



Pioneer Protocol for Monitoring Pesticides in Water, State of São Paulo, Brazil

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Abstract

Pesticides protect crops against pests, but are harmful to human health when ingested through contaminated food and water. While developed countries seek to ban the use of pesticides, developing countries use many of these chemicals, already banned in developed countries. Brazil is the world's largest producer of crops for humans and animals and the state of São Paulo is one of the largest consumers of these chemicals in the country. This research sought to create a methodology for the investigation of pesticides in water, avoiding unnecessary laboratory expenses, aiming at protecting human health.

Keywords: Pesticides; Clean Water; Chemicals; Methodology

Abbreviations: EU: European Union; GUS: Groundwater Ubiquity Score.

Introduction

Pesticides destroy pests and weeds and are a widely used tool in agricultural practice in developed and developing countries, reducing losses in rural production. However, excessive use of these pesticides contaminates food leading to possible adverse effects of these chemicals on human health [1].

Many of these chemicals that have been banned by industrialized countries since the end of the 20th century are still used in developing countries [2]. There is epidemiological evidence of a relationship between pesticides and cancer, especially in workers who apply them to crops on a daily basis [3].

The European Union (EU) plans to reduce the global use of chemical pesticides by 50% by 2030 [4]. Brazil is a world

leader in the production of food of plant origin, both for human and animal consumption. Agriculture and livestock are fundamental economic activities that maintain the positive balance of its economy. As a result, the registration and use of pesticides in Brazil has grown at an accelerated pace [5]. Antagonistic to the EU, Brazil has approved more pesticides and is the world leader in the use of these chemicals.

The state of São Paulo, Brazil, is the largest consumer of pesticides in the country. Water can be contaminated by these chemicals, exposing populations to risks.

Developing countries do not have a methodological protocol to define which pesticides are potential contaminants in their supply sources, causing unnecessary costs in laboratory analyzes and failures in monitoring. The objective of this research was the application of a pioneering methodology for defines these chemicals.

Methods

The pioneering protocol for monitoring pesticides in water was developed and applied in the state of São Paulo, located in the southeastern region of Brazil, which has an

area of 248.209 km² (3.0% of the Brazilian territory) and a population of 44 million inhabitants. It is the most populous and economically richest state [6]. The location of the State of São Paulo is shown in Figure 1.



Figure1: State of São Paulo, Brazil

Data Survey

Data available in official Brazilian databases were verified. Based on these data, a methodological protocol was defined and applied in the state of São Paulo, for monitoring pesticides in drinking water, consisting of the steps:

- 1) Calculation of the semi-annual average of the volumes of the most sold pesticides in the last 5 years;
- 2) Mapping of river basins, main agricultural crops by basin and agricultural defensives most used in these plantations;
- 3) Identification of priority pesticides for water contamination;
- 4) Application of the main pesticide measurement indices in each of them: Groundwater (GUS), Leaching (LEACH) and Priority (PI);
- 5) Definition of priority pesticides for water monitoring

To define priority pesticides, the list of pesticides approved for use in the country was used, with 491 active ingredients. Based on data on agricultural production in the state of São Paulo over a period of 5 years, available on the official website of the state government, the main agricultural crops were listed and the river basins were mapped.

The pesticides approved for commercialization in Brazil and the pesticides used in the main crops in the areas planted in the São Paulo state and therefore with potential for contamination of water basins were investigated.

Taking into account that the potential to find pesticides in bodies of water is influenced by different variables that include the volume of pesticides used, the application form and its behavior in the environment, it was used for the definition of priority pesticides the combination of three indexes: Groundwater Ubiquity Score – GUS, Leaching Index – LEACH and the Priority Index – IP. After the application of these indexes in each pesticide, there were elected the priority pesticides for water monitoring.

Results

Calculation of the semi-annual average of the volumes of the most sold pesticides in the last 5 years: Of the 491 active principles that are authorized for use in Brazil, 371 did not have all the information necessary for the calculation of indexes. There were 120 pesticides with highest sales volume and simultaneously with potential for water contamination were listed.

