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Herbicides *vis-a-vis* other pesticides: An overview on use and potential hazards

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ABSTRACT

Modern agriculture depends on the four main factors *viz*: seed, water, fertilizers and pesticides. The total number of pests attacking major crops has increased significantly from 1940s. Therefore, the demand of pesticides especially herbicides in agriculture is increasing. Farmers are facing shortages of labour for hand weeding crop fields as people are moving to urban from rural areas. Herbicides are cheaper and more readily available than labour for hand weeding. This review article focuses on the status of using herbicides *vis a vis* other pesticides and their uses and potential hazards. All pesticides must be toxic to be effective against the pests they are intended to control. Because of being toxic, pesticides are potentially hazardous to humans, animals, other organisms, and the environment. Therefore, users of the pesticides must understand the relative toxicity and potential health effects of the products they use. Pesticides are classified based on the oral and dermal lethal dose, 50% values (to the rat) of the active principles. Globally, 35% of the 158 insecticides fall under extremely hazardous and highly hazardous categories, compared to only about 4% in case of herbicides. Under the slightly hazardous group, the number of herbicides is two times higher as compared to insecticides. The number of herbicides that are unlikely to present acute hazard is as much as 37.1% of the total as compared to 12.6% insecticides. Thus, herbicides as a pesticide category are safer or less hazardous than other pesticides especially insecticides. But it is not intended to give clear chit to herbicides because the ultimate toxicity depends on the formulation. The formulation of pesticides may be thousand times more toxic than their active principles. Thus, there is need to set maximum residue limits (MRLs) based on formulation rather than on the basis of active principles.

INTRODUCTION

Agriculture is the soul of Indian economy as it brings home the bread to nearly 60% of the population and supplies it to the remainder (Prasad *et al.* 2016). In India, agriculture has come a long way since independence, with chronic food scarcity giving way to grain self-sufficiency, despite about three-fold increase in population. This made Indian agriculture transform from subsistence farming to modern farming. Modern agriculture depends on the four main factors *viz*: seed, water, fertilizers and pesticides. About 35-45% crop production is lost due to diseases, insects and weeds, while 35% crop produces are lost during storage (OPCI, Outlook of Pesticide Consumption in India 2014).Hence, pesticides are the integral part of modern agriculture.

The total number of pests attacking major crops has increased significantly from 1940's (**Table 1**) (FICCI 2015). For instance, the number of pests which are harmful for crops such as rice has increased from 10 to 17 whereas for wheat have increased from 2 to 19. The increased damage to crops from pests and subsequent losses pose a serious threat to food security and further underscores the importance of agrochemicals.

Pesticides are inevitable to prevent pre- and post-harvest losses, which have assumed

Table 1. Crop-wise demographic increase in pest population

Crop	1940s		At present	
	Total pests	Serious pests	Total pests	Serious pests
Rice	35	10	240	17
Wheat	20	2	100	19
Sugarcane	28	2	240	43
Peanut	10	4	100	12
Mustard	10	4	38	12
Pulses	30	6	250	34

(Source: FICCI 2015)

significance during recent times in agriculture. The growing popularity of synthetic pesticides in agriculture has over shadowed the traditional methods of plant protection to manage insect-pest, diseases and weeds. Undoubtedly, pesticides are said to have contributed to the food security by way of avoidance of post-harvest losses. Pesticides like all other inputs play an important role in increasing agricultural production. However, there is a growing awareness about the ill-effect of pesticides on human and animal health, environment, natural resources and sustainability of agriculture production. The problem of pesticide usage is not over now; in many countries, the old persistent, bio-accumulative pesticides have been banned. Many new products have been developed and used in large quantities. For many of these products today we still do not have sufficient amount of knowledge about their possible risks and adverse effects on the environment and humans. Several of them appear to have a bad environmental impact.

Pesticide use and Indian market overview

Indian Agrochemical Industry size was estimated to be US$ 3.8 billion in year 2012. Over the 12th plan period, the segment is expected to grow at 12-13% per annum to reach 7.0 billion (FICCI 2015). The Indian domestic demand is growing at the rate of 8-9% and export demand at 15-16%. The per capita consumption of pesticides in India is 0.6 kg which is lowest in the world. The per ha pesticide consumption in China and the USA is 13 and 7 kg, respectively. The main reason for low per ha consumption of pesticides in India is low purchasing power of farmers and small land holdings. The majority of agricultural farmland belongs to marginal farmers but maximum contribution to the produce is also from marginal farmers. The large-scale farming is increasing and therefore, there is good scope for increase of per ha consumption of pesticides in India. (http//:www.newsagropages.com/News/News Detail—10649.htm).

The Indian crop protection industry is expected to grow at a compound annual growth rate (CAGR) of 12% to reach United State dollar (USD) 7.5 billion by 2019. Exports currently constitute almost 50% of the Indian crop protection industry and are expected to grow at a CAGR of 16% to reach USD 4.2 billion by 2019, resulting in 60% share in the Indian crop protection industry. The domestic market on the other hand would grow at 8% CAGR, as it is predominantly monsoon dependent, to reach USD 3.3 billion by 2019. Globally, India is the fourth largest producer of crop protection chemicals, after the United States, Japan and China.

