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Functional Tools for Pesticide Risk Assessment and Management

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Deliverable DL5

State-of-art review on bound residues

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RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	

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Foreword

The present literature review was prepared within the context of the work package WP1 ('Integrated knowledge reviews') of the FOOTPRINT project.

The preferred reference to the present document is as follows:

Barriuso E. & Benoît P. (2006). State-of-the-art review on bound residues. Report DL#5 of the FP6 EU-funded FOOTPRINT project [www.eu-footprint.org], 79p.

1 INTRODUCTION

Non-extractable residues or bound residues (BR) are a particular state of pesticide residues characterised by their non-extractability using current extraction methods. In the present document, we will focus on pesticide bound residues in soils although it should be noted that this concept is extensively used for other organic chemicals (organic pollutants, drugs, veterinarian products) and other matrices (plants, animals) (Khan, 1982; Burgat-Sacaze et al., 1986; Sandermann, 2004). It is a kinetic process starting as soon as the pesticide is in contact with soil and should be included along other dissipation processes such as metabolite formation or mineralization (Fig. 1).

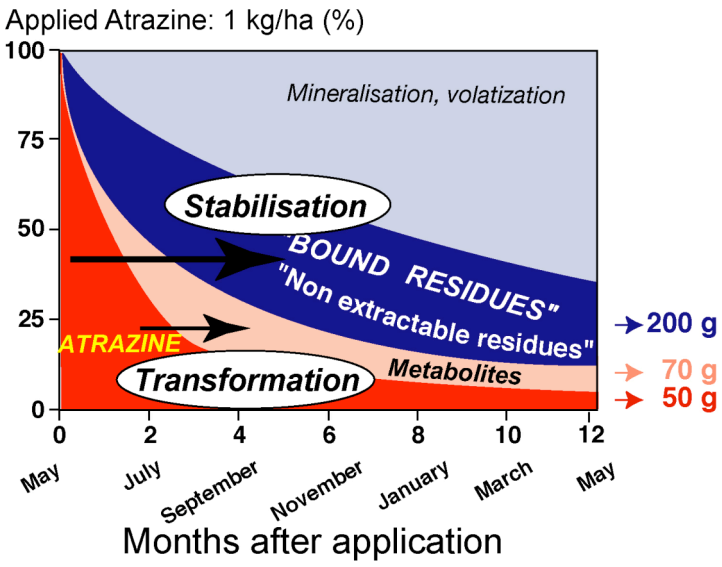

Figure 1. Evolution of atrazine concentration in soils and overall balance among atrazine, metabolites, bound residues and other dissipation process.
Bound residues could be considered as a stabilisation process concurrent to degradation process giving identifiable (extractable) metabolites
(Data from Barriuso & Koskinen, 1996)

The aim of the present report is to update the available knowledge on the formation of pesticide bound residues in soils. In pesticide risk assessment procedures, bound residues are usually implicitly taken into account in the description of the dissipation kinetics. Dissipation constants or half lives (DT50) are composite parameters resulting from the addition of different dissipation processes, each of which having a specific kinetic. Bound residues will be considered both as a process contributing to pesticide dissipation and as process decreasing pesticide availability, thereby provoking a transient pesticide stabilisation which may lead to a subsequent slow release. The first consequence of the BR formation is a decrease in availability of pesticide residues with is concurrent with an increase of persistence in soil. The stabilisation process leading to BR is in competition with the degradation process. An

increase in the stabilisation induces generally a decrease in the recovery of extractable metabolites and in the mineralization. The concepts and the hypotheses used to explain the formation of bound residues will have a direct influence on the way they should be described in pesticide fate models. If BR are considered a true dissipation process, they could be described as an irreversible process. However, if BR formation is considered as a stabilisation process, the concepts of non-reversible sorption or slow sorption/desorption kinetics must be considered.

The magnitude of BR formation can be typically assessed from degradation studies for aerobic and water/sediment systems, and for anaerobic and lysimeter studies when necessary. BR are explicitly considered in the decision making process for the placement of pesticides on the market in Europe. According to Annex VI of the Council Directive 91/414/EEC, if non-extractable residues are formed in amounts exceeding 70 % of the initial dose after 100 days with a mineralization rate of less than 5 % in 100 days, no authorisation shall be granted. The directive and the "guidance document on persistence in soils" also utilize the "unless clause" when the above criteria is not met. Hence, no authorization shall be granted *unless* it is scientifically demonstrated that there is no accumulation in soil under field conditions at levels such that i) unacceptable residues in succeeding crops occur, and/or ii) unacceptable phytotoxic effects on succeeding crops occur, and/or, iii) there is a potential unacceptable impact on the environment. Two challenges have to be met. The first one is to adopt recognised and agreed methods and experimental or modelling tools to evaluate BR phytoxicity, environmental impact and residue carry-over. The second challenge is the evaluation of the significance of BR concerning the ecotoxicological relevancy or their capacity to contribute to the non-point pollution of the water bodies through the slow release of the stabilised pesticides as BR. Craven (2000) indicated that there is no agreement amongst EU Member States on how BR should be treated. The possible key to this question could be BR "bioavailability" (Craven, 2000). The current approach which is most often adopted is to treat soil BR in the same way as persistent compounds (Craven & Hoy, 2005). Thus, for these authors, the full range of environmental fate, long term effects and crop residue tests required to identify any risks posed by BR are brought into play. This position is however not consensual. The Scientific Committee on Plants (SCP) provided a view on the issue in 1999 after analysis of the available literature. The SCP noted that small fractions of BR may be released by a variety of processes and become potentially bioavailable. The opinion of the SCP (1999) is that the fractions of BR which are released are low and any concern over their ecotoxicology or effect on succeeding crops should have been addressed during studies required under Annex II and III for the active substance and relevant metabolites. Thus, for the SCP, the fractions released from BR have little significance from a regulatory viewpoint.

The present literature review attempts to i) provide knowledge which can be used to discuss the issues raised above, ii) identify available data on the kinetics of BR formation, and, iii) evaluate the quantity of actives involved in BR formation. The relationship between the extent of BR formation and relevant soil and pesticides properties or experimental conditions will be analysed. Finally, the potential for linking the characteristics of the release of BR and the nature of the pesticide and the experimental conditions will be explored. The overall aim of the present work is to propose the principles, the parameters and the sets of experimental data that can be used to simulate BR formation and subsequent release within the FOOTPRINT modelling tools.

2 DEFINITION AND SCIENTIFIC INFORMATION ON BOUND RESIDUES

2.1 Definitions

The first research activities on BR started at the end of the 1960s and concerned BR in plants or vegetal constituents while the first publications concerning BR in soils appeared in the 1970s (Lichtenstein et al., 1977; Khan, 1982). In 1975, the American Institute of Biological Sciences, Environmental Task Group proposed a first definition for BR: “bound pesticide residues in the soil are non-extractable and chemically unidentifiable pesticide residues remaining in the fulvic acids, humic acids, and humin fractions after exhaustive sequential extraction with nonpolar organic and polar solvents”. Roberts (1984), from the definition of Kearney (1982), provided additional details on the extraction method and requirements on the chemical nature of the residues: “bound residues represent the chemical species (active ingredient, metabolites and fragments) originating from pesticides, used according to good agricultural practice, that are unextracted by methods which do not significantly change the chemical nature of these residues”. These non-extractable residues are considered to exclude fragments, recycled through metabolic pathways leading to naturally occurring products. This definition was adopted by the International Union of Pure and Applied Chemistry (IUPAC), and is roughly the position adopted in the Uniform Principles in the EU directive (CEC, 1997).

Other definitions or position statements appear periodically in the literature. The notion of biological activity of BR and the possibility soil structure modifications was introduced by Calderbank (1989): “BR in soils could be defined as residues of the intact pesticide or degradation products derived from it that are no longer able to exert their original biological activity to any significant extend and/or cannot be extracted from the soil by extraction

methods which do not degrade the compound unless such methods are able to destroy the soil structure without affecting the compound". The introduction of the biological activity consideration allowed avoiding the issue of the extraction methods, but the biological approach remains controversial and is not used in the literature. The last consensual BR definition came from Führ et al. (1998): BR represent compounds in soils, plants or animals which persist in the matrix in the form of the parent substance or its metabolite(s) after extraction. The extraction method must not substantially change the compounds themselves or the structure of the matrix".

Beyond the conceptual definition of the BR, it is necessary to consider an operational definition, depending on the techniques allowing the quantification and the identification of the BR. Classical analytical chemistry techniques cannot be used because most techniques need a previous extraction of the residues, BR being unextractable by definition. Hence, only the use of isotopic techniques, mainly with the radioisotope ^{14}C, allows a quantification of BR in practice. BR are studied in incubations of soils treated with pesticides labelled with ^{14}C. After incubation for a target duration, soils are exhaustively extracted. The unextracted radioactivity remaining in the soil is measured by liquid scintillation counting of the total ^{14}C-CO_2 recovered by combustion of the soil samples. Thus, the operational definition of BR corresponds to the unextracted radioactivity remaining in the soil. Due to the destructive approach used for BR quantification (combustion), it is very difficult to give information on nature of BR. In practice, it is impossible to know whether BR are the intact pesticides, their metabolites or ^{14}C recycled in microbial biomass or in soil organic matter. For this purpose, additional techniques and laborious protocols using degradative techniques are needed to allow a partial degradation of the soil structure or constituents with liberation of ^{14}C labelled compounds originating from the ^{14}C-pesticide.

2.2 Bibliometric analysis of the BR literature

Bibliographic databases were consulted with regard to the presence of papers dealing with BR. CAB Abstracts of the ISI Web of Knowledge platform were explored in May 2006. All types of available documents were searched on the period extending from 1973 to the present time. A search for the term "bound residues" in the titles, descriptors and abstracts of documents yielded 549 references:

413 references contained "bound residues" and "pesticide";

332 references contained "bound residues" and "soil";

291 references contained "bound residues" and "pesticide" and "soil".

There were 158 references containing “Bound residues” in their title, indicating that it is an important subject of the paper, of which only 42 concerned soil and pesticides. The number of available papers increased at the beginning of the 1990s. Most of the papers identified before the year 2000 dealt with domains other than soil or pesticides. However in the last five-year period (2000-2005), a significant proportion of the papers dealing with bound residues were on pesticide and soil (Fig. 2).

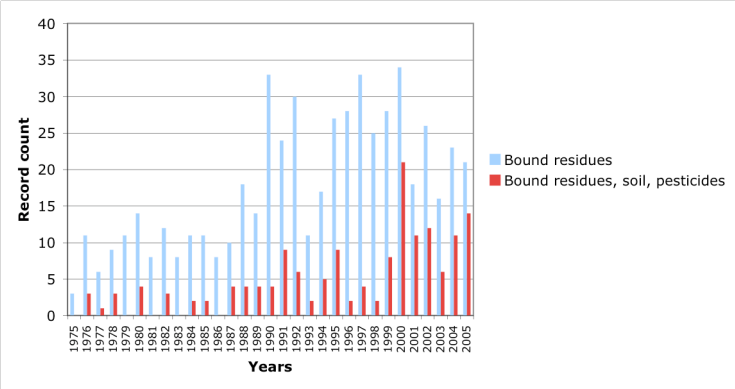

Figure 2. Records counts over time identified on CAB Abstracts database by descriptor “bound residues” and part of which corresponding to the “bound residues + soil + pesticides”

Few authors published intensively in this area. Figure 3 provides an analysis of the distribution of the records with the descriptor “bound residues”, sorted by the field “authors”. The pioneer publications were from Lichtenstein while Khan and Führ contributed most to the area until 1995. The increase in counts between 1995 and 2000 corresponds mainly to the publications of Barriuso, Scheunert and Burauel (the latter coming from the same team as Führ). One interest of this kind of bibliometric analysis is to identify the main team working in a given area. This can be interesting to identify grey literature, additional data or information, and experts able to give a pertinent discernment of our work.

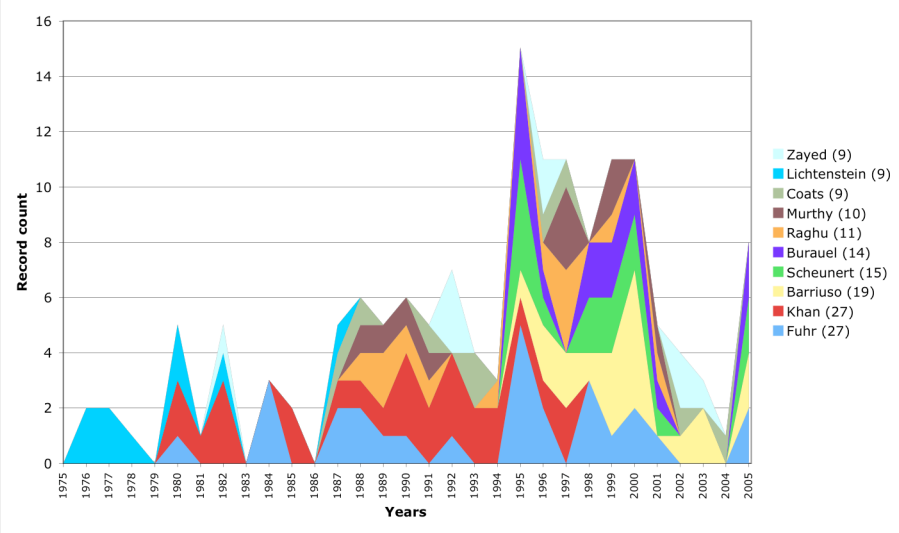

Figure 3. Records counts over time from the main authors which publications were identified with descriptor “bound residues + soil + pesticides” in the CAB Abstracts database

To detail the content of the records identified, an analysis of the main other descriptors found in the 549 records containing "bound residues" was undertaken (Fig. 4). The descriptors associated with "bound residues" can be classified in relation to the concerned compounds, the associated process, the identified factors and the considered effects. The main chemicals involved are pesticides, especially herbicides (37 % of selected records), then insecticides (22 %), and finally fungicides (6 %). Among the herbicides, atrazine was intensively associated to "bound residues" studies (11 % of the selected records, representing 61 records). Atrazine is the only chemical with a large number of publications and is thus probably the only chemical allowing a exhaustive study of bound residues in different contexts and experimental conditions. The main process associated with "bound residues" is "degradation" (26 % of the selected records presenting 141 records). A large number of similar descriptors are pointed out with a high score, e.g. "biodegradation", "decomposition", mineralization", "metabolites". The other process associated with "bound residues" was "sorption" (11 % of records).

Concerning factors, "soil organic matter" was found in 40 "bound residues" records (7 % of selected records). A specific reference to the humic acids is mentioned in 5 % of records. "Soil types" represented 57 records (10 %). Some references associated "bound residues" with specific plants like "wheat" (43 records) and "maize" (31 records).

Field: Descriptor	Record Count	% of 549
residues	246	44.8 %
soil	240	43.7 %
herbicides	203	37.0 %
degradation	141	25.7 %
pesticides	131	23.9 %
insecticides	123	22.4 %
pesticide residues	111	20.2 %
agricultural entomology	105	19.1 %
insecticide residues	89	16.2 %
herbicide residues	88	16.0 %
nontarget effects	64	11.7 %
atrazine	61	11.1 %
biodegradation	61	11.1 %
decomposition	60	10.9 %
sorption	58	10.6 %
soil types	57	10.4 %
mineralization	54	9.8 %
metabolism	52	9.5 %
environment	50	9.1 %
persistence	47	8.6 %
metabolites	46	8.4 %
wheat	43	7.8 %
drug residues	42	7.7 %
Triticum	42	7.7 %
soil organic matter	40	7.3 %
uptake	38	6.9 %
USA	37	6.7 %
soil pollution	36	6.6 %
interactions	35	6.4 %
rats	35	6.4 %
fungicides	34	6.2 %
polluted soils	34	6.2 %
stored products	33	6.0 %
maize	31	5.6 %
techniques	31	5.6 %
Zea mays	31	5.6 %
analytical methods	30	5.5 %
humic acids	29	5.3 %
cereals	28	5.1 %
microorganisms	27	4.9 %
bioavailability	26	4.7 %
microbial degradation	26	4.7 %
toxicity	26	4.7 %

Figure 4. Analyse of the descriptors found together to the descriptor "bound residues" in CAB Abstracts database

The interest concerning the effects of bound residues appears to be mainly driven by environmental concerns, with environmental descriptors ranking highly: "environment" – 50 records, "persistence" – 47 records, "soil

pollution" – 36 records. "Bioavailability" (26 records), "uptake" (38 records), and "toxicity" (26 records) were other effects often associated to "bound residues".

A large part of the documents identified (12 % of the selected records, representing 66 records) originated from the *Journal of Agricultural and Food Chemistry* (Figure 5). This journal publishes papers in all the areas interesting bound residues (soils, plants, food, water, analytical methods, …). The journal has an impact factor (IF) of 2.507. The others identified sources are environmental publications such as *Chemosphere* (7 % of records, IF 2.297), *Journal of Environmental Science and Health* (5 % of records, IF 0.862), *Environmental Science & Technology* (3.5 % of records, IF 4.054). Two particular sources must be pointed out, both contributing to 1 % of the selected records: the first is an old book coming from a symposium of the ACS in 1975, the second is a special issue of the journal *Environmental Pollution* published in 2000 (Vol. 108 – N° 1) (Jones et al., 2000).

Field: Source Title	Record Count	% of 549	Bar Chart
Journal of Agricultural and Food Chemistry	66	12.0 %	
Chemosphere	38	6.9 %	
Journal of Environmental Science and Health. Part B, Pesticides, Food Contaminants, and Agricultural Wastes	28	5.1 %	
Pesticide Science	22	4.0 %	
Environmental Science & Technology	19	3.5 %	
Journal of Environmental Quality	17	3.1 %	
Environmental Pollution	15	2.7 %	
Environmental Toxicology and Chemistry	12	2.2 %	
Journal of Pesticide Science	11	2.0 %	
Soil Biology & Biochemistry	11	2.0 %	
Drug Metabolism Reviews	10	1.8 %	
Bulletin of Environmental Contamination and Toxicology	8	1.5 %	
Pesquisa Agropecuaria Brasileira	6	1.1 %	
Special issue: non-extractable residues in soil and sediments: characterisation and environmental significance.	6	1.1 %	
Bound and Conjugated Pesticide Residues; ed. by D.D. Kaufman, G.G. Still, G.D. Paulson, S.K. Bandal. A symposium sponsored by the Division of Pesticide Chemistry, Colorado, 1975 (ACS Symposium Series 29).	5	0.9 %	
Bulletin of the National Research Centre (Cairo)	5	0.9 %	
International Journal of Environmental Analytical Chemistry	5	0.9 %	
Pest Management Science	5	0.9 %	
Pesticide Biochemistry and Physiology	5	0.9 %	
Residue Reviews	5	0.9 %	
Revista Brasileira de Ciencia do Solo	5	0.9 %	
Biology and Fertility of Soils	4	0.7 %	
Food Additives and Contaminants	4	0.7 %	
Human and environmental exposure to xenobiotics. Proceedings of the XI Symposium Pesticide Chemistry, Cremona, Italy, 11-15 September, 1999.	4	0.7 %	
ACS Symposium Series	3	0.5 %	

Figure 5. Main bibliographic sources identified with descriptor "bound residues" in CAB Abstracts database sorted by the record count.

3 PROPORTION OF APPLIED PESTICIDES FORMING BOUND RESIDUES

3.1 Dependency of bound residues on the extraction methods

By definition, BR are non-extractable residues, and are thus depending on the technique used for the extraction. This point introduces an arbitrary character of these residues and the data reported on BR (amount of BR, chemical nature) should therefore be attached to the extraction procedure used. To quantify BR, an "exhaustive extraction" of the extractable residues is required. The problem is to define the accepted degree of the denaturation of the matrices containing pesticides residues, and when the "total" extraction is reached. Another problem is the lack of standardisation of laboratory procedures for pesticide extraction from soil. Such a standardisation does not seem possible because extraction must be adapted and optimised to the nature of the pesticides and their metabolites, and very often to the matrices (soil types). The objective of this optimisation is to propose extraction methods maximising the extraction efficiency (SANCO, 2006). It is interesting to note that the objective of these methods is to extract the residues, not to recover BR. BR are the proportion that optimised extraction methods are not able to extract.

The requirement on the extraction efficacy corresponds to a mean recovery at each fortification level inside the range 70 – 110 % (91/414/EC; SANCO, 2004). Thus extraction methods have been developed with fortified soil samples, which are extracted often a few hours or days after pesticide fortification. It is considered that the extraction yields are independent of the residence time of pesticides in soils, although it is known that this assumption does not hold. On the other hand, an extraction efficiency of only 70 % of the applied amount is accepted during fortification experiments. This points out the problem of pesticide recovery from the soil. By default, a proportion of BR between 0 and 30 % could correspond to "methodological noise". This would explain the aspect of some BR formation kinetics with a basal noise corresponding to the extraction yield at the beginning of the soil incubation. An important point here is to become aware of the different nature and interactions of these quickly-formed BR, in relation to the methodological noise and the BR time-dependent formation during soil incubations.

