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Pesticides, Inhalation Toxicity and Risk for Operators

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Abstract

Background: Some pesticides, chemical compounds used in agriculture, can be so toxic to pose a risk to operators. In Europe phytosanitary management is entrusted to regulations, such as No. 1107/2009 among others, aimed to achieve high-standard-protection for humans, animals and environment. Furthermore, the European Community, through the Prior Informed Consent (PIC) Regulation no. 649/2012, carries out the Rotterdam Convention that promotes shared responsibility in relation to marketing of banned or severely restricted pesticides in its territory. It is essential though to develop expertise to spot and evaluate any dangerous substance that could affect both environment and public health.

Methods: This study analyzes the inhalation toxicity for 307 pesticides included in the PIC Regulation by means of in silico techniques, toxicological databases (Toxnet, Cameo, Toxin and Toxin Target Database, PubChem, Environmental Protection Agency and ECHA) and computational chemistry tools (QSAR toolbox with Trend Analysis methods; products' SDS). The quantitative damage estimation is obtained applying the probit function (Green Book of TNO Organization) to in vivo toxicity reported in the literature.

Results: From all 307 listed pesticides, we extracted 15, reported in the PIC Regulation, that hold an LC50 toxicity comparable to traditional chemical warfare agents such as Sarin, Tabun and Soman. Therefore, they are dangerous for both operators and exposed population. Our results are compliant with the European Community ban applied for 11 of such substances and circulation limit for 4 allowing their export, except for respecting an express refusal by the importing country.

Conclusions: In silico techniques are fundamental for the management of all information connected to the risk estimate and allow to promptly highlight any dangerous characteristics. In this case, we confirm the need to raise awareness among operators regarding the pesticide inhalation toxicity and to disseminate the ethical green message of Bamako Convention: anything restricted or prohibited in importing countries is hazardous waste.

Keywords: Dual Use; Inhalation Toxicity; Pesticides; TIM (Toxic Industrial Material); WMD (Weapon of Mass Destruction)

Introduction

The use of chemicals as pesticides in agriculture has been strongly regulated in Europe, especially following major chemical disasters such as the Bophal disaster **[1]** which precisely involved the production of a pesticide. The adoption of the European Regulation Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) **[2]**, is aimed at discouraging the use of chemicals considered harmful to the environment and, at the same time, at adopting new chemicals less harmful to humans and the environment. In addition, the European Community has, with PIC Regulation no. 649/2012 **[3]** boosted the control of exports and imports of chemicals deemed hazardous, with the aim at increasing a shared responsibility and collaboration in international trade with the aim of safeguarding human health (for operators and the population possibly exposed) and protecting the environment, especially in developing countries. In this sense, the Bamako Convention **[4]** aims to prevent imports in African countries of all types of hazardous chemical and radioactive waste.

Aim

The purpose of this article is to investigate the risk of inhalation toxicity of pesticides listed in the PIC Regulation, by providing a match for the inhalation toxicity of certain chemicals in the chemical weapons category (Sarin, Soman, Tabun and Vx). In addition, export profiles for the last 16 years are analyzed to track any exports to Bamako Convention countries.

Materials and Methods

From the above-mentioned databases the inhalation toxicity LC50 values of 307 substances listed in the PIC Regulation "pesticides" are extracted and filled with all available information from the Chemical Safety Data Sheets. QSAR toolbox computational chemistry software is used in order to estimate all not available parameters and to perform Trend Analysis. Conversion factors (0.50 for the mouse and 0.25 for the rat) are applied to inhalation toxicity comparison values expressed in ppm. All data are ranked by "a" Probitparameter described in the vulnerability analysis models **[5]** that expresses the sensitivity of the human body to the inhaled substance (the greater the number, the greater the toxicity hypothesized towards the human body):

$$a=5-\ln\{[LC50_{(human)}]^n\}xt.$$

Where LC50 is the tabulated toxicity reported in human or guinea pigs, "n" is given by default as 2 in this formula, and "t" is the exposure time. "a" parameter, therefore, allows the comparison of all studied compounds with different LC50 concentration and different exposure time.

Results

LC50 data was retrieved for 130 substances directly from the Databases, while for 128 substances from QSAR analysis (Trend Analysis). No LC50 data could be assessed for 49 substances neither from the databases nor by computational chemistry (regression line not computable).

From the whole set of compounds, 15 substances show inhalation toxicity are selected and listed in **(Table 1)** taking into account the parameter "a" from the least toxic nervine Chemical Warfare Agents (CWA)agent , Tabun to the most toxic Vx (Tabun, Sarin, Soman and Vxare highlighted).