The crop protection companies in India can be categorized into three types –Multi-National, Indian including public sector companies and small sector units (http://ficci.in/study page.asp?spid=20541 &sectorid=7). The Indian crop protection industry is dominated by generic products with more than 80% of molecules being non-patented. This results in very low entry barriers for the industry. Hence, strong distribution network, appropriate pricing, brand recall and dealer margins are some of the critical factors for companies to succeed. Crop protection chemicals are manufactured as technical grades and converted into formulations for agricultural use. (http://www.careratings.com/upload/NewsFiles/SplAnalysis/Outlook%20of%20Indian%20Pesticide%20Industry.pdf).

The Indian agrochemical value chain comprises of technical grade manufacturers, formulators producing the end products, distributors and end use customers. According to the Pesticide Monitoring Unit, Government Of India (GOI), there are about 125 technical grade manufacturers, including about 10 multinationals, more than 800 formulators and over 145,000 distributors in India (http://www.tsmg.com/download/reports/Indian_Agrochemicals_Industry_2013.pdf). More than 60 technical grade pesticides are being manufactured indigenously. In India, top 10 companies control almost 75-80% of the market share (FICCI 2015). The market share of large players depends primarily on product portfolio and introduction of new molecules. The market has seen a number of mergers and acquisitions with large players buying out small manufacturers. Companies are also looking for strategic alliances and partnerships in order to expand their market reach.

Domestic market by product category

The Indian crop protection market is dominated by insecticides, which form almost 60% of the domestic crop protection chemicals market (FICCI 2015). The major applications are found in rice and cotton. Fungicides and herbicides are the largest growing segments accounting for 18% and 16% respectively of the total crop protection chemicals market, respectively. Rice and wheat crops are the major application areas for herbicides. Increasing labour costs and labour shortage are key growth drivers for herbicides.

The fungicides find application in fruits, vegetables and rice. The key growth drivers for fungicides include a shift in agriculture from cash crops to fruits and vegetables and government support for exports of fruits and vegetables. Bio-pesticides include all biological materials organisms which can be used to control pests. Currently, bio-pesticides constitute only 3% of the Indian crop protection market; however, there are significant growth opportunities for this product segment due to increasing concerns of safety and toxicity of pesticides, stringent regulations and government support.

Erstwhile Andhra Pradesh (Seemandhra and Telangana), Maharashtra and Punjab are top three states contributing to 45% of pesticide consumption in India. The top seven states together account for more than 70% of crop protection chemicals usage in India.

Since 2005, the value of the herbicide market in India has doubled (Philips 2013). The Indian market for herbicides is expected to grow about 40% annually (Frabotta 2011). The adoption of herbicides has gained impetus over conventional weeding practices and has increased the herbicide consumption to approximately 90% in developed countries, Latin America 70%, Europe 67% and Asia 84% (WAP 2014).

Annual usage of herbicides in the world was about 1814369.48 tonnes in the 1953, increasing to nearly 54884676.77 tonnes at the end of 2013 (WAP 2014). Since then, at the end of each five years, 15-24% increments occurred. The herbicide industry is quite significant in dollar terms. Annual expenditures by users of herbicides totalled about USD 33 billion in 1953 and USD 998 at the end of 2013. It is clear from the figure that, there is a sharp increasing trend in consuming herbicides which triggers to increase the market expenditure for herbicides (Hossain 2015). In future, by the end of 2025, it is supposed that the herbicides consumption to be increased by 68.03 million tonnes which will costs around USD 2000.

Area treated with pesticides

As per the input surveys conducted under the aegis of agricultural census (GOI 2016), the cultivated area treated with the pesticides has increased in the last two decades. Around 40% of the total cultivated area is treated with pesticides. Approximately, 65-70% of the cultivated area treated with pesticides is irrigated. As regard to pesticide usage, land holding size-wise, medium size land holding are treated the most, followed by the small and marginal land holding. At a micro level, on an average 65% of the area under the fibre crops are treated with pesticides followed by fruits (50%), vegetables (46%), spices (43%), oilseeds (28%) and pulses (23%).(https://eands.dacnet.nic.in/PDF/State_of_Indian_Agriculture,2015-16.pdf).

Until recently in India, herbicides were used on 10% of the wheat hectares to control grass weed species and on 20–25% of the hectares to control broadleaf species (Chatrath 2006). It is inevitable that, herbicide use will increase in the world agriculture, not only because millions of people are leaving rural areas, creating shortages of hand weeders, but also the need to increase crop yields. Hand weeding has never been a very efficient method of weed control often performed too late and not frequently enough. In many parts of the world, herbicides are being increasingly used to replace tillage in order to improve environmental conditions. In comparison with tillage, herbicide use reduces erosion, fuel use, greenhouse gas emissions and nutrient run-off and conserves water (Hossain 2015).

Ecological effects of pesticides

The first warning signal about pesticides danger came in 1962, when Rachel Carson, an American courageous woman scientist, wrote down her nature observation and pointed out sudden dying of birds caused by indiscriminate spraying of pesticides (DDT). Her book, Silent Spring, became a landmark. It changed the existing view on pesticides and has stimulated public concern on pesticides and their impact on health and the environment. Silent Spring facilitated the ban of the DDT in 1972 in the United States. More research has been done and several dangerous and persistent organic pesticides like dieldrin, endosulfan and lindane have been banned or restricted since that time.

