HAZARDOUS WASTE GENERATION IN TURKISH PESTICIDE INDUSTRY

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ABSTRACT

The aim of this study is to assess the contribution of pesticide industry to the total amount of hazardous waste generation in Turkey. While conducting the study the hazardous waste list defined by Commission Decision on Hazardous Wastes, was used as a base format and the average unit hazardous waste generation expressed as kg hazardous waste per ton of production were explored accordingly. In order to realize this target pesticides with highest production levels and the most commonly used production technologies were defined. A detailed investigation was performed to enlighten the applied technologies and processes, raw material and auxiliary inputs, waste generating parts of the production processes, quantity and quality of wastes etc. on a representative manufacturing plant. Data collected by The Ministry of Environment and Urban Planning on the amount of hazardous waste generation arising from industrial installations and the findings of the field study were evaluated together.

Pesticide active ingredients namely, methamidophos, humic acid, copper sulphate production facilities and powder, granule and liquid pesticide formulation plants were covered. For pesticide synthesis sector values ranging from 7 to 56 kg of hazardous waste generation per ton of active ingredient produced were obtained. On the other hand 45 to 80 kg of hazardous waste generation per ton production were found for pesticide formulation. The evaluation of the unit hazardous waste generation factors with the capacities of Turkish pesticide plants showed that 27200 - 42800 ton hazardous waste was produced annually from this sector. This amount yielded 2 to 3.2 % of the total hazardous waste generation in Turkey.

Keywords: hazardous waste, industry, pesticide, active ingredients, formulation, powder, granule, liquid, methamidophos, humic acid, copper sulphate.

1. Introduction

Since the wastes generated during the production of pesticides can be characterized as toxic and/or carcinogenic and/or bioaccumulative and/or refractory for treatment, this industry falls into the category of sectors which have a high potential to harm the environment (Maele-Fabry *et al*., 2006; Chen *et al*., 2007; Maele-Fabry *et al*., 2007; Li *et al*., 2009; WHO, 2009; Salles *et al*., 2010; Ye *et al*., 2010; Zolgharnein *et al*., 2011; Bouya *et al*., 2012; Shen *et al*., 2013). On a global basis, around 500 compounds are inscribed as either pesticides or their metabolites (Reddy and Kim, 2015). The wastes arising from both pesticide synthesis and formulation plants can peregrinate long distances with atmospheric movements, groundwater flow etc. (EU, 2007; Syed and Malik, 2011).There are research activities dealing with the degradation of pesticides by various methods such as ozonation, photolysis, adsorption, biotreatment and their combinations (Maldonado *et al*., 2006; Lafi *et al*., 2006; Chen *et al*., 2007; Li *et al*., 2009; Salles *et al*., 2010; Zolgharnein *et al*., 2011; Reddy and Kim, 2015). However degradation by-products can sometimes observed to be more hazardous than the parent pesticide (Reddy and Kim, 2015). Substance recovery from segregated process waste streams is stated to be a promising future solution to waste problem in pesticide industry (Shen *et al*.,2013).

Within all the wastes generated from pesticide production industries, the most significant part in terms of negative impacts on the environment is quoted as the hazardous wastes. Knowing the amount of hazardous waste production for an industrial sector is of crucial importance in prescribing the in-plant control measures, treatment requirements and managing the disposal alternatives. Since the amount of hazardous waste generation per product depends on the production methods applied, a case specific approach gathering the local discrepancies is required. Apart from few studies (Germirli Babuna *et al*., 2014; Zhu *et al*., 2014), in general reliable data on unit hazardous waste generation originating from pesticide industry is not available. 180 kg TOC/batch mother liquor is reported to be produced during pesticide manufacturing (EU, 2006; IFC, 2007). Besides 200 kg of waste generation per ton of active ingredient production and 3-4 kg of waste production per ton of formulation are stated in literature (World Bank Group, 1998; EU, 2006; IFC, 2007). In another study 208 kg waste generation per ton pesticide is reported (Rahman *et al.*, 2014). The mentioned figures are not developed by separately quoting the hazardous wastes and they might cover solid wastes. Since the hazardous wastes can be solid or liquid in nature, it is important to differentiate it from other types of nonhazardous wastes i.e. solid wastes and wastewaters.

