



Schriftelijke Statenvragen van de Statenfractie van de PvdD over normoverschrijding dinoterb, ingediend op 5 juni 2024, en de antwoorden daarop van het college van Gedeputeerde Staten zoals vastgesteld op 2 juli 2024 (3278217).

INLEIDING

Onlangs bereikte ons een bericht over de stof dinoterb dat is aangetroffen in monsters. Dinoterb is de werkzame stof voor herbiciden (gewasbeschermingsmiddelen om onkruid te bestrijden) die vanaf 1974 werd gebruikt. Het mag sinds 1 juli 1998 niet meer gebruikt worden in de landbouw. Dinoterb is een verboden pesticide die kanker verwekt en schadelijk is voor natuur en volksgezondheid.

Uit de gegevens van de Bestrijdingsmiddelenatlas blijkt dat vooral in 2013 en in 2022 in Noord-Holland normoverschrijdende gehalten zijn vastgesteld. In de tussenliggende jaren was het aantal normoverschrijdingen veel lager. Incidenteel zijn ook in andere regio's te hoge waarden van dinoterb gemeten.

In een rapport van Royal HASKoningDHV¹ (meetronde 2018, publicatie 4-6-2020) over Flevoland valt in paragraaf 2.3 op pagina 10 te lezen: "De stof dinoterb (een bestrijdingsmiddel) gaf volgens het laboratorium (AL-West) vals positieve waarnemingen. De waarnemingen boven de rapportagegrens zijn verwijderd uit het databestand. Voor dinoterb blijven daarom alleen meldingen over onder de rapportagegrens."

Vragen:

1. Kan het college van GS uitleggen hoe het kan dat de stof dinoterb nog steeds wordt aangetroffen in de monsters, terwijl deze stof al lange tijd is verboden?
2. Hoe komt het dat de metingen van dinoterb vals positieve waarnemingen gaven en waarom zijn deze waarnemingen verwijderd uit de database?

Antwoord op vraag 1 en 2:

Dinoterb is niet vastgesteld in het Flevolandse grondwater.

Uw vraag gaat over het rapport "Grondwaterkwaliteit provincie Flevoland, Meetronde 2018" uit 2020. De provincie meet elke 3 jaar de grondwaterkwaliteit in haar grondwatermeetnet, waarbij eens in de 6 jaar een uitgebreide meting. Dit rapport gaat over de uitgebreide meting van 2018.

Bij de analyse van de monsters is een verontreiniging in het laboratorium opgetreden waardoor dinoterb ten onrechte werd aangetoond in de resultaten. Het bleek dat het laboratoriummateriaal verontreinigd was met dinoterb. U treft de verklaring van het laboratorium aan in de bijlage.

(bijlage #3282442 Dinoterb Statement West 190306 signed.pdf)

Dit is de reden dat de analyseresultaten niet zijn meegenomen in de rapportage.

3. Zijn er naast deze vals positieve waarnemingen nog meer metingen uit de database verwijderd? En zo ja, waarom?

Antwoord:

Nee.



PROVINCIE FLEVOLAND

4. *Maakt het college zich net als de Partij voor de Dieren zorgen over de aanwezigheid van dinoterb in deze monsters?*

Antwoord:

Nee. Er is geen dinoterb aangetroffen

5. *Is het college voornemens de bron van de aanwezigheid van dinoterb te gaan achterhalen?*

Antwoord:

Nee. Er is geen dinoterb aangetroffen.

De bron van dinoterb was een verontreiniging in het laboratorium. De stof is dus niet aangetroffen in de monsters zelf, maar is een fout bij de analyses. Dit heet in vaktermen "vals positief".

6. *Is het college bekend met gevolgen die de aanwezigheid van dinoterb in het oppervlaktewater heeft op de gezondheid van mensen en de staat van instandhouding van dieren in Flevoland? Zo ja, op basis van welke gegevens of onderzoeken? Zo nee, gaat het college zich hierover informeren?*

Antwoord:

Ja. Dinoterb is een toxische stof, dit is de reden waarom de stof ook niet meer is toegelaten.