Soil contamination

Persistence of pesticides in soil can vary from few hours to many years in case of organochlorine pesticides. Despite organocarbon pesticides were banned or restricted in many countries, they are still detected in soils (Shegunova *et al.* 2007, Toan *et al.* 2007, Li *et al.* 2008, Hildebrandt *et al.* 2009, Jiang *et al.* 2009, Ferencz and Balog 2010).

Water contamination

Pesticides can get into water via drift during pesticide spraying, by runoff from a treated area, and leaching through the soil. In some cases, pesticides can be applied directly onto water surface. Pandey *et al.* (2011) reported that pesticides has caused both surface sediment and river water pollution as several registered pesticides have been detected in the river Yamuna in Delhi. Similar studies also reported the pesticides detection in other rivers in India. In addition, Pandey *et al*. (2011) also reported some cases of pesticides contamination in monitoring studies in other places in the world, such as: (1) coastal marine sediment in Singapore; (2) Ebro river delta, Mediterranean Sea; (3) Paranoa lake in Brazil; (4) Coastal lagoon watershed in Argentina; (5) Bay of Ohuira in Mexico; (6) Haleji lake in Pakistan; (7) some stream sediment in Spain; (8) Lake Orta sediments in Italy; (9) Uluabat lake in Turkey and (10) Pearl river estuary in China etc. Pesticides are in detectable level in the UK groundwater (Stuart *et al.* 2012) while, in the US, it has been reported that 100% of major rivers and streams and 33% of major aquifers contained at least one pesticide at detectable levels (Koleva and Schneider 2010).

Although quantity control and residues monitoring are important, these cannot ensure that all pesticides will be used correctly and safely. There must also be systems in place to deal with toxic chemicals if they are found in drinking water. With regard to recommendations for the future, some investment is required in training farmers on correct application methods for pesticides. Otherwise, potential dangers to drinking water can be ignored. It may be appropriate to sell pesticides only to those who can produce written evidence of having received the necessary safety training. In addition, an existing risk assessment already established should further be enhanced by which the pesticides entering groundwater, their toxicity and potential risks to drinking water and the environment can be assessed. Zhao and Pei (2012) have reviewed the four aspects of such risk evaluation including the establishment of a theoretical system, comprehensive consideration of the impact factors, the development of validation methods and combined evaluation methods and the strengthening of monitoring work and groundwater pollution risk assessment in arid areas. In relation to drinking water quality assurance, there should be an increase in the sampling rates of water supplies, especially during times of maximum pesticide application.

Effects on organisms

Fungicides were found to be toxic to soil fungi and actinomycetes and caused changes in the microbial community structure (Liebich *et al.* 2003, Pal *et al*. 2005). Nitrification bacteria are very sensitive to pesticides influence. Inhibition of nitrification was proved by sulphonylurea herbicides (Gigliotti and Allievi 2001). Some pesticides (Benomyl, Dimethoate) can also negatively affect symbiotic mycorrhizal fungi, which facilitate plant nutrient uptake (Menendez *et al.* 1999, Chiocchio *et al.* 2000). Glyphosate affected predatory arthropods (spiders and ground beetle) in agricultural field, caused behavioural changes and influenced long-term surviving even in residual exposure. These results also suggest that herbicides can affect arthropod community dynamics separate from their impact on the plant community and may influence biological control in agroecosystems (Evans *et al*. 2010). Scientific literature addressing the influence of pesticides on the growth and reproduction of earthworm is reviewed by Yasmin and D'Souza (2010). Majority of the studies have used mortality as an endpoint rather than subtler endpoints such as reproductive output. It is now emphasized that, whereas higher concentrations of a pollutant can easily be assessed with the acute (mortality) test, contaminated soils with lower (sublethal) pollutant concentrations require more sensitive test methods such as reproduction test in their risk assessment. Lower bumblebee and butterfly species richness was found in the more intensively farmed basin with higher pesticide loads (Brittain *et al.* 2010). Several articles reported negative effects of pesticides butterflies populations (Longley and Sotherton 1997, White and Kerr 2007, Adamski *et al.* 2009). Carbaryl has been found toxic for several amphibian species, additional combination with predatory stress caused higher mortality (Relyea 2003). Also, herbicide glyphosate caused high mortality of tadpoles and juvenile frogs in an outdoor mesocosms study (Relyea 2005b). Insecticide and herbicide application can lead to reduction of chick survival and bird population. Evidences of this important indirect effect of pesticides have been reported (Moreby and Southway 1999, Boatman *et al.* 2004, Taylor *et al.* 2006). A recent review about this topic and possible mitigation measures were published by Royal Society for the Protection of Birds in the UK (Bright *et al.* 2008).

Toxicity risks of agricultural pesticides to fishes are pivotal. The 96h LC_{50} and 95% lower and upper confidence limits, respectively, for the following pesticides were determined (Kreutz et al. 2008): glyphosate (7.3 mg/L; 6.5–8.3), atrazine (10.2 mg/L; 9.1–11.5), atrazine + simazine (10.5 mg/L; 8.9–12.4), mesotrione (532.0 mg/L; 476.5–594), tebuconazole (5.3 mg/L; 4.9–5.7), methylparathion (4.8 mg/L; 4.3–5.3), strobulurin and triazol (9.9 mg/L; 8.7–11.2). Diflubenzuron was also tested and caused no fish mortality up to 1 g/L. The toxic concentration of these pesticides to silver catfish fingerlings fell above the concentration used for application in the field and except following accidental application or misplacing of empty recipients, it should not cause fish mortality.

