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Pesticide-Derived Aromatic Amines and Their Biotransformation

Jean-Marie Dupret, Julien Dairou, Florent Busi, Philippe Silar, Marta Martins, Christian Mougin, Fernando Rodrigues-Lima and Angelique Cocaign[1]

1. Introduction

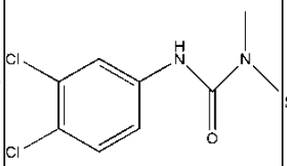
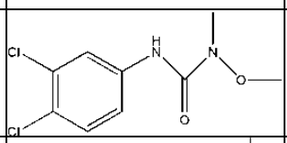
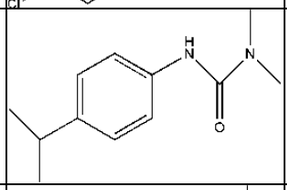
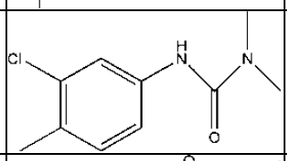
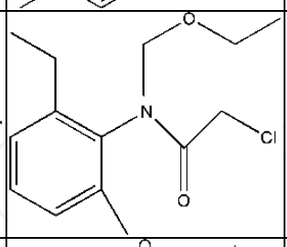
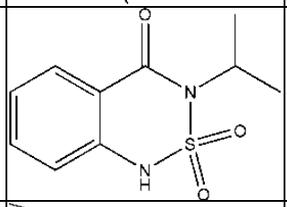
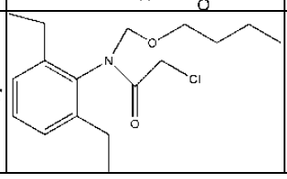
Aromatic amines (AA) are an important and diversified class of pollutants, including industrial products, drugs, combustion products, pesticides or dyes. Some AA, in particular pesticide-derived AA, are persistent in soils and ground waters and exhibit potential toxicity. These compounds may accumulate in the environment, where they have noxious effects. This is especially true for 3,4 dichloroaniline (3,4-DCA), a by-product of aniline-derived herbicides such as diuron. In treated soil, diuron is transformed into 3,4-DCA and then acetylated by soil bacteria and fungi into the less toxic acetyl-DCA. Microorganisms are thus good candidates to be used for decontamination of AA-polluted soils, a process known as bioremediation. Recent data indicate that filamentous fungi represent promising candidates for bioremediation of AA-contaminated soils. However, fundamental research is still needed to better understand the potential of fungi in metabolizing these pollutants.

2. Aromatic amines, an important and diversified class of pollutants

AA constitute an important and diversified class of pollutants. Many AA are toxic to most living organisms due to their genotoxic or cytotoxic properties (Kim & Guengerich, 2005). AA account for 12% of the 415 chemicals known or strongly suspected to be carcinogenic in humans (USA National Toxicology Program, 2005). AA are common by-products of chemical manufacturing (pesticides, dyestuffs, rubbers or pharmaceuticals), coal and gasoline combustion or pyrolysis reactions (Palmiotto et al., 2001). The presence of AA in ground waters or soil samples subject to industrial, agricultural or urban pollution is an increasing concern, particularly for persistent toxic AA contaminants, such as pesticide-derived anilines (Gan et al., 2004).

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Major reports on pesticide-derived AA contaminations are listed in Table 1, including the chemical sources of contaminants. 3,4-dichloroaniline (3,4-DCA), a highly toxic pesticide-derived AA, is persistent in soil, surface and ground waters. This compound is the major breakdown product of the phenylurea herbicides diuron and linuron, and of the anilide propanil. At the cellular level, 3,4-DCA is known to activate the Ahr/Cyp1a1 pathway (Voelker et al., 2008; Ito et al., 2010). In the same way, the metabolite 3,5-dichloroaniline (3,5-DCA) is more toxic and persistent than its parent vinclozolin. In particular, toxicity of 3,5-DCA has been shown to be related to anti-androgenic activity (Lee et al., 2008).

