that about 20 % of the ^{137}Cs in Eastern Europe (Moscow area, Belarus, Ukraine) was of non-Chernobyl origin (Smith et al. 1993). Radiocaesium accumulation in basidiomycetes appears to be species dependent, with influences exerted by soil properties. Significantly higher activities may be found in mycorrhizal species compared to saprotrophic and parasitic fungi (Smith et al. 1993). Smith et al. (1993) found that many prized edible mycorrhizal fungi may contain unacceptably high levels of ^{137}Cs, that is, at levels of greater than 1000 Bq (kg dry wt)$^{-1}$. It has also been demonstrated that the fungal component of soil can immobilise the total Chernobyl radiocaesium fallout received in upland grasslands (Dighton et al. 1991) although grazing of fruiting bodies by animals may lead to radiocaesium transfer along the food chain (Baaken and Olson 1990).

G. Fungi as Bioindicators of Metal and Radionuclide Contamination

As mentioned above, higher fungi growing on contaminated sites can show significantly elevated concentrations of metals in their fruiting bodies, and some experiments have demonstrated a correlation between the quantities of metals in a growth substrate and the amounts subsequently found in the fruiting bodies (Wondratschek and Roder 1993). The concept of bioindicators has been usually discussed in terms of reaction indicators and accumulation indicators. Reaction indicators may comprise individual organisms and/or communities which may decline or disappear (sensitive species) or show increases (tolerant species). For accumulation indicators, the indicator organism is analysed for the pollutant. Some organisms, in theory, can therefore serve as both reaction and accumulation indicators. As described previously, alteration of macrofungal communities by metal pollution has frequently been recorded. Ruhling et al. (1984) noted a decline from about 40 species per 100 m^2 to about 15 species near the source of metal contamination (smelter emissions), with only *Laccaria laccata* increasing in frequency at more polluted locations. Other higher fungi which are apparently tolerant of high metal pollution include *Amanita muscaria* and several species of *Boletus*; some *Russula* species, on the other hand, appear metal sensitive (Wondratschek and Roder 1993).

Fungi possess several advantages over plants as metal accumulation indicators. The fruiting bodies may accumulate greater amounts of metals than plants, while the large area of mycelium ensures contact with and translocation from a large area of soil. Furthermore, fruiting bodies may project above the ground for only a short period, thereby minimising contamination from aerial or wet deposition of metal pollutants. Sporophores are also easily harvested and amenable to rapid chemical analysis (Mejstrik and Lepsova 1993). However, it is debatable whether a sufficiently clear relationship exists between indicator species and the metal pollution under consideration. For mercury, wide variations in metal content of fruiting bodies occur in different species sampled at the same site, ranging over as much as three orders of magnitude, with some species showing extremely high Hg accumulation values. Mercury concentrations in fungi generally occur in the range 0.03–21.6 mg (kg dry wt)$^{-1}$ although concentrations greater than 100 mg (kg dry wt)$^{-1}$ have been recorded from polluted sites. Despite this, several macrofungi have been suggested as being suitable bioindicators of mercury pollution (see Mejstrik and Lepsova 1993; Wondratschek and Roder 1993) (Table 5.1).

Table 5.1 Higher fungi proposed as bioindicators for metal pollution based on metal analyses of fruiting bodies (see Mejstrik and Lepsova 1993; Wondratschek and Roder 1993)

Species	Metal(s)
Agaricus arvensis	Hg, Cd
Agaricus campestris	Hg, Cd
Agaricus edulis	Hg, Cd
Agaricus haemorrhoidarius	Hg
Agaricus xanthodermus	Hg
Agaricus sp.	Pb, Zn, Cu
Amanita rubescens	Hg
Amanita strobiliformis	Hg
Coprinus comatus	Hg
Lycoperdon perlatum	Hg
Lycoperdon sp.	Pb, Zn, Cu
Marasmius oreades	Hg
Mycena pura	Hg, Cd

A wide variation in Cd content has also been recorded in macrofungi with ranges of reported values from <0.1–229 mg (kg dry wt)$^{-1}$ (Tyler 1980). However, there is frequently a lack of correlation between the fungal Cd content and the Cd content of the soil (Wondratschek and Roder 1993). Compared to other common metal pollutants, lower concentrations of Pb tend to be found in macrofungi, with much of the Pb content being derived from aerial sources. Levels of Pb around 0.4–36 mg (kg dry wt)$^{-1}$ have been reported in sporophores, with higher levels occurring in urban areas (Tyler 1980). Zinc, an essential metal for fungal growth and metabolism, occurs at high concentrations within fungi, 50–300 mg (kg dry wt)$^{-1}$ (Tyler 1980), with a few genera apparently showing high affinities for the metal (Table 5.1). Copper may also be found at high levels (20–450 mg (kg dry wt)$^{-1}$) in higher fungi (Tyler 1980). However, with both Cu and Zn, there is a tendency for metal concentrations in fruiting bodies to be independent of soil concentrations which reduces their value as bioindicators (Gast et al. 1988).