REGULATION	SUBSTANCE	CAS	LC50	PPM	TIME/ANIMAL	LC50 Hu. Ppm	PARAMETER "a"	STATE
CWA	TABUN	77-81-6	15mg/m^3[1]	2,26	30' mouse	1,13	1,354	L
CWA	SARIN	107-44-8	9 mg/m^3[2]	1,57	60' mouse	0,785	1,39	L
PIC PESTICIDES	PROPANIL	709-98-8	1.25 mg/Lair[1]	1,25	4hr rat	0,313	1,846	S
PIC PESTICIDES	DIELDRIN	60-57-1	13 mg/m^3 [2]	0,83	4hr rat	0,208	2,665	S
PIC PESTICIDES	OMETHOATE	1113-02-6	.5 mg/L[1]	1,5	1hr rat	0,375	2,867	L
PIC PESTICIDES	NICOTINE	54-11-5	2.3 mg/L[3]	2,3	20' rat	0,575	3,111	L
PIC PESTICIDES	LINDANE	58-89-9	1.56 mg/L [1]	1,56	30' rat	0,39	3,482	S
PIC PESTICIDES	TRIAZOPHOS	24017-47-8	0.61 mg/L [1]	0,61	1hr rat	0,153	4,667	L
PIC PESTICIDES	TOLYLFLUANID	731-27-1	0.26 mg/L [1]	0,26	4hr rat	0,065	4,986	S
PIC PESTICIDES	TOXAPHENE	8001-35-2	0.26 mg/L [1]	0,26	4hr rat	0,065	4,986	S
PIC PESTICIDES	AZOCYCLOTIN	41083-11-8	0.2 mg /l [1]	0,2	4hr rat	0,05	5,511	S
PIC PESTICIDES	CYFLUTHRIN	68359-37-5	0.1 mg/L [1]	0,1	4hr rat	0,025	6,897	L
CWA	SOMAN	96-64-0	1mg/m [2]	0,13	30' mouse	0,065	7,066	L
PIC PESTICIDES	MONOCROTOPHOS	6923-22-4	0.08 mg/L [1]	0,08	4 hr rat	0,02	7,343	S
PIC PESTICIDES	METHOMYL	16752-77-5	0,06 mg/l [1]	0,06	4 hr rat	0,015	7,919	S
PIC PESTICIDES	CHLORFENVINPHOS	470-90-6	0.05 mg/L [1]	0,05	4hr rat	0,013	8,283	L
PIC PESTICIDES	FENTIN ACETATE	900-95-8	0.044 mg/l [1]	0,044	air/4hr rat	0,011	8,539	S
PIC PESTICIDES	CADUSAFOS	95465-99-9	0.026 mg/l [1]	0,026	4hr rat	0,007	9,591	L
CWA	VX	50782-69-9	0,16 mg/m^3 [2]	0,015	4hr rat	0,004	10,74	L

Table 1: Pic substances listed in order of toxicity by comparison with CWA (in green), in the table the references 1, 2 and 3 refer to the reference databases, respectively 1 for ToxNet, 2 for Pubchem and 3 for Db Echa, S and L are the physical state L for liquid, S for Solid .

Parameter "a" of probity function permits to sort substances with different units of measurement, different concentrations, duration of exposure and data sources according to their toxicity.

The geographical dispersion profile of the exported substances compliant with PIC Regulation of the last sixteen years is visualized in **(Figure 1).** Almost no PIC chemicals are imported into European countries that are a fundamental goal of the principles of the regulation.

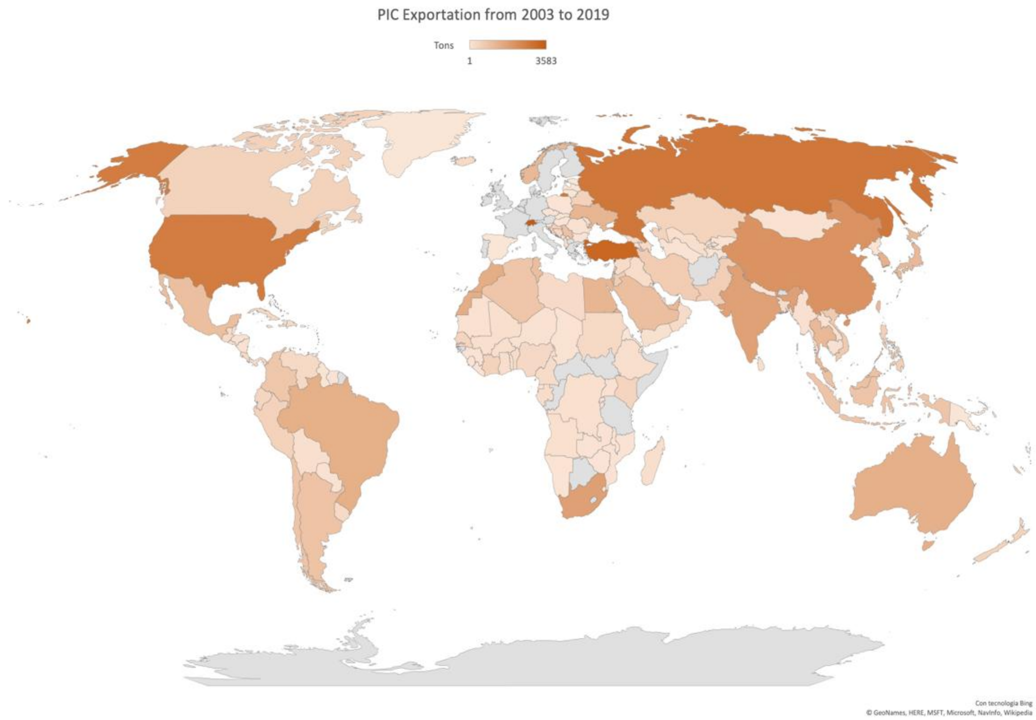

Figure 1: export levels of PIC substances in tons from 2003 to 2019 worldwide (Db ECHA).

Conclusions

The study shows that the PIC pesticides regulation includes fifteen compounds holding inhalation toxicity equal or exceeding the toxicity of some of the most dangerous nervine CWA. This is an evident concern and implies a possible exposition of both professionals and population. In fact, Europe has banned these substances but despite the signing of the Bamako Convention they continue to be exported to African countries. This highlights the need for a shared approach to the problem through the adoption of regulations that cannot be applied by a single continent. From this point of view, words such as prevention in the workplace for operators or for the reduction of the consequences of accidents for industries is to be considered mandatory. Just as it is important to maintain a traceability of the flows of these chemicals and at the same time trying to reduce the trade of these dangerous substances (as in the intentions of the Bamako Convention), for the welfare of people and the planet.

Acknowledgments:

All of the authors listed have equally contributed for this work.

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