UNIVERSITÀ DI PARMA

Biotransformation in plant of chemicals: a focus on modified mycotoxins

Chiara Dall'Asta

OUTLINE of the TALK

The Yin & Yang of Biotransformation exerted by plants

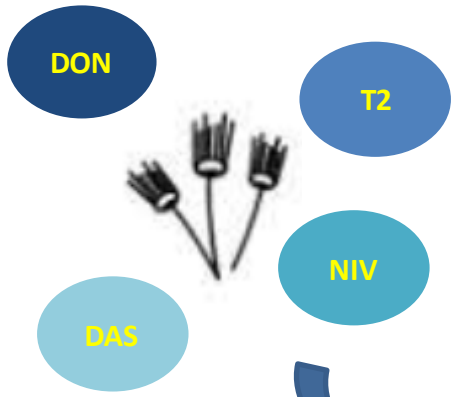
Modified mycotoxins as a case study

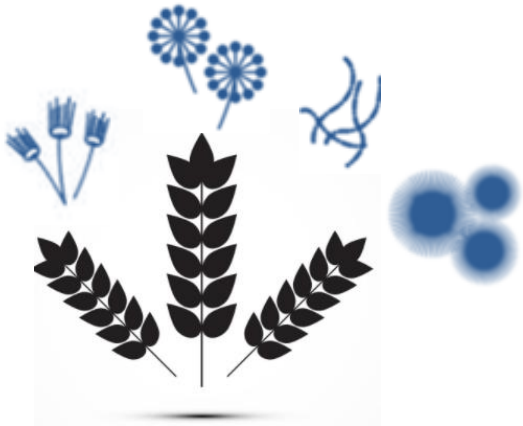
Which Impact for Risk Assessment?

A challenge or an opportunity?

WHAT WE KNOW ABOUT CO-OCCURRENCE?