Potential pollution source	Use	Structure	Reported sites of pollution	Aromatic amine derivative contaminants	References
diuron	herbicide (no longer used)		soils, waste waters, sewage sludges, surface waters	3,4-dichloroaniline	(Vroumsia et al., 1996; Ghanem et al., 2007; Albers et al., 2008; Badawi et al., 2009; Vercraene-Eairmal et al., 2010)
linuron	herbicide		soils	3,4-dichloroaniline	(Kolpin et al., 1998; Badawi et al., 2009; Heidler & Halden, 2009; Woudneh et al., 2009)
isoproturon	herbicide		soils, shallow ground waters	4-isopropylaniline	(Vroumsia et al., 1996; Spliid & Koppen, 1998; Muller et al., 2002; Hussain et al., 2009; Mosleh, 2009)
chlorotoluron	herbicide		soils, surface waters	3-chloro-4-methylaniline	(Vroumsia et al., 1996; Muller et al., 2002; Badawi et al., 2009)
acetochlor	herbicide (no longer used)		soils, ground waters	2-methyl-6-ethylaniline 2,6-diethylaniline	(Kolpin et al., 1998; Barbash et al., 2001; Osano et al., 2002; Dictor et al., 2008; Vercraene-Eairmal et al., 2010)
bentazon	herbicide		soils	2-amino N-isopropylbenzamide	(Kim et al., 1997)
butachlor	herbicide (no longer used)		soils	2,6-diethylaniline	(Ye et al., 2002)

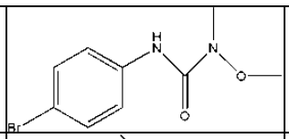
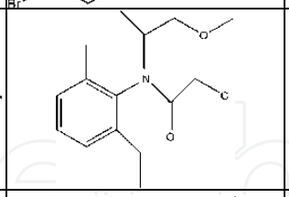
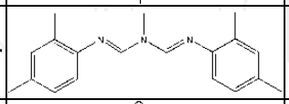
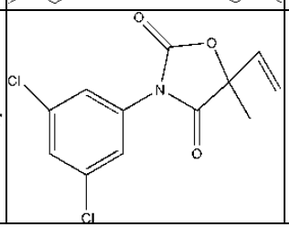
metobromuron	herbicide		soils	4-bromoaniline	(Van Eerd et al., 2003)
metolachlor	herbicide (no longer used)		ground and surface waters	2-ethyl-6-methylaniline	(Osano et al., 2002; Focazio et al., 2008; Huang et al., 2008; Vercraene-Eairmal et al., 2010)
amitraz	pesticide (no longer used)		soils, surface waters	2,4-dimethylaniline	(Osano et al., 2002)
vinclozolin	fongicide (no longer used)		soils	3,5-dichloroaniline	(Lee et al., 2008)

Table 1. Pesticide contaminants and their AA derivatives.

3. The fate of pesticide-derived aromatic amines in the soil environment

In the environment, organic pollutants can be degraded by different biological (Van Eerd et al., 2003), chemical (Sarmah & Sabadie, 2002) or photochemical (Katagi, 2004; Nelieu et al., 2009) processes. Furthermore, in soils, the occurrence and kinetics of degradation processes are modulated by retention through reversible or irreversible adsorption on soil components. Soils present a variety of complex and heterogeneous characteristics; among them, clay and organic contents as well as pH are known as the main properties driving its reactivity and thus the fate of chemicals (Calvet, 1989).

In addition, soils are complex ecosystems of many species, including plants, fauna and microorganisms (Spaink, 2002). Living organisms use several enzymatic pathways, including a variety of xenobiotic-metabolizing enzymes (XME) to protect themselves against the potentially toxic effects of the natural products and xenobiotics present in their environment. Overall, the metabolic fate of xenobiotics involves a two phase metabolism including cytochrome P450-mediated phase I reactions and transferase-mediated conjugation reactions (Phase II). Plant XME include cytochromes P450 (Morant et al., 2003) and glutathione *S*-transferases (Pflugmacher et al., 2000). XME are also expressed in soil microorganisms. Presently, most studies focus on bacterial XME (Van Eerd et al., 2003).

By-products of aniline-derived herbicides (such as 3,4-DCA) are among the most toxic chemicals found in soil (Dearfield et al., 1999; Harvey et al., 2002). The XME-dependent N-acetylation of these chemicals has been shown to detoxify them (Tweedy et al., 1970; Tixier et al., 2002) and has been reported to occur in soil bacteria such as *Pseudomonas sp.* (Vol'nova et al., 1980; Travkin et al., 2003; Westwood et al., 2005) and *Mesorhizobium loti* (Rodrigues-Lima et al., 2006). This pathway has also been described in filamentous fungi such as *Podospora anserina* (Martins et al., 2009).

