Text (Theo v.d. Trenck)

1. "**EVALUATION OF HETEROCYCLIC COMPOUNDS AND REFERENCE VALUES FOR THE MANAGEMENT OF GROUNDWATER CONTAMINATIONS**".

I am going to present the results of the LAWA-Subcommittee "**Significance Thresholds for NSO-Het**", which were approved by the **GERMAN FEDERAL STATES' WATER CONSORTIUM** and are published in the internet under the link indicated in the bottom line of my title slide.

2. The German Federal Soil Protection Ordinance (1999) contains**TRIGGER VALUES** for the **soil→groundwater** path. One of these is a value of **0.2 µg/l** for total polycyclic aromatic hydrocarbons (**PAH**) in the **soil leachate** as well as in the **groundwater** itself. PAH are contained in the **tar oil** (créosote) from gasworks or manufactured gas plants. The value for the PAH-sum includes relevant heterocyclic compounds (NSO-Het). But **NSO-Het** have been included in the investigations **very rarely** in the past.

3. The next slide shows 3 heterocyclic compounds as an example:
Carbazole (with a Nitogen-hetero-atom), **Dibenzothiophene** (with a Sulfur-hetero-atom), and **Dibenzofuran** (with an Oxygen-hetero-atom) and their hydrocarbon analog Fluorene.

4. Starting in 2003, the **German Ministry of Research** (BMBF) financed 74 projects as a **joint effort** (KORA) to investigate **natural attenuation processes** on sites contaminated with tar oil. **KORA** stands for 'Controlled natural attenuation for the remediation of contaminated groundwater and soil'. Natural attenuation of pollutants can be observed mainly in the groundwater plume. Because of their greater water solubility, NSO-Het can travel over longer distances with the groundwater plume. That is why in the course of KORA **NSO-Het were also analyzed** besides PAH. And **20** heterocyclic **priority** pollutants were identified according to the properties of substance and site (ARCADIS, 2007).

5. In the course of KORA, 256 heterocyclic compounds were identified altogether. Including isomers 51 substances were named as priority pollutants.
Another working group (Altlastenforum) was based on KORA. The 'Altlastenforum' also considered the **center** of the contamination and consequently expanded the set of priority pollutants to 71 (including isomers).
The LAWA-subcommittee revised the prioritization procedure emphasizing **toxic effect** and **mobility** and added the 10 pollutants ranked highest plus their isomers. This resulted in 92 substances, for which the data were searched.
Sufficient data to derive **trigger-** or **reference-values** were found for only 12 of these 92 NSO-Het. The cumulative value of **0.2** µg/l for PAH + NSO-Het remains in effect for all the others.

6. This slide shows the Pollutant Priority according to Mobility, Persistence, and Toxicity for Humans and the Ecosystem. All these categories were classified by assigning 1 to 5 points and weighted according to their importance. The 3 criteria blocks carry a weight of 6 (mobility & persistence), 6 (human tox) or 5 (ecotox).

7. The 10 substances of highest rank were added (plus isomers and substances of equal rank) to yield a total of 92 priority pollutants.

8. Slide 8 shows the priority pollutants added because of their toxic potential. Only one of these (coumarin) was characterized by sufficient data. Its priority was 161 points and a significance threshold of 4.7 µg/l was derived for this compound. (The significance threshold of 14 µg/l for Piperazine was too uncertain because of a huge assessment factor of 6000, that had to be incorporated.)

9. The Significance Thresholds are **Criteria for Contaminated Groundwater**. How were they derived?
The significance threshold substantiates
(for single substances or groups of substances) the concept of „damage“ in the German Water Act (WHG, 2009).

10. A damaging alteration of the water is **defined** as changes of the properties of a body of water, which impair the public welfare, especially the public water supply.
The **purpose** of the law is to protect a body of water against detrimental changes of its properties…
and to compensate (as much as possible) impairments, that are **not insignificant**.
All activities are to be carried out in such a way that a detrimental change of the water quality should not be feared.
Examples are **groundwater pollution abatement** (§ 48) and the handling of **substances hazardous to water** (§ 62).

11. What magnitude of groundwater impairment is ‚not insignificant‘? Concentrations in groundwater can be classified as insignificant only if
•no relevant ecotoxicological effects are exerted in or due to the groundwater, and
•the groundwater complies with the requirements of the GERMAN DRINKING WATER ORDINANCE (or VALUES derived correspondingly).

12. According to the German Drinking Water Ordinance Groundwater contaminants without a drinking water limit value must meet 3 criteria. Their concentration must be: Harmless for human health, minimized (at reasonable expense according to the best available technology), and aesthetically unobjectionable.

