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relana® Communication Note 21-03

Statement about the presence of

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

in food products

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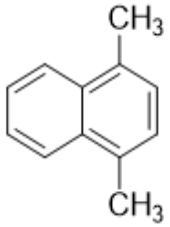
1. Introduction

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 is 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 (as an MRL is set for potatoes only) 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.
In particular, 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)

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, only 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 empty.

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.

3. Analytical approach

The multi residue method QuEChERS is appropriate to detect and quantify 1,4-DMN (commonly by the GC/MSMS module). 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 5, last paragraph).

4. Assessment of findings of 1,4-DMN in potatoes and other plant food products

EFSA Reasoned Opinion

In the "Summary Table" (see below) of the "Reasoned opinion on the setting of a new MRL for 1,4-dimethylnaphthalene in potatoes" of the EFSA article [**EFSA** Journal 2014;12(6):3735] it is mentioned on page 3 related to "other plant commodities":

"0.01mg/kg (is) not appropriate to cover 1,4-DMN natural background level in plants"

An additional remark mentions:

"*Limited quantitative information is available on 1,4-DMN natural background level in plants. Natural levels up to 0.061 mg/kg reported in potato tuber."*

SUMMARY TABLE

Code number (a)	Commodity	Existing EU MRL (mg/kg)	Proposed EU MRL (mg/kg)	Justification for the proposal
Enforcement residue definition: 1,4-DMN				
211000	Potatoes	0.01*	15	The consumer risk assessment could not be finalised since MRLs could not be proposed for products of animal origin and since no reliable processing and conversion factors could be derived from the available studies. However, based on the available data, the additional contribution of the residues present in animal matrices is not expected to result in an exceedance of the ADI value.
-	Other plant commodities	0.01*	0.01mg/kg not appropriate to cover 1,4-DMN natural background level in plants	Limited quantitative information is available on 1,4-DMN natural background level in plants. Natural levels up to 0.061 mg/kg reported in potato tuber.

Page 15 of this EFSA opinion provides more detail:

*“In addition, in the supervised residue trials where samples were analysed for 1,4-DMN prior to applications, the background levels in whole potatoes were mostly below the limit of quantifications (<0.005 to <0.07 mg/kg), with some positive values in the range of 0.015 to 0.061 mg/*kg.”

Finally, most of the background levels of 1,4-DMN cited by EFSA are between 0.005 and 0.07 mg/kg in whole potatoes, with levels between 0.015 and 0.061 mg/kg appearing to have occurred only in isolated cases ("some positive values"). The reliability of the data cannot be verified, as it is not known how and under which cultivation conditions the reported levels were determined. The number of data sets is also not stated in the EFSA Opinion.

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) are 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.

Conclusion of the 2 documents (EFSA and Oteef):

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. Summary and Conclusion

Recommendation for the assessment of 1,4-DMN contents in (organic) ***potatoes***

In untreated potatoes the natural content of 1,4-DMN is about 0.004 mg/kg. Higher contents (between 0.015 mg/kg and 0.061 mg/kg) have only been reported in isolated cases. The natural levels in potatoes in the range of 0.041 to 0.076 mg/kg reported in one study were possibly influenced by contaminated laboratory reagent blanks and thus their validity was questioned.

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. As the Implementing Regulation to the Organic Farming Regulation [reg (EC) no 889/2008] requires in Article 26:
"Operators [...] shall in particular ensure that precautionary measures are taken to avoid the risk of contamination by unauthorised substances or products",
it is recommended to inform the control body in case of 1,4-DMN levels above 0.01 mg/kg in order to eliminate possible sources of contamination.

Nevertheless, it can be assumed that levels < 0.1 mg/kg are very unlikely to be due to deliberate use of 1,4-DMN. This is also stated by EFSA:
"EFSA is therefore of the opinion that, for the rest of the plant commodities, a default value of 0.10 mg/kg would be more appropriate to cover the possible natural background levels of 1,4-DMN in plants, although this proposal is not fully supported by a sufficient number of data. This default value of 0.1 mg/kg was therefore used as input value for chronic consumer intake calculations."

As a **preliminary** approach, we recommend tolerating levels of 1,4-DMN in organic potatoes up to a level of **0.05 mg/kg** (the expanded measurement uncertainty of 50% might by applied, too). This proposal of relana® is of course subject to the approval and agreement of the responsible organic control bodies resp. the related competent authorities. As soon as a sufficiently large number of analytical results are available, the recommended level will be reviewed by relana® and - if necessary - adjusted. In that case an updated version of this document will be published.

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

Recommendation for the assessment of 1,4-DMN levels in other plant products

For all products - except potatoes - listed in Annex I of Regulation (EC) No 396/2005, the default value of 0.01 mg/kg (therein Article 18, para. 2 b) has to be applied. Nevertheless, as described above, different sources of entry are known and should be checked.

According to current knowledge, 1,4-DMN findings in plant products other than potatoes cannot be explained by the natural presence of 1,4-DMN. The EFSA Opinion [1] states as follows:

"EFSA is therefore of the opinion that, for the rest of the plant commodities, a default value of 0.10 mg/kg would be more appropriate to cover the possible natural background levels of 1,4-DMN in plants, although this proposal is not fully supported by a sufficient number of data."
However, this also means that no reliable data are available to prove possible natural contents**.**

Taking into consideration other sources like discussed above we suggest the possibility of a default value of 0.1 mg/kg for all products except potatoes recommended here as a first approach worth considering.
Nevertheless, this could quickly become obsolete due to corresponding lower data. In our view, it is more likely that the levels of 1,4-DMN found so far are caused by cross-contamination or by co-formulants of pesticide formulations (e.g., petroleum resp. naphtha).

Acknowledgment

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

References

PPDB: Pesticide Properties DataBase, University of Herfordshire, UK, http://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm, access on 24.06.202

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

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OTEEF 2008 Mohammed Dhafer Yahya Oteef, "*Analysis of the potato sprout inhibitor 1,4-Dimethylnaphthalene: HPLC Method development and applications*", Thesis submitted for the degree of Doctor of Philosophy, University of Glasgow, Faculty of Physical Sciences Department of Chemistry Analytical Chemistry Section, UK June 2008. Ebenfalls unter: http://theses.gla.ac.uk/319/2/2008OTEEF1PHD.pdf

Anastassiades Michelangelo „Overview of pesticide-relevant compounds originating from sources other than pesticide use", 12th European Pesticide Residue Workshop, 22th-25th May 2018, Munich, Germany

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

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