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On the ranking of chemicals based on their PBT characteristics: Comparison of different ranking methodologies using selected POPs as an illustrative example

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HIGHLIGHTS

- Ranking of POPs based on persistence, bioaccumulation and toxicity.
- Comparison of ranking methods: simple additive ranking, utility function, partial order ranking.
- Total ranks vs. averaged ranks.
- Relative importance of parameters.

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ABSTRACT

Knowledge of the environmental behavior of chemicals is a fundamental part of the risk assessment process. The present paper discusses various methods of ranking of a series of persistent organic pollutants (POPs) according to the persistence, bioaccumulation and toxicity (PBT) characteristics. Traditionally ranking has been done as an absolute (total) ranking applying various multicriteria data analysis methods like simple additive ranking (SAR) or various utility functions (UFs) based rankings. An attractive alternative to these ranking methodologies appears to be partial order ranking (POR). The present paper compares different ranking methods like SAR, UF and POR. Significant discrepancies between the rankings are noted and it is concluded that partial order ranking, as a method without any pre-assumptions concerning possible relation between the single parameters, appears as the most attractive ranking methodology. In addition to the initial ranking partial order methodology offers a wide variety of analytical tools to elucidate the interplay between the objects to be ranked and the ranking parameters. In the present study is included an analysis of the relative importance of the single P, B and T parameters.

1. Introduction

Persistent organic pollutants, POPs, are a global problem. A series of POPs were banned by the adoption of the Stockholm Convention in 2001 (Stockholm Convention, 2008) such as the obsolete pesticides (OPs) like DDT, Aldrin, Dieldrin, Heptachlor, Chlordane and Lindane. Compounds like DDT and HCH (hexachloro cyclohexane) has been widely used after World War II. They have seriously affected not only the environment, but also human health, e.g., by possessing endocrine disrupting effects (Our Stolen Future, 2011).

The major environmental problem, in addition to the toxicity of these compounds, is associated with their persistency as well as the bioaccumulating ability. Hence, these compounds are classified as so-called PBT (persistent, bioaccumulating, toxic) – or vPvB (very persistent, very bioaccumulating) compounds with reference to the European chemicals regulation REACH (EC, 2006). The background for the discrepancy PBT/vPvB can roughly be expressed that if the substances are 'sufficiently' persistent and bioaccumulating the toxicity can be regarded as secondary. We seek in this paper documentation for that.

For PBT or vPvB compounds the assessment must include an exposure analysis as well as a risk characterization. It must be remembered that according to REACH (EC, 2006; article 57 and 59) authorisation should not be granted for, among others, substances having PBT or vPvB properties.

Further, in order to characterize such types of compounds, their mutual ranking according to their PBT characteristics appears of interest. This has traditionally been done, e.g., by applying various multicritiria decision data analysis (MCDA). In the present study we have included ranking methodologies such as simple additive ranking (SAR) (Talente, 2007), ranking based on a utility function

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(UF) (Talente, 2007) and partial order ranking (POR) (Bruggemann et al., 2001; Bruggemann and Carlsen, 2006; Bruggemann and Patil, 2010; Bruggemann and Patil, 2011) the latter with special emphasis on a ranking according to average ranks (Bruggemann et al., 2004; Talente, 2007; Bruggemann and Carlsen, 2011), respectively. Earlier studies have made comparisons based on different ranking method applying the various indexes for exposure and effects as used in the combined monitoring-based and modeling-based priority setting scheme (COMMPS) (Lerche et al., 2002; Pavan and Worth, 2007).

2. Methodology

2.1. Chemicals

A series of 12 persistent organic pollutants, POPs, all covered by the Stockholm Convention (Stockholm Convention, 2008) has been chosen to illustrate the discrepancies between the single types of rankings. In Table 1 the selected compounds are summarized including CAS No.'s and SMILES notations as appropriate input for the subsequent EPI Suite (EPA, 2011) calculations.

The ranking of the compounds was performed according to their PBT (Persistence, Bioaccumulation, Toxic) properties as calculated by the EPI Suite QSAR models (EPA, 2011) (vide infra), despite the fact that for several of the compounds investigated experimental data are available.

2.2. Data generation

Values for three parameters to elucidate the PBT characteristics of the single compounds were generated applying the QSAR modeling software EPI Suite (EPA, 2011). Thus, persistence was estimated applying the BioWin3 model for ultimate biodegradation potential (BDP3), bioaccumulation by the model BCFBAF and toxicity as the LC50 values for fish as calculated by the EcoSAR model. In order to carry out the partial order ranking it is necessary that the single parameters have the same orientation, e.g., low to high. In the present case the low a low value of BDP3 corresponds to a high persistence. Analogously, a low LC50 value corresponds to a high toxicity whereas a high BCF value corresponds to a high bioaccumulation. Hence, actual input values for ranking were P = 1/BDP3, B = logBCF and T = 1/LC50, respectively, in order to secure the same orientation of the three parameters, i.e. the highest values correspond to highest persistence, bioaccumulation and toxicity, respectively.

