Verband der Mineralfarben-industrie e. V.

VdMi – UBA Discussion
UBA-Prioritization List vPvM / PMT

UBA Dessau

April 10th 2024

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Verband der Mineralfarben-industrie e. V.

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2. Why we are here today
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4. Mobility criteria and their applicability
5. Discussion

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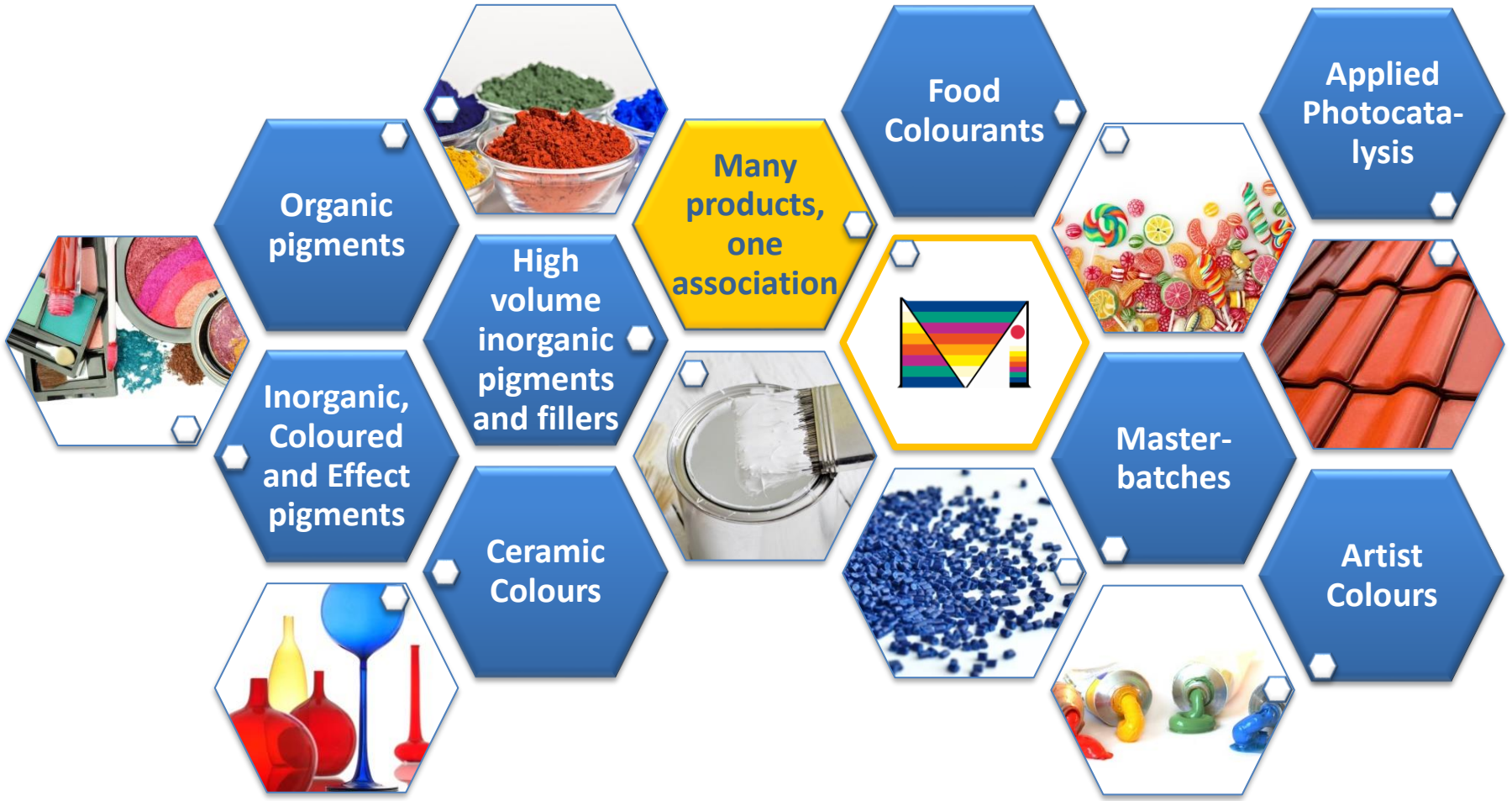
VdMi - Who we are

Verband der Mineralfarben-industrie e. V.

