Environ. Sci. Technol. **2008,** *42,* 1845–1854

Formation of Pesticide Nonextractable (Bound) Residues in Soil: Magnitude, Controlling Factors and Reversibility

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Received August 29, 2007. Revised manuscript received December 8, 2007. Accepted December 17, 2007.

The analysis of the coherent data on nonextractable (bound) residues (NER) from the literature and EU pesticide registration dossiers allows the identification of general trends, in spite of the large variability and heterogeneity of data. About 50% of the pesticides reviewed exhibit a low proportion of NER (less than 30% of the initial amount) while only 12% of pesticides have a proportion of NER exceeding 70%. The lowest proportion of NER was found for dinitroanilines (<20%), and the largest value was obtained for carbamates, and in particular dithiocarbamates. The presence of chemical reactive groups, such as aniline or phenol, tends to yield a larger proportion of NER. NER originating from *N*-heteroatomic ring were found to be lower than those from phenyl-ring structures. Among the environmental factors affecting the formation of NER, microbial activity has a direct and significant effect. Concerning the NER uptake or their bioavailability, consistent data suggest that only a small percentage of the total amounts of NER can be released. The analysis of NER formation kinetics showed that incubation experiments are often stopped too early to allow a correct evaluation of the NER maturation phase. Therefore, there is a need for longer term experiments to evaluate the tail of the NER formation kinetics. Still, the heterogeneity of the NER data between pesticides and for specific pesticides calls for great care in the interpretation of the data and their generalization.

Introduction

The first research activities on pesticide nonextractable residues (NER) in soils, initially referred to as "bound residues", were initiated in the mid-1970s (*1, 2*), whereas earlier work had been conducted on plants or vegetal constituents. Definitions or position statements on bound residues appear periodically in the literature (*3*−*6*). The last consensual definition for bound residues was provide by Führ (*7*): "bound residues 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 bound residues, operational definitions depend upon the techniques used for its quantification. Classical analytical chemistry techniques cannot be used because most techniques are based on an earlier extraction of the residues, and bon residues are nonextractable residues (NER) by definition. In this context, NER benefit from an operational definition which is dependent on extraction techniques, incubation times, and other experimental conditions used for soil incubation. It should be noted that this technical dependency is of the same nature as that for the measurement of total extractable residues. The only technique which does not rely on a preceding extraction and which allows a quantification of NER relies on the use of isotopes, usually ^{14}C. NER are typically studied in incubations of soils treated with pesticides labeled with ^{14}C. After incubation for a target duration, soils are exhaustively extracted. The unextracted radioactivity remaining in the soil, the operational definition of NER, is measured by liquid scintillation counting of the total $^{14}C-CO_2$ recovered after combustion of the soil samples. Due to the destructive nature of the approach, it cannot determine whether NER measured 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 are needed to allow a partial degradation of the soil structure or constituents with liberation of ^{14}C labeled compounds originating from the ^{14}C-pesticide (*8*). Also the use of the stable isotopes ^{13}C and ^{15}N allowed to give information on NER nature and their formation mechanisms (*9*−*12*).

In pesticide risk assessment procedures, NER are usually accounted for the description of dissipation kinetics. Dissipation constants or half-lives (DT50s) are composite parameters resulting from the amalgamation of various dissipation processes, each of which having a specific kinetic. NER formation is typically considered both as a process contributing to pesticide dissipation and as a process decreasing pesticide availability, thereby provoking a transient pesticide stabilization which may lead to a subsequent slow release. The first consequence of the NER formation is a decrease in availability of pesticide residues with a concurrent increase of persistence in soil. The concepts and hypotheses used to explain the formation of NER in soils will have a direct influence on the way they should be described in pesticide fate models. If NER are considered as a true dissipation process, they could be described as an irreversible sink. In contrast, if NER formation is considered as a

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10.1021/es7021736 CCC: $40.75
Published on Web 02/07/2008

stabilization process, the concepts of nonreversible sorption or slow sorption/desorption kinetics must be considered.

NER are explicitly considered in the decision making process for the placement of pesticides on the market in Europe: no authorization of active ingredient shall be granted if NER are formed in amounts exceeding 70% of the initial dose after 100 days with a mineralization rate of less than 5% in 100 days (*5*). The EU directive also consider an "unless clause" when the above criterion 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 residue levels 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. The challenge is to reach an agreement on the experimental methods and/or modeling tools to evaluate NER phytotoxicity, their environmental impact, and their potential carryover. Craven (*13*) indicated that there is no agreement among EU Member States on how NER should be treated. The current approach, which is typically adopted within the EU, is to treat soil NER in the same way as persistent compounds (*14*). This represents an evolution from the position formulated by the EU Scientific Committee on Plants (SCP) in 1999 based on an analysis of the available literature (*15*). The SCP considered at the time that the fractions of NER which are released are low and any concern over their ecotoxicology or effect on succeeding crops should have been addressed during studies required for the active substance and relevant metabolites (*5*). The actual position of the EU authorities for pesticide regulation and the questions for a better took into account the NER are well summarized in the cited papers (*13, 14*).

The review below attempts to provide knowledge and Supporting Information on NER formation, the governing factors involved and aspects of potential reversibility and environmental release. The review work allows the identification of general trends in NER formation which support the creation of a functional typology based on kinetics data, molecular properties and contributing environmental factors.

The Formation of Nonextractable Residues. *Kinetics of Bound Nonextractable Residues Formation.* The magnitude of NER depends on the experimental methodology to extract pesticide residues in soil. A consensus would need agreement on (i) the degree of denaturation of the matrices containing pesticides residues and (ii) a criteria to define when "total" extraction is reached. With regard to this latter aspect, the requirement on the extraction efficiency corresponds to a mean recovery at a number of fortification level inside the range 70–110% (*5, 16*). Extraction methods have been developed with fortified soil samples, which are often extracted a few hours or days after pesticide fortification. It is therefore considered in practice that the extraction efficiency is independent of the residence time of the pesticide in soil, although it is known that this assumption does not hold. If an extraction efficiency of only 70% of the applied amount is accepted, it is implicitly assumed that a proportion of NER between 0 and 30% would correspond to a "methodological or background noise".

Because of the importance given to quickly formed NER in a regulatory context, it is essential that knowledge is gained on the time-dependent formation of NER during soil incubations. Very few publications were specifically focused on the kinetics of NER formation. Some representative examples of NER formation curves are provided in Figure 1 (*17*). NER formation kinetics can be broken down into three steps:

(i) The first step 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 corresponds to the rapidly formed (or "flash") NER which are related to the "methodological noise" described above and which usually represent <10% of the applied compound, but can reach 30% in some instances (methodological quality threshold). Other examples in the literature can be found for (% NER at zero time) triticonazole (<10%) (*18*), endosulfan (<12%) (*19*), atrazine (20−25%) (*20*), chlorothalonil (5−40%) (*21*), paraquat (>90%) (*22*). The main explanation for these "flash" NER is the difficulty of the solvent to compete with the soil−pesticide interactions (paraquat is an extreme case) or to access hidden sites in organo−mineral colloids protecting diffusing pesticides. It should, however, be noted that the use of inappropriate extraction solvents can be a factor in the "flash" NER formation.

(ii) The second step in NER kinetics is a "formation step", characterized by its kinetics rate. When the rate is high, a NER plateau is quickly reached and high levels of NERs are usually generated (see metazachlor and metamitron, Figure 1). In other cases, the NER formation rate is low and a plateau is not reached (see trifluralin and sulcotrione, Figure 1); this behavior is often associated with a low proportion of NER.

(iii) The third step corresponds to the fate of NER when their formation rate decreases. This step can be considered as a NER "maturation stage". Roughly, three situations can be found: (i) a "plateau" is reached and the NER proportion remains "stable" during time; (ii) the NER formation carries on at a lower rate indicating a continuous "incorporation" of new residues in the NER pool; or (iii) the NER proportion decreases with a "release" rate. A stable "plateau" situation is exemplified by metazachlor and metamitron in the Toulouse soil, while a continuous NER "incorporation" is observed for trifluralin and sulcotrione, and a NER "release" is obtained for metamitron in the Dijon and Châlons soils (Figure 1).

It should be noted that these general considerations about NER kinetics should be taken with care as the shape of the kinetics curves depends on soil type, incubation conditions, and time range. Very often, the total incubation time only covers the first step of NER formation and this may lead to inadequate inferences regarding NER formation and the absence of a plateau. Table S1 (Supporting Information) provides a categorization of the literature data based on the three steps of NER formation described above. The table also highlights instances in which a release of NER has been observed. Long-term experiments which allow a more complete study of NER formation are seldom reported in the literature because of the inappropriateness of laboratory microcosm studies to conduct incubation experiments over long periods. Some results of small microcosm studies conducted over durations exceeding one year are nevertheless available (*23−29*). Other experimental devices such as lysimeters or field incubation studies may be used to study the long-term fate of NER (*30−36*). The underlying data are usually not reported in papers appearing in journals, but the data are presented in gray-literature reports such as Ph.D. theses, e.g, for 2,4-D (*37*); for metsulfuron-methyl (*38*); or for glyphosate (*39*).