Nonetheless, the data obtained will be useful to study the long-term effect of these products on the hematological, biochemical, hormonal and immunological parameters of silver catfish and related fish species.

Effect on biodiversity

If biodiversity is to be restored, there must be a world-wide shift towards farming with minimal use of pesticides over large areas (Geiger *et al.* 2010). A recent study conducted in agriculture area in Netherlands estimated the impact of insecticides, herbicides and fungicides drift on terrestrial biodiversity outside the treated area. This study suggests that increasing unsprayed buffer zones around crops is critical to the success of any new strategy to prevent the harmful impact of pesticides (de Jong *et al.* 2008).

Pesticide hazard

Toxicity is a measure of the capacity of a substance to cause injury or death, and is related to the dose. It is an intrinsic property of the substance. The dose-response relationship is a way of quantifying acute toxicity, and the LD_{50} is a crude estimate of the dose needed to kill 50% of the test animals when they are exposed to the chemical by the oral, dermal or inhalation route. The value is usually expressed in milligrams of chemical per kilogram bodyweight of the test animal. The smaller the LD50 value, the greater is the acute toxicity of the chemical.

Hazard represents the potential for injury to occur. It is a function of the toxicity of the chemical and degree of exposure. Even a highly toxic chemical presents little hazard to man when the means of exposure are largely eliminated.

Risk is the probability of a hazard occurring under specified conditions. Safety, the reciprocal of risk, is the probability that harm will not occur under specified conditions.

When satisfied that an adequate assessment has been made of all the potentially hazardous components of the product, the next step is to assess the risks that may arise from the proposed use. These include risk to the applicator, the consumer of treated crops, beneficial species or wildlife, and to the environment. The risks are minimized if the user follows the appropriate warning and precautionary statements on the label. It is the responsibility of the manufacturer/supplier and regulator to ensure that the safety statements are adequate to minimize the risks, and that the benefits of using the product outweigh any risks involved.

Potential hazard is assessed on the formulation or product in the pack and therefore takes into account the properties of the solvents, diluents or other adjuvants, in addition to the active ingredient (WHO 2010). The WHO Recommended Classification of Pesticides by Hazard is widely used and is based on the oral and dermal LD50 values (to the rat). The more restrictive class is always chosen from the oral and dermal LD50 classifications. From these values, one of four coloured bands is assigned with a corresponding hazard statement and one of two hazard symbols, which denote classification of hazard in use, is placed along the bottom of the label.

Criteria for classification

WHO presently uses the Acute Toxicity Hazard Categories from the Global Harmonized System (GHS) as the starting point for classification. This change is consistent with the 1975 World Health Assembly Resolution which envisaged that the WHO Classification would be further developed with time in consultation with countries, international agencies and regional bodies. The Global Harmonized System (GHS) meets this requirement as a classification system with global acceptance following extensive international consultation.

Based on this system the pesticides active principles are classified (WHO 2010) (**Table 2**). However, the final classification of any product is intended to be by formulation.

Abbreviations :AC-acaricide, AP -aphicide ,B-bacteriostat (soil), FM–fumigant, F-fungicide, other than for seed treatment, FST-fungicide, for seed treatment, H –herbicide, I-insecticide, IGR-insect growth regulator, Ix-ixodicide (for tick control), L-larvicide, M-molluscicide, MT-miticide, N –nematocide, O- other use for plant pathogens, PGR-plant growth regulator , R-rodenticide, RP-repellant (species), S- applied to soil: not used with herbicides or plant growth regulators SY -synergist

As per the WHO classification (**Table 2**) of pesticides globally 35% of the 158 insecticides fall under the extremely hazardous and highly hazardous category, compared to only about 4% in case of herbicides. Under the slightly hazardous group, the number of herbicides is two times higher as

WHO Class	LD_{50} for the rat (mg/kg body weight)	
	Oral	Dermal
Ia Extremely hazardous	< 5	< 50
Ib Highly hazardous	5–50	50–200
II Moderately hazardous	50–2000	200–2000
III Slightly hazardous	Over 2000	Over 2000
U Unlikely to present acute hazard	5000 or higher	

Table 2. Classification of pesticides according to toxicity, expressed as LD_{50} (mg/kg) based on WHO classification scheme (after WHO 2010)