Many mycotoxins per fungi

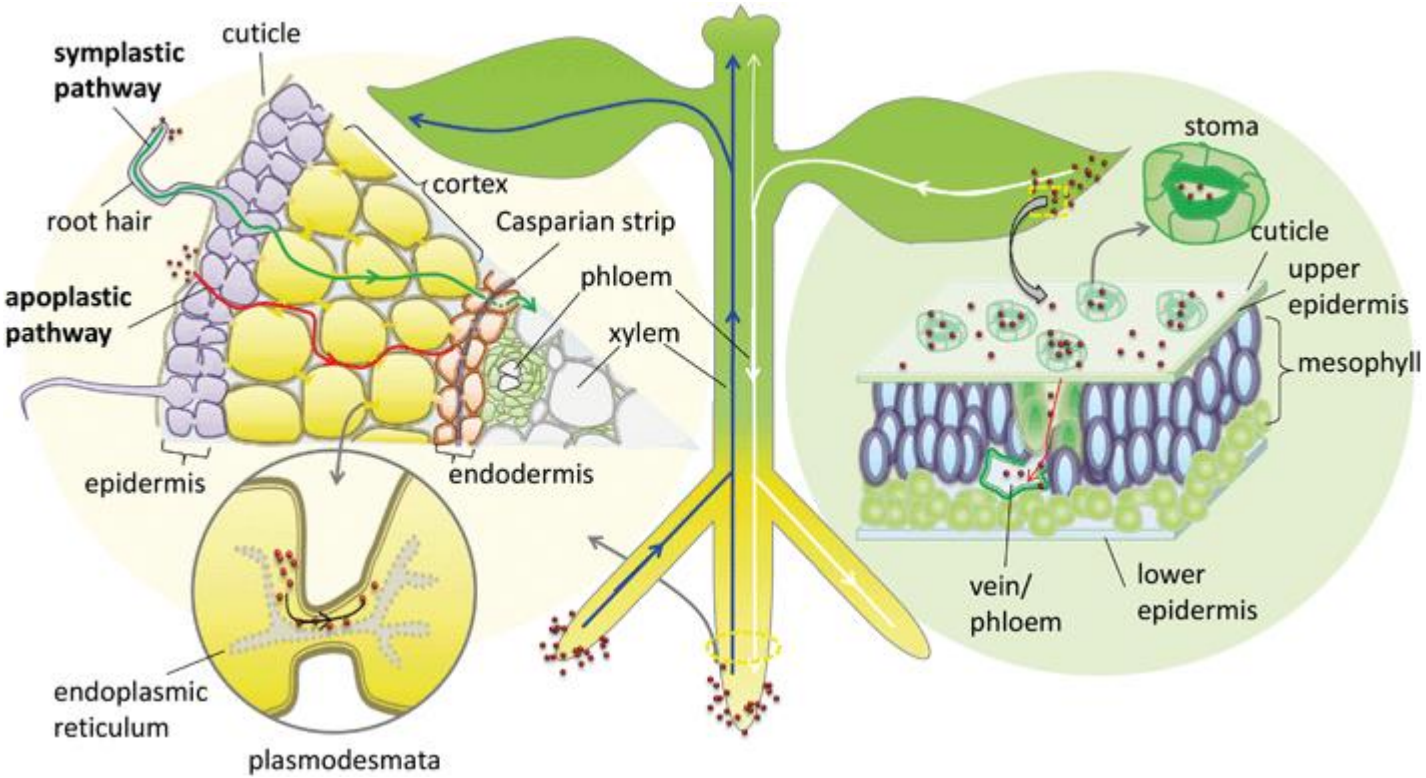




Many fungi per crop

Many crops per meal

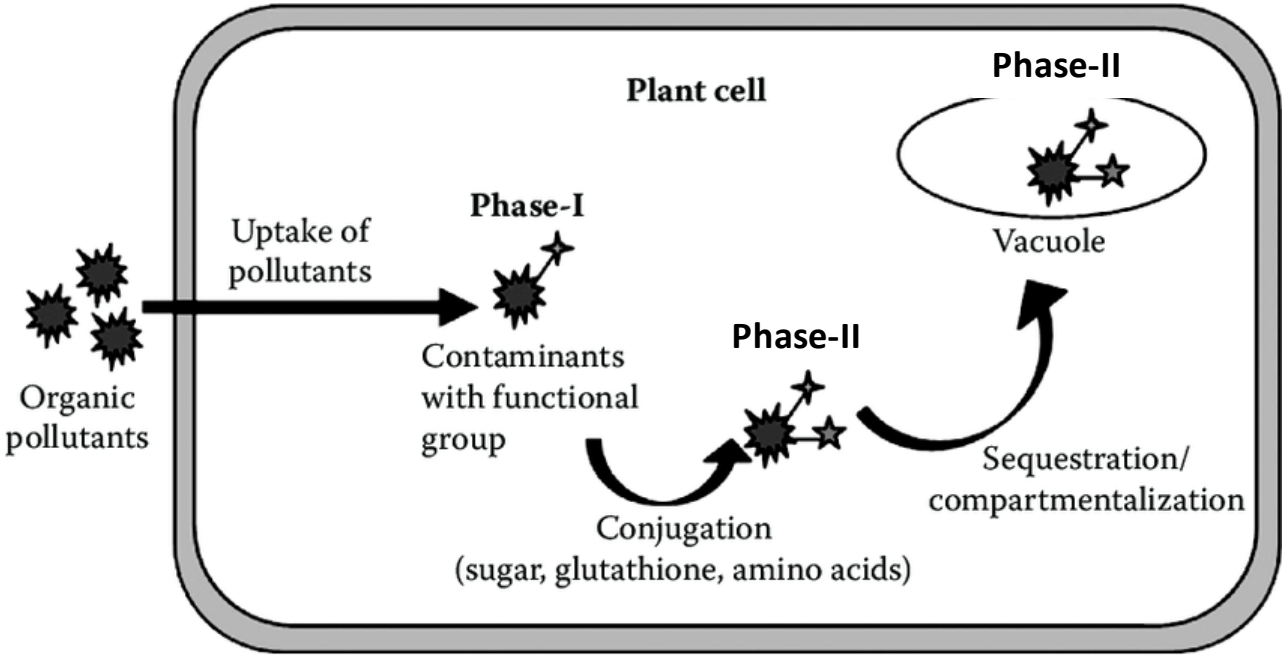
PLANT UPTAKE of CONTAMINANTS



What we call «contaminants» or «residues», are just «xenobiotics» for the plant.

Xenobiotics can be uptaken by plant according to their polarity, translocated and metabolised.

THE GREEN LIVER SYSTEM



Generally, Phase II metabolites have little or no **phytotoxicity** and may be stored in cellular organelles.