Verband der Mineralfarbenindustrie e. V. (VdMi) – our products

raw material producers

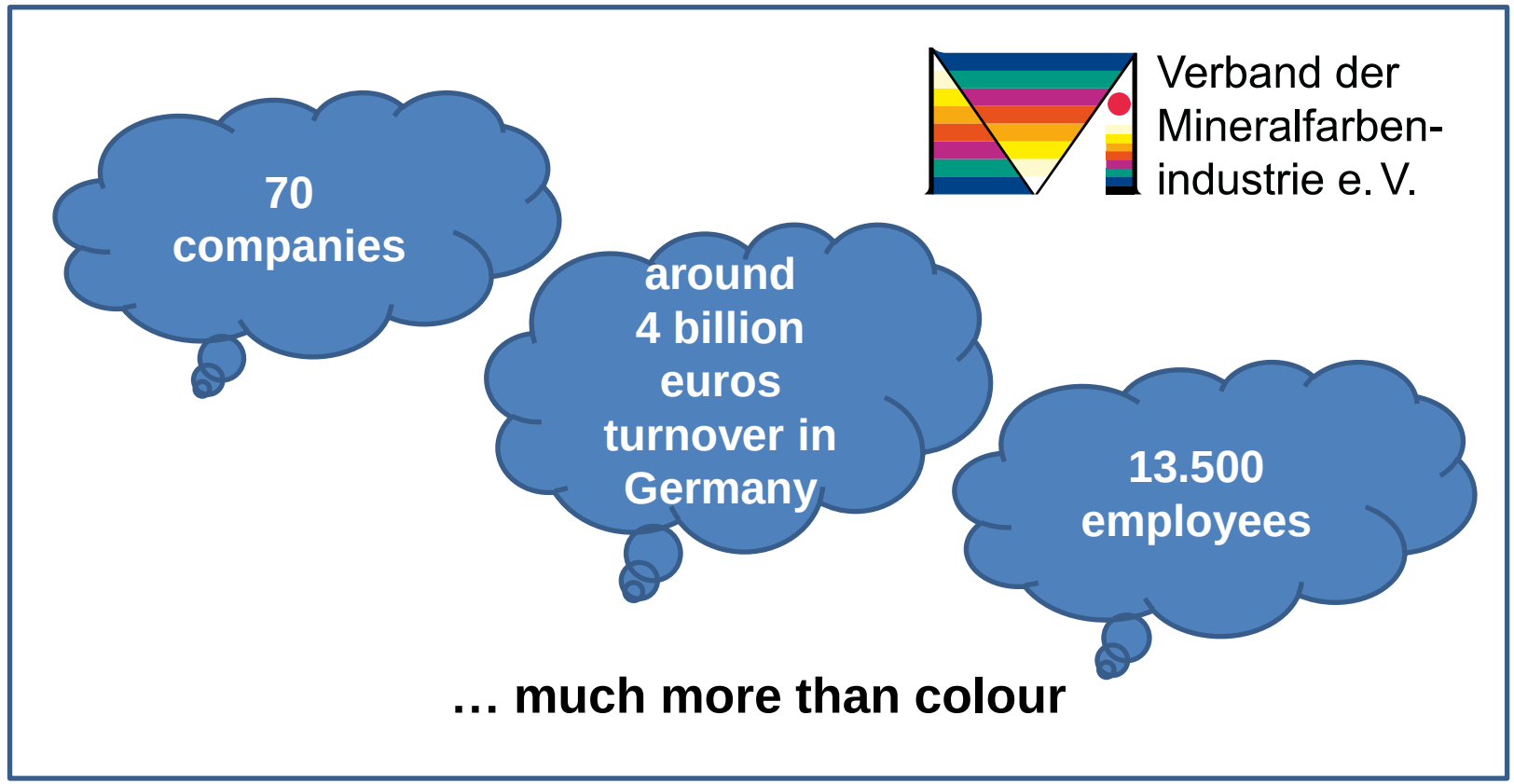
users



VdMi - Who we are

Verband der Mineralfarben-industrie e. V.

VdMi – figures and facts



The member companies in VdMi consider themselves as part of the German Chemical Industry. VdMi represents therefore a sub-sector, which employs a good 13,500 people in about 70 companies and has an annual turnover of around 4 billion euros in Germany. More than half of the companies are SMEs.

Source: Members employee query 2022

VdMi - Who we are

Verband der Mineralfarbenindustrie e. V.

Participants of today's meeting

Participants VdMi and its member companies

- [redacted] Colors & Effects Switzerland AG – Sun Chemical
- [redacted] Colors & Effects Switzerland AG - Sun Chemical
- [redacted] Heubach Colorants Germany GmbH
- [redacted] Heubach Colorants Germany GmbH
- [redacted] Heubach Colorants Germany GmbH
- [redacted] VdMi
- [redacted] VdMi

Participants Umweltbundesamt /BauA

- [redacted] (BauA)
- [redacted] (UBA - Chemikalien)
- [redacted] (UBA - Chemikalien)
- [redacted] (UBA - Chemikalien)
- [redacted] (UBA - Chemikalien)
- [redacted] (UBA - Chemikalien)
- [redacted] (UBA - Chemikalien)

Why we are here today

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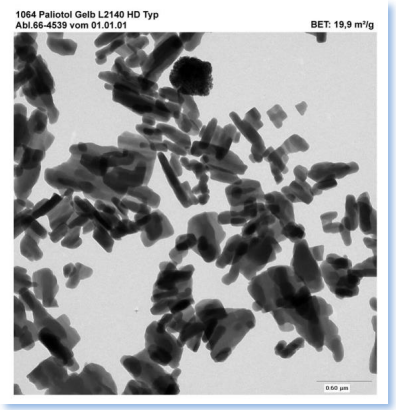

In order to better protect the environment, the German Environment Agency (UBA) is of the opinion that the simplified procedure for identifying a SVHC based on a harmonised classification under CLP should be extended to new hazard classes, like PMT and vPvM (UBA, 2022).

3.2.2 Mobility in the aquatic environment

A substance fulfils the 'mobility in the aquatic environment' criterion (M) in the following situation:

The water solubility (SW) at pH 6–8 and 12 °C is ≥150 µg/L and the log K_{oc} at pH 6–8 and 12 °C is ≤4.5.

This criterion is identical with the proposed mobility criterion (M) in Kalberlah et al. (2014).

4.2 Local authorities and water suppliers

The UBA list of PMT/vPvM substances in the REACH registration data base is fit for purpose and ready to use for local authorities water suppliers and producers of drinking water, as well as water researchers, as they can immediately add the substances to their monitoring programs.

C.I. Name	CAS Number	Water solubility [mg/L]	Octanol solubility [mg/L]
Pigment Yellow 12	6358-85-6	0.0004	0.0498
Pigment Yellow 13	5102-83-0	0.0004	0.0223
Pigment Yellow 14	5468-75-7	0.0008	0.0026
Pigment Yellow 152	31775-20-9	0.0106	0.1400
Pigment Yellow 17	4531-49-1	0.0026	0.0068
Pigment Yellow 176	90268-24-9	0.0020	0.0410
Pigment Yellow 81	22094-93-5	0.0026	0.0086
Pigment Yellow 83	5567-15-7	0.0081	0.0085

UBA		C.I. Name	CAS Number
vPvM	High-Priority_A	Pigment Yellow 81	22094-93-5
vPvM	Moderate-Priority_B	Pigment Yellow 152	31775-20-9
vPvM	High-Priority_A	Pigment Yellow 139	36888-99-0
vPvM	High-Priority_A	Pigment Yellow 17	4531-49-1
vPvM	High-Priority_A	Pigment Yellow 13	5102-83-0
vPvM	High-Priority_A	Pigment Yellow 14	5468-75-7
vPvM	High-Priority_A	Pigment Yellow 83	5567-15-7
vPvM	High-Priority_A	Pigment Yellow 12	6358-85-6