In parallel to the finalization of optimised and repeatable extraction methods for pesticide residue analysis, extraction methods more specifically adapted to the study of BR have been developed. The objectives of these methods are to get information on the nature of BR, to evaluate the residue availability or to know the main mechanisms implicated in their formation. Most of these procedures allow a speciation of pesticides on the basis of the

extracting conditions, the extractant strength, or on the association of BR to soil fractions or soil constituents. Some methods and results will be described below. The question remains of knowing why the supplementary extracted residues of pesticide is considered as BR, in other words, why this more efficient technique is not used to evaluate the extractability of pesticides in the first place.

Very few publications were specifically focused on the kinetics of BR formation. These kinetics are found as a result of the overall balance of the ^{14}C residues coming from the ^{14}C-pesticides, bound residues becoming a supplementary compartment together with the mineralized and the extractable fractions. Figure 6 show an example of the typical data found in the literature showing evolution of the radioactivity, during a target time, among different measured compartments and for different pesticides and soils (Mamy et al., 2005).
Figure 6 allows the identification of three steps in the formation of BR.

First, the first step in the kinetics depends on the extractability at the beginning of the soil incubation (usually 24 h after pesticide application). The extraction yields depend on the extraction method, the nature of the pesticides and the soil properties. This has been discussed above, and corresponds to the rapidly formed (or "flash") BR related to the "methodological noise". This is usually <10 %, but can be up to 30 % (methodological quality threshold). This is demonstrated for glyphosate in Fig. 6 (Mamy et al., 2005). Other examples can be found for (% BR at zero time) triticonazole (<10 %) (Beigel et al., 1999), endosulfan (<12 %) (Monteiro et al., 1989), atrazine (20 to 25 %) (Weaver et al., 2004), chlorothalonil (5 to 40 %) (Regitano et al., 2001), paraquat (>90 %) (Mordaunt et al., 2005). The main explanation of these BR is the difficulty of the solvent to compete with the soil-pesticide interactions (paraquat is an extreme case) or to access to hidden sites in organo-mineral colloids by diffusion.

The second step to consider in BR kinetics is the "formation step" and associated kinetics rates. When these rates are high, a BR plateau is quickly reached, usually associated with a high level of BR. This is the case of the metazachlor and metamitron in Fig. 6. In other cases, the BR formation rate is low and a plateau is not reached (trifluraline and sulcotrione are examples in the Fig. 6). This behaviour is often associated with a low proportion of BR.

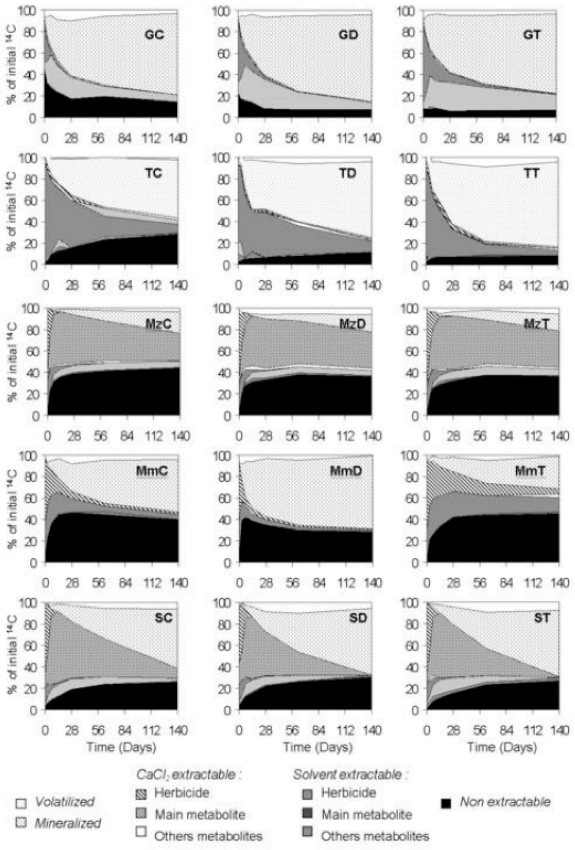

Figure 6. Exemples of bound (non extractables) residues kinetics (dark areas) for different pesticides and soils.

Glyphosate (G), trifluralin (T), metazachlor (Mz), metamitron (Mm) and sulcotrione (S) in Châlons (C), Dijon (D) and Toulouse (T) soils.

Distribution of the initial radioactivity between the different analyzed fractions and between active ingredients and their metabolites (From Mamy et al., 2005).

The third step to consider is the fate of BR when their formation rate decreases. This step can be considered as a BR "maturation stage". Roughly, three situations can be found (Fig. 7), (i) a "plateau" is reached and the BR proportion remains stable during time, (ii) the BR formation carries on at a lower rate indicating a continuous "incorporation" of new residues in the BR pool, or (iii) the BR proportion decreases with a "release" rate. These

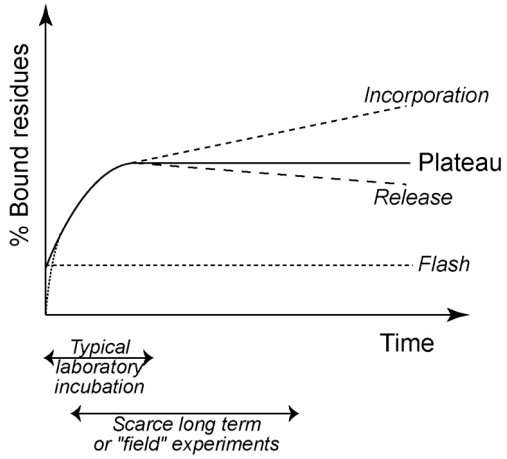

Figure 7. Schematic drawing of the different kinetics of bound residues evolution found in the literature.

three situations are illustrated in Fig. 6. A stable "plateau" situation corresponds to the fate of metazachlor and metamitron BR in the Toulouse soil. A continuous BR "incorporation" is observed for trifluralin and sulcotrione. And a BR "release" is shown for metamitron. Other examples found in the literature are synthesised in Table 1; the references used are not exhaustive, but are examples of the data set of BR kinetics with complementary data on mineralization and extractability of pesticides residues.

Table 1. Selected bibliography containing kinetic data on bound residues formation.
Analyse of the kinetic shapes in relation to the discussed criteria: initial BR proportion, rate on BR formation, identification of a BR plateau and long-term evolution of plateau when existing.

Pesticide	Initial BR	Rate	Plateau (time)	Maturation (final time)	Reference
2,4-D	< 5 %	High	Yes (10 d)	Release (60 d)	Boivin et al., 2005
Acetochlor	< 5 %	High	Yes (90 d)	Release (371 d)	Loor-Vela et al., 2003
Alachlor	< 5 %	High	Yes (28 d)	Incorporation (80 d)	Laabs et al., 2002
Atrazine	< 10 %	Low	Yes (200 d)	Stable (326 d)	Assaf & Turco, 1994
Atrazine	?	Low	No (180 d)		Winkelman & Klaine, 1991
Atrazine	< 5 %	Low	No (91 d)		Mordaunt et al., 2005
Atrazine	< 10%	High	Yes (60 d)	Release (154 d)	Miller et al., 1997
Atrazine	< 20%	High	No (56 d)		Hang et al., 2003
Atrazine	?	High	Yes (60 d)	Release (360 d)	Nakagawa et al., 1996
Bentazone	< 10 %	Low	Yes (60 d)	Stable (inc.) (160 d)	Boivin et al., 2004
Chlorothalonil	< 40 %	High	Yes (7 d)	Stable (90 d)	Regitano et al., 2001
Chlorpyrifos	< 5 %	Low	No (97 d)		Yücel et al., 1999
Chlorpyrifos	< 5 %	Low	No (80 d)		Laabs et al., 2002
Cloransulam	< 5 %	High	Yes (120 d)	Release Inc. (357 d)	Wolt et al., 1996
Cyprodinil	< 10 %	Low	No (200d) (yes, 100 d)		Dec et al., 1997
DDT	< 5 %	High	Yes (7 d)	Incorporation (28 d)	Lichtenstein et al., 1977
Deltamethrin	< 10 %	Low	Yes (30 d)	Stable (80 d)	Laabs et al., 2002
Dialllate	< 5 %	High	Yes (28 d)	Release (210 d)	Anderson & Domsch, 1980
Dicamba	< 5 %	High	Yes (40 d)	Release (91 d)	Mordaunt et al., 2005
Dicamba	<10 %	High	Yes (14 d)	Release (90d)	Gevao et al., 2005
Dieldrin	< 5 %	Low	No (28 d)		Lichtenstein et al., 1977
Dimethenamid	< 10 %	High	Yes (30 d)	Stable (inc.) (142 d)	Crawford et al., 2002
Dyfonate	< 5 %	High	Yes (14 d)	Stable (28 d)	Lichtenstein et al., 1977
Endosulfan	<20 %	Low	No (160 d)		Monteiro et al., 1989
Endosulfan	< 5 %	Low	No (80 d)		Laabs et al., 2002
Flupropacil	< 5 %	Low	No		Vithala & White, 1996
Isoproturon	< 5 %	Low	Yes (40 d)	Incorporation (91 d)	Mordaunt et al., 2005
Isoproturon	< 10 %	Low	No (40 d)		Benoit et al. 1999
Lindane	< 5 %	Low	Yes (70 d)	Release (91 d)	Mordaunt et al., 2005
Metamitron	< 5 %	High	Yes (28 d)	Release (stable) (84 d)	Mamy et al., 2005
Metazachlor	< 5 %	High	Yes (14 d)	Stable (84 d)	Mamy et al., 2005
Metsulfuron	< 5 %	High	Yes (20 d)	Incorporation (100 d)	Pons & Barriuso, 1998
Monocrotofos	< 5 %	High	Yes (4 d)	Stable (80 d)	Laabs et al., 2002
Paraquat	< 5 %	High	Yes (1 d)	Stable (91 d)	Mordaunt et al., 2005
Parathion	< 5 %	High	Yes (7 d)	Incorporation (28 d)	Lichtenstein et al., 1977
Phosalone	< 5 %	High	Yes (14 d)	Incorporation (84 d)	Ambrosi et al., 1977
Prometryne	< 5%	Low	No (150 d)		Khan & Hamilton, 1980
Propiconazole	< 5 %	Low	No (12 m)		Kim et al., 2003
Prosulfuron	< 20 %	High	Yes (20 d)	Stable (release (105 d)	Hultgren et al., 2002
Simazine	< 5 %	Low	Yes (50 d)	Incorporation (80 d)	Laabs et al., 2002
Sulcotrione	< 5 %	Low	Yes (56 d)	Incorporation (84 d)	Mamy et al., 2005
Triallate	< 5 %	High	Yes (140 d)	Release (365 d)	Anderson & Domsch, 1980
Trifluraline	< 5 %	Low	No (140 d)		Mamy et al., 2005
Trifluraline	< 5 %	Low	No (80 d)		Laabs et al., 2002
Trifluraline	< 5 %	Low	No (91 d)		Mordaunt et al., 2005
Triticonazole	<10 %	Low	Yes (100 d)	Stable (130 d)	Beigel et al., 1999

General considerations about the kinetics should be taken with care as the shape of the kinetics curves depends of the incubation time range. Very often, the incubation time

concerns the first period of the BR formation. Thus, incubation may stop in the BR "formation step", before reaching a plateau, and authors may inadequately conclude that a continuous incorporation of new BR is happening. Long-term experiments allowing to look at the fate of BR are very scarce in the literature. The main reason is the experimental significance of this kind of experimentation, the accumulation of analytical errors inducing a large imprecision, and, above all, the incompatibility of laboratory microcosm studies to conduct long-term incubation maintaining biological and physico-chemical soil properties. However, some results coming from small microcosm studies followed over one year are available in the literature (Khan et al., 1988; Khan et al., 1989; Assaf & Turco, 1994; Nakagawa et al., 1996; Kim et al., 2003; Wolt et al., 1996; Loor-Vela et al., 2003). Other experimental devices such as lysimeters or field incubation studies may in theory be used to study the long-term fate of bound residues, but they cannot be used in practice due to the need to use radioactive materials (Helling & Krivonak, 1978; Smith, 1979; Sing & Agarwal, 1992; Barriuso & Koskinen, 1996; Burauel et al., 1998; Burauel & Führ, 2000; Edzang-Ondo, 2005).

In the context of the FOOPRINT project, datasets of BR kinetics can be analysed to develop a mathematical model of BR formation. It should be noted that datasets fit for this purpose are usually not reported in the literature and are presented in grey-literature reports such as PhD theses, e.g. Benoit (1994) for 2,4-D; Beigel (1997) for triticonazole; Pons (1997) for metsulfuron-methyl; Abdelhafid (1998) for atrazine; Dakhel (1998) for amitrole ; Loiseau (2001) for atrazine; Boivin (2003) for 2,4-D, isoproturon and bentazone; Saffih-Hdadi (2003) for parathion; Madrigal-Monarrez (2004) for isoproturon; Mamy (2004) for glyphosate, trifluralin, metazachlor, metamitron and sulcotrione; Edzang-Ondo (2005) for atrazine and isoproturon. Most of the literature datasets allow the simulation of the formation step. Datasets containing a BR "release" phase (Table 1, and cited thesis reports) can also be used to model the reversibility of BR storage. Indications on models found in the literature are discussed further below.

3.2 Proportion of bound residues at a target duration

If the literature on pesticides behaviour in soils is relatively abundant, the multiplicity of the experimental conditions used for soil incubations prevents the identification of comparative parameters for different pesticides and/or soils. An exception is the generation of BR data within the context of pesticide registration. The proportion of BR at 100 days in incubation experiments is used in the EU Council Directive 91/414/EEC for risk assessment purposes, and a threshold of 70 % of BR is used to launch additional studies to inform of the nature and

the specific risk of BR. Review reports containing this information are available at the site http://ec.europa.eu/food/plant/protection/evaluation/. These documents were reviewed and BR data BR for the aerobic degradation route were extracted. The number of review documents available is 97, which represents ca. 15 % of the total number of pesticides (645) in the FOOTPRINT-PPDB (Pesticide Properties Database, www.eu-footprint.org/ppdb.html). In spite of the limited coverage, the data will nevertheless be used for modelling purposes because they are quality-assured and they usually correspond to homogeneous experimental conditions (incubation duration, temperature, soil water content). Data are shown in Annex 1. The pesticide name, its chemical family (from FOOTPRINT-PPDB), its chemical structure, and the mineralization and BR data from the aerobic degradation route in soils are summarized in the Annex 1. Most of the data originate from soil incubations at 20°C and a soil water content equivalent at 50 % of the water holding capacity. The target duration is 100 days, but when other durations are used, they are indicated.

Figures 8 and 9 give a representation of the BR data from Annex 1. The bar length represents the interval between the maximum and minimum proportion of BR. Pesticides were sorted by an increasing order of the minimum (Fig. 8) or maximum (Fig. 9) proportion of BR. All pesticides formed BR in soils at different proportions according to the pesticide nature and probably to experimental conditions. For a given pesticide, the variability of the BR proportion can be very large. The proposed classification in these figures reveals that the proportion of BR varied from <10 % of the applied pesticide to >70 %. If the "methodological noise" of 30 %, corresponding to the minimum requirement of the extraction method is retained as a reference, about 50 % of pesticides had a low proportion of BR (Table 2). Only 12 % of pesticides had a BR proportion higher than 70 %, the threshold used in risk assessment procedures (Table 2).

Table 2. Classification of some pesticides in three classes according to the bound residues amount found in the EU "end points".

« Methodological noise » Low BR level < 30 %	Intermediate situation 30 % < BR < 70 %	Threshold risk assessment High BR level > 70 %
Molinate	Flurtamone	Thiophanate-methyl
S-Metolachlor	2,4-DB	Metalaxyl-M
Isoxaflutole	Acetamiprid	Phenmedipham
Trifloxystrobin	Picoxystrobin	Bromoxynil
Pendimethalin	Glyphosate	Iprodione
Azoxystrobin	Ethofumesate	Chlorpropham
Flazasulfuron	MCPA-acid	Cinidon-ethyl
Carfentrazone-ethyl	Mesotrione	Bentazone
Pyraflufen-ethyl	Zoxamide	Maneb
Imazamox	Flupyrsulfuron-methyl	Foramsulfuron
Ethoxysulfuron	Iodosulfuron	
Benalaxyl	Thifensulfuron-methyl	
lambda-Cyhalothrin	Milbemecin	
Amitrole	Sulfosulfuron	
Glyphosate trimesium	*beta*-Cyfluthrin	
Maleic hydrazide	Cyfluthrin	
Oxadiargyl	Prosulfuron	
Chlorpyrifos	Dimethenamid-P	
Metsulfuron methyl	Ioxynil	
Fosthiazate	Cyhalofop-butyl	
Daminozide	Silthiofam	
Triasulfuron	Mancozeb	
Quinoxyfen	Forchlorfenuron	
Tepraloxydim	Propiconazole	
Etoxazole	Fenamidone	
Chlorpyrifos-methyl	Kresoxim-Methyl	
Deltamethrin	Mecoprop	
Mepanipyrim	Famoxadone	
Spiroxamine	Indoxacarb	
Propyzamide	Pyraclostrobin	
Methoxyfenozide	Flufenacet	
Iprovalicarb	Mesosulfuron	
2,4-D	Alpha-Cypermethrin	
Fluroxypyr	Cypermethrin	
Thiacloprid	Florasulam	
Cyclanilide	Oxasulfuron	
MCPB	Acibenzolar-s-methyl	
	Pyridate	
	Pymetrozine	
	Flumioxazine	
	Chlorotoluron	
	Chlorothalonil	
	Cyazofamid	
	Propoxycarbazone	
	Picolinafen	
	Metiram	
	Imazosulfuron	
	Bifenazate	
	Desmedipham	
	Isoproturon	

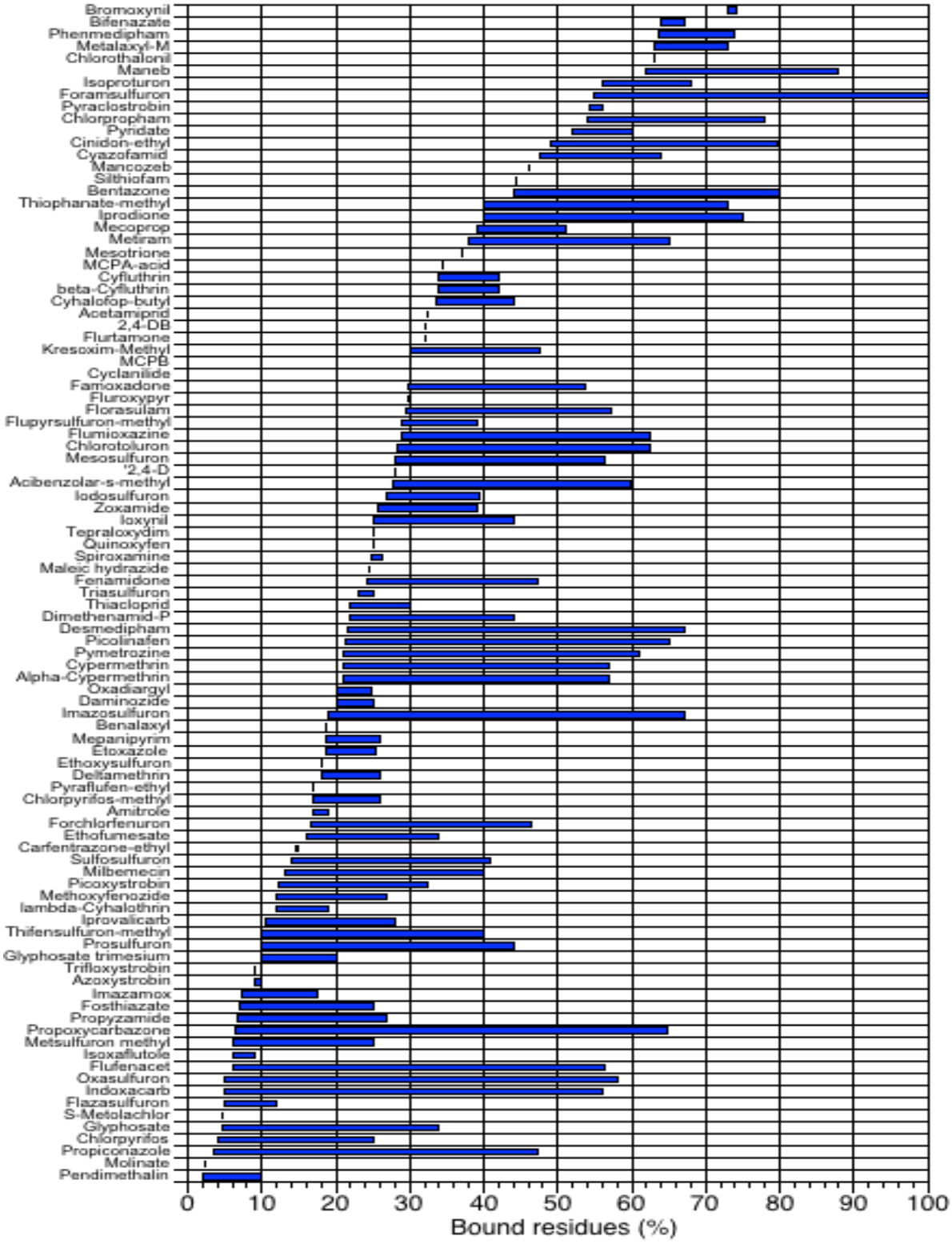

Figure 8. Intervals of bound residues amount and pesticide classification according to the minimum proportion of bound residues reported in the EU "end-points" of the corresponding review report for each pesticide (data provided in Annex 1).

