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relana® Communication Note 21-03

Statement about the presence of

1,4-Dimethylnaphthalene (1,4-DMN)

in food products

Updated Version 2023/01/30

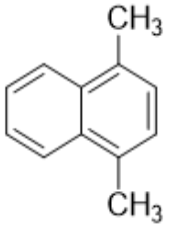
1. Introduction

1,4-dimethylnaphthalene (1,4-DMN) is a growth inhibitor (sprouting inhibitor) applied on potatoes. It has a very low aqueous solubility and is highly volatile. 1,4-DMN is approved in the EU by implementing regulation (EU) No. 192/2014 to be used on potatoes.
The approval of the commonly used growth inhibitor chlorpropham was not extended (implementing Reg. (EU) No. 2019/989), and the phase out was dated 8. October 2020. Therefore, a substitute for chlorpropham was sought and found with 1,4-DMN.
The high volatility of 1,4-DMN causes rapid dispersion through the air and poses a high risk of cross-contamination of non-treated goods. Such a cross-contamination is critical for all products other than potatoes (MRL is set at 15 mg/kg) and of course for products from organic agriculture.
As 1,4-DMN is belonging to the chemical group of polyaromatic hydrocarbons (PAH), its presence in the environment and thus in food products can also be caused by other sources and uses than as a growth inhibitor. This aspect must be taken into consideration when interpretating findings of 1,4-DMN in products other than conventionally produced potatoes.

2. Basic information about 1,4-DMN

1,4-Dimethylnaphthalene (1,4-DMN) is an aromatic hydrocarbon with the following properties [**PPDB** and **BCPC**]:

Structural formular:



<u>Properties</u>

Chemical name: 1,4-dimethylnaphthalene
Other names: 1,4-DMN; naphthalene, 1,4-dimethyl
Trade names: 1,4SIGHT, 1,4SEED, 1,4SHIP
CAS number: 571-58-4
Composition: $C_{12}H_{12}$

Molecular weight: 156.2g/mol
Boiling point: 264°C
Solubility in water: 5.1ppm (thus slightly soluble in water)
Solubility in organic solvents (g/l, 20-25 °C): Soluble in acetone (>250), 1,2-dichloroethane (248), ethyl acetate (>250), n-heptane (239), methanol (>250), xylene (248) (thus good solubility in organic solvents)
Vapour pressure at 20 °C (mPa): 2500 (therefore highly volatile)
Octanol-water partition coefficient at pH 7, 20 °C: Log P 4.37 (thus lipophilic, fat-loving)
Stability: Stable, >14 d (dark, 55 °C). Decomposes to 14 % in 14 days (light, 55 °C).

In summary, 1,4-DMN has a very low solubility in water, is lipophilic and very volatile.

Mechanism of action / application:

1,4-DMN is a growth inhibitor used on potatoes.
1,4-DMN is used as a post-harvest agent. 1,4-DMN is used as a plant growth regulator to inhibit sprouting of potatoes during storage and transport. It is commonly applied in closed storage areas as a thermal (heated) aerosol mist. Applications of hot dipping or cold fogging of harvested potatoes are also known.

1,4-DMN also occurs naturally in potatoes (Solanum tuberosum L.). The pure extract is a pale yellow to colourless liquid and smells like petroleum distillates.
1,4-DMN inhibits germination and etiolated growth in stored potatoes and thus prolongs the effective storage time while maintaining tuber quality.

Authorisation status (EU):

Authorised under Regulation (EC) No 1107/2009 (current updates: implementing regulation (EU) No. 192/2014 and implementing regulation (EU) No. 2020/2007), current authorisation period: 01/07/2014 - 30/06/2025.

Toxicological characteristics:

ADI: 0.1 mg/kg body weight (bw)/day (EFSA 2013).
ARfD: Not Applicable (EFSA 2013)
AOEL 0.32 mg/kg bw/day (EFSA 2013)

3. Analytical approach

The multi residue method QuEChERS is appropriate to detect and quantify 1,4-DMN (commonly by the GC/MSMS module) according to the residue definition for enforcement (“1,4-dimethylnaphthalene”). To identify possible sources other than the use as a sprouting inhibitor, it is meaningful to include other Dimethylnaphthalene isomers into the analytical scope, too (see at page 4).

4. 1,4-DMN in potatoes and other products of plant origin

PHD thesis of M.D.Y. Oteef

According to the dissertation by Mr Oteef [**OTEEF** 2008 PHD], the natural content of 1,4-DMN in potatoes (see pages 242/243) is about 4 µg/kg potato fresh weight.