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UBA Mobility Assessment of Organic Pigments

- Organic pigments published on UBA list in September 2023 classified as vPvM and in 10 of 11 cases as High-priority A

C.I. Name	Substance group	CAS	Octanol Solubility [mg/L]	Water Solubility [mg/L]	calculated log Pow	UBA	Assessment	UBA (min logDow) used for the Assessment
Pigment Yellow 12	Diarylide	6358-85-6	0.0498	**0.0004**	2.1	vPvM	High-Priority_A	2.1
Pigment Yellow 13	Diarylide	5102-83-0	0.0223	**0.00035**	1.8	vPvM	High-Priority_A	1.8
Pigment Yellow 14	Diarylide	5468-75-7	0.0026	**0.0008**	0.5	vPvM	High-Priority_A	0.5
Pigment Yellow 17	Diarylide	4531-49-1	0.0068	**0.0026**	0.4	vPvM	High-Priority_A	0.4
Pigment Yellow 81	Diarylide	22094-93-5	0.0086	**0.0026**	0.5	vPvM	High-Priority_A	0.5
Pigment Yellow 83	Diarylide	5567-15-7	0.0085	**0.0081**	0.02	vPvM	High-Priority_A	0.0
Pigment Yellow 126	Diarylide	90268-23-8	0.145	**0.0057**	1.4	vPvM	High-Priority_A	1.4
Pigment Yellow 127	Diarylide	68610-86-6	0.0275	**0.0043**	0.81	vPvM	High-Priority_A	0.8
Pigment Yellow 152	Diarylide	31775-20-9	0.140	**0.0106**	1.1	vPvM	Moderate-Priority_B	1.1
Pigment Yellow 176	Diarylide	90268-24-9	0.041	**0.002**	1.3	vPvM	High-Priority_A	1.3
Pigment Yellow 139	Isoindoline	36888-99-0	0.0059	**0.0029**	0.31	vPvM	High-Priority_A	-5.70

Why we are here today

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- “Final Report Prioritised PMT/vPvM substances in the REACH registration database” (UBA-Texte 21/2023) published in September 2023 includes a list of chemicals identified as PMT or vPvM and considered being SVHC by the authors
- List includes also several organic pigments, many of them flagged as “high Priority” (A)
- How did UBA come to the conclusion that organic pigments are mobile or even very mobile?
- It is the role of the lead registrant of a given substance to assess whether a substance will be classified as M/vM according to CLP
- Classification of organic pigments as vPvM substances is not correct (false positive) as the criteria do not apply to the insoluble chemicals
- The pigments need to be removed from the list as they are not potential contaminants of water resources

Properties of Organic Pigments

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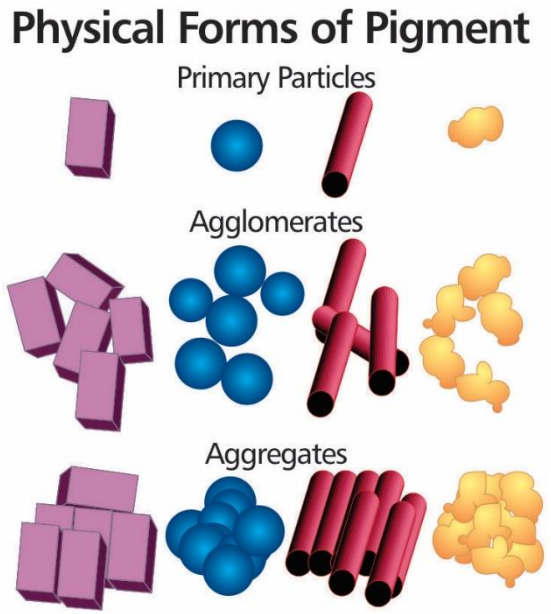
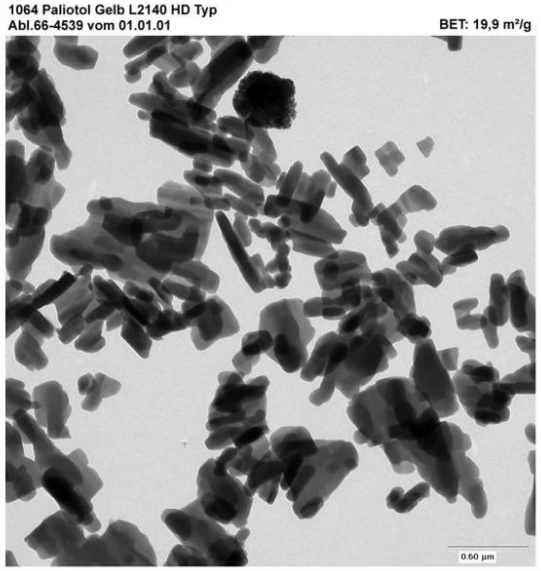


1.1

Definition: Pigments and Dyes

Colourants are classified as either pigments or dyes. Pigments are inorganic or organic, coloured, white or black materials that are practically insoluble in the medium in which they are incorporated. Dyes, unlike pigments, do dissolve dur-

K. Hunger et al.; **Industrial Organic Pigments**; 4th Edition 2018



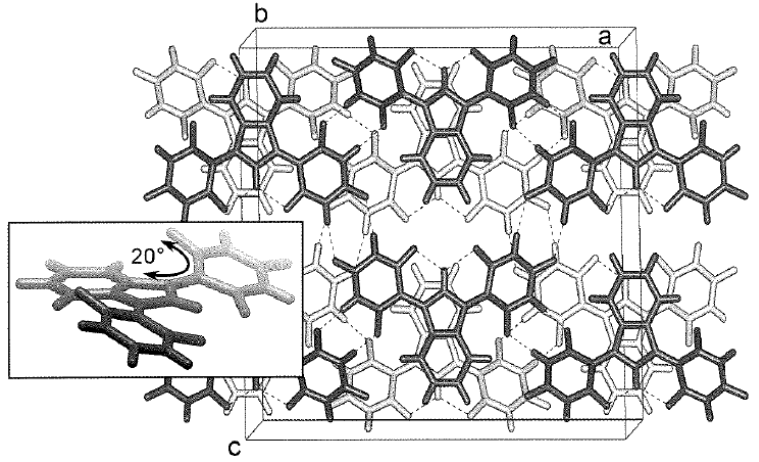
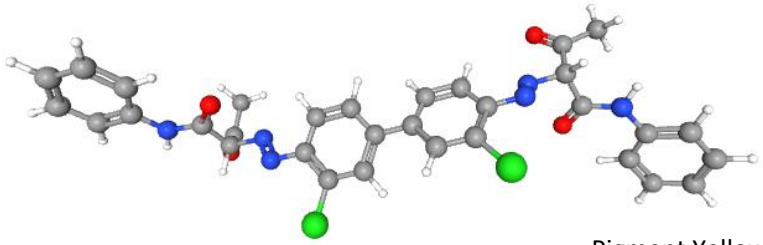