7. *Het lijkt erop dat er geen landelijke richtlijn is wat wel en niet gemeten wordt aan stoffen zoals dinoterb. Door verschillende werkwijzen ontstaat er nu ruis over wat wel en geen juiste metingen zijn. Is de provincie voornemens zich in te zetten voor een landelijke richtlijn met eenduidige werkwijze, bijv. in IPO-verband? Zo nee, waarom niet?*

Antwoord:

De provincie stemt wel af over het meetpakket in IPO-verband.

De meetronden in het grondwater worden in heel Nederland op vergelijkbare wijze uitgevoerd. Ook wordt landelijk het zelfde analysepakket gehanteerd. Dit bevat een zeer ruim spectrum aan stoffen die geanalyseerd worden. In 2018 (de ronde waarover is gerapporteerd) bestond het pakket uit:

- 49 algemene stoffen,
- 192 bestrijdingsmiddelen,
- 95 geneesmiddelen,
- 121 overige verontreinigende stoffen.

We zien regelmatig arbeiders (veelal arbeidsmigranten) werken in de bollen velden in Flevoland. Zij dragen daarbij geen beschermende kleding of mondkapjes.

8. *Zijn deze medewerkers op de hoogte (gebracht) van de gevaren van blootstelling aan de gewasbeschermingsmiddelen die op grote schaal worden toegepast in de bollenteelt?*
9. *Is het college van PS het met de Partij voor de Dieren eens dat deze medewerkers beschermd horen te worden tegen blootstelling aan deze middelen?*

Antwoord op vraag 8 en 9:

De Nederlandse Arbeidsinspectie van het Ministerie van Sociale Zaken en Werkgelegenheid is het bevoegd gezag voor "Oneerlijk, onveilig, ongezond werk of arbeidsuitbuiting melden", niet de provincie.

Dr.Blasy-Dr.Busse

Niederlassung der AGROLAB Labor GmbH, Bruckberg
Moosstr. 6a, 82279 Eching am Ammersee, Germany
Tel.: +49 8143 79-01, Fax: +49 8143 72-14
eching@agrolab.de www.agrolab.de



Dr.Blasy-Dr.Busse - Niederlassung der AGROLAB Labor GmbH

AL-West B.V. - Deventer
Dortmundstraat 16B
7418 BH Deventer
Niederlande

Ansprechpartner

Dr. Michael Maier

Tel.: [REDACTED]

Fax: [REDACTED]

E-Mail: [REDACTED]@agrolab.de

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Statement on Dinoterb values

Dear customer,

hereby you receive a statement about the withdrawal of Dinoterb values. Below, please find a root-cause-analysis and our corrective actions:

Root-cause-analysis

- In our lab two types of disposable glass vials are used: small vials for analysis and larger vials for retain samples
- Our (daily) internal quality control system recognized blank values of Dinoterb in a batch of small vials before the measured values were released, hence:
 - the measured values were blocked
 - the samples were analyzed again with a method that was not affected by blank problems
 - the manufacturer was contacted who confirmed that we received glass ware that had (by accident) only minor quality and that will be substituted
- This triggered a preventive action, where we checked our process systematically for further potential sources of blank values. In the end we could pinpoint a source of contamination in our current batch of retain vials. Although it is disposable glass ware, the glass itself is a contamination source for Dinoterb (and neither the septum nor the packing or any other process step).
- In contrast to the vials for analysis, these retain vials were not part of the daily quality control (see below)
- This circumstance is critical for all samples, whose measurements have been repeated internally (because values were not within working range, the matrix disturbed the initial measurement or samples had to be filtered). External repeaters, triggered by clients, have been repeated from the original bottle and are not biased
- The earliest samples where we cannot exclude a contamination was measured on July 24 2017 and the last on January 15 2019.