Soil bacteria	Filamentous fungi
Pseudomonas aeruginosa (Westwood et al., 2005)	*Aspergillus niger, Beauveria bassiana, Cunninghamellae chinulata, Mortierella isabellina* (Tixier et al., 2002)
Mesorhizobium loti (Rodrigues-Lima et al., 2006)	*Podospora anserina* (Martins et al., 2009)

Table 2. Examples of species involved in microbial conversion of 3,4-DCA into 3,4-AcDCA.

The herbicide metobromuron is metabolized to 4-bromoaniline (4-BA), which is detoxified by certain soil microbes to acetyl-4-bromoaniline (Tweedy et al., 1970; Van Eerd et al., 2003).

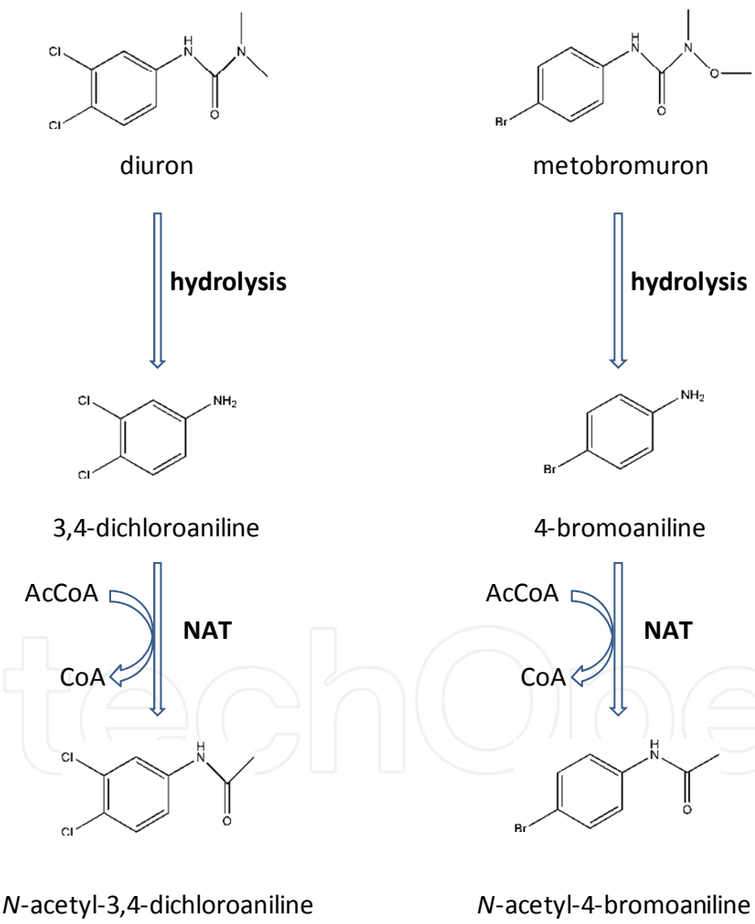


Fig. 1. Biotransformation of diuron and metobromuron by microorganisms.

4. Strategies for bioremediation of aromatic amine-contaminated soils

Soil contamination with pesticides and their derivatives is a major concern in industrialized countries. Exploiting the metabolic capability of microorganisms to transform pollutants is a

promising approach for bioremediation (degradation of pollutants using living beings) of contaminated soils.

Bioremediation is the use of living organisms for *in situ* treatment of contaminated soils, sediments or waters (Schnoor, 1997). Although bacteria are the most common group of organisms used for bioremediation, the use of plants (phytoremediation) and algae (phycoremediation) have been reported, whereas animals (zooremediation) are much more rarely considered (Gifford et al., 2007). The use of filamentous fungi (mycoremediation) may offer promising alternatives (Mougin, 2002; D'Annibale et al., 2006; Harms et al., 2011).

Phytoremediation has successfully been applied for remediation of soils contaminated with heavy metals or other xenobiotics. A form of phytoremediation is rhizoremediation or phytoremediation of the rhizosphere. Indeed, root exudates, soil bacteria and mycorrhizal fungi participate in degradation of organic chemicals in close proximity to the roots. Although the importance of the rhizosphere community for degradation of anthropic xenobiotics has been recognized, very little is known about the exact composition of the degrading populations (Kuiper et al., 2004).