In Table 2 the calculated descriptor values for the 12 compounds are given.

2.3. Ranking methodologies

A series of ranking methodologies has been applied including linear ordering based on simple additive ranking (SAR) and a utility function (UF) as well as a ranking based on the COMMPS procedure. These ranking methods, where for all objects a mutual order relation $x < y$ exists, are called complete, total or linear orders. Further partial order ranking including a weak linear ordering (i.e. allowing tied ranks) based on average ranks was carried out.

2.3.1. Simple additive ranking

The Simple Additive Ranking (SAR) method is including in the DART software (Talente, 2007). The ranking is based on an individual ranking of each object based on the single parameters separately followed by a subsequent aggregation of the possibly weighted ranks by arithmetic mean. Thus, the eventual rank of the ith object, R_i, is calculated as

$$R_i = \frac{\sum_{j=1}^{p} w_j \cdot r_{ij}}{n} \quad (1)$$

where j refers to the parameters. Thus, w_j is the weight of the jth parameter and r_{ij} the ranking of the ith object with regard to the jth parameter. Subsequently the ranks are normalized.

2.3.2. Utility function

The ranking based on a utility function (UF) is included in the DART software (Talente, 2007). The ranking procedure to some extent mimics that of the SAR, but here the single parameters are transformed into a so-called utility, u_{ij}, by a function, f, that transforms the single object values, r_{ij}, into values between 0 and 1, i and j referring to objects and the parameters, respectively (Norstad, 2011).

$$U_j(i) = f_i(r_j(i)) \quad (2)$$

In the present study a linear transformation function has been applied. The single utilities may be weighted and the overall utility is thus calculated by

$$\Gamma(r_i) = \sum_{j=1}^{p} w_j \cdot u_j(i) \quad (3)$$

where w_j are the single weights and

$$\sum_{j=1}^{p} w_j = 1 \quad (4)$$

2.3.3. Partial order ranking

Partial Order Ranking is a simple principle, which a priori includes "$\leqslant$" as the only mathematical relation among the objects (Bruggemann et al., 2001; Bruggemann and Carlsen, 2006; Bruggemann and Patil, 2010; Bruggemann and Patil, 2011). If a system is considered, which can be described by a series of descriptors r_j, a given object A, characterized by the a set of descriptors r_j(A), $j = 1, \ldots, m$ can be compared to another object B, characterized by the descriptors r_j(B), through comparison of the single descrip-

Table 1
Chemicals included in the study.

ID	CAS No.	Trivial name	Smiles
DDT	50-29-3	p,p-DDT	Clc1ccc(cc1)C(c2ccc(Cl)cc2)C(Cl)(Cl)Cl
DDD	72-54-8	p,p-DDD	ClC(Cl)C(c1ccc(Cl)cc1)c2ccc(Cl)cc2
DDE	72-55-9	p,p-DDE	Clc1ccc(cc1)\C(=C(/Cl)Cl)c2ccc(Cl)cc2
MEC	72-43-5	Methoxychlor	ClC(Cl)(Cl)C(c1ccc(OC)cc1)c2ccc(OC)cc2
ALD	309-00-2	Aldrin	ClC3=C(Cl)C4(Cl)C2C1CC(C=C1)C2C3(Cl)C4(Cl)Cl
DIE	60-57-1	Dieldrin	ClC4=C(Cl)C5(Cl)C3C1CC(C2OC12)C3C4(Cl)C5(Cl)Cl
HCl	76-44-8	Heptachlor	ClC1C=CC2C1C3(Cl)C(=C(Cl)C2(Cl)C3(Cl)Cl)Cl
CHL	57-74-9	Chlordane	ClC1CC2C(C1Cl)C3(Cl)C(=C(Cl)C2(Cl)C3(Cl)Cl)Cl
LIN	58-88-9	Lindane (-HCH)	ClC1C(Cl)C(Cl)C(Cl)C(Cl)C1Cl
HCB	118-74-1	Hexachlorbenzene	c(c(c(c(c1Cl)Cl)Cl)Cl)(c1Cl)Cl
PCN	82-68-8	Pentachlor nitrobenzene	O=N(=O)c(c(c(c(c1Cl)Cl)Cl)Cl)c1Cl
PCP	87-86-5	Pentachlor phenol	Clc1c(O)c(Cl)c(Cl)c(Cl)c1Cl