Petroleum & Coal
ISSN 1337-7027

Available online at www.vurup.sk/petroleum-coal
Petroleum & Coal 54 (3) 220-224, 2012

THE PERSISTENCE, BIOACCUMULATION AND TOXIC ESTIMATION OF SOME SULFUR COMPOUNDS IN THE ENVIRONMENT

Yana Koleva[1*], Yordanka Tasheva[2]

[1]Department of Organic Chemistry, University "Prof. Assen Zlatarov", 1 Prof. Yakimov str., 8010 Bourgas, Bulgaria, [2]Department of Industrial Technology and Management, University "Prof. Assen Zlatarov", 1 Prof. Yakimov str., 8010 Bourgas,Bulgaria
E-mail: yanuriana@abv.bg, jtasheva_2006@abv.bg

Received February 23, 2012, Accepted September 10, 2012

Abstract

Persistent, Bioaccumulative and Toxic (PBT) substances are carbon-based chemicals that resist degradation in the environment and accumulate in the tissues of living organisms, where they can produce undesirable effects on human health or the environment at certain exposure levels. The limited empirical data, the high test costs together with the regulatory constraints and the international push for reduced animal testing motivates a greater reliance on QSAR models in PBT assessment. The aim of this work was to study the persistence, bioaccumulation and toxicity of S-containing compounds in the environment. Their persistence, bioaccumulation and toxicity were investigated on QSAR models in PBT assessment. The results show that the S-containing compounds are not persistent (one exception is phenanthro [4,5-bcd] thiophene) and bioaccumulative, but they are toxic to aquatic and terrestrial species (exceptions are some of S-containing compounds).

Key words: sulphur compounds; persistence; bioaccumulation and toxicity.

1. Introduction

Energy supply and demand play an increasingly vital role in our national security and for the economic output. The fossil fuels (coal, oil and gas) have been formed from organic remains of prehistoric plants and animals. They are a non-renewable source of energy. Over 85 % of our energy demand is met by the combustion of fossil fuels [1], which may be associated with environmental pollution.

The origin of Organic Sulfur Compounds (OSC) can be explained by three major pathways, namely biosynthesis, formation during early diagenesis and by reaction of elemental sulfur and hydrocarbons, but none of them has been proved to conclusively occur in fossil material [1].

Sulfur exists in both aliphatic and aromatic forms in the crude oil. A few typical parent structures of sulphur compounds can be considered (thiol, sulphide, disulfide, thiane, thiophene, benzothiophene, dibenzothiophene, phenanthro[4,5-bcd] thiophene) [1].

The exhaust gases from motor vehicles contribute to air pollution through release of SOx [2-4]. Sulfur is also a well-known poison for catalytic converters. Therefore there is a need to reduce sulfur level in fuels. More and more severe environmental legislations are introduced [2, 5, 6]. Industrial research is aimed at finding the best methods and catalysts for ultra-deep desulfurization. The challenge is to remove the sulfur impurities with a minimal olefin saturation since olefins provide a fairly good octane number [6, 7].

Persistent Organic Pollutants (POPs) and Persistent, Bioaccumulative and Toxic (PBT) substances are carbon-based chemicals that resist degradation in the environment and accumulate in the tissues of living organisms, where they can produce undesirable effects on human health or the environment at certain exposure levels [8]. The aim of this work was to study the persistence, bioaccumulation and toxicity of S-containing compounds in the environment.

2. Experimental

Compound Data. S-containing compounds with CAS number and Name of compound are presented in Table 1.

Table 1. PBT Profiler estimate of S-containing compounds

CAS number	Name of compound	Persistence		Bio accumulation	Toxicity
		Media (water, soil, sediment, air) Half-life (days)	Percent in each Medium	BCF	Fish ChV (mg/l)
108-98-5	Benzenethiol	15; 30; 140; 1.4	24%, 70%, 0%, 5%	21	0.003
74-93-1	Methyl mercaptan	15; 30; 140; 0.46	75%, 11%, 0%, 13%	3.2	0.77
75-18-3	Dimethyl sulphide	15; 30; 140; 4.2	51%, 14%, 0%, 35%	3.2	41
139-66-2	1,1`-Thiobis benzene	15; 30; 140; 0.62	21%, 71%, 7%, 1%	400	0.17
1613-51-0	Thiane	15; 30; 140; 0.67	34%, 60%, 0%, 6%	15	4.7
110-02-1	Thiophene	15; 30; 140; 1.7	53%, 24%, 0%, 23%	7.3	1.3
95-15-8	Thianaphthene	15; 30; 140; 0.54	20%, 78%, 0%, 2%	53	1.6
132-65-0	Dibenzo thiophene	15; 30; 140; 2	21%, 70%, 6%, 3%	360	0.21
30796-92-0	Phenanthro [4,5-bcd] thiophene	38; 75; 340; 0.3	12%, 63%, 25%, 0%	860	0.06

Criteria used by the PBT Profiler. The PBT Profiler is a screening-level tool that provides estimates of the persistence, bioaccumulation, and chronic fish toxicity potential of chemical compounds. It was designed used when data are not available. In order to help interested parties make informed decision on a chemical's PBT characteristics, the PBT profiler auto-matically identifies chemicals that may persist in the environment and bioaccumulate in the food chain. These chemicals are identified using thresholds published by the EPA [9].

