Code Number and Title:

LRI-ECO24: Prediction of Non-Extractable Residues (NER) using structural information ('structural alerts')

Background

Many different mechanisms are responsible for the formation of non-extractable residues (NER). The main types of interactions involved in the formation of NER are:

- sorption between the chemical and/or its transformation products and the matrix, e.g. organic matter, pH and total exchange capacity
- binding of a chemical and/or its transformation products to the matrix, e.g. covalent and ionic bonds
- physical sequestration of a chemical and/or its transformation products into the matrix

Generally, chemicals which are most strongly associated with sediment or soil (and least bio-accessible) are either covalently bound to the matrix, or physically sequestered and trapped in the pores of the matrix. Other interactions which have been shown to lead to NER or slowly desorbed residues included ionic binding and ligand exchange. A review of pesticide literature[1] indicates that the degree of NER formation of compounds in soils and sediments is dependent on the presence of appropriate chemical groups and their respective binding strengths. Molecules with electron-rich functional groups, e.g. double bonded oxygen or sulphur in carbamates and dithiocarbamates result in higher NER formation. These reactive groups are generally polarised and are therefore more likely to interact with sediment or soil via electrostatic forces (ionic bonding) or hydrogen bonding. Conversely, the abundance of electronegative (electron withdrawing) functional groups within dinitroanilines and N-heteroatomic ring may reduce any polarising effect and result in lower NER formation. The presence of reactive groups, such as aniline or phenol, generally led to a higher percentage of NER formation.

On the limited data acquired to date, only rudimentary predictions are feasible. However, it is considered that with further literature research to provide more data, it would be possible to develop so-called 'structural alerts' to predict which substances are likely to sorb to sediment and/or soil and which subsequently may form NER. Presently, the use of structural alerts to predict NER formation is not a definitive approach, though recent ECETOC Task Forces[2-3] have both identified the potential of such a technique. However, several parameters need to be taken into consideration, including the structure of the compound, the behaviour of the potential transformation products, the binding

forces involved in NER formation (between relevant structural groups and the matrix) as well as the characteristics of the adsorbent (sediment or soil).

Objectives and scope

The proposed RfP includes thorough researching of literature to identify most up-to-date information on the formation of NER in sediment and soil. The project would then develop appropriate rules to identify structural alerts. The formation of biogenic NER[4] will also be considered within this project. If suitable data are identified from the literature, then the key parameters affecting NER formation will be used to develop polyparameter linear free energy relationships (ppLFERs)[5-6] or artificial neural networks (ANNs)[7-8] to design a prediction tool for identification of key structural alerts in NER formation.

Deliverables

The final report shall contain an executive summary (2 pages max), a main part (max. 50 pages) and a detailed bibliography. It is expected that the findings will be developed into at least one peer reviewed publication, following production of poster(s) and presentation(s) at suitable scientific conference(s).

Cost and Timing

Start in early 2014, duration 2 years

Budget in the order of €150.000

Partnering/Co-funding

Applicants should provide an indication of additional partners and funding opportunities that can be appropriately leveraged as part of their proposal. Partners can include, but are not limited to industry, government/regulatory organizations, research institutes, etc. Statements from potential partners should be included in the proposal package.

Fit with LRI objectives/Possible regulatory and policy impact involvements/ Dissemination

Applicants should provide information on the fit of their proposal with LRI objectives and an indication on how and where they could play a role in the regulatory and policy areas. Dissemination plans should also be laid down.

References

1. Barriuso E, Benoit P, Dubus IG (2008). Formation of pesticide nonextractable (bound) residues in soil: magnitude, controlling factors and reversibility. Environ Sci Technol 42(6):1845-1854.
2. ECETOC (2012). Understanding the relationship between extraction technique and bioavailability. ECETOC Technical Report 117, Brussels.
3. ECETOC (2012). Development of interim guidance for the inclusion of non-extractable residues (NER) in the risk assessment of chemicals. ECETOC Technical Report 118, Brussels.
4. Nowak KM, Miltner A, Gehre M, Schaffer A, Kastner M. 2011. Formation and fate of bound residues from microbial biomass during 2,4-D degradation in soil. Environ Sci Technol 45:999-1006.
5. Goss KU and Schwarzenbach RP (2001). Linear free energy relationships used to evaluare equilibrium partitioning of organic compounds, Environ. Sci. Technol. 35(1): 1-9.
6. Undemann E, Czub G and McLachlan MS (2011). Modeling bioaccumulation in humans using poly-parameter linear free energy relationships (PPLERS), Sci Total Environ 409(9), 1726-1731.
7. Balabin RM and Lomakina EI (2009). Neural network approach to quantum-chemistry data: Accurate preiction of density functional theory energies.. J. Chem. Phys. 131(7):074104.doi:10.1063/1.3206326(http://dx.doi.org/10.1063%2F1.3206326). PMID 19708729 (//www.ncbi.nlm.nih.gov/pubmed/19708729).
8. Graves A, Liwicki M, Fernandez S, Bertolami R, Bunke H and Schmidhuber J (2009). A novel connectionist system for improved unconstrained handwriring recognition. IEEE Transactions on pattern analysis and machine intelligence 31(5).

DEADLINE FOR SUBMISSIONS: 1 September 2013

Please see www.cefic-lri.org for general LRI objectives information, project proposal form and further guidance for grant applications. For further assistance do not hesitate to contact lri@cefic.be.