Science of the Total Environment 454–455 (2013) 149–153

Contents lists available at SciVerse ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Discrete mathematical data analysis approach: A valuable assessment method for sustainable chemistry

Kristina Voigt [a,*], Hagen Scherb [a], Rainer Bruggemann [b], Karl-Werner Schramm [c]

[a] Helmholtz Zentrum Muenchen, Institute of Biomathematics and Biometry, 85764 Neuherberg, Germany
[b] Leibniz-Institute of Fresh Water Ecology and Inland Fisheries, Berlin, Germany
[c] PPM-Molecular Exposomics, 85764 Neuherberg, Germany

HIGHLIGHTS

- Data analysis for environmental health is of upmost importance.
- The method of partial order ranking proves to be a valuable method.
- Persistent Organic Pollutants are still a great problem in breast milk worldwide.
- Partial order ranking can be of great support in sustainable chemistry.

ARTICLE INFO

Article history:
Received 13 July 2012
Received in revised form 22 February 2013
Accepted 28 February 2013
Available online 27 March 2013

Keywords:
Sustainable chemistry
Persistent Organic Pollutants (POPs)
Partial order
Hasse diagram technique
PyHasse software
Chemometrics

ABSTRACT

Sustainable/Green Chemistry is a chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances. In this respect, metrical scientific disciplines like Chemometrics are important, because they indicate criteria for chemicals being hazardous or not.

We demonstrated that sustainable principles in the disciplines Green Chemistry, Green Engineering, and Sustainability in Information Technology have main aspects in common. The use of non-hazardous chemicals or the more efficient use of chemical substances is one of these aspects. We take a closer look on the topic of the hazards of chemical substances. Our research focuses on data analyses concerning environmental chemicals named Persistent Organic Pollutants (POPs), which are found all over the world and pose a large risk to environment as well as to humans. The evaluation of the data is a major step in the elucidation of the danger of these chemicals. The data analysis method demonstrated here, is based on the theory of partially ordered sets and provides a generalized ranking. In our approach we investigate data sets of breast milk samples of women in Denmark, Finland, and Turkey which contained measurable levels of 20 POPs. The goal is twofold: On the one side the hazardous chemicals are to be identified and on the other side possible differences among the three nations should be detected, because in that case possible different uptake mechanisms may be supposed. The data analysis is performed by the free available software package PyHasse, written by the third author.

We conclude that the data analysis method can well be applied for distinguishing between more or less dangerous existing chemicals. Furthermore, it should be used in sustainable chemistry in the same manner for detecting more and less sustainable chemicals.

1. Introduction

The most intractable pollutants are nuclear wastes, hazardous wastes, and wastes that threaten global biogeochemical processes, such as greenhouse gases, chemically the hardest to sequester or detoxify, physiologically the hardest for our senses to detect, economically and politically the most difficult to regulate (Meadows et al., 2004). We focus in this paper on human-synthesized chemicals, called Persistent Organic Pollutants (POPs). They have never before existed on the planet, and therefore no organisms have evolved in nature to break them down and render them harmless. Every day thousands of tons of hazardous wastes are generated in the world, much of them in the industrialized countries. Slowly there is recognition to the problem. Then there are contaminants that pollute the earth as a whole. These global pollutants, no matter who generates them, affect everyone.

1.1. Sustainable chemistry

Green Chemistry, also called sustainable chemistry, is a chemical philosophy encouraging the design of products and processes that

* Corresponding author. Tel.: +49 89 31874029; fax: +49 89 31873029.
E-mail address: kvoigt@helmholtz-muenchen.de (K. Voigt).

0048-9697/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.scitotenv.2013.02.098

reduce or eliminate the use and generation of hazardous substances. The focus is on minimizing the hazard and maximizing the efficiency of any chemical choice. It is an innovative, non-regulatory, economically-driven approach towards sustainability. Sustainability and sustainable development are effectively ethical concepts, expressing desirable outcomes from an economic and social framework. The important matter of principle becomes a victim of the desire to set targets and measure progress. Hence the involvement of measures and metrics is evident. Disciplines like, e.g. Chemometrics, Environmetrics, Biometrics, Chemoinformatics, Environmental Informatics, etc. should play an important role in the whole sustainability debate. Currently, many chemicals are produced to be persistent so that they retain their chemical structure long enough to do their work. This especially applies to POPs. The degradation is an extremely important concept of sustainable chemistry. Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment according to the 12 principles of Paul Anastas set up already in 1998 (Anastas and Warner, 1998; Anastas, 2009). According to Kummerer (2007) sustainability should be considered from the very beginning of the design of chemicals.

1.2. Persistent Organic Pollutants

Persistent Organic Pollutants (POPs) are found world-wide. Environmental and human exposure to POPs has been the subject of scientific investigation and political regulation for almost 40 years. The signature of the Stockholm Convention on Persistent Organic Pollutants (http://www.pops.int) in May 2001, and its amendments in 2011, are one of the most obvious and important results of this scientific and political discussion. Martin Scheringer formulated important ideas on the role of science and politics in coping with this major environmental and health subject (Scheringer, 2004). The role of Chemometrics, Environmetrics and Environmental Modeling was published by the same author (Scheringer, 2009).