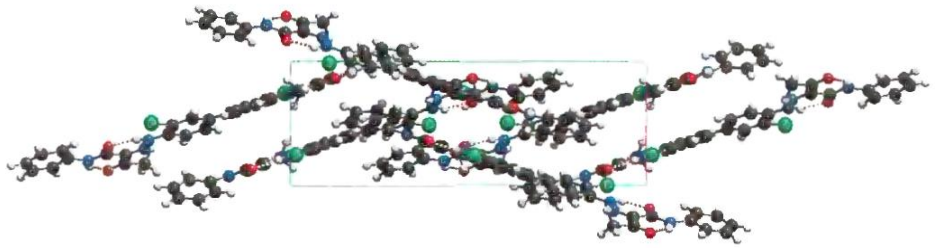
Figure 14.11 Molecular structure and packing diagram of P.Y. 139. Dashed lines represent intra- and intermolecular hydrogen bonds.

Effect of Pigment Properties on Solubility



Pigment Yellow 12

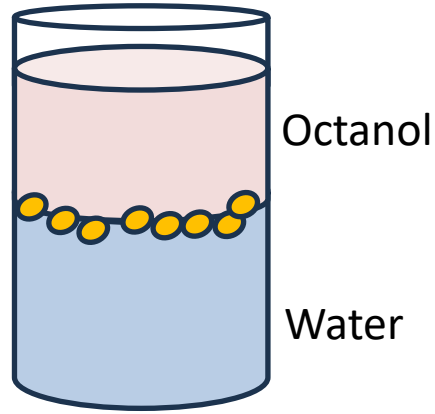
- Planar or nearly planar molecules forming rigid and efficiently packed structures within the crystal lattice
- Efficient packing results in high densities and high lattice energies → extremely low solubility in water and organic solvents



Pigment Yellow 12

K. Hunger et al.; **Industrial Organic Pigments**; 4th Edition 2018

- Pow measurements according to OECD standards technically not feasible due to extremely low solubility in both media
  - → no equilibrium distribution at the interface between octanol and water
- Solubility in octanol (Co) and water (Cw) determined separately (ECHA guidance R11), quotient Log(Co/Cw) calculated afterwards
- Calculated logPow of limited suitability for mobility assessment of pigments



Insoluble in both, water and octanol e.g. organic pigment
→ no partition in any medium

Calc. Pow = Sol_{oc}/Sol_w

0.0498 mg/L / 0.0004 mg/L = 125

logPow = 2.1

Misleading artifact, not lipophilic

Effect of Pigment Properties on Solubility

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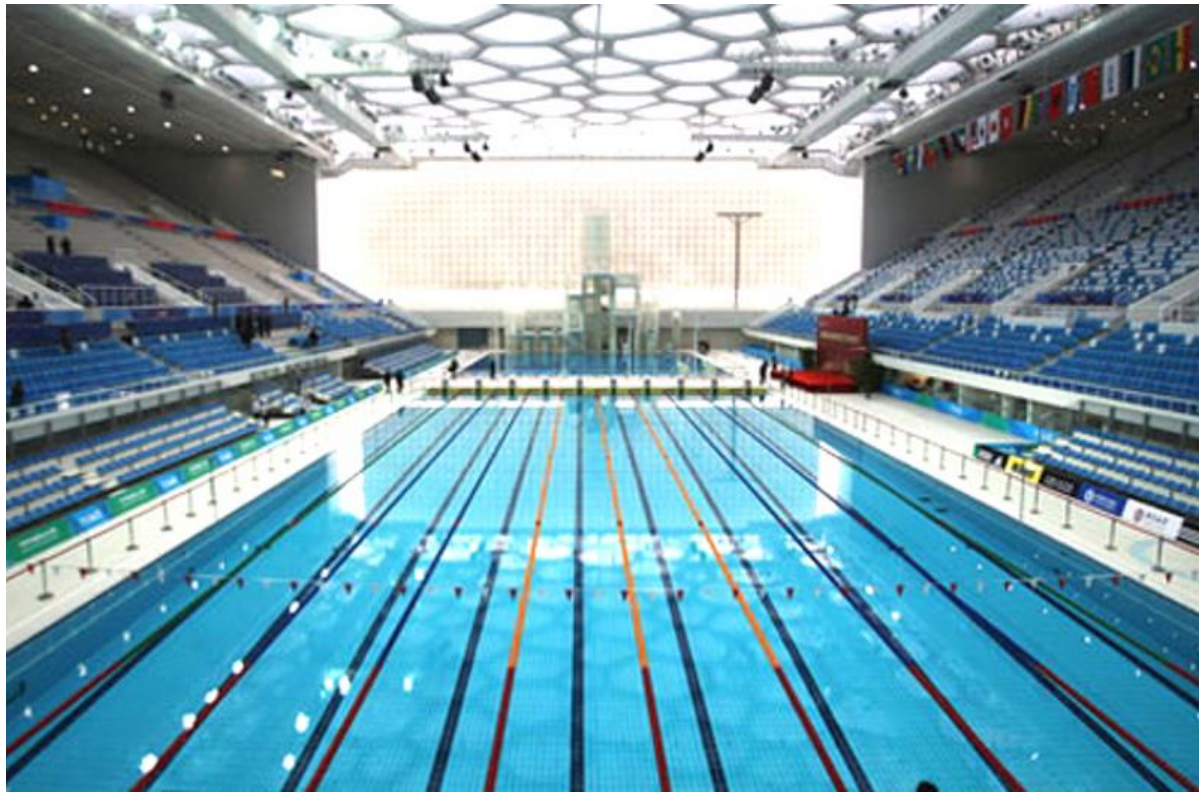