Although the use of combined action between plants and microorganism is a promising strategy for bioremediation, other approaches may be proposed. Whereas it is known that the rhizosphere contains a great proportion of gram-negative bacteria such as *Pseudomonas sp.* (Kuiper et al., 2004), soil microbiological characteristics are generally more complex. Especially, it must be pointed out that the fungal/bacterial ratio in soil has shown the predominant contribution of fungi (Gilbertson, 1980; Durrieu, 1993; Boer et al., 2005). Due to the low substrate specificity of their degradative enzyme machinery (e.g. laccase, lignine peroxidase...), fungi are able to perform the breakdown of a wide range of organic pollutants in contaminated soils (Mougin et al., 2003, Tortella et al., 2005; D'Annibale et al., 2006). Thus, use of soil fungi may be a promising step for setting up new bioremediation development strategies.

However, the field of mycoremediation remains still to be explored (Harms et al., 2011). The best species suitable for such task are not well characterized and presently research focus on a few species, like *Fusarium* (many of them may belong to plant pathogenic species) or white-rots (i.e., basidiomycetes fungi that efficiently degrade lignin) (Mougin et al., 2002, Tortella et al., 2005; Chulalaksananukul et al., 2006; McErlean et al., 2006; Mougin et al., 2009).

Although a still limited number of data is available, bioremediation appears to induce reduced cost in comparison to conventional process such as incineration (Wood, 2008; Vangronsveld et al., 2009). *In situ* bioremediation techniques are in general less expensive since they avoid soil excavation and transport. Finally, soils treated by bioremediation may be re-used, at least for industrial crops, if acceptable target pollutant levels are reached (Mougin et al., 2009). However, current strategies generally categorized into *ex situ* and *in situ* bioremediation have not yet yielded the expected efficiency (Pandey et al., 2009). Fundamental research is needed to reduce cost and to increase performance of bioremediation techniques. A promising strategy is to explore the metabolic diversity of microorganisms and their ability to degrade pollutants. In the eyes of EU's regulation on genetic modified organisms (GMO) (European Commission DG ENV, 2010), the use of non-GMO with no pathogenic potential will be of great interest for future bioremediation approaches.

Exploiting the ability of microorganisms to transform AA pollutants is a promising approach for bioremediation of contaminated soils. Most studies focused on conversion of 3,4-DCA into its acetylated form. First, it has been shown that acetylated 3,4-DCA is less

toxic than 3,4-DCA; second, some soil bacteria and fungi strains are able to acetylate 3,4-DCA (Tixier et al., 2002; Westwood et al., 2005). Although aniline derivatives undergo complex transformations in soils, including mineralization (biodegradation), co-metabolic and condensation reactions, binding to humus complexes (Albers et al., 2008) and mineralization (Mougin et al., 2009), studies opened up new possibilities in bioremediation (Rodrigues-Lima et al., 2006; Martins et al., 2009, Mougin et al., 2009), as detailed below.

The major detoxification pathway of AA depends on the activity of arylamine *N*-acetyltransferase enzymes (NAT) (Dupret & Rodrigues-Lima, 2005). NAT catalyze the acetyl-CoA-dependent *N*- and/or *O*- acetylation of AA and their N-hydroxylated metabolites. The *N*-acetylation reaction leads to the detoxification of AA through the production of arylacetamides that are chemically stable. In humans, variations of NAT activity have long been associated with susceptibility to different cancers in relation with exposure to certain AA (Hein, 2002).

