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Classification of herbicides according to chemical family for weed resistance management strategies – an update

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Summary

There are inaccuracies in the chemical families of the WSSA and HRAC herbicide classification systems which could limit their practical use in herbicide-based weed management strategies. In essence, these inaccuracies could be divided into four parts: (i) the nomenclature of many of the chemical families is not correct, (ii) distinct active ingredients are grouped in same chemical families, (iii) many chemical families have been repeated in at least two modes of action/herbicide groups, and (iv) many active ingredients have not been assigned to chemical family, herbicide group or mode of action. The aim of this study was to revise the current classifications and to propose corrections for the current ones. Detailed investigations on chemical structure of the active ingredients of the registered herbicides showed that some moieties have the same mechanisms of action. According to this study, these moieties have been assigned to the names of chemical families and active ingredients are then classified within the chemical families accordingly. This study has 119 chemical families, compared with 145 in the WSSA system and 58 in the HRAC system. A major priority of this study is the number of active ingredients covered; we included 410 active ingredients with known mechanisms of action and herbicide groups, more than 100 active ingredients more than the current classification systems. Overall, this study provides better opportunities for the management of resistance to herbicides through the application of improved pure and applied knowledge.

Keywords: herbicide resistance, cross-resistance, chemical structure, active ingredient, mode of action, Herbicide Resistance Action Committee.

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Introduction

Weed resistance to herbicides has become a major concern in crop production worldwide that necessitates special attention. Resistance to herbicides is often attributed to lack of rotational programmes of herbicides and to continuous applications of herbicides with the same sites of action (Beckie *et al.*, 2006). There are numerous studies about the advantages of rotational application of herbicide groups in delaying the evolution of herbicide-resistant weeds (Stephenson *et al.*, 1990; Gill, 1995; Itoh *et al.*, 1999; Singh *et al.*, 1999; Hartmann *et al.*, 2000; Légère *et al.*, 2000; Hashem *et al.*, 2001; Schmidt *et al.*, 2004). Thus, a true understanding of the sites of action of herbicides is essential for strategic planning of herbicide-based weed control.

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An effective way to design a good rotational herbicide programme would be to use classification systems of these chemicals. Currently, there are two systems of classification for herbicides: one that belongs to the WSSA (2007) and the other that has been developed by the HRAC (2010). The former classification system uses numbers, whilst the latter uses letters for classifying herbicides. Generally, the WSSA system includes 200 active ingredients and 145 chemical families and the HRAC system covers 291 active ingredients grouped in 58 chemical families. However, these two systems both have problems with the designation of chemical families that have negative implications for chemical management of weeds. In a broad sense, we divide these difficulties into two aspects. From a chemistry point of view, (i) there are many active ingredients with unknown chemical family, (ii) there are some mistakes in the nomenclature of chemical families, and (iii) some active ingredients have been grouped in a chemical family when they are distinct. In the latter case, such an issue may result in incorrect decision-making over the selection of herbicides to be used in a rotational programme. As an example, if two distinct active ingredients are grouped in the same chemical family, it may be incorrectly inferred that as these two active ingredients are members of a same chemical family, they will show the same cross-resistances. From a weed management point of view, there are 100 active ingredients that have not been assigned to any mechanism of action, chemical family and herbicide group in both classification systems. This poses difficulties in weed management programmes and could potentially accelerate the occurrence of resistance.

Considering the shortcomings stated above, this study aimed at revising the current classification systems, with the ultimate goals of correcting the record and in supporting better planning of weed management strategies regarding rotational applications of herbicides. The objectives of this study can be summarised as follows: (i) corrections to be made in the nomenclature of chemical families based on the rules that govern organic chemistry, (ii) distinct active ingredients that have been grouped in one chemical family to be shifted to appropriate families, (iii) active ingredients with unknown chemical family and many active ingredients repeated with at least two mechanisms of action/herbicide groups to be assigned to appropriate chemical family and (iv) over 100 active ingredients with known mechanisms of action, herbicide groups and chemical families to be added to both classification systems. The authors note that a mechanism of action directly depends on its active ingredient; thus, the mechanism of action of most active ingredients can be identified merely on the basis of the chemical structure. As a result, the names of some chemical families (as it stems from the active ingredients) are partially or thoroughly revised. Addition of more than 100 active ingredients may also be an important step towards decreasing the occurrence of herbicide resistance.

Chemical basis of this study

The basis of the new classification system relies on the fact that it is the active ingredient that determines its respective chemical family and ultimately the mechanism of action it demonstrates (or it should be grouped in). However, less familiarity with rules that govern the nomenclature of organic compounds is the main cause of mistakes that exist in the HRAC and WSSA classifications. Some examples will be given to clarify this. Chemical family aryloxyphenoxypropionate (WSSA group 1 and HRAC group A) exist in both classifications. This chemical family includes some aromatic active ingredients, for example clodinafop, fenoxaprop, fluazifop, haloxyfop, propaquizafop and quizalofop. However, the correct name should be hydroxyphenoxyisopropionic acid. The justification is that according to IUPAC (1979), the term 'aryl' refers to a univalent aromatic hydrocarbon that only contains carbon and hydrogen atoms. However, in the current classification systems, the term 'aryl' has been used for aromatic compounds that also contain other chemical elements other than carbon and hydrogen, such as nitrogen; using the term 'aryl' for a heterocyclic aromatic compound is not correct. Also, according to the WSSA and HRAC systems, the chemical family of the active ingredients clethodim and tralkoxydim from acetyl CoA carboxylase (ACCase) inhibitors is cyclohexanedione. Cyclohexane consists of a six-membered ring with six carbon atoms that are connected to each other with six single bonds, whilst such a chemical structure belongs to cyclohexene. The difference between cyclohexene and cyclohexane relates to the replacement of a single bond by a double bond in the ring of the latter. The suffix '-dione' in cyclohexanedione indicates the replacement of two $>CH_2$ groups by >CO in the ring, whilst in the active ingredients of this chemical family, one $>CH_2$ group is replaced by >CO in the ring. Thus, the nomenclature of this chemical family should be hydroxyoxocyclohexenecarbaldehyde oxime. As another example, 32 active ingredients within the photosystem II inhibitors have the moiety (moiety is a part of a molecule that may include either whole functional groups or parts of functional groups as substructures; a functional group has similar chemical properties whenever it occurs in different compounds) triazinediamine and thus their chemical family in this study is named triazinediamine. Within the

Table 1 The numbers of mechanisms of action, herbicide groups, chemical families and active ingredients in each classification system

Classification systems	Mechanisms of action	HRAC groups	WSSA groups	Chemical families	Active ingredients
This study	16	23	28	119	430
HRAC (2010)	16	23	26	58	291
WSSA (2007)	16	22	28	145	200

HRAC system, the name of the chemical family of these active ingredients is triazine. Although triazine exists in all active ingredients within this chemical family, such a nomenclature is not correct because triazine also exists in some active ingredients of acetohydroxy acid synthase (AHAS) or acetolactate synthase (ALS) inhibitors. However, all 32 active ingredients within photosystem II inhibitors have two amine groups in their chemical structure, and thus, the more appropriate nomenclature for the chemical family of these active ingredients should be triazinediamine.

One principle used in naming the chemical families in this study is as follows. Some active ingredients have different forms, such as acid or ester. An example is diclofop (acid form) and diclofop-methyl (ester form). However, because different forms of a compound have the same mechanism of action (possibly with different degrees of effectiveness), where the moiety of the active ingredient is an ester, the chemical family is named as an acid form, to prevent an excessive number of chemical families. Also, in the presented classification, only the acid form of an active ingredient is mentioned, as an example to show the position of an active ingredient within a mechanism of action, chemical family and herbicide group. Also, although the classification of the active ingredients within the chemical families has been based on their similarity regarding their moieties, in some cases the nomenclature has not been solely based on the chemical structure of the moiety. However, such an approach does not interfere with differences in the active ingredients and has been aimed at improving readability.

