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Occurrence and Distribution of Pesticide Residues in Soil as a Result of Long-Term Application

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Executive Summary

Pesticides have been widely used in agriculture for the better part of the past century. While they are known to save farmers time and money, negative effects on human and environmental health have been well described. National and international bodies have identified diffuse pollution by pesticides as a major concern. However, the actual occurrence and distribution of pesticides in the soil is poorly understood, despite soil's vital role in global biogeochemical cycles. Determination of a wide variety pesticide residues in the soil on a regional scale has historically been difficult and expensive.

In this study, a new methodology is used to extract up to 250 pesticides from the soil. The actual occurrence and distribution of pesticide residues in the soil is determined in two contrasting European agricultural systems: annual rotation of root and cereal crops in the Dutch Atlantic climate and permanent cultivation of oranges in the Spanish Mediterranean climate. This study is also novel in that it incorporates interviews from local experts in linking management practices to pollutant levels.

Indeed some pesticides are still present in the soil, even after forty years since application. With this study, it becomes evident that pesticide residues are probably mobile in the environment via particulate transport and that the concentration of some compounds in the soil exceed acceptable risk levels. However, heterogeneity is still great as compounds behave variably between fields. Assessment of residues on a regional scale may provide more useful assessment of risk to public and environmental health. This study makes further analysis of the risks associated with residues actually present in the soil more feasible.

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Definitions of Selected Terms

Active substance- the main chemical producing the desired effect in a pesticide. The compounds mentioned in this report are all active substances. However, pesticides are sold as mixtures with other substances to facilitate application.

Adsorption- see *sorption*

Degradation is the process of reducing pesticide residue levels in soil.

Fungicide- a chemical intended to inhibit the growth of or kill fungal pests.

Herbicide- a chemical intended to inhibit the growth of or kill plant pests, namely weeds.

Insecticide- a chemical intended to inhibit the growth of or kill insect pests.

Metabolite- a degraded daughter compound of the originally applied product.

(MRL) Maximum residue level- the maximum amount of a compound that a person can consume without seeing negative health effects. Usually expressed in a unit of mass per unit of time. Levels may be specific to a compound and/or crop.

Pesticide- a product intended to destroy or inhibit the growth of any pest or weed that threatens crop productivity.

(POP) Persistent Organic Pollutant- a chemical listed on the UN treaty, the Stockholm Convention, which presents compounds with high persistence in the environment and potential for negative environmental effects. Nine of the twelve compounds on the list are pesticides.

Sorption- an umbrella term for adsorption and absorption. *Absorption* is the incorporation of one substance into another. *Adsorption* is the binding of ions or molecules from one substance to the ions or molecules of another substance. For this study, absorption is irrelevant and adsorption and sorption are used interchangeably.

1 Introduction

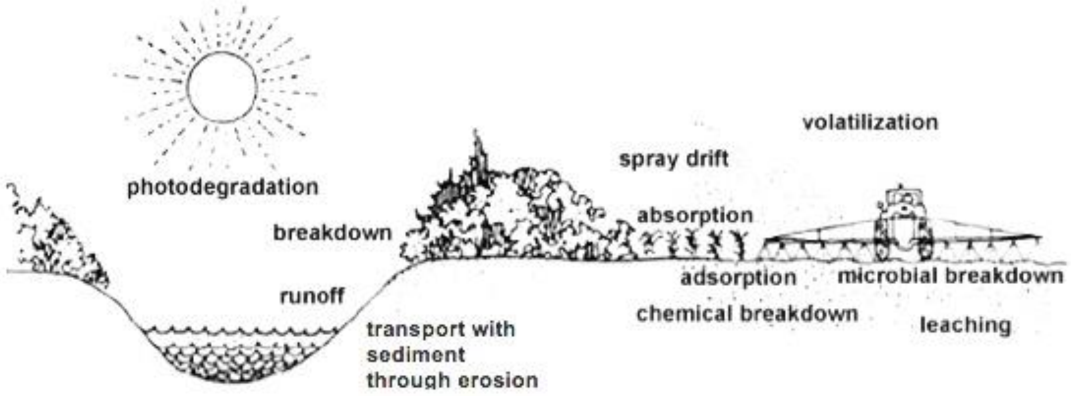


Figure 1: Scheme of potential fates of pesticide residues in the environment (MABA, n.d.)

A *pesticide* is a chemical product intended to destroy or inhibit the growth of any pest that threatens crop productivity. Pesticides are divided by functional groups where *fungicides, herbicides and insecticides* eliminate fungal, weed and insect pests respectively. While pesticides can be used for control of disease-carrying insects, this report will focus on use in agriculture, which accounts for 80% of global pesticide consumption (USEPA, 2011). With these products, farmers are able to increase crop yields while saving time and money (Hart & Pimentel, 2002). However, less than 0.1% of pesticides reach the target, the rest is left in the air, soil and water (Pimentel & Levithan, 1986). The natural follow up question is: What is the fate of pesticides that do not reach the target organisms?

Environmental impacts of pesticide use are widespread, well documented, and of global concern. Beneficial soil macro-organisms and nitrification bacteria are especially vulnerable to pesticide application, leading to increased dependence on synthetic fertilizers (Lang & Cai, 2009). Mixtures of pesticides have been shown to have a synergistic effect, killing endangered salmon (Laetz et al., 2009). Finally, when it comes to public health, pesticide use results in afflictions for both farmers and residents of the surrounding community (Antle & Pingali, 1994; van der Mark et al., 2012; Ruiz-Suárez et al., 2014). Pollution of pesticides from agriculture is considered a threat to fresh water quality for human consumption (European Commission, 2007; EEA, 2010). In fact nine of the twelve persistent organic pollutants (POPs) banned under the Stockholm Convention are pesticides (Schafer & Kegley, 2002). To address these wide ranging concerns, a thorough understanding of the distribution and fate of pesticide residues is necessary.

So far, most ecological concern with pesticide residues has been focused on the impact of application on water bodies, although Fig. 1 illustrates that there are many potential pathways of pesticide distribution in the environment (Arias-Estevez et al., 2008). In this report, the focus is on the process of 'adsorption' or 'sorption' of residues to the soil. Soil is a sink from which pesticide residues can be released into water or air (Shegunova et al., 2007). Understanding the fate and distribution of pesticide residues in soil is of interest because all water that will become groundwater passes through soil at some point. Gilliom et al. (1999) found that 50% of wells they studied were contaminated with pesticide residues, likely coming from leaching from the soil. Governments have established acceptable limits for how many residues are permissible in potable water.

Controls also exist for food quality. Some pesticides are fat-soluble and thus pose a threat with long-term exposure through food. Maximum Residue Levels (MRLs), the acceptable maximum level a person can consume before being negatively affected, are established per compound and per crop by various bodies including the FAO, WHO, EU and national governments. Residues in the soil are known to translocate into the material of many cereals, fruits and vegetables and thus may accumulate in meat (USDA, 2014; JMPR, 2005). In 2013, almost a quarter of all carrots screened for residues of persistent pesticides contained DDT metabolites (USDA, 2014). These pesticides must be biologically available in the soil following decades since the most recent application. Understanding the concentration and distribution of pesticide residues in soil is crucial for determining the transportability of these residues into water bodies, non-target organisms, and humans.

Some soil characteristics universally increase the likelihood of a pesticide binding to the soil and thus persisting in the environment. Clay content and soil organic matter are considered to be two of the most important factors positively influencing the potential for residues to bind to the soil (Andreu & Picó, 2004; Kah et al., 2007; Arias-Estévez et al., 2008). However, other factors like pH have different effects on different compounds (Kah et al., 2007). Furthermore, the likelihood of persistence of residues can even be influenced by conditions at the time of application, like soil water content following a rainfall event (Ghadiri & Rose, 2001; Arias-Estévez et al., 2008). Even under controlled laboratory conditions, there are marked differences in the ability of different soil types to contain and degrade residues (Kah et al., 2007). The list of potential factors influencing persistence of pesticides in soil is wide ranging (see Table 1) and includes factors impossible to simulate in a laboratory or generalize in models.

This means that prediction of degradation rates on a large scale is often unrealistic. In order to understand the quantity and distribution of pesticide residues, field data is necessary. Only field observations will offer the ability to understand the dynamics of pesticide distribution in the environment and associated risks. Aware of the enormous range of potential relationships between environmental factors and pesticide persistence, the aim of this study is not to try to explain the mechanisms behind the rates of degradation of the different compounds. The goal instead is to describe what mixtures of pesticides and metabolites occur under field conditions in an Atlantic climate on a crop rotation including cereals and root vegetables and in a Mediterranean climate where oranges are produced as a permanent crop.

1.1 Theory

1.1.1 Factors Influencing Residue Persistence and Ecological Availability

The formation of residues in the soil depends on how strongly the chemical binds to soil components, how readily the chemical degrades and, environmental conditions at the time of application (Arias-Estevez et al., 2008). The processes that govern persistence of residues in soils are sorption and degradation. *Sorption* is the process through which pesticides bind to soil particles. Higher rates of sorption occur where organic matter and clay content is highest in the soil (Arias-Estevez et al., 2008). Microbial activity, which has a great influence on the sorption of a pesticide to the soil, increases with these factors (Penn State Extension, 2001). The influence of pH on persistence of residues varies with the pH of the compound itself (Dubus et al., 2001; Barriuso et al., 2008). While organic matter, clay content, pH and microbial activity are widely cited as the most important factors in the sorption of a compound to the soil, relationships between these factors in the field are poorly understood.

Once residues bind through sorption, *degradation* is the process of reducing residue levels in soil. Puzzlingly, degradation rates are also usually governed by microbial activity and carbon content (Guo et al., 2000; Kah et al., 2007). pH also plays a role because as values reach 8-8.5, microbial activity can be limited (Kah et al., 2007). Laboratory studies exist that seek to describe the relationship of sorption to degradation, but these studies often only examine one potential factor and compound at a time (Guo et al., 2000; Park et al., 2004). General consensus is that over time, degradation rate slows to the point that remaining residues are inert and not biologically available (Barriuso et al., 2007; Arias-Estévez et al., 2008). Degradation rates correlate with similar factors as sorption rates, leaving little to go on when predicting the distribution of pesticide residues in agricultural soil.

Table 1: Factors that influence persistence of residues in soil, summarized from Arias-Estévez et al., 2008

Properties of the Pesticide	Properties of the Soil	Properties of the Site	Climatic Variables
Chemical Nature	Clay content	Elevation (slope, aspect)	Wind movement
Volatility	Structure	Plant cover (species, density, distribution, historical)	Temperature
Application of pesticide (method, time of year, frequency, amount)	Compaction	Microbial populations (species, density, distribution)	Solar radiation
Formulation	Organic matter content	Use of fertilizers (chemical and natural)	Precipitation
Concentration	Soil moisture	Combination with other pesticides	
Solubility	pH	Tillage	
	Mineral content	Irrigation (type, amount, frequency)	
	Iron-oxides	Adjacent environments (hedges, water bodies)	

Even when the pesticides are fully bound to the soil, they are still mobile in the ecosystem through particulate transport with erosion and through macropores in the soil via colloid flow (Borgaard & Gimsing, 2008). Following rainfall events, pesticide residues can be transported along with soil particles (Worrall et al., 1999; Hesketh et al., 2001; Michel et al., 2014). Also, residues can be made biologically available through microbial activity, but mechanisms and relationships in play are not well understood (Gevao et al., 2000). Due to the translocation of residues through erosion and the potential uptake of residues by crops, further analysis of the presence and distribution of these residues is merited.