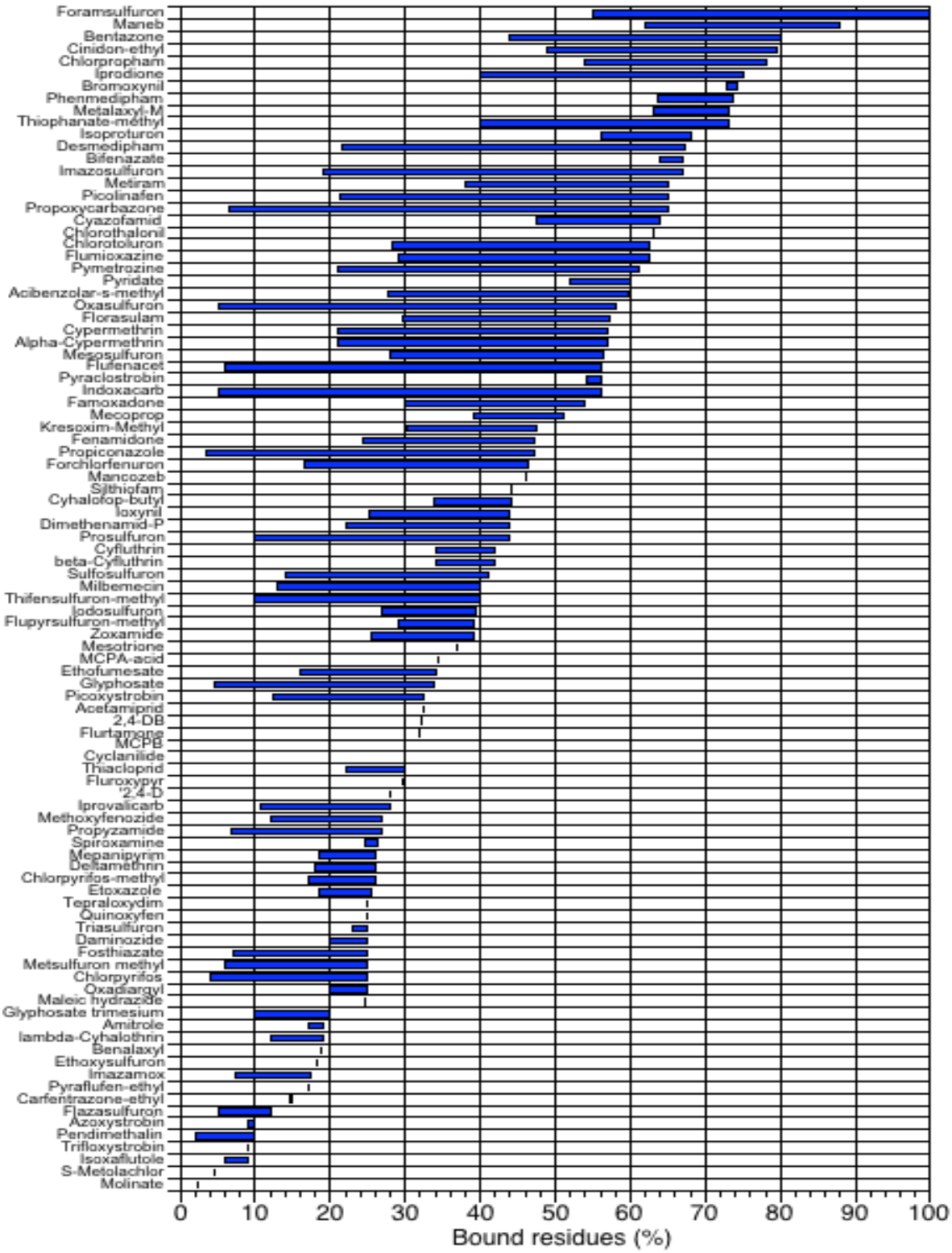

Figure 9. Intervals of bound residues amount and pesticide classification according to the maximum proportion of bound residues reported in the EU "end-points" of the corresponding review report for each pesticide (data provided in Annex 1).

The number of individual pesticides representing a given chemical family is not enough to build an exhaustive classification of importance of BR formation by pesticide family. A preliminary analysis was done with the available data coming from the EU "end-points" when there are >2 pesticides by family. In spite of these approximations, of the heterogeneous values and of the different numbers of pesticides in each family, this preliminary analysis can be used to propose a classification of pesticide families according to the tendency to form BR (Fig. 10). The best families represented in the analysis (i.e. those with the largest number of different pesticides) were the sulfonylureas, pyrethroids and strobilurins. Organophosphates are the compounds forming the least BR. The proportion of BR of the dinitroanilines is low (< 20 %), however, only pendimethalin data was available in the finalised EU "end-points". The highest proportion of BR was found for carbamates, and in particular the dithiocarbamates. However, it should be noted that the largest variability of the BR proportion was found for carbamates. This analysis needs to be enlarged in the future using additional data.

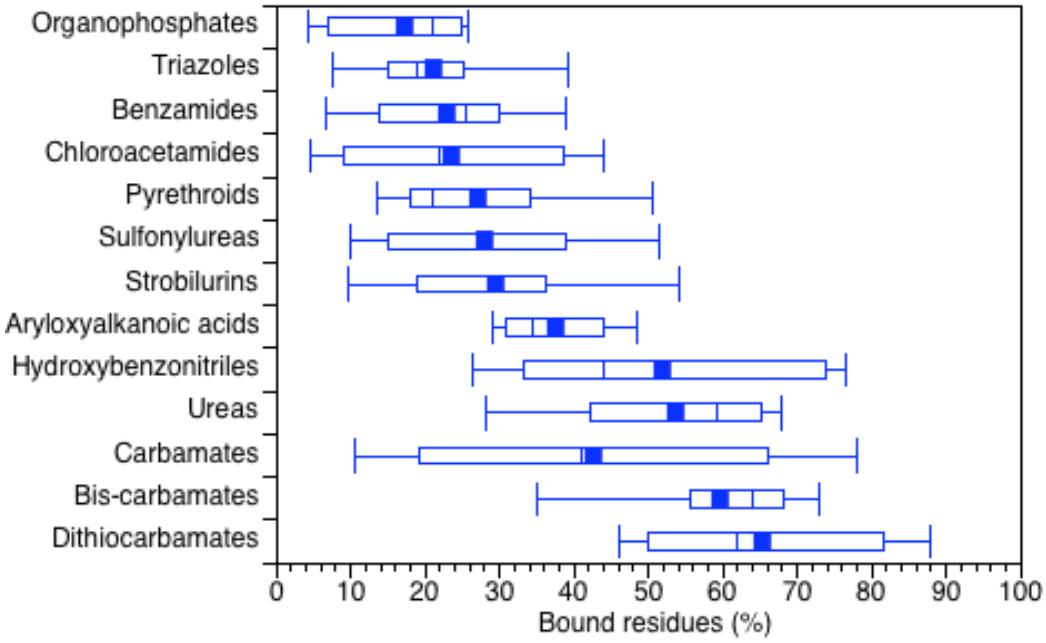

Figure 10. Box plot showing the classification of the pesticide families according to its capacities to form bound residues.

Plotted data corresponded to the BR rang found in EU "end-points" mixed for all pesticides of the same family and corresponding to a target incubation duration near of 100 days. All used data are summarised in the Annex 1.

All data presented above come from direct measurements of the non-extractable ^{14}C. The experimental determination procedure consisted in a combustion of the soil samples containing the non extractable ^{14}C-pesticide residues, a trapping of the $^{14}CO_2$, and a determination of the radioactivity by liquid scintillation counting. In these conditions, no

information is available on the nature of the ^{14}C and the proportion of BR formation is dependent on the position of the ^{14}C-labeling in the pesticide chemical structure. If the ^{14}C labelling is in a labile molecular group (i.e. one which can easily be mineralised), the BR formation will tend to be low. In contrast, if a stable moiety of the molecule is ^{14}C labelled, the proportion of BR can be higher. The different positions of the ^{14}C labelling in the pesticide molecule is very useful to specify degradation routes. If the proportion of ^{14}C incorporation in BR depends on the location of the ^{14}C in the molecule, this is an indication of a breakdown of the molecule before BR formation. On the contrary, the independency of the BR proportion for the location of labelled moiety may give an indication of the incorporation of the total molecule in BR without degradation. As an example, cloramsulam-methyle has the same kinetics of BR formation and the same proportion whether the labelling is on the phenyl or on the pyrimidine moieties (Wolt et al., 1996). However, for risk assessment, the location of the ^{14}C in the molecule can induce different values of BR. Table 2 provides examples focused on molecules containing two or more aromatic rings which show differences in BR formation depending on the location of the labelling. Examples were selected to point out the different behaviour of ^{14}C-N-heteroatomic rings compared with the ^{14}C-phenyl in the same compound. Other pesticides were also selected to try to evaluate the dependence of BR formation upon the nature of the N-ring.

Table 2. Proportion of BR (in % of the applied radioactivity) related to the position of the ^{14}C-labeling for the molecules containing different rings.

Comparison for a same pesticide of the BR coming from a phenyl-^{l4}C-laveling and a N-heteroatomic-^{14}C-laveling. Calculation of the relationship of the BR formed with ^{14}C-N-ring and ^{14}C-phenyl (data from EU pesticide review reports – Annex 1).

Pesticide	Phenyl	Pyridine	Pyrimidine	Indol	Imidazole	Thiadiazole	Triazole	Triazine	N-ring/phenyl
Forchlorfenuron	24 - 46	23 - 25							0.3
Picolinafen	44 - 65	21 – 23							0.4
Picoxystrobin	22 -32	12 - 32							0.8
Foramsulfuron	74 - 103		55 - 93						0.8
Mepanipyrim	26		19						0.7
Mesosulfuron	56		28 - 55						0.7
Oxasulfuron	21 - 27		40 - 58						2.0
Cinidon-ethyl	80			49					0.6
Cyazofamid	48				64				1.3
Flufenacet	30 - 56					6			0.1
Propiconazole	23 - 27						14 - 16		0.6
Metsulfuron methyl	15 - 25							18	0.9
Prosulfuron	12 - 44							10	0.4
Triasulfuron	25							23	0.9
Fluroxypyr		30							--
Flupyrsulfuron-methyl		29	39						--
Imazamox		17							--
Sulfosulfuron		15			14				--
Amitrole							17 - 19		--
Thifensulfuron-methyl								10	--

In general, when ^{14}C-labeling was supported by a N-heteroatomic ring, the proportion of BR was lower than in the same molecule with a phenyl-ring ^{14}C-labelling. Two exceptions were

noted, for cyazofamid, and oxasulfuron. These data allows a classification of the capacity of aromatic rings to form BR (Fig. 11). It appears that ^{14}C in thiadiazole, triazole pyridine and triazine rings is the little incorporated in BR compared to other rings. The ranges of BR formation were large when the ^{14}C-labelling was in phenyl, imidazole and pyrimidine moieties.

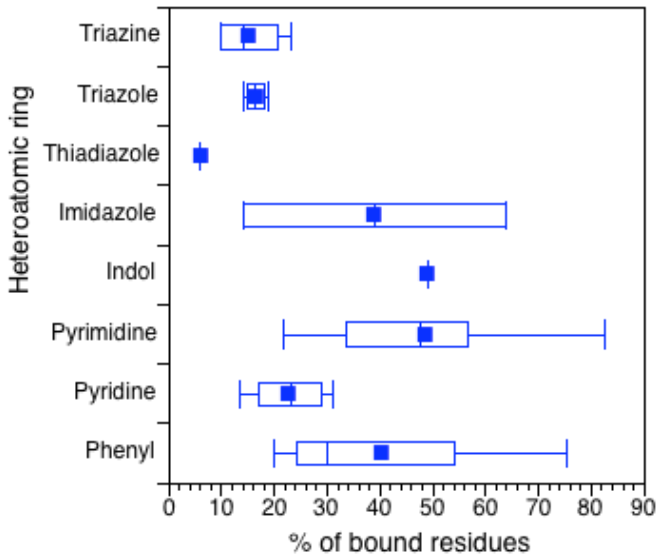

Figure 11. Box plot of the proportion of bound residues formed in relation to the nature of N-heteroatomatic ring or phenyl containing the ^{14}C-laveling

In addition to the data originating from the EU "end points", results on BR formation coming from the published literature are summarised in Table 3. Only results from incubation with a duration of ca. 100 days or more were retained. The duration time which corresponds to the maximum incubation time is reported and differs according to the datasets. These data supported the results of the Annex 1 and Figures 7 and 8, mainly for some selected families like the dinitroanlines and the triazines. Most of data reported in the literature were found to be consistent, although it should be noted that some results were out of these ranges, probably due to the enlarged incubation times found in the literature.

Table 3. Non exhaustive complementary data on bound residues amount for different pesticides and different incubation durations.

Only results coming from duration close to 100 days or higher were reported.

Name	Familly	% Bound residues (duration, days)	Reference
Cyprodinil	Anilinopyrimidine	54 (197 d)	Dec et al., 1997
2,4-D	Aryloxyalkanoic acid	14 (90 d)	Khan, 1995
2,4-D	Aryloxyalkanoic acid	44.9 (90 d)	Xie et al., 1997
2,4-D	Aryloxyalkanoic acid	44.9 (250 d)	Barriuso et al., 1997
Diclofop-methyl	Aryloxyphenopropionate	37 (180 d)	Smith, 1979
Dicamba	Benzoic acid	67.4 (91 d)	Mordaunt et al., 2005
Bentazone	Benzothiazinone	25.9 – 56.7 (105 d)	Lee et al., 1988
Bentazone	Benzothiazinone	32 – 65 (160 d)	Boivin et al., 2004
Paraquat	Bipyridylium	92 (91 d)	Mordaunt et al., 2005
Carbetamide	Carbamate	48.1 (250 d)	Barriuso et al., 1997
Acetochlor	Chloroacetamide	40.3 (371 d)	Loor-Vela et al., 2003
Alachlor	Chloroacetamide	40.3 – 45.1 (140 d)	Gan et al., 1995
Metazachlor	Chloroacetamide	35 – 46 (140 d)	Mamy et al., 2005
Metolachlor	Chloroacetamide	27.6 – 36.9 (120 d)	Rice et al., 2002
Dimethenamid	Chloroacetimide	57 – 63 (142 d)	Crawford et al., 2002
Chlorothalonil	Chloronitrile	18 – 46 (90 d)	Regitano et al., 2001
Butralin	Dinitroaniline	17 (150 d)	Helling & Krivonak, 1978
Chlornidine	Dinitroaniline	17 (150 d)	Helling & Krivonak, 1978
Dinitramine	Dinitroaniline	8 (150 d)	Helling & Krivonak, 1978
Fluchloralin	Dinitroaniline	21 (150 d)	Helling & Krivonak, 1978
Oryzalin	Dinitroaniline	6 – 36 (<1000 d)	Helling & Krivonak, 1978
Pendimethalin	Dinitroaniline	45.4 (250 d)	Barriuso et al., 1997
Profluralin	Dinitroaniline	11 (150 d)	Helling & Krivonak, 1978
Trifluralin	Dinitroaniline	8 (360 d)	Helling & Krivonak, 1978
Trifluralin	Dinitroaniline	7 (150 d)	Helling & Krivonak, 1978
Trifluralin	Dinitroaniline	21.3 (91 d)	Mordaunt et al., 2005
Trifluralin	Dinitroaniline	8 – 27 (140 d)	Mamy et al., 2005
Acifluorfen	Diphenyl ether	15 (210 d)	Celi et al., 1997
Fonofos	Ethylphosphonothioate	21.8 (130 d)	Khan & Bélanger, 1987
Glyphosate	Glycine derivative	6 – 13 (140 d)	Mamy et al., 2005
Endosulfan	Organochlorine	23 – 34 (160 d)	Monteiro et al., 1989
Chlorpyrifos	Organophosphate	11.7 (97 d)	Yücel et al., 1999
Oxadiazon	Oxidiazole	1.9 – 13.3 (175 d)	Ambrosi et al., 1977
Cypermethrin	Pyrethroid	23 (168 d)	Roberts & Standen, 1981
Deltamethrin	Pyrethroid	19.2 (180 d)	Khan et al., 1988
Metsulfuron-methyl	Sulfonylurea	11.4 – 48.1 (98 d)	Pons & Barriuso, 1998
Metsulfuron-methyl	Sulfonylurea	47.8 (250 d)	Barriuso et al., 1997
Metsulfuron-methyl	Sulfonylurea	19.3 – 52.6 (180 d)	Ye et al., 2005
Prosulfuron	Sulfonylurea	29.2 – 48.1 (104 d)	Hultgren et al., 2002
Diallate	Thiocarbamate	10 (210 d)	Anderson & Domsch, 1980
Triallate	Thiocarbamate	31,1 (365 d)	Anderson & Domsch, 1980
Atrazine	Triazine	16.6 (90 d)	Xie et al., 1997
Atrazine	Triazine	54 (320 d)	Assaf & Turco, 1993
Atrazine	Triazine	19.1 – 29.7 (360 d)	Nakagawa et al., 1996
Atrazine	Triazine	49.8 (154 d)	Miller et al., 1997
Atrazine	Triazine	26.2 (91 d)	Mordaunt et al., 2005
Atrazine	Triazine	39.4 (180 d)	Winkelmann &Klaine, 1991
Atrazine	Triazine	62 – 73 (120 d)	Kruger et al., 1997
Atrazine	Triazine	10.4 (250 d)	Barriuso et al., 1997
Atrazine	Triazine	54 (365 d)	Khan, 1995
Atrazine	Triazine	29 – 53 (180 d)	Edzang-Ondo, 2005
Promethryn	Triazine	43 (150 d)	Khan & Hamilton, 1980
Prometryn	Triazine	57.4 (365 d)	Khan, 1995
Prometryn	Triazine	43 (150 d)	Khan, 1982
Simazine	Triazine	20.3 (250 d)	Barriuso et al., 1997
Terbutryn	Triazine	54.6 (250 d)	Barriuso et al., 1997
Metamitron	Triazinone	28 – 45 (140 d)	Mamy et al., 2005
Propiconazole	Triazole	60 – 74 (365 d)	Kim et al., 2003
Triticonazole	Triazole	21 – 36 (150 d)	Beigel et al., 1999
Sulcotrione	Triketone	23 – 30 (140 d)	Mamy et al., 2005
Dimefuron	Urea	68.1 (250 d)	Barriuso et al., 1997
Diuron	Urea	20 (180 d)	Khan, 1995
Isoproturon	Urea	64.5 (91 d)	Mordaunt et al., 2005
Isoproturon	Urea	47 – 66 (180 d)	Edzang-Ondo, 2005
Methbenzthiazuron	Urea	41 (111 d)	Führ & Mittelstaedt, 1980
Cloransulam	- - -	44 -78 (357 d)	Wolt et al., 1996
Flupropacil	- - -	15 (238 d)	Vithala & White, 1996
Lindane	- - -	8 (91 d)	Mordaunt et al., 2005

4 MECHANISMS IMPLICATED IN PESTICIDE BOUND RESIDUES FORMATION

4.1 Inventory of hypothesised mechanisms involved in bound residues formation

The dependence of pesticide behaviour in soils with soil organic matter is related to more or less specific interactions or reactivities (Ahmad et al., 2001; Martin-Neto et al., 2001). Physical interactions are responsible for sorption and colloidal entrapment, chemical interactions imply establishment of covalent bounds, and biological interactions concern pesticide transformation and incorporation into the soil microbial biomass. All these interactions are space and time dependent. Spatially, sorption and degradation depend on the accessibility of sorption sites and degrading microorganisms (Alexander, 2000), respectively. Pesticide availability in soils is time dependent, and decreases with increasing pesticide residence time because of the evolution of the initial interactions between the pesticide and the soil constituents. The initial physico-chemical interactions responsible for sorption are reversible, but they can become less or non reversible with time, leading to the stabilization of the pesticide residues under less available and less biodegradable forms (Khan, 1982). Various hypotheses have been proposed to explain BR formation: chemical binding to soil organic matter constituents, oxidative coupling with phenolic soil constituents and incorporation into phenolic co-polymers, bioincorporation in cellular structures through metabolic activity of soil microorganisms, blocking of internal voids of soil organic constituents and soil microorganisms (Mathur & Morley, 1975; Wolf & Martin, 1976; Khan, 1982; Bertin et al., 1991; Bollag et al., 1992; Bollag & Myers, 1992). All of these hypotheses point out the fundamental role of soil organic matter and soil microorganisms. However, White (1976) indicated early that some interactions with soil mineral constituents (clays) could contribute to BR. This type of interactions can be determinant in the deeper soil horizons where the organic matter contents are low. The interactions leading to BR formation can be classified into two categories: those implying the establishment of the chemical bonding (corresponding to a “chemical stabilisation”) and those implying a sequestration or physical trapping into the organic constituents. In addition, soil microbial biomass is an additional soil compartment to be considered because it can directly stock pesticide residues under non extractable forms. It also plays a fundamental role on pesticide dynamics and in BR remobilisation.