Highlighting the differences between the WSSA, HRAC and present classification systems

As observed, this study has 119 chemical families compared with 145 in the WSSA (2007) system and 58 in the HRAC (2010) system (Table 1). In total, the present study covered 430 active ingredients, which was 230 and 139 compounds more than the WSSA and HRAC systems, respectively. The number of chemical families included in each mechanism of action in this study showed decreases, increases or no change compared with the WSSA and HRAC systems (Table 2). The highest increases in number of families have been in the unknown, carotenoid biosynthesis inhibitors, photosystem II inhibitors, synthetic auxins and mitosis inhibitors. Compared with the WSSA system, most of

Table 2 The numbers of chemical families in each mechanism of action in different classification systems

	No. chemical families		
Mechanisms of action	This study	HRAC (2010)	WSSA (2007)
Acetyl CoA carboxylase inhibitors	4	3	11
Acetolactate synthase or acetohydroxy acid synthase (AHAS) inhibitors	9	5	14
Photosystem II inhibitors	21	11	30
Photosystem I inhibitors	1	1	4
Protoporphyrinogen oxidase (PPG oxidase or protox) inhibitors	13	8	15
Carotenoid biosynthesis inhibitors	13	1	20
Enolpyruvylshikimate-3-phosphate synthase inhibitors	2	1	1
Glutamine synthetase inhibitors	2	1	1
Dihydropteroate synthetase inhibitors	1	1	3
Mitosis inhibitors	18	11	15
Cellulose inhibitors	5	4	5
Oxidative phosphorylation uncouplers	1	1	1
Fatty acid and lipid biosynthesis inhibitors	3	4	6
Synthetic auxins	12	4	10
Auxin transport inhibitors	2	2	2
Unknown	12	0	7

Table 3 New active ingredients added to the HRAC (2010) classification system with their corresponding chemical families, herbicide groups and mechanisms of action

Chemical families	New active ingredients	Mechanisms of action	HRAC groups	WSSA groups*
Hydroxyoxocyclohexen-ecarbaldehyde oxime	Cloproxydim	Acetyl CoA carboxylase inhibitors	A	1
Hydroxyphenoxyisopropionamide	Isoxapyrifop			
Hydroxyphenoxyisopropionic acid	Chlorazifop, Clofop, Fenthiaprop, Kuicaoxi, Trifop, Trifopsime			
Benzoyltriazinediol	Triafamone	Acetolactate synthase or acetohydroxy acid synthase inhibitors	B	2
Phenoxypyrimidinediol	Pyribambenz-isopropyl			
Sulfonylurea	Iofensulfuron, Metazosulfuron, Methiopyrisulfuron, Monosulfuron, Zuomihuanglong			
Aminotriazinedione	Ametridione	Photosystem II inhibitors	C_1	5
Aminotriazinone	Amibuzin, Ethiozin, Isomethiozin			
Carbamoyloxycarbanilic acid	Chlorprocarb, Phenisopham			
Phenyl aminopyridazone	Brompyrazon			
Pyrimidinediamine	Iprymidam, Tioclorim			
Triazinediamine	Atraton, Aziprotryne = Aziprotryn, Chlorazine, CP 17029, Cyanatryn, Cyprazine, Dipropetryn, Eglinazine, Fucaojing, Ipazine, Mesoprazine, Methometon, Methoprotryne = Methoprotryn, Procyazine, Proglinazine, Sebuthylazine, Secbumeton, Simeton			
Uracil	Isocil			
Benzothiazolylurea	Benzthiazuron		C_2	7
Chlorophenyl acrylamide	Chloranocryl = Dicryl			
Chlorophenyl valeramide	Erlujixiancaoan, Monalide			
Isoxazolylurea	Monisouron			
Phenylthiourea	Methiuron			
Phenylurea	Bromuron, Buturon, Chloreturon, Defenuron, Difenoxuron, Fluothiuron, Metobenzuron, Monuron, Parafluron, Tetrafluron			
Thiadiazolylurea	Buthiuron, Thiazafluron			
Dihalohydroxybenzonitrile	Bromobonil, Chloroxynil, Iodobonil		C_3	6
Pyridinium	Cyperquat, Diethamquat, Morfamquat	Photosystem I inhibitors	D	22
Nitrophenoxybenzene	Chlornitrofen, Etnipromid, Fluorodifen, Fluoronitrofen, Fucaomi, Furyloxyfen, Nitrofen, Nitrofluorfen	Protoporphyrinogen oxidase (PPG oxidase or protox) inhibitors	E	14
Phenylpyrazole	Nipyraclofen			
Phenylpyrroledione	Chlorphthalim, Flumipropyn			
Phenyltrifluoromethyluracil	Flupropacil, Tiafenacil			
Trifluoromethylphenoxy-pyridinecarboxamide	Flufenican	Carotenoid biosynthesis inhibitors	F_1	12
Trifluoromethylphenyl -aminopyridazone	Metflurazon			
Dioxocyclohexanecarbaldehyde	Fenquinotrione, Ketospiradox		F_2	28 (27)
Pyrazolecarbaldehyde	Tolpyralate			
Phosphonomethylglycinamide	Huangcaoling	Enolpyruvylshikimate-3-phosphate synthetase inhibitor	G	9
Sulfanilylcarbamic acid	Carbasulam, Fenasulam	Dihydropteroate synthetase inhibitors	I	18

Table 3 (Continued)

Chemical families	New active ingredients	Mechanisms of action	HRAC groups	WSSA groups*
Dinitroaniline	Chlornidine, Dipropalin, Fluchloralin, Isopropalin, Methalpropalin, Nitralin, Prodiamine, Profluralin, Prosulfalin	Mitosis inhibitors	K_1	3
Phosphoramidothioic acid	DMPA, Shuangjiaancaolin			
Carbanilic acid	Barban, BCPC, CEPC, Chlorbufam, CPPC, Swep		K_2	23
Chloroacetamide	Butenachlor, Allidochlor = CDAA, CDEA, Delachlor, Diethatyl, Ethachlor, Ethaprochlor, Prynachlor, Terbuchlor, Xylachlor		K_3	15
Sulfonylisoxazoline	Fenoxasulfone			
Sulfonyltriazolecarboxamide	Epronaz			
Trifluoromethanesulfonanilide	Mefluidide, Perfluidone			
Dinitrophenol	Dinofenate, Dinoprop, Dinosam, Etinofen, Medinoterb	Oxidative phosphorylation uncouplers	M	24
Thiocarbamic acid	Di-allate = Diallate, Ethiolate, Isopolinate, Methiobencarb	Fatty acid and lipid biosynthesis inhibitors	N	8
Chlorobenzoic acid	Tricamba	Synthetic auxins	O	4
Chlorophenoxyacetic acid	2,4,5-T, 3,4-DA, 4-CPA			
Chlorophenoxybutyric acid	2,4,5-TB, 3,4-DB, 4-CPB			
Chlorophenoxyisopropionic acid	3,4-DP, 4-CPP, Cloprop, Fenoprop			
Chlorophenylacetic acid	Chlorfenac = Fenac			
Chlorophenylpropionic acid	Chlorfenprop			
Chloropicolinic acid	Halauxifen			
Chloropyrimidinecarboxylic acid	Aminocyclopyrachlor			
Organic arsenic	CMA, MAA, MAMA	Unknown	Z	17

*Group number enclosed in parenthesis is the new number suggested by WSSA (2011) instead of the adjacent number out of the parenthesis.

the mechanisms of action showed decreases in their number of chemical families. The number of chemical families in the unknown, mitosis inhibitors, synthetic auxins, enolpyruvylshikimate-3-phosphate (EPSP) synthase inhibitors and glutamine synthetase inhibitors increased, whilst numbers in the cellulose and auxin transport inhibitors, and oxidative phosphorylation uncouplers remained unchanged.