Mapping of water basins, main agricultural crops per basin and pesticides most used in these plantations and identification of priority pesticides for water contamination. There are 22 water basins. The main crops in terms of planted area in São Paulo state were brachiaria (41.0%), sugar cane (31.0%), and eucalyptus (5.0%), orange (4.0%) and others crops (19.0%). There are 10 main agricultural crops, with sugar cane representing more than 60% of the planted area in the state.

Application of the main pesticide measurement indexes in each one: Groundwater (GUS), Leaching (LEACH) and Priority (PI) and definition of priority pesticides for water monitoring. The results show that the indexes GUS, LEACH

and IP prioritization produced a distinct from the pesticides studied, which was expected since they are based on information and different parameters. These results are shown in Table 1.

Active ingredient	Ranking	GUS	Ranking	LEACH	Ranking	IP
Diuron	15 th	3,35E+00	22 nd	4,54E+08	1 st	10,8
Carbofuran	12 th	3,49E+00	31 st	5,81E+07	2 nd	10,8
Glyphosate	48 th	3,17E-01	12 th	5,76E+11	3 th	10
Atrazine	7 th	4,40E+00	25 th	1,88E+08	4 th	9
Imazetapir	1 st	7,67E+00	4 th	2,91E+15	5 th	8,4
Imidacloprido	5 th	4,74E+00	6 th	7,74E+14	6 th	8,4
Sulfentrazona	6 th	4,47E+00	8 th	1,57E+12	7 th	8,4
Tebutiurum	3 rd	6,31E+00	16 th	1,69E+10	8 th	8
Clorotalonil	38 th	1,15E+00	52 nd	2,06E+04	9 th	7,9
Acephate	29 th	1,68E+00	13 th	4,81E+11	10 th	7,2
Methamidophos	52 nd	0,00E+00	19 th	3,54E+09	11 th	7,2
Imazapique	2 nd	6,44E+00	2 nd	4,26E+15	12 th	7,2
Imazapir	8 th	3,95E+00	5 th	9,20E+14	13 th	7,2
Simazine	17 th	3,00E+00	29 th	9,08E+07	14 th	7,2
Clomazona	18 th	2,93E+00	41 st	2,07E+06	15 th	7,2
Cyromazine	25 th	2,02E+00	14 th	3,22E+11	16 th	6,6
Azoxystrobin	21 th	2,53E+00	10 th	1,40E+12	17 th	6,2
Glufosinate-ammonium salt	33 rd	1,44E+00	3 rd	3,83E+15	18 th	6
Methomyl	9 th	3,93E+00	17 th	1,15E+10	19 th	6
Diquate dibromide	59 th	-5,48E+00	18 th	3,82E+09	20 th	6
Prometryn	10 th	3,80E+00	34 th	1,63E+07	21 th	6
Linurom	26 th	1,97E+00	38 th	3,38E+06	22 th	6
Metolachlor	23 th	2,45E+00	40 th	2,31E+06	23 th	6
Aldicarb	44 th	4,88E-01	45 th	1,45E+06	24 th	6
Chlorpyrifos	51 th	4,53E-03	58 th	1,69E+02	25 th	5,9
Nicossulfurom	13 th	3,44E+00	1 st	7,03E+19	26 th	5,6
Tebuconazole	20 th	2,78E+00	20 th	1,68E+09	27 th	5,5
Dimetomorfe	30 th	1,62E+00	27 th	1,40E+08	28 th	5
Quincloraque	4 th	5,65E+00	37 th	9,38E+06	29 th	5
Alachlor	22 th	2,45E+00	42 nd	1,67E+06	30 th	5
Endossulfam	55 th	-1,34E-01	55 th	4,09E+03	31 st	4,9
Halossulfurom-methyl	16 th	3,26E+00	7 th	2,24E+12	32 nd	4,8
Setoxidim	27 th	1,97E+00	33 rd	2,33E+07	33 rd	4,8
Propargito	58 th	-9,82E-01	53 rd	1,08E+04	34 th	4,6
Mancozeb	50 th	6,68E-02	35 th	1,57E+07	35 th	4,5
Malathion	41 st	7,33E-01	49 th	4,36E+05	36 th	4,5