- Pigment Yellow 139 has a water solubility of 2.9 µg/L
- An Olympic size swimming pool of 50 x 25 m contains 2.5 million liters of water
- **138 swimming pools (345 million liters water) would be required to dissolve 1 kg of Pigment Yellow 139**

Effect of Pigment Properties on Ionization

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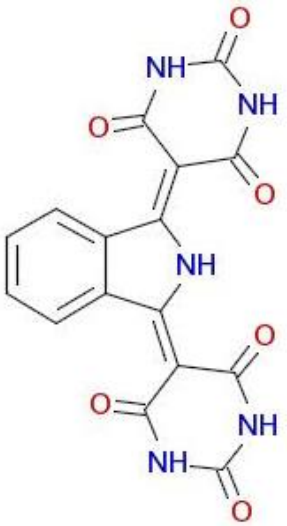
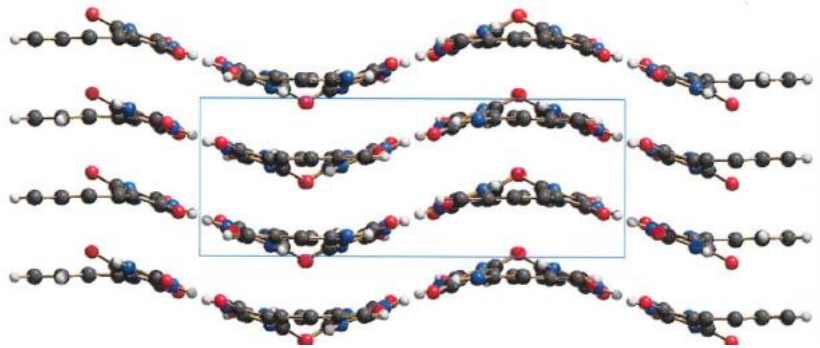
- Pigment particles do not dissolve in water due to their high lattice energy and dense crystal structure, they cannot be ionized under environmental conditions
- Breaking the bonds between neighboring molecules in the crystal structure to introduce or release ions into / from these non-polar molecules is energetically impossible
- Pigment molecules within the crystal are always present as neutral species



Pigment Yellow 139 (CAS 36888-99-0)

- Contains “barbituric acid”, appears ionizable
- Prerequisite for introduction of e.g. H^+ is dissolution in water
- 2.9 µg/L water → Pigment cannot dissolve → requires far too much energy to ionize the barbituric acid groups
- min LogDow of -5.7 for the charged molecule as used by UBA is not appropriate



Effect of Pigment Properties on Ionization

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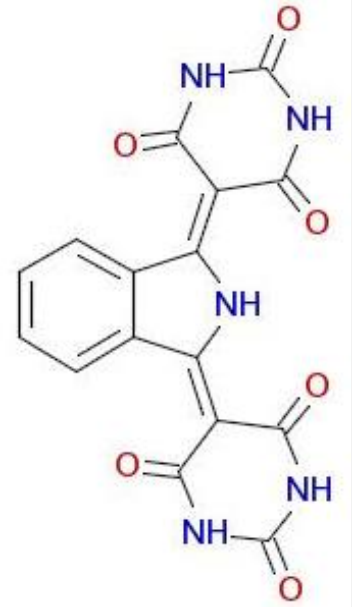
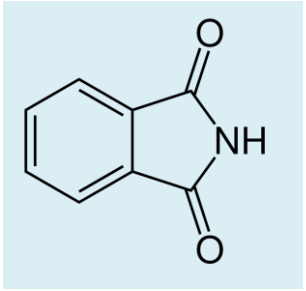
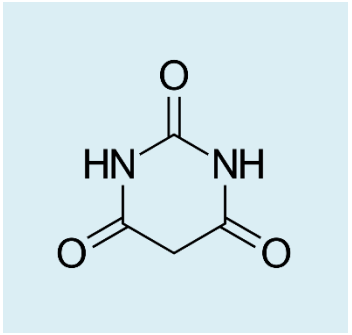


Pigment Yellow 139
Water solubility 2.9 µg/L
Not ionizable

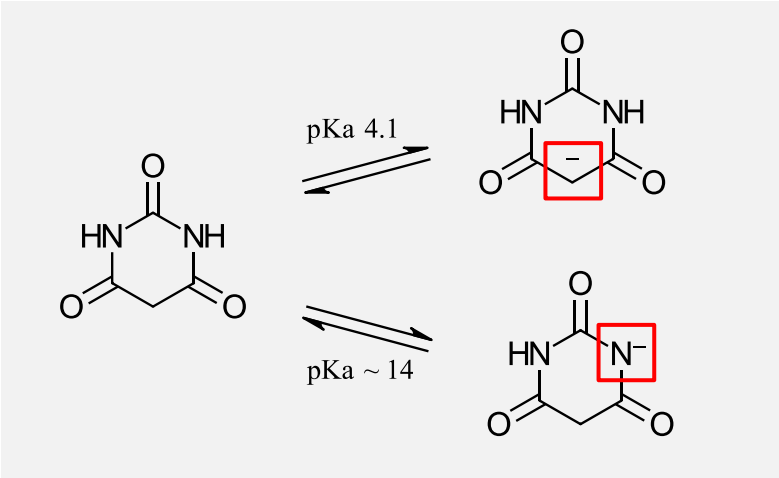


Phthalimide (PI)
PI is water soluble (~ 360 mg/L)
logPow 1.15
pKa is 8.3 in H_2O
Likely ionizable



Barbituric acid (BA)
Raw material for PY 139
BA is water soluble (10 g/L)
logPow – 2.39 (OECD 107)
pKa is 4.1 in H_2O
Ionizable