Turkey is among the top ten higher pesticide using countries in the world (Verma *et al.*, 2014). According to 2010 data, annually 60792,4 ton pesticide is consumed on the total agricultural area of 390120 km^2 in Turkey (Verma *et al.*, 2014). Although all the pesticide applied on land area are not manufactured in Turkey, there exist factories with different sizes producing pesticide active ingredients and formulation.

In this context the objective of this study is to develop unit hazardous waste generation for Turkish pesticide manufacturing industry. In order to fulfill this aim the production of methamidophos, humic acid, copper sulphate together with liquid, granule and powder pesticide formulations are evaluated. By using the obtained unit hazardous waste generation factors and the production capacities, the annual amount of hazardous waste production for Turkish pesticide industry is brought to light.

2. Adopted methodology

Hazardous waste list put forth by Commission Decision on Hazardous Wastes (EU, 2000), is used as a base format to determine the average unit hazardous waste generation factors expressed as "kg hazardous waste per ton product". Table 1 tabulates the mentioned hazardous waste list defined for pesticide production (EU, 2000).

The following information on Turkish pesticide manufacturing plants

i. Production capacities related to different pesticide synthesis (i.e. glyphosate, trifuralin, copper sulphate, methamidophos etc.)
ii. Production capacities related to pesticide formulation (liquid, granule, powder)
iii. The most commonly applied production technologies are gathered.

Pesticides with highest production levels and the most commonly used production technologies are defined and further studies are concentrated on them. As a parallel task, a detailed investigation is carried out to enlighten the applied technologies and processes, raw material and auxiliary inputs, waste generating parts of the production processes, quantity and quality of wastes etc.on a representative manufacturing plant. During the entire research, the opinion of a production expert (who is in the sector for more than 30 years) is used as an important tool.

The Ministry of Environment and Urban Planning collects data on the amount of hazardous waste generation arising from industrial installations on an annual basis. The declarations of the pesticide manufacturing plants (that are obtained from The Ministry of Environment and Urban Planning) and the findings of the field study are evaluated together with the help of expert opinion and the obtained results are given as average unit hazardous waste generation.

Table 1. Hazardous waste codes and related waste definition for pesticide manufacturing (EU, 2000)

Waste Code	Waste Definition
07	Wastes from organic chemical processes
07 04	wastes from the manufacture, formulation, supply and use (MFSU) of organic plant protection products, wood preserving agents and other biocides
07 04 01	aqueous washing liquids and mother liquors
07 04 03	organic halogenated solvents, washing liquids and mother liquors
07 04 04	other organic solvents, washing liquids and mother liquids
07 04 07	halogenated still bottoms and reaction residues
07 04 08	other still bottoms and reaction residues
07 04 09	halogenated filter cakes and spent absorbents
07 04 10	other filter cakes and spent absorbents
07 04 11	sludges from on-site effluent treatment containing dangerous substances
07 04 13	solid wastes containing dangerous substances

3. Results and discussion

Table 2 presents the unit hazardous waste generation figures for pesticide formulation. As can be seen from Table 2, between 45 to 80 kg of hazardous waste generation per ton of pesticide formulation is obtained.

Unit hazardous waste generation figures for the manufacturing of pesticide active ingredients are tabulated in Table 3. This table gathers the results attained in this study and the literature data. Accept for acephate all the figures are in accordance with each other. The high level of unit hazardous waste generation (200 kg hazardous waste/ton acephate) given by Zhu *et al*., 2014, can be attributed to the fact that this literature data considers most of the solid waste as hazardous waste.