PHASE II – chemical conjugation of parent compounds with polar groups

The ability of plants to modify xenobiotics is based on its enzymatic machinery:

- Monoxygenase reaction (hydroxylation)
- P450 mediated reactions

Therefore, the genetic backgroud and possible modification in the CYPs superfamily may lead to metabolic RESISTANCE

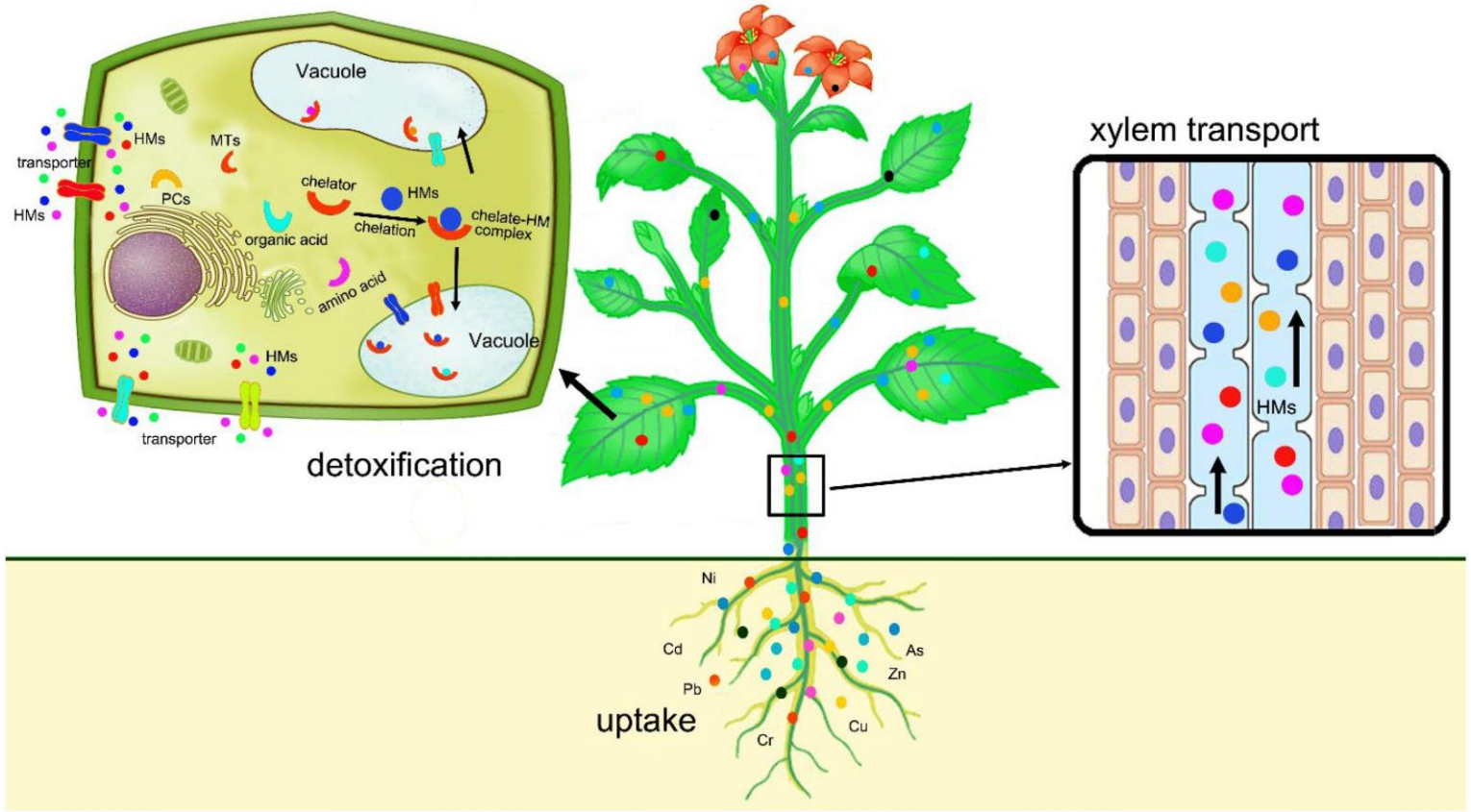
blackgrass

ryegrass

First documented cases of metabolic resistance (CYP-mediated) towards herbicides

PHYTOREMEDIATION: The ability of plants to uptake contaminats from soil and biotrasform them