- The moieties of Pigment Yellow 139, phthalimide and barbituric acid, have a comparably high water solubility
- The pigment itself however has completely different properties: poorly soluble and not ionizable



Effect of Pigment Properties on Mobility

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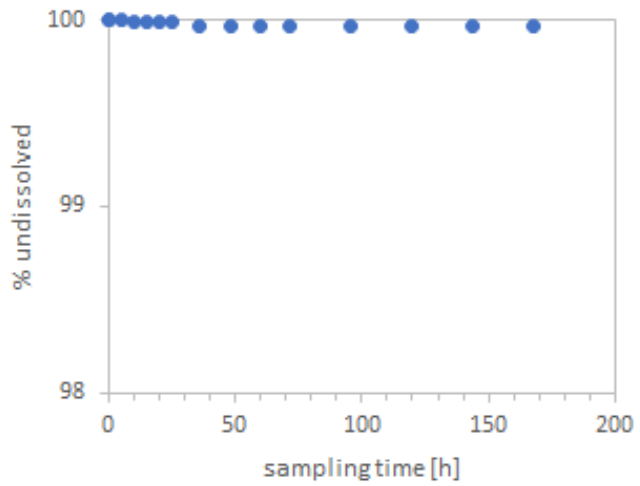
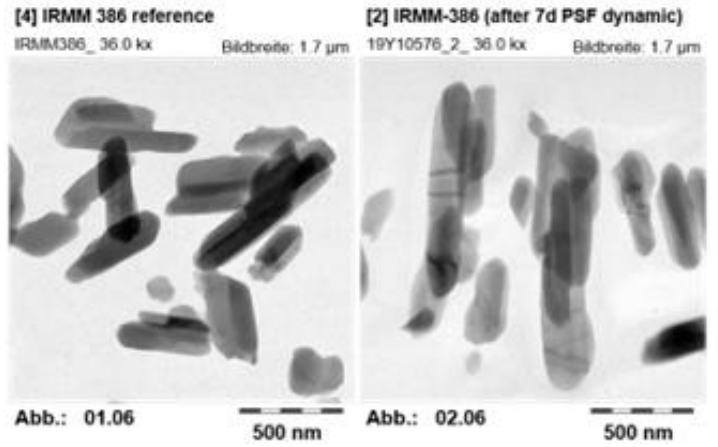
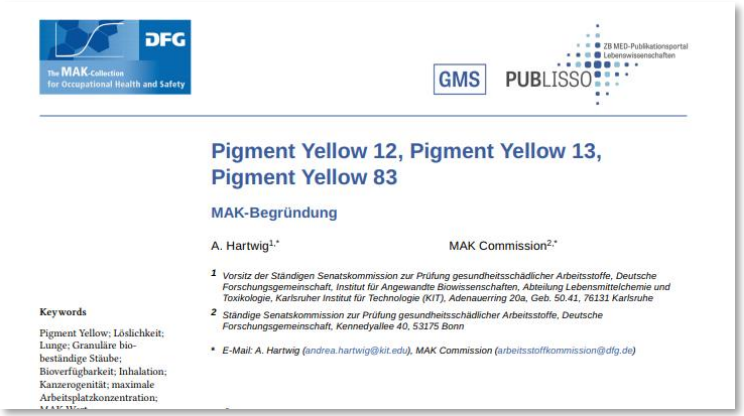


Dynamic dissolution of Pigment Yellow 139 in pH 4.5 PSF with detection by UV-Vis. The pigment shows a dissolution rate of 0.013 ng/cm²/h and is therefore clearly below the cut-off of insoluble materials.



TEM analysis of remaining solids after dynamic dissolution in comparison to reference before dynamic dissolution. No change of particle size after 7 treatment days.

- The dynamic dissolution assay is an abiotic flow-through method to determine the biodissolution of materials in relevant lung fluids. Transmission Electron Microscopy (TEM) was used to evaluate potential shrinkage or re-crystallization of the remaining particles after 7 days of dissolution. Pigment samples for TEM are carefully dispersed to enable evaluation of single particles.
- TEM analysis and dynamic dissolution were used for the re-assessment of the water hazard class of PY 12, 13 and 83 via MAK commission in 2019.


DFG The MAK-Collection for Occupational Health and Safety

GMS PUBLISSO

Pigment Yellow 12, Pigment Yellow 13, Pigment Yellow 83

MAK-Begründung

A. Hartwig[1,*] MAK Commission[2,*]

[1] Vorsitz der Ständigen Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe, Deutsche Forschungsgemeinschaft, Institut für Angewandte Biowissenschaften, Abteilung Lebensmittelchemie und Toxikologie, Karlsruher Institut für Technologie (KIT), Adenauerring 20a, Geb. 50.41, 76131 Karlsruhe

[2] Ständige Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe, Deutsche Forschungsgemeinschaft, Kennedyallee 40, 53175 Bonn

* E-Mail: A. Hartwig (andrea.hartwig@kit.edu), MAK Commission (arbeitsstoffkommission@dfg.de)

Keywords

Pigment Yellow; Löslichkeit; Lunge; Granuläre biobeständige Stäube; Bioverfügbarkeit; Inhalation; Kanzerogenität; maximale Arbeitsplatzkonzentration;