It is clear that many factors contribute to the wide variations in recorded metal contents of macrofungal fruiting bodies, even in the same species sampled at the same site. Despite numerous studies, most investigations tend to be contradictory and provide little useful information (Wondratschek and Roder 1993). Apart from organism-related factors, environmental factors are of paramount importance in relation to metal accumulation by higher fungi and include physicochemical soil properties like moisture and temperature, all of which influence metal availability as well as the physiological activity of the fungus. It can be concluded, therefore, that a perfect fungal bioindicator does not exist, although macrofungi may be useful in determining the extent of a polluted or unpolluted area.

H. Bioremediation, Biotechnology and Bioprocessing

Several fungal metal and mineral transformations have potential for the treatment of environmental pollution (Gadd 2004a, 2005; Pumpel and Paknikar 2001). While several fungal-based systems have received interest in the context of bioremediation of organic pollutants, there has not been so much attention given to metals. However, it should be stressed that fungi will be components of the microbiota in any metal-polluted sites where their activities may contribute to natural attenuation of the pollutants and will also be involved in many soil and waste treatment processes, revegetation strategies and effluent treatments. Fungi were clearly important in remediation of selenium-contaminated soils (Thompson-Eagle and Frankenberger 1992). In addition, fungal mineral-solubilising properties are important in plant nutrition and soil fertility especially regarding phosphates. In addition to bioremediation, metal and mineral transformations have applications in other areas of biotechnology and bioprocessing, including biosensors, biocatalysis, electricity generation and nanotechnology.

1. Bioleaching

Fungal solubilisation of metals from solid minerals and metal and mineral wastes, including contaminated soil, for metal recovery, recycling and bioremediation purposes have all been investigated, although fungal systems cannot compare with the established bacterial bioleaching processes and may be more suited to bioreactor applications. Metals can be solubilised from fly ash (originating from municipal solid waste incineration), contaminated soil, electronic scrap and other waste materials by fungal activity (Brandl 2001; Brandl and Faramarzi 2006).

2. Biosorption and Bioaccumulation

Biosorption is a physicochemical process, simply defined as ‘the removal of substances from solution by biological material’. It is a property of both living and dead organisms (and their components) and has been proposed as a promising biotechnology for the removal (and/or recovery) of metals, radionuclides and organic pollutants for many years because of its simplicity, analogous operation to conventional ion exchange technology and apparent efficiency (Gadd 1986, 2001a, b, 2009; Volesky 1990; Garnham et al. 1992; Gadd and White 1990, 1993; Wang and Chen 2006, 2009). Modification of biomass has been attempted to improve efficiency or selectivity of microbial biosorbents. Fungal–clay biomineral sorbents combined the sorptive advantages of the individual counterparts, i.e. the high density of metal-binding sites per unit area and high sorption capacity of fungal biomass, high sorption affinity and the high surface area per unit weight mechanical strength and efficient sorption at high metal concentrations of the clay minerals (Fomina and Gadd 2002). *S. cerevisiae* mutants (*pmr1*Δ) hypersensitive to heavy metals due to increased metal uptake have been investigated for the ability to remove Mn^{2+}, Cu^{2+}, Co^{2+} or Cd^{2+} from synthetic effluents by a combination of biosorption and intracellular uptake (Ruta et al. 2010). Phytochelatins (PCs) are metal-binding cysteine-rich peptides, enzymatically synthesised in plants and certain fungi from glutathione in response to heavy metal stress. Overexpression of PC synthase in bacteria could be a means of improving the metal content of organisms for bioremediation (Valls et al. 2000).

3. Metalloid Bioremediation

Microbial responses to arsenic of bioremedial potential include chelation, compartmentalisation, exclusion and immobilisation. Attempts to engineer an arsenic accumulating microbe have involved modification of natural resistance mechanisms and development of novel or hybrid pathways into an easily manipulated organism. Thus, PC synthase from *S. pombe* (SpPCS) has been expressed in *E. coli*, resulting in higher As accumulation, these steps being combined in an arsenic efflux deletion *E. coli* strain to achieve the highest reported arsenic accumulation in *E. coli* of 16.8 μmol/g cells (Tsai et al. 2009). A yeast strain coexpressing AtPCS and cysteine desulphhydrase, an aminotransferase that converts cysteine into hydrogen sulphide under aerobic conditions, was used to elevate As accumulation by formation of PC–metal–sulphide complexes (Tsai et al. 2009). The ability of fungi, along with bacteria, to transform metalloids has been utilised successfully in the bioremediation of contaminated land and water. Selenium methylation results in volatilisation, a process which has been used to remove selenium from contaminated sites (Thompson-Eagle and Frankenberger 1992).