It has been studied to «clean» polluted soils/waters, i.e. heavy metals

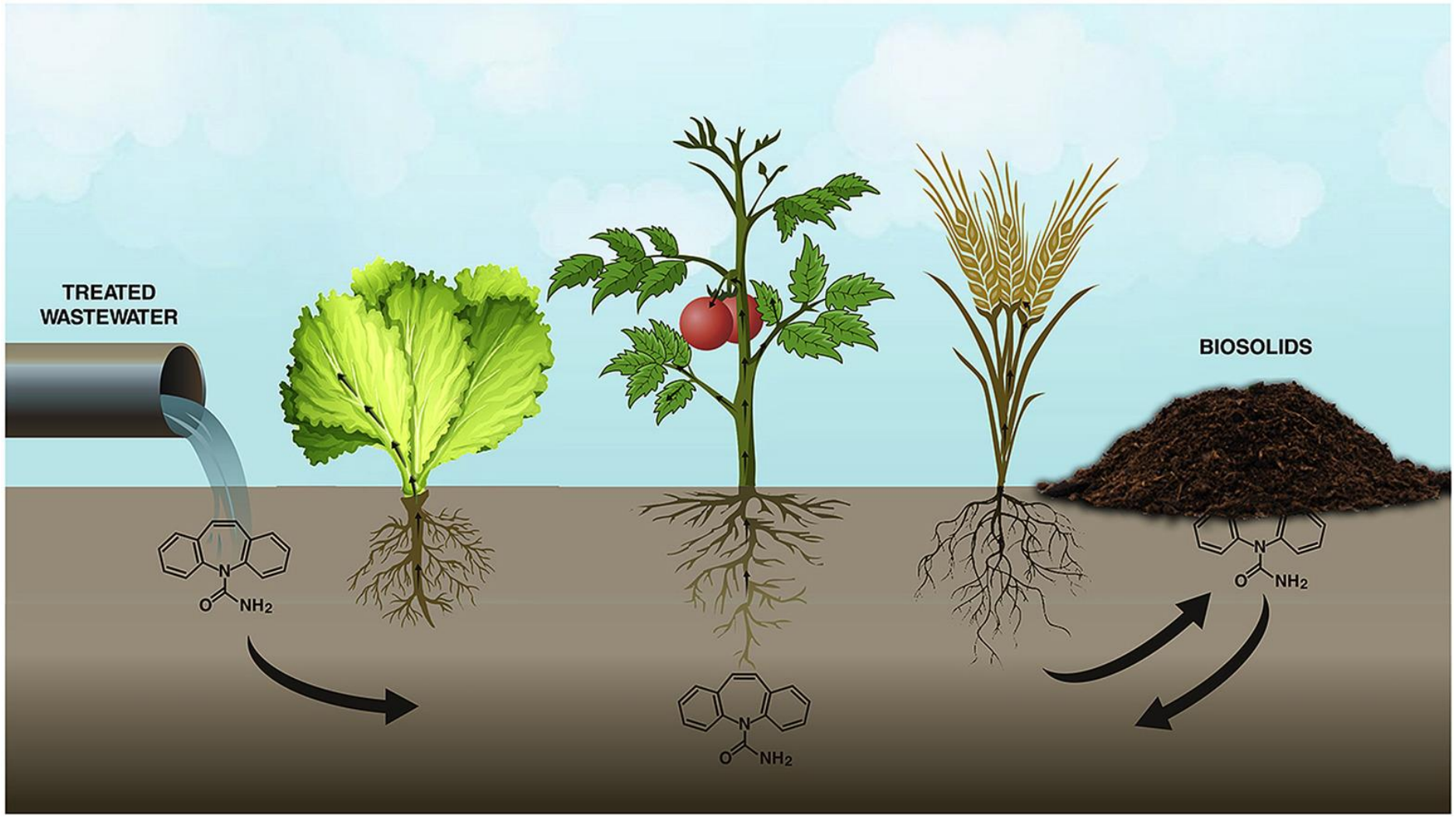


Source: https://doi.org/10.3389/fpls.2020.00359

However, when it comes to EDIBLE PLANTS, the phenomenon can be of concern

➔ **Cadmium enrichment in rice**

PHYTOREMEDIATION OR MASKING?