13. The assessment according to the Drinking Water Ordinance and the ecotoxicological assessment are carried out in parallel. The **lower** value of the two is **relevant**. In both cases **effective laws (limit values or EQS)** have the highest priority (1. – blue).
Values based on data from the toxicological literature have a lower priority (2. – violet).
If the lower value is taken from an effective law, it becomes the ***significance threshold*** without further consideration.
2nd priority values are checked whether they are **lower than 0.01 µg**/l. This value is the **lower limit** of the Significance Threshold. Significance Thresholds lower than this value are possible only, if they are based on a proven effect at this concentration (not on an AF).

14. Predicted no effect concentrations (PNEC) are calculated by dividing the lowest **NOEC** of the most sensitive species (algae, crustaceans, fish) by an assessment fachtor of **10 or greater**.
Values derived **according to the DRINKING WATER ORDINANCE are based on the TDI** (for non-carcinogens) or an **added life time risk of 10^{-6}** (for carcinogens) or the **odor detection threshold** **if it is the lowest value.**

15. This shows the **Benzothiophene** data sheet as an **example**. The table contains the results of the scheme of the significance threshold derivation followed by an explanation, the toxicological assessment, the ecotoxicological assessment, the references and the analytical methods.

16. 24 substances were characterized by **ecotox** data, 8 substances were characterized by **human tox** data. Therefore significance thresholds should be possible for 24 substances, **but…**

17. The results of the human-toxicological and ecotoxicological assessments may be very far apart from each other.
For instance, the human tox value for Piperazine is quite uncertain.
It would be 14 µg/l but contains a large AF of 6000. The PNEC is **90x** higher. Compliance with the piperazine-**PNEC** obviously does **not suffiently protect** the gw as **dw-resource**.
Therefore, the PNECs were double-checked by means of the **health related indication value** (HRIV) for non-assessable substances.
The HRIV can be regarded as the upper bound of the precautionary zone. It is **as high as possible** and **as low as necessary** to compensate the lack of data.
With the **HRIV** the **Federal Environment Agency** has created a criterion, that includes

- **Precautionary** aspects and the
- Experience from the **assessments** of dw-contaminants conducted **earlier**

in order to **bridge** the toxicological **data gap**.

18. The slide shows the **HRIV** as the **upper bound of the precautionary** zone and the lower bound of the zone of concern.
The **basic** HRIV for non-assessable pollutants is **0.1** µg/l.
With more **exonerating data** about a compound, the HRIV can be **raised up to 10** µg/l.
For **strong** genotoxins the HRIV has to be lowered to **0.01** µg/l.

19. Here you can see the **List of Values** (the German abbreviation GFS means ***Significance Thesholds***)

- Coumarin: **Human** toxicology is **relevant** (4.7 < 8)
- Dibenzofuran: **Ecotoxicology** is **relevant** (0.4 < 120)
- Quinoline: **Human** toxicology is **relevant** (0.002 < 0.4; but **no effect** was demonstrated at 0.002 ➔ 0.01 µg/l)

20. 19 continued:
- Pyridine: **Odor** detection threshold is **relevan**t (**0.5** < 1.1 < 3.5)
- 2,3-Dimethylbenzofuran: **Ecotoxicology** is **relevant** (0.3 = only criterion and HRIV = 0.1 ➔ is not further off than a factor of 3, which is marginal)
- ∼ 4 ∼2-Methylbenzofuran, 3-Methylbenzothiophene, 5-Methylbenzothiophene, Benzothiophene-1,1-dioxide: **Ecotoxicology** is **relevant** because it is the only criterion. The HRIV = 0.1 µg/l; the **difference > factor 3 ➔ no GFS**-value was derived.

21. 19 continued:
5 more substances without sufficient data, therefore no significance threshold could be derived. But the value of 0.2 µg/l for the lumped parameter ΣPAH applies, because it is not off the HRIV (health related indication value).

22. Summary 1

23. Summary 2

24. The new trigger values were derived by the ***subcommittee*** SIGNIFFICANCE THRESHOLDS FOR HETEROCYCLES and mandated and published by the GERMAN STATES' WATER CONSORTIUM. The ***subcommittee*** consisted of 3 members of the German Federal Environment Agency (Dieter, Konietzka, Six) and one member each from the Saarland (Frank), Hesse (Herrmann), Hamburg (Moll, chair), Bavaria (Stockerl), and Baden-Württemberg.
Thank you very much for your interest!