Tables 3 and 4 show the active ingredients added to the lists released by the HRAC and WSSA in 2010 and 2007 respectively. A marked increase in the number of active ingredients within the classification is undoubtedly an important achievement of this study. As explained before, it is the chemical structure of the active ingredient which determines its mechanism of action. Based on this fact, detailed investigations on chemical structure of the active ingredients of the registered herbicides showed that some moieties have same mechanisms of action. According to this study, these moieties have been assigned to the names of chemical families and active ingredients are then classified within the chemical families accordingly. Such a classification method resulted in the addition of more than 100 active ingredients, with known mechanisms of action and HRAC and WSSA groups, to the current list of active ingredients in HRAC and WSSA classifications. For instance, the new active ingredient metazosulfuron does not exist in HRAC (2010) and WSSA (2007) classifications. In this study and as a result of having the same moiety with active ingredients within sulfonylurea chemical family, it has been grouped under AHAS or ALS inhibitors from groups B (HRAC) & 2 (WSSA). Lee *et al.* (2011) also studied metazosulfuron for paddy weeds control and found it an efficient herbicide with very limited environmental side effects. The obsolete herbicide chlorprocarb is an example of a herbicide where the mechanism of action of has not been identified to date. However, because chlorprocarb includes carbamoyloxycarbanilic acid, it could be grouped as a photosystem II inhibitor, based on the current approach to chemical family nomenclature.

As shown, the present classification has 139 active ingredients more than the HRAC system and 230 active ingredients more than the WSSA system. It should also be noted that Table 3 only consists of those active ingredients for which an agreement exists

Table 4 New active ingredients added to the WSSA (2007) classification system with their corresponding chemical families, herbicide groups and mechanisms of action

Chemical families	New active ingredients	Mechanisms of action	HRAC groups	WSSA groups*
Hydroxyoxocyclohexenecarbaldehyde oxime	Cloproxydim, Profoxydim	Acetyl CoA carboxylase inhibitors	A	1
Hydroxyphenoxyisopropionamide	Isoxapyrifop			
Hydroxyphenoxyisopropionic acid	Chlorazifop, Clofop, Fenthiaprop, Kuicaoxi, Trifop, Trifopsime			
Benzoyltriazinediol	Triafamone	Acetolactate synthase or acetohydroxy acid synthase inhibitors	B	2
Phenoxypyrimidinediol	Pyriminobac, Pyribambenz-isopropyl			
Phenylhydroxymethylpyrimidinediol	Pyrimisulfan			
Phenylthiopyrimidinediol	Pyriftalid			
Sulfonylaminocarbonyltriazolinone	Thiencarbazone-methyl			
Sulfonylurea	Iofensulfuron, Mesosulfuron, Metazosulfuron, Methiopyrisulfuron, Monosulfuron, Orthosulfamuron, Oxasulfuron, Propyrisulfuron, Tritosulfuron, Zuomihuanglong			
Triazolopyrimidinesulfonamide	Metosulam, Pyroxsulam			
Aminotriazinedione	Ametridione	Photosystem II inhibitors	C_1	5
Aminotriazinone	Amibuzin, Ethiozin, Isomethiozin			
Carbamoyloxycarbanilic acid	Chlorprocarb, Phenisopham			
Phenyl aminopyridazone	Brompyrazon			
Pyrimidinediamine	Iprymidam, Tioclorim			
Triazinediamine	Atraton, Aziprotryne = Aziprotryn, Chlorazine, CP 17029, Cyanatryn, Cyprazine, Dimethametryn, Dipropetryn, Eglinazine, Fucaojing, Ipazine, Mesoprazine, Methometon, Methoprotryne = Methoprotryn, Procyazine, Proglinazine, Propazine, Sebuthylazine, Secbumeton, Simeton, Terbutryn = Terbutryne			
Uracil	Isocil, Lenacil			
Dibromohydroxybenzaldehyde oxime	Bromofenoxim		C_3	6
Dihalohydroxybenzonitrile	Bromobonil, Chloroxynil, Iodobonil			
Phenylpyridazinol	Pyridafol			
Benzothiazolylurea	Benzthiazuron		C_2	7
Chlorophenyl acrylamide	Chloranocryl = Dicryl			
Chlorophenyl valeramide	Erlujixiancaoan, Monalide, Pentanochlor = Solan			
Isoxazolylurea	Isouron, Monisouron			
Phenylthiourea	Methiuron			
Phenylurea	Bromuron, Buturon, Chlorbromuron, Chloreturon, Chloroxuron, Defenuron, Difenoxuron, Fenuron, Fluothiuron, Metobenzuron, Metobromuron, Monuron, Neburon, Parafluron, Tetrafluron			
Thiadiazolylurea	Buthiuron, Ethidimuron, Thiazafluron			
Pyridinium	Cyperquat, Diethamquat, Morfamquat	Photosystem I inhibitors	D	22

Table 4 (Continued)

Chemical families	New active ingredients	Mechanisms of action	HRAC groups	WSSA groups*
Bipyrazole	Pyraclonil	Protoporphyrinogen oxidase (PPG oxidase or protox) inhibitors	E	14
Nitrophenoxybenzene	Chlomethoxyfen, Chlornitrofen, Etnipromid, Fluorodifen, Fluoronitrofen, Fucaomi, Furyloxyfen, Halosafen, Nitrofen, Nitrofluorfen			
Phenylimidazolidinedione	Profluazol			
Phenyliminothiadiazoline	Thidiazimin			
Phenyloxazolidinedione	Pentoxazone			
Phenylpyrazole	Fluazolate, Nipyraclofen			
Phenylpyrroledione	Chlorphthalim, Cinidon-ethyl, Flumipropyn			
Phenyltriazolinone	Bencarbazone			
Phenyltrifluoromethyluracil	Benzfendizone, Flupropacil, Saflufenacil, Tiafenacil			
Trifluoromethylphenoxychlorobenzene	Ethoxyfen			
Trifluoromethylphenoxypyridinecarboxamide	Flufenican	Carotenoid biosynthesis inhibitors	F_1	12
Trifluoromethylphenyl aminopyridazone	Metflurazon			
Dioxocyclohexanecarbaldehyde	Fenquinotrione, Ketospiradox, Tefuryltrione, Tembotrione		F_2	28 (27)
Isoxazolecarbaldehyde	Isoxachlortole			
Oxobicyclooctenecarbaldehyde	Benzobicyclon, Bicyclopyrone			
Pyrazolecarbaldehyde	Pyrasulfotole, Tolpyralate			
Phosphonomethylglycinamide	Huangcaoling	Enolpyruvylshikimate-3-phosphate synthase inhibitor	G	9
Hydroxy methylphosphinoylhomoalaninamide	Bilanafos	Glutamine synthetase inhibitor	H	10
Sulfanilylcarbamic acid	Carbasulam, Fenasulam	Dihydropteroate synthetase inhibitors	I	18
Benzyl propionamide	Tebutam = Butam	Mitosis inhibitors	K_1	3
Dinitroaniline	Butralin, Chlornidine, Dinitramine, Dipropalin, Fluchloralin, Isopropalin, Methalpropalin, Nitralin, Profluralin, Prosulfalin			
Phosphoramidothioic acid	Amiprophos, Butamifos, DMPA, Shuangjiaancaolin			
Carbamoylmethylphosphorodithioic acid	Piperophos		K_3	15
Chloroacetamide	Allidochlor = CDAA, Butenachlor, CDEA, Delachlor, Diethatyl, Dimethachlor, Ethachlor, Ethaprochlor, Pethoxamid, Propisochlor, Prynachlor, Terbuchlor, Xylachlor			
Diphenylacetamide	Diphenamid			
Naphthoxyisopropionamide	Naproanilide			
Phenyloxotriazolinecarboxamide	Ipfencarbazone			
Sulfonylisoxazoline	Fenoxasulfone, Pyroxasulfone			
Sulfonyltriazolecarboxamide	Cafenstrole, Epronaz			
Trifluoromethanesulfonanilide	Mefluidide, Perfluidone			
Carbanilic acid	Barban, BCPC, CEPC, Chlorbufam, Chlorpropham, CPPC, Propham, Swep		K_2	23
Dichlorobenzothioamide	Chlorthiamid	Cellulose inhibitors	L	20
Phenyltriazolecarboxamide	Flupoxam			(28)
Fluoromethyltriazinediamine	Indaziflam, Triaziflam			(29)