Effect of Pigment Properties on Mobility

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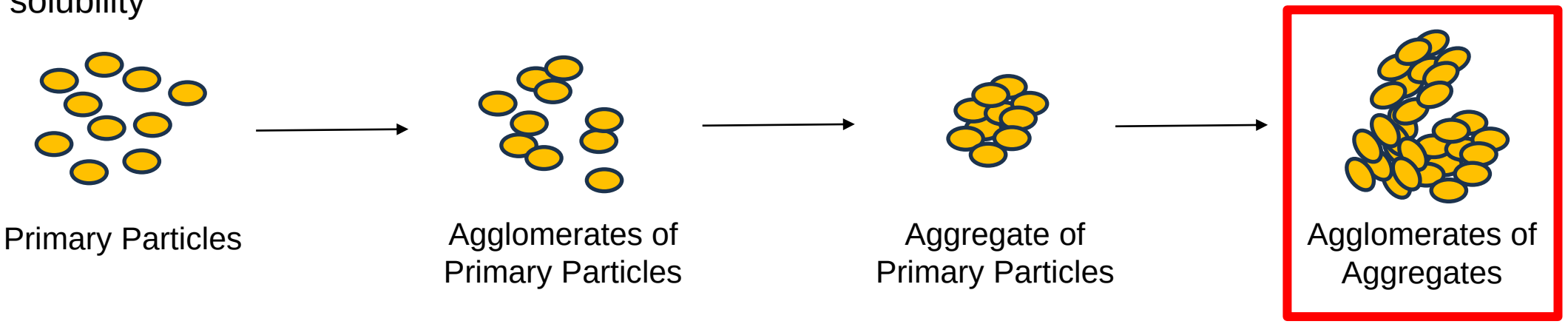
- Van der Waals or Coulomb forces cause primary particles and aggregates to grow together, forming larger agglomerates (visible pigment particles) with a non-polar surface, being hydrophobic
- Strong hydrogen bonds of amide groups within the crystal lattice result in highest densities. E.g. Pigment Yellow 139 is considered as molecule with highest density in comparison to similar compounds with C, H, N, O.
- Transport of agglomerates within soil layers not expected due to the particle size and negligible solubility



Aggregation state in nature

UBA Mobility Criteria and their Inapplicability

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Box 3a. M/vM criteria proposed in 2019 by UBA

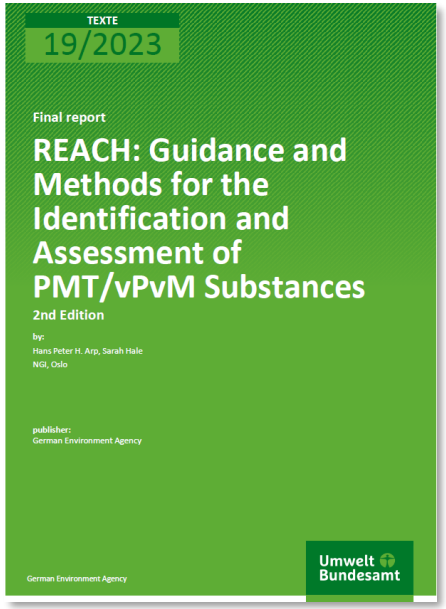
A substance fulfils the mobile criterion (M) in the following situation:

- (a) the lowest organic carbon-water coefficient log K_{OC} over the pH range of 4-9 is less than 4.0

A substance fulfils the very mobile criterion (vM) in the following situation:

- (b) the lowest organic carbon-water coefficient log K_{OC} over the pH range of 4-9 is less than 3.0

Source: Neumann and Schliebner (2019)



If no K_{OC} data is available, screening for mobility is recommended. Recommended screening parameters for mobility are the octanol-water partition coefficient (K_{OW}) or the pH-dependant octanol-water coefficient for ionisable substances (D_{OW}), as shown in Box 3c.

Box 3c. Indication of M and vM properties

- (a) For ionisable substances, the lowest pH dependent octanol-water distribution coefficient (D_{OW}) experimentally determined between pH 4-9 in accordance with Section 7.8 of Annex VII of REACH or estimated by QSAR models in accordance with Section 1.3 of Annex XI of REACH.
- (b) For other substances, the octanol-water partition coefficient (K_{OW}) experimentally determined in accordance with Section 7.8 of Annex VII of REACH or estimated by QSAR models in accordance with Section 1.3 of Annex XI of REACH.
- (c) Other information provided that its suitability and reliability can be reasonably demonstrated.

Source: Neumann and Schliebner (2019)

And what if the chemical is neither soluble in water nor octanol? (Insoluble in terms of <150 µg/L?)

UBA Mobility Criteria and their Inapplicability

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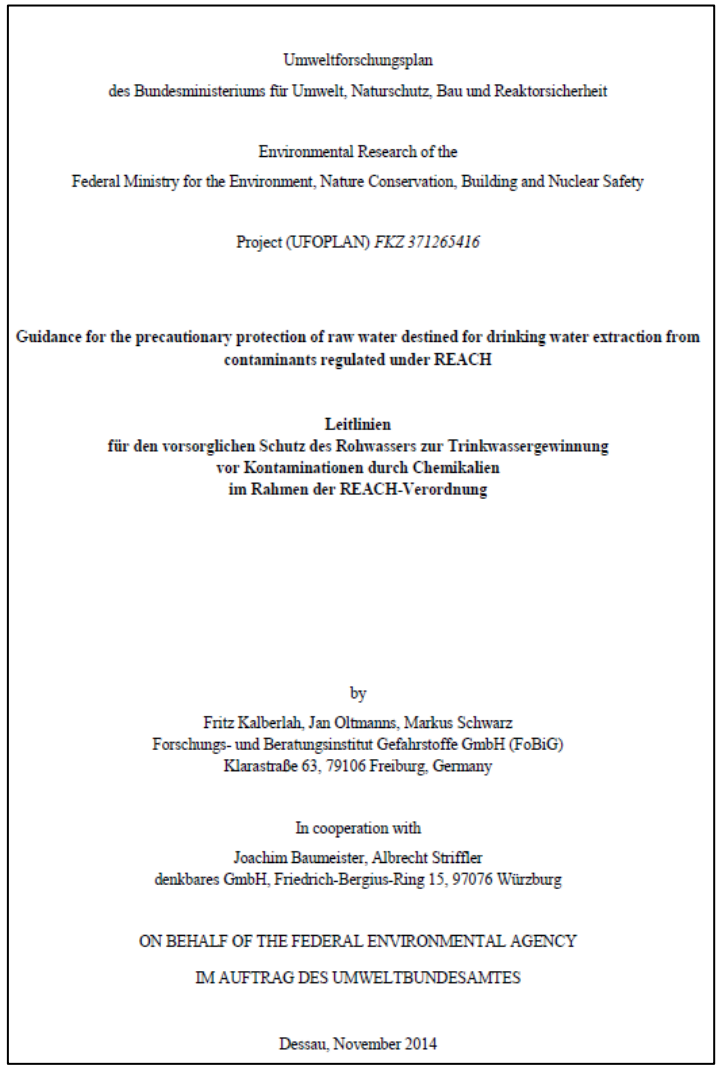

