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ACCOUNTING FOR PHOTO DEGRADATION IN THE PBT ASSESSMENT OF CHEMICALS

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INTRODUCTION and OBJECTIVES

Photo degradation (PhoDeg) in water may be an important removal mechanism of chemical substances from the environment, in particular for chemicals that resist biodegradation. Two main mechanisms of photolysis have been described in the aquatic environment: (1) Direct photolysis, occurring when a given chemical absorbs light and as a consequence of that absorption undergoes transformation. (2) Indirect photolysis, occurring either when another excited species transfer their energy to the chemical (sensitized photolysis) or when reactive (non-excited) compound present in the media (e.g. hydroxyl radicals) react with the chemical. Photo reactivity of chemicals cannot be estimated from chemical structure by means of QSARs. PhoDeg rates in water are obtained from laboratory measurements. Information on PhoDeg is often neglected in P-assessment of chemicals, due to lack of systematic procedures to translate such information into “half-lives in water”. However, REACH regulation requires that chemical substances be assessed with respect to persistence, bioaccumulation and toxicity (PBT). The REACH Guidance specifies an Integrated Testing Strategy for carrying out persistency assessments indicating that Information on PhoDeg may be used in the assessment of (non) persistence. Although the spirit of the regulation is clear, still unclear how to deal with some specific issues: (1) Extrapolation of measured PhoDeg rates in water under laboratory conditions to half-lives in natural water; (2) Definition of relevant environmental characteristics for evaluating “half-lives in water”; (3) Identification of environmental compartments which need to be considered “relevant”. The OBJECTIVES of the present work are to evaluate and apply the current knowledge on quantitative description/prediction of PhoDeg rates in water and to propose a modeling procedure to account for photo degradation in P assessment of chemicals.

MODELING

Currently used model algorithms originate largely from laboratory research and model development, carried out more than twenty years ago by the US EPA and have been applied in water quality modeling since 1982 (EXAMS). The early models considered direct photolysis only. Although knowledge of indirect PhoDeg processes has increased, this has not led to improvement of modeling PhoDeg. An update of the multimedia mass balance model SimpleBox to better account for PhoDeg of chemicals in the environment is proposed in this work. The model algorithm adopts the standard procedures for deriving a first-order rate constant for direct PhoDeg in clean (completely transparent) water from GSOLAR-calculated solar irradiance tables, the substance’s absorption spectrum, and a laboratory-measured quantum yield. The clean-water rate constant is extrapolated to natural water conditions by use of modifiers:

\[ k_{phot} = \frac{1}{\Delta t} \times \sum_{i} \frac{A_{i}}{z_{i}} \times C_{i} \times (AF - \text{DOM factor} \times pH factor) \]

The factor AF (light attenuation factor) corrects for the absorption of light in the water column. AF-values for various waters are based on measured light attenuation coefficients \( K_z \) and the water depths \( d \).

It has not been possible to formulate generic derivations for the modifiers DOMfactor and pHFactor.

CONCLUSIONS and RECOMMENDATIONS

Quantitative knowledge of the rate of photo degradation in water can be applied for the purpose of P-assessment under REACH as follows:

- Rates of direct photolysis in clear water can be obtained by standard procedures and should be made available from registration dossiers.
- The influence of DOM on direct photolysis can be accounted for.
- The influence of DOM on indirect PhoDeg and the influence of pH can be accounted for, if only experimental knowledge is available.
- PhoDeg in natural waters is much slower than in clear (laboratory) water: \( t_{1/2} \approx 400 \text{ days} \) in clear water, while \( t_{1/2} \approx 50 \text{ days} \) in natural waters.
- For the purpose of P-assessment, “half-life in water” can be derived as the weighted average of half-lives in the various water types, typically modeled in environmental risk assessment of chemicals, using modeled steady-state mass fractions in the various waters as weighting factors.

Relative importance of dissolved organic matter (DOM) and pH

Published evidence indicates that acid-base speciation can dramatically influence the rate of direct photolysis: rates can be up to 35 times higher at neutral pH, compared to lab. pH. Presence of DOM may influences PhoDeg rates in various ways (see scheme above), two mechanisms being the most studied: (i) UV light absorption by humic materials decreases the irradiance, particularly in deeper waters; (ii) light absorbed by DOM can be transferred to the chemical substance, indirectly enhancing the photo degradation. Enhancement up to a factor of 19, as well as depression by a factor of 8 have been reported. Decrease of PhoDeg rates as a result of light absorption by DOM can be quantified and accounted for in models. However, insufficient basis to formulate generic procedures to account for enhancement of indirect PhoDeg by DOM, or the influence of pH on direct PhoDeg was found. P-assessment of photo sensitive substances requires that the influence of DOM and pH be described. Knowledge of direct PhoDeg rates in optically thin water, as measured/extrapolated in the EPA and OECD procedures is insufficient. Particularly experimental knowledge of the rate of indirect PhoDeg may be helpful.

Application to example substances

The calculation procedure was tested with a number of chemicals, some of which have been considered to be labeled (Persistent) According to REACH guidelines, a chemical is persistent if its half-life in water exceeds a critical value (40 and 60 days for fresh and sea water, respectively). Persistent chemicals that do not hydrolyze or biodegrade could turn out from-Pollutant the PhoDeg half-life in water is smaller than 40 days. The table below lists estimated PhoDeg half-lives in various waters and overall half-lives \( t_{1/2} \text{(photo)} \) in all waters, calculated by weighted averaging of half-lives in the various waters \( t_{1/2} \text{(water)} \) using the steady-state mass distributions \( m_j \) as weighting factors. This analysis demonstrates how musk xylene, if not degraded by other mechanisms, will be VP since its overall half life in water is greater than 60 days. The polybrominated diphenyl ethers (PBDEs) have overall half lives in water well below 40 days and with respect to this compartment would not fulfill the P criterion. Note that most of these example chemicals are particle-bounded, so even if PhoDeg in water may reduce their environmental half-lives the contribution to their overall TIEgree of persistence in terms of persistent/not persistent in the environment may not be significant.

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