Nonextractable Residues Formation and the Nature of Pesticides. Although the literature on pesticide behavior in soils is relatively abundant, the variability of experimental conditions used for soil incubations prevents the construction of a reliable comparative data set for different pesticides and soils. This variability is reduced to some extent when the data on NER formation are generated within the context of pesticide registration. Review reports containing information on NER formation were available from the EU Directorate General for Health and Consumer Protection for ca. 100 pesticides in 2007. NER data for the aerobic degradation route were extracted from these reviews reports. In spite of the

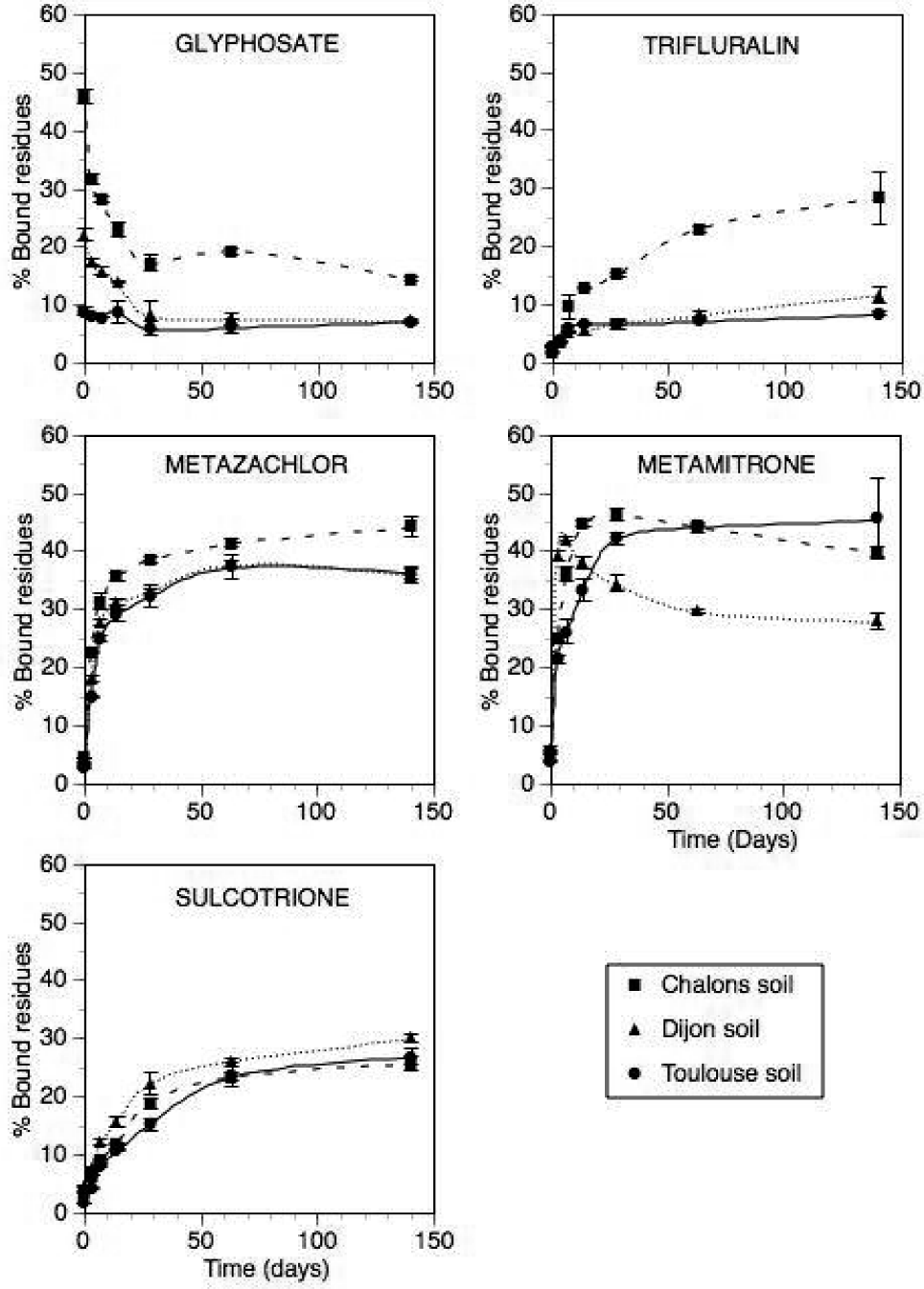

FIGURE 1. Exemples of nonextractable (bound) residues kinetics for different pesticides (glyphosate, trifluralin, metazachlor, metamitron and sulcotrione) and three different soils (Châlons, Dijon and Toulouse soils). Data from Mamy et al. (*17*).

limited coverage of the overall spectrum of active substances, the data set is interesting because studies undertaken for registration purposes are quality-assured and undertaken under a reduced variability of the experimental conditions. Still, although all studies conducted rely on soil incubation experiments undertaken at 20 °C and a soil–water content equivalent to 50% WHC, the potential for variability remains significant given that the soil type and the extraction methods are not fixed. The proportions of bound residues formed in these registration studies are provided as Supporting Information.

All pesticides reviewed formed NER in soils at different degree depending on the nature of the pesticide, and a significant variability in the proportion of NER formed for a given pesticide was noted (Figure 2). If the "methodological noise" of 30%, corresponding to the minimum requirement of the extraction method is retained as a reference, about 40% of pesticides considered had a low proportion of NER (i.e., comparable to the methodological noise). Only 10 pesticides were categorized as having a proportion of NER higher than the risk assessment threshold of 70% (see Table S2, Supporting Information).

Data on NER amount were grouped by pesticide family when there were more than two pesticides by family (Figure 3). The best families represented (i.e., those with the largest number of active ingredients) were the sulfonylureas, pyrethroids, and strobilurins. Organophosphates are the compounds forming the least NER. The largest proportion of NER was found for carbamates, and in particular, for dithiocarbamates. The large variability noted within families is linked to the process responsible for NER formation and to the part of the molecule directly involved in NER formation.

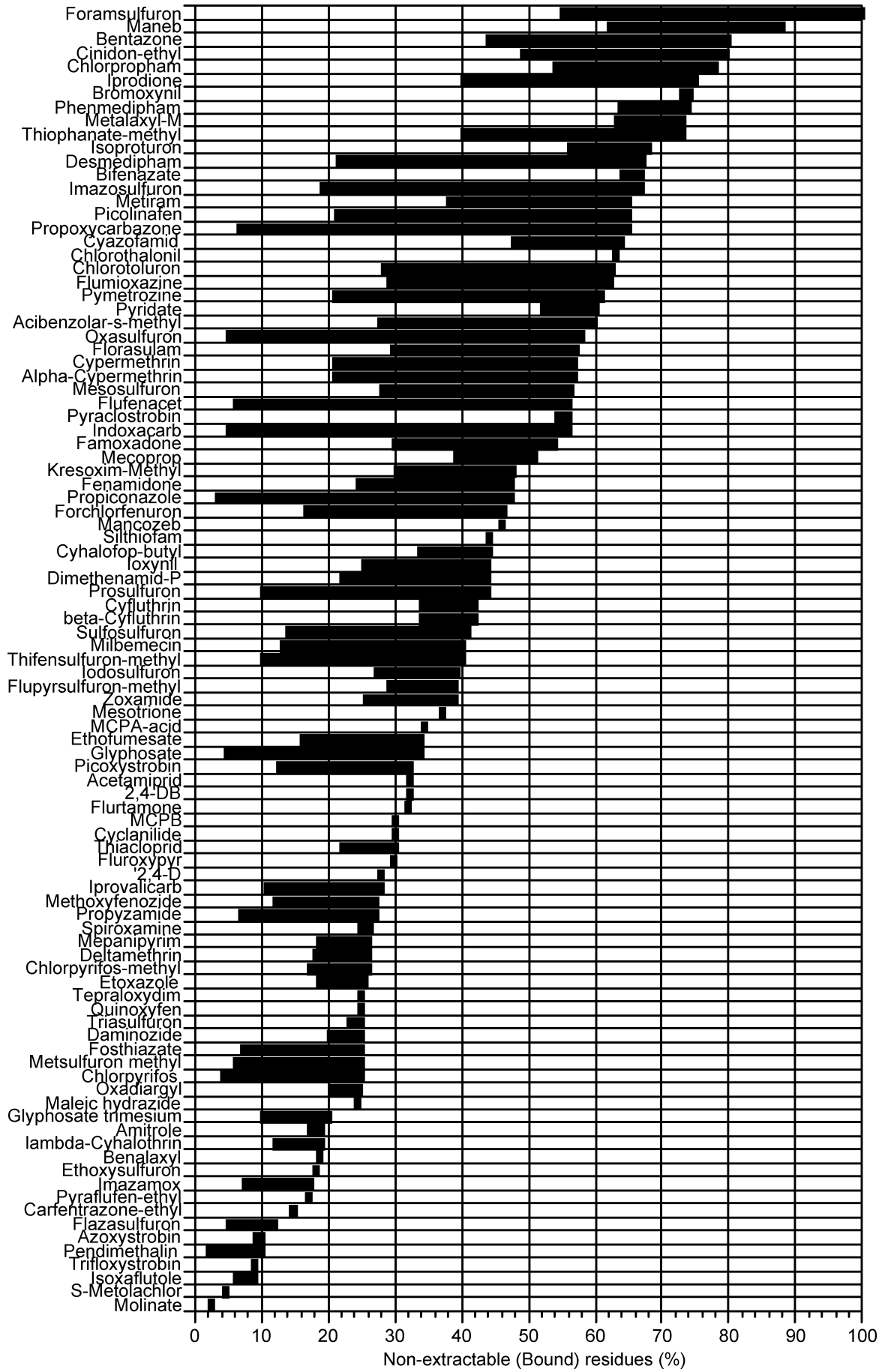

FIGURE 2. Classification of pesticides according to the proportion of bound residues formed (from EU end points data). The horizontal extents of the bars indicate the variability in the data.