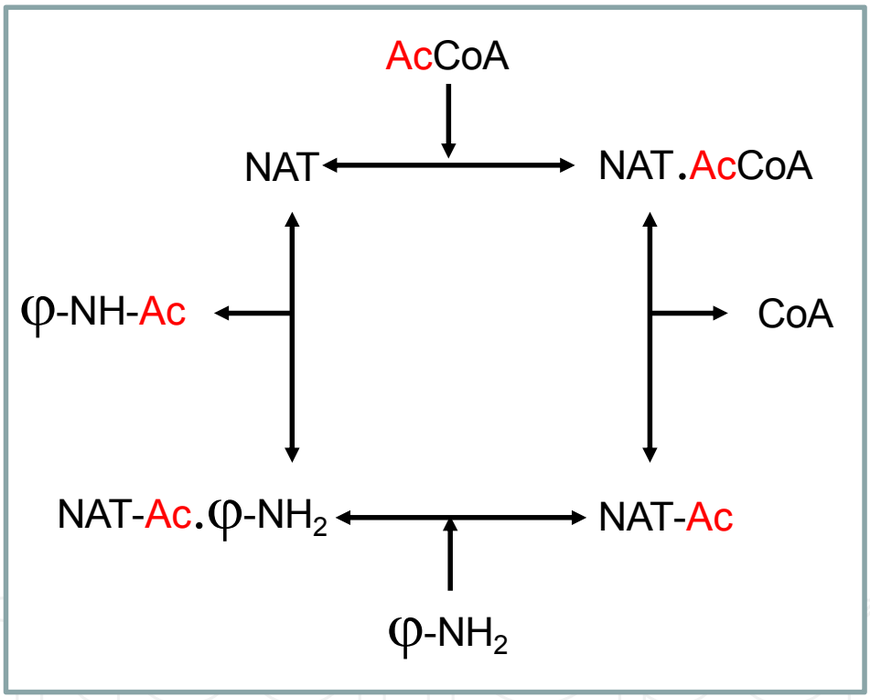


Fig. 2. Reaction mechanism of NAT enzymes

Using the potential detoxifying properties of NAT enzymes expressed in soil microorganisms, putative AA bioremediation pathways were explored using soil bacteria or filamentous fungi.

Legume plants and nitrogen-fixing roots represent a promising plant-bacterial rhizoremediation system, which turned the attention of biotechnologists in recent years. Two NAT enzymes were characterized in Mesorhizobium loti, a rhizobial nitrogen-fixing bacterium that lives in symbiosis with several species of the genus Lotus, including Lotus

corniculatus and Lotus japonicus. These two enzymes were shown to catalyze the N-acetylation of several known NAT substrates including aniline-derived pesticide residues (3,4-DCA, 4-BA and 4-iodoaniline). The existence of a functional NAT-dependent acetylation pathway in the root nodules of Lotus japonicus inoculated with M. loti was also demonstrated. M. loti was the first non-eukaryotic organism shown to express two catalytically active NAT isoforms. This work also provided the first evidence for acquisition of a xenobiotic detoxification pathway by a plant through symbiosis with a soil microbe (Rodrigues-Lima et al., 2006). As many aromatic pollutants are detoxified by the NAT-dependent pathway, these results opened up new possibilities in the field of rhizoremediation for aromatic soil pollutants. Indeed, leguminous plants grow in a wide variety of environments; moreover, root systems penetrate from 50 cm to a few meters into the soil. However, technical constraints are important and fungal remediation represents a promising alternative for AA bioremediation.

To date the potential of fungi in bioremediation is not well understood although these organisms form the large majority of the soil microorganisms (Harms et al., 2011). Indeed, it has been estimated that in a typical soil 80% of the biomass, with the exception of the plant roots, is of fungal origin (Gilbertson, 1980; Durrieu, 1993) and fungi out compete bacteria in many degradation processes or synergize their activity (Boer et al., 2005). Fungi efficiently secrete in the medium a large array of enzymes involved in cellulose/lignin degradation, which have been shown to display xenobiotic-metabolizing enzyme (XME) activities (Tortella et al., 2005; McErlean et al., 2006). They also produce and encounter many secondary metabolites (Misiek & Hoffmeister, 2007), including harmful polyketides, cyclic peptides, alkaloids and others, for which they must have detoxifying enzymes with XME activities (Glenn & Bacon, 2009).

Filamentous fungi are able to degrade aromatic ring containing compounds. The most efficient species in term of known enzymatic capacity are white-rot fungi such as *Pleurotus*, *Trametes* or *Phanerochaetes*. Lignin modifying enzymes from white rots, such as lignin peroxidases (LiP), manganese-dependent peroxidases (MnP) and laccases play key roles in degradation reactions. So far, fungal remediation studies using white rots have been performed on polycyclic aromatic hydrocarbons, nitro-aromatic compounds, or endocrine-disrupting phenolic chemicals (Mougin et al., 2009). However, white rots are not very competitive in soils. Therefore, the use of a cosmopolitan fungus to bioremediate AA-contaminated soils is a promising alternative.