Table 2: Unit hazardous waste generation figures for pesticide formulation

Waste Code	Liquid Pesticide Formulation (kg hazardous waste/ton product)	Powder/Granule Pesticide Formulation (kg hazardous waste/ton product)
07 04 01	30-40	30-40
07 04 03	5-10	3-5
07 04 04	10-20	5-10
07 04 09		1
07 04 10		1
07 04 11	4-6	4-6
07 04 13	1-4	1-4
TOTAL	50-80	45-67

According to the figures given in Table 3, values ranging from 10 to 56 kg of hazardous waste generation per ton of pesticide synthesis are observed.

It should be noted that the obtained unit hazardous waste generation figures corresponds to the most commonly applied production technologies in Turkey. As an example the most frequently applied methamidophos production route is illustrated in Figure 1 and that of tetramethrin, acephate and glyphosate are shown in Figure 2. The unit hazardous waste generation figures presented in this study are developed for the mentioned production flowcharts.

By complying the data shown in Table 2 and Table 3 with the data on realized pesticide production obtained from state agencies (DPT, 2008; MARA, 2010), the amount of annual hazardous waste generation originating from pesticide production is calculated as given in Table 4.

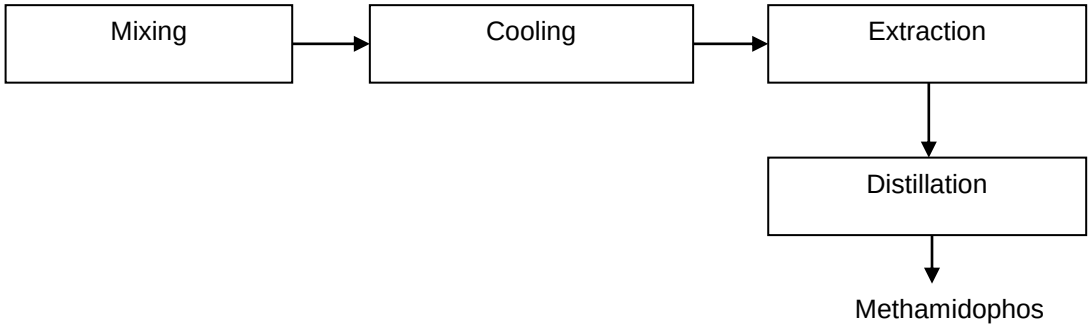

Figure 1. Methamidophos production flowchart

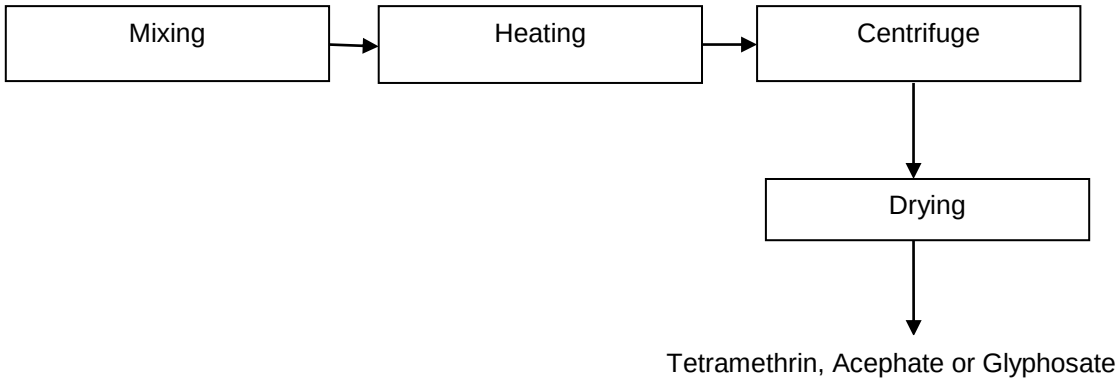

Figure 2: Tetramethrin, Acephate and Glyphosate production flowchart (Germirli Babuna *et al*., 2014