1.1.2 Existing Knowledge on Residue Presence and Distribution

Large-scale monitoring of a wide range of residues in the field has historically been difficult due to previous methods of extracting residues from the soil for analysis being complex, costly and covering only a narrow spectrum of compounds (Lehotay, 2011). The QuEChERS method, described in the methodology chapter, is able to extract a broad range of compounds from food and soil at a lower cost (Lehotay, 2011). Only recently has an adequate methodology for extracting and measuring a broad spectrum of residues been available.

Table 2: Span of previous studies of pesticide persistence on a regional scale.

	Oldal et al., 2006	Shegunova et al., 2007	Ruzickova et al., 2008	Ferencz & Balog, 2010	Pose-Juan et al., 2015
Location	Hungary	Czech Republic	Czech Republic plus Western Balkan countries	Romania	Spain
Scale	Nation-wide (93,000 km^2)	Nation-wide (79,000 km^2)	Region-wide (288,800 km^2)	County-wide (6,714 km^2)	Region-wide (5,000 km^2)
N Compounds Analyzed	10	10	6	70	17
N Soil Samples	24	19	47	20	17
Notable Compounds Detected	Only atrazine was detected in two of the 24 soil samples	Only organochlorine compounds tested. Heptachlor epoxide is the most frequently occurring.	Only organochlorines tested. DDT and HCH metabolites frequently found	Many classes tested. DDT found most frequently at concentrations up to 50 ppb. Samples taken from 50cm deep.	Many classes tested. Herbicides are most frequently found.

Previous field screenings determine the presence of relatively few pesticides for a broad regional or national assessment of risk to public health. Most of these studies are in eastern European countries recently entered into the EU (Oldal et al., 2006; Shegunova et al., 2007; Ruzickova et al., 2008; Ferencz & Balog, 2010). Most of these studies focus on organochlorines (see Table 2). Meanwhile, other studies try to make a global assessment of pesticide transport and residence time based on literature review, but it is difficult to make any universal conclusions due to variation in the climate, physical traits of soil, pesticide application method and frequency and chemical composition of pesticides applied (Gevao et al., 2000; Farenhorst, 2006; Kah et al., 2007; Arias-Estevez et al., 2008).

1.2 Measures for Determining Likelihood of Long-term Persistence

There are three measures used throughout this report to describe the likelihood for a pesticide to persist in the soil: log KoW and DT_{50}.

log KoW or octanol-water partition coefficient is an important measure for understanding the environmental fate of pesticides. It describes the ratio between concentrations of a given pesticide between an organic solvent (octanol) and water (Noble, 1993). It is expressed in a unitless measure ranging from 2-7. Compounds with low log KoW values are more water soluble and therefore leach readily, while compounds with high values are fat soluble and more likely to bioaccumulate, thus posing more risk to humans and animals (Zachariah, 2011). While log KoW is fairly easy to measure, its values become unreliable for particularly non-polar compounds, as any value above 4 is difficult to reliably estimate and is considered to have high potential to adsorb to soil and bioaccumulate (Pontolillo & Eagenhouse, 2001). This coefficient is in the nature of the compound itself and would not vary under different conditions in the field.

Half-life, or DT_{50}, is another important value used to understand the environmental fate of a pesticide. DT_{50} describes the time it takes for 50% of the original dosage to of the pesticide to degrade (Kah et al., 2007). For some compounds the DT_{50} is only hours, and for others, decades. DT_{50} for a given compound is known to vary in different environmental conditions and to be much shorter in the laboratory than in the field, this is probably due to more active microbial life (Miyamoto & Kearney, 1985). For example, glyphosate degradation under laboratory and field conditions has been shown to range from 1-130 days (Landry et al., 2005; Tomlin, 2009). DT_{50} values for metabolites are difficult to measure due to the non-uniformity of degradation rates, with a wide range of estimated values (Yang et al., 2015). Thus, DT_{50} alone is not an objective measure of the persistence of a compound, but serves to make comparisons between the likelihood of different compounds to persist in soil. In Appendix I are collected DT_{50} values for almost all of the compounds studied. Whenever possible the value reported represents the upper estimate from field conditions, but in some cases only laboratory results are available.

1.3 Objective and Research Questions

Laboratory studies have been helpful in distinguishing which factors may influence the persistence of pesticide residues in the soil. Yet even in a controlled environment, great variation in sorption and degradation rates is present. Policymakers have expressed concern in pesticide pollution, but so far, field-based studies have taken only few samples on a regional level and analyzed a select few pesticides. If the aim is to make a better assessment of risks associated with diffuse pollution from pesticides in agricultural regions, then the study must focus on the actual occurrence and distribution of pesticide residues in the environment.

Objective: To assess the occurrence and distribution of pesticides in agricultural soil within and between fields under typical cultivation systems as a result of long-term application in the Netherlands and Spain.

Main Research Question: How are pesticide residues distributed in agricultural soil in the Netherlands and Spain? Are there patterns in the distribution of residues found within and between fields?

> *RQ 1*: Which pesticide residues still occur in agricultural soil following decades of application?
>
> > *Sub Question 1: How do management practices influence the persistence of pesticide residues?*
> > *Sub Question 2: Are pesticide residues transported from the field through soil erosion into connected water bodies?*
>
> *RQ 2:* What relationships can be found in the distribution of pesticide residues? How heterogeneous is pesticide residue distribution on a field scale?
>
> > *Sub Question 1: How do soil pH and organic matter content relate to the distribution of pesticide residues?*
> > *Sub Question 2: Do patterns differ between the Netherlands and Spain?*
>
> *RQ 3*: Which environmental risks are associated to the residues actually found in soil?

Hypotheses:

> *H 1:* Most likely to be present are old persistent compounds, which are known to have long residence times, low water solubility, and potential for bioaccumulation, like DDT (Shegunova et al., 2007; Lamberth et al., 2013). Such compounds will be found in equal measure in sites that have converted to organic management as in those still managed conventionally. Otherwise, the compounds found will have relatively high K_d, log KoW and DT_{50} values.
>
> Residue levels will be higher in the sediment than in nearby soil because degradation rates are limited under the anaerobic conditions and decreased photodegradation found in canals. Underwater, pesticides can accumulate in sediment (Ghadiri & Rose, 2001; Bach et al, 2005).
>
> *H 2*: Residue quantities will correlate positively with organic matter and clay content (Samuel & Pillai, 1991; Kah et al., 2007). It is difficult to hypothesize which differences are present between the Netherlands and Spain. For example, residues quantities may be lower on Spanish orchards because open spaces and low rainfall enhance photodegradation

(Baycon et al., 2003; Osborn, et al., 2010). On the other hand, in the Netherlands residues may be lost through leaching or runoff, and dosages of many individual pesticides may be too low to accumulate over time. The diversity of potential factors in the literature makes it difficult to form a confident hypothesis.

H 3: Currently there is little monitoring of pollution in soil (Eurostat, 2007). Threshold values are infrequently included in national legislation. There is little evidence to support a hypothesis either way if residues will be higher or lower than established risk levels following 50 years of pesticide application.

2 Materials and Methods

2.1 Site Description

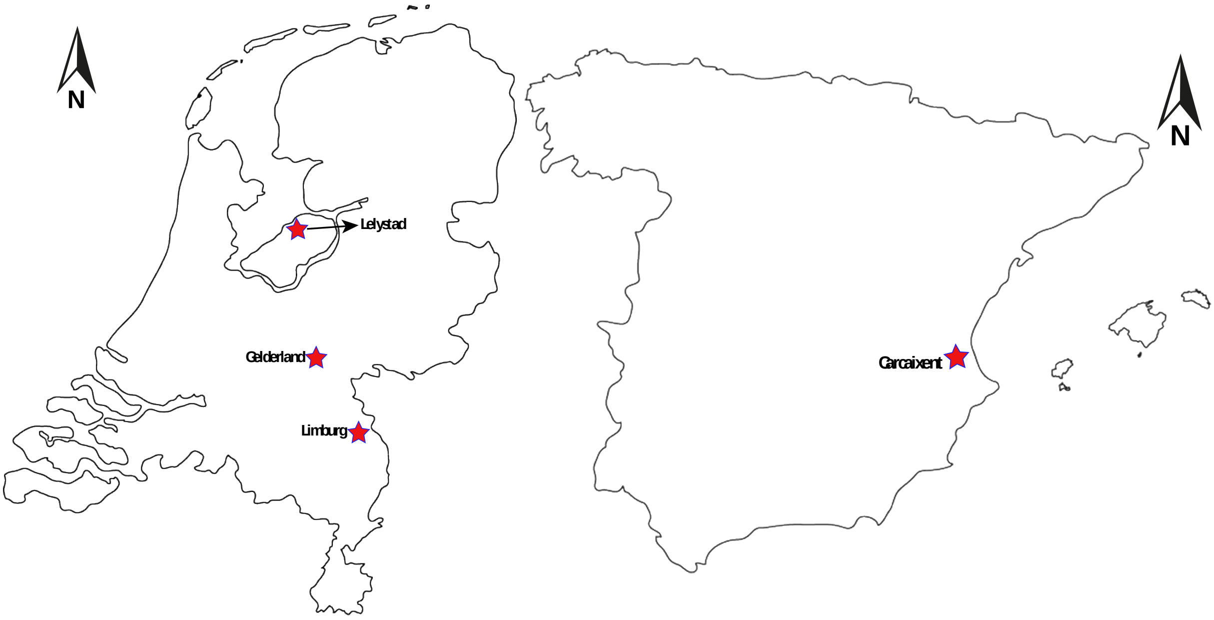


Figure 2: Maps of the Netherlands and Spain highlighting the study locations (Outline source: worldatlas.com).

2.1.1 Netherlands

The Netherlands is the second most intense user of pesticides in the European Union, after Belgium. While it accounts for only 2.3% of total product volume used in on arable land (Eurostat, 2007), the Netherlands uses an average of 10 kg of active substance per ha of arable land from 1992-2010 (FAOSTAT, 2015). Due to the intensity of use of pesticides, the Netherlands is an interesting study area.

The three farms selected for this study are research farms affiliated with Wageningen University in three different provinces in the Netherlands. Each of the farms practices a typical Dutch crop rotation, a 5-7 year long rotation where crops like maize, wheat, barley, sugar beets, potatoes and cover crops (ie: alfalfa, hay) are grown interchangeably. The three sites are discussed separately due to the geographic spread of the sites (Fig. 2). A summary of physical characteristics of the soil can be found in Table 2.

2.1.1.A. Flevoland

Flevoland is comprised of land reclaimed from the sea during the middle of the 20th century. The reclamation process involved the establishment of the province using clay-rich sediment from the Zuiderzee in the center of the Netherlands. This soil is nutrient-rich and well suited for agriculture. Average annual rainfall is 820 mm/ year (van Eertwegh et al., 2006).

The farm studied in Flevoland has been in operation since 1971. The groundwater lies relatively close to the surface at 80cm deep. The soil here is clay-rich. The farm is managed with traditional pesticide use and the typical crop rotation described above. The farmers believe that there is a large amount of runoff and sedimentation in their canals. Annually, sediment must be removed.

2.1.1.B Limburg

The topsoil in Limburg is an anthrosol with a humus-enriched A horizon (20cm deep, according to farmers) overlaying very sandy, porous soil (Boesten & van der Pas, 2000). The managers mention that there is negligible sediment transport runoff from their fields, due to a high likelihood of infiltration of rainwater due to the sandiness of the soil. Annual average precipitation is 750mm/ year (Tiktak et al., 1998). This farm has been in operation since 1955. While most of the farm is managed similarly to the farm in Flevoland, some parcels have been managed organically for approximately 20 years. These organic sites are all adjacent to each other, but there is no protection between the organic fields and nearby conventionally managed plots.

2.1.1.C. Gelderland

At this farm, the soil ranges from sand to peat. The farm has also been managed since the mid 20th century, but records of pesticide application rates only date back until 1995. Annual average precipitation is 735mm/ year (Jacobs et al., 2010). Some fields on the site have been managed organically for 20 years, but are not always far or protected from nearby conventional fields.