Persistence criteria. The PBT Profiler combines the persistence criteria for water, soil, and sediment and highlights chemicals with an estimated half-life ≥ 2 months and < 6 months as persistent and those with an estimated half-life ≥ 6 months as very persistent. The half-life in air is not used in the PBT Profiler's Persistence summary (chemicals with an estimated half-life > 2 days are considered as persistent). The PBT Profiler uses 30 days in a month for its comparisons.

Bioaccumulation criteria. The PBT Profiler combines the bioaccumulation criteria and highlights chemicals with a BCF ≥ 1000 and < 5000 as bioaccumulative and those with a BCF ≥ 5000 as very bioaccumulative.

Toxicity criteria. To highlight a chemical that may be chronically toxic to fish, the PBT profiler uses the following criteria: Fish ChV (Chronic Value) > 10 mg/l (low concern), Fish ChV = 0.1 - 10 mg/l (moderate concern) and Fish ChV < 0.1 mg/l (high concern).

Acute Aquatic Toxicity Data. Toxicity values of some sulfur compounds to *Tetrahymena pyriformis* were obtained from the literature [10] and reported in Table 2. Population growth impairment was assessed after 40h with the common ciliate *T. pyriformis*.

Acute Terrestrial Toxicity Data. The experimental data for rat (oral LD_{50} values) were collected from the literature [11].

EcoSAR software. EcoSAR is a user-friendly computer programme developed and routinely applied by the US EPA for predicting aquatic toxicity to fish, daphnids and algae [12]. This software was used for grouping of the chemicals.

Log P. Data for the logarithm of the 1-octanol-water partition coefficient (log P) were obtained from the KOWWIN software [13]. Where possible measured log P values were verified and used in preference to calculated values.

Baseline models. In this study several models were used for non-polar compounds to aquatic and terrestrial species to determine the acute toxicity of organic sulfur compounds (Tables 2).

Table 2. Experimental and predicted values of S-containing compounds

CAS number	Name of compound	EcoSAR classification	logP	Exp. T. pyriformis log(1/IGC_{50}), mmol/l	Pred. T. pyriformis log(1/IGC_{50}), mmol/l /TR	Exp. oral Rat LD_{50} mmol/kg	Pred. oral Rat LD_{50} mmol/kg / TR
108-98-5	Benzenethiol	Phenol	2.52[a]	1.66	-0.04/ 1.70	0.42	40.89/ 97.52
74-93-1	Methyl mercaptan	Thiol (mercaptan)	0.78[b]				
75-18-3	Dimethyl sulphide	Neutral organic	0.92[b]			53.11	32.22/ 0.61
139-66-2	1,1`-Thiobis benzene	Neutral organic	4.45[a]			2.92	20.25/ 6.94
1613-51-0	Thiane	Neutral organic	2.28[b]				
110-02-1	Thiophene	Thiophene	1.81[a]			16.64	46.87/ 2.82
95-15-8	Thianaphthene	Neutral organic	3.12[a]	0.26	0.42/ -0.16		
132-65-0	Dibenzo thiophene	Neutral organic	4.38[a]				
30796-92-0	Phenanthro [4,5-bcd] thiophene	Neutral organic	4.95[a]				

[a]*Experimental value of logP;* [b]*Calculated value of logP.*

Baseline model (saturated alcohols and ketones) of *Tetrahymena pyriformis* [14]:

$$\log(1/IGC_{50}) = 0.78*\log P - 2.01 \quad (1)$$

n = 87 R^2 = 0.96 s = 0.20 F = 2131

Baseline model (saturated alcohols and ketones) of Rat (oral LD_{50}) [15]:

$$\log(1/LD_{50}) = 0.805*\log P - 0.971*\log(0.0807*10^{\log P}+1) + 0.984 \quad (2)$$

n = 54 R^2 = 0.824 s = 0.208 F = 35.3

Excess toxicity. The property - excess toxicity - was used to define the toxicity of chemicals (reactive or nonrective) [6]. The extent of excess toxicity was determined as the toxic ratio (TR), which was calculated by the following equations 3-4 [15, 16]:

$$TR = \log(1/C)exp - \log(1/C)calc \quad (3)$$

$$TR = (\text{predicted baseline toxicity})/(\text{observed toxicity}) \quad (4)$$

Mode of action. For environmental toxicants four broad classes of mode of action have been identified – from class I to class IV [17, 18].

