Improved test system to determine chemical degradation in laboratory water/sediment systems – experimental results

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1. Introduction

The degradability of chemicals in different environmental compartments plays a crucial role in regulatory decision-making in different legislative frameworks. Degradation half-lives are used for persistence assessment but also for exposure modelling e.g. in the FOCUS models used in the risk assessment of plant protection products and veterinary pharmaceuticals, or in the EUSES model for risk assessment of industrial chemicals. Several study types for laboratory investigation of the fate of chemicals in different compartments are described in OECD-Guidelines. As those studies on the one hand should represent the maximum range of different environmental conditions as a higher tier simulation test, but on the other hand have to be as standardized as possible to enable reproducible lab performance, there are still uncertainties with regard to performance, evaluation and interpretation.

The OECD 308 guideline on “Aerobic and Anaerobic Transformation in Aquatic Sediment Systems” has been used since 2002 extensively in pesticide registration as well as for the assessment of industrial chemicals. But particular for OECD 308 several shortcomings have been identified and discussed over the years in workshops and the scientific literature: the combination of degradation and sorption, which makes it impossible to locate where and how degradation occurs; the unrealistic water-sediment ratio of 3:1 which often result in high levels of non extractable residues (NER) and huge anaerobic areas in the sediment. Thus, a derivation of a compartment specific degradation half-live is hardly possible from OECD 308.

In the last years the OECD 309 guideline, that is intended to determine biodegradation in aerobic natural waters, became more important for regulation. It is run at low sediment concentrations under fully aerobic conditions as a laboratory shake flask test. With suspended sediment concentrations between 0.01 and 1 g suspended solids (SS)/L it is related to OECD 308, but might potentially exhibit several advantages over OECD 308 for determining biodegradation.

This CEFIC-funded project (LRI-ECO18) should (i) help to better understand the value and information content of the existing OECD 308 protocol, and (ii) help to develop an improved test strategy for assessing persistence in sediment and surface water in a consistent and robust manner. For this purpose a set of four reference chemicals are investigated applying OECD 308 and 309 methods but also modified 308 and 309 experimental setup to bridge the gap between the two standard methods. In addition sorption coefficients are obtained with the sediments used in the study. With these experimental data set robust degradation data and disentangling of sorption and degradability - while clearly distinguishing between aerobic or anaerobic conditions - will be obtained by advanced parameter estimation techniques (refer to Honti, M.).

This presentation will focus on experimental methods and the current status of data determination within the CEFIC project including first results and conclusions about the influence of the experimental setup on the results. The aim is to develop alternative test systems that close the gap between OECD 308 and 309, and where some of the major points of criticism of OECD 308 are addressed.

2. Materials and methods

For the current approach OECD 308 and OECD 309 are seen as two extremes:

- OECD 308 as a simulation approach with an unrealistically high water-sed ratio of 3:1, semi-aerobic conditions (at least in the sediment) and substance distribution by diffusion processes only.
- OECD 309 as a simulation approach with only small amounts of sediment (water-sed ratio: 1000:1) serving as inoculum rather than adsorbant, aerobic conditions and substance distribution close to partitioning equilibrium through continuous shaking.

To bridge the gap between those two extremes, both systems are modified carefully:

- OECD 308 is modified with stirring in the water column without disturbing the sediment and a thinner sediment layer (water-sed ratio: 10:1) to achieve as aerobic conditions as possible and suppress the significance of diffusion.
- OECD 309 is modified to contain higher sediment concentrations (water-sed ratio: 100:1), aiming towards reflecting a fully aerobic, but disturbed sediment system.

The set of four ^{14}C-labelled reference substances are primarily be chosen to span the relevant range of sorption and biodegradability. The set thus include two rather weakly sorbing compounds with high and low biodegradability, and two strongly sorbing compounds with high and low biodegradability:

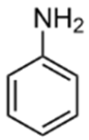	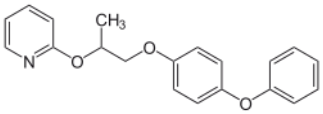	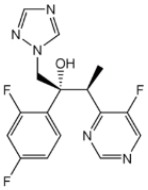	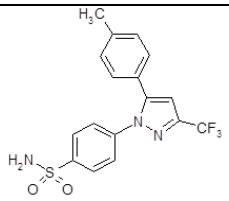
Aniline (weak sorb, high deg)	Pyriproxifen (strong sorb, high deg)	Voriconazole (weak sorb, low deg)	Celecoxib (strong sorb, low deg)

Figure 1: chemical structure formulas of the selected reference substances .

For the project two natural sediments with different textures and high and low OC according to OECD 308 are used. To ensure same phys-chem sediment properties throughout the entire project, the sediments were sampled freshly just once and portions were stored frozen (-20°C) until the respective experiments. Prior to start of the experiments the sediments were allowed to pre-incubate under experimental conditions at 20°C in the dark for 3 weeks.

Sorption coefficients (Kd, Koc) for all four substances and the two sediments were determined experimentally in accordance to OECD 106 guidance

3. Results and discussion

The experiments are not yet finished. Complete data sets from all 4 test systems are available for Aniline and Voriconazole.

The behaviour of Aniline as a ready degradable substance reflect very well the effect of the different conditions in the four test systems. The rapid dissapearance of Aniline from the systems is caused by two major processes: generation of irreversible bound residues (NER) to sediment by covalent binding and mineralisation (release of $^{14}CO_2$) by biodegradation. Both are competing processes as bound residues are no longer available for biodegradation. This is pictured by the results where the processes has difference significance depending on water/sediment ratio and OC-content of the sediment.

With Voriconazole again results fit very well to the respective system setups although the primary dissipation process is different from the Aniline experiments. Voriconazole turned out to be very stable in the water/sediment system, the only reduction process is the slow generation of NER. But besides that the reversible sorption the sediment is the driving the dissipation of Voriconazole. Thus, on the basis of the 106-like sorption experiments with Voriconazole a very good prediction of the results from the water/sediment systems is possible.

Results from the two other reference substances will help to further improve the understanding on the dominating dissipation processes and are as such important for the development of the advanced parameter estimation techniques.

4. Conclusions

Data determined so far in the laboratory experiments are well suited for the advanced parameter estimation techniques, as they are reasonable and reflect perfect the various test system conditions for different dissipation processes. As such they are a perfect basis for development of an advanced evaluation of water/sediment laboratory tests. The variation of the test systems might help to improve the experimental setup and to overcome some of the criticism on the current OECD 308.

Acknowledgement - The authors thank the European Chemical Industry Council (Cefic) for founding the current project (Cefic LRI-ECO 18)