Carbaryl	37 th	1,16E + 00	44 th	1,49E + 06	37 th	4,4
Dimethoate	40 th	8,91E-01	21 th	5,51E + 08	38 th	4,3
Thiophanate-methyl	54 th	0,00E+00	43 th	1,66E+06	39 th	4,3
Phosmet	47 th	3,59E-01	50 th	9,27E + 04	40 th	4,2
Fenarimol	14 th	3,41E + 00	30 th	9,04E + 07	41 st	4,1
Acetamiprido	32 nd	1,46E + 00	39 th	2,81E + 06	42 nd	4
Fipronil	19 th	2,89E + 00	23 th	3,34E + 08	43 th	3,8
Cresoxim-Methyl	45 th	4,09E-01	47 th	5,32E + 05	44 th	3,4
Metidationa	42 nd	7.00E- 01	48 th	4,88E + 05	45 th	3,4
Propanil	46 th	3,87E-01	46 th	6,46E + 05	46 th	3,2
Fludioxonil	31 th	1,59E+00	32 nd	3,89E + 07	47 th	3,1
Propiconazole	24 th	2.20E + 00	36 th	1,21E+07	48 th	3,1
Permethrin	57 th	-8,78E-01	57 th	2,10E + 02	49 th	2,8
Formetanato hydrochloride	34 th	1,29E + 00	9 th	1,48E+12	50 th	2,5
Metiram	53 rd	0,00E+00	24 th	2,12E + 08	51 th	2,1
Acibenzolar-S-Methyl	43 th	5,77E-01	54 th	8,48E + 03	52 nd	2,1
Cletodim	39 th	9,23E-01	28 th	1,16E + 08	53 rd	2
Dissulfotom	36 th	1.22E + 00	56 th	2,88E + 03	54 th	1,8
Triflumizol	35 th	1,23E + 00	26 th	1,66E+08	55 th	1,6
Amitraz	56 th	-7,14E-01	59 th	1,05E + 02	56 th	1,4
Profenofós	49 th	2,10E-01	51 th	3,10E + 04	57 th	0,9

Table1: Values of the indexes calculated and their ratings for the 57 active principles.

Through the application of the indexes in each pesticide, PI index was the most specific and sensitive, as it was the only one that admitted the sales volume for calculation. For water monitoring were defined the main pesticides in São Paulo state.

Discussion

The need to identify priority substances in order to monitor pesticide residues in the environment has been shown to be a major challenge for managing institutions due to the large number of active principles in use, which have specific properties about the behavior in the environment and the effects on human health [7].

Such challenge has been expanded in developing countries, not only as a result of the large number of licensed active principles, but also on grounds of disability public policies of restriction and control of economic and technological resources necessary. This challenge has been extended by these countries as being targets of banned products in developed countries [2,8].

The Priority Index, which takes into account the volume of pesticides used and information about the methods of implementation may be more suitable for defining priorities of monitoring in surface water bodies by surveillance services of water for human consumption.

The sales volume is an indicator of the amount of pesticides used is a fundamental parameter and in this way, the IP is a more representative index in this case, in particular in developing countries such as Brazil, which do not have adequate information about the volume of pesticides that is effectively used in every culture and also, there are no effective programs of control of the use of pesticides.

Conclusions

In contexts where the volume of sales of pesticides is the main data, the PI index is the best measure. This methodological protocol is relevant especially for developing countries in the definition of pesticide monitoring in springs, avoiding unnecessary laboratory expenses, monitoring risks and protecting health.

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