Table 4 (Continued)

Chemical families	New active ingredients	Mechanisms of action	HRAC groups	WSSA groups*
Dinitrophenol	Dinofenate, Dinoprop, Dinosam, Dinoseb, DNOC, Etinofen, Medinoterb	Oxidative phosphorylation uncouplers	M	24
Thiocarbamic acid	Di-allate = Diallate, Dimepiperate, Ethiolate, Isopolinate, Methiobencarb, Orbencarb, Tiocarbazil	Fatty acid and lipid biosynthesis inhibitors	N	8
Dihydrobenzofuranyl sulphonate	Benfuresate			16
Chlorobenzoic acid	2,3,6-TBA, Chloramben, Tricamba	Synthetic auxins	O	4
Chlorooxobenzothiazolylacetic acid	Benazolin			
Chlorophenoxyacetic acid	2,4,5-T, 3,4-DA, 4-CPA			
Chlorophenoxybutyric acid	2,4,5-TB, 3,4-DB, 4-CPB			
Chlorophenoxyisopropionamide	Clomeprop			
Chlorophenoxyisopropionic acid	3,4-DP, 4-CPP, Cloprop, Fenoprop			
Chlorophenylacetic acid	Chlorfenac = Fenac			
Chlorophenylpropionic acid	Chlorfenprop			
Chloropicolinic acid	Halauxifen			
Chloropyrimidinecarboxylic acid	Aminocyclopyrachlor			
Chloroquinolinecarboxylic acid	Quinmerac			
Organic arsenic	CMA, MAA, MAMA	Unknown	Z	17
Benzanilide	Etobenzanid			27 (26)
Benzyl butyramide	Bromobutide			
Benzyldihydrooxazinone	Oxaziclomefone			
Benzylurea	Cumyluron, Daimuron, Methyldymron			
Fluorenecarboxylic acid	Chlorflurenol = Chlorflurecol			
Pelargonic acid	Oleic acid			
Phenyl pyridylthiocarbamate	Pyributicarb			

*Group numbers enclosed in parenthesis are the new numbers suggested by WSSA (2011) instead of the adjacent number out of the parenthesis or they are being suggested for the first time (such as group number 29).

on their mechanisms of action according to the HRAC and WSSA. This is also a reason of why the number of new active ingredients in Table 3 does not match with the corresponding number given in Table 1. Having more active ingredients with known chemical family, mechanism of action and herbicide group (i) increases the flexibility in designing herbicide rotational programmes and (ii) decreases the chance of occurrence of cross-resistance. Knowing about herbicide chemical family grouping could serve as a short-term strategy for managing resistance to site of action (Beckie *et al*., 2006).

To further explain the benefits of this study in terms of herbicide resistance management, we give some examples. The chemical families of active ingredients hexazinone and metribuzin are aminotriazinedione and aminotriazinone, whilst according to HRAC (2010) classification, both active ingredients have been grouped in the triazinone chemical family. The suffix '-one' in triazinone indicates the replacement of one $>CH_2$ group by >CO in the triazine ring, whilst in hexazinone, two $>CH_2$ groups are replaced by >CO in the ring. Thus, attributing hexazinone to the triazinone chemical family is not correct. Accordingly, the correct name for this compound is triazinedione. Such a mistake in the nomenclature of this chemical family has resulted in classification of hexazinone and metribuzin in one chemical family. The considerable difference between the resistance levels of these two herbicides (Table 5) in the study of Perez-Jones *et al*. (2009) clearly shows that these two herbicides belong to different chemical families. However, one interpretation of the Perez-Jones *et al*. (2009) study is that these two herbicides belong to a same chemical family, but they

Table 5 Comparison of the resistance level to selected herbicides in the chemical families of HRAC and this study

Species	Herbicides	Chemical families		Resistance ratio	References
		HRAC (2010)	This study		
Amaranthus hybridus (L.) Amach	Diuron	Urea	Phenylurea	1.4	Fuerst *et al.* (1986)
	Tebuthiuron		Thiadiazolylurea	22	
Kochia scoparia (L.) Schrad	Diuron		Phenylurea	6.8	Mengistu *et al.* (2005)
	Tebuthiuron		Thiadiazolylurea	37.7	
Capsella bursa-pastoris (L.) Medik	Hexazinone	Triazinone	Aminotriazinedione	22.3	Perez-Jones *et al.* (2009)
	Metribuzin		Aminotriazinone	3.9	

had shown different resistance levels. In the WSSA (2007) classification system, two and three chemical families have been attributed to hexazinone and metribuzin respectively. Such an uncertainty in chemical families does not allow their usage in resistance studies, which may have implications for herbicide resistance. As another example, according to HRAC (2010), the chemical family of active ingredients diuron and tebuthiuron is urea, whilst this is not correct according to this study. Although urea exists in both active ingredients, due to considerable differences in the chemical structure of these two active ingredients, they are grouped in different chemical families in this study. Significant difference between the resistance level of diuron and tebuthiuron (Table 5), as founded by Mengistu *et al.* (2005) and Fuerst *et al.* (1986), clearly shows that these two herbicides do not belong to a same chemical family. Such a great difference in resistance level should not occur between herbicides of the same chemical family. In this study, the presence of urea in the chemical structure of the two active ingredients is not an acceptable reason for classification of these two active ingredients in a same family, because urea alone does not result in a same mechanism of action. In the WSSA (2007) classification, three chemical families have been attributed to these two active ingredients; thus one cannot use their chemical families in resistance studies. As another example, active ingredient metoxuron from photosystem II inhibitors has been classified under group 5 (C_1 in HRAC) in the WSSA 2007 classification system. This grouping has not been changed in the 2011 version of WSSA classification. However, this active ingredient is classified under group C_2 (group 7 in WSSA) in HRAC 2010 classification system. According to this study, this active ingredient contains the moiety phenylurea, and this moiety exists in groups 7 (WSSA) and C_2 (HRAC) in both classification systems. Thus, metoxuron should be classified under a same group.

The mistakes in the nomenclature of the chemical families in the HRAC and WSSA systems are shown in Tables S1 and S2 respectively. As observed, there are 17 and 27 chemical families in the HRAC and WSSA systems, respectively, which have mistakes in their nomenclature. Corrections were made based on the chemical structure of the active ingredient. For instance, currently the chemical family of the active ingredients oxadiargyl and oxadiazon from protoporphyrinogen oxidase (PPG oxidase or protox) inhibitors is oxadiazole. Oxadiazole consists of a five-membered ring with two carbon atoms, two nitrogen atoms and one oxygen atom that are connected to each other by two double bonds and three single bonds. However, in the active ingredients of this family, one $>CH_2$ group is replaced by >CO in the ring. Thus, the correct nomenclature for this compound is oxadiazolone.