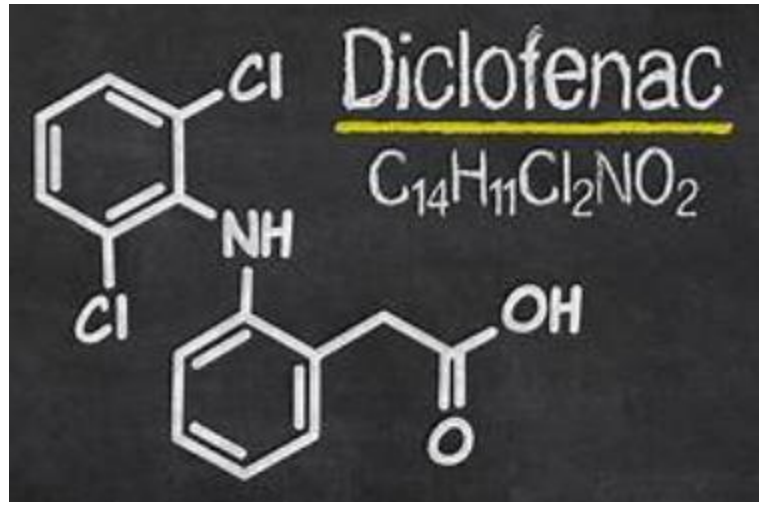


Analytical and Bioanalytical Chemistry (2020) 412:1817–1824
https://doi.org/10.1007/s00216-020-02429-7

RESEARCH PAPER

A new analytical workflow using HPLC with drift-tube ion-mobility quadrupole time-of-flight/mass spectrometry for the detection of drug-related metabolites in plants

Franz Mlynek[1] · Markus Himmelsbach[1] · Wolfgang Buchberger[1] · Christian W. Klampfl[1]



>30 metabolites of diclofenac in edible plants

Science of the Total Environment 766 (2021) 144499

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Uptake, accumulation and impact of antiretroviral and antiviral pharmaceutical compounds in lettuce

Preston Akenga [a,b], Antony Gachanja [c], Mark F. Fitzsimons [a], Alan Tappin [a], Sean C

Environmental Science Nano

REVIEW

Uptake, translocation, and transformation of metal-based nanoparticles in plants: recent advances and methodological challenges†

Jitao Lv,[a] Peter Christie [a] and Shuzhen Zhang [*ab]

Journal of Chromatography A 1613 (2020) 460673

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Investigations on the uptake and transformation of sunscreen ingredients in duckweed (*Lemna gibba*) and *Cyperus alternifolius* using high-performance liquid chromatography drift-tube ion-mobility quadrupole time-of-flight mass spectrometry

Alexandra Seyer, Franz Mlynek, Markus Himmelsbach, Wolfgang Buchberger, Christian W. Klampfl*

Institute of Analytical Chemistry, Johannes Kepler University Linz, Altenberger Strasse 69, 4040 Linz, Austria

IN THE MEANSWHILE, SCIENTISTS…

(knowledge from one field does not easily enter other fields)

1983: J.D. Miller – „masked“ fusarium mycotoxins …?

CANADIAN JOURNAL OF PLANT PATHOLOGY 7: 132-134, 1985

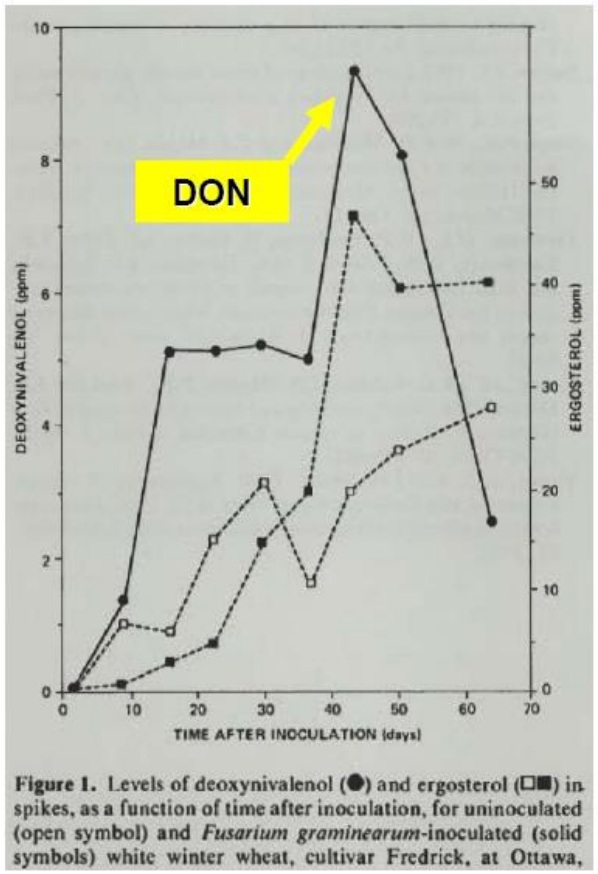


Figure 1. Levels of deoxynivalenol (●) and ergosterol (□■) in spikes, as a function of time after inoculation, for uninoculated (open symbol) and *Fusarium graminearum*-inoculated (solid symbols) white winter wheat, cultivar Fredrick, at Ottawa,