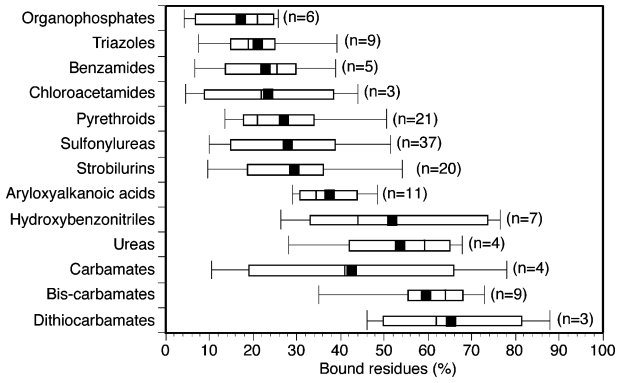

FIGURE 3. Box plot showing a classification of pesticide families according to their capacities to form nonextratable (bound) residues. Plotted data corresponded to the proportion of NER formation reported in the EU review documents and are for experiments with a target duration of ca. 100 days.

It should be noted that this part may be different to the functional group responsible for the family name.

All data presented above originate from measurements of the nonextractable ^{14}C through combustion of the soil samples containing the NER. Under these experimental conditions, the proportion of NER is dependent on the position of the ^{14}C-labeling in the pesticide chemical structure. If the ^{14}C-labeling is positioned on a labile molecular fragment (i.e., one which can easily be mineralized), the NER formation will tend to be low. In contrast, if a stable moiety of the compound is ^{14}C-labeled, the proportion of NER will appear high. Variations in the proportion of ^{14}C incorporation in NER in result to different locations of the ^{14}C in the molecule are an indication of a breakdown of the molecule before NER formation. On the contrary, an independence of the results would suggest an incorporation of the whole molecule under a NER form without degradation. As an example, cloramsulam-methyl presents the same kinetics of NER formation and the same proportion of NER formed whether the labeling is positioned on the phenyl or on the pyrimidine moieties (*28*). Table S3 (Supporting Information) provides examples of compounds which contain two or more aromatic rings and which show differences in NER formation depending on the location of the labeling. In general, when the ^{14}C-labeling was supported by a *N*-heteroatomic ring, the proportion of NER was found to be lower than for the same molecule with a phenyl-ring ^{14}C-labeling (Table S3, Supporting Information). Two exceptions were however noted (cyazofamid and oxasulfuron). The ^{14}C in thiadiazole, triazole, pyridine, and triazine rings appears to be little incorporated in NER compared to other rings (Figure 4). The ranges of NER formation are larger when the ^{14}C-labeling was in phenyl, imidazole and pyrimidine moieties (Figure 4).

Factors Governing the Formation of Nonextractable Residues. *Nonextractable Residues and Pesticide Molecular Properties.* Relatively few publications have investigated the relationships between NER formation and molecular properties. Some general publications point out the low capacity to form NER of the dinitroanilines, in comparison to triazines (simazine) or chloroacetamides (alachlor) (*40*). In general, pesticides or metabolites supporting "free" reactive chemical groups, such as aniline or phenol, have a tendency to give a larger proportion of NER (*41–44*). The degradation of pesticides presenting metabolites with hydroxyl or amine groups leads to an increase in NER formation by chemical bounding as their metabolites are more reactive than the parent compound (*43, 45–49*). The result of these different reactivities between the parent and its metabolites is a competition between degradation and the formation of NER.

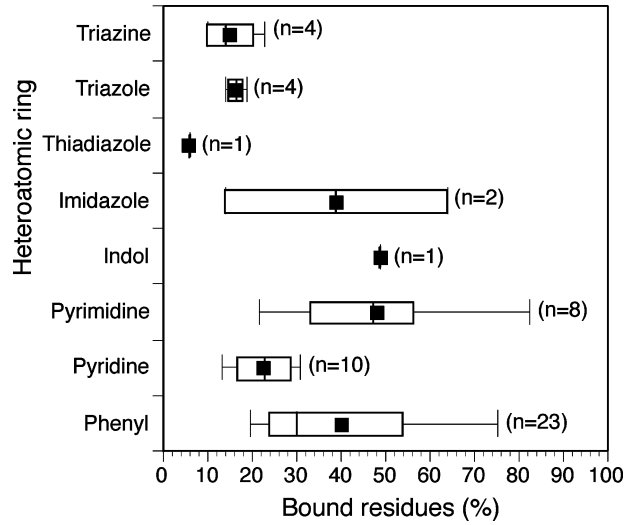

FIGURE 4. Box plot of the proportion of nonextratable (bound) residues formed in relation to the nature of the *N*-heteroatomatic ring or phenyl containing the ^{14}C-labelling.

If it is the parent compound which is involved in NER formation, then rapid degradation competes with NER formation. If, on the other hand, it is the metabolite which is involved in NER formation, then rapid degradation may lead to an extensive formation of NER.

Pesticides with a large number of electronegative substituents, such as the halogens, tend to form lower NER than similar compounds with a smaller number of substituents (*50*). The electronegativity of the substituent induces modifications of the electronic distribution in the molecular orbitals, and the dipolar moment increases with an increase in the number of halogens. Approaches aimed at linking pesticide environmental and molecular properties, e.g., for sorption (*51*), are typically based on (i) the generation of a large number of molecular properties using quantitative structure–activity relationships; (ii) statistical analyses aiming at relating environmental and structural traits. In the field of NER, Barriuso et al. (*52*) suggested that the distribution of the electronic density could promote nucleophile or electrophile attacks and that differences between energy levels of the frontier molecular orbitals HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) could be used as an indicator of the chemical reactivity. The best correlation with the amount of NER for a limited number of pesticides was in effect found for the LUMO energy. The calculations of these kind of molecular indicators are only valid if the compound (pesticide or metabolite) reacting with soil is known. In the present instance, we assumed that the parent compound was directly involved in NER formation.

Nonextractable Residues and Soil Properties. The formation of NER for most pesticides is usually correlated to the soil biological activity and to the amount of soil organic matter in the soil (*53–55*). The nature of the organic matter also influences the formation of NER for some pesticides. For instance, the nonhumified fraction of the organic matter appears to display the largest affinity to form NER for atrazine (*33, 56, 57*). The total microbial activity has a direct effect on NER formation as evidenced in pesticide incubation experiments which involve soil samples taken at different depths in a profile and which reveal low NER formation for deeper soil samples which usually have a low microbial activity (*45, 58–62*). In general terms, most environmental factors affecting biological activity, such as temperature or soil moisture content, are likely to have an influence on NER formation. Anderson (*63*) has shown that variation in soil–water content from 2 to 19% had little effect on the

formation of NER for diallate (the lowest formation was found at an intermediary water content of 12%), but provoked an increase in triallate NER. In the case of clorasulam-methyl, variations in the water content between 20 and 60% WHC had no influence on NER content (*64*). However, it should be noted that the range of variation in water contents in these two studies was fairly limited. Larger water content variations resulted in differences in NER formation for MCPA (*65*), atrazine (*60, 66*), carbofuran (*67*), metolachlor (*62*), prosulfuron (*68*), carbaryl (*69*), and isofenphos (*70*). In general, NER amounts increase with increasing water content until the soil reaches saturation. With regard to temperature effects, Cupples et al. (*64*) reported an increase in NER content for clorasulam-methyl when the temperature was increased from 5 to 50 °C for a same length of study. Increased NER formation with temperature has been reported for other pesticides: isofenphos (*70*), MCPA (*65*), flumetsulam (*71*), clomazone (*72*), methabenzthiazuron (*73*).