Four well known fungal species (*Fusarium graminearum*, *Phycomyces blakesleeanus*, *Podospora anserina*, and *Rhizopus oryzae*) from different ecosystems (natural habitats of fungi are wheat (*F. graminearum*), soil (*R. oryzae*; *P. blakesleeanus*), dung (*P. anserina*) or soil/dung (*C. globosum*)), for which complete genome sequences are available, were screened for radial growth in the presence of three toxic AA: 3,4-DCA (pesticide residue), 2-aminofluorene (2-AF, carcinogen), and 4-butoxyaniline (4-BOA, chemical intermediate) (Martins et al., 2009). The growth of *R. oryzae* and *P. blakesleeanus* was almost completely abolished by these three AA at concentrations of 100–250 μM in standard minimal growth medium. In the same conditions, little effect on growth was observed in the other two studied species (*P. anserina* and *F. graminearum*), suggesting that they have mechanisms of tolerance to AA. Genomic DNA sequence analysis indicated that *P. anserina* had two putative NAT enzymes and that *F. graminearum* had three such enzymes, whereas the two sensitive fungi had no genes encoding NAT enzymes.

The bioremediation potential of *Podospora anserina* was explored. *P. anserina* only reproduces by sexual means, it is a cosmopolitan non-pathogenic species and its spread is easy to control. In addition, its genome has been sequenced and powerful genetic tools permit to construct single and double deletion mutants. Two NAT enzymes, PaNAT1 and PaNAT2, were characterized in *P. anserina*. PaNAT2 was systematically more active than PaNAT1. Targeted gene disruption experiments revealed that PaNAT2 was required for the growth and survival of the fungus in the presence of toxic AA.