Deoxynivalenol in an experimental *Fusarium graminearum* infection of wheat

J. David Miller and J. Christopher Young

The decline in DON concentrations between weeks 6 and 9 is consistent with a similar pattern observed in an experimental infection of field corn with *F. graminearum* (Miller et al. 1983b). Rapid declines in DON concentrations after a peak in naturally infected wheat also have been observed (Scott et al. 1984). This is of some practical importance because the timing of harvest may influence the DON concentration in the crop. The basis of these declines appears to be the breakdown of DON by plant enzymes (Miller et al. 1983b, unpublished). This is the first example of a mycotoxin degradation in vivo by plant cells. This phenomenon is being studied in our laboratory.

"Fast decrease in DON after a peak» in naturally infected as well as inoculated wheat

Strange trend probably due to "…the breakdown of DON driven by plant enzymes"

2005: F. Berthiller – «DON-3-glucoside, the first Fusarium masked mycotoxin isolated ever»

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

J. Agric. Food Chem. **2005**, *53*, 3421–3425 **3421**

Masked Mycotoxins: Determination of a Deoxynivalenol Glucoside in Artificially and Naturally Contaminated Wheat by Liquid Chromatography–Tandem Mass Spectrometry

Franz Berthiller,† Chiara Dall'Asta,† Rainer Schuhmacher,*,†
Marc Lemmens,‡ Gerhard Adam,§ and Rudolf Krska†

Mycotoxins are poisonous, low molecular weight secondary metabolites of molds. The topic of conjugated or masked mycotoxins first caught attention in the mid-1980s because in some cases of mycotoxicoses, clinical observations in animals did not correlate with the low mycotoxin content determined in the corresponding feed. The unexpected high toxicity could for instance be attributed to the occurrence of undetected, conjugated forms of mycotoxins that hydrolyze to the precursor toxins in the digestive tracts of animals (*1*). It was shown that

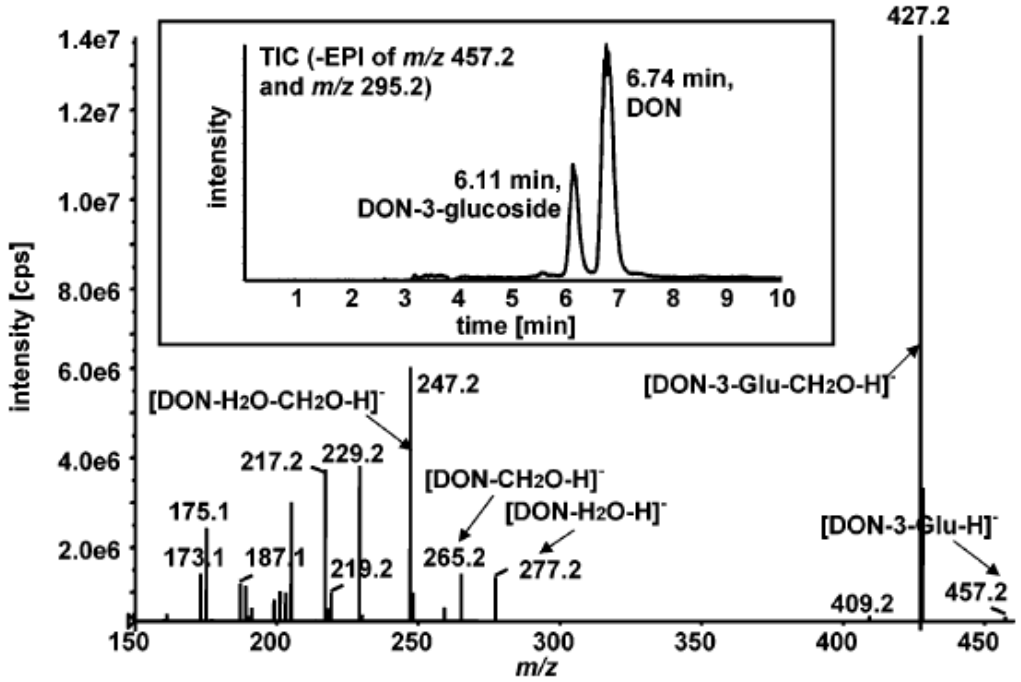


Figure 4. MS/MS (EPI) spectrum of the LC peak at 6.11 min and total ion chromatogram (TIC) of wheat extract (*m/z* 457.2 and *m/z* 295.2) after purification with MycoSep 230 column, APCI negative ion mode, CE (–30 eV).