Table 4: The amount of annual hazardous waste generation in Turkish pesticide industry

Waste Code	Amount of Hazardous Waste (ton/year)	
	Minimum	Maximum
070401	16696	22409
070403	2513	4854
070404	4757	9499
070407	73	111
070408	055	
070409	155	
070410	149	
070411	2240	3357
070413	572	2218
TOTAL	27156	42753

The total amount of hazardous waste generated by Turkish pesticide industry is in the range of 27200-42800 tons per year. On the other hand the total amount of all hazardous wastes in Turkey is stated to be 1350000 tons per year (HAWAMAN, 2009). Therefore the contribution of pesticide sector to the total hazardous wastes is around 2 to 3.2 %.

4. Conclusions

Three pesticide active ingredients manufacturing (methamidophos, humic acid, copper sulphate) and powder, granule and liquid pesticide formulation industries in Turkey are investigated in terms of their hazardous waste generation. Values ranging from 7 to 56 kg of hazardous waste generation per ton of active ingredient produced are obtained for pesticide synthesis sector. 45 to 80 kg of hazardous waste generation per ton of formulation are attained. The evaluation of the unit hazardous waste generation factors and the realized pesticide production levels showed that 27200 - 42800 ton hazardous waste is produced annually by Turkish pesticide sector. Thus it can be concluded that the contribution of pesticide production to the total hazardous waste generation in Turkey is 2 to 3.2 %.

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Table 3. Unit hazardous waste generation figures for the manufacturing of pesticide active ingredients (kg hazardous waste/ton product)

Name of the Pesticide Active Ingredient	WASTE CODE									
	070401	**070403**	**070404**	**070407**	**070408**	**070409**	**070410**	**070411**	**070413**	**TOTAL**
2,4 D Acid	20-30[a]	5[a]		5-10[a]		1[a]		3-5[a]	1[a]	35-56[a]
Acephate	5-10[a]		3-5[a]		1[a]		1[a]	0.5[a]	0.5[a]	11-18[a] 200[b]
Tetramethrin	5-10[a]		3-5[a]		1[a]		1[a]	0.5[a]	0.5[a]	11-18[a]
2,4 D isooctyl ester	5-10[a]	2-4[a]	1[a]					1[a]	1[a]	10-17[a]
Propanil (liquid)	10-20[a]	3-5[a]		1-3[a]		0.5[a]		3-5[a]	0.5[a]	18-34[a]
Propanil (solid)	10-20[a]	3-5[a]		10[a]		0.5[a]		3-5[a]	0.5[a]	27-41[a]
Glyphosate	5-10[a]		3-5[a]		1[a]			1[a]	10[a]	20-27[a]
Fenvalerate	10-20[a]		5[a]					1[a]	1[a]	17-27[a] 20.4[b]
Cypermethrin	10-20[a]		5[a]					1[a]	1[a]	17-27[a] 31.9[b]
Alfa cypermethrin	10-20[a]		5[a]				1[a]	1[a]	1[a]	18-28[a]
Trifuralin	15-30[a]	5-8[a]		10[a]		0.5[a]		3-5[a]	0.5[a]	34-54[a]
Copper sulphate	5-10[c]							1[c]	1[c]	7-12[c]
Humic acid	5-10[c]							1[c]	1[c]	7-12[c]
Methamidophos	10-20[c]		5[c]					1[c]	1[c]	17-27[c]

[a]: Germirli Babuna *et al*., 2014
[b]: Zhu *et al*., 2014
[c]: This study

WASTE CODES
070401: aqueous washing liquids and mother liquors
070403: organic halogenated solvents, washing liquids and mother liquors
070404: other organic solvents, washing liquids and mother liquids
070407: halogenated still bottoms and reaction residues
070408: other still bottoms and reaction residues
070409: halogenated filter cakes and spent absorbents
070410: other filter cakes and spent absorbents
070411: sludges from on-site effluent treatment containing dangerous substances
070413: solid wastes containing dangerous substances