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- Unfortunately the degree of contamination varies over time. Hence we cannot correct positive results for a certain value, but we have to withdraw all positive results of Dinoterb to exclude the potential of false positive values.
- the majority of our Dinoterb samples can be analyzed directly from the original bottle; consequently, the above mentioned blank problem did not appear as a systematic trend in our data base

Existing (routine-)measures that were already active prior to the incident

- We participate twice a year in an independent round robin test for Dinoterb - always successful
- The method, including Dinoterb, is regularly requalified - unfortunately the retain samples were not included in these tests
- There are several positive and negative quality controls every day, if these values are not within the nominal range, all measured values are blocked and cannot be exported into the database (as described in the second bullet point on page one)
- These control samples cover the complete measuring procedure, which is a demand of our internal quality guidelines
- However, the retain vials have not been recognized as part of the complete process
- Within the past three years we received four complaints about Dinoterb values; although these complaints were thoroughly carried out, they did not deliver a hint towards the retain vials (please find details in appendix)

Ad-hoc measures

- Immediate conversion of the method to ensure blank free measurements
- The retain vials were integrated into the daily routine quality control to maintain an immediate detection of quality problems (of the supplier)
- Review of all historical values that could be affected
- checking whether there might be a similar problem elsewhere in the laboratory
 - all lab processes were screened for blind spots concerning quality controls
 - this is not the case, since in all other cases the original bottle is used as retain sample
 - all these containers are regularly monitored

The following measures are still running

- Close contact with the glass vial manufacturer to find out the real root-cause of the problem, since Dinoterb is not expected to appear in disposable glass vials. As we know now, Dinoterb can be used as a polymerization inhibitor and stem from plastic used during production steps.
- The process of having extra-vials for retain samples is under discussion



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We apologize once again for any inconvenience. As described above, we perform a strict quality control on every single measurement. However, we had a blind spot in our overall process with respect to quality problems of our supplier that is covered now. The immediately initiated root-cause-analysis and the resulting measures shall show you that the quality of your results is our top priority.

Yours sincerely

Dr. Michael Maier

Department leader chemistry

Dr. Sibylle Steinbeiss

Site manager

Appendix - QS check in case of complaints

General Scheme

1. Complaint is started by customer relationship manager
2. Lab manager gets informed
3. Standard Control points are checked by lab manager
 - a. Check of calibration
 - b. Check of positive and negative control
 - c. Check of recovery rate (if applicable)
 - d. Check of working range
 - e. Check of internal standard
 - f. Check of integration (for chromatography)
 - g. Check of qualifier (for mass spectrometry)
 - h. Check of cross contamination by other samples can be excluded
 - i. Check of repeater / Dilution
 - j. Check of data transfer
4. When indicated, customer relationship manager and lab manager define additional measures
5. Measures are documented and client gets feedback

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Individual cases (December 2016 – January 2018)

1. 13.12.2016 Dinoterb too high
 - a. Standard control points were OK
 - b. Sample contained matrix that biased the analysis, (internal standard too low), hence measurement was made after dilution -> internal standard was OK and Dinoterb values were higher -> this was interpreted as a "normal" matrix effect and reported
 - c. It was checked that the addition of thiosulphate as matrix inhibitor does not influence the analysis
2. 03.01.2017 Dinoterb too high
 - a. Standard control points were OK
 - b. Sample was contaminated by another sample -> this was clarified and immediately corrected
3. 28.11.2017 Dinoterb too low after reanalysis
 - a. Standard control points were OK
 - b. Bentazone – a pesticide that is measured by the same method - was checked as well and showed similar results in both measurements -> proof that the method is working well in general and samples were not mixed by accident
 - c. Sampling times were checked – repeater was measured after one month
 - d. Literature was checked that indicates a potential half-life time of Dinoterb of approximately 10 days
 - e. It was concluded that Dinoterb degraded in the sample
4. Dinoterb 10x higher than reported in the last 10 years - is the method changed
 - a. Standard control points were OK
 - b. Reference material was double checked
 - c. The calibration curves were compared over the months and years – no systematic changes were found (in case of degraded material the sample concentrations would be overestimated)
 - d. Systematic analysis of recent samples showed no systematic trend
 - e. All samples that were part of the complaint had to be diluted
 - f. the method was not changed

Re-interpretation of these cases from today's point of view

1. the sample was contaminated during dilution in the retain vials
2. individual case that was solved immediately
3. very first measurement was not successful and was repeated internally from the contaminated retain vial -> first measurement positive; second measurement was made from the original bottle -> negative
4. the samples were contaminated during dilution in the retain vials

Evaluation of actions

In all (four) cases the standard control points were checked. Doing so, 99% of typical mistakes are covered. Moreover, additional measures were taken by looking at the bigger picture. However, we have to admit that the idea of disposable (= single-use) glass vials that release a pesticide was out of our scope.