THE LONG ROAD TO MODIFIED MYCOTOXINS

Gareis et al 1990

Berthiller et al. 2005

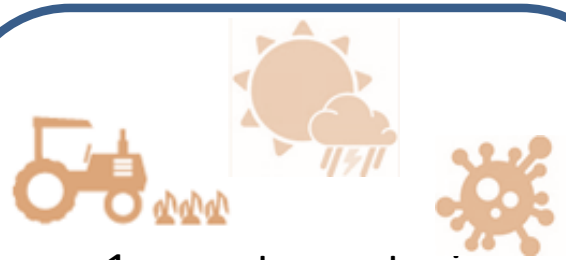
Berthiller et al. 2012

Rychlik et al. 2013

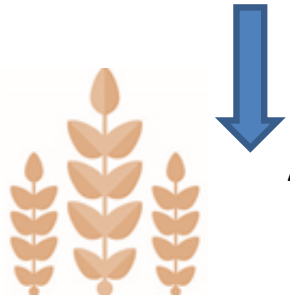
EFSA Opinion, 2014

Modified mycotoxins – mycotoxins structurally modified as an effect of a metabolic process exerted by a living organism (i.e. plants, fungi, mammals), or as an effect of food processing. Masked mycotoxins *senso strictu* are included in this definition.

WHAT IS KNOWN IN 2021

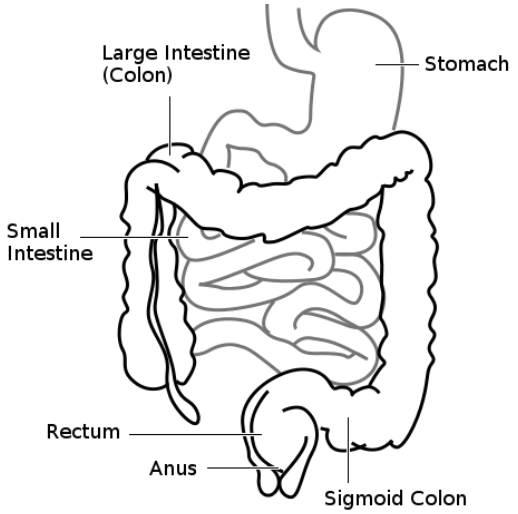


1 parent mycotoxin

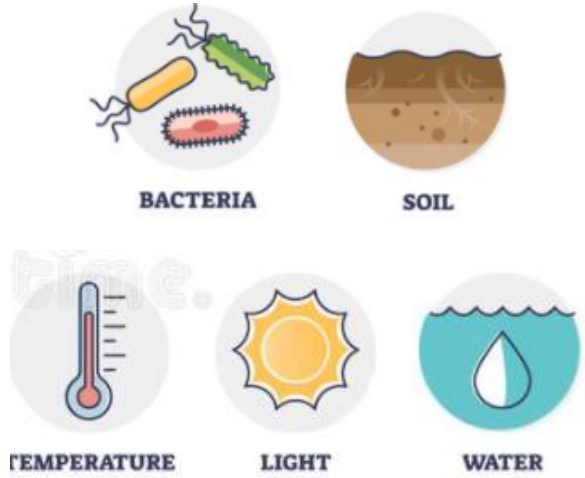


A pool of modified mycotoxins

The spectrum of modified forms generated in plants from the same prent compound may vary according to the plant genetic background



Masked mycotoxins are less toxic than parent compounds *per se*; they are not cleaved *enzymatically* in the stomach, but they are totally cleaved in the gut by *resident microbiota*



The biotransformation in plant may be affected by biotic and abiotic stressors *(i.e. climate, insects, other pathogens, multiple chemicals in soil/water)*

A CHALLENGE OR AN OPPORTUNITY?

Plants modify mycotoxins to get rid of them, as part of their natural defence system.
Their biotransformation in planta minimises the spread of the fungus. Therefore, breeders are exploiting this mechanism to breed more resistant/resilient crops.

➔ The overall mycotoxin load is reduced, BUT the proportion of masked mycotoxins becomes more prominent.