Mr Oteef has cited another reference:
Another study (2006) on the natural 1,4-DMN levels in potatoes was conducted in a commercial laboratory as part of the approval process of 1,4-DMN with the authorities in the USA. In this study, potatoes were grown in a controlled environment greenhouse for the purpose of the study. 1,4-DMN was extracted from the potato skin using a solvent extraction method. Natural 1,4-DMN has been reported to be present in potato peel at a concentration of 20 ppb (µg/kg), which is equivalent to about 2 to 3 µg/kg fresh weight of potato ("John Forsythe, personal communication", [2] page 243).
This study suggests a similar level of natural 1,4-DMN as the values of about 4 ppb (µg/kg) determined by Mr Oteef on the basis of potato fresh weight.

Mr Oteef's thesis also refers to a study reporting levels in the range of 41-76 µg/kg (fresh weight basis, page 243) in organically grown potatoes from a commercial shop. However, these results have been challenged:
For example, the thesis points out that despite the fact that the experiment was conducted in a controlled environment to ensure maximum accuracy, trace amounts (about 2 ppb, µg/l) of 1,4-DMN were present in the laboratory reagent blank (i.e. reagents used for analysis such as solvents). This level of contamination could have influenced the level of natural 1,4-DMN reported in this study, according to Mr Oteef. The contamination could be because the analysing laboratory routinely analyses potatoes that have been treated conventionally and thus also with 1,4-DMN. In routine analyses of conventional potato samples, 1,4-DMN is present in much higher concentrations and can thus contaminate other (untreated potato) samples.

Summary

The 2 studies indicate that natural levels of 1,4-DMN in potatoes are approx. 4 ppb (µg/kg). Another study cited, reported levels of 41-76 ppb (µg/kg) (fresh weight basis) for untreated potatoes, but these are critically questioned due to increased contamination risks from laboratory reagent blank.

Analogies to chlorpropham

The authorisation of the active ingredient chlorpropham was not renewed and the phase-out period ended on 8 October 2020 (implementing reg. (EU) No. 2019/989). Chlorpropham was also used as a sprout inhibitor to prevent sprouting of potatoes after harvest. Chlorpropham, like 1,4-DMN, has very low water solubility, is lipophilic and very volatile.

The fact that organic potatoes show chlorpropham levels although chlorpropham has never been used in the processing plants (or not for many years) can be explained by the

- high mobility of chlorpropham due to low evaporation pressure (also applies to for 1,4-DMN)
- binding/adsorption of chlorpropham to particles/dust and to walls/ceilings and surfaces of machines/technical equipment due to its physical/chemical properties (also applies to 1,4-DMN)
- permanent release of low concentrations of chlorpropham from the contaminated areas and thus permanent risk of contamination of untreated products, directly or via transport crates/boxes (also applies to 1,4-DMN).

These properties of chlorpropham have led to major problems in the past related to organic potatoes that had been processed in parallel to conventional potatoes. It can be assumed that the contamination risks associated with the use of 1,4-DMN are comparable to those of chlorpropham.

Other sources of inputs of 1,4-DMN

In a presentation by Michelangelo Anastassiades [**Anastassiades**, slide no. 65] during the European Pesticide Residue Workshop (EPRW) 2018, he pointed out other possible sources of 1-4 DMN findings. On the one hand, these are petroleum oils, which are used directly as pesticides or are added to plant protection products as co-formulants or are also added to plant protection products as carriers.

The relana® member Labor Friedle detected levels of 0,081 mg/kg 1,4-DMN in conventional parsley. After investigations, the source of this 1,4-DMN result was identified as "*solvent naphtha (petroleum), highly aromatic*", which was present in the applied pesticide formulation "Score" (with Difenoconazole as active ingredient). This interpretation is based on the presence of additional Dimethylnaphthalene isomers, and Monoethylnaphthalene isomers which are characteristic for the different fractions of petroleum (f.ex. Naphtha fractions). Fertilisers, which also contain petroleum oils, are also a potential source of contamination with 1,4-DMN.