In literature reviews on BR such as those of Calderbank (1989) or Gevao et al. (2000), soil-pesticide interactions are considered to be initially responsible for pesticide adsorption phenomena which then contribute to BR formation. However, adsorption is a physico-

chemical process, and it is intrinsically reversible. When the adsorption becomes non reversible, with apparition of hysteretic systems during the desorption process, this can be interpreted as a modification of the initial interaction into the soil interfaces or by the inadequacy of the solvent used for desorption, which is not competitive enough to displace the adsorbed pesticide. Hence, the hypothesis that adsorption mechanisms are responsible for BR formation does not seem appropriate. Most of the interactions implicated in pesticide adsorption can be breakable either by desorption with water if they are reversible, or by use of a solvent or solvent mixture enough competitive.

Other physical diffusive mass transfer mechanisms into the micro or nano-porositty of soil aggregates and colloidal constituents can be responsible for the disappearance of the pesticide from the solution, contributing to slow sorption and BR formation (Brusseau et al., 1991). They are often invocated to explain hysteresis during adsorption/desorption experiments, and they are phenomenologically combined with adsorption under the term “sorption”. The kinetics of these diffusion processes is lower than those of adsorption and its reversibility could be lower than interfacial interactions. This mechanism is responsible for the trapping or sequestration, which can be described as a slow sorption (Pignatello & Xing, 1996). Diffusion/adsorption coupling can contribute to the delocalisation of pesticide residues into the soil voids with a potential preservation again biodegradation and with a decrease in solvent accessibility. Pesticides or their metabolites may remain intact, but become non-extractable. The kinetic interferences between these different processes, provoking a decrease in pesticide availability, are often mentioned in the literature by the term “ageing”. Increased contact between pesticides (or their metabolites) reduces the fraction that can be extracted by “mild” extraction procedures (Gevao et al., 2000). The mild character of extraction makes the difference between ageing and BR formation. Different processes are proposed to explain “ageing: sorption onto soil particles, diffusion into spatially remote areas, such as soil micropores, entrapment within soil organic matter. All of these phenomena can also be implicated in BR formation.

4.2 Microbiological component of bound residues

Several publications showed a relationship between soil microbial activity and the extent of BR for a given pesticide. Some results showed that an increase in soil microbial activity increased BR formation. Otherwise, an increase of the pesticide degradation can be accompanied by an increase in the proportion of BR. The more illustrative experiments are when incubations are done in parallel in sterile and non sterile conditions. One example is presented in Fig. 12, which shows that the inhibition of the microbiological activity by soil

sterilisation leads to a decrease in BR for 2,4-D and its metabolites (Benoit & Barriuso, 1997). When the microbiological activity was decreased, the extractible fractions had a low variation during incubation. With a normal microbiological activity, the residues extractability decreased quickly with a progressive increase in BR. This exemplifies the indirect role of soil microorganisms in BR formation through the partial degradation of the pesticides, leading to the production of metabolites with a chemical reactivity higher that the initial pesticide. In the example presented in Figure 12, chloro-phenols could be coming from 2,4-D degradation.

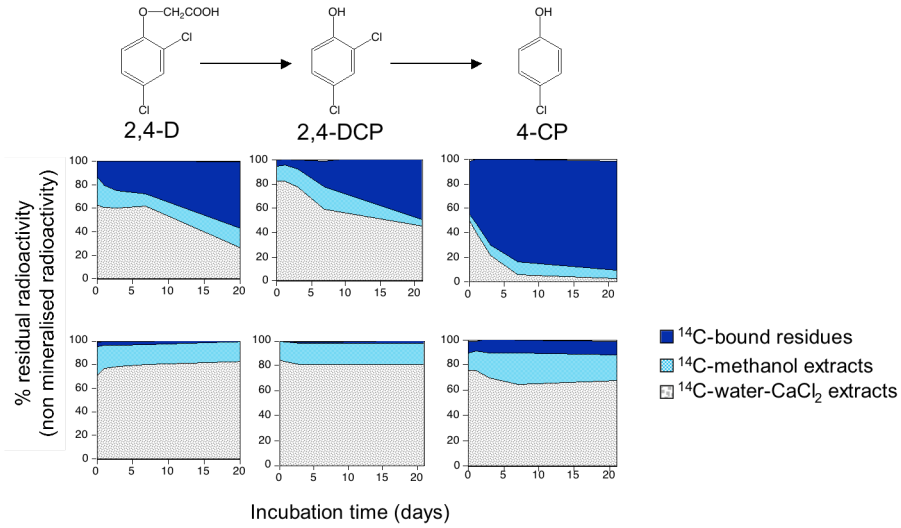

Figure 12. Overall balance of the radioactivity distribution between extractible fractions and bound residues during incubation in sterile and non sterile conditions of 14C-2,4-D, 14C-2,4-DCP (2,4 dichlorophenol) and 14C-4-CP (4 chlorophenol) (Benoit & Barriuso, 1997).

If the indirect participation of the soil microbial activity can be demonstrated with the sterile / non-sterile experiments, an important point is the quantitative evaluation of the direct BR stock in the soil microbial biomass. This can originate from a passive accumulation of pesticide residues or as a consequence of the metabolic microbial pathways. Microorganisms can absorb large amounts of pesticides (Wolf & Martin, 1975; Percich & Lockwood, 1978). The contribution of the soil microbial biomass to BR can be estimated using fumigation techniques used for the C and N-microbial biomass measurements (Stott et al., 1983; Soulas et al., 1984). The application of these techniques to soils incubated with ^{14}C-pesticides allows the estimation of ^{14}C amount incorporated into the soil microbial biomass. Table 4 gives some examples for different ^{14}C-uniformly-ring labelled pesticides (Houot et al., 1997). ^{14}C into the biomass represented between 0.7 and 10 % of the initial ^{14}C-pesticide. Supposing that the total biomass incorporated ^{14}C is the microbial component of BR, the residues associated to the microbial biomass could contribute between 3 and 20% to the total amount of BR. The

largest proportion of ^{14}C- incorporation in biomass was found with pesticides without Cl substituents. These pesticides also showed the largest mineralization during incubation, which could be an indication of a metabolic pathway of incorporation with the use of part of pesticide carbon to synthesise biochemical cellular constituents.

Table 4. Proportion of bound residues incorporated into the soil microbial biomass estimated by fumigation-extraction for different pesticides uniformaly-^{14}C-ring labeled (Houot et al., 1997).

Pesticide	Family	% ^{14}C applied	% ^{14}C of bound residues
2,4-D	Aryloxyalkanoic acid	1.3 ± 0.2	2.9 ± 0.4
Carbetamide	Carbamate	2.9 ± 0.6	17.2 ± 1.3
Pendimethalin	Dinitroaniline	2.1 ± 0.1	4.7 ± 0.2
Metsulfuron-methyl	Sulfonylurea	5.5 ± 2.1	18.4 ± 4.3
Terbutryn	Triazine	2.0 ± 1.6	8.1 ± 2.9
Atrazine	Triazine	0.7 ± 0.1	6.9 ± 0.3
Simazine	Triazine	0.8 ± 0.1	4.0 ± 0.5
Dimefuron	Urea	2.2 ± 0.4	3.2 ± 0.6

From a risk assessment point of view, it is important to know the chemical nature of the pesticides residues incorporated into the biomass. If there is a conservation of the pesticide or metabolite structure, it remains a concern for risk assessment because the high turnover of microbial biomass may lead to a possible release of residues. If these residues are recycled as C-biomass and the structure corresponded to the other biochemical cellular constituents, then these residues is of no relevance to the risk assessment. It is known that fungal biomass can stock pesticides or metabolites without degradation (Kaufman & Blake, 1970). Usually it is considered that bacteria are more active on pesticide degradation by endo-cellular mechanisms. Little information is available on nature of ^{14}C coming from pesticides found into the bacterial biomass. Sequential extractions, allowing extract different biochemical families from the bacterial and fungal biomass growing in presence of ^{14}C-pesticides, were used to identify

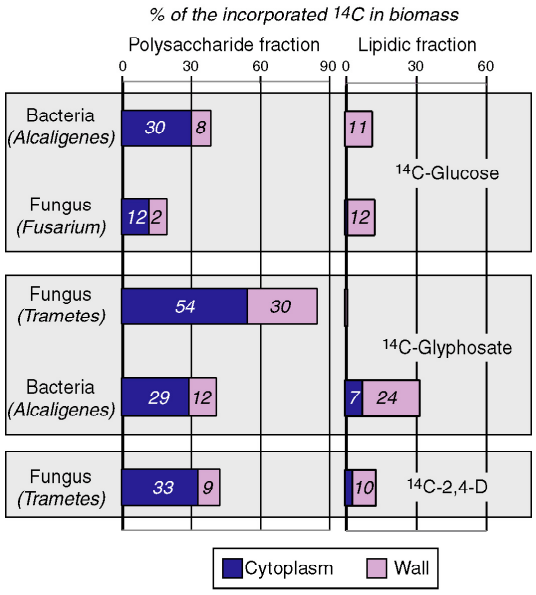

Figure 13. Distribution of the radioactivity among the polysaccharide and lipidic fractions of the fungal and bacterial biomass growing in pure culture in presence of ^{14}C-glyphosate and ^{14}C-2,4-D as C source.
Culture with ^{14}C-glucose were used as reference (Charnay et al., 2004)

the possible route of ^{14}C incorporation into the biomass by Charnay et al., (2004). ^{14}C was associated to the lipid, polysaccharide and protein biomass fractions (Fig. 13). In the case of the glyphosate and 2,4-D, most of the incorporated ^{14}C into the biomass was associated to the polysaccharide fractions, coming from 40 to 85 % of the ^{14}C-biomass. The highest proportion was found in the fungal biomass in the case of glyphosate.

4.3 Chemical and physical component of bound residues

Because soil organic matter is directly implicated in the formation of BR, early methods used to study soil organic matter were applied to soil samples containing BR to accede at the complementary information on BR. Soil organic matter is a heterogeneous set of compounds with different origin, nature and properties, and spatially distributed within the soil aggregates conditioning their accessibility (Christensen, 2001). Most of the soil organic matter studies are based on the application of techniques allowing to reduce its heterogeneity and to separate more homogeneous fractions. Chemical fractionation techniques and molecular size fractionation separate fractions with more homogeneous properties. The classical chemical fractionation of soil organic matter consists in solubilising organic constituents with alkaline solvents followed by acidification of the alkaline extract to flocculate part of the solubilised organic compounds. The separation of these fractions is based on the relative density distribution of the functional groups in relation to the macromolecular size of the compounds. Others methods, like soil physical fractionation methods, separate fractions of different density and/or size at the soil particle scale. These techniques separate fresh or poorly humified organic matter from humified organic matter; the former being localized in the coarsest (or lightest) fractions, and the latter in the finest (or heaviest) fractions (Balesdent et al., 1987; Christensen, 2001).

The first techniques to study BR, which are still being used, were the use of alkaline extractions and the fractionation into humic and fulvic acids and humine, measuring the ^{14}C associated with each humic fraction. Numerous results on the overall balance of the ^{14}C-BR among these fractions can be found in the literature. Table 5 which summarizes some representative examples highlights the high variability of the results and the difficulty to generalise this kind of results.

Beyond the quantification of ^{14}C-BR among the humic fractions, soil organic matter fractionation techniques allow information to be gained on the relative contribution of physical trapping and chemical bound mechanisms involved in BR formation (Barriuso et al., 1991; Loiseau & Barriuso, 2002). Coupling physical and chemical soil fractionation can be

used to evaluate, more or less quantitatively, the risk of BR mobilisation or the reversibility degree of the stabilisation under BR. The part of BR associated with incompletely decomposed plant materials that are preferentially located in the coarsest fractions, during a soil size particles fraction, could be released during their decomposition or humification. On the other hand, BR associated with dispersible fine clay fractions or with soluble humic fractions, such as fulvic acids, would present a high mobilization risk in case of leaching of particles or soluble organic matter.

Table 5. Examples of the distribution of 14C of bound residues for different pesticides among the humic fractions (humin, fulvic and humic acides) separated by alkaline extration and acid precipitation.

Pesticide	Family	% applied	% of Bound residues			Reference
		Bound residues	Fulvic acids	Humic acids	Humin	
Cyprodinil	Anilinopyrimidine	54.1	20	14	50	Dec et al., 1997
Cyprodinil	Anilinopyrimidine	58.3	22	24	42	Dec et al., 1997
Bentazone	Benzothiazinone	46.6	30	22	48	Lee et al., 1988
Bentazone	Benzothiazinone	56.7	43	19	37	Lee et al., 1988
Bentazone	Benzothiazinone	44	36	23	41	Lee et al., 1988
Carbaryl	Carbamate	12.5	10	3	86	Murthy & Raghu, 1991
Carbaryl	Carbamate	35.7	19	2	79	Murthy & Raghu, 1991
Carbaryl	Carbamate	78.0	11	2	87	Murthy & Raghu, 1991
Butralin	Dinitroaniline	3	51	7	42	Helling & Krivonak, 1978
Butralin	Dinitroaniline	17	53	21	26	Helling & Krivonak, 1978
Chlornidine	Dinitroaniline	17	54	16	30	Helling & Krivonak, 1978
Dinitramine	Dinitroaniline	8	47	15	38	Helling & Krivonak, 1978
Fluchloralin	Dinitroaniline	21	60	25	15	Helling & Krivonak, 1978
Profluralin	Dinitroaniline	11	53	16	31	Helling & Krivonak, 1978
Trifluralin	Dinitroaniline	7	47	15	38	Helling & Krivonak, 1978
Phosalone	Organophosphate	74.9	45	30	26	Ambrossi et al., 1977
Phosalone	Organophosphate	79.3	57	25	17	Ambrossi et al., 1977
Atrazine	Triazine	?	48	14	38	Schiavon et al. 1978
Atrazine	Triazine	?	17	13	61	Munier-Lamy et al., 2002
Atrazine	Triazine	?	18	20	45	Munier-Lamy et al., 2002
Atrazine	Triazine	22.6	14	1	85	Loiseau et al., 2000
Atrazine	Triazine	44	41	0	54	Loiseau et al., 2000
Atrazine	Triazine	20	39	22	38	Benoit et al., 2000
Atrazine	Triazine	40	32	7	60	Barriuso et al., 1991
Atrazine	Triazine	16	62	12	25	Barriuso et al., 1991
Atrazine	Triazine	15	47	13	40	Barriuso et al., 1991
Propiconazole	Triazole	23.2	28	10	62	Kim et al., 2003

From a mechanistic point of view, these fractionation techniques provide supplementary information. For example, the capacity of organic constituents of different soil size fractions to form atrazine BR decreased with the particle size (Barriuso et al., 1991; Barriuso et al., 2000; Barriuso & Koskinen, 1996), as shown in Fig. 14. The coarsest fractions, containing non-humified organic matter, had the largest atrazine binding capacity. The relative affinity of soil organic matter to form BR was high in the non humified fractions. The general trend of BR location in the soil particle size was confirmed for atrazine in different soils and incubation conditions. However, similar experiments undertaken with isoproturon have shown that most BR were in the finest fraction (<20 μm) where most organic C was located.

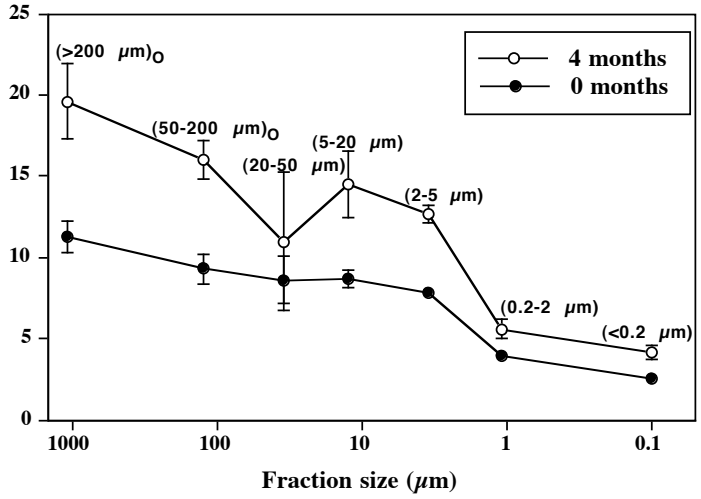

Figure 14. Variation with particle size of the relative concentration of atrazine bound residues, expressed as ^{14}C-atrazine equivalent per fraction C content, in soil sampled 0 and 4 months after application (Barriuso & Koskinen, 1996).

Indeed, for isoproturon, the humified organic matter had the highest affinity to form isoproturon BR (Benoit et al., 2000). The different behaviour between atrazine and isoproturon could be related to the different supposed mechanisms of BR formation. For atrazine, non reactive physical mechanisms could be the main mechanism at play although it should be noted that fungal mycelium co-located on the coarsest fractions could also play an important role (Wolf & Martin, 1975; Barriuso et al., 1991). For isoproturon, the main mechanism of BR formation is probably the reactive chemical incorporation of aniline, an isoproturon metabolite, through a reaction with humified organic matter into the finest fractions (Lehr et al., 1996; Scheunert & Reuter 2000).

Additional experiments were done to evaluate the mineralization rate of atrazine BR of each fraction (Barriuso et al., 1994). Mineralization rates strongly depended on the fraction size, and progressively increased with decreasing size fraction. After 100 days of incubation, nearly 8 % of ^{14}C-BR of the finest fraction (<0.2 μm) were mineralized. In contrast, less than 1% of BR of the coarsest fraction (>200 μm) had evolved as CO_2. These incubation tests allow the evaluation of the the availability of bound residues and their potential for biological remobilization (Barriuso et al., 2000).

Soil size fractionation followed by alkaline extraction, before and after HF treatment, and then acid hydrolysis was applied to the soils containing atrazine BR (Loiseau & Barriuso, 2002). Colloidal dispersion resulting from the alkaline extraction made soluble the BR associated to fulvic and humic acids. The analysis of BR recovered with fulvic acids indicated that these residues were probably entrapped, whereas the BR recovered with humic acids

were "chemically bound" to this fraction. Dec et al. (1997), using ^{13}C-cyprodinil found that some residues associated with fulvic acids consisted in the intact molecule which was apparently sequestered, whereas most residues associated with humic acids were chemically bound. Acid hydrolysis of the humic acids which were not dialyzable at 5000 Da confirmed the formation of BR via chemical bonding, and suggested a chemical bond between the triazinic ring and HA through the –OH group of hydroxy-atrazine, or an hetero-atomic bond with the 1st carbon of the triazinic ring after substition of the chlorine atom. Identification of hydroxy-atrazine in the hydrolysates of humin can also be due to the disruption of a chemical bond between atrazine and/or hydroxy-atrazine and the organic matter. In all cases, no chemical bond can be hypothesized between the –NH- groups of the atrazine's lateral chains and organic matter (Loiseau & Barriuso, 2002).

Applying the different steps of the chemical fractionation set-up at two different soils (Fig. 15), 78 to 89 % of the bound residues were solubilised. From 20 to 50 % of the BR of the fraction <20 µm were identified as the intact atrazine and its main derivatives, indicating that this proportion of BR were probably formed by entrapment in voids of the soil organic matter. 13 to 30 % of the bound residues were associated to humic acids, they were not dialyzable and were released by acid hydrolysis, indicating that these BR were chemically bound to humic acids.