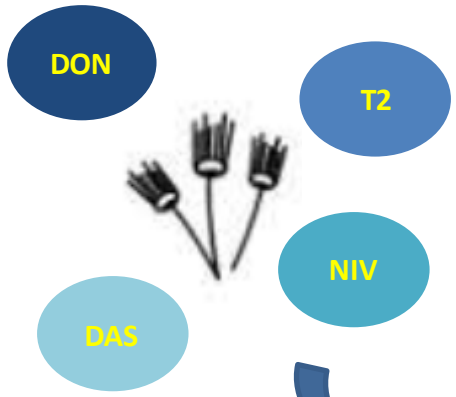
Fungi might adapt themselves to new conditions, and start producing mycotoxins less prone to biotransformation

➔ The reported rise of 3-acetyl-DON producing fungi in Canada and the USA Midwest might be explained by the inability of the plant to immediately detoxify the compound to DON-3-glucoside.

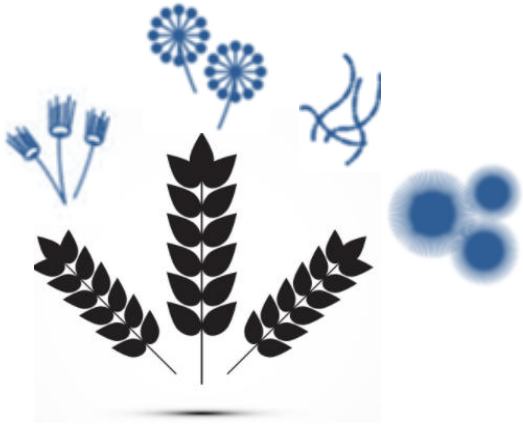
Little to nothing is known so far about the modulation of plant biosynthetic machinery by the co-occurrence of different chemicals in soil/water. Effects of soil microbiome should be considered as well.

WHAT WE KNOW ABOUT CO-OCCURRENCE?

Many mycotoxins per fungi



Many crops per meal



Many fungi per crop

A system approach

Innovative agro-ecological APProaches to achieving resilience to climate CHANGE in Mediterranean countries

Italy, France, Algeria, Tunisia, Morocco. A well-balanced collection of partners dedicated to **re-design innovative farming systems for the Mediterranean area**.

New Perennial Grains (NPGs)

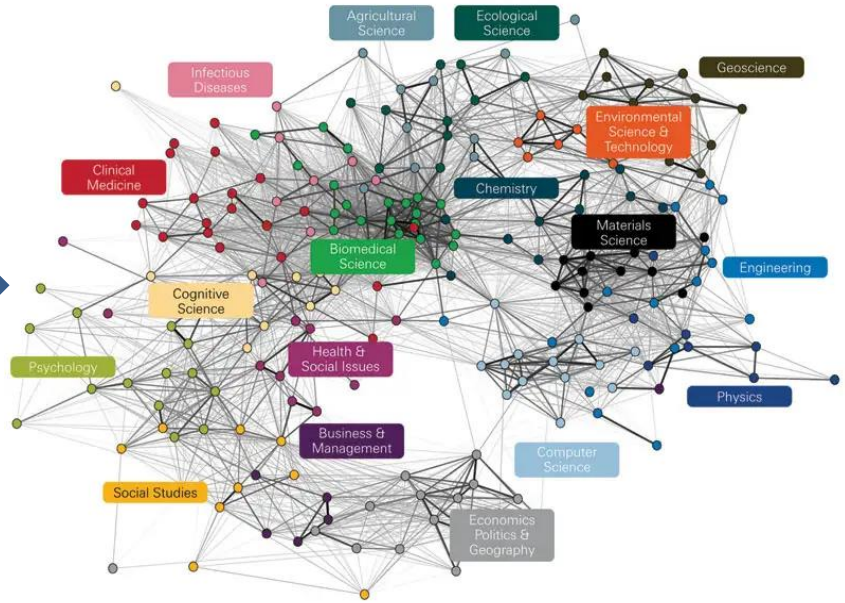
NPGs are new species obtained by hybridization and/or domestication holding great potential in **ameliorating soil physical-chemical properties, biodiversity and food web composition**. The longer growing season of NPGs, *their more extensive root systems*, and the permanent soil cover, make them more competitive against weeds and more effective at capturing nutrients and water.

Take home message

The assessment of multiple chemicals in our diet is much more complex than expected

Fundamental science is needed to tackle the complexity

Proper risk assessment methodologies should be implemented under the ONE HEALTH approach



ONE SCIENCE APPROACH

THANK YOU FOR YOUR ATTENTION

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