A specific analysis looking for soils factors influencing NER formation was undertaken for metsulfuron-methyl (*74*). 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 sulfonylureas (*75*). Accordingly, these authors found that NER increased when soil pH decreased. Similar results were found for another sulfonylurea, prosulfuron (*68*). On the contrary, NER for carbaryl, which hydrolyzes to 1-naphtol, was found to increase when the soil pH increased from 4.2 (12% of NER) to 8.3 (78% of NER) (*69*). The same trend was found for the organophosphate isofenphos, NER being more largely formed in an alkaline soil compared to soils having neutral and acidic conditions (*70*). Similar findings were reported for cyprodinil with stronger binding at higher soil pH (*76*).

Variations in the redox potential can be encountered during drying/wetting cycles, in particular at low depths in hydromorphic soils and in riparian buffer zones. The decrease in the oxidoreduction potential was found to decrease the amount of the formation of NER for isoproturon (*77*). In the case of organochlorines, such as DDT, an increase in water content increased the proportion of NER (*78*). This can be explained by the creation of anaerobic microenvironments for the microbial degradation which normally contributes to the reductive dechlorination. Other information on the effect of flooded soil conditions onto pesticide degradation and NER formation can be found for acetochlor (*29*), atrazine (*20, 60, 79*), carbaryl (*69*), carbofuran (*80*), dimethenamid (*81*), fluometuron (*20*), metolachlor (*62*), and nitrofen (*82*).

Nonextractable Residues and Agronomic Practices. Agronomic practices directly or indirectly modifying the factors regulating the behavior of pesticides in soils will have an influence on the formation of NER. 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 experiments is the decrease of the yields of NER when pesticide application rates increase (*83, 84*). Repeated applications can induce specific microbial activities which are able to quickly degrade the pesticide. Barriuso and Houot (*85*) showed that when the soils were treated every year in a maize−maize rotation, atrazine mineralization was fast and the proportion of NER was very low. In contrast, atrazine mineralization was slow with a high proportion of NER formation in the soil which was cropped under wheat or grass and which did not receive atrazine applications. There is, therefore, an apparent competition between pesticide mineralization and NER formation (*85, 86*). In the case of carbofuran, repeated applications lead to an increase in the mineralization rate, but also to a strong increase in NER formation (*44*). 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 micro-organisms adapted to consume triazine-N. For carbofuran, the adapted degradation increases the speed of the oxidation and hydrolysis process. An increase in NER formation with repeated pesticide applications was also found for prometryn (*87*) and deltamethrin (*88*). However, others investigations showed that repeated applications of pesticides to a soil containing NER can provoke a decrease in NER proportion, as for prometryn (*89*) and some arylphenoxyacetic acids (*90*).

The use of organic amendments increases the soil organic stock and can partially modify the nature of organic matter. In general, an increase in organic matter content leads to an increase in NER, as demonstrated for compost additions (*91*). The effect of compost addition depends on the nature of the pesticide (see Figure S1, Supporting Information). For atrazine, the specific activity responsible for accelerated degradation was largely inhibited, with an increase in NER (*91*). A similar effect was found for other triazines (simazine and terbutryne). However, no effect of compost addition on NER was found for the other pesticides studied (pendimethalin, carbetamide, 2,4-D, or metsulfuron-methyl). A decrease in NER was even found for dimefuron when the proportion of compost was increased (Figure S1, Supporting Information). The decrease in mineralization which was also observed for dimefuron can be attributed to an increase in sorption following the addition of exogenous organic matter (*91*).

The addition of a carbon source, which can be easily utilized by microorganisms, will lead to an increase in microbial activity and will affect pesticide behavior. Abdelhafid and colleagues (*54, 55*) have shown that glucose addition did not modify atrazine mineralization, but increased the formation of NER. The authors hypothesized that the increase in NER was linked to the atrazine incorporation in the growing microbial biomass. The simultaneous addition of glucose and mineral N leads to an inhibition of atrazine mineralization and the formation of a larger proportion of NER. The competition between atrazine-degrading microorganisms and the total heterotrophic soil microflora probably contributed to the decrease in atrazine mineralization allowing its stabilization under NER. Gerstl and Helling (*92*) conducted an experiment on the addition of different mineral and organic amendments on soil previously incubated with methyl-parathion. The proportion of the NER after the addition of amendments was 46% of the initial parathion. The release of methyl-parathion NER could not be demonstrated, but both NER and extractable ^{14}C were mineralized.

The management of crop residues and/or the introduction of reduced till or nontillage systems will modify the proportion and the location of the fresh organic matter. A mulch at the soil surface will intercept part of the applied pesticide. The pesticide intercepted is likely to evolve differently to that directly applied onto the soil. Very often pesticide incubated on mulch or fresh organic matter resulted in a higher proportion of NER than those incubated directly in soils (*39, 55, 93, 94*), and the increase in the humification degree of the vegetal residues increased the proportion of NER (*47*). Increase in NER when straw was incorporated into the soil was also found for methabenzthiazuron (*73*) or when bromoxynil was incubated on maize residues (*95*). The formation of NER for 2,4-D and chlorophenols incubated with straw strongly decreased in sterile conditions (*96*). Wanner et al. (*97*) showed that the addition of straw to soil increases the soil microbial biomass and the proportion of NER from dithianon.

Reversibility and Availability of Nonextractable Residues. The formation of NER leads to a decrease in the toxicity and bioavailability of pesticides. In spite of the position concerning the non relevancy of NER for the ecotoxicological risk assessment from a regulatory viewpoint, environment concerns may arise if the stock of NER changes and if a proportion of NER is released. The release of NER was intensively studied from early on. The following articles are considered key in this field: microbial and physicochemical release (*98–103*); bioavailibity (*104–106*); plant uptake (*30, 76, 98, 107–114*); or earthworms uptake (*98, 109, 115, 116*).

Release, bioavailability, and uptake by plants or earthworms only represent a small percentage of the total amounts of NER. Ionic modifications and the addition of nitrogen to the soil can induce a partial release of some NER, as demonstrated for NER of chloro-aniline which were released by addition of N-ammonic fertilizers (*117*), and for prometryn NER which were released by addition of ammoniac-N and nitrate-N (*100*). 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 NER for prometryn (*100*). During the incubation of soil containing NER of cypermethrin, 21−37% of NER were mineralized after a 18 week incubation (*108*). Incubation experiments conducted with NER of methyl-parathion have shown that NER were very slowly released and that the soil microflora was able to mineralize NER directly, without any appreciable build-up of ^{14}C activity in the extractable phase (*92*). From a carry-over point of view, NER derived from metsulfuron-methyl in soil have been demonstrated to have the potential to induce phytotoxic effect on plants such as rape seedling (*118–120*).

Soil column leaching experiments have demonstrated that NER 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 (*121*), atrazine (*122*) or its metabolite deethylatrazine (*123*) 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 NER were still found at the bottom of the columns. The exact origin of these NER found deep in the column is difficult to establish. These could result from the leaching of NER formed near the soil surface, hence indicating an intrinsic or facilitated mobility, or from the formation of NER at various depths following the leaching of the parent and its metabolites down the column.

In conclusion, gaining detailed information regarding how NER are formed and subsequently released is essential if NER are to be included in environmental risk assessments. However, the explicit consideration of NER in environmental risk assessment would require more intensive long-term experiments. However, classical reduced microcosms used for laboratory incubations are probably not adapted and incubation devices must be reconsidered. NER formation can be conceptually interpreted as flow mass using an approach based on kinetic compartment models. The concepts of "slow sorption" can be quite easily implemented in pesticide fate models through a kinetics approach. This slow sorption could evolve to an irreversible sorption pool 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 issue with this kind of approach is the lack of information regarding the exact nature of the NER as the information is required to convert ^{14}C-NER into ^{14}C-parent pesticide or ^{14}C-metabolites.

The definition and use of overall factors involved in the formation of NER is a challenge because most of the factors are interdependent and because the supporting data are incomplete, occasionally not coherent, and strongly pesticide-dependent. A significant effort toward greater standardization of experimental protocols is needed so that robust comparisons of data originating from different laboratories can be performed. The generation of consistent databases would also allow the prediction of the behavior of new compounds with regard to their potential for NER formation. In the end, the important matter is not so much how the residue is defined, but the question of the reversibility between unavailable and available forms of the residues and their biological availability. Accounting for potential biological effects may lead to improved risk assessments.

Supporting Information Available

Categorization of the literature data on NER based on their formation kinetics. Data extracted from the available "endpoints" of the EU review-reports: ranges of mineralized and NER proportion in aerobic conditions. Synthetic complementary data on NER amount for different pesticides and different incubation durations (only results coming from duration close to 100 days or higher were reported). This material is available free of charge via the Internet at http://pubs.acs.org.

Acknowledgments

This review was undertaken as part of the European project FOOTPRINT ((Functional tools for pesticide risk assessment and management, Project SSPI-CT-2005-022704, www.eu-footprint.org). The funding of the work by the European Commission through its Sixth Framework Programme is gratefully acknowledged.

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ES7021736

The Formation of Pesticide Non-extractable (Bound) Residues in Soil: Magnitude, Controlling Factors and Reversibility

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Supporting Information

Summary

This document provides additional information on categorisation of the literature data on NER formation based on the kinetics characteristics of the NER formation (Table S1).

Data extracted from the available « end-points » (EU Registration Data) allowed to propose a classification of some pesticides into categories related to the NER proportion (Table S2).

Table S3 provides examples from EU registration reports of compounds which contain two or more aromatic rings and which show differences in NER formation depending on the location of the labelling.

All available data from the EU review-reports were ranged by chemical families (Table S4), and ranges of mineralized and bound residues proportion in aerobic conditions were given (Table S4).

Finally, Figure S1 showed caculated data on modification of non-extractable (bound) residues amount of different pesticides when the organic matter was increased by addition of different proportions of compost to soil *(91)*.

TABLE S1. Categorisation of the Literature Data on NER Formation Based on the Presence/Absence and Magnitude of Three Steps: i) Initial or "Flash" NER, ii) Time to Reach a NER Plateau, and iii) Long-term NER Evolution. The Table also Provides the Total Length of the Incubation Study

Rate of NER formation	Pesticide	Initial NER	Plateau time	Maturation (final time)	Reference
High	2,4-D	< 5 %	10 d	Release (60 d)	(*124*)
	Acetochlor	< 5 %	90 d	Release (371 d)	(*29*)
	Alachlor	< 5 %	28 d	Incorporation (80 d)	(*40*)
	Atrazine	< 10%	60 d	Release (154 d)	(*61*)
	Atrazine	?	60 d	Release (360 d)	(*26*)
	Chlorothalonil	< 40 %	7 d	Stable (90 d)	(*21*)
	Cloransulam	< 5 %	120 d	Release Inc. (357 d)	(*28*)
	DDT	< 5 %	7 d	Incorporation (28 d)	(*1*)
	Dialllate	< 5 %	28 d	Release (210 d)	(*125*)
	Dicamba	< 5 %	40 d	Release (91 d)	(*22*)
	Dicamba	<10 %	14 d	Release (90 d)	(*126*)
	Dimethenamid	< 10 %	30 d	Stable (inc.) (142 d)	(*81*)
	Dyfonate	< 5 %	14 d	Stable (28 d)	(*1*)
	Metamitron	< 5 %	28 d	Release (stable (84 d)	(*17*)
	Metazachlor	< 5 %	14 d	Stable (84 d)	(*17*)
	Metsulfuron	< 5 %	20 d	Incorporation (100 d)	(*75*)
	Monocrotofos	< 5 %	4 d	Stable (80 d)	(*40*)
	Paraquat	< 5 %	1 d	Stable (91 d)	(*22*)
	Parathion	< 5 %	7 d	Incorporation (28 d)	(*1*)
	Phosalone	< 5 %	14 d	Incorporation (84 d)	(*127*)
	Prosulfuron	< 20 %	20 d	Stable (release (105 d)	(*68*)
	Triallate	< 5 %	140 d	Release (365 d)	(*125*)
Low	Atrazine	< 10 %	200 d	Stable (326 d)	(*25*)
	Bentazone	< 10 %	60 d	Stable (inc.) (160 d)	(*129*)
	Deltamethrin	< 10 %	30 d	Stable (80 d)	(*40*)
	Isoproturon	< 5 %	40 d	Incorporation (91 d)	(*22*)
	Lindane	< 5 %	70 d	Release (91 d)	(*22*)
	Simazine	< 5 %	50 d	Incorporation (80 d)	(*40*)
	Sulcotrione	< 5 %	56 d	Incorporation (84 d)	(*17*)
	Triticonazole	<10 %	100 d	Stable (130 d)	(*18*)

Additional references:

(124) Boivin, A.; Amellal, S.; Schiavon, M.; Genuchten, M. T. V. 2,4-Dichlorophenoxyacetic acid (2,4-D) sorption and degradation dynamics in three agricultural soils. *Environ. Pollut.* **2005**, *138*, 92-99.

(125) Anderson, J. P. E.; Domsch, K. H. Relationship between herbicide concentration and the rates of enzymatic degradation of ^{14}C-diallate and ^{14}C-triallate in soil. *Arch. Environ. Contam. Toxicol.* **1980**, *9*, 259-268.

(126) Gevao, B.; Jones, K. C.; Semple, K. T. Formation and release of non-extractable ^{14}C-Dicamba residues in soil under sterile and non-sterile regimes. *Environ. Pollut.* **2005**, *133*, 17-24.

(127) Ambrosi, D.; Kearney, P. C.; Macchia, J. A. Persistence and metabolism of oxadiazon in soils. *J. Agric. Food Chem.* **1977**, *25*, 868-872.

(128) Boivin, A.; Cherrier, R.; Perrin-Ganier, C.; Schiavon, M. Time effect on bentazone sorption and degradation in soil. *Pest Manag. Sci.* **2004**, *60*, 809-814.

TABLE S2. Classification of some Pesticides Reviewed into Categories of NER Formation Percentage (Based on EU Registration Data)

Low NER level < 30 %	Low intermediate NER level 30%<NER<50%	High intermediate NER level 50%<NER<70%	High NER level > 70 %*
2,4-D	2,4-DB	Acibenzolar-s-methyl	Bentazone
Amitrole	Acetamiprid	Alpha-Cypermethrin	Bromoxynil
Azoxystrobin	*beta*-Cyfluthrin	Bifenazate	Chlorpropham
Benalaxyl	Cyfluthrin	Chlorothalonil	Cinidon-ethyl
Carfentrazone-ethyl	Cyhalofop-butyl	Chlorotoluron	Foramsulfuron
Chlorpyrifos	Dimethenamid-P	Cyazofamid	Iprodione
Chlorpyrifos-methyl	Ethofumesate	Cypermethrin	Maneb
Cyclanilide	Fenamidone	Desmedipham	Metalaxyl-M
Daminozide	Flupyrsulfuron-methyl	Famoxadone	Phenmedipham
Deltamethrin	Forchlorfenuron	Florasulam	Thiophanate-methyl
Ethoxysulfuron	Glyphosate	Flufenacet	
Etoxazole	Iodosulfuron	Flumioxazine	
Flazasulfuron	Ioxynil	Imazosulfuron	
Fluroxypyr	Kresoxim-Methyl	Indoxacarb	
Fosthiazate	Mancozeb	Isoproturon	
Glyphosate trimesium	MCPA-acid	Mesosulfuron	
Imazamox	Mecoprop	Metiram	
Iprovalicarb	Mesotrione	Oxasulfuron	
Isoxaflutole	Milbemecin	Picolinafen	
lambda-Cyhalothrin	Picoxystrobin	Propoxycarbazone	
Maleic hydrazide	Propiconazole	Pymetrozine	
MCPB	Prosulfuron	Pyraclostrobin	
Mepanipyrim	Silthiofam	Pyridate	
Methoxyfenozide	Sulfosulfuron		
Metsulfuron methyl	Thifensulfuron-methyl		
Molinate	Zoxamide		
Oxadiargyl			
Pendimethalin			
Propyzamide			
Pyraflufen-ethyl			
Quinoxyfen			
S-Metolachlor			
Spiroxamine			
Tepraloxydim			
Thiacloprid			
Triasulfuron			
Trifloxystrobin			

* Threshold used in the EU for additional studies on bound residues.

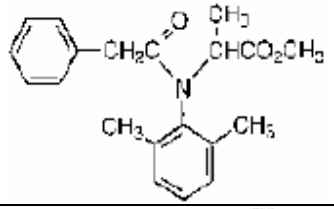
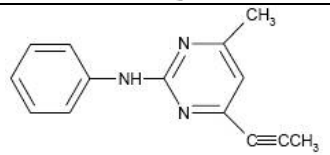
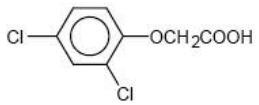
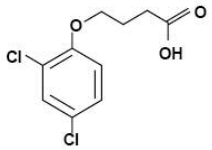
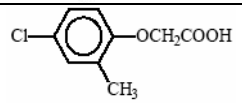
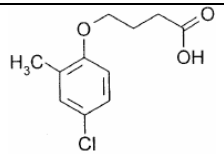
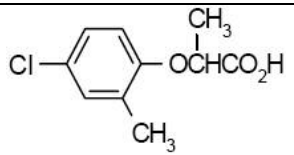
TABLE S3. Proportion of NER (in %) Related to the Position of the ^{14}C-labelling for Selected Compounds Containing Different Rings. Data Extracted from EU Registration Documents