Another inaccuracy in the current classifications was that some chemical families were repeated in at least two mechanisms of action/herbicide groups, whilst the active ingredients within a chemical family have only one mechanism of action/herbicide group (Tables 6 and 7). For instance, the substituted urea chemical family in the WSSA system has been repeated in groups 5 and 7 within photosystem II inhibitors, which means that this chemical family has two sites of action. The new classification and corrections of nomenclature have solved this issue. Another example is that fluometuron in the HRAC (2010) classification has two mechanisms of action, that is photosystem II inhibitor and carotenoid biosynthesis inhibitor. Fluometuron appears to be selectively toxic to one or more light-mediated biochemical reactions required for the formation and function of photosynthetic pigments

Table 6 Chemical families repeated in two mechanisms of action in the HRAC (2010) classification system

Chemical families	HRAC groups
Benzamide	K_1 & L
Benzoic acid	K_1 & O
Carbamate	I & K_2
Diphenyl ether	E & F_3
Nitrile	C_3 & L
Triazolinone	C_1 & E

Table 7 Chemical families repeated in at least two mechanisms of action/herbicide groups in the WSSA (2007) classification system

Chemical families	WSSA groups
Acetamide	7 & 15
Amide	3 & 7 & 12 & 14 & 15 & 21
Anilide	1 & 12 & 15
Arsenical	17 & 27
Benzonitrile	6 & 20
Carbanilate	5 & 23
Nitrile	6 & 20
Nitrodiphenylether	11 & 14
Nitrophenylether	11 & 14
Organic arsenical	17 & 27
Organophosphorus	8 & 9 & 10 & 18 & 27
Phenylurea	5 & 7
Pyrazole	2 & 14 & 15 & 27 & 28
Pyridazinone	5 & 12 & 14
Pyridine	3 & 4 & 12
Quaternary ammonium	22 & 27
Substituted amide	3 & 7 & 15
Substituted urea	5 & 7
Sulphonamide	2 & 18
Triazolone	2 & 14
Uracil	5 & 14

and organelles (Sikka & Pramer, 1968). However, according to the WSSA (2007) classification, being a photosystem II inhibitor has only been accepted as the valid mechanism of action for this active ingredient. On the other hand, further investigation of the chemical structure of fluometuron shows that it includes the phenylurea moiety. This moiety exists in some of photosystem II inhibitor active ingredients. Thus, fluometuron may also have the same mechanism of action. The difference between fluometuron and photosystem II inhibitor active ingredients is the presence of a trifluoromethyl group in the former active ingredient. Thus, when WSSA, similar to HRAC, classified this active ingredient as a carotenoid biosynthesis inhibitor, we can call its chemical family trifluoromethylphenylurea with this mechanism of action. Also, as the chemical structure of parafluron and fluometuron is very similar to each other, it has the same mechanism of action and group as fluometuron.

Classification of active ingredients within chemical families according to their chemical structure may result in further understanding of the biochemical basis of active ingredients. For instance, the difference in

Table 8 Target-site (ALS/AHAS gene) herbicide resistance to ALS/AHAS inhibitors in the sulfonylurea herbicides

Mutation*	Substitution	Species	Herbicides	Resistance index†	References
Asp 376	Glu	*Raphanus raphanistrum* L.	Chlorsulfuron Sulfometuron	VH	Yu *et al.* (2012)
Pro 197	Leu	*Amaranthus retroflexus* L.	Rimsulfuron Tribenuron-methyl Triflusulfuron-methyl	M	Sibony *et al.* (2001)
			Amidosulfuron Chlorimuron-ethyl Metsulfuron-methyl Nicosulfuron Sulfometuron-methyl Triasulfuron	H	
			Chlorsulfuron Thifensulfuron-methyl	VH	
	Ser	*Bromus tectorum* L.	Primisulfuron Sulfosulfuron		Park & Mallory-Smith (2004)
		Papaver rhoeas L.	Chlorsulfuron Metsulfuron-methyl	L	Durán-Prado *et al.*, (2004)
			Rimsulfuron Sulfometuron-methyl Tribenuron-methyl	H	
	Thr	*Lactuca serriola* L.	Chlorsulfuron Sulfometuron–methyl Triasulfuron	VH	Preston *et al.* (2006)
Trp 574	Leu	*Amaranthus retroflexus* L.	Nicosulfuron	H	Scarabel *et al.* (2007)
			Oxasulfuron Thifensulfuron-methyl	VH	

*Amino acid number is standardised to the *Arabidopsis thaliana* sequence.

†Resistance index defined as effective herbicide dose reducing growth or survival by 50% compared with the non-treated control (ED_{50}) of the resistance compared with the susceptible biotype: L = low resistance (2–5), M = moderate resistance (6–10), H = high resistance (11–100) and VH = very high resistance (>100).

Table 9 Active ingredients of this study according to mechanism of action, herbicide group and chemical family

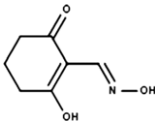
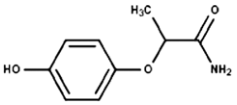
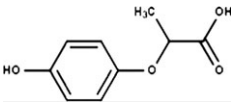
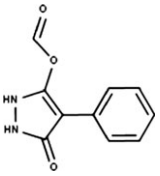
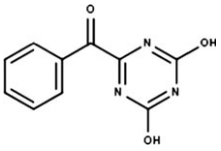
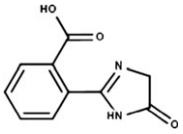
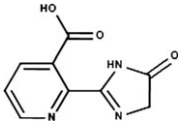
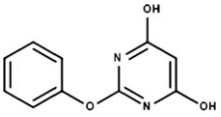
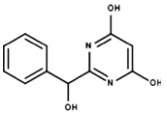
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
A	Acetyl CoA carboxylase inhibitors	Hydroxyoxocyclohexenecarbaldehyde oxime 	Alloxydim, Butroxydim, *Clethodim*, Cloproxydim, *Cycloxydim*, *Profoxydim*, Sethoxydim, *Tepraloxydim*, *Tralkoxydim*	1
		Hydroxyphenoxyisopropionamide 	Isoxapyrifop, Metamifop	
		Hydroxyphenoxyisopropionic acid 	Chlorazifop, *Clodinafop*, Clofop, *Cyhalofop-butyl*, *Diclofop*, *Fenoxaprop-P*, Fenthiaprop, *Fluazifop-P*, *Haloxyfop-P*, Kuicaoxi, *Propaquizafop*, *Quizalofop-P*, Trifop, Trifopsime	
		Phenyloxopyrazolinyl formate 	*Pinoxaden*	
B	Acetolactate synthase or acetohydroxy acid synthase inhibitors	Benzoyltriazinediol 	Triafamone	2
		Oxoimidazolinylbenzoic acid 	Imazamethabenz	
		Oxoimidazolinylnicotinic acid 	*Imazamox*, Imazapic, Imazapyr, *Imazaquin*, Imazethapyr	
		Phenoxypyrimidinediol 	*Bispyribac*, Pyribambenz-isopropyl, Pyribenzoxim, Pyriminobac	
		Phenylhydroxymethylpyrimidinediol 	Pyrimisulfan	

Table 9 (Continued)