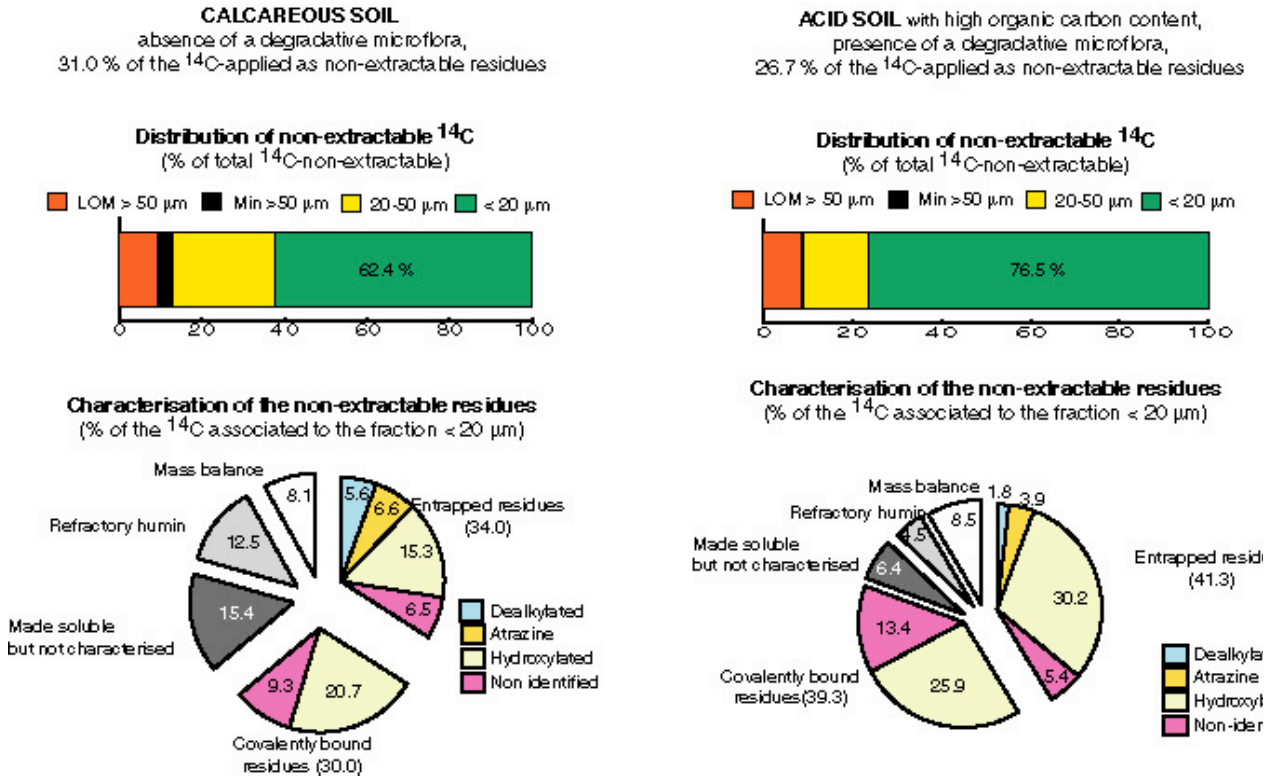

Figure 15. Characterization of bound residues in the fraction <20 µm from two soils: a calcareous soil and an organic acid soil, by application of a fractionation protocole using physical and chemical treatments (data from Loiseau & Barriuso, 2002).

Specific methods were developed to study BR associated to humin which can be essential for BR for the more hydrophobic chemicals. Humin was isolated by the traditional alkalin extraction and then fractionated into bound-humic acids, bound-lipids and mineral components using a methyl-isobutylketone (MIBK) portioning method proposed by Rice & MacCarthy (1989).

4.4 Information on the bound residues nature

Application of more efficient extraction techniques than those typically used for pesticide extraction have allowed the extraction of additional compounds which can be analysed by chromatographic techniques (Northcott & Jones, 2000). Techniques used are for example, high-temperature distillation (Khan & Hamilton, 1980; Capriel et al., 1985), thermoanalytical methods (Khan, 1982a, b; Alzaga et al., 1995) or the use of supercritical methanol (Scheunert et al., 1992) or carbon dioxide (Khan, 1995) extraction. However, Ye et al. (2005) reported results from Guo et al. (1998) showing that in the case of chlorsulfuron and its metabolites, these techniques can destroy the original molecular structure. Hence, results obtained using these rather drastic extraction methods may not represent the "true" composition of BR.

Coupling physical and chemical soil fractionation methods, as described in the precedent paragraph, allows to dissolve soil organic matter and to recover part of the BR in a soluble state, thereby allowing the use of chromatographic methods to identify the chemical nature of some BR (Loiseau et al., 2000). Alkaline hydrolysis is also used if the pesticide or its metabolites are stable enough. For instance, Schwarzbauer et al. (2003) performed an alkaline hydrolysis to study BR for DDT.

From the results of the experiment illustrated in Fig. 15, about 30 % of the BR can be identified as the initial non-degraded pesticide (atrazine) or its close metabolites. These results cannot be generalized, since the nature of the pesticide and the experimental conditions (soil type, incubation parameters) are important factors. Theses methods are very time consuming and it is not possible to be certain that the solubilised BR were not transformed during the more aggressive steps of the solubilisation protocol (alkaline extraction favouring oxidative reaction, hydrolysis in the acid conditions).

Other approaches providing information on BR mechanisms and the subsequent analysis of the nature of BR is silylation (Dec et al., 1997b). A part of BR associated to the humic acids can be solubilised by silylation, allowing to differentiate between sequestration and covalent

binding. The substitution of active hydrogen atoms of various functional groups of the humic substances with silyl groups disaggregates the humic compounds in smaller fragments which are held together by H bonds and other non-covalent interactions. Unlike entrapped chemicals, covalently bound residues are not released by this derivatization. In the case of cyprodinil, Dec et al. (1997b) analyzed the silyled residues and identified two mechanisms of BR formation: sequestration of the unaltered or only slightly altered cyprodinil, and molecular cleavage followed by covalent binding. Similar approaches coupling silylation and MNR were used to study BR for anilazine (Haider et al, 1992; Klaus et al. 1998).

Others techniques tried to avoid the denaturation stages or to reduce the duration of analysis. Liquid chromatography with mass spectrometry and different ionization methods have been directly used to analyse BR associated to the soluble fractions as dissolved organic matter (Klaus et al., 2000; Ye et al. 2004). Some authors use spectrometric methods as NMR and applied them to BR obtained from the soil incubation with pesticides labelled with ^{13}C or ^{15}N (Thorn et al., 1992; Hatcher et al., 1993; Thorn et al., 1996; Dec et al., 1997; Witte et al., 1998; Benoit & Preston, 2000; Berns et al., 2005). NMR allows the identification of the signals specific of the structural functional groups that can be attached to the initial structure of the pesticide or its metabolites (Fig. 16). Similar information was found using ^{15}N-labelled simazine, incubated with ^{15}N-depleted compost to reduce the amount of background signal (Berns et al., 2005). Specific signals corresponding to the metabolites of simazine, resulting from N-dealkylation, were detected. Other fragments coming from the triazine ring destruction were also detected. The NMR information is only qualitative, indicating the presence or the preservation of the structure. The biggest problem of these techniques is related to the low sensibility and the high natural noise, which means that that a high enrichment of the labelled pesticides is required and that concentration 10 to 1000 times that used in the field must be used.

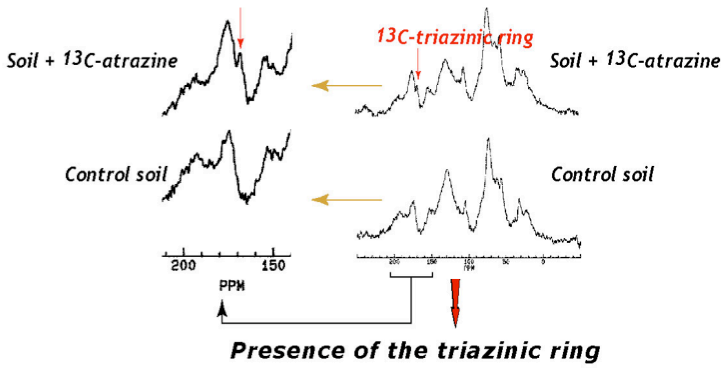

Figure 16. Identification of the presence of the triazincic ring on the bound residues recovered after incubation of a soil with ring-^{13}C-atrazine (data from Benoit & Preston, 2000).

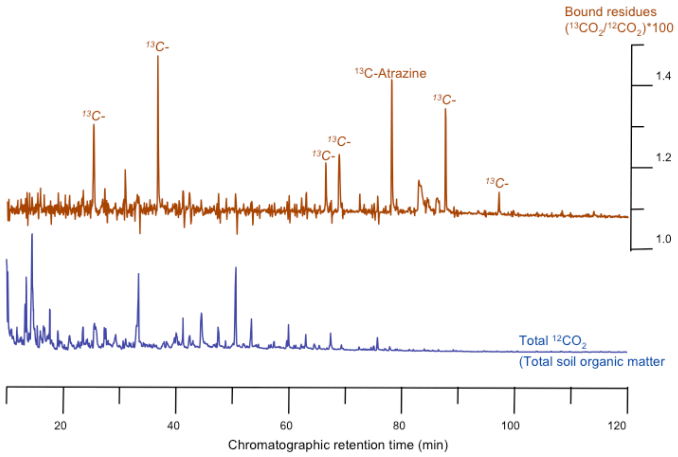

Figure 17. Identification of atrazine residues and others labelled fragments coming from the bound residues of ^{13}C-atrazine obtained after incubation in a soil.
Results of isotopic mass spectrometry detection of the pyrolysis fragments separated by gas chromatography (data from Dignac et al., 2004).

Other degradative techniques allow the release of part of BR. Pyrolysis of soil or humic fractions containing BR allows the direct chromatographic analysis of the compounds released by thermal desorption or cracking of chemical bound responsible of the BR formation (Khan & Hamilton, 1980; Loiseau, 2001; Schwarzbauer et al., 2003). Pyrolysis released up 90 % of prometryn BR (Khan & Hamilton, 1980) allowing identification of 50% of the total BR as parent compound. The use of ^{13}C-labeled pesticides and the coupling pyrolysis – gas chromatography – atomic mass spectrometry allows an improvement in detection selectivity (Fig. 17) with an identification of the isotopically-enriched compounds originating from the labelled pesticide (Guthrie et al, 1999; Loiseau, 2001; Dignac et al., 2004).

5 FACTORS DETERMINING THE RATE OF BOUND RESIDUES FORMATION

5.1 Pesticide molecular properties

Relatively few publications have investigated the relationships between BR formation and molecular properties. Some general publications point out the low capacity to form BR of the dinitoanilines, in comparaison to triazines (simazine) or (chloroacetamides) (alachlor) (Laabs et al., 2002). Most of these publications concern chemical reactivity, mainly through the oxydative coupling phenomena. In general, pesticides or their metabolites supporting chemical reactive groups, like aniline or phenol, tend to give a large proportion of BR (Katan

& Lichtenstein, 1977; Helling & Krikovack, 1978; Bollag et al., 1980; Talebi & Walker, 1993). Thus, the degradation of some pesticides releasing metabolites with hydroxyl or amine groups leads to an increase in BR formation by chemical bounding, the metabolites being more reactive than the initial pesticide (Bollag, et al., 1980; Schiavon, 1988; Winkelmann & Klaine, 1991; Benoit et al., 1999; Knauber et al., 2000; Chilom et al., 2004). On the other hand, pesticides with a high number of electronegative substituents, as the halogens, tend to form lower BR than similar molecules with a lower content of substituents (Scheunert & Korte, 1985). The substituent electronegativity induces the modification of the electronic distribution into the molecular orbitals. Thus, the dipolar moment increases with an increase in the number of halogens. Parameters linking environmental properties and molecular structure were mainly used to explain the link between adsorption properties and degradation. These approaches are based on quantitative structure-activity relationships and on the statistical treatment of selected molecular parameters and target environment parameters, mainly sorption coefficients (Reddy & Locke, 1994). A preliminarily work in the area of BR was done previously (Barriuso et al., 2004), in which it was proposed that the distribution of the electronic density can promote nucleophile or electrophile attacks. Hence, the difference between the energy levels of the frontier molecular orbitals HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) can be used as a good indicator of the chemical reactivity. The best correlation with the amount of BR for a limited number of pesticides was found for the LUMO energy (Fig. 18).

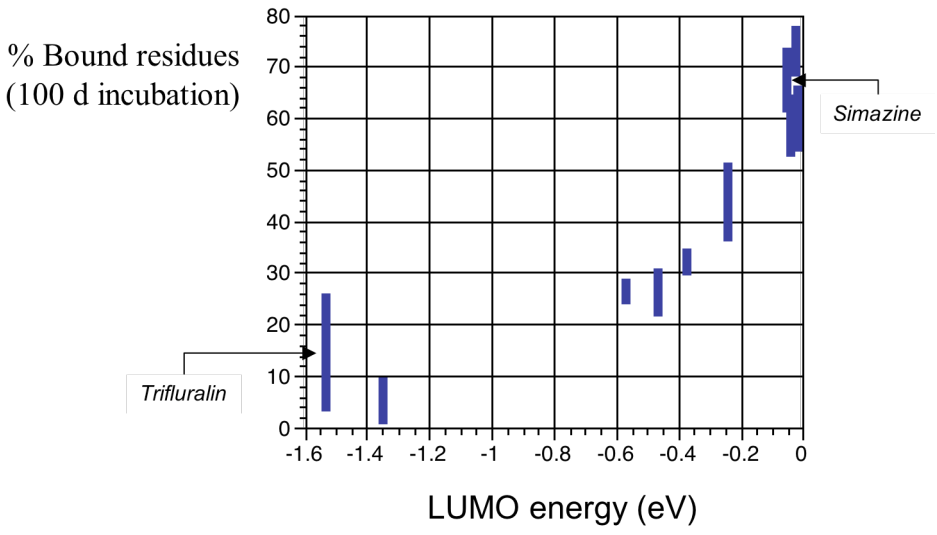

Figure 18. Relationship between the energy of the lowest unoccupied molecular orbital (eV) and the bound residues amount from the selected pesticides (Barriuso et al., 2004).
Data on bound residues was from the EU review reports.

The exploratory results of Barriuso et al. (2004) were extended for the present report to a large number of pesticides. The additional data used in the analysis were part of BR intervals from EU "end-points" (Annex 1). For the selected pesticides, descriptors allowing the estimation of the structure-activity relationship (SAR) were calculated using routines available on the software Chem3D (ChemOffice, CambridgeSoft). Various SAR descriptors were calculated using semi-empirical MOPAC and *ab initio* Gaussian methods, applied to the building structure made on ChemDraw and after optimal geometry conformation by minimising energy. A statistical analysis using the maximum and minimum values of BR for up to 33 pesticides confirmed that LUMO energy is positively correlated with BR, but only with the minimum value of BR. The correlation coefficient was low (0.364) with a probability >95%. No other significant correlation was found when considering all the parameters. This kind of analysis suffers from two issues. The first issue is the coherence of the global data and the large range of BR proportion coming from the EU "end-points". The second issue is related to the pathways of BR formation. If the molecule implicated in BR is not the initial pesticide, but a metabolite, metabolite SAR descriptors for this metabolite have to be used instead of those for the parent compound. The approach will need to be more thoroughly conducted using a more coherent dataset, taking into account hypotheses on BR formation through metabolites. Table 6 provides a summary of the SAR indicators with a significant linear correlation (P>95 %) which was found when pesticides were split into two groups: either pesticides given ≥ 40 % of BR, or pesticides with DT50 ≥ 60 days. The maximum BR from the EU "end-points" was mainly correlated to the topological index (Balaban Index) for pesticides with high BR level (> 40 %). The minimum BR from the EU "end-points" was mainly correlated to the orbital energy, only for the low persistent pesticides.

Table 6. Identification of the molecular descriptors significantly (P>95%) correlated with the minimum or maximum bound residues content from the EU "end-points" for 33 pesticides regrouped in function of its bound residues level or its persistence.

	Low bound residues content BR < 40 %	High bound residues content BR > 40 %	Low persistent pesticides DT50 < 60 d
Minimum BR			• HOMO energy[5] (0.480) • LUMO energy[6] (0.483)
Maximum BR	• Total Energy[3] (-0.498)	• Dipole/dipole[1] (-0.676) • Electronic Energy[2] (0.711) • Total Energy[3] (0.635) • Balaban Index[4] (-0.858) • Molecular diameter (-0.662)	

[1] *Dipole/dipole: sum of the electrostatic energy terms resulting from interaction of two dipoles*
[2] *Electronic Energy: total electronic energy at 298°K*
[3] *Total Energy: sum of Electronic Energy and Repulsion Energy*
[4] *Balaban Index: also called the average distance sum connectivity index is a distance-based topological index derived from the adjacency and distance matrices of molecular graphs*
[5] *HOMO energy: Energy of the highest occupied molecular orbital*
[6] *LUMO energy: Energy of the lowest unoccupied molecular orbital*

5.2 Bound residues and soil properties

It was mentioned earlier in this report that the formation of BR for most of the pesticides is correlated to the soil biological activity and to the soil organic matter (Kaufman & Blake, 1973; Abdelhafid et al., 2000a, b). Most of environmental factors affecting biological activity, such as temperature or soil moisture content, should therefore have an influence on BR formation. Other factors related to the dynamics of the micro-organism populations (e.g. soil pH, agronomic history, fertiliser, organic amendments) are expected to also modify the formation kinetics and the amounts of BR formed.

The total microbial activity has a direct effect on BR formation. This can be evidenced during pesticide incubation in soil samples coming from different depths of the same soil, with the deeper soil samples having usually a low microbial activity and reaching low BR amount (Schiavon, 1988; Baluch et al., 1993; Stolpe & Shea, 1995; Kruger et al., 1997; Miller et al., 1997; Rice et al., 2002).

Some works have shown results on the effects of temperature and water content on pesticide behaviour with information on BR. Anderson (1981) has shown that variation in soil water content from 2 to 19 % had little effect on the formation of BR for diallate (the lowest formation was found at an intermediary water content of 12 %), but provoked an increase in triallate BR. In the case of clorasulam-methyl, variations in the water content between 20 and 60 % WHC had no influence on BR content (Cupples et al., 2000). However, it should be noted that the range of water content variation was small. It has been shown for other pesticides that a larger water content range influences the BR formation of MCPA (Helweg, 1987), atrazine (Kruger et al., 1993, 1997), carbofuran (Ou et al., 1982), metolachlor (Rice et al., 2002), prosulfuron (Hultgren et al., 2002), carbaryl (Murthy & Raghu, 1991) and isofenphos (Abou-Assaf & Coats, 1987). In general, BR amounts increase with the water content until soil saturation.

Cupples et al. (2000) found a continuous increase in BR content for clorasulam-methyl when the temperature was increased from 5 to 50°C. Increased BR formation with temperature has been reported for other pesticides: MCPA (Helweg, 1987), flumetsulam (Lehmann et al., 1993), clomazone (Mervosh et al., 1995), methabenzthiazuron (Printz et al., 1995), isofenphos (Abou-Assaf & Coats, 1987).

If the amount of BR is generally correlated to the soil organic amount, the nature of the organic matter also influences the formation of BR for some pesticides. The example on the

largest affinity of the non-humified organic matter to form BR of atrazine was commented earlier (Barriuso et al., 1991; Barriuso & Koskinen, 1996; Benoit et al., 2000).

A specific analysis looking for soils factors influencing BR formation was done for metsulfuron-methyl (Ye et al., 2005). As all sulfonylureas, metsulfuron-methyl degradation is largely affected by soil pH. The pH-dependent hydrolysis of the sulfonylurea bridge to form phenyl sulfonamide is the primary transformation process of the sulfonylureas. Thus, these authors found a negative correlation between soil pH and the amount of BR. Similar results were found for another sulfonylurea, prosulfuron (Hultgren et al., 2002). These authors have worked with four different soils and found hat degradation and BR formation rate increased when the pH decreased. On the contrary, BR for carbaryl, which hydrolyzes to 1-naphtol, increased when soil pH increased from 4.2 (12 % of BR) to 8.3 (78 % of BR) (Muthy & Raghu, 1991). The same trend was found for the organophosphate isofenphos, its BR being greatest in alkaline soil compared with neutral and acidic soils (Abou-Assaf & Coats, 1987). Similar findings were reported for cyprodinil with stronger binding at higher soil pH (Dec et al., 1997).

Figure 19 gives an example of the modifications induced on the global behaviour of isoproturon when the redox potential was modified (Charnay et al., 2001). The decrease in oxydoreduction potential dramatically decreased the amount of the BR. Variation in the redox potential can be encountered during dry/wet cycles, particularly on the superficial depth of the hydromorphic soils and on the riparian buffer zones. In the case of organochlorines, such as DDT, the increase in water content increased the proportion of BR (Boul, 1996).

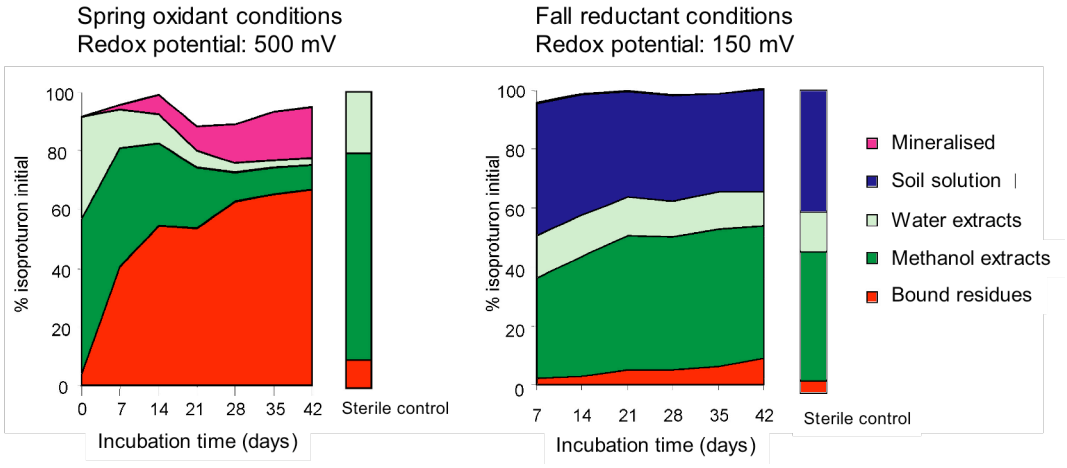

Figure 19. Effect of the oxydoreduction conditions on the isoprotuton behaviour and the bound residues formation (Charnay et al., 2001)

This is explained by the creation of anaerobic microenvironments for the microbial degradation which normally contributed to the reductive dechlorination. Other information on anaerobic degradation or on the effect of flooded soil conditions on pesticide degradation and BR formation can be found for acetochlor (Loor-Vela et al., 2003), atrazine (Kruger et al., 1997; Mersie et al., 1998; Weaver et al., 2004), carbaryl (Murthy & Raghu, 1991), carbofuran (Kale et al., 2001), dimethenamid (Crawford et al., 2002), fluometuron (Weaver et al., 2004), metolachlor (Rice et al., 2002) and nitrofen (Kale et at., 1997).

5.3 Agronomic factors

All agronomic practices modifying directly or indirectly the factors regulating the pesticide behaviour in soils will have an influence on the formation of BR. This not only concerns the modifications of the biological activity involved in pesticide degradation, but also the modifications of the nature or amount of the soil organic matter.

A general effect observed during laboratory experiment is the decrease of the yields BR proportion when the pesticide application rates increase (Racke & Lichtenstein, 1987; Gan et al., 1995).

A modification of the specific microbiological activity implicated in pesticide degradation has been often found when the same pesticide is repeatedly applied onto the same soil. Repeated applications can induce specific microbial activities which are able to quickly degrade the pesticide. This phenomenon is known in the literature as “accelerated degradation”. Figure 20 shows the example of the modification of the capacity for atrazine degradation by repeated applications. When the soils were treated every year in a maize-maize rotation, the atrazine mineralization had a high rate and the proportion of BR was very low. In contrast, atrazine mineralization was slow with a high proportion of BR formation in the soil which was cropped under a wheat-grass rotation and which did not receive atrazine applications. The amount of extractable atrazine was always greater in the never-treated field than in the soil treated annually with atrazine. The main difference between the soils was the apparent competition between the two competitive processes, pesticide mineralization and BR formation (Houot et al., 2000).

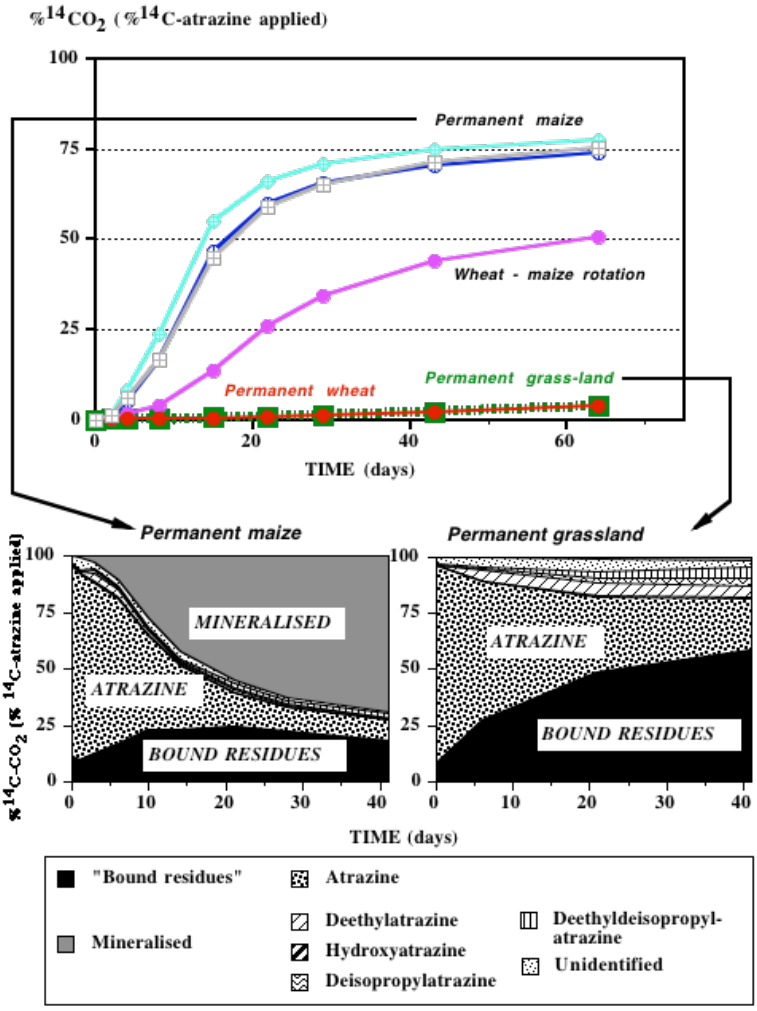

Figure 20. Consequences on bound residues formation of the apparition of a specific microbial activity responsible of the accelerated pesticide degradation (from Barriuso & Houot, 1996).
Case of the atrazine applied to the soil adapted (maize monoculture) or non adapted (wheat or permanent grass) to the atrazine degradation

In the case of carbofuran, repeated applications lead to an increase in the mineralization rate, but above all to a strong increase in BR formation (Talebi & Walker, 1993). This is an illustration of the importance of degradation pathways and intermediate degradation products. In the case of atrazine, adapted degradation implied the opening of the triazine ring by adapted micro-organisms to consume N-triazine. For carbofuran, the adapted degradation increases the speed of the oxidation and hydrolysis process. An increase in BR formation with repeated pesticide applications was also found for prometryn (Khan & Hamilton, 1980) and detamethrin (Zhang et al., 1984). However, others works showed that repeated applications of pesticides to a soil containing BR can provoke a decrease in BR proportion, as for prometryn (Khan et al., 1989) and some arylphenoxyacetic acids (Smith & Aubin, 1991).

Agronomic practices can directly affect the soil organic matter. The use of organic amendments increases the soil organic amount and can partially modify the nature of organic matter. In general, an increase in organic matter content leads to an increase in BR, as demonstrated for compost additions (Barriuso et al., 1997). The actual effect depends of the pesticide nature. It was found to be very significant for atrazine with a high inhibition of the specific activity responsible for accelerated degradation, and for an increase in BR (Fig. 21). A similar effect was found for other triazines (simazine and terbutryne). However, no effect of compost addition on BR was found for the other pesticides studied (pendimethalin, carbetamide, 2,4-D or metsulfuron-methyl). A decrease in BR was found for dimefuron when the proportion of compost increased. For this herbicide, the addition of compost decreased mineralization and BR, most of residues remaining extractable. This is due to an increase in sorption when organic matter, with a preservation against microbial degraders. These results provide an example of the different BR formation pathways, depending on the pesticide degradation route and the difficulty in deriving simple rules based on organic matter amendments

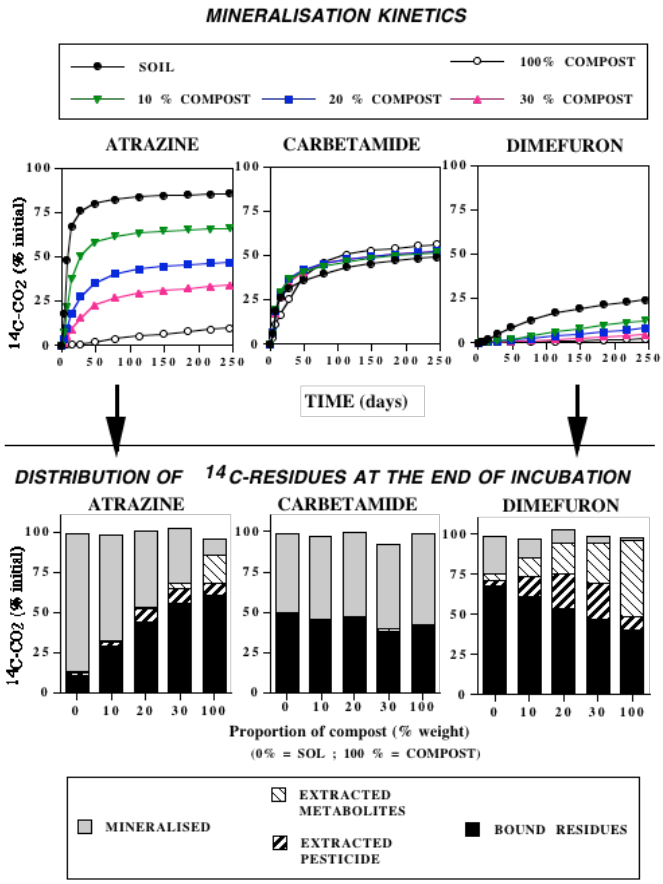

Figure 21. Modification of mineralisation kinetics and 14C-residues distribution of 14C-ring-pesticides (atrazine, carbetamide and dimefuron) by adition to soil of different proportions of compost during laboratory incubations in controlled conditionsatrazine behaviour by compost addition (from Barriuso et al., 1997)

The addition of a source of carbon which can be easily utilised by microorganisms will lead to an increase in micro-organisms activity and will affect pesticide behaviour. Abdelhafid et al. (2000a, b) have shown that microbial activation by glucose addition did not modify atrazine mineralization, but increased the formation of BR (Abdelhafid et al., 2000a). The authors hypothetised that atrazine trapping by the growing microbial biomass was involved in the increase in BR. In the same work, the simultaneous addition of glucose and mineral N lead to an inhibition of atrazine mineralization and the formation of a large proportion of BR. The competition between atrazine-degrading micro-organisms and the total heterotrophic soil microflora probably contributed to the decrease in atrazine mineralization allowing its stabilisation under BR. Gerstl & Helling (1985) conducted an experiment on the addition of different mineral and organic amendments on soil previously incubated with methyl-parathion. The proportion of the BR after the addition of amendments was 46 % of the initial parathion. The release of methyl-parathion BR could not be demonstrated, but both BR and extractable ^{14}C were mineralized.

The management of crop residues and/or the introduction of reduced till or non-tillage systems will modify the proportion and the location of the fresh non-humified organic matter. A mulch at the soil surface will intercept part of the applied pesticide. The evolution of the intercepted pesticide will be different from what happens to the pesticide directly applied on the soil (Fig. 22). Very often pesticide incubated on mulch or fresh organic matter gave a higher proportion of BR than those incubated directly in soils (Abdelhafid et al., 2000b; Rampoldi et al., 2002; Mamy, 2004), and the increase of the humification degree of the vegetal residues increased the proportion of BR (Benoit et al., 1999). Increase in BR when straw was incorporated into the soil was also found for methabenzthiazuron (Printz et al., 1995) or when bromoxynil was incubated on maize residues (Rosenbrock et al., 2004). Wanner et al. (2005) showed that the addition of straw to soil increases the soil microbial biomass and then the proportion of incorporated ^{14}C from ^{14}C-dithianon.

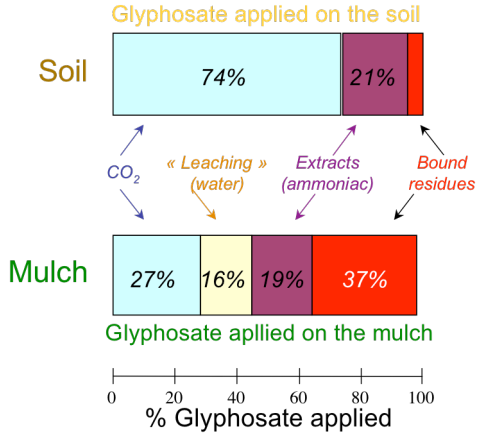

Figure 22. Modification of glyphosate behaviour and the bound residues formation when glyphosate was applied directly on soils or on the mulch (data from Rampoldi et al., 2004).

6 REVERSIBILITY AND AVAILABILITY OF BOUND RESIDUES

The formation of BR leads to a decrease in the toxicity and in the bioavailability of pesticides. In spite of the position of the Scientific Committee on Plants concerning the non relevancy of BR for the ecotoxicological risk assessment from a regulatory view point, environment concerns may arise if the stock of BR changes and if part of BR are released. The release of BR was intensively studied from early on. The following articles are considered key in this field:

(1) Microbial and physicochemical release (Fuhremann & Lichtenstein, 1978; Khan & Ivarson, 1981, 1982; Yee et al., 1985; Dec et al., 1988; Khan & Behki, 1990; Hayar et al. 1997);

(2) Bioavailibity (Aly & Dauterman, 1992; Scheunert et al., 1995; Mathew et al., 1998);

(3) Plant uptake (Fuhremann & Lichtenstein, 1978; Helling & Krivonak, 1978; Führ & Mittelstaedt, 1980; Roberts & Standen, 1981; Haque et al., 1982; Mostafa et al., 1982; Kloskowski et al., 1986; Nelson & Khan, 1990; Verma & Pillai, 1991; Dec et al., 1997; Tiryaki et al., 1997);

(4) Earthworms uptake (Fuhremann & Lichtenstein, 1978; Haque et al., 1982; Ebert, 1992; Gevao et al., 2001).

From a general point of view, values observed for release, bioavailability and uptake only represented a small percentage of the total amounts of BR. Ionic modifications and the addition of nitrogen to the soil can induce a partial release of some BR, as demonstrated for chloro-aniline BR which were released by addition of N-ammonic fertilisers (Saxena & Bartha, 1983), and for prometryn BR which were released by addition of N-ammoniac and N-nitrate (Yee et al., 1985). Additional experiments with modification of soil pH have shown that an increase from pH 4 to pH 8 induces a release of up to 25% of the initial BR for prometryn (Yee et al., 1985)

During the incubation of soil containing BR of cypermethrin, 21-37 % of BR were mineralised after a 18-week incubation (Roberts & Standen, 1981). Incubation experiments conducted with BR of methyl-parathion have shown that BR were very slowly released and that the soil microflora was able to mineralize BR directly, without any appreciable build-up of ^{14}C activity in the extractable phase (Gerstl & Helling, 1985).

From a carry-over point of view, BR derived from metsulfuron-methyl in soil and have the potential to induce phytotoxic effect on plant such as rape seedling (Ye, 2003; Ye et al., 2004) and rice (Li et al., 2005; Ye et al., 2004).

Soil column leaching experiments have demonstrated that BR are usually mainly concentrated in the top of the column, indicating a low leaching capacity of these residues. However, although the bulk of residues of isoproturon (Benoit et al., 2000), atrazine (Kruger et al., 1993) or its metabolite deethylatrazine (Kruger et al., 1996) was confined to the first few cm of soil columns, it should be noted that the extractability of the residues decreased with depth and that significant proportions of bound residues were still found at the bottom of the columns. The exact origin of these BR found deep in the column is difficult to establish. These could result from the leaching of BR formed near the soil surface, hence indicating an intrinsic or facilitated mobility, or from the formation of BR at various depths following the leaching of the parent and its metabolites down the column.

7 CONCLUSIONS & PERSPECTIVES

The present review aimed at providing a summary of the current knowledge on bound residues (Khan, 1982; Calderbank, 1989; Bertin & Schiavon, 1989; Burauel et al., 1998; Gevao et al., 2000; Northcott & Jones, 2000). Gaining detailed information regarding how BR are formed and subsequently released is essential if BR are to be included in pesticide fate models and environmental indicators. BR formation can be conceptually interpreted under the basis of flow mass. The scheme of Fig. 23 proposes an approach based on kinetic compartment models. The compartment size can be operatively defined using sequential extraction techniques allowing separate labile (soluble in water) and more hardly retained fractions (soluble in organic solvents).

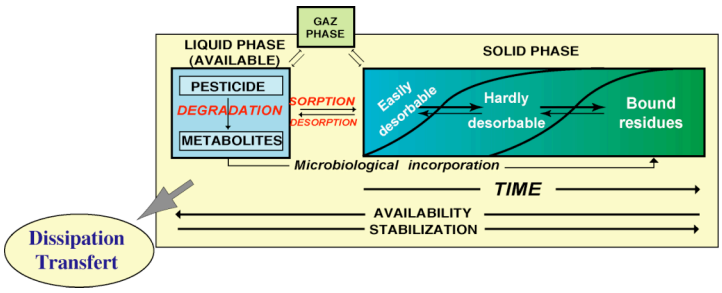

Figure 23. Time dependency of pesticide distribution in liquid and solid phases showing bound residues formation as a consequence of the evolution of the retention processes in the solid phase (from Barriuso, 1994).

This approach was used early by Hamaker & Goring (1976) who used a compartment model with two connected sorption compartments, one of them being BR. They suggest that the formation of BR may be responsible for the deviation from first order degradation kinetics. In

their model, the degradable pesticide (labile compartment) was in equilibrium with the BR compartment which was assumed to be unavailable for degradation. This model was used to estimate pesticide residues which would accumulate following repeated applications. The above model was based on the parent substance forming BR in equilibrium with the soil solution and also assumes that BR are unavailable for degradation, except when in equilibrium with the unbound residues. However, there is evidence in the literature that BR may be subject to slow degradation. Figure 24 demonstrates that a compartmental approach presented above is capable of describing experimental incubation data. The proportion of BR in each compartment is determined through sequential extractions.

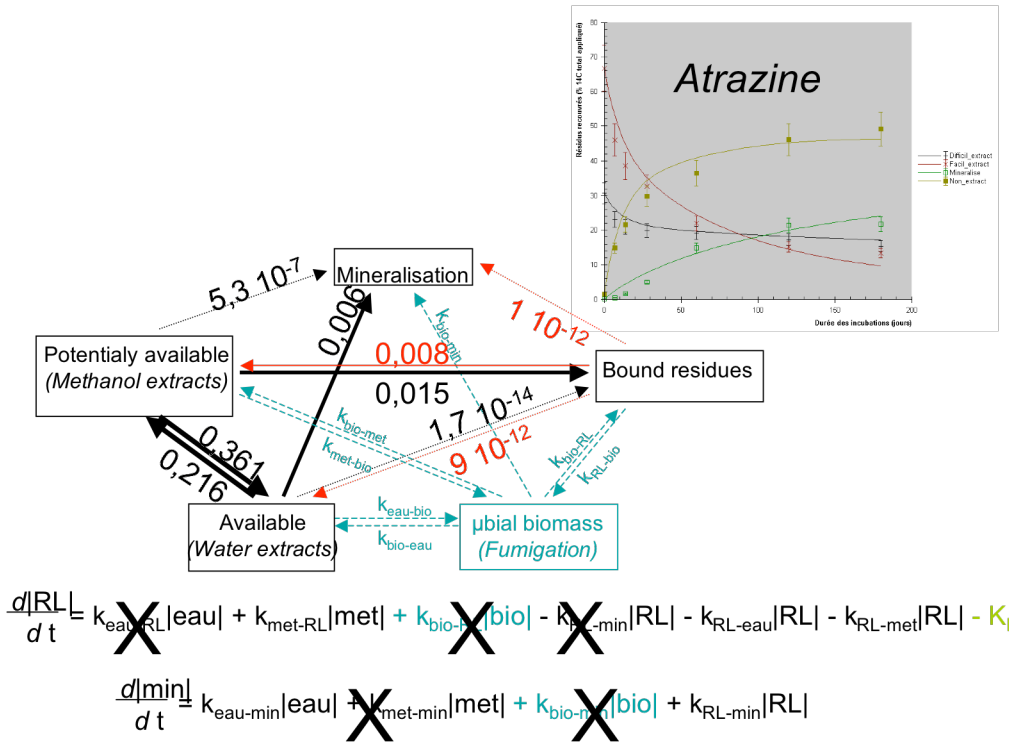

Figure 24. Example of application of the compartment model to describe ^{14}C-residues from the atrazine during soil incubation allowing to estimate the rate the significant flow between compartments and the rate constant (from Edzang-Ondo, 2005)

Others models based on the sequential equilibrium can be found in the literature (for example, Locke, 1992; Selim & Zhu, 2005). The multisite (or multireaction) approach (Selim & Zhu, 2005) allows description of linear and nonlinear processes of the equilibrium and/or kinetic (reversible and irreversible) type. The concepts of the "slow sorption" can be quite easily implemented in pesticide fate models through a kinetics approach This slow sorption could evolve to an irreversible sorption by suppressing desorption from the "slow sorption" sites, or adjusting equilibrium constants of these sites to high values, thereby creating "restrictive sites" or sites with an irreversible retention. The main problem with this kind of approach is

the lack of information regarding the exact nature of the pesticide as the information is required to convert ^{14}C-BR into ^{14}C-parent pesticide or ^{14}C-metabolites.

Although the approach has been used in the past, it appears difficult to introduce overall factors implied in the formation of BR because most of the factors are interdependent, because the available data are incomplete, sometimes not coherent, and strongly pesticide-dependent. For instance, microbiological activity is an important factor in BR formation, but it is dependent on the population dynamics, can be modified by environmental conditions or genetic adaptation which cannot be predicted. An alternative approach would be define the compartments on the basis of mechanisms which are believed to be responsible for BR formation. BR factors can be grouped by mechanisms and their effects should be easily identified. Barraclough et al. (2005) proposed a conceptual approach based on possible routes of BR formation along these lines. Entrapped BR can be described by a diffusion pathway into the colloidal organic matter, which can be simulated by the classical diffusion equation relating the diameters of molecules and pores. Another idea of Barraclough et al. (2005) was to relate the BR release to the turnover of the organic matter fraction to which the BR is associated. In the same way, Fig 25 shows a representation of a conceptual model can be used to elaborate a compartment model on the basis of BR mechanisms: physical trapping, chemical covalent bounding and microbial biomass incorporation. The difficulty with all these approaches is the identification of analytical techniques suitable to estimate the size of the various compartments. The techniques reviewed in the present report which allow the speciation of BR by coupling degradative releasing and chromatographic identification are time consuming, difficult to reproduce and often incompatible with the need for numerous data to precise fluxes between different compartments.

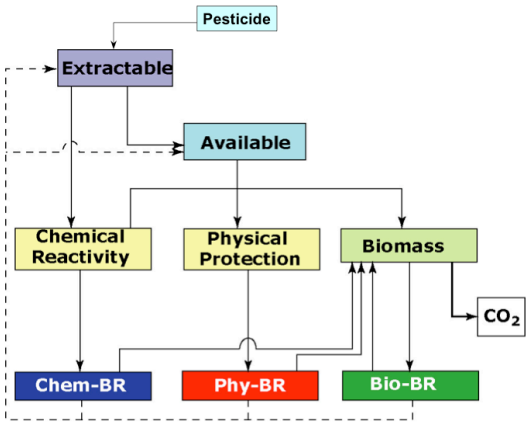

Figure 25. Conceptual model of bound residues formation on the basis of the main supposed mechanisms and that can be quantified by coupling of different spetiation techniques (from Barriuso & Benoit, 2003).

In the end, the important matter is not so much how the residue is defined, but the question of its biological availability (Calderbank, 1989; Gevao et al., 2003). In the absence of information on the nature and on the degree of reversibility of the stabilised residues as BR, it seems necessary to consider BR aspects in a broader context of pollution. The idea is to propose the definition of different pesticide pollution levels according to specific "variable" thresholds in relation to the target or to the methods used (Figure 26). The "biocidal pollution" can be defined by a concentration threshold for which a toxic action is observable. This pollution level is directly related to the pesticide bioavailability, in relation to the concentration of pesticides in the soil water. It is the most perceptible pollution level as it results for instance in fish mortality, crop phytotoxicity or the inhibition of soil microbial activity. The critical threshold can be defined using bioassays or bio-indicators. The "chemical pollution" corresponds to the presence of xenobiotic organic molecules in soils. The concentration threshold is related to the extraction yield and the sensibility of the analytical methods used for their quantification. The "ecological pollution" is defined in relation to any manifestation of pesticides or of their degradation products in the short or long term. This pollution level includes biocidal and chemical pollution, and has a concentration threshold lower than the two others.

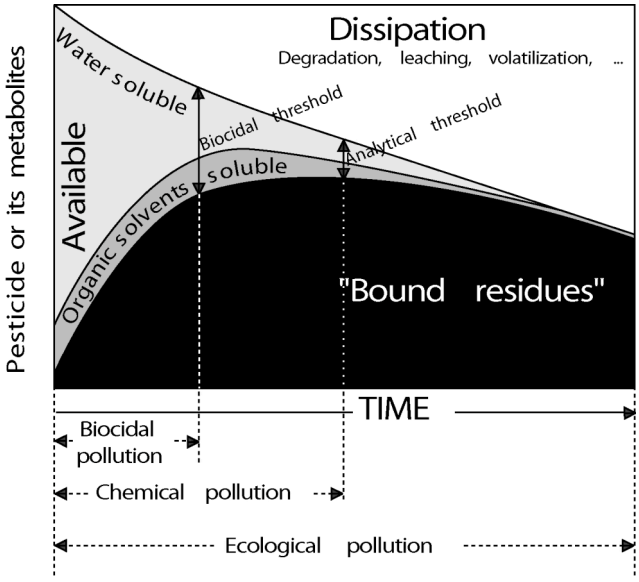

Figure 26. Soil pollution levels and pesticide behaviour in soils in relation with time (from Barriuso, 1994)

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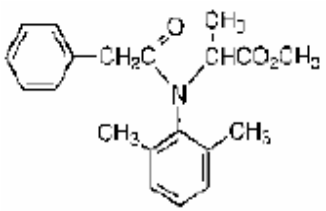
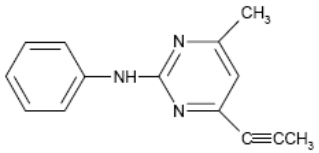
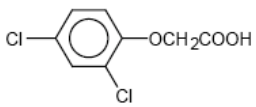
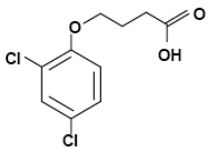
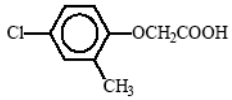
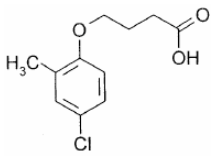
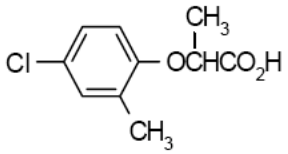
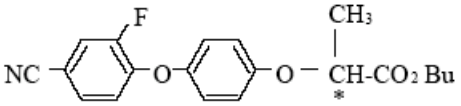
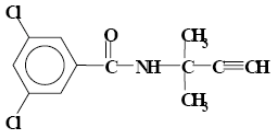
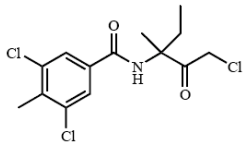
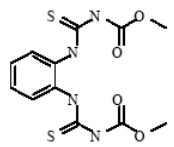
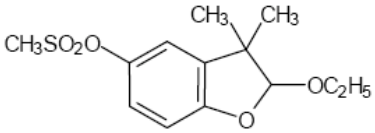
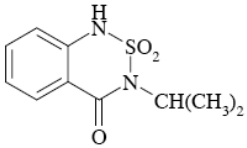
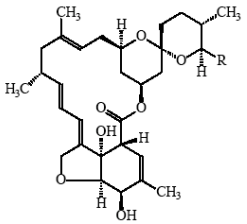
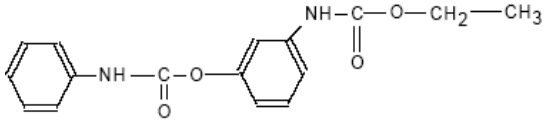
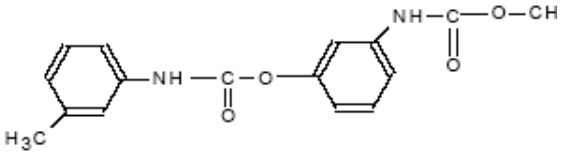
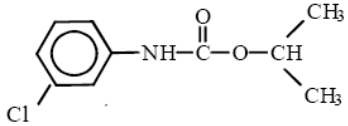
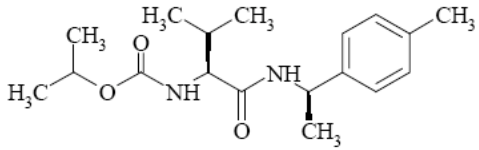
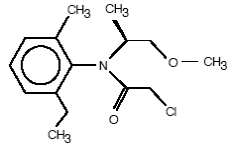
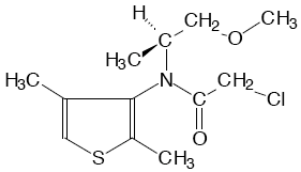
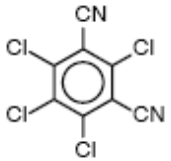
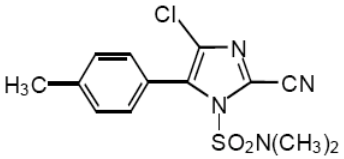
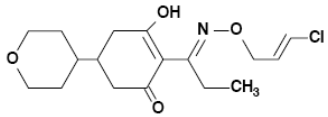
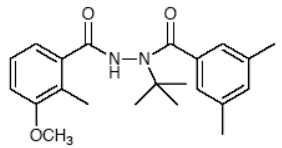
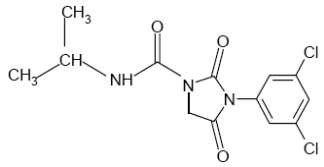
ANNEX 1

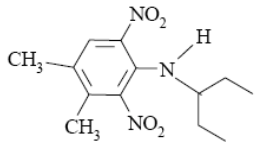
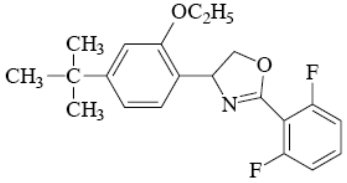
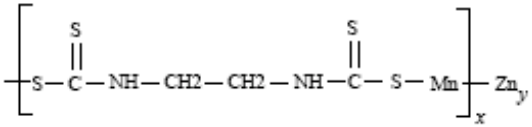
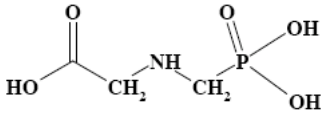
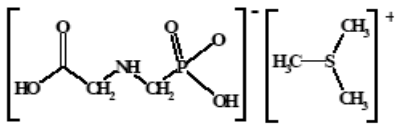
Data extracted from the available “end-points” of the EU review-reports: ranges of mineralised and bound residues proportion in aerobic conditions

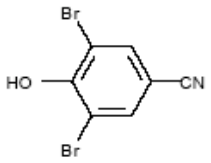
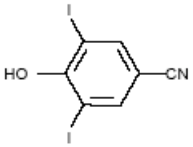
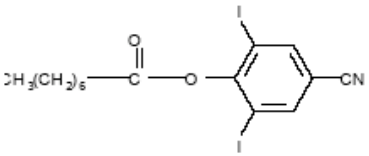
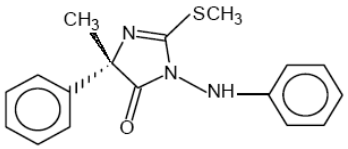
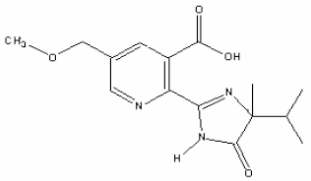
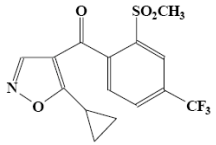
Name		Structure	Mineralization	Bound residues
Benalaxyl	Acylalanine		25 – 26 % (100 d)	18.8% (133 d)
Mepanipyrim	Anilinopyrimidine		5.4 % (120 d, phenyl) 2.4% (120 d, pyrimidin)	26.0 % (120 d, phenyl) 18.6 % (120 d, pyrimidin)
2,4-D	Aryloxyalkanoic acid		36 % (114 d)	27.9 % (114 d)
2,4-DB	Aryloxyalkanoic acid		42.1 % (118 d)	33.2% (118 d)
MCPA-acid	Aryloxyalkanoic acid		54 % (91 d) 67 % (209 d)	34.4 % (91 d) 30 % (209 d)
MCPB	Aryloxyalkanoic acid		58 % (120 d)	30 % (120 d)

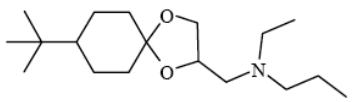
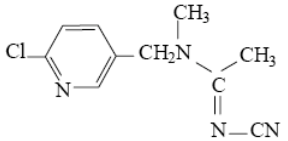
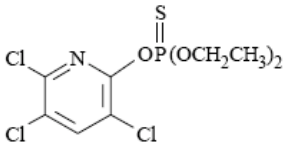
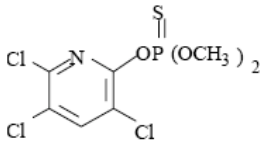
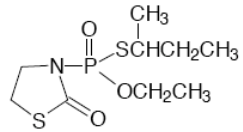
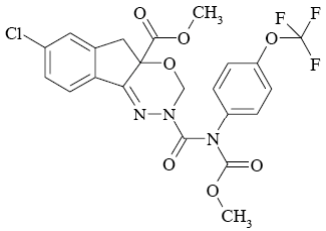
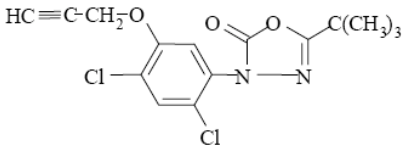
Mecoprop	Aryloxyalkanoic acid		42 - 51 % 25 - 52 % (91 d)	43 – 51 % 39 – 47 % (91 d)
Cyhalofop-butyl	Aryloxyphenoxypropionic herbicide		36.1 - 46.3 % (120 d)	33.7 - 44.2 % (120 d)
Propyzamide; pronamide (USA);	Benzamide		3.4 % (90 d) 33 – 48 % (120 d)	6.8 % (90 d) 16 – 27 % (80 d)
Zoxamide	Benzamide		34.4 - 57.8 % (120-122 d, phenyl)	25.6 – 39 % (28-120 d, phenyl)
Thiophanate-methyl	Benzimidazole		7.3 - 25.7 % (120 d)	40 -73 % (120 d)
Ethofumesate	Benzofuran		6 – 13 %	16 – 34 %
Bentazone	Benzothiazinone		6 - 9 % (90 d) 2 % (60 d)	44 - 74 % (90d) 80% (100d)

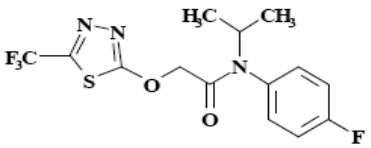
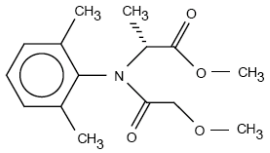
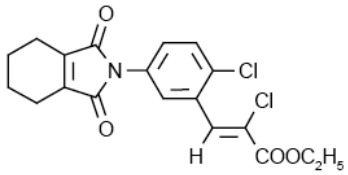
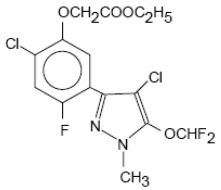
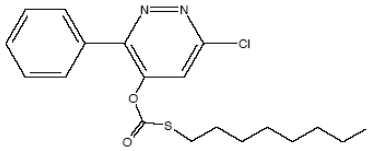
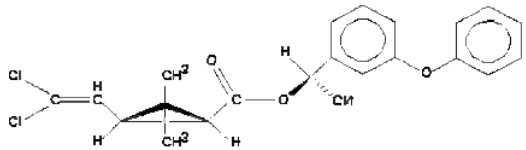
Milbemecin (Milbemectin)	Biopesticide		14 – 35 % (120 d)	13 – 40 % (91-120 d)
Desmedipham	Bis-carbamate		21.4 - 37.8 % (100 d, both labels) 7.5 - 46.4 % (112 d, both labels) 14 - 19 % (90 d, AP-label)	55.8 - 67.2 % (100 d, both labels) 21.5 - 55.0 % (112 d, both labels) 64 % (90 d, AP-label)
Phenmedipham	Bis-carbamate		13.3 – 16.5 % (120 d, AP) 9.7 – 11.3 % (120 d, phenoxy)	63.6 – 64.1 % (120 d, AP) 71.3 – 73.8 % (120 d, phenoxy)
Chlorpropham	Carbamate		15 – 30 % (200 days)	54 – 78 %
Iprovalicarb	Carbamate		17.1 - 59.5 %	10.6 - 27.9 %
S-Metolachlor	Chloroacetamide		15. 3% (90 d)	4.6 % (90 d)

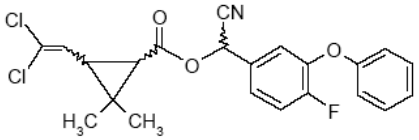
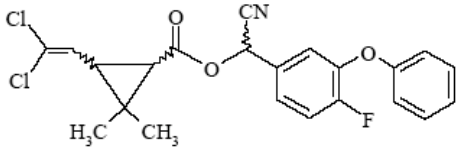
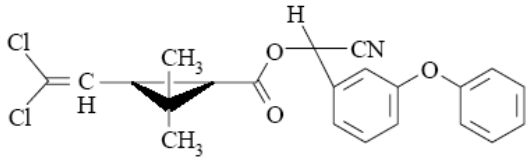
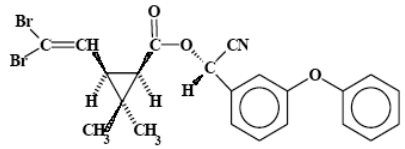
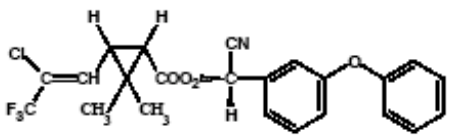
Dimethenamid-P	Chloroacetimide		8 - 36 % (120 d, thienyl)	22 - 44 % (120 d, thienyl)
Chlorothalonil	Chloronitrile		23.8% (92 days)	63% (90 days)
Cyazofamid	Cyanoimidazole		14.4 % (45 d, phenyl) 11.9 % (59 d, imidazole))	47.6 % (59 d, phenyl) 64 % (45 d, imidazole)
Tepraloxydim	Cyclohexadione oxime		66 %	25 %
Methoxyfenozide	Diacylhydrazine		0.9 - 3.6 % (120 d, A-ring, 25°C) 2.6 % (120 d, B-ring, 25°C) 2.7 % (120 d, t-label, 25°C)	12 – 27 % (120 d, A-ring, 25°C) 26 % (120 d, B-ring, 25°C) 24 % (120 d, t-label, 25°C)
Iprodione	Dicarboximide		5 % (phenyl)	40 - 75 %

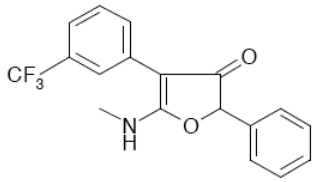
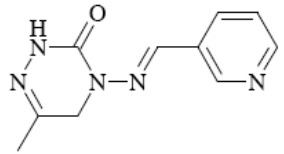
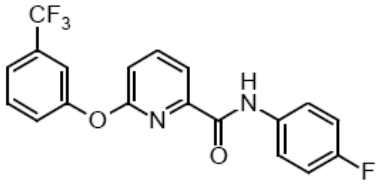
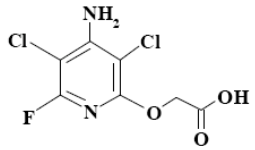
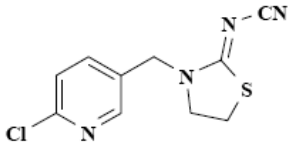
Pendimethalin	Dinitroaniline		1.7 - 2.4 %	2 -10 % (90 d)
Etoxazole	Diphenyl oxazoline		7.0 % (90 d, t-butylphenyl) 15.8 % (269 d, t-butylphenyl) 48.0 % (90 d, difluorophenyl) 56.4 % (269 d, difluorophenyl)	18.6 % (90 d, t-butylphenyl) 27.5 % (269 d, t-butylphenyl) 25.5 % (90 d, difluorophenyl) 23.0 % (269 d, difluorophenyl)
Mancozeb	Dithiocarbamate		31.5 - 51.8% (93 d)	46.1 % (93 d)
Maneb	Dithiocarbamate	[-SCS.NHCH$_2$CH$_2$NHCS.S-Mn-]$_X$	16 – 23 % (32 d)	62 – 88 % (32 d)
Glyphosate	Glycine derivative		46.8 – 55.3 % (28 d) 5.8 – 9.3 % (112 d) 34.7 – 41.4 % (84 d) 69.7 – 80.1 % (150 d) 32.7 % (112 d) 79.6 % (100 d)	8.5 – 40.3 % (28 d) 4.6 – 13.5 % (112 d) 16.7 – 33.9 % (84 d) 5.1 – 8.8 % (150 d) 13.9 % (112 d) 8.4 % (100 d)
Glyphosate trimesium	Glycine derivative		37 % (21 d) 75 % (150 d) 46 % (9 d, trimesium) 74 % (150 d, trimesium)	32 % (21 d) 20 % (150 d) 26 % (9 d, trimesium) 10 % (150 d, trimesium)

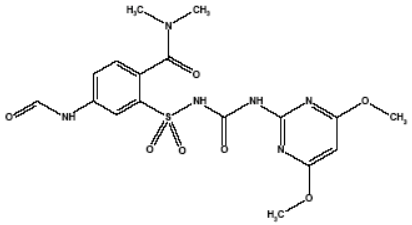
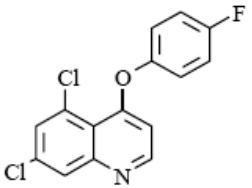
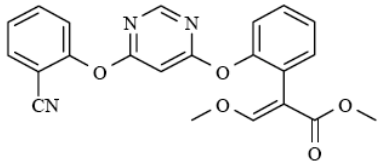
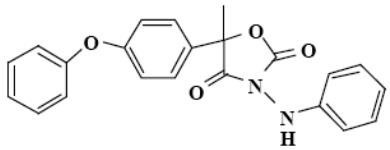
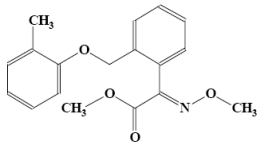
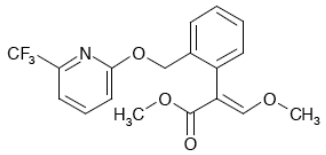
Bromoxynil	Hydroxybenzonitrile		27.3 - 33.6 % (28 d)	72.9 - 74.2 % (28 d); max: 95.2 % (7 d)
Ioxynil	Hydroxybenzonitrile	 	27.3 % (48 d, phenyl) 50.2 - 54.7 % (120 d, octanoate) 60.5 - 66.3 % (128 d, phenyl)	77 % (48 d, phenyl) 38.6 - 44.0 % (120 d, octanoate) 25.2 - 31.6 % (128 d, phenyl)
Fenamidone	Imidazole		3.6 - 9.3 % (90 d, C-phenyl 5 % (90 d, N-phenyl)	24.3 - 37.4 % (90 d, C-phenyl) 47.3 % (90 d, N-phenyl)
Imazamox	Imidazolinone		0.8 - 23.6 % (122 d, pyridine) 1.6 - 21.3 % (90 d, 25°C)	17.5 % (122 d, pyridine) 7.3 % (90 d, 25°C)
Isoxaflutole	Isoxazole		1 %	6 % 9 % (120 d)

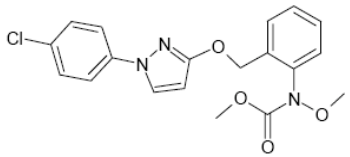
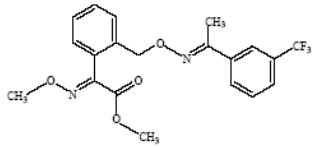
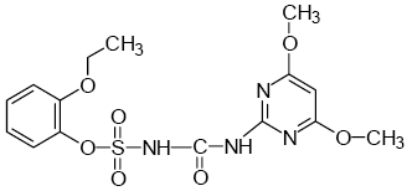
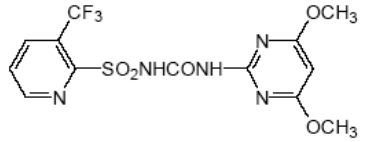
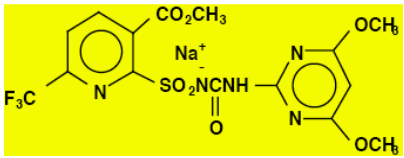
Spiroxamine	Morpholine		30.7 - 44.7 %	24.7 - 26.4 %
Acetamiprid	Neonicotinoid		9.6 % (120 d)	32.3 % (120 d)
Chlorpyrifos	Organophosphate		82 % (120 d) 5 – 50 % (other studies)	4 % (120 d) 25 % (other studies)
Chlorpyrifos-methyl	Organophosphate		23 – 69 %	17 – 26 %
Fosthiazate	Organophosphate		67 % (84 d, thiazolidine) 27 % (84 d, butyl)	7 % (56 d, thiazolidine) 25 % (56 d, butyl)
Indoxacarb	Oxadiazine		12.5 – 29 % (indanone) 1.9 - 8.4 % (trifluoromethoxyphenyl)	39 – 45 % (indanone) 5 – 56 % (trifluoromethoxyphenyl)
Oxadiargyl	Oxidiazole		5.1 – 10.4 % (92-125 d)	20.0 – 24.8 % (92-125 d)

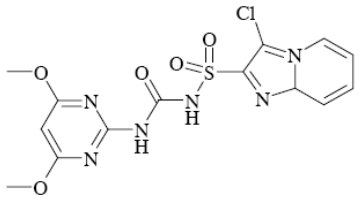
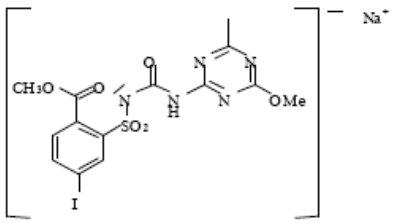
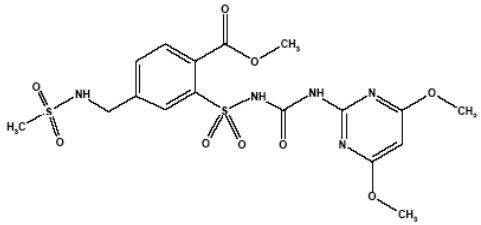
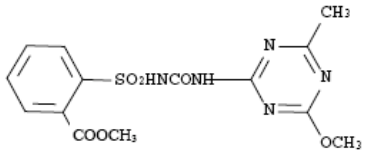
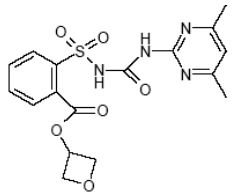
Flufenacet	Oxyacetamide		10.2 - 20.8 % (90 d, fluorophenyl) 31.9 % (90 d, thiadiazole)	29.9 - 56.2 % (90 d, fluorophenyl) 6.0 % (90 d, thiadiazole)
Metalaxyl-M	Phenylamide		22 – 33 % (84 d)	63 – 73 % (84 d)
Cinidon-ethyl	Phenylphthalimide		6.1 % (118 d, phenyl) 40.7% (90 d, indole)	79.6 % (118 d, phenyl) 49.2 % (90 d, indole)
Pyraflufen-ethyl	Phenylpyrazole		2.53 %	17 %
Pyridate	Phenylpyridazine		19 - 26 %	52 - 60 %
Alpha-Cypermethrin	Pyrethroid		20 - 47% (168 d, cis-isomers of cypermethrin, both labels)	21 - 57% (168 d, cis-isomers of cypermethrin, both labels)

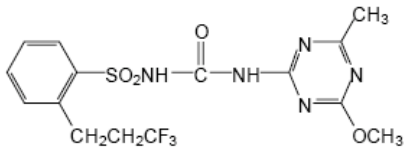
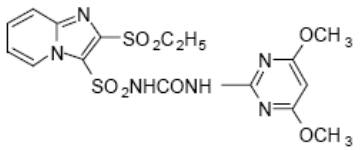
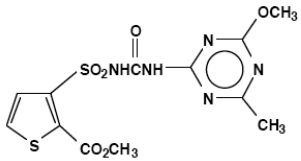
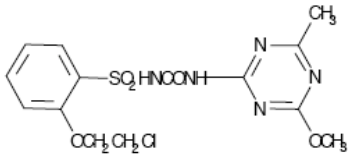
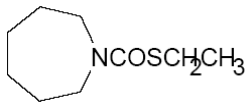
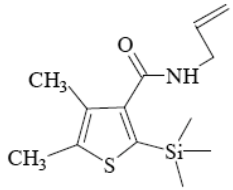
beta-Cyfluthrin	Pyrethroid		36 % (190 d) 23 % (84 d)	42 % (190 d) 34 % (84 d)
Cyfluthrin	Pyrethroid		23 % (84 d) 36 % (190 d)	34 % (84 d) 42 % (190 d)
Cypermethrin	Pyrethroid		20 – 47 % (168 d, cis-isomers) 48 – 61 % (168 d, trans-isomers)	21 – 57 % (168 d, cis-isomers) 26 – 45 % (168 d, trans-isomers)
Deltamethrin	Pyrethroid		61 – 65 % (64 d, benzyl) 52 % (90 d, benzyl) 52 – 58 % (128 d, phenoxy) 62% (64 d, cyano), 62 – 69 % (128 d, cyano) 60 % (64 d, vinyl) 50 – 70 % (64 d, vinyl) 36 % (90 d, gem)	18 – 26 % (64 d, benzyl) 18 % (90 d, benzyl 24 - 31 % (128 d, phenoxy) 20 % (64 d, cyano) 10 – 17 % (128 d, cyano) 21 % (64 d, vinyl) 14 – 18 % (64 d, vinyl) 48 % (90 d, gem)
lambda-Cyhalothrin	Pyrethroid		25 – 59 % (92 d, cyclopropane)	12-19% (92 d, cyclopropane)

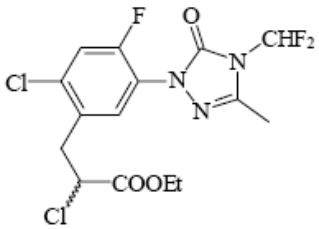
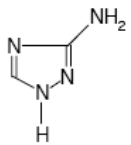
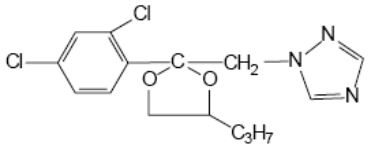
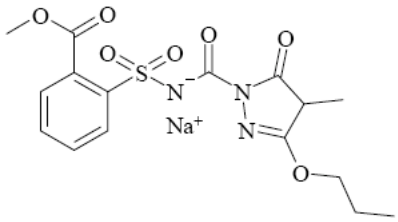
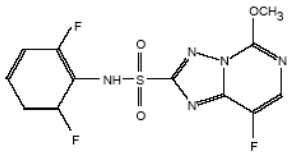
Flurtamone	Pyridazinone		24 - 40 % (366 d)	32 % (366 d)
Pymetrozine	Pyridine		3 - 15 % (90 ...92 d)	21 - 61 % (90 d, 20 -25 °C)
Picolinafen	Pyridinecarboxamide		17.4 % (61 d, aniline) 22.8 - 43.0 % (100 d, pyridine)	43.9 % (61 d, aniline), 65 % (134 d, aniline) 21.2 % (100 d, pyridine) 22.7 (60 d, pyridine)
Fluroxypyr	Pyridinecarboxylic acid		65 %	29.7 %
Thiacloprid	Pyridylmethylamine		6.5 - 34 %	22 - 30 %

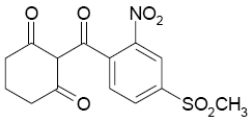
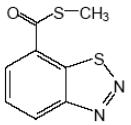
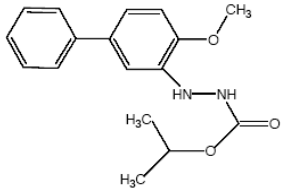
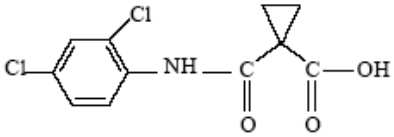
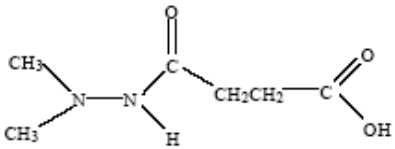
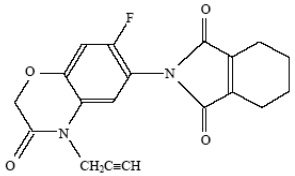
Foramsulfuron	Pyrimidinylsulfonylurea		0.3 - 1.2 % (80-107 d, phenyl) 2.5 – 16.3 % (80-107 d, pyrimidyl)	74 – 103 % (80-107 d, phenyl) 55 - 93 % (80-107 d, pyrimidyl)
Quinoxyfen	Quinoline		1.9 % (200 d)	25 % (200 d)
Azoxystrobin	Strobilurin		2 - 2.5 % (100 d) 11 - 14 % (360 d)	9 - 10 % (100 d) 18 - 24 % (360 d)
Famoxadone	Strobilurin		11.8 % (90 d, phenylamino) 13.0 - 32.2 % (90 d, phenoxyphenyl)	53.8 % (90 d, henylamino) 29.9 - 51.4 % (90 d, phenoxyphenyl)
Kresoxim-Methyl	Strobilurin		17.2 - 35.2 % (91 d)	30.1 - 47.6 % (91 d)
Picoxystrobin	Strobilurin		17.9 - 32.5 % (119 d, pyridinyl) 13.4 - 22.0 % (119 d, pyridinyl) 22.95 % (120 d, pyridinyl)	12.4 - 20.6 % (119 d, pyridinyl) 16.2 - 32.4 % (119 d, pyridinyl) 19.65 % (120 d, pyridinyl)

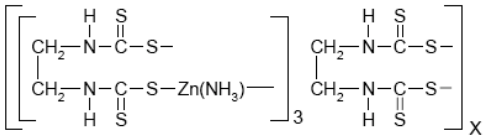
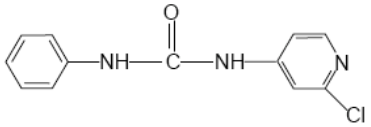
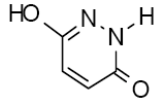
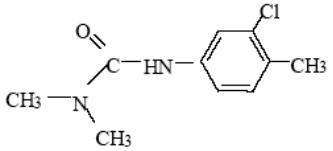
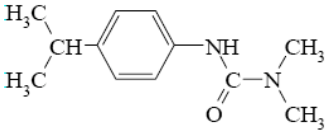
			42.1 - 54.4 % (113 d, phenyl) 29.9 - 42.8 % (119 d, phenyl) 4 % (87 d, tolyl) 5 % (91 d, chlorophenyl)	30.0 - 32.2 % (113 d, phenyl) 22.4 - 28.6 % (119 d, phenyl) 54.3 % (87 d, tolyl) 56.1 % (91 d, chlorophenyl)
Pyraclostrobin	Strobilurin			
Trifloxystrobin	Strobilurin		4 - 64% (105-365 d, GP) 57 % (365 d, TP)	9 – 27 % (105-365 d, GP) 27 % (365 d, TP)
Ethoxysulfuron	Sulfonylurea		16.6 %	18.2 %
Flazasulfuron	Sulfonylurea		2 - 5 %	5 - 12 %
Flupyrsulfuron-methyl	Sulfonylurea		< 2 % (both labels)	29 % (90 d, pyridine) 39 % (90 d, pyrimidine)

Imazosulfuron	Sulfonylurea		3 – 10 % (120 d)	19 – 67 % (120 d)
Iodosulfuron	Sulfonylurea		3.3 - 11.6 % (86 d) 2.1 % (91 d) 2.2 – 29.9 % (120 d)	36.7 - 32.9 % (86 d) 28.0 - 32.4 % (91 d) 27.0 - 39.3 % (120 d)
Mesosulfuron	Sulfonylurea		6.7 % (90 d, phenyl) 6.1 - 46.8 % (90 d, pyrimidyl)	56.3 % (90 d, phenyl) 28.0 - 54.8 % (90 d, pyrimidyl)
Metsulfuron methyl	Sulfonylurea		32 % (112 d, phenyl) 11.4 % (90 d, triazine) 10 % (triazine amine) 38 % (455 d)	12 - 25 % (98 d, phenyl) 17.6 % (90 d, triazine) 6 % (triazine amine) 10 % (455 d)
Oxasulfuron	Sulfonylurea		36 - 57 % (105 d, phenyl) 21 – 25 % (128 d, pyrimidinyl) 51 – 80 % (79-120 d, oxetanyl)	21 - 27 % (105 d, phenyl) 40-58% (128 d, pyrimidinyl) 5 – 30 % (79-120 d, oxetanyl)

Prosulfuron	Sulfonylurea		< 5 % (phenyl & triazine) 9 % (180d, phenyl) 45 % (180d, triazine)	12 - 44 % moiety (90 d, phenyl) 10 % (90 d, triazine)
Sulfosulfuron	Sulfonylurea		1.6 % (imidazo) 2.2 % (225 d, imidazo) 8.1 % (pyridine) 13 % (225 d, pyridine)	14 % (imidazo) 41 % (225 d, imidazo) 15 % (pyridine) 33 % (225 d, pyridine)
Thifensulfuron-methyl	Sulfonylurea			27 - 40 % (thiophene) 40 - 48 % (365 d, thiophene) 10 % (triazine amine) 38 % (455 d, triazine amine)
Triasulfuron	Sulfonylurea		2 % (70 d, triazine) 21 % (365 d, traizine) 2 % (84 d, phenyl) 14 % (365 d, phenyl)	23 % (70 d, triazine) 42 % (365 d, triazine) 25 % (84 d, phenyl) 57 % (365 d, phenyl)
Molinate	Thiocarbamate		0.96% (30 d, 30ºC)	2.39 % (30 d, 30ºC)
Silthiofam	Thiophene		10.62 % (120 d)	44.27 % (120 d)

Carfentrazone-ethyl	Triaolinone		< 3 % (phenyl and carbonyl)	14.5 – 15 % (phenyl and carbonyl)
Amitrole	Triazole		20 - 60 % (7 d, 25 °C)	17 - 19 % (100 d) max of 20 - 50 % (7 d)
Propiconazole	Triazole		0.2 - 0.5 % (84-105 d, triazole) 2.0 % (120 d, triazole) 29.3 - 35.4 % (84 d, phenyl	14.1 - 15.5 % (84 d, triazole), 47.3 % (120 d, triazole) 3.4 – 24.6 % (105 d, triazole) 23.3 - 27.3 % (84 d, phenyl)
Propoxycarbazone	Triazolone		9.1 - 41.9 % (88-98 d phenyl) 21.7 - 49.0 % (180-361 d, phenyl) -label: 1.3 - 8.9 % (93-117d, triazolinone) 2.6 - 12.6 % (18-365 d, triazolinone)	6.5 - 29.5 % (88-98 d, phenyl) 8.2 - 28.3 % (180-361 d, phenyl) 8.9 - 64.9 %(93-117d, triazolinone) 17.9 - 65.7 % (182-365 d, triazolinone)
Florasulam	Triazolopyrimidine		4.8 - 13.5 %	29.6 - 57.1 %

Mesotrione	Triketone		75%	37%
Acibenzolar-s-methyl	Unclassified		7.5 - 44.1 % (90 d, phenyl)	27.7 - 59.8 % (90 d, phenyl)
Bifenazate	Unclassified		15.2 - 23.0 % (119 d)	64.0 - 67.3% (119 d)
Cyclanilide	Unclassified		4.3 % (120 d)	30 % (120 d)
Daminozide	Unclassified		20 – 59 % (2 - 64 d)	20 – 25 % (2 - 3 d)
Flumioxazine	Unclassified		13.5 % (100 d, phenyl, 20° C) 5.6 % (59 d, phenyl, 25°C) 11.5 % (181 d, phenyl, 25°C) 54.9 % (91 d, THP, 25°C)	62.4 % (100 d, phenyl, 20°C) 71.3 % (59 d, phenyl, 25°C) 73.6 % (181 d, phenyl, 25°C) 29 % (91 d, THP, 25°C)

Metiram	Unclassified		28 – 41 % (90-365 d)	38 – 65 % (90-365 d)
Forchlorfenuron	Unclassified		3.07 % (90 d, phenyl) 15.7 – 25.4 % (120 d, phenyl) 2.9 – 5.0 % (120 d, pyridine)	16.6 % (90 d, phenyl) 23.6 – 46.4 % (120 d, phenyl) 23.5 – 25.2 % (120 d, pyridine)
Maleic hydrazide	Unclassified		71.6 % (90 d)	24.5 % (90 d)
Chlorotoluron	Urea		6.4 - 13.3 %	28.2 - 62.6 %
Isoproturon	Urea		10 - 22 %	56 – 68 %