Class	Main use	Pesticides
Extremely hazardous (Class 1a)	I	Chlorethoxyfos; Chlormephos; Disulfoton; EPN; Mevinphos; Parathion; Parathion-methyl; Phoratek; Phosphamidon; Sulfotep; Tebupirimfos
	R	Brodifacoum; Bromadiolone; Bromethalin; Chlorophacinone; Difenacoum; Difethialone; Diphacinone; Flocoumafen; Sodium fluoroacetate
	I-S	Aldicarb (0.93 mg/kg); Ethoprophos; Terbufos
	FM	Calcium cyanide
	F	Captafol
	FST	Hexachlorobenzene; Phenylmercury acetate
	F-S	Mercuric chloride
Highly hazardous (Class 1b)	I	Azinphos-ethyl; Azinphos-methyl; Butocarboxim; Butoxycarboxim; Calcium arsenate; Carbofuran; Chlorfenvinphos; *Cyfluthrin; Beta-cyfluthrin;* Zeta-cypermethrin; Demeton-S-methyl; Dichlorvos; Dicrotophos; Ethiofencarb; Famphur; Flucythrinate; Heptenophos; Isoxathion; Mecarbam; Methamidophos; Methidathion; Methiocarb; Methomyl; Monocrotophos; Omethoate; Oxamyl; Oxydemeton-methyl; Propetamphos; Thiometon; Triazophos; Vamidothion
	R	3-Chloro-1,2-propanediol; Coumatetralyl; Fluoroacetamide; Sodium arsenite; Sodium cyanide; Strychnine; Thallium sulphate; Warfarin; Zinc phosphide
	AC	Formetanate
	I-S	DNOC; Furathiocarb; Tefluthrin; Thiofanox
	O	Mercuric oxide
	AC, MT	Coumaphos;
	N	Fenamiphos
	N,I	Cadusafos
	L	Lead arsenate; Paris green
	I,F, H	Pentachlorophenol
	F	Blasticidin-S; Edifenphos;
	H	Acrolein; Allyl alcohol; Dinoterb; DNOC
Moderately hazardous (Class II)	I	Acephate; Alanycarb; Allethrin; Azamethiphos; Bendiocarb; Benfuracarb; Bensultap; Bifenthrin; Bioallethrin; Carbaryl; Carbosulfuron; Cartap; Chlordane; Chlorpyrifos; Cyanophos; Cypermethrin; Alpha-cypermethrin; Cyphenothrin; DDT; Deltamethrin; Diazinon; Dimethoate; Endosulfan; Esfenvalerate; Ethion; Fenitrothion; Fenobucarb; Fenpropathrin; Fenvalerate; Fipronil; Gamma-HCH; HCH; Hydramethylnon; Imidacloprid; *Indoxacarb;* Isoprocarb; Lambda-cyhalothrin; Methacrifos; Metolcarb; Naled; permethrin; Phenthoate; Phosalone; Phoxim; Pitimiphos-methyl; Prallethrin; profenofos; Propoxur; Prothiofos; Pyraclofos; Pyrethrins; Pyridaphenthion; Quinalphos; Rotenone; Sulfluramid; Thiocyclam; Thiodicarb; Tralomethrin; Trichlorfon; XMC; Xylylcarb
	Ix	Cyhalothrin
	I, MT	Chlorfenapyr
	MT	Tebufenpyrad,
	AC	Amitraz; Azocyclotin; Cyhexatin; Dicofol; Fenazaquin; *Fenpyroximate;* Pyridaben;
	R	Chloralose
	M	Metaldehyde
	L	Fenothiocarb
	I, L	Fenthion
	I, AC	Phosmet
	AP	Pirimicarb; Triazamate
	FM	Dichlorobenzene
	B	Bronopol
	B-S	Nitrapyrin
	F	Azaconazole; Bromuconazole; Butylamine; Copper hydroxide; Copper oxychloride; Copper sulphate; Cuprous oxide; Cymoxanil; Cyproconazole; Dichlorophen; Difenoconazole; Diniconazole; Dithianon; Dodine; Fenpropidin; Fentin acetate; Fentin hydroxide; Ferimzone; Flufenacet; Fluoroglycofen; Flusilazole; Fuberidazole; Furalaxyl; Imazalil; Iminoctadine; Iprobenfos; Isoprothiolane; Mercurous chloride; Metalaxyl; Metconazole; Methasulfocarb; Myclobutanil; Nabam; Nuarimol; Octhilinone; Oxadixyl; Procloraz; Propiconazole; Pyrazophos; Pyroquilon; Spiroxamine; Tebuconazole; Tetraconazole; Thiram; Triadimefon; Tricyclazole; Tridemorph; Triflumizole; Ziram
	F-S	Dazomet; Metam-sodium; Methyl isothiocyanate
	F,FST	Flutriafol
	AC,F	Dinobuton; Dinocap
	FST	Guazatine; triadiamenol
	H	Acifluorfen; Alachlor; Ametryn; Anilofos; Bensulide; Bentazone; Bilanafos; Bromoxynil; Butamifos; Butralin; Butoxydim; Clomazone; Cyanazine; 2,4-D; 2,4-DB; Dicamba; Dichlorprop; Diclofop; Difenzoquat; Dimepiperate; Dimethachlor; Dimethipin; *Dimethenamid;* Dimethylarsinic acid; Diphenamid; Diquat; Endothal-sodium; EPTC; Fluchloralin; Fluxofenim; Fomesafen; Glufosinate; Haloxyfop; Hexazinone; Ioxynil; Ioxynil octanoate; Isoproturon; Isouron; MCPA; MCPA-thioethyl; MCPB; Mecoprop; Mecoprop-P; Mefluidide; Metamitron; Methylarsonic acid; Metribuzin; Molinate; Paraquat; Pebulate; Pendimethalin; Piperphos; Propachlor; Propanil; Prosulfocarb; Pyrazoxyfen; Quinoclamine; Quizalofop; Quizalofop-p-tefuryl; Simetryn; Sodium chlorate; 2,3,6-TBA; TCA; Tebuthiuron; Terbumeton; Thiobencarb; Tralkoxydim; Triclopyr
	PGR	Chlormequat; 4-CPA; Flurprimidol; Mepiquat; 2-Napthyloxyacetic acid Paclobutrazol; Uniconazole
Slightly hazardous (Class III)	I	*Bacillus thuringiensis;* Buprofezin; Chlorpyrifos methyl; Empenthrin; Flufenoxuron; tau-Fluvalinate; Halofenozide; Malathion; Resmethrin; Spinosad; Spirotetramat; Timephos; Tetrachlorvinphos
	L	Cyromazine; Diflubenzuron
	MT	Fenbutatin