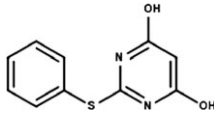
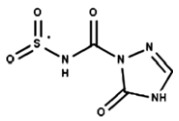
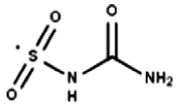
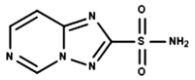
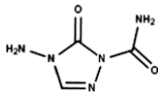
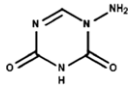
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Phenylthiopyrimidinediol 	Pyriftalid, Pyrithiobac	
		Sulfonylaminocarbonyltriazolinone 	Flucarbazone, *Propoxycarbazone*, *Thiencarbazone-methyl*	
		Sulfonylurea 	*Amidosulfuron*, *Azimsulfuron*, *Bensulfuron-methyl*, Chlorimuron, *Chlorsulfuron*, Cinosulfuron, Cyclosulfamuron, *Ethametsulfuron-methyl*, Ethoxysulfuron, *Flazasulfuron*, Flucetosulfuron, *Flupyrsulfuron-methyl-sodium*, *Foramsulfuron*, *Halosulfuron-methyl*, *Imazosulfuron*, *Iodosulfuron*, Iofensulfuron, *Mesosulfuron*, Metazosulfuron, Methiopyrisulfuron, *Metsulfuron-methyl*, Monosulfuron, *Nicosulfuron*, *Orthosulfamuron*, *Oxasulfuron*, Primisulfuron, Propyrisulfuron, *Prosulfuron*, Pyrazosulfuron, *Rimsulfuron*, Sulfometuron, *Sulfosulfuron*, *Thifensulfuron-methyl* = *Thiameturon-methyl*, *Triasulfuron*, *Tribenuron*, Trifloxysulfuron, *Triflusulfuron-methyl*, *Tritosulfuron*, Zuomihuanglong	
		Triazolopyrimidinesulfonamide 	Cloransulam, Diclosulam, *Florasulam*, Flumetsulam, *Metosulam*, *Penoxsulam*, *Pyroxsulam*	
C_1	Photosystem II inhibitors	Aminooxotriazolinecarboxamide 	Amicarbazone	5
		Aminotriazinedione 	Ametridione, Hexazinone	
		Aminotriazinone 	Amibuzin, Ethiozin, Isomethiozin, *Metamitron*, *Metribuzin*	

Table 9 (Continued)

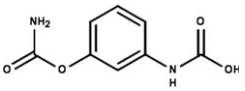
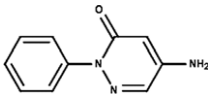
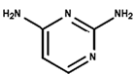
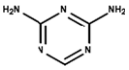
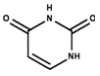
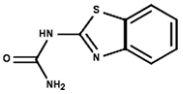
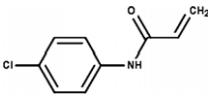
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Carbamoyloxycarbanilic acid 	Chlorprocarb, *Desmedipham*, Phenisopham, *Phenmedipham*	
		Phenyl aminopyridazone 	Brompyrazon, *Chloridazon* = *Pyrazon*	
		Pyrimidinediamine 	Iprymidam, Tioclorim	
		Triazinediamine 	Ametryn = Ametryne, Atraton, Atrazine, Aziprotryne = Aziprotryn, Chlorazine, CP 17029, Cyanatryn, Cyanazine, Cyprazine, Desmetryn = Desmetryne, Dimethametryn, Dipropetryn, Eglinazine, Fucaojing, Ipazine, Mesoprazine, Methometon, Methoprotryne = Methoprotryn, Procyazine, Proglinazine, Prometon, Prometryn = Prometryne, Propazine, Sebuthylazine, Secbumeton, Simazine, Simeton, Simetryn = Simetryne, Terbumeton, *Terbuthylazine*, Terbutryn = Terbutryne, Trietazine	
		Uracil 	Bromacil, Isocil, *Lenacil*, Terbacil	
C_2		Benzothiazolylurea 	Benzthiazuron, Methabenzthiazuron = Methibenzuron	7
		Chlorophenyl acrylamide 	Chloranocryl = Dicryl	
		Chlorophenyl propionamide	Propanil	

Table 9 (Continued)

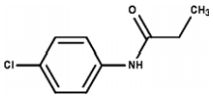
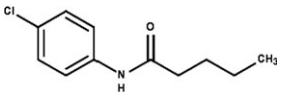
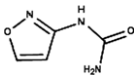
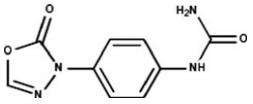
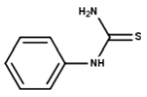
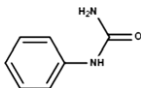
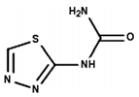
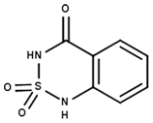
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
				
		Chlorophenyl valeramide	Erlujixiancaoan, Monalide, Pentanochlor = Solan	
				
		Isoxazolylurea	Isouron, Monisouron	
				
		Oxooxadiazolylphenylurea	Dimefuron	
				
		Phenylthiourea	Methiuron	
				
		Phenylurea	Bromuron, Buturon, Chlorbromuron, Chloreturon, *Chlorotoluron = Chlortoluron*, Chloroxuron, Defenuron, Difenoxuron, *Diuron*, Fenuron, *Fluometuron*, Fluothiuron, *Isoproturon*, *Linuron*, Metobenzuron, *Metobromuron*, Metoxuron, Monolinuron, Monuron, Neburon, Parafluron, Siduron, Tetrafluron	
				
		Thiadiazolylurea	Buthiuron, Ethidimuron, Tebuthiuron, Thiazafluron	
				
C_3		Benzothiadiazinanonedioxide	*Bentazone = Bentazon*	6
				
		Dibromohydroxybenzaldehyde oxime	Bromofenoxim	

Table 9 (Continued)

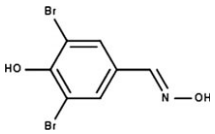
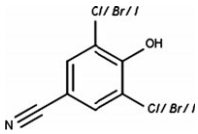
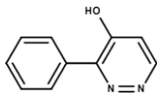
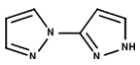
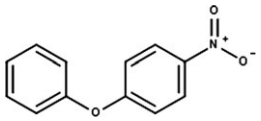
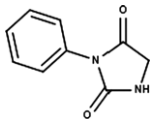
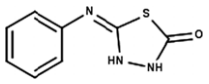
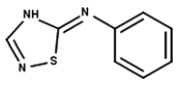
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
				
		Dihalohydroxybenzonitrile	Bromobonil, *Bromoxynil*, Chloroxynil, Iodobonil, *Ioxynil*	
				
		Phenylpyridazinol	Pyridafol, *Pyridate*	
				
D	Photosystem I inhibitors	Pyridinium	Cyperquat, Diethamquat, *Diquat*, Morfamquat, Paraquat	22
				
E	Protoporphyrinogen oxidase (PPG oxidase or protox) inhibitors	Bipyrazole	Pyraclonil	14
				
		Nitrophenoxybenzene	Acifluorfen, *Bifenox*, Chlomethoxyfen, Chlornitrofen, Etnipromid, Fluorodifen, Fluoroglycofen, Fluoronitrofen, Fomesafen, Fucaomi, Furyloxyfen, Halosafen, Lactofen, Nitrofen, Nitrofluorfen, *Oxyfluorfen*	
				
		Phenylimidazolidinedione	Profluazol	
				
		Phenyliminothiadiazolidone	Fluthiacet	
				
		Phenyliminothiadiazoline	Thidiazimin	
				
		Phenyloxadiazolone	*Oxadiargyl*, *Oxadiazon*	

Table 9 (Continued)

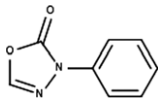
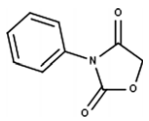
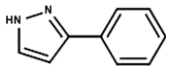
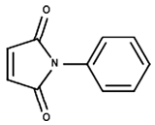
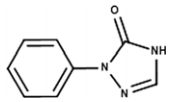
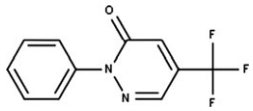
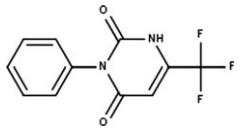
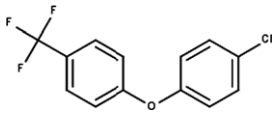
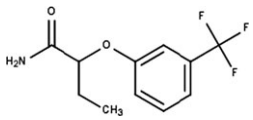
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
				
		Phenyloxazolidinedione	Pentoxazone	
				
		Phenylpyrazole	Fluazolate, Nipyraclofen, *Pyraflufen-ethyl*	
				
		Phenylpyrroledione	Chlorphthalim, *Cinidon-ethyl*, Flumiclorac, *Flumioxazin*, Flumipropyn	
				
		Phenyltriazolinone	Azafenidin, Bencarbazone, *Carfentrazone-ethyl*, Sulfentrazone	
				