3. Results and Discussion

The results of estimation of S-containing compounds for persistence, bioaccumulation and toxicity are presented in Table 1.

PBT chemicals are those that persist in the environment. They generally occur in low concentrations, and can be transported throughout the biosphere. They can be bioconcentrated in aquatic organisms and transported up food chains to humans, birds, and wild mammals. Exposure to PBT chemicals is generally through the diet and is the result of chronic exposure. Chronic exposures lead to chronic toxicity, and not acute toxicity. That is, chronically toxic chemicals affect processes other than survival. Therefore, it would be possible for organisms to survive the acute effects of such chemicals (i.e., not die) yet still undergo adverse effects from long-term exposure (e.g., chronic exposure may adversely effect growth or reproduction). In order to best estimate the effects of PBT chemicals on the environment, the fish chronic toxicity is used in the PBT Profiler. The EcoSAR program also estimates a variety other aquatic toxicity endpoints depending on the structure of the chemical (Table 2).

These include the acute toxicity of a chemical to fish (both fresh and saltwater), water fleas (daphnids), and green algae. For some chemical classes, endpoints for other organisms may be estimated (e.g., earthworms).

The PBT profiler uses a well-defined set of procedures to predict the persistence, bioaccumulation, and toxicity of chemical compounds when experimental data are not available. The persistence, bioaccumulation, and fish chronic toxicity values estimated by the PBT profiler are automatically compared to criteria published by the EPA.

Analysis of data in Table 1 reveals that as all S-containing compounds are not persistence (one exception is phenanthro [4,5-bcd] thiophene) and bioacculumative, but they are toxic (Fish ChV) for the more compounds (one exception is dimethyl sulfide). The S-containing compounds can be classified as low, moderate and high toxic (Fish ChV, mg/l). The sulphur compound with low toxic (>10 mg/l) is dimethyl sulphide. The compounds with moderate toxic (0.1-10 mg/l) are methyl mercaptan, 1,1`-thiobis benzene, thiane, thiophene, thianaphthene and dibenzo thiophene. Finally, chemicals with high toxic (< 0.1 mg/l) are benzenethiol and phenanthro [4,5-bcd] thiophene.

There are several modes of action for acute toxicity. The S-containing compounds were classified as neutral organics, thiols (mercaptans), thiophenes, phenols from the EcoSAR software. Data is given Table 2.

For the organic sulfur compounds mode(s) of toxic action, where toxicity is observed to be (or not to be) in excess of narcosis, the possible mechanism is (ir)reversible, i.e. the toxicity is (not) observed to be related to hydrophobicity and is (not) in excess of baseline toxicity for the compounds (Fig. 1).

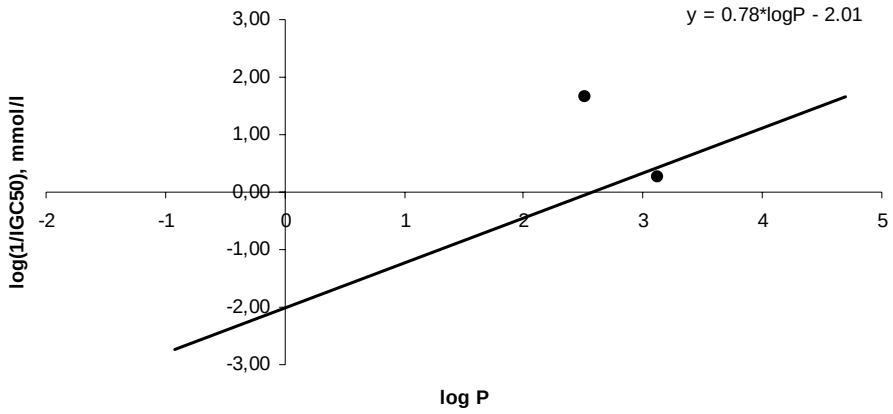

Fig. 1. Plot of toxicity to *Tetrahymena pyriformis* vs log P for S-containing compounds showing baseline toxicity.

Therefore, among sulfur compounds are recognized narcotics and reactive chemicals. A number of reliable baseline equations are available for different organisms (aquatic (*Tetrahymena pyriformis*) and terrestrial (Rat)) and endpoints (IGC_{50}, LD_{50}). Baseline models (eqs 1-2) for different species (aquatic and terrestrial) were applied to S-containing compounds (Table 2). On the basis of calculated and experimental values for acute toxicity, the toxicity ratio (TR) as the ratio of the calculated baseline toxicity over the experimentally determined value was calculated. A TR-value less than one could indicate rapid hydrolysis and/or biotransformation of the parent compound by the organism to non-toxic metabolites [19].