4. Mycoremediation and the Mycorrhizosphere

Mycorrhizal associations may have application in the general area of phytoremediation (Rosen et al. 2005; Gohre and Paszkowski 2006): phytoremediation is the use of plants to remove or detoxify environmental pollutants (Salt et al. 1998). Mycorrhizas may enhance phytoextraction by increasing plant biomass, and some studies have shown increased plant accumulation of metals, especially when inoculated with mycorrhizal fungi isolated from metalliferous environments. However, the potential impact of mycorrhizal fungi on bioremediation may be dependent on many factors including their metal tolerance and the nutritional status of contaminated soils (Meharg 2003). In addition, some studies have shown mycorrhizas can reduce plant metal uptake (Tullio et al. 2003). Arbuscular mycorrhizas (AMs) depressed translocation of zinc to shoots of host plants by binding of metals in mycorrhizal structures and immobilisation of metals in the mycorrhizosphere (Christie et al. 2004). Local conditions in metal-contaminated sites may determine the relationship between the plant and the AM fungus, and detrimental, neutral and beneficial interactions have all been documented (Meharg and Cairney 2000a, b). A protective metal-binding effect of ectomycorrhizal fungi (EcM) has been postulated (e.g. Leyval et al. 1997). A Cu-adapted *Suillus luteus* isolate provided protection against Cu toxicity in pine seedlings exposed to elevated Cu. Such a metal-adapted *Suillus–Pinus* combination might be suitable for large-scale land reclamation at phytotoxic metalliferous and industrial sites (Adriaensen et al. 2005). Ectomycorrhizal fungi persistently fixed Cd(II) and Pb(II) and formed an efficient biological barrier that reduced the movement of these metals in birch tissues (Krupa and Kozdroj 2004). Such mycorrhizal metal immobilisation around plant roots, including biomineral formation, may also assist soil remediation and revegetation. Naturally occurring soil organic compounds can stabilise potentially toxic metals like Cu, Cd, Pb and Mn. The insoluble glycoprotein, glomalin, produced in copious amounts on hyphae of arbuscular mycorrhizal fungi can sequester such metals and could be considered a useful stabilisation phenomenon (Gonzalez-Chavez et al. 2004). Phytostabilisation strategies may reduce the dispersion of uranium (U) and the environmental risks of U-contaminated soils. *Glomus intraradices* increased root U concentration and content, but decreased shoot U concentrations. AM fungi and root hairs improved not only P acquisition but also root uptake of U, and the mycorrhiza generally decreased U translocation from plant root to shoot (Rufyikiri et al. 2004; Chen et al. 2005a, b).

For ericaceous mycorrhizas, host protection has been observed in, for example, *Calluna*, *Erica* and *Vaccinium* spp. growing on Cu- and Zn-polluted and/or naturally metalliferous soils, the fungus preventing metal translocation to plant shoots (Bradley et al. 1981, 1982). Further, ericaceous plants are generally found on nutrient-deficient soils, and it is likely the mycorrhiza could additionally benefit the plants by enhanced nutrient uptake (Smith and Read 1997). The development of stress-tolerant plant–mycorrhizal associations may therefore be a promising strategy for phytoremediation and soil amelioration (Schutzendubel and Polle 2002). Ericoid mycorrhizal fungal endophytes, and sometimes their plant hosts, can evolve toxic metal resistance which enables ericoid mycorrhizal plants to colonise polluted soil (Perotto et al. 2002; Martino et al. 2003). This seems to be a major factor in the success of ericoid mycorrhizal taxa in a range of harsh environments (Cairney and Meharg 2003).