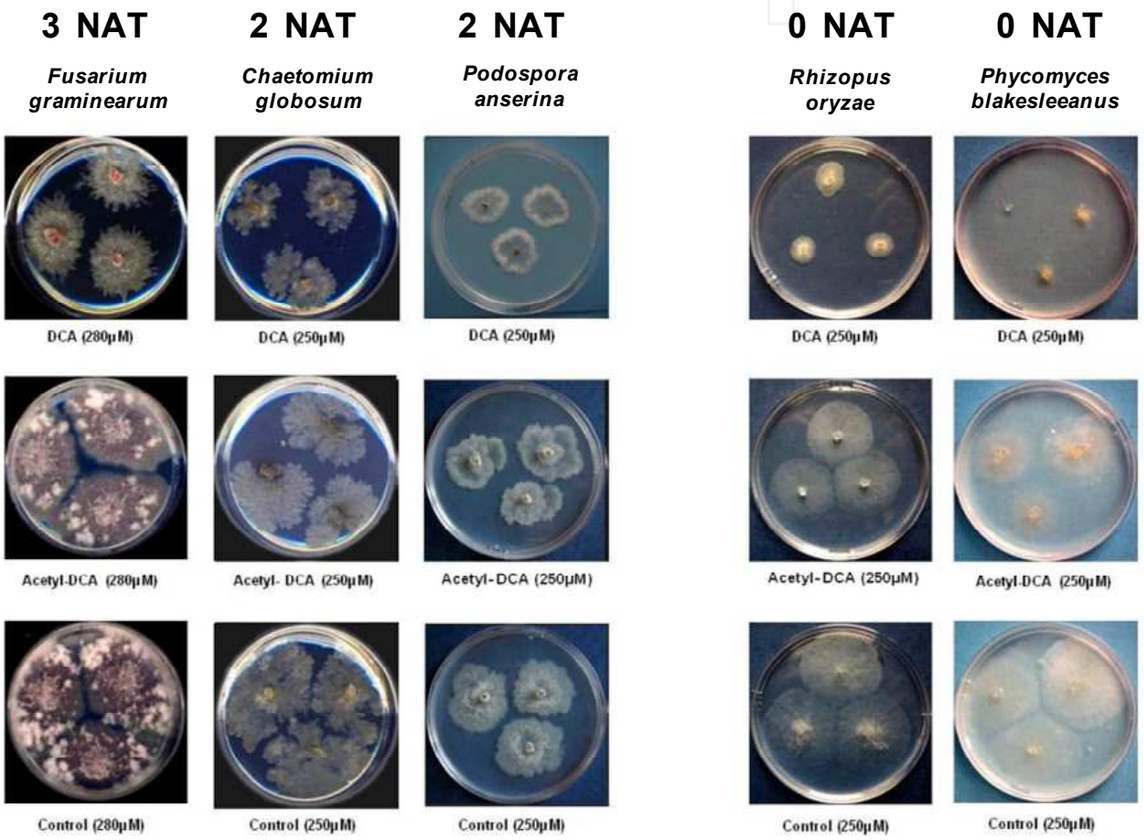


Fig. 3. NAT genes in fungi and tolerance to 3,4-DCA in five species.
The figure shows that three common fungal species, Fusarium graminearum, Chaetomium globosum and Podospora anserina tolerate 3,4-DCA at concentrations of 250 µM. By contrast, two other species, Rhizopus oryzae and Phycomyces blakesleeanus, are much less tolerant to this compound. In all cases, acetylated 3,4-DCA is less toxic than 3,4-DCA. Finally, the presence, in species of the left columns, of NAT genes appears to be associated with tolerance to 3,4-DCA.

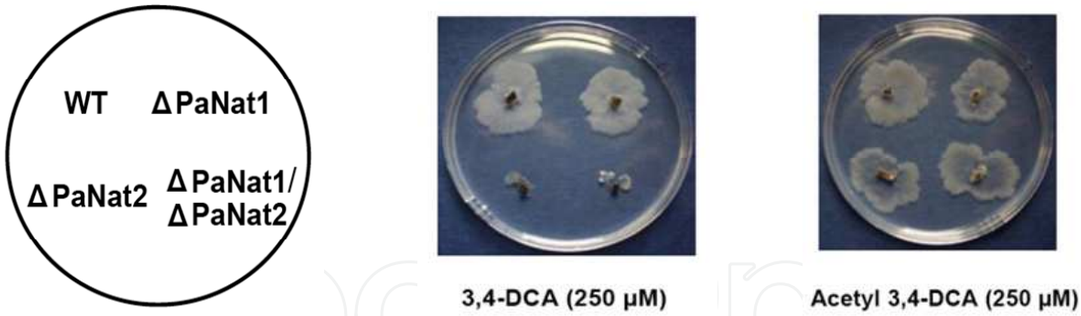


Fig. 4. PaNAT2 plays a key role in P. anserina tolerance to 3,4-DCA.
The figure shows that the radial growth of strains lacking PaNAT2 was strongly impaired in the presence of 3,4-dichloroaniline (3,4-DCA). Conversely, acetylated 3,4-DCA was much less toxic. Tested mutants lacked either one (ΔPaNat1 or ΔPaNat2) or both (ΔPaNat1/2) NAT genes. Petri dish contained the indicated strains grown on M2-agar medium with 3,4-DCA or its acetylated form at the indicated final concentration. Photographs were taken after 3 days of growth at 27°C.