4. Conclusion

A series of aliphatic and aromatic sulfur-containing compounds were evaluated in the *T. pyriformis* population growth impairment assay (IGC_{50}) and oral Rat (LD_{50}) for acute toxicity. The endpoints are a result of different routes of exposure in various species. The effect of a chemical is dependent on the species, route of exposure, and dose. The structure of sulfur compounds is varied, suggesting a different reactivity (non-covalent and covalent interactions).

The levels of certain PBTs in the environment have been reduced by eliminating or reducing releases and adopting alternatives, but recovery times are slow because these chemicals do not break down to harmless byproducts easily or quickly. The analyses of results of this work have been shown that the S-containing compounds are not persistent (one exception is phenanthro [4,5-bcd] thiophene) and bioaccumulative, but they are toxic to

fish (exceptions are aliphatic S-containing compounds). Therefore, the persistence and toxicity for the S-containing compounds vary as a function of the structure of the compound (aliphatic and aromatic).

References

[1] Ulman M., "Development of Separation Methods and ChemicalTransformations for Structural Elucidation of Large Organic Compounds in Petroleum Fractions", Münster, Germany, (2008).

[2] Babich I.V. and Moulijn J. A., Science and technology of novel processes for deep desulfurization of oil refinery streams: a review, *Fuel*, 82, 607 (2003).

[3] Shiraishi Y., Hirai T. and Komasawa I., A novel desulfurizationprocess for fuel oils based on the formation and subsequent precipitation of S-alkylsulfonium salts. 4. Desulfurization and simultaneous denitrogenation of vacuum gas oil, *Industrial & Engineering Chemistry Research*, 40, 3398 (2001).

[4] Hirai T., Ogawa K. and Komasawa I., Desulfurization Process for Dibenzothiophenes from Light Oil by Photochemical-Reaction and Liquid-Liquid-Extraction, *Industrial & Engineering Chemistry Research*, 35, 586 (1996).

[5] Bej S.K., Maity S.K. and Turaga U.T., Search for an efficient4,6-DMDBT hydro-desulfurization catalyst: a review of recent studies, *Energy & Fuels*, 18, 1227 (2004).

[6] Brunet S., Mey D., Pérot G., Bouchy C. and Diehl F., On the hydrodesulfurization of FCC gasoline: a review, *AppliedCatalysis A: General*, 278, 143 (2005).

[7] Shafi R. and Hutchings G.J., Hydrodesulfurization of hindereddibenzothiophenes: an overview, *Catalysis Today*, 59, 423 (2000).

[8] Pavan M. and Worth A., Review of QSAR Models for ReadyBiodegradation, European Commission Directorate – General Joint Research Centre Institute for Health and Consumer Protection, (2006).

[9] Criteria used by the PBT Profiler: http://www.pbtprofiler.net/criteria.asp

[10] Schultz T.W., Sinks G.D., Miller L.A., Population Growth Impairment of Sulfur-Containing Compounds to *Tetrahymena pyriformis*, *Environmental Toxicology*, 16, 543 (2001).

[11] http://chem.sis.nlm.nih.gov/chemidplus/.

[12] http://www.epa.gov/oppt/newchems/tools/21ecosar.htm.

[13] http://www.epa.gov/oppt/exposure/pubs/episuite.htm.

[14] Ellison C.M., Cronin M.T.D., Madden J.C., Schultz T.W., Definition of the structural domain of the baseline non-polar narcosis model for *Tetrahymena pyriformis*, *SAR and QSAR in Environmental Research*, 19, 751 (2008).

15] Lipnick R.L., Outliers-Their origin and use in the classification of molecular mechanisms of toxicity**,** *Science of the Total Environment*, 109, 131 (1991).

[16] Nendza M. and Müller M., Discriminating toxicant classes by mode of action: 3. Substructure indicators, *SAR and QSAR in Environmental Research*, 18, 155 (2007).

[17] Russom C.L., Bradbury S.P., Broderius S.J., Hammermeister D.E. and Drummond R.A., Predicting modes of toxic action from chemical structure: Acute toxicity in fathead minnow *(Pimephales promelas)*, *Environ. Toxicol. Chem.*, 16, 948 (1997).

[18] Verhaar H.J.M., van Leeuwen C.J., Hermens J.L.M., Classifying environmental pollutants. 1. Structure activity relationships for prediction of aquatic toxicity, *Chemosphere*, 25, 471 (1992).

[19] Aptula A.O. and Roberts D.W., Mechanistic applicability domains for non animal-based prediction of toxicological end points: General principles and application to reactive toxicity, *Chem. Res. Tox.*, 19, 1097 (2006).