5. Maximum residue levels for 1,4 Dimethylnaphthalene in products of plant origin

Maximum residue levels for 1,4-DMN according to Regulation (EC) No 396/2005

Commission Regulation (EU) 2015/399 set maximum residue levels for 1,4-DMN, among others. There, recital 1 states:

"*For 1,4-dimethylnaphthalene […], no specific MRLs have been set in those Annexes, nor have the substances been included in Annex IV to that Regulation, so the default value of 0.01 mg/kg applies.*"

In Regulation (EU) 2015/399, a maximum residue level of 15 mg/kg for potatoes (code number 0211000) exists. The column for MRLs of 1,4-DMN for all other groups and individual products to which the MRL apply is not filled.

Thus, for all products except potatoes, the default value of 0.01 mg/kg according to Article 18(1)(b) of Regulation (EC) No 396/2005 applies.

Due to findings of 1,4-Dimethylnaphthalene also in other products of plant origin (others than potatoes), laboratories were confronted with the assessment of 1,4-DMN findings. As a laboratory finding at or above the reporting limit only provides evidence about the presence of an analyte - but cannot make any statement about *how* the analyte got into the sample (deliberate application, contamination etc.?) - the assessment according to Reg. (EC) 396/2005 taking into consideration the default MRL (0,01 mg/kg) was critically discussed from a scientific perspective.

These aspects have now been considered in setting new maximum residue levels for 1,4-DMN: In regulation (EU) 2022/1346, a maximum residue level of 15 mg/kg is set for potatoes (code number 0211000). For other products of plant origin, the MRL is set at 0,05 mg/kg. Reg. (EU) 2022/2007 applies from 22 February 2023.

Recital 2 of Reg. (EU) 2022/1346:
For 1,4-dimethylnaphthalene the European Food Safety Authority ("the Authority"), submitted a reasoned opinion on the existing MRLs to the Commission and the Member States […]. The Authority proposed to change the residue definition for products of animal origin. The Authority considered that, as 1,4-dimethylnaphthalene could naturally occur in plant products, setting MRLs for products of plant origin at the Limit of Determination (LOD) could be inappropriate. […]

Remark:
According to the EFSA reasoned opinion [**EFSA** 2021] the residue definition for risk assessment is "sum of 1,4-dimethylnaphthalene, M21 and its conjugates, expressed as 1,4-dimethylnaphthalene".

6. Summary and Conclusion

In analogy to chlorpropham findings in **organic** potatoes about possible causes and sources of input, these causes / sources appear to be similar to 1,4-DMN.

Cross-contamination during storage and/or processing can lead to increased findings of 1,4-DMN.
The Organic Farming Regulation [reg (EU) 2018/848] requires in Article 28:
"*In order to avoid contamination with products or substances that are not authorised […] for use in organic production, operators shall take […] precautionary measures at every stage of production, preparation and distribution: […]"*

According to the reasoned opinion of EFSA [**EFSA** 2021], 1,4-DMN is authorised only for indoor post-harvest treatment of stored potatoes (excluding seed potatoes). As a conclusion, operators of organic potatoes run a high risk of contamination in case of processing organic potatoes in premises of conventional potato producers. Findings of 1,4-dimethylnaphthalene that cannot be linked to this kind of cross-contamination should be carefully investigated for other possible sources of contamination.

Conventionally produced potatoes that do not exceed the MRL for 1,4-DMN of 15 mg/kg (considering the expanded measurement uncertainty) follow the requirements of Regulation (EC) No. 396/2005.

For all products of plant origin - except potatoes - listed in Annex I of Regulation (EC) No 396/2005, the new MRLs of 0,05 mg/kg according to Reg. (EU) 2022/1346 must be applied from 22 February 2023 (considering the expanded measurement uncertainty).

The residue definition for risk assessment (like f.ex. for calculation of the ARfD exhaustion) also includes the sum of 1,4-dimethylnaphthalene, M21 and its conjugates. It is therefore different from the residue definition for enforcement (compliance with MRL) which is 1,4-dimethylnaphthalene only.

References

PPDB: Pesticide Properties DataBase, University of Herfordshire, UK, http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm, access on 30.01.2023

BCPC: British Crop Protection Council, UK, e-Pesticide Manual, https://www.bcpc.org/my-account, access on 24.06.2021

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Regulations and **Implementing Regulations** of the EU: allocated in the text

Acknowledgment

Relevant information was provided by:
Labor Friedle GmbH, Tegernheim, Germany

relana® communication note

This communication note is a literary property of relana®, based on the contribution and the knowledge of the members of the relana® laboratory quality circle. The aim of this publication is to increase knowledge and to provide expertise to all relevant and interested stakeholders in order to achieve best practices on analytical services related to food and feed testing. Everybody is invited to make use of this communication note and to circulate it wherever meaningful.