Umweltforschungsplan

des Bundesministeriums für Umwelt, Naturschutz, Bau und Reaktorsicherheit

Environmental Research of the

Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety

Project (UFOPLAN) *FKZ 371265416*

Guidance for the precautionary protection of raw water destined for drinking water extraction from contaminants regulated under REACH

Leitlinien
für den vorsorglichen Schutz des Rohwassers zur Trinkwassergewinnung
vor Kontaminationen durch Chemikalien
im Rahmen der REACH-Verordnung

by

Fritz Kalberlah, Jan Oltmanns, Markus Schwarz
Forschungs- und Beratungsinstitut Gefahrstoffe GmbH (FoBiG)
Klarastraße 63, 79106 Freiburg, Germany

In cooperation with

Joachim Baumeister, Albrecht Striffler
denkbares GmbH, Friedrich-Bergius-Ring 15, 97076 Würzburg

ON BEHALF OF THE FEDERAL ENVIRONMENTAL AGENCY

IM AUFTRAG DES UMWELTBUNDESAMTES

Dessau, November 2014

UBA Texte 09/2018:

"A substance fulfils the 'mobility in the aquatic environment' criterion (M) in the following situation:

The water solubility (SW) at pH 6–8 and 12 °C is ≥150 µg/L and the log Koc at pH 6–8 and 12 °C is ≤4.5.

This criterion is identical with the proposed mobility criterion (M) in Kalberlah et al. (2014)."

Organic pigments were excluded at that time in a Project (UFOPLAN) FKZ 371265416* on behalf of UBA:

*"Certain **organic pigments** may for example fall into the class of **low concern**, being **highly insoluble in water** and often at the same time of **very low solubility in octanol**. Given a density higher than water, they would be expected to **partition by gravity to the solid phase** and to **reside there essentially unaltered**.*
*To exclude these and similar compound groups, a **water solubility cut-off of 150 µg/L** is introduced, at or below which a substance is not regarded to be pervious to ground - or surface water. This criterion therefore can be included into an **early tier of mobility assessment** (tier M1)."*

UBA Mobility Criteria and their Inapplicability

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DTU Library

How many potential vPvM/PMT substances have been registered under REACH? - vPvM/PMT-screening by using the Danish (Q)SAR database

Holmberg, Rikke; Wedebye, Eva Bay; Nikolov, Nikolai Georgiev; Tyle, Henrik

Publication date:
2021

Document Version
Publisher's PDF, also known as Versio

Link back to DTU Orbit

Citation (APA):
Holmberg, R., Wedebye, E. B., Nikolov, *have been registered under REACH?* - Tekniske Universitet (DTU).

vM/M Screening scenario		S_w>0.15mg/L UBA criteria proposal	Without S_w criteria	Difference
1 MCI (v)M K_{oc}MCI:	M: vM:	245 (11.8%) 1,248 (60.2%)	292 (14.0%) 1,254 (60.5%)	53
2 UBA: (v)M D_{min}UBA	M: vM:	208 (10.0%) 1,224 (59.0%)	229 (11.3%) 1,249 (60.2%)	46
3 EPI: (v)M D_{min}EPI:	M: vM:	199 (9.6%) 1,329 (64.1%)	227 (11.0%) 1,362 (65.7%)	61
4 DK: (v)M D_{min}	M: vM:	212 (10.2%) 1,395 (67.3%)	268 (12.9%) 1,436 (69.3%)	97

Table 5: Results of application of screening criteria with and without the Sw-part on the 2073 REACH substances for the four vM/M-screening scenarios carried forward

The numbers in the table refer to number of selected substances out of the 2073 mono-constituent REACH substances (>10tpa/manufacturer or importer). # excluding vM substances i.e. M_{excl}

- Later adaptation of the M-screening criteria in 2019 led to removal of the water solubility threshold because water solubility was considered “neither a suitable property to set a threshold for the assessment of mobility, nor for the screening” (Holmberg et al., 2019) and was removed (UBA 127/2019)
- A QSAR assessment indicated that “for these scenarios there is **not a great influence** of whether the Sw part of the vM and M criteria set are included or not.” (Holmberg et al., 2019) and finally due to “**simplicity reasons**” water solubility was excluded from the mobility criteria
- Removal of the water solubility cut-off leads to false positive results applying the M-criteria for insoluble, solid chemicals

UBA Mobility Criteria and their Inapplicability

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- Cut-off value of 150 µg/L as proposed by Kalberlah et al. (2014) and as included in the mobility criteria (UBA 2018) is an opportunity to prevent overestimation of mobility for substances with low solubility

- Water solubility of the listed pigments is far below the cut-off value: 0.35 µg/L (Pigment Yellow 13) - 10.6 µg/L (Pigment Yellow 152)

- Removal of the water solubility cut-off for “simplicity reasons” (Holmberg et al., 2019) and low impact is hardly comprehensible from a scientific point of view

- Listing and prioritizing false positive chemicals is not acceptable, even more with regard to the call to action to authorities and NGO’s

Conclusion

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- Remove the pigments from this list in the report
- Consider to adapt your assessment criteria
  - Consider to include the threshold of water solubility again
  - Consider that there are other properties that may hamper mobility assessments e.g. ionization or elsewhere Kow is not appropriate
- More transparency in the prioritization would be appreciated

Discussion

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- What is the scientific justification that the cut-off threshold of 150 µg/L water solubility was removed by UBA?
- What does it mean for the mobility assessment of substances such as pigments where partitioning coefficient is not an appropriate criterion to assess mobility and leads to an unrealistic overestimation of risk?
- EU-Reach-Registration tonnages and reported uses cannot solely explain the prioritization and none of the pigments prioritized by UBA were detected in the environment so far (UBA 126/2019). So, based on which rationale were the eleven pigments prioritized by UBA?
- Is the UBA priority list intended to be updated on a regular basis? What is the procedure for a reassessment of the already listed substances?

Thank you

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