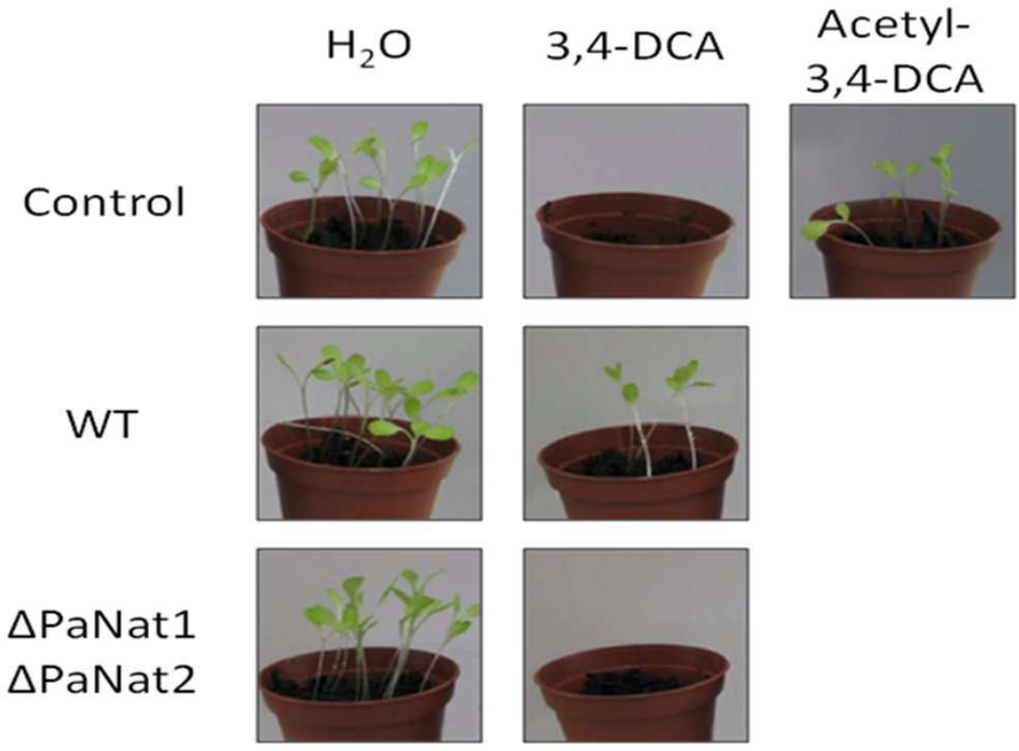


Fig. 5. Remediation of soil samples contaminated with 3,4-DCA.
3,4-DCA-contaminated soils (20 g/pot, 80 mg of 3,4-DCA/kg of soil) were inoculated every 24 hours, over a period of three days, with 0.5 g of wild-type Podospora anserina or with NAT-deleted strains (ΔPaNat 1/2 strains) and incubated for 72h at 25°C. Lactuca sativa seeds were sown and allowed to germinate and grown for 8 days at 25°C. Controls were set up with acetyl-3,4-DCA (80 mg/kg of soil) and water. Germination and growth were abolished in soils contaminated with 3,4-DCA. Conversely, in contaminated soils treated with P. anserina, seed germination and growth were restored.

Finally, proof-of-concept remediation experiments were performed where *P. anserina*, through its PaNAT2 enzyme, was able to detoxify 3,4-DCA in experimentally contaminated soil samples. 3,4-DCA concentration (80 mg/kg of soils) used were higher than concentrations observed in contaminated soils (around 0.02 to 5 mg/kg of dry soils). These findings provided a basis for new systems based on fungi for the bioremediation of contaminated soils (Martins et al., 2009).

Overall, given the detoxifying activity of NAT enzymes, the presence of NAT genes in many fungi (Martins et al., 2009; Martins et al., 2010) and the fungal biomass in fungi-bearing soils, these studies show that fungal bioremediation of pesticide-derived AA represent a promising perspective.

5. Conclusion

What are the remediation potential of bacteria and fungi for pesticide-derived AA? This question is still open. Whereas bacteria are abundant, fungi represent the largest biomass in soils. Moreover, the NAT activity of fungi seems to be higher than that of bacteria. So our preliminary studies suggest that fungi represent better candidates for bioremediation of AA-contaminated soils. Given the fungal biomass in fungi-bearing soils, these reports keep with promising perspectives in the field of bioremediation for a variety of toxic AA. Such perspectives should now be assessed in field studies.

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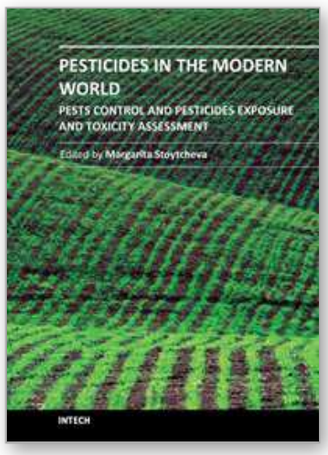
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Pesticides in the Modern World - Pests Control and Pesticides Exposure and Toxicity Assessment

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The present book is a collection of selected original research articles and reviews providing adequate and up-to-date information related to pesticides control, assessment, and toxicity. The first section covers a large spectrum of issues associated with the ecological, molecular, and biotechnological approaches to the understanding of the biological control, the mechanism of the biocontrol agents action, and the related effects. Second section provides recent information on biomarkers currently used to evaluate pesticide exposure, effects, and genetic susceptibility of a number of organisms. Some antioxidant enzymes and vitamins as biochemical markers for pesticide toxicity are examined. The inhibition of the cholinesterases as a specific biomarker for organophosphate and carbamate pesticides is commented, too. The third book section addresses to a variety of pesticides toxic effects and related issues including: the molecular mechanisms involved in pesticides-induced toxicity, fish histopathological, physiological, and DNA changes provoked by pesticides exposure, anticoagulant rodenticides mode of action, the potential of the cholinesterase inhibiting organophosphorus and carbamate pesticides, the effects of pesticides on bumblebee, spiders and scorpions, the metabolic fate of the pesticide-derived aromatic amines, etc.

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