The past and the present of environmental chemicals have proven that many chemicals found in the environment and human body are very persistent. This is e.g. the case for Persistent Organic Pollutants. The aforementioned Stockholm Convention is a global treaty to protect human health and the environment from chemicals that remain intact in the environment for long periods, become widely distributed geographically, accumulate in the fatty tissue of humans and wildlife, and have adverse effects to human health or to the environment. Exposure to Persistent Organic Pollutants can lead to serious health effects including certain cancers, birth defects, infertility, dysfunctional immune and reproductive systems, greater susceptibility to disease and even diminished intelligence (Edwards and Myers, 2007). Given their long range transport, no single government acting alone can protect its citizens or its environment from POPs. In response to this global problem, the Stockholm Convention, which was adopted in 2001 and entered into force in 2004, requires parties to take measures to eliminate or reduce the release of POPs into the environment. The Convention is administered by the United Nations Environment Programme based in Geneva, Switzerland (UNEP, 2011). Over the last 20 years, endocrine disruption research has shown how chemicals in our environment can profoundly affect development, growth, maturation, and reproduction by mimicking hormones or interacting with hormone receptors. One important mechanism of endocrine disruption is altered gene expression, mediated by inappropriate activation or deactivation of receptors that act as transcription factors. Yet, receptor-mediated changes in gene expression are just the tip of the iceberg. There are many more mechanisms of gene regulation that are potentially susceptible to alteration by environmental influences. In a recently performed study by Lyche et al. (2010) it could be demonstrated again that increased weight and the regulation of genes associated with weight homeostasis and insulin signaling suggest that environmental pollution by POPs may affect the endocrine regulation of the metabolism, possibly leading to increased weight gain and obesity.

A lot of evidence is given that there is a strong relationship between the exposure of women with chemicals and the development of cryptorchidism (malformation of the testis in the male offspring). The association between congenital cryptorchidism and some persistent pesticides in breast milk as a proxy for maternal exposure suggests that testicular descent in the fetus may be adversely affected. It has been demonstrated in case–control studies that prenatal exposure to some pesticides can adversely affect male reproductive health in animals. A possible human association between maternal exposure to POPs used as pesticides and cryptorchidism among male children has been investigated. These investigations have shown striking differences in semen quality and testicular cancer rate between Denmark and Finland. Since malformation of the testis is a shared risk factor for these conditions, a joint prospective study for the prevalence of congenital cryptorchidism was executed in Denmark (1997–2001) and Finland (1997–1999). These data have already been analyzed by classical statistical methods (Boisen et al., 2004; Shen et al., 2008). The studies suggested an association between congenital cryptorchidism and some persistent organochlorine pesticides present in mothers' breast milk. Thus, prenatal exposure to persistent organochlorine pesticides may adversely affect testicular descent in boys.

In Turkey the monitoring of pesticides is comprehensively described in a recent paper (Cok et al., 2012). In a newly performed Turkish–German collaboration study in the Taurus Mountain area in Turkey, breast milk samples were analyzed for POPs (Turgut et al., 2011).

2. Materials and methods

2.1. Data analysis method: Hasse diagram technique

The data analysis method is the method of partially ordered sets. Partial order theory is a discipline of Discrete Mathematics and one may consider partial order theory as an example of mathematics without arithmetic. A good overview can be found in Bruggemann and Carlsen (2006) and Bruggemann and Patil (2010, 2011).

Partial order theory will only be briefly outlined in this paper in order to support the understanding of the data analyses steps.

First step: We need a set of objects. We call this set of objects the ground set, and denote it as G. Objects can be chemicals, strategies (for example: water management), geographical units, environmental and chemical databases, etc. When speaking in a mathematical context, objects are often denoted as “elements”.

Second step: We need an operation between any two objects. As our aim is an evaluation, we must compare the objects. Is object “a” better than object “b”? If objects a and b are comparable we write $a \perp b$, albeit this generally important symbol is actually not needed in the analysis.

Third step: We do not only want that two objects are comparable, but we also would like to know the orientation: Is “a” better or worse than “b”? Therefore the signs $\leq$ and $\geq$ are introduced: $a \leq b$ “may” denote that a is better than b, $a \geq b$ “may” indicate that a is worse b.

Fourth step: Why “may”? The essential point is that we have to define, when we will consider object a as better than b, i.e. the signs “$\leq$” and “$\geq$” alone do not help in an evaluation procedure, we must give them an appropriate sense, i.e. an appropriate orientation.

Fifth step: The indicator values are the basis for comparisons by which objects are characterized. We call the indicators q_i and the value of an object “a” of the ith indicator, $q_i(a)$. After performing the appropriate orientation we define:

$$a \geq b \text{ if and only if } q_i(a) \geq q_i(b) \text{ for all indicators, } i = 1,\ldots,m.$$

By this definition, objects can be not only positioned relatively to each other, but due to the underlying indicator values we know,