Class	Main use	Pesticides
	RP (insect; dog/cats)	Diethyltoluamide (insect); Undecan-2-one (Dog/cats)
	I, F	Sulphur
	AC, F	Chinomethionate
	AC	Clofentezine; diafenthiuron; Propargite
	F	Benalaxyl; Biphenyl; Borax; Buprimate; Butylate; Chlozolinate; Dicloran; Dmethirimol; dimethomorph; Etridiazole; Fenarimol; Fenbuconazole; Fenpropimorph; Flamprop-M; hexaconazole; Iprodione; Ofurace; Oxycarboxin; Penconazole; 2-phenylphenol; Pimaricin; Probenazole; Prifenox; Pyrimethanil; Thiabendazole; Tritaconazole
	FST	Carboxin; Hymexazol
	H	Acetochlor; Alloxydim; Ammonium sulfamate; Asulam; Atrazine; Benazolin; Bensuresate; Bispyribac; Butachlor; Chloridazon; Chlorimurion; Chlorthal-dimethyl; Cinmethylin; Clopyralid; Cyloate; Cycloxydim; Dichlobenil; dichlormid; Diflufenican; Dimefuron; Dimethametryn; dinitramine; diuron; Dodemorph; Esprocarb; Fluazifop-p-butyl; fluorochloridone; Fosamine; Glyphosate; Linuron; Metazachlor;Methabenzthiazuron; methyldymron; Metobromuron; Metolachlor; Metoxuron; monolinuron; Prometon; Prometryn; Pyridate; Pyrithiobac sodium; Quinclorac; Sethoxydim; TCA; Terbuthylazine; Terbutryn; Triallate; Trietazine
	PGR	Ancymidol; Ethephon; 1-Naphthylacetic acid; Thidiazuron
	SY	N-octylbicycloheptene dicarboximide
Acute hazard	I	Bioresmethrin; Chlorantraniliprole; Cryolite; Cycloprothrin; Etofenprox; Fenoxycarb; Hexaflumuron; Methoxychlor; Methozyfenozide; Novaluron; Noviflumuron; Phenothrin
	MT	Acrinathrin
	M	Niclosamide
	IGR	Chlorfluazuron; Methoprene;
	RP (bird)	Anthraquinone (birds); Dimethyl phthalate (insect); Dipropyl isocinchomerate (fly); Ethyl butylacetylasminopropionate
	AC	Bifenazate; Bromopropylate; Flucycloxuron; Hexythiazox
	F	Azoxystrobin; Benomyl; Bitertanol; Boscalid; Captan; Carbendazim; Carpropamid; Chlorothalonil; Diclofluanid; Diclomezine; Diethofencarb; Dimethomorph; Flutolanil; Folpet; Fosetyl; Imibenconazole; Iprovalicarb; Kasugamycin; Mancozeb; Mandipropamid; Maneb; Mepanipyrim; Mepronil; Metiram; nitrithal-isopropyl; Oxine-copper; Pencycuron; Phosphorus acid; Phthalide; Procymidone; Propamocarb; Tolylfluanid; Trifloxystrobin; Triforine; Validamycin; Vinclozolin; Zineb; Zoxamide
	FST	Ethrimol; Fenfuram; Fenpiclonil
	H	Aclonifen; Aminopyralid; Amitrole; Azimsulfuron; Benfluralin; Benoxacor; Bensulfuron methyl; Bifenox; Bromacil; Bromobutide; Carbetamide; Chlorasulam methyl; Chlorotoluron; Chlorsulfuron; Cinosulfuron; Clomeprop; Cyclosulfamuron; Cyhalofop; Daimuron; Dalapon; Daminozide; Desmedipham; Diclosulam; Dithiopyr; Ethalfluralin; Ethoflumesate; Fenchlorazole; Fenclorim; florasulam; Flucarbazone-sodium; Flumetsulam; Flumeturon; Flupropanate; flupyrsulfuron; fluridone; fluroxypyr; Fluthiacet; Imazamethabenzmethyl; Imazapyr; Imazaquin; Imazethapyr; Isozaben; Lenacil, Mefenacet; Metosulam; metsulfuron methyl; Napropamide, Neburon; Nicosulfuron; Norflurazon; Oryzalin; Oxabetrinil; Oxadiazon; Oxyfluorfen; Penoxulam; Pentanochlor; Phenmedipham; Picloram; Pretilachlor; Pimisulfuron; Prodiamine; Propaquizafop; Propazine; Propham; Propineb; Propizamide; Triasulfuron; Tribenuron; Trifluralin; Triflusulfuron-methyl
	PGR	Chlorpropham; Cloxyfonac; Dikegulac; Flumetralin; Flurenol; Gibberellic acid; Inabenfide; Maleic hydrazide; 2-(1-Naphthyl) Acetamide; Naptalam; Triflumuron
	SY	Piperonyl butoxide

compared to insecticides. The number of herbicides that are unlikely to present acute hazard is as much as 37.1% of the total as compared to 12.6% insecticides. Thus it may be noted that herbicides as a pesticide category are safer or less hazardous than other pesticides especially insecticides.