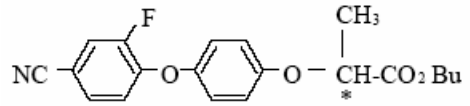
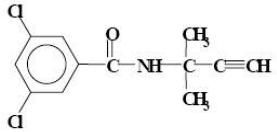
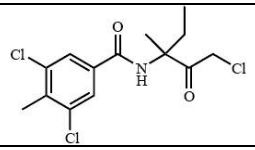
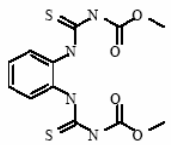
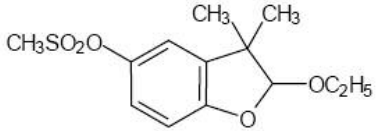
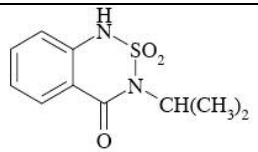
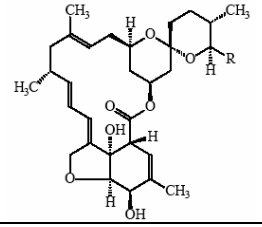
	Phenyl[a]	Pyridine	Pyrimidine	Indol	Imidazole	Thiadiazole	Triazole	Triazine	N-ring/phenyl[b]
Forchlorfenuron	24 - 46	23 - 25							0.3
Picolinafen	44 - 65	21 – 23							0.4
Picoxystrobin	22 -32	12 - 32							0.8
Foramsulfuron	74 - 103		55 - 93						0.8
Mepanipyrim	26		19						0.7
Mesosulfuron	56		28 - 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	--

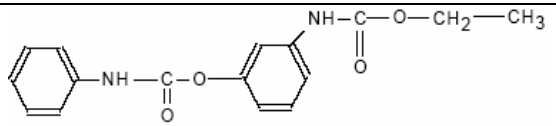
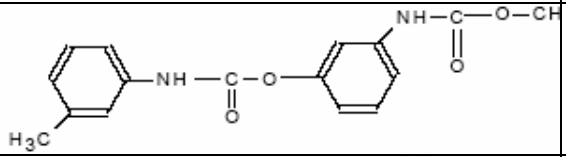
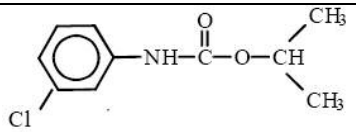
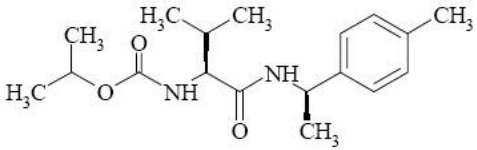
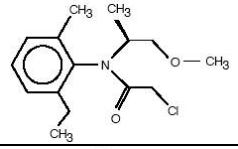
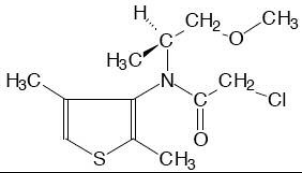
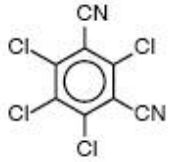
[a] The phenyl range presented incorporates data for NER originating from a phenyl-^{14}C-labelling and a N-heteratomic-^{14}C-labelling. [b] Ratio of the proportions of NER formed for compounds with ^{14}C-N-ring and ^{14}C-phenyl.

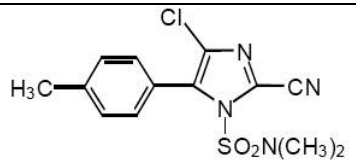
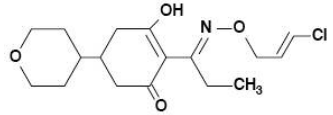
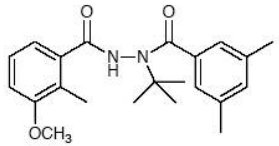
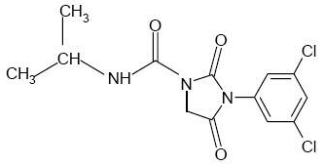
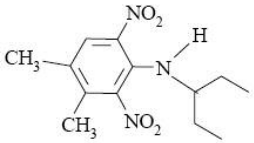
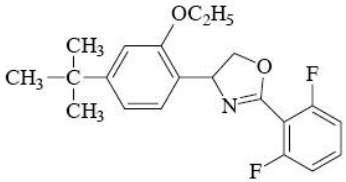
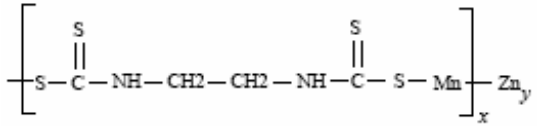
TABLE S4. Data from the Available "end-points" (2007) of the EU review-reports for pesticide registration:

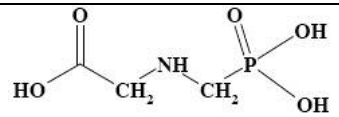
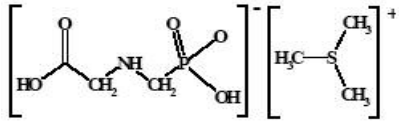
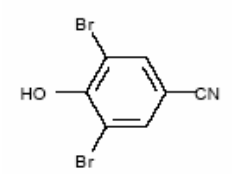
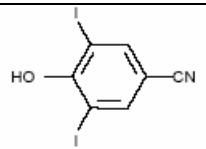
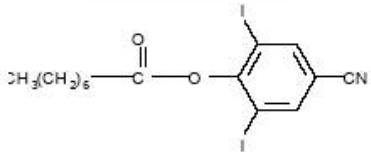
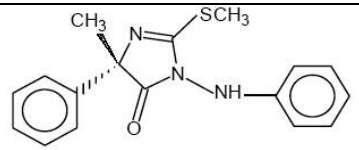
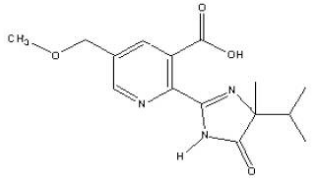
Ranges of Mineralized and Non-extractable (Bound) Residues Proportion in Aerobic Conditions

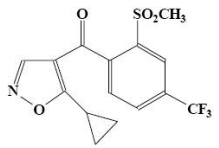
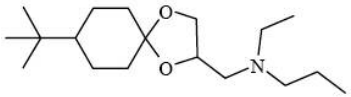
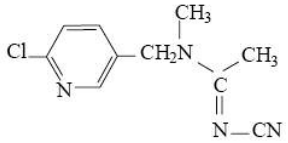
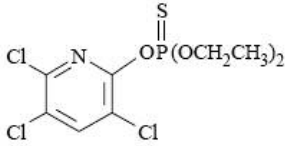
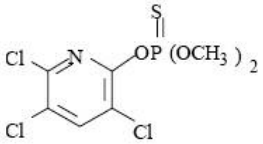
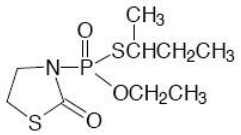
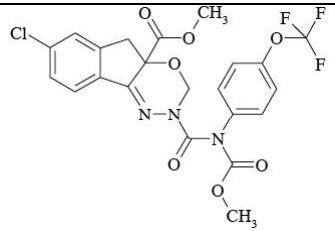
Name	Family	Structure	Mineralization	Non-Extracted Residues (NER)
Benalaxyl	Acylalanine		25 – 26 % (100 d)	18.8% (133 d)
Mepanipyrim	Anilinopyrimidine		5.4 % (120 d, phenyl) 2.4% (120 d, pyrimidin)	26.0 % (120 d, phenyl) 18.6 % (120 d, pyrimidin)
2,4-D	Aryloxyalkanoic acid		36 % (114 d)	27.9 % (114 d)
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)

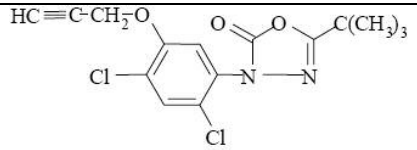
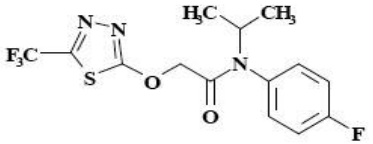
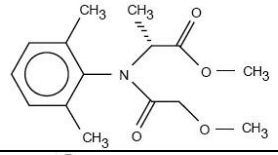
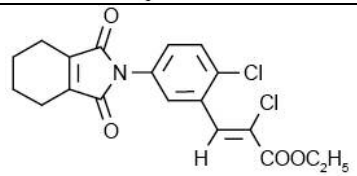
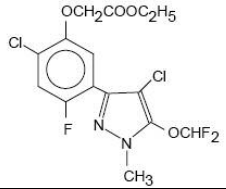
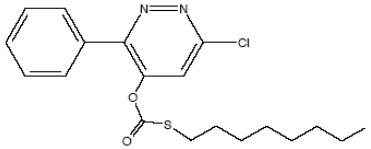
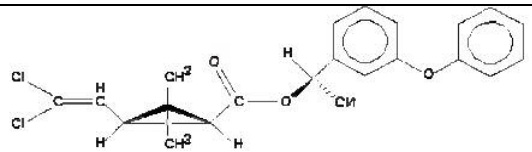
Cyhalofop-butyl	Aryloxyphenoxypropionic herbicide		36.1 - 46.3 % (120 d)	33.7 - 44.2 % (120 d)
Propyzamide; pronamide (USA);	Benzamide		3.4 % (90 d) 33 – 48 % (120 d)	6.8 % (90 d) 16 – 27 % (80 d)
Zoxamide	Benzamide		34.4 - 57.8 % (120-122 d, phenyl)	25.6 – 39 % (28-120 d, phenyl)
Thiophanate-methyl	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)

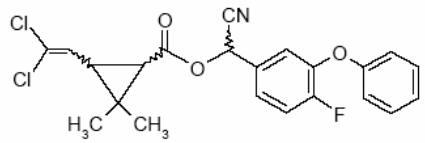
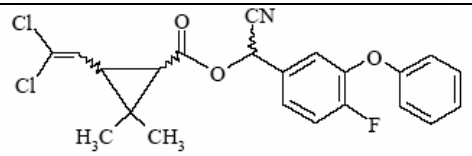
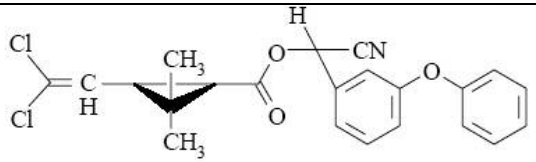
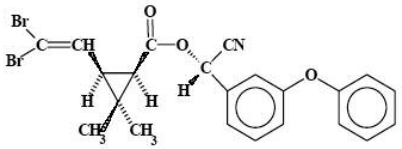
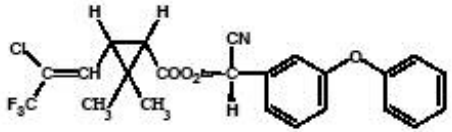
Desmedipham	Bis-carbamate		21.4 - 37.8 % (100 d, both labels) 7.5 - 46.4 % (112 d, both labels) 14 - 19 % (90 d, AP-label)	55.8 - 67.2 % (100 d, both labels) 21.5 - 55.0 % (112 d, both labels) 64 % (90 d, AP-label)
Phenmedipham	Bis-carbamate		13.3 – 16.5 % (120 d, AP) 9.7 – 11.3 % (120 d, phenoxy)	63.6 – 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)

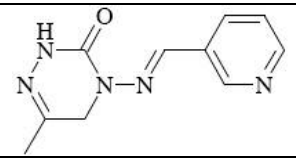
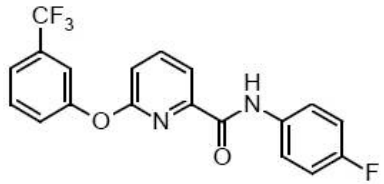
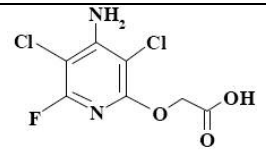
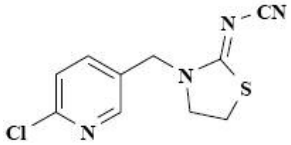
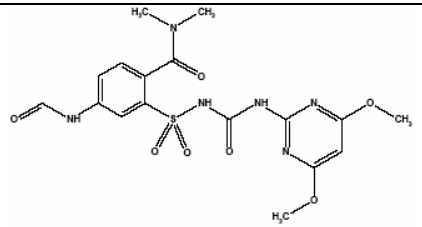
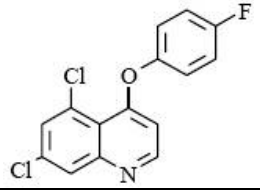
Cyazofamid	Cyanoimidazole		14.4 % (45 d, phenyl) 11.9 % (59 d, imidazole))	47.6 % (59 d, phenyl) 64 % (45 d, imidazole)
Tepraloxydim	Cyclohexadione oxime		66 %	25 %
Methoxyfenozide	Diacylhydrazine		0.9 - 3.6 % (120 d, A-ring, 25°C) 2.6 % (120 d, B-ring, 25°C) 2.7 % (120 d, t-label, 25°C)	12 – 27 % (120 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)

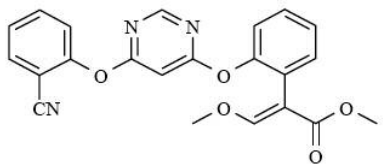
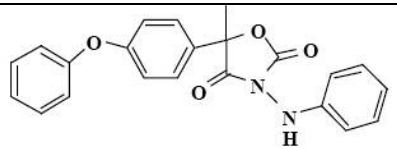
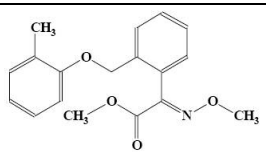
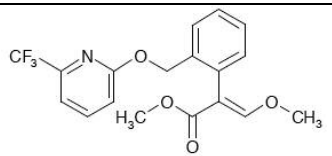
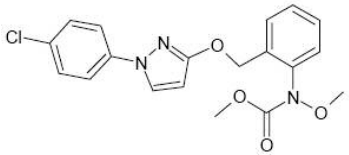
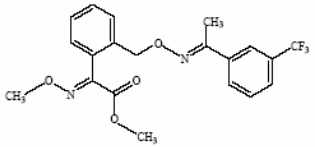
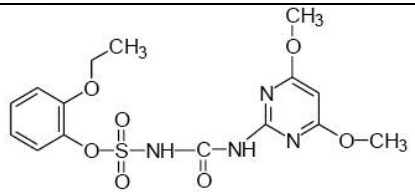
Glyphosate	Glycine derivative		46.8 – 55.3 % (28 d) 5.8 – 9.3 % (112 d) 34.7 – 41.4 % (84 d) 69.7 – 80.1 % (150 d) 32.7 % (112 d) 79.6 % (100 d)	8.5 – 40.3 % (28 d) 4.6 – 13.5 % (112 d) 16.7 – 33.9 % (84 d) 5.1 – 8.8 % (150 d) 13.9 % (112 d) 8.4 % (100 d)
Glyphosate trimesium	Glycine derivative		37 % (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)

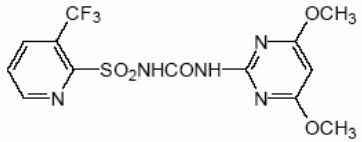
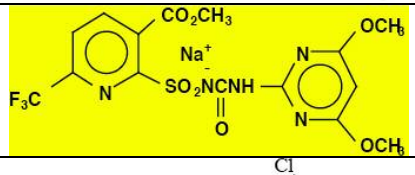
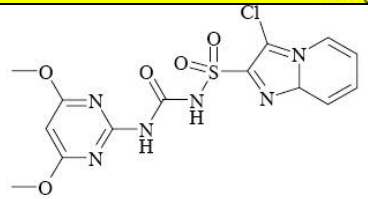
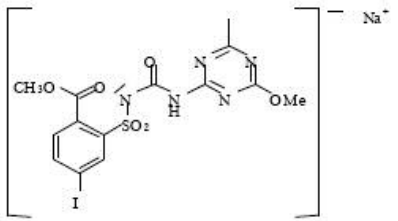
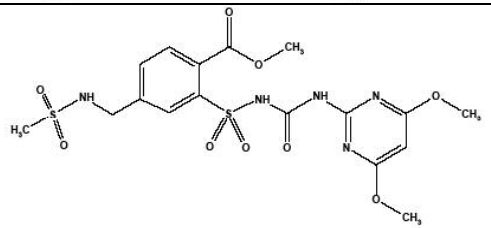
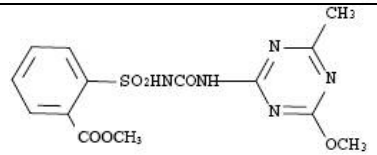
Isoxaflutole	Isoxazole		1 %	6 % 9 % (120 d)
Spiroxamine	Morpholine		30.7 - 44.7 %	24.7 - 26.4 %
Acetamiprid	Neonicotinoid		9.6 % (120 d)	32.3 % (120 d)
Chlorpyrifos	Organophosphate		82 % (120 d) 5 – 50 % (other studies)	4 % (120 d) 25 % (other studies)
Chlorpyrifos-methyl	Organophosphate		23 – 69 %	17 – 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)

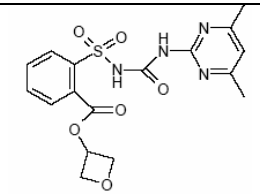
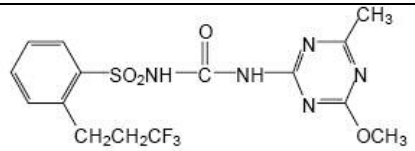
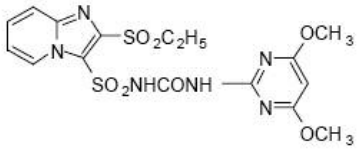
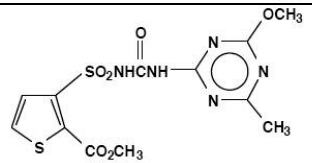
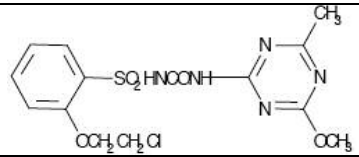
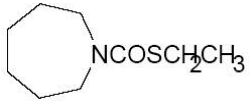
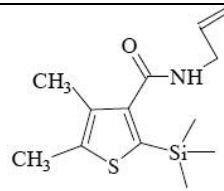
Oxadiargyl	Oxidiazole		5.1 – 10.4 % (92-125 d)	20.0 – 24.8 % (92-125 d)
Flufenacet	Oxyacetamide		10.2 - 20.8 % (90 d, fluorophenyl) 31.9 % (90 d, thiadiazole)	29.9 - 56.2 % (90 d, fluorophenyl) 6.0 % (90 d, thiadiazole)
Metalaxyl-M	Phenylamide		22 – 33 % (84 d)	63 – 73 % (84 d)
Cinidon-ethyl	Phenylphthalimide		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)

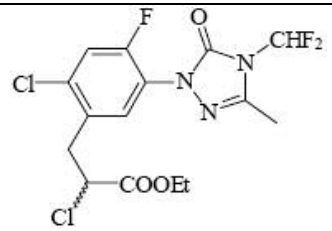
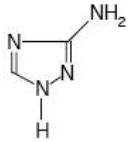
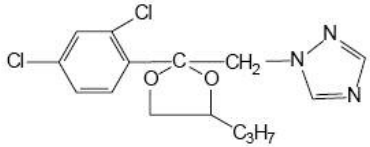
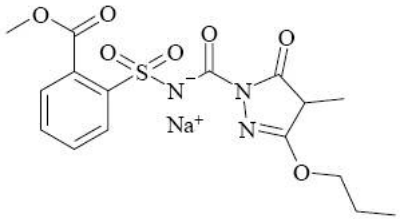
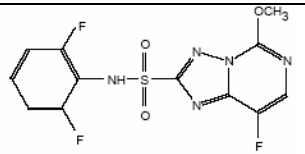
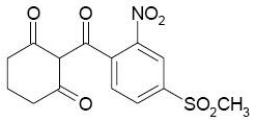
beta-Cyfluthrin	Pyrethroid		36 % (190 d) 23 % (84 d)	42 % (190 d) 34 % (84 d)
Cyfluthrin	Pyrethroid		23 % (84 d) 36 % (190 d)	34 % (84 d) 42 % (190 d)
Cypermethrin	Pyrethroid		20 – 47 % (168 d, cis-isomers) 48 – 61 % (168 d, trans-isomers)	21 – 57 % (168 d, cis-isomers) 26 – 45 % (168 d, trans-isomers)
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)

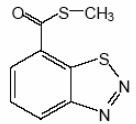
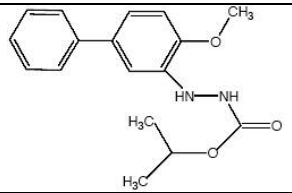
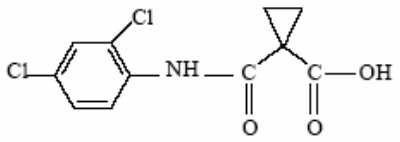
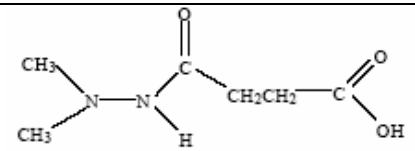
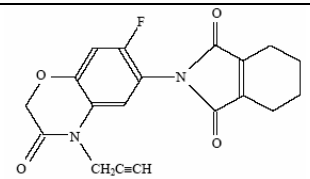
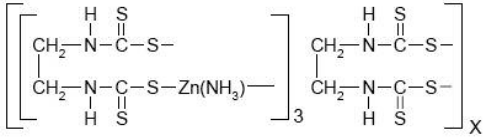
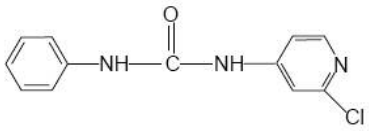
Pymetrozine	Pyridine		3 - 15 % (90 ...92 d)	21 - 61 % (90 d, 20 -25 °C)
Picolinafen	Pyridinecarboxamide		17.4 % (61 d, aniline) 22.8 - 43.0 % (100 d, pyridine)	43.9 % (61 d, aniline), 65 % (134 d, aniline) 21.2 % (100 d, pyridine) 22.7 (60 d, pyridine)
Fluroxypyr	Pyridinecarboxylic acid		65 %	29.7 %
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)

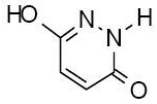
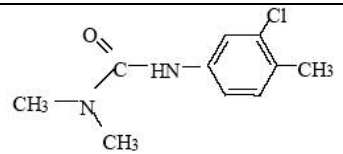
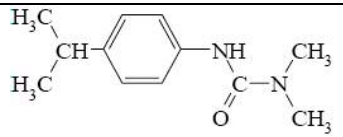
Azoxystrobin	Strobilurin		2 - 2.5 % (100 d) 11 - 14 % (360 d)	9 - 10 % (100 d) 18 - 24 % (360 d)
Famoxadone	Strobilurin		11.8 % (90 d, phenylamino) 13.0 - 32.2 % (90 d, phenoxyphenyl)	53.8 % (90 d, henylamino) 29.9 - 51.4 % (90 d, phenoxyphenyl)
Kresoxim-Methyl	Strobilurin		17.2 - 35.2 % (91 d)	30.1 - 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) 42.1 - 54.4 % (113 d, phenyl) 29.9 - 42.8 % (119 d, phenyl)	12.4 - 20.6 % (119 d, pyridinyl) 16.2 - 32.4 % (119 d, pyridinyl) 19.65 % (120 d, pyridinyl) 30.0 - 32.2 % (113 d, phenyl) 22.4 - 28.6 % (119 d, phenyl)
Pyraclostrobin	Strobilurin		4 % (87 d, tolyl) 5 % (91 d, chlorophenyl)	54.3 % (87 d, tolyl) 56.1 % (91 d, chlorophenyl)
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 %

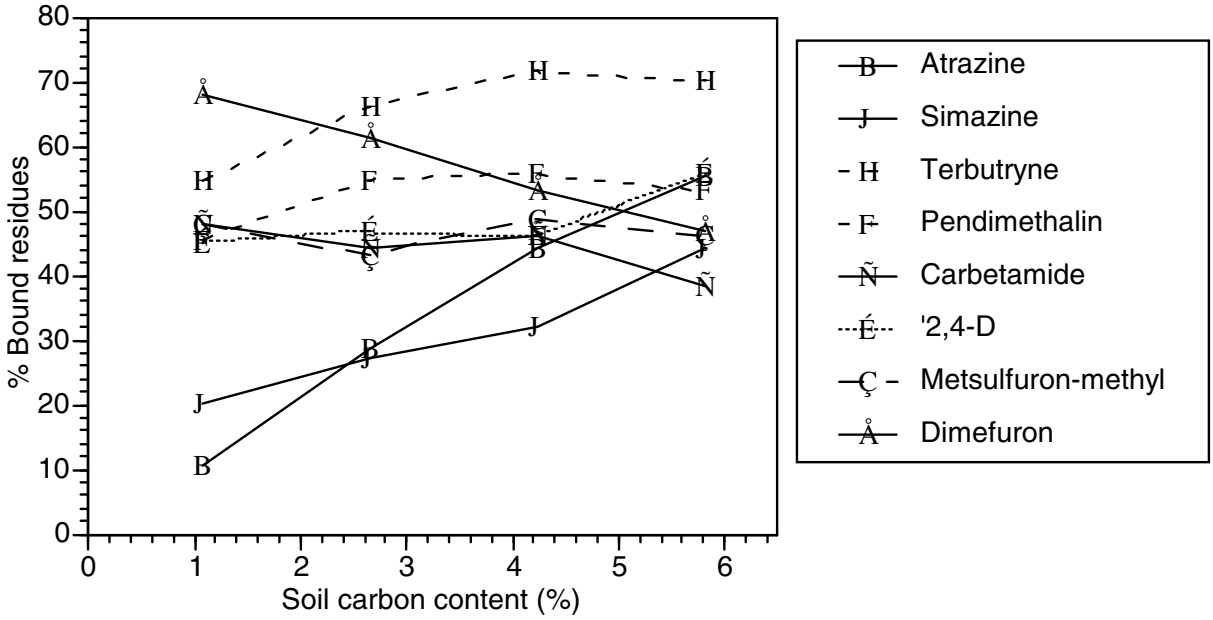


FIGURE S1. Modification of non-extractable (bound) residues amount of different pesticides in relation to the proportion of soil organic matter after 250 days of incubation in controlled laboratory conditions. The soil organic matter was increased by addition of different proportions of compost to soil. Recalculated data from Barriuso et al. (*91*).