The importance of mycorrhizas in plant phosphorus nutrition has been appreciated for a long time, and their ability to dissolve and transform calcium-containing insoluble compounds and minerals (calcium phosphates, carbonate and sulphate) has been widely studied (Callot et al. 1985a, b; Lapeyrie et al. 1990, 1991; Gharieb and Gadd 1999). However, toxic metal mineral solubilisation has received little attention, though this should be considered in any revegetation, natural attenuation or phytoremediation strategies. The ectomycorrhizal fungi *Suillus granulatus* and *Pisolithus tinctorius* can promote the release of cadmium and phosphorus from rock phosphate (Leyval and Joner 2001), while the ericoid mycorrhizal fungus *Oidiodendron maius* can solubilise zinc oxide and phosphate (Martino et al. 2003). Many ericoid mycorrhizal and ectomycorrhizal fungi are able to solubilise zinc, cadmium, copper phosphates and lead chlorophosphate (pyromorphite) releasing phosphate and metals (Fomina et al. 2004). Both non-mycorrhizal *Pinus sylvestris* and pines infected with the ectomycorrhizal *Paxillus involutus* could enhance zinc phosphate dissolution, withstand metal toxicity and acquire the mobilised phosphorus (Fomina et al. 2006).

5. Nanoparticle Formation and Nanobiotechnology

Metal-containing micro-/nanoparticles have applications as new ceramic–metal (cermet) or organic–metal (orgmet) composites or structured materials for a variety of applications (Hennebel et al. 2009). The use of metal-accumulating microbes for the production of nanoparticles, and their assembly, may allow control over size, morphology, composition and crystallographic orientation. The production of such biomimetic materials is relevant to the production of new advanced materials, with applications in metal and radionuclide bioremediation, antimicrobial treatments (e.g. nano-silver), solar energy and electrical battery applications and microelectronics (Dameron et al. 1989; Klaus-Joerger et al. 2001). Because of their high specific surface area and high catalytic properties, biogenic metal products also offer potential for sorption and degradation of organic contaminants, as well as a variety of other applications, e.g. electricity generation in fuel cells, novel catalysts and sensors. Biogenic Mn oxides can sequester metals like Pb, Zn, Co, Ni, As and Cr and also oxidise certain organic pollutants (Hennebel et al. 2009). In contrast to bacteria, rather less attention has been given to fungal systems in this context although fungal reductive transformations of metalloids and Ag and Au species to nano- or colloidal forms are well known, as well as metal-containing reactive crystallites (Dameron et al. 1989) and Mn oxides (Miyata et al. 2004, 2007).

6. Soil Treatment Processes

The application to soils of certain amendments that immobilise metals, e.g., lime or phosphate treatment, has demonstrated enhanced natural remediation resulting in improved vegetation growth, increased microbial activity and diversity and reduced off-site metal transport. However, while long-term stability of certain metal complexes and compounds has been shown in model systems (Adriano et al. 2004), the influence of plant roots and its microbial and mycorrhizal associations on such stability has often been neglected. For example, pyromorphite ($Pb_5(PO_4)_3Cl$), which can form in urban and industrially contaminated soils, can be solubilised by phosphate-solubilising fungi, with concomitant production of lead oxalate (Sayer et al. 1999; Fomina et al. 2004). The ability of free-living and mycorrhizal fungi to transform pyromorphite (and other toxic metal-containing minerals) should be taken into account in risk assessments of the long-term environmental consequences of in situ chemical remediation techniques, revegetation strategies or natural attenuation of contaminated sites. The bioweathering potential of fungi has been envisaged as a possible means for the bioremediation of asbestos-rich soils. Several fungi could extract iron from asbestos mineral fibres (e.g. 7.3 % from crocidolite and 33.6 % from chrysotile by a *Verticillium* sp.), thereby removing the reactive iron ions responsible for DNA damage (Daghino et al. 2006).

VI. Conclusions

It is clear from the above that fungi are of importance in the transformation of both organic and inorganic pollutants in the natural environment. While pollutants may exhibit toxicity and cause changes in fungal community composition, fungi possess a range of mechanisms that confer resistance or tolerance, many of these resulting in pollutant transformation to less toxic forms. Such activities are part of natural biogeochemical cycles for major elements such as C, N, O, P and S but also metals, metalloids and radionuclides, as well as having applications in the bioremediation and natural attenuation of polluted habitats. However, pollutant interactions are complex and greatly influenced by environmental factors. While the theoretical response of fungi to pollutants can readily be speculated upon, some effects are difficult to demonstrate and quantify because of the inadequacy of several common techniques used to study fungal populations and their activities. Despite this, newly developed approaches using molecular biology and biomarkers are allowing a better understanding of community structure and responses to environmental factors, including pollutants. Growth media containing low and therefore more realistic concentrations of available carbon should also be used if in vitro techniques are employed to help determine the effects of pollutants on fungal growth. However, it is clear that because of the complexity of the fungal growth form and their multiplicity of biological responses and interactions with pollutants, coupled with the complexity of the terrestrial (and other) environments, a wealth of knowledge still awaits discovery.

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