The other points those can be substantiated in favour of herbicides in comparison to other pesticides are as follow:

Lower pesticide load: With the advent of new herbicides, the application rates have come down drastically. Sulfonylureas, for example, are applied at very low rates a.i (4-30 g/ha) which lead to low herbicides load in the environment. Many herbicides are tightly bound to soil organic matter with little risk of their horizontal or vertical movement. Further as the Indian agriculture is predominant by marginal and small farmers, there is little chance of a large scale use of a single herbicide and thereby possibility of contamination of surface and ground water.

Lower or no residues in food and environment: The waiting period between application and crop harvest is longer in herbicides in comparison to insecticides and fungicides. More the interval more will be the exposure of the herbicide to pressures of degradation or dissipation acting on them. Thus by default the interval between application and crop harvest is very long which ensures their degradation and dissipation to sub-toxic levels. This is in direct contrast to other pesticides which are quite often used at the later stages of crop growth especially flowering and fruiting stages. Thus, there are good chances of findings residues of such pesticides on the crop produce.

The above discussion is not intended to give clear chit to herbicides. Some are distinctly different from other pesticides as discussed below:

-Herbicides are crop specific and different chemicals are used to control the same weed. For example, atrazine is used in maize and butachlor in rice to control the same *Echinochloa* sp this is referred to as selectivity.

-Herbicide dose is of great importance. At higher dose herbicides may significantly damage the crop while other pesticides may not affect the crop.

-Uniform application is critical with herbicides. That is why these are recommended at active ingredient basis and applied after calibration of the sprayers. The other pesticides are applied at recommended concentration.

-Cautious application is of great concern as any spray drift reaching the susceptible crop plants grown in the adjoining fields may damage them.

-There is need to educate farmers about the dangers of using herbicides meant for Herbicide resistant crops(HRCs) on non-herbicide resistant crops while it is not relevant in the case of insecticides. For instance, insecticides could be safely used both in Bt-cotton as well as in non-Bt cotton.

Other methods of classification

According to its chemical structure, pesticides are classified into different families, ranging from organochlorine and organophosphorus compounds to inorganic compounds. The most common way to classify them based on their chemical structure is split into four main groups (Garcia *et al* 2012): Organochlorine (stable compounds too persistent in the environment and tend to accumulate in fatty tissue (Waliszewski *et al*. 2002, 2003 a, b, 2004); Organophosphates **(**they are esters derived from phosphoric acid. In man act on the central nervous system by inhibiting acetyl cholinesterase, Sorgob and Vilanova 2002); Carbamates **(**they are esters derived from acids or dimethyl N-methyl carbamic acid are used as insecticides, herbicides, fungicides and nematicides. Are less persistent than organochlorines and organophosphates), Pyrethroids **(**they originate from natural insecticide derived from pyrethrum extract derived from chrysanthemum flowers, known as pyrethrins) and others (triazine herbicides, ureic, hormonal, amides, nitro compounds, benzimidazoles, ftalamidas, bipyridyl compounds, ethylene dibromide, sulfur containing compounds, copper or mercury).

Effect of formulation

Pesticides are used throughout the world as mixtures called formulations. They contain adjuvants, which are often kept confidential and are called inerts by the manufacturing companies, plus a declared active principle, which is usually tested alone. Mesnage *et al*. (2014) tested the toxicity of nine pesticides, comparing active principles and their formulations, on three human cell lines (HepG2, HEK293, and JEG3). Glyphosate, isoproturon, fluroxypyr, pirimicarb, imidacloprid, acetamiprid, tebuconazole, epoxiconazole, and prochloraz constitute, respectively, the active principles of three major herbicides, three insecticides, and three fungicides. They measured mitochondrial activities, membrane degradations, and caspases 3/7 activities. Fungicides were the most toxic from concentrations 300–600 times lower than agricultural dilutions, followed by herbicides and then insecticides, with very similar profiles in all cell types. Despite its relatively benign reputation, Glyphosate was among the most toxic herbicides and insecticides tested. Most importantly, eight formulations out of nine were up to one thousand times more toxic than their active principles. Their results challenge the relevance of the acceptable daily intake for pesticides because this norm is calculated from the toxicity of the active principle alone. Chronic tests on pesticides may not reflect relevant environmental exposures if only one ingredient of these mixtures is tested alone.

The previous investigation by Mesnage *et al.* (2013) showed unexpected active principles for human cell toxicity in the adjuvants of glyphosate-based herbicides. Ethoxylated adjuvants found in glyphosate based herbicides were up to 10000 times more toxic than the so-called active AP glyphosate (Mesnage *et al.* 2013) and are better candidates for secondary side effects. This may explain in vivo long-term toxicity from 0.1 ppb of the formulation and other toxicities that were not explained by a consideration of glyphosate alone (Seralini *et al.* 2013; Gasnier *et al.* 2009; Peluso *et al.* 1998; Walsh *et al*. 2000). These adjuvants also have serious consequences to the health of humans and rats in acute exposures (Bradberry *et al.* 2004; Adam *et al.* 1997).

Adjuvants in pesticides are generally declared as inerts, and for this reason they are not tested in long-term regulatory experiments. It is thus very surprising that they amplify up to 1000 times the toxicity of their active principles in 100% of the cases where they are indicated to be present by the manufacturer. In fact, the differential toxicity between formulations of pesticides and their active principles now appears to be a general feature of pesticides toxicology. As we have seen, the role of adjuvants is to increase AP solubility and to protect it from degradation, increasing its half-life, helping cell penetration, and thus enhancing its pesticidal activity (Marutani and Edirveerasingam 2006) and consequently side effects. They can even add their own toxicity (Mesnage 2013). The definition of adjuvants as "inerts" is thus nonsense; even if the US Environmental Protection Agency has recently changed the appellation for "other ingredients" pesticide adjuvants should be considered as toxic "active" compounds.

Government initiatives

The "Monitoring of Pesticide Residues at National Level" scheme has been initiated for monitoring and analysis of pesticide residues in agricultural commodities in different agro-ecological regions of the country. During the last five years, the incidence of residues in various commodities has shown an increase from 1.2 to 2.6% (GOI 2016).

In 2005, the Joint Parliamentary Committee (JPC) set out a clear agenda for governments to ensure the safe use of pesticides (Bhushan *et al.* 2013). The committee recommended to make mandatory the setting of maximum residue limits (MRL) for pesticides before registering it, setting MRLs for deemed registered pesticides, reviewing the set MRLs for compliance with the Acceptable Daily Intake (ADI) of pesticides and monitoring pesticide residues regularly. In their paper, (Bhushan *et al.* 2013) reviewed the state of pesticide regulations in India from a food safety perspective in the light of the recommendations made by the JPC. Pesticide use in India is regulated by the Central Insecticides Board and Registration Committee (CIBRC) and the Food Safety and Standards Authority of India (FSSAI). The CIBRC registers pesticides for crops while the FSSAI sets the maximum residue limits of pesticides for the crops it has been registered for. It was reported that recommendations of JPC have not been followed properly. Of the 234 pesticides registered in the country, the FSSAI has not set MRLs for 59 pesticides. A review of MRL status of 20 commonly used and recommended pesticides showed that the MRLs set for 18 pesticides are not complete. MRLs have not been set for all the crops these pesticides have been registered for. A few MRLs have been set for crops for which the corresponding pesticide is not registered. MRLs have been set for broad groups like fruits, vegetables and food grains rather than specific crops while the pesticides have been registered for specific crops. In the paper, the Theoretical Maximum Daily Intakes (TMDI) for 20 pesticides was calculated to check the compliance of these pesticides with ADI. The TMDIs of seven pesticides was above the corresponding ADIs for adults while TMDIs for nine pesticides was higher than ADI for children. The comparison of TMDIs with reference doses (RfD), US EPA equivalent of ADI, showed that they were higher than corresponding RfDs for six and eight pesticides for adults and children, respectively. A review of 11 important crops in India was done—wheat, paddy, apple, mango, potato, cauliflower, black pepper, cardamom, tea, sugarcane and cotton. The paper shows that the pesticide recommendations made by state agriculture universities, agriculture departments and other boards for a crop do not adhere to the pesticides that the CIBRC has registered for those crops. The agriculture universities, departments and boards have recommended many pesticides that have not been registered for some crops. Recommendations of waiting periods for pesticides are not complete. An analysis of 10 common pesticides showed that waiting periods for many of their registered uses (crop-pest/weed/disease combination) have not been recommended. The farmers were found to be unaware of the registered pesticides. They mostly followed the pesticides as the dealers recommended them. The outreach of state agriculture universities and departments to the farmers was minimal.

The DAC&FW have taken a number of measures to ensure that chemical pesticides are employed as a last resort to pest management. The department has revised 68 Integrated Pest Management (IPM) Packages of Practices for major crops giving impetus to ecological and cultural techniques of pest management (GOI 2016). Capacity building and training programmes are held annually to sensitize stakeholders (farmers, extension officers, pesticides dealers, *etc*) about various facets of pest management. "Grow Safe Food" campaign has been launched to create awareness among the stakeholders regarding judicious use of Plant Protection chemicals. Efforts are in the pipeline to explore usage of Information Technology (IT) in pest management to ensure that pest assessment report and advisories thereon are disseminated on real time basis. In India, the Bureau of Indian Standards (BIS) adopted the 'Requirements for Good Agricultural Practices' in 2010. It recommends practices for every stage of farming from land preparation to post harvest supply chain (Bureau of Indian Standards 2010).

Conclusion

Pesticides are inevitable to prevent losses in agriculture. The number of pests attacking crops has increased from 1940s. The demand of pesticides especially herbicides is increasing due to shortage of labour in agriculture. Based on active principle herbicides as a category are less hazardous than the insecticides but it is intended not to give clear chit to herbicides; after all the ultimate toxicity depends on the formulation. Therefore, residual limits need to be set based on formulations. The recommendations made for pesticides in India are unsatisfactory at multiple levels. There is lack of uniformity in the recommendations. Therefore, it is difficult to either set the MRLs of a pesticide for appropriate food commodities or to monitor pesticide residues. The State Agricultural Universities do not consider the recommendations of Central Insecticide Board and Registration Committee (CIBRC) while recommending pesticides. They have their own research mechanism that they follow. This leads to the difference between recommendations and makes it difficult to monitor the pesticides residues in crops. The MRLs need to be completed for all pesticides and for all crops the pesticides have been recommended for. The MRLs for some commodities like fruits and vegetables need to be revised and brought down to a level at which the TMDIs do not exceed ADIs.

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