		Phenyltrifluoromethylpyridazone	Flufenpyr	
				
		Phenyltrifluoromethyluracil	Benzfendizone, Butafenacil, Flupropacil, Saflufenacil, Tiafenacil	
				
		Trifluoromethylphenoxychlorobenzene	Ethoxyfen	
				
F_1	Carotenoid biosynthesis nhibitors	Trifluoromethylphenoxybutyramide	*Beflubutamid*	12
				

Table 9 (Continued)

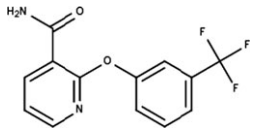
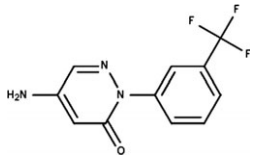
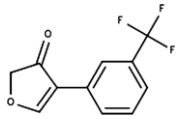
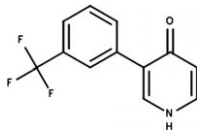
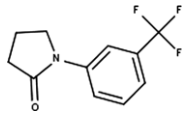
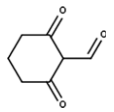
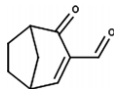
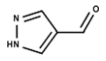
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Trifluoromethylphenoxypyridinecarboxamide	*Diflufenican*, Flufenican, *Picolinafen*	
				
		Trifluoromethylphenyl aminopyridazone	Metflurazon, Norflurazon	
				
		Trifluoromethylphenylfuranone	*Flurtamone*	
				
		Trifluoromethylphenylpyridone	Fluridone	
				
		Trifluoromethylphenylpyrrolidone	*Flurochloridone* = *Fluorochloridone*	
				
F_2		Dioxocyclohexanecarbaldehyde	Fenquinotrione, Ketospiradox, *Mesotrione*, *Sulcotrione*, Tefuryltrione, *Tembotrione*	28 (27)
				
		Isoxazolecarbaldehyde	Isoxachlortole, *Isoxaflutole*	
				
		Oxobicyclooctenecarbaldehyde	Benzobicyclon, Bicyclopyrone	
				
		Pyrazolecarbaldehyde	Benzofenap, Pyrasulfotole, Pyrazolynate, Pyrazoxyfen, Tolpyralate, *Topramezone*	
				

Table 9 (Continued)

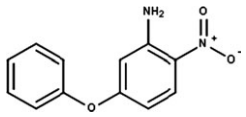
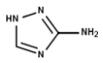
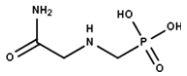
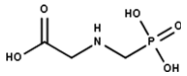
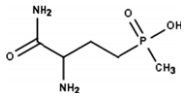
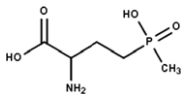
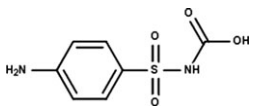
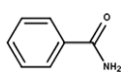
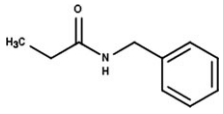
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
F_3		Phenoxynitroaniline	*Aclonifen*	11
				
		Triazolamine	*Amitrole*	
				
F_4		Isoxazolidone	*Clomazone*	13
				
G	Enolpyruvylshikimate-3-phosphate synthase inhibitors	Phosphonomethylglycinamide	Huangcaoling	9
				
		Phosphonomethylglycine	*Glyphosate*	
				
H	Glutamine synthetase inhibitors	Hydroxy methylphosphinoylhomoalaninamide	Bilanafos	10
				
		Hydroxy methylphosphinoylhomoalanine	*Glufosinate-ammonium*	
				
I	Dihydropteroate synthetase inhibitors	Sulfanilylcarbamic acid	Asulam, Carbasulam, Fenasulam	18
				
K_1	Mitosis inhibitors	Benzamide	*Propyzamide* = *Pronamide*	3
				
		Benzyl propionamide	Tebutam = Butam	
				

Table 9 (Continued)

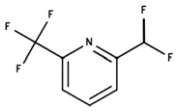
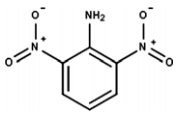
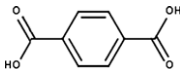
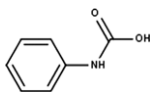
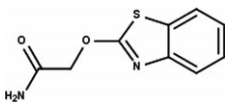
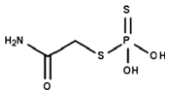
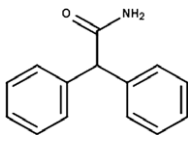
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Difluoromethyltrifluoromethylpyridine	Dithiopyr, Thiazopyr	
				
		Dinitroaniline	*Benfluralin* = *Benefin*, Butralin, Chlornidine, Dinitramine, Dipropalin, Ethalfluralin, Fluchloralin, Isopropalin, Methalpropalin, Nitralin, *Oryzalin*, *Pendimethalin*, Prodiamine, Profluralin, Prosulfalin, Trifluralin	
				
		Phosphoramidothioic acid	Amiprophos, Butamifos, DMPA, Shuangjiaancaolin	
				
		Terephthalic acid	Chlorthal	
				
K_2		Carbanilic acid	Barban, BCPC, *Carbetamide*, CEPC, Chlorbufam, *Chlorpropham*, CPPC, Propham, Swep	23
				
K_3		Benzothiazolyloxyacetamide	Mefenacet	15
				
		Carbamoylmethylphosphorodithioic acid	Anilofos, Piperophos	
				
		Chloroacetamide	Acetochlor, Alachlor, Allidochlor = CDAA, Butachlor, Butenachlor, CDEA, Delachlor, Diethatyl, *Dimethachlor*, *Dimethenamid-P*, Ethachlor, Ethaprochlor, *Metazachlor*, *Pethoxamid*, Pretilachlor, Propachlor, Propisochlor, Prynachlor, *S-metolachlor*, Terbuchlor, Thenylchlor, Xylachlor	
				
		Diphenylacetamide	Diphenamid	
				

Table 9 (Continued)

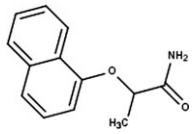
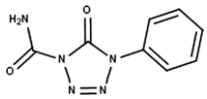
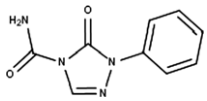
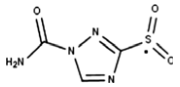
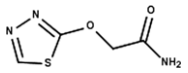
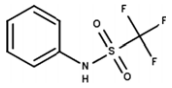
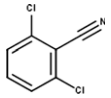
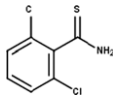
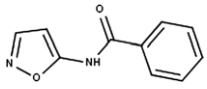
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Naphthoxyisopropionamide	Naproanilide, *Napropamide*	
				
		Phenyloxotetrazolinecarboxamide	Fentrazamide	
				
		Phenyloxotriazolinecarboxamide	Ipfencarbazone	
				
		Sulfonylisoxazoline	Fenoxasulfone, Pyroxasulfone	
				
		Sulfonyltriazolecarboxamide	Cafenstrole, Epronaz	
				
		Thiadiazolyloxyacetamide	*Flufenacet*	
				
		Trifluoromethanesulfonanilide	Mefluidide, Perfluidone	
				
L	Cellulose inhibitors	Dichlorobenzonitrile	Dichlobenil	20
				
		Dichlorobenzothioamide	Chlorthiamid	
				
		Isoxazolyl benzamide	*Isoxaben*	21
				

Table 9 (Continued)

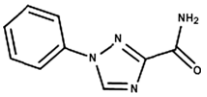
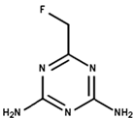
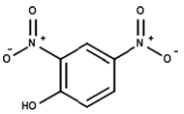
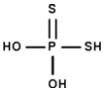
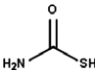
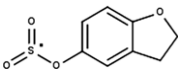
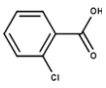
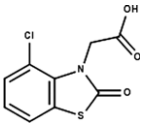
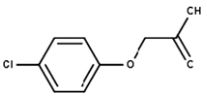
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Phenyltriazolecarboxamide	Flupoxam	(28)
				
		Fluoromethyltriazinediamine	Indaziflam, Triaziflam	(29)
				
M	Oxidative phosphorylation uncouplers	Dinitrophenol	Dinofenate, Dinoprop, Dinosam, Dinoseb, Dinoterb, DNOC, Etinofen, Medinoterb	24
				
N	Fatty acid and lipid biosynthesis inhibitors	Phosphorodithioic acid	Bensulide	8
				
		Thiocarbamic acid	Butylate, Cycloate, Di-allate = Diallate, Dimepiperate, EPTC, Esprocarb, Ethiolate, Isopolinate, Methiobencarb, *Molinate*, Orbencarb, Pebulate, *Prosulfocarb*, Thiobencarb, Tiocarbazil, *Tri-allate* = *Triallate*, Vernolate	
				
		Dihydrobenzofuranyl sulphonate	Benfuresate, *Ethofumesate*	16
				
O	Synthetic auxins	Chlorobenzoic acid	2,3,6-TBA, Chloramben, *Dicamba*, Tricamba	4
				
		Chlorooxobenzothiazolylacetic acid	Benazolin	
				
		Chlorophenoxyacetic acid	2,4,5-T, *2,4-D*, 3,4-DA, 4-CPA, *MCPA*	
				

Table 9 (Continued)

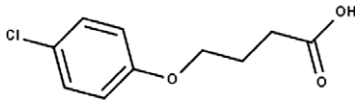
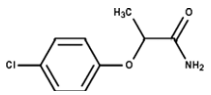
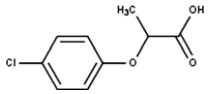
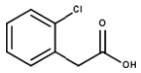
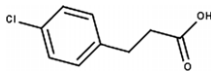
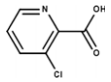
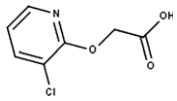
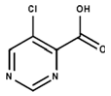
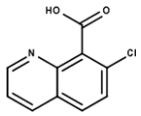
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Chlorophenoxybutyric acid 	2,4,5-TB, *2,4-DB*, 3,4-DB, 4-CPB, *MCPB*	
		Chlorophenoxyisopropionamide 	Clomeprop	
		Chlorophenoxyisopropionic acid 	3,4-DP, 4-CPP, Cloprop, *Dichlorprop-P*, Fenoprop, *Mecoprop*	
		Chlorophenylacetic acid 	Chlorfenac = Fenac	
		Chlorophenylpropionic acid 	Chlorfenprop	
		Chloropicolinic acid 	*Aminopyralid*, Halauxifen, *Clopyralid*, *Picloram*	
		Chloropyridyloxyacetic acid 	*Fluroxypyr*, *Triclopyr*	
		Chloropyrimidinecarboxylic acid 	Aminocyclopyrachlor	
		Chloroquinolinecarboxylic acid 	Quinclorac, *Quinmerac*	
P	Auxin transport inhibitors	Phthalamic acid	Naptalam	19

Table 9 (Continued)

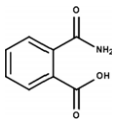
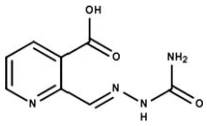
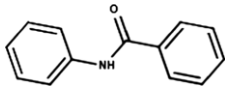
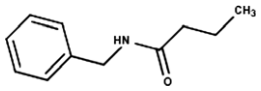
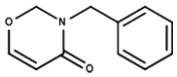
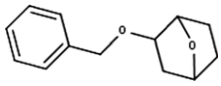
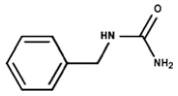
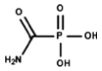
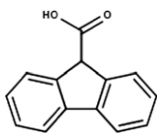
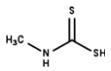
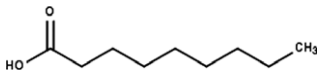
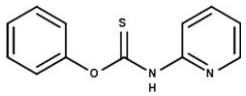
HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
				
		Semicarbazonomethylnicotinic acid	Diflufenzopyr	
				
Z	Unknown	Organic arsenic 	CMA, DSMA, MAA, MAMA, MSMA	17
		Benzanilide	Etobenzanid	27 (26)
				
		Benzyl butyramide	Bromobutide	
				
		Benzyldihydrooxazinone	Oxaziclomefone	
				
		Benzyloxyoxabicycloheptane	Cinmethylin	
				
		Benzylurea	Cumyluron, Daimuron, Methyldymron	
				
		Carbamoylphosphonic acid	Fosamine	
				
		Fluorenecarboxylic acid	Chlorflurenol = Chlorflurecol	
				

Table 9 (Continued)

HRAC groups	Mechanisms of action	Chemical families*	Active ingredients†	WSSA groups‡
		Methyldithiocarbamic acid	*Dazomet, Metam = Metham*	
				
		Pelargonic acid	*Oleic acid, Pelargonic acid*	
				
		Phenyl pyridylthiocarbamate	Pyributicarb	
				
		Pyrazolium	Difenzoquat	
				

*The position of substituents and heteroatoms of rings in the chemical structure are based on the majority of active ingredients within a chemical family. Thus, it is possible that such positions in a few active ingredients differ slightly from that shown in the chemical structure.
†The italicised active ingredients approved for use or known to be used in at least one European Union country (EU Pesticides database available at: http://ec.europa.eu/sanco_pesticides/public/index.cfm?event = homepage&language = EN#).
‡Group numbers enclosed in parenthesis are the new numbers suggested by WSSA (2011) instead of the adjacent number out of the parenthesis or they are being suggested for the first time (such as group number 29).

chemical structure of prothioconazole compared to triazole compounds led Parker *et al.* (2011) to probe the biochemical basis of the demethylation inhibitor's affinity to the target protein. Further investigation of the fungicide interaction with the target protein revealed that prothioconazole interacts with CYP51 in a novel way that is distinct from other azole fungicides (Parker *et al.*, 2011). Classification of active ingredients according to their chemical structure provides a way for the study of resistance in active ingredients with similar chemical structure. Based on this study, all active ingredients in a chemical family have a same moiety although being different from each other. As the active ingredients within a chemical family have the same mechanism of action and moiety, thus they may have similar pattern of resistance. Nevertheless, differences between the active ingredients within a chemical family may result in more than one pattern of resistance in that family (Table 8).

Conclusions

Tables S3 and S4 show the current and new nomenclatures for chemical families of HRAC (2010) and WSSA (2007) classification systems, along with their active ingredients and herbicide groups. Overall, it seems that the present study (Table 9) provides better opportunity for managing herbicide resistance in weeds. Including over 100 extra active ingredients with known chemical families, mechanisms of action and herbicide groups opens up new opportunities for researchers and farmers to design more flexible rotational herbicide programmes and to decrease the risk of occurrence of herbicide (cross)resistance. As herbicides of chemical families within a mechanism of action play an important role in the evolution of cross-resistant weed biotypes, the replacements, additions and omissions that have been adjusted in the present study should have promising consequences for herbicide-based weed management strategies.

Acknowledgements

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1 The mistakes in the nomenclature of the chemical families in the HRAC (2010) classification system with their corresponding new chemical families, active ingredients, and HRAC groups.

Table S2 The mistakes in the nomenclature of the chemical families in the WSSA (2007) classification system with their corresponding new chemical families, active ingredients, and WSSA groups.

Table S3 The current and new nomenclatures for chemical families of the HRAC (2010) classification system, along with their active ingredients and HRAC groups.

Table S4 The current and new nomenclatures for chemical families of the WSSA (2007) classification system, along with their active ingredients and WSSA groups.