In Gelderland canals surround the fields, collecting sediment. This sediment is removed from the canals annually and placed on a compost pile together with organic waste from the farm. This mixture is then applied to one particular field, also managed conventionally, with pesticides being applied in similar doses to other fields at this farm. One should not assume that all residues present here come exclusively from the sediment. Nevertheless, the farmers believe that this field is where residues are most likely to accumulate.

Table 3: Soil properties of the study sites in the Netherlands. N= 3 for %OM and pH, N=1 for texture analysis.

	Flevoland	Limburg	Gelderland
Clay %	15	<1	7
Silt %	33	7	12
Sand %	44	87	77
Mean OM %	3.2	4.2	3.5
Mean pH	7.89	6.65	7.06

2.1.2 Spain

While the average intensity of pesticide use from 1992- 2003 is lower in Spain than in the Netherlands at 1.7 kg of active substance per ha of arable land, Spain accounts for 14% of total use of pesticides in the EU, accounting for 26% of the insecticide use (Eurostat, 2007; FAOSTAT, 2015).

Citrus is also the third-most intensive crop with regard to use of plant protection products in Europe (after grapes and other fruit trees), with an average of 5.83 kg active substance/ha (Eurostat, 2007). Therefore, analysis of citrus plantations in Spain is of interest.

The area selected for this study is the municipality of Carcaixent in east-central Spain. The municipality lies 40 km south of the city of Valencia, in prime citrus producing territory in a valley along the River Júcar. The first commercial orange grove in the world was planted in 1781 in Carcaixent itself, giving Carcaixent the nickname "The Birthplace of the Orange" (Mora, 1991). This has remained vital to the municipality's heritage in the following centuries. Recently, in the face of competition from cheaper sources of fruit, farmers in Carcaixent are increasingly moving toward organic farm-to-table production. Many organic farmers in the municipality now sell their fruit as a premium product direct to European consumers.

The climate in Carcaixent is typical for the Mediterranean region. The average annual temperature is 17^{o}C, with a winter average of 11^{o}C and a summer average of 25^{o}C. Rains are infrequent, and vary in amount from year to year but when they occur they can be torrential, especially in the autumn (Ferrer Pérez, 1985; Ajuntament de Carcaixent, 2011).

There are essentially two zones to the municipality: a flood prone, clay rich region to the west, and a sand rich zone to the east near some mountains. The river floods at very irregular times, sometimes going years without overflowing from the banks. But when the river does overflow, it brings with it much fine sediment that is deposited around the area (Ferrer Pérez, 1985). However, the frequency is such that many farmers in the flood zone use the water as a major source for irrigation. Cemented drainage ditches surround fields in the clay-rich region (Fig. 5). These *acequias* serve as sources for irrigation water, but are primarily used to guide runoff from flooding away from the fields. This zone is further referred to as the clay-rich zone.

The clay and sandy zones are divided by a ravine that more or less corresponds to the modern railroad (Fig. 3). On the other side of the ravine is the zone from here on referred to as the sandy zone. The soil in the sandy zone has coarser sediment coming from the surrounding limestone mountains. In this zone today most farmers depend on drip irrigation.

Both the social and environmental background have lead to the emergence of four principal soil-management groups for orange production in the municipality: Organically managed farms in the sandy region (Os), Organically managed farms in the clay-rich region (Oc), Conventionally managed farms in the sandy region (Cs) and Conventionally managed farms in the clay-rich region (Cc). Table 4 illustrates the physical differences between the four categories.

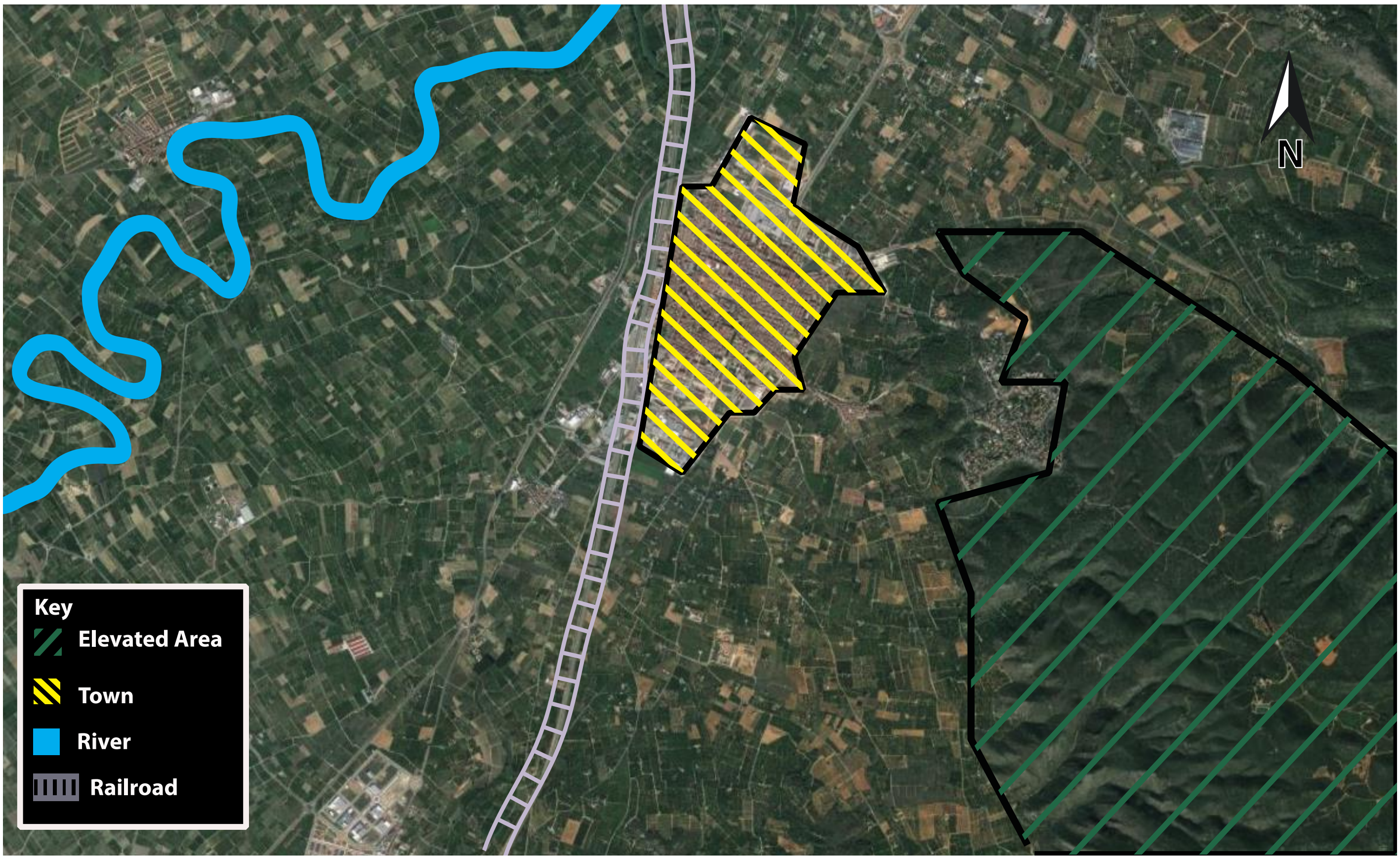


Figure 3: Map of Carcaixent. The clay-rich zone is between the train tracks and the river, the sandy zone between the train tracks and the elevated area. Original image source: GoogleMaps

Table 4: Soil properties of the study sites in Spain N= 3 for %OM and pH, N=1 for texture analysis

	Organic Sand (Os)	Organic Clay (Oc)	Conventional Sand (Cs)	Conventional Clay (Cc)	Sediment
Clay %	11	17	11	18	23
Silt %	5	30	34	13	38
Sand %	83	21	46	31	10
OM%	2.2	5.3	2.4	3.4	5.3
pH	8.01	8.09	8.03	8.14	7.95

2.2 Experimental Design- the Netherlands

In the Netherlands, data collection was intended as a screening, and to contrast to Spanish findings. Soil was collected at farms in three provinces in the Netherlands.

In Flevoland, three samples were taken from three different points on one field. In Limburg, six total plots were studied, three being managed organically for the past 15 or so years, and three conventionally managed plots. Finally, in

Gelderland, three conventionally managed and two organic fields were studied. Additionally, a sample was taken from a field where compost made from sediment dredged from canals and green waste from previous crops was added to the soil each year. This field is referred to from here forward as the field where compost was applied. From this farm samples were taken from the field with added sediment. All samples were taken in early December 2014. This paragraph is summarized in Table 5a.

At each site, soil samples were taken from the topsoil (0-20cm) using a small (~3cm diameter) soil auger. A few cores were taken within a small area on each field (approximately 5m diameter zone), and mixed together in a plastic bag indicating the location. These plastic bags were then kept in a cool room.

The physical characteristics of each of the sites were also analyzed, with organic matter (OM) being measured as a percentage of dry weight at 550°C, and pH using a standard instrument after shaking 10g of soil in 25mL demi water. Representative soil samples were also taken to a private agricultural services lab for texture analysis. See the findings in the site description in Table 3.

2.3 Experimental Design- Spain

Spanish samples were taken following a more organized sampling methodology in order to better understand the distribution of residues within and between fields. As mentioned in the site description, there are essentially four categories of farms: Oc, Os, Cc, Cs as previously mentioned. See Table 5b for a description of how many samples were taken for each category.

To analyze the heterogeneity of pesticide residue distribution on an orchard, samples were taken both between two trees and between two rows of trees. The samples taken between two trees are here forward referred to as "Row" samples, and those between two rows are called "Inter-row" samples. Figure 4 illustrates these locations in a field. This series of row/ inter-row samples was repeated three times per field. Therefore each field has six sampling points. At each point, samples from two depths were taken: one from the topsoil (10-20cm deep) and one sample from the second horizon, at approximately 30cm depth.

Table 5a: Sample distribution in the Netherlands.

	Flevoland	Limburg	Gelderland
Number of organic fields	0	3	2
Number of conventional fields	1	3	3
Number of samples per field	3	1	1
Number of compost samples	0	0	1
Total Samples	3	6	6

Table 5b: Sample distribution in Spain. In the case of the extra farm in the Cc category, the spatial distribution samples were taken at a different location than the general samples. That explains the extra samples for the conventional clay fields. The "number of unique farms in category" row tells us how many managers there are in that category. For example, the same individual manages two of the fields selected for the organic sand category.

	Soil-management group			
	Os	**Oc**	**Cs**	**Cc**
Number of fields	3	3	3	4
Number of unique farms in this category	2	2	3	3
Number of "Row" points per field	3	3	3	3
Number of "Inter-row" points per field	3	3	3	3
Number of sample depths per point (both row and inter-row)	2	2	2	2
Number of spatial distribution points	-	-	3	5
Number of sample depths per spatial distribution points	-	-	2	2
TOTAL per field	12	12	18	18
TOTAL per category	36	36	54	54
Number of sediment samples	-	-	-	5

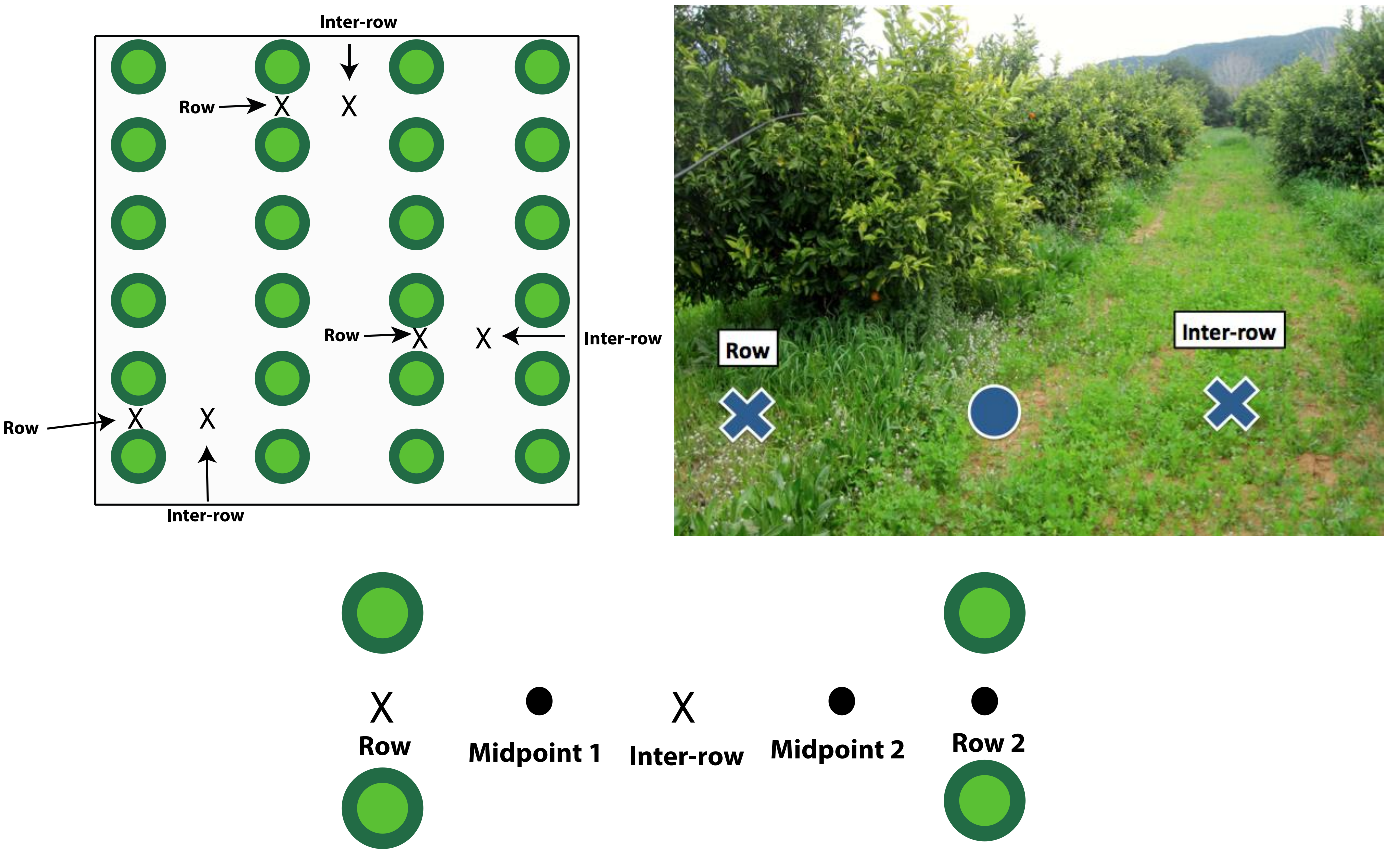


Figure 4: Sampling schematic. The image in the top left is a birds-eye view of how sampling was conducted in a field with "X"s representing sampling points. The image on the right represents how these idealized points are actually arranged onsite. Finally, the image on the bottom illustrates the sampling design for spatial variability. The row/ inter-row samples indicated in this figure correspond to the position of the "X"s in the bottom image.

Furthermore, at each conventionally managed field, the sampling was expanded around one of the row/inter-row pairs to better understand the distribution of residues in space. Samples were taken at two depths from the row on the other side of the inter-row sample (labeled as 'Row 2' in Fig. 4), what would be off the right hand side of the image in Fig 1, as well as samples from the two midpoints between the row and inter-row samples (labeled as 'Midpoint 1' and 'Midpoint 2' in Fig. 4).

Finally, samples were taken from *acequias* adjacent to the Cc fields; the bottom of these *acequias* contains sediment from the floodwaters coming off of the fields. Five total sediment samples were taken from two ditches.

All samples were collected in labeled plastic bags and were stored in a dark, dry place. Upon return to the Netherlands, they were frozen until needed for laboratory analysis. The samples were also taken for physical analysis in the same manner as in the Netherlands. The results are found in Table 4.

A total of 185 samples were taken from Spain. Five of these samples are of sediment in nearby *acequias* or drainage ditches, the remaining 180 come from agricultural sites. The samples come in equal quantities from sandy or clay rich soil. The sandy zone is located at a relatively higher altitude than the clay zone, which is a flood-prone region close to the river. Approximately two-thirds of the samples come from conventionally managed sites, using agrochemicals today, and one third come from organic farms.

In sum, the primary divisions of the samples are organic v. conventional management, topsoil v. subsoil, row v. inter-row and sand v. clay soil.

Figure 5: An *acequia* with collected sediment.

2.4 Interviews/ Historical Data

Interviews and historical data were collected in the Netherlands to understand: age of organic fields, pesticide application methods and quantities, and canal maintenance procedures. At the farm in Gelderland historical data going back until 1995 for all conventional fields was compiled (Appendix II). Similar data is available in paper logbooks going back until 1971 in Flevoland, and 1952 in Limburg. Given the similar crop rotation patterns and experience of the managers, the farmers' behavior is assumed to be similar between sites.

In Spain a questionnaire was developed to ask farmers the same questions as in the Netherlands (Appendix IV). The bulk of data regarding historical pesticide use in Carcaixent came from an interview with the owner of an agricultural services shop. The owner of the store is a local expert, having sold pesticides to farmers in the area since 1971. He provided estimates of pesticides used on orange trees from 1960 to the present (Appendix III). These opinions were confirmed with local farmers and managers at an experimental research farm.

2.5 Selection of Compounds for Analysis

For the Dutch samples all 250 compounds for which analysis is possible (full list in Appendix I) were studied. Most compounds on this list are in the amide, carbamate, organochlorine and organophosphorous groups. A pre-selection of compounds to analyze in Spain was made to economize on effort. This selection is based on the list of compounds recommended in interviews with local experts. This list was supplemented by compounds identified by Eurostat as likely to have been used in Spanish citrus production (Eurostat, 2007). Seventy compounds were finally analyzed in Spain (Appendix I).

Some metabolites were also analyzed. Metabolites of DDT including DDE p-p', DDE o-p', DDD p-p', DDD o-p' and DDMU were measured, because some metabolites, particularly DDE are known to be more toxic and persistent than the original compound (Pontolillo & Eagenhouse, 2011). Aminomethylphosphonic acid (AMPA) is the main metabolite of the widely used herbicide, glyphosate (Yang et al., 2015). It is relevant due to the widespread use of glyphosate. Tetrahydrophthalimide (THPI) and phthalimide (PTI) are metabolites of the fungicides captan and folpet respectively. Stock solutions were available for these compounds, thus they were included in analysis.

2.6 Extraction of Residues

Two methods of extraction are necessary to analyze the full range of compounds due to differences in pesticide properties. Acidified organic solvents like methanol, acetonitrile and acetone are best for extracting a broad spectrum of pesticide residues (Mol et al., 2008). However, glyphosate has a very low log KoW value (-3.3), meaning that it is insoluble in organic solvents. Therefore, it must be extracted from the soil using a strong base (Yang et al., 2015).

2.6.1 General Screening

All except two of the compounds studied can be extracted from the soil matrix using the same method. The extraction method is the QuEChERS method modified for the extraction from soil by the staff at the RIKILT Food Safety Lab at Wageningen University (Lehotay, 2011; Anastassiades et al., 2013). The process involves mixing 5 g of homogenized sample together with 5mL water and 10mL of the extraction solvent (CH_3CN + 1% HAc)in a 50ml test tube. This is then agitated in a head-over-head shaker for 30 min. To each tube 1g of NaAc and 4g $MgSO_4$ is added. The tubes are then centrifuged for 3500rpm for 5 minutes. The resulting supernatant is then prepared for either GC or LC analysis. 13-C Caffeine is used as an internal standard, and a stock solution was prepared for all pesticides studied as a reference (10µg/mL) as the reference standard. All stock solutions and standards are stored at 4^oC for both extraction procedures.

To prepare the vials for LC, 125µL of the supernatant is transferred into a 0.45µm filter vial, add 125µL of the extraction solvent and 250µL millipore water. The vials are ready for LC analysis.

Preparation of the extract for GC analysis involves adding 250 µL of the supernatant and 250µL of the extraction solvent to a vial prepared with 50mg PSA and 150mg $Mg2SO_4$. These vials are centrifuged for 5 minutes at 13000 rpm. 150µL of the supernatant from this cleanup process is then transferred into a brown glass vial for GC analysis.

2.6.2 Glyphosate/ AMPA

The extraction method for glyphosate follows that of Yang et al. (2015), but is summarized here. For this process, the compound is extracted from the soil using 10mL of a strong base, 0.6M KOH for 2g of each soil sample. This is then centrifuged at 3500rpm for 15 minutes. 1mL of this supernatant is transferred to a different tube to which 80µL HCL 6M is added in order to adjust the pH to about 9 for deritivization.

For the deritivization of the standard mix, 0.5mL Sodium Tetraborate Buffer 5% and 0.5 mL 6.5mM FMOC-Cl are added. Here, 40µL of a mixture of isotopically-labeled glyphosate and AMPA is added to each extract as an internal standard. After waiting for 30min at room temperature, 50µL of formic acid is added. 0.5 mL of this mixture is transferred to a filter vial for LC analysis.

2.7 GC-MS/MS, LC-MS/MS use

Analyte-specific settings regarding the expected transitions and retention time for the pesticides listed in Appendix I are described in the Appendices of Mol et. al, 2008.

2.7.1 GC-MS/MS

The pesticides that require analysis with GC-MS/MS are generally non-polar. Non-polar pesticides are more likely to be fat-soluble with high log KoW values and therefore be bio-accumulative. Therefore, in recent decades many of these compounds have been banned.

2.7.2 LC-MS/MS

Pesticides analyzed by LC-MS/MS are typically more recent and polar. If a compound is polar, it can be analyzed using either a positive or negative ion, according to the standard procedures at the RIKILT laboratory. The LC-MS machine cannot analyze both negative and positive ions at the same time, so in order to quantify the residues of compounds able to be analyzed on the LC, two separate trials are needed: one for compounds measured with positive ions, the second for negative ions.

2.8 Quantification of Residues

The resulting data obtained from the LC-MS/MS and GC-MS/MS is transferred to the software recommended by the machine manufacturers for the integration of peak area.

A calibration curve was prepared (for GC ranging from 0-100ng/mL and for LC ranging from 0 to 250ng/mL) to verify the linearity of detection by the system, but residues were quantified using point-calibration.

The acceptable range for recovery of the standards for all compounds is 70-120%. For the ion ratio of each sample, +/- 30% of the average ion ratio of the standards was accepted.

The LOQ was considered to be 0.01µg/g or 10 ppb for the compounds extracted with the QuEChERS method and 0.05µg/g or 50ppb for Glyphosate and AMPA.

2.9 Statistical Analysis

Statistical analysis was conducted on the Spanish samples. There were too few samples taken in the Netherlands to merit any statistical test. All statistical analysis was done using IPM SPSS Version 22.

For many of the pesticides analyzed, most samples tested negative with the data containing many zeros, so the data was not normally distributed. Therefore, non-parametric tests including Chi-Square, Mann-Whitney, and Kruskall-Wallis were conducted. Samples taken from midpoints of the spatial distribution sites were excluded from these tests because they did not fit in with the row vs. inter-row factor. Instead for these samples, a paired t-test was used to better understand significant spatial relationships.

A series of Chi-Square tests compared frequency of occurrence between the first order divisions in the aggregate (topsoil vs. subsoil, clay vs. sand, row vs. inter row, organic vs. conventional). All samples were coded with a 0 or 1 for each compound to represent if that compound is present or absent. For this analysis management and soil type were not paired together, but simply compared by one set of factors at a time. The tests were conducted separately for each compound.

Mann-Whitney U tests were conducted for the same categories as the Chi-Square tests, for all of the positive samples. However, rather than comparing presence and absence between the groups, the measured concentration of each positive data point was used.

The Kruskall-Wallis test was conducted combining factors to determine if groups correlated with each other. Here again, only samples that tested positive were used. The four principle soil and management categories (Os, Oc, Cs, Cc) were paired together with the remaining first-level factors (topsoil vs. subsoil, row vs. inter-row). Finally, a Dunn post-hoc test was conducted on the groups that showed significant differences between groups. The tests were conducted separately for each compound.

Spearman's rho correlations were conducted between physical factors (pH, organic matter and clay content) for the most abundant compounds in both the Netherlands and Spain.

3. Results

3.1 Compounds Applied in the Netherlands and Spain

The results of the interviews with experts in the Netherlands and Spain on historical use of pesticides are recorded as timelines in Appendices II and III. The Dutch record (Appendix II) has a high level of precision, in diagnosing exact dosage of individual compounds on individual fields, but only goes back to 1995. In contrast the Spanish record (Appendix III) gives us a general understanding of pesticide use municipality-wide for the past 50 years.

3.2 Netherlands

3.2.1 Compounds Present in the Soil

A wide range of compounds is present (<LOQ) across the three Dutch sites. Of the 250 compounds analyzed, 18 compounds were present in at least one sample. Those present are outlined in Table 6. Ten of the pesticides found are fungicides. The majority of the compounds present in the soil have a log KoW coefficient of 3 or higher. A notable exception is glyphosate/ AMPA. While this particular coefficient has a low value, its half-life (DT_{50}) in the field is approximately 130 days.

Table 6: Compounds present in Dutch soil and their abundance and frequencies. Log Kow and DT_{50} values are not listed for AMPA, due to the unpredictability of metabolites (see chapter 1.2). N=10 according to the sampling described in Table 5a. The field where compost is added to the soil is included in this value.

Compound	Function	Log KoW	DT_{50} (days)	% Samples where Present- Conventional Fields (N=10)	Min-Max Concentrations (ppb)	Category
AMPA	Herbicide			50%	50-540	Organophosphorus
Azoxystrobin	Fungicide	2.5	70	10%	20	Antibiotic
Bixafen	Fungicide	3.3	360	10%	10	Amide
Boscalid	Fungicide	3.0	200	60%	20-40	Pyridine
Cyproconazole	Fungicide	3.1	40	10%	20	Conazole
DDT (Σ metabolites)	Insecticide	6.8	30 (years)	10%	55	Organochlorine
Difenoconazole	Fungicide	4.4	318	10%	30	Conazole
Diflufenican	Herbicide	4.2	280	30%	30-40	Amide
Epoxiconazole	Fungicide	3.3	90	40%	10-20	Conazole
Fluopicolide	Fungicide	3.3	415	70%	10-110	Pyridine
Fluoxastrobin	Fungicide	2.9	184	10%	80	Antibiotic
Glyphosate	Herbicide	-3.2	130	30%	50-202	Organophosphorus
Linuron	Herbicide	3.0	60	20%	10	Urea
Mandipropamid	Fungicide	3.2	24	30%	20-60	Amide
Metolachlor	Herbicide	2.1	90	20%	40-100	Amide
Pencycuron	Fungicide	4.7	64	10%	20	Urea
Prosulfocarb	Herbicide	4.7	49	10%	30	Carbamate
Terbuthylazine	Herbicide	3.4	149	10%	20	Triazine

The sample with the highest total concentration of pesticide residues was one of the three samples from Flevoland (601 ppb). This particular sample contained three compounds: AMPA, Fluopicolide and Glyphosate. The sample with the greatest variety of compounds is one of the three taken from Limburg, with eight compounds present and a total residue concentration of 195 ppb. Thus, an increase in the number of compounds present does not necessarily indicate high levels of total concentration.

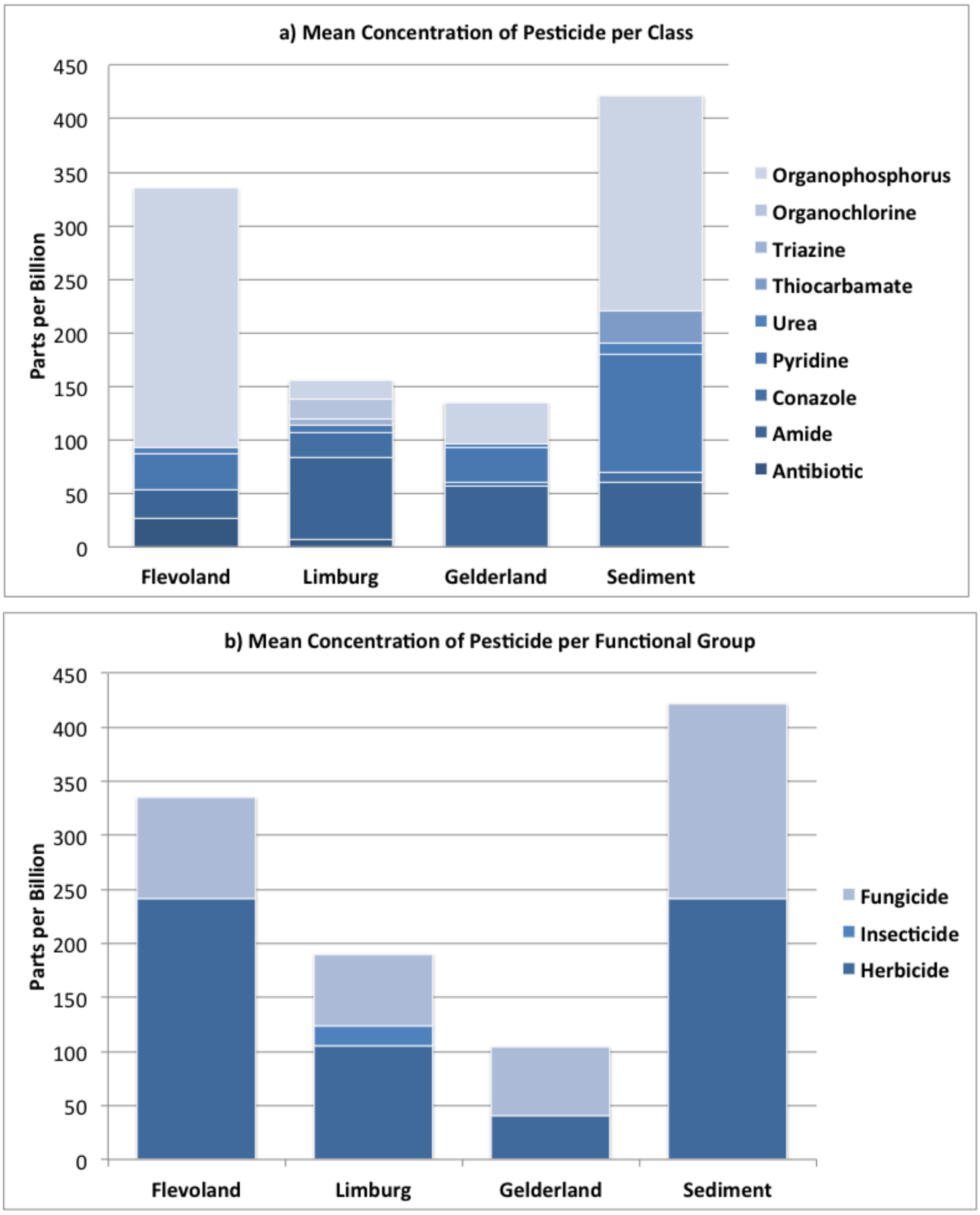


Figure 6 a+b: Mean concentration of pesticides in conventionally managed soil in the Netherlands separated by location. Figure 7 a divides the pesticides by chemical class. Figure 7b divides the concentration by function. N= 3 for each of the locations (Flevoland, Limburg, and Gelderland) and N=1 for the compost. When calculating the mean, negative results are incorporated.

Considering the group of samples as a whole, 80% of the conventional samples taken contain a total concentration of <100ppb, 30% of 100-300ppb and 10% with 300-600ppb. The highest concentrations were found in AMPA in Flevoland (max. 540 ppb) and glyphosate in Gelderland (max. 220 ppb). The samples collected in Flevoland have the highest mean concentration of pesticides of any of the traditional fields, especially AMPA. The overall concentration of pesticides in the compost is about 100ppb higher than the mean for the fields in Flevoland.

If AMPA is excluded from the Figure 7a below, the sum total of mean pesticide residues detected is between 90-140 ppb for the soil samples. The compost site (N=1), though has a concentration of 220 ppb (again excluding AMPA). The bulk of this difference comes from the increased concentration of the pyridine fluopicolide, which has a mean value here three times larger than that of any of the other three sites.

Despite the fact that 10 of the 18 substances detected are fungicides, Figure 6b above shows that, in general herbicides, despite their lower frequency, are found in concentrations similar to those of fungicides. Again AMPA and glyphosate contribute the bulk of the herbicide concentration in the soil.

The organic samples were excluded from Figure 1 above. The only compound detected in organic sites were DDT metabolites (DDT-p’p’ and DDE-p’p’) in one of the three organic fields examined in Limburg. The organic sample contained a sum total of 72 ppb, which is slightly higher than the concentration found in the conventional soil (55ppb). Like in the organic samples, DDT metabolites were only found in one of three conventional samples taken from the farm in Limburg. The organic samples taken from Gelderland were free of pesticides. No organic samples were taken in Flevoland.

3.2.2 Distribution of residues between sites

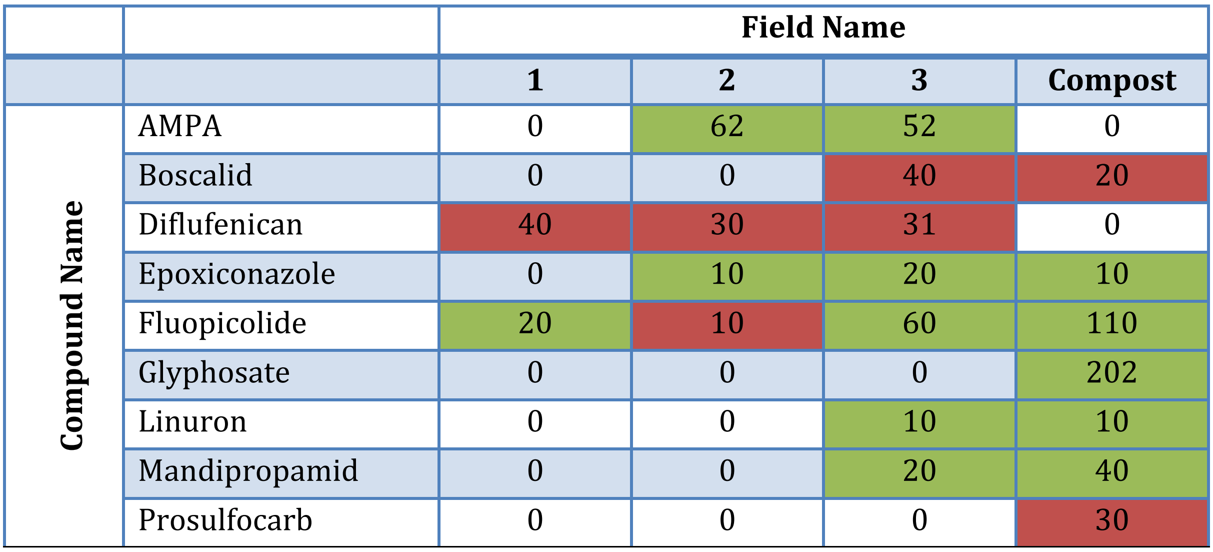
The distribution and abundance of compounds between the three sites are fully described in Table 7. Limburg has the greatest diversity of compounds present while if a compound is present in Gelderland, it is likely to be present in two or three fields.

Focusing on one site, in Gelderland, a comprehensive historical record is available from 1995-present for the four fields studied. They are listed individually in Table 8. Even older records are available in Limburg and Flevoland, but were not compiled for the present study. The historical data is listed in full in Appendix II. In general, the concentration of all pesticides on the field with compost applied is higher than the other fields. Dosage rates are similar for this field as they are for the other three fields, but the presence of pesticide residues is significantly higher on this field. This is due to the application of the mixed compost, where residues are transferred with no record.

Table 7: Presence and abundance of different compounds distributed between sites. The compost sample is excluded from the calculation of the mean values. All organic samples were included, and the compost sample was excluded. See Table 5a for a thorough sampling methodology. Mean value (in ppb) taken from positive results only.

	Flevoland		**Limburg**		**Gelderland**	
Compound	N	x̄± SD	N	x̄± SD	N	x̄± SD
AMPA	2	295 ± 346	1	51	2	57±7
Azoxystrobin	n.d.	n.d.	1	20	n.d.	n.d.
Bixafen	n.d.	n.d.	n.d.	n.d.	1	10
Boscalid	1	20	3	30 ±10	1	40
Cyproconazole	n.d.	n.d.	1	20	n.d.	n.d.
DDT (Σ metabolites)	n.d.	n.d.	2	68.5 ±19	n.d.	n.d.
Difenoconazole	n.d.	n.d.	1	30	n.d.	n.d.
Diflufenican	n.d.	n.d.	n.d.	n.d.	3	33±6
Epoxiconazole	n.d.	n.d.	1	20	2	15±7
Fluopicolide	2	50±57	1	20	3	30± 26
Fluoxastrobin	1	80	n.d.	n.d.	n.d.	n.d.
Glyphosate	2	68± 24	n.d.	n.d.	n.d.	n.d.
Linuron	n.d.	n.d.	n.d.	n.d.	1	10
Mandipropamid	1	60	n.d.	n.d.	1	20
Metolachlor	n.d.	n.d.	2	70	n.d.	n.d.
Pencycuron	1	20	n.d.	n.d.	n.d.	n.d.
Prosulfocarb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Terbuthylazine	n.d.	n.d.	1	20	n.d.	n.d.

Table 8: Concentration of pesticides (ppb) found in four fields in Gelderland. See Appendix II for the record of historical application rates for these fields. Cells highlighted in green can be easily explained in the record. Those in red require are not easily explained, and will be discussed in a future chapter.



		Field Name			
		1	**2**	**3**	**Compost**
Compound Name	AMPA	0	62	52	0
	Boscalid	0	0	40	20
	Diflufenican	40	30	31	0
	Epoxiconazole	0	10	20	10
	Fluopicolide	20	10	60	110
	Glyphosate	0	0	0	202
	Linuron	0	0	10	10
	Mandipropamid	0	0	20	40
	Prosulfocarb	0	0	0	30

Prosulfocarb is not found on any of the other fields, but is present on the field where compost has been applied. However, on this field no prosulfocarb is found in the historical record. Although diflufenican is present on three of the four fields, it is absent from the historical record. Boscalid is found on 2 of 4 sites, but is absent from the historical record. Fluopicolide was not applied on field 2, but was applied on the adjacent site, field 1.

Epoxiconazole was last applied on field 2 in 2008, but was still detected in the soil 7 years later. The same compound was last applied on field 1 in 2000, but is now absent. Somewhere in between 7 and 15 years following application, epoxiconazole is no longer detectable. Similarly, mandipropamid was applied to both field 3 and the field with compost applied in 2013, and was detected. It was applied on field 1 in 2011, but was not detected today. While two years after application, mandipropamid is still detected, four years later it is absent.

3.3 Spain

3.3.1 Compounds present in the soil

Table 9: Compounds present in Spanish soil and their frequencies between management categories. Log Kow and DT_{50} values are not listed for AMPA, due to the unpredictability of metabolites (see chapter 1.2). For Glyphosate and AMPA N=57 Organic, N= 108 Conventional and N= 5 Sediment. For Oxyfluorfen N= 70 Organic, N=108 Conventional and N=5 Sediment. For DDT, Chlorpyrifos, Ethion and THPI N= 12 Organic, N=12 Conventional and N= 2 Sediment. The differences in N is due to the differences in the machines used for each compound.

Compound	Function	Log KoW	DT_{50} (days)	% Samples where Present (All Fields)	% Samples where Present (Organic)	% Samples where Present (Conventional)	% Samples where Present (Sediment)	Category
AMPA	Herbicide			51%	9%	72%	100%	Organophosphorus
Chlorpyrifos	Insecticide	4.7	30	2%	0%	4%	100%	Organophosphorus
DDT (Σ metabolites)	Insecticide	~6.5	30 (years)	46%	58%	33%	0%	Organochlorine
Ethion	Insecticide	4.3	150	2%	0%	4%	0%	Organophosphorus
Glyphosate	Herbicide	-3.3	130	10%	4%	13%	100%	Organophosphorus
Oxyfluorfen	Herbicide	4.5	35	16%	0%	22%	80%	Diphenyl Ether
THPI (Captan Metabolite)	Fungicide			2%	0%	4%	0%	Dicarboxamide

Overall seven compounds were detected in Spanish soil, fewer than the 18 compounds detected in the Dutch samples. Table 9 is a summary of all of the samples detected and their frequency. Fewer compounds were tested for Spain than for the Netherlands (74 vs. 250). Similar to the Dutch sites, AMPA was found to be the most common compound, with over 50% of samples testing positive. Three compounds (Chlorpyrifos, Ethion and THPI) were found in only one soil sample each. Therefore, the only compounds for which statistical analysis is possible are AMPA, DDT, glyphosate and oxyfluorfen.

Of these four compounds, three are herbicides currently in use in the municipality today. DDT is found in almost 50% of the samples, including organic samples, but is a banned insecticide, that has not been sold since the mid-late 1970s.

3.3.2 Patterning of the presence vs. absence of compounds

In order to better understand the frequency of occurrence of the pesticides, a Chi-Square test was performed on the presence or absence of each of the compounds between the four first-level factors. The results are shown in Table 10. In this test only the pattern across the paired 'first-level' factors is considered. All Spanish samples were aggregated together for this analysis.

Table 10: Frequency of occurrence divided by first level factors. Values represent the percentage of samples in that category that are positive for the given sample. ***= $p<0.001$, **= $0.001<p<0.01$, *= $0.01<p<0.05$ following a Chi-Square test. For Glyphosate and AMPA N=126. For Oxyfluorfen N= 140. For DDT, Chlorpyrifos, Ethion and THPI N= 48. The differences in N are due to the differences in the machines used for each compound. Spatial distribution and sediment samples are excluded from this test. += given compound occurred only once in all samples.

	AMPA	Chlorpyrifos +	Σ DDT	Ethion +	Glyphosate	Oxyfluorfen	THPI +
Organic/ Conventional	**8%/ 72% ***	0%/4%	59%/33%	0%/4%	**4%/13%**	**0%/23%***	4%/0%
Topsoil/ Subsoil	**55%/ 33% ***	0%/4%	54%/38%	0%/4%	**15%/2%***	16%/7%	4%/0%
Sand/ Clay	50%/37%	0%/4%	46%/46%	4%/0%	6%/12%	**18%/6%***	4%/0%
Row/ Inter-row	42%/45%	0%/4%	46%/46%	4%/0%	10%/8%	9%/14%	4%/0%

A few significant relationships are evident between the factors. First, AMPA and Glyphosate are found more often in conventional and topsoil samples. Likewise, oxyfluorfen is found in the conventionally managed samples, but in the sand more often than in the clay. There was no significant difference in the occurrence between the top and subsoil. DDT exhibits no significant trend between any groups, with equal likelihood of occurrence across all categories. Chlorpyrifos, ethion and THPI are only found in one soil sample each, so no conclusions can be drawn for these compounds.

The three compounds that show up only once are found as follows: ethion was found in a conventionally managed subsoil sample in the sandy zone in a row (86ppb). Chlorpyrifos was found in a conventionally managed subsoil inter-row sample in the clay zone (12 ppb). THPI was found in the topsoil of a sample in a row on an organic farm in the sandy region, but its concentration cannot be confidently quantified due to its instability during laboratory analysis.

3.3.3 Patterning of residues across the four principal soil groups

Recall from the methodology the four major soil groups identified for this study in Carcaixent: Organically managed farms in the sandy region (Os), Organically managed farms in the clay-rich region (Oc), Conventionally managed farms in the sandy region (Cs) and Conventionally managed farms in the clay-rich region (Cc). From this point forward, the Spanish samples are considered not in the aggregate, but divided into one of these four categories.

When considering the data represented in Table 10, it is important to couple the findings here with those of Fig. 7 and Table 11 below. The medians represented in Figure 7 are only representative of the positive results. Table 11 shows that often the frequency of positive results is quite low.

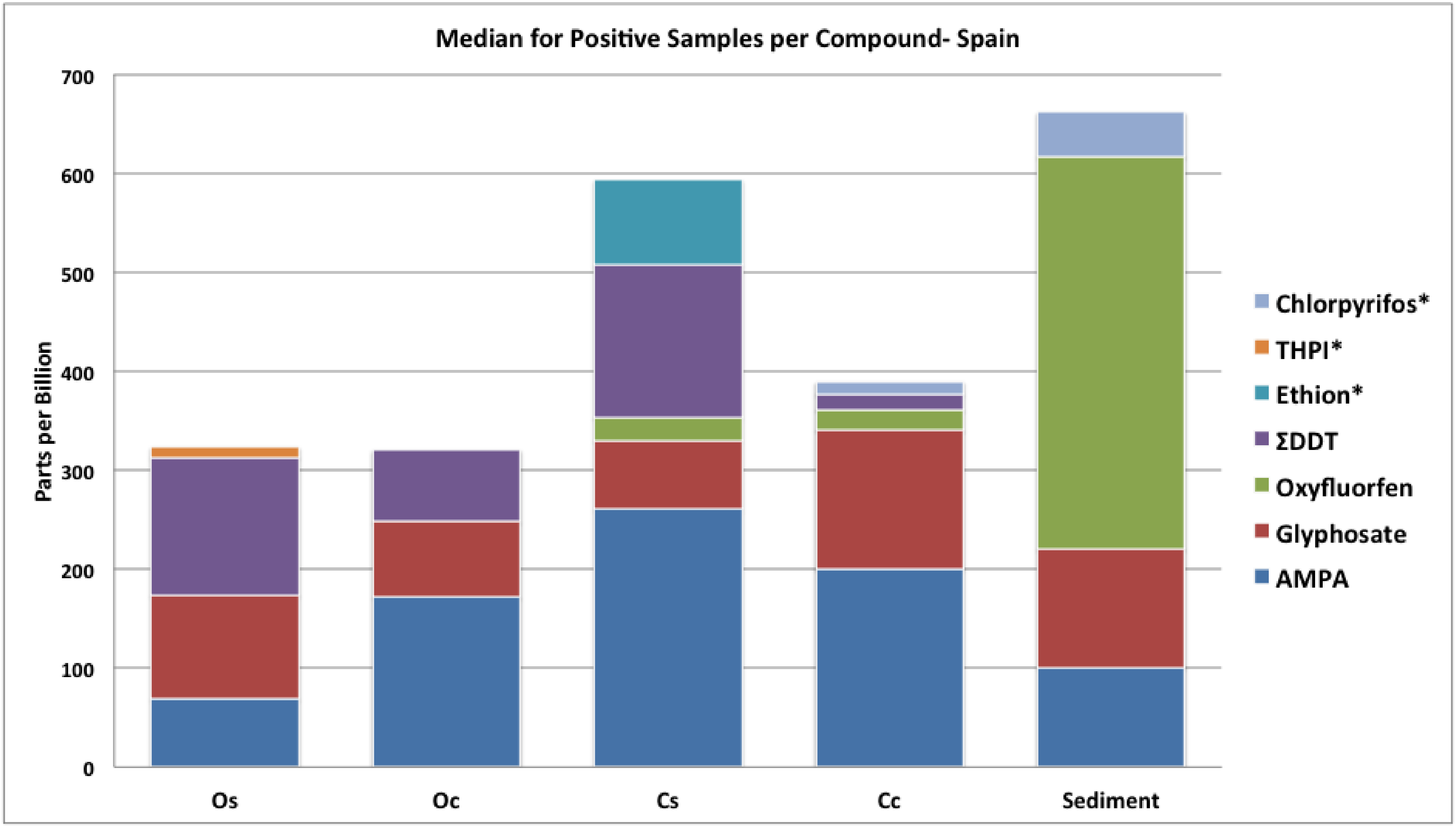


Figure 7: Median concentration of pesticide residues divided by soil-management category. The median values presented here is the median of the positive samples only. The compounds with the star next to the name indicate compounds that were only present once in a soil sample.

Table 11: Pesticide concentrations of positive samples and frequencies of each pesticide divided by soil-management category. N.d. indicates that no conclusions can be made for this group.

		Os	Oc	Os	Cc	Sediment
AMPA	**N**	32	25	52	56	5
	N positive	3	2	46	33	5
	$\bar{x}$ positive samples	69	322	260.5	201	101
	Min- Max Concent. (ppb)	69-118	51-593	53-1626	50-1090	83-2441
Chlorpyrifos	**N**	12	12	12	12	2
	N positive	n.d.	n.d.	n.d.	1	2
	$\bar{x}$ positive samples	n.d.	n.d.	n.d.	12	44.5
	Min- Max Concent. (ppb)	n.d.	n.d.	n.d.	n.d.	17-72
Σ DDT	**N**	12	12	12	12	2
	N positive	10	4	1	7	n.d.
	$\bar{x}$ positive samples	139.5	72.5	154	16	n.d.
	Min- Max Concent. (ppb)	52-713	55-88	n.d.	11- 94	n.d.
Ethion	**N**	12	12	12	12	2
	N positive	n.d.	n.d.	1	n.d.	n.d.
	$\bar{x}$ positive samples	n.d.	n.d.	86	n.d.	n.d.
	Min- Max Concent. (ppb)	n.d.	n.d.	n.d.	n.d.	n.d.
Glyphosate	**N**	32	25	52	56	5
	N positive	1	1	6	9	5
	$\bar{x}$ positive samples	105	76	70	140	120
	Min- Max Concent. (ppb)	n.d.	n.d.	60-99	60-180	90-7791
Oxyfluorfen	**N total**	34	36	52	56	5
	N positive	0	0	12	4	4
	$\bar{x}$ positive samples ppb	n.d.	n.d.	23	20.5	396.5
	Min- Max Concent. (ppb)	n.d.	n.d.	11-172	10-85	148-1550
THPI	**N**	12	12	12	12	2
	N positive	1	n.d.	n.d.	n.d.	n.d.
	$\bar{x}$ positive samples	~10	n.d.	n.d.	n.d.	n.d.
	Min- Max Concent. (ppb)	n.d.	n.d.	n.d.	n.d.	n.d.

3.3.4 Patterning of residues within and between groups

After understanding the differences between groups for the frequency of occurrence, it is important to see if the magnitude of the positives varies between groups. In order to measure this, the data is divided into a series of groups illustrating possible relationships between factors. The difference between groups is measured through a series of Kruskal-Wallis tests.

Table 8 shows the results of these tests. What is reported is the median value for each pesticide per each category listed in the left column. None of the relationships are significant, except for DDT between the groups of the "first level division" of our four original soil types. There is a difference between the four groups (p=0.005), and have described the relationships in the top-right cell of this chart. The conventional clay group is statistically different from both organic groups, but the same as the conventional sand group. The organic groups and the conventional sand group are statistically identical.

Mann Whitney tests were also conducted for each compound for each compound in the aggregate. So rather than looking at the differences between top and subsoil only for organic samples, only the difference between two factors was analyzed. For each compound the groups were sand vs. clay, topsoil vs. subsoil and row vs. inter-row. Out of the 12 potential relationships, only two possible relationships were found to be significant. First, the difference between top and subsoil for AMPA was significant (p= 0.034), with higher concentrations being found in the topsoil than in the subsoil. Second, the difference between sand and clay was also significant for DDT (p=0.000), with higher concentrations found in the sand rather than clay.

3.3.5 Patterning within a field- spatial distribution of compounds

Although the aim was to compare the spatial distribution for all compounds, there were simply not enough positive samples for compounds other than AMPA. The data was too sparse to draw any trends.

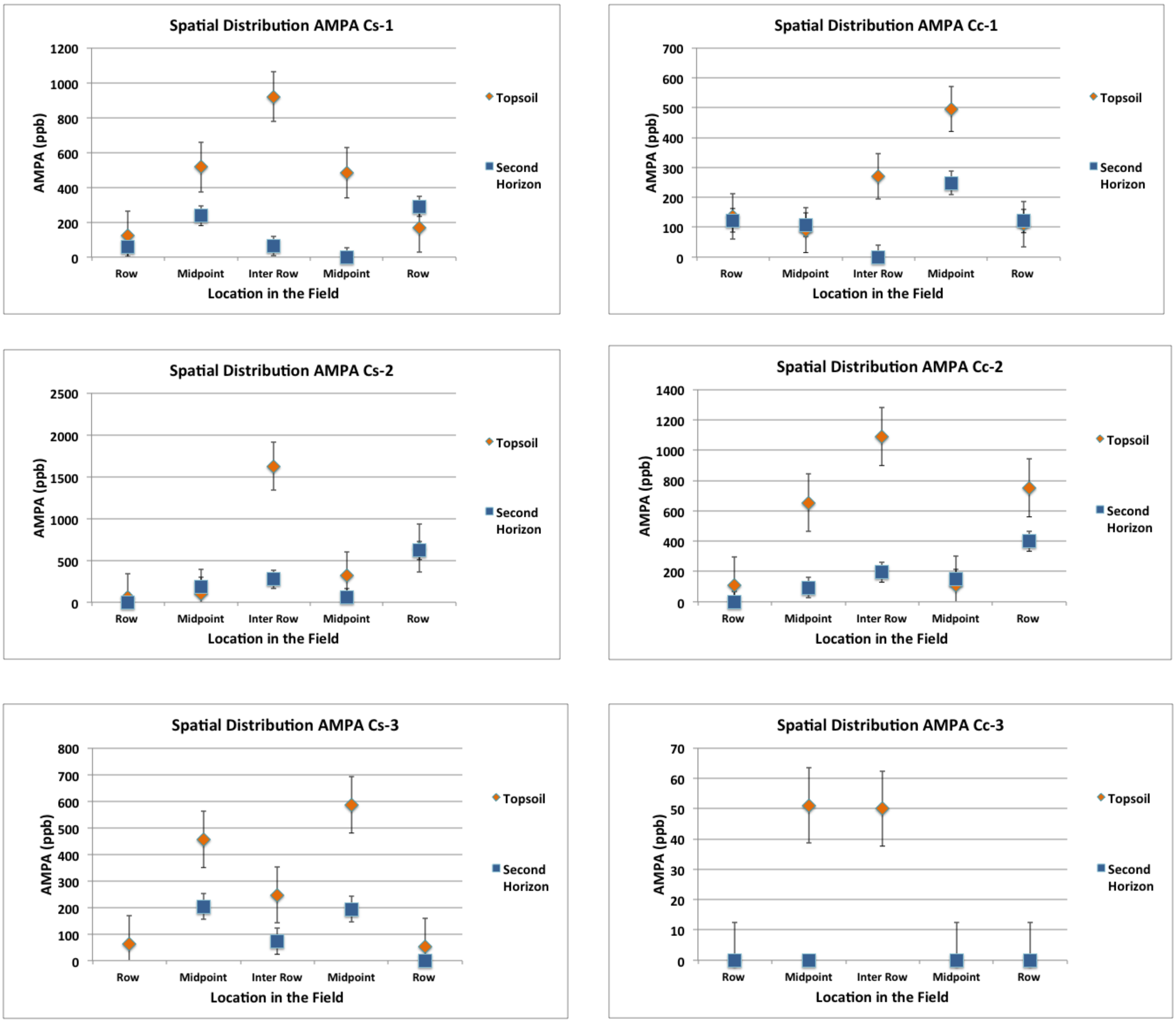
Considering the spatial distribution of AMPA across the conventionally managed fields, little patterning is visible on first glance of Fig. 8. However, analyses using a paired-samples t-test reveal that indeed topsoil samples are significantly higher than the corresponding subsoil sample (p=0.001). So although there are some subsoil samples that have a concentration of AMPA higher than others in the topsoil, by linking the top and subsoil samples from the same point, a trend is evident.

Furthermore, there is a similar significant relationship (p=0.03) between the topsoil samples in the row and the corresponding inter-row sample. Again, while in the aggregate trends are not recognizable, pairing related points reveals some trends. There was no significant relationship between topsoil samples in the row and corresponding midpoint samples or between the midpoint and inter-row samples. The midpoints show no significant difference from the extremes.

Table 12: Median values (ppb) for positive samples of each compound divided by the sub-groupings in the left-most column. Os= Organically Managed in sandy soil, Oc= Organically managed in clay soil, Cs= Conventionally managed in sandy soil, Cc= Conventionally managed in clay soil. The number of samples in each category is represented in parentheses. A hash mark indicates that no samples within that group were positive for that compound.

	Oxyfluorfen	AMPA	Glyphosate	Σ DDT
Division 1: First Level Division				
Os	-	69 (N=3)	105 (N=1)	**139.5 (N=10) (a)**
Oc	-	322 (N=2)	76 (N=1)	**72.5 (N=4) (ac)**
Cs	24 (N=18)	260.5 (N=46)	70 (N=6)	**154 (N= 1) (a)**
Cc	18 (N=10)	265.5 (N=38)	140 (N=14)	**16 (N=7) (bd)**
Division 2: Topsoil vs. Subsoil in Organic Samples				
Os Top	-	69 (N=3)	69 (N=1)	139.5 (N=6)
Os Bottom	-	-	-	270.5 (N=4)
Oc Top	-	593 (N=1)	76 (N=1)	72.5 (N=2)
Oc Bottom	-	51 (N=1)	-	71.5 (N=2)
Division 3: Topsoil vs. Subsoil in Conventional Samples				
Cs Top	24 (N=11)	488.5 (N=26)	70 (N=5)	154 (N=1)
Cs Bottom	22 (N=7)	220.5 (N=20)	60 (N=1)	-
Cc Top	17 (N=6)	265.5 (N=20)	140 (N=7)	15 (N=4)
Cc Bottom	24 (N=4)	150 (N=13)	120 (N=2)	19 (N=3)
Division 4: Row vs. Inter-row in Organic Samples				
Os Row	-	69 (N=1)	-	116 (N=5)
Os Inter-row	-	93.5 (N=2)	105 (N=1)	150 (N=5)
Oc Row	-	322 (N=2)	76 (N=1)	88 (N= 2)
Oc Inter-row	-	-	-	56 (N=2)
Division 5: Row vs. Inter-row in Conventional Samples				
Cs Row	33.5 (N=4)	174.5 (N=12)	-	-
Cs Inter-row	28 (N=8)	399 (N=18)	84.5 (N=2)	154 (N=1)
Cc Row	32 (N=2)	261 (N=11)	140 (N=4)	15 (N=4)
Cc Inter-row	26 (N=2)	270 (N=9)	140 (N=2)	16 (N=3)
Division 6: Row vs. Inter-row in Top and Subsoil				
Topsoil Row	11.5 (N=6)	309.5 (N=16)	80 (N=5)	93.5 (N=6)
Topsoil Inter-row	27.5 (N=6)	382 (N=17)	105 (N=5)	129 (N=7)
Subsoil Row	-	136 (N=10)	140 (N=1)	52 (N=5)
Subsoil Inter-row	19 (N=4)	225 (N=12)	-	74.5 (N=4)

Figure 8: Spatial distribution of AMPA concentration (ppb) on a site level. Sites Cs 1-3 represent the three individual Cs sites and Cc 1-3 represent the three individual Cc sites. The error bars represent the Standard Error.



3.3.6 Relationship between concentrations and pH and organic matter

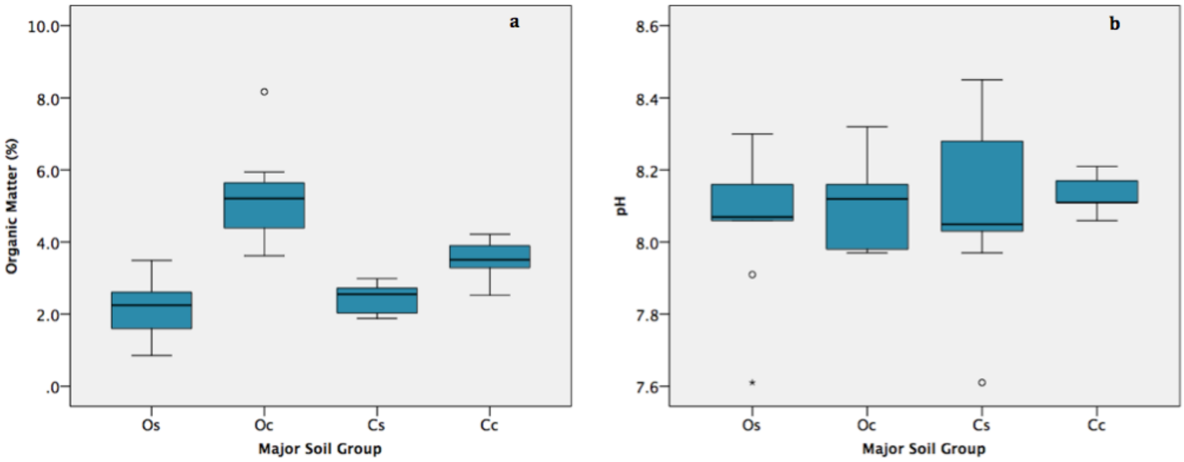


Figure 9: Boxplots of physical traits between major soil-management groups.

A Kruskal-Wallis test shows that indeed the four groups have different concentrations of organic matter (p<0.001) with the Os group being statistically identical to the Cs and Cc groups as illustrated in Figure 9. pH does not vary significantly between groups (p=0.78). Therefore, it is not relevant to continue examining the relationship between pH and the pesticide concentrations. Soil organic matter does physically differ between the categories selected with samples categorized as “clay-rich” also having a higher organic matter percentage.

With a limited number of samples taken for physical analysis, and the few samples that tested positively for DDT and oxyfluorfen residues, it is difficult to run a correlation between the pesticides detected and organic matter. But indeed Fig. 10 shows a negative correlation between organic matter concentration and concentration of residues. Meanwhile, in previous statistical tests, glyphosate and AMPA exhibited no significant relationship with soil type. However here there is a slightly positive trend between organic matter content and concentration of residues

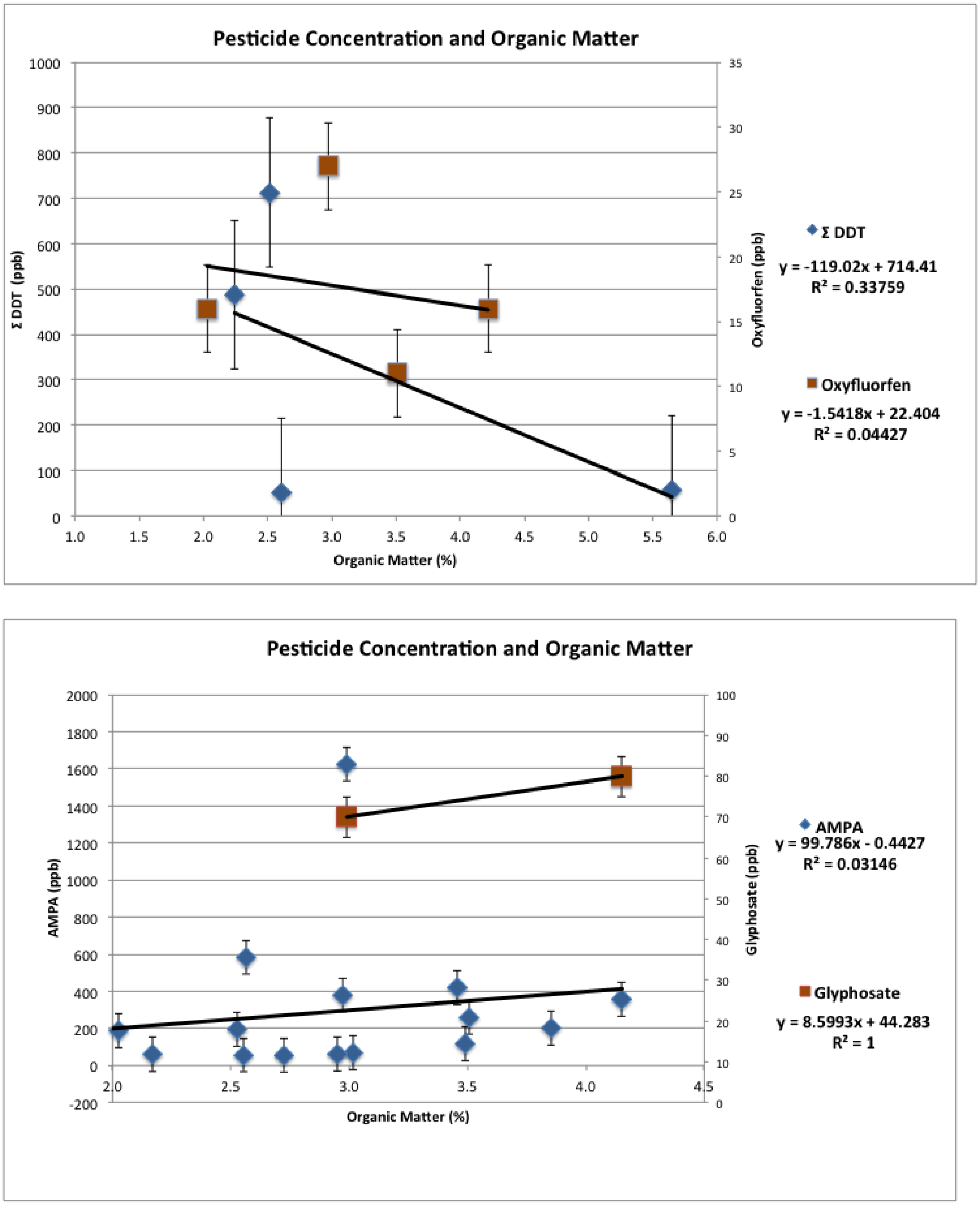


Figure 10: Correlations between pesticides and organic matter. Standard error is indicated. Glyphosate/ AMPA and DDT and Oxyfluorfen are listed separately due to the differences in their chemical nature.

3.3.6 Relationship between concentrations and clay content

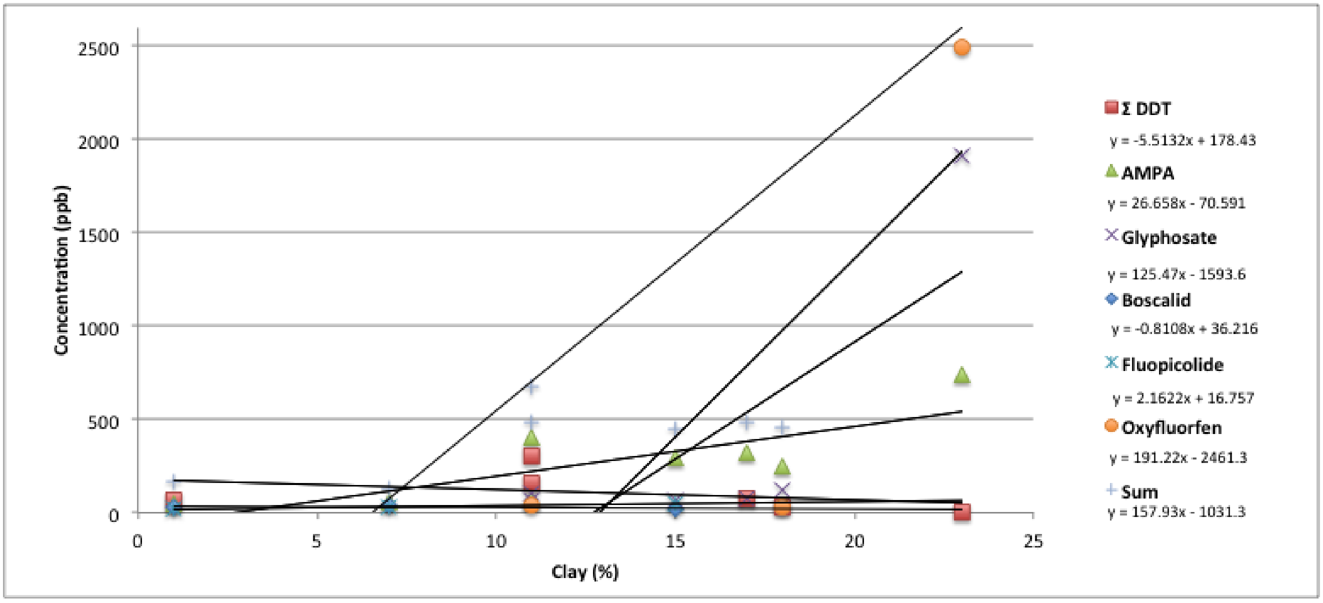


Figure 11: Linear relationships between clay content and pesticide concentration. The average was calculated for each group from which a physical sample was taken. Only positive samples from both Dutch and Spanish samples are included. The compounds selected are found in at least 50% of the Dutch or Spanish samples. The "Sum" value is the sum of all of the averages for each point.

Figure 11 shows how pesticide residues increase with clay content. As only eight samples were taken for physical analysis, the average for all samples within that category was taken. Both Dutch and Spanish samples are included. All trends are positive, except DDT and Boscalid. However, as evident in Table 13, the sample size is too small to make any significant conclusions except for AMPA.

Table 13: Spearman's rho correlations between clay content and average pesticide concentrations as described in Fig. 11.

	N	Spearman's ρ	p
AMPA	8	**.743**	**0.035**
Boscalid	3	.667	1.00
Σ DDT	6	-.638	.173
Fluopicolide	3	.667	1.00
Glyphosate	6	.667	.148
Oxyfluorfen	3	.500	.667
SUM	8	.083	.647

3.3.7 Sediment

Comparing residue concentration in soil and sediment, DDT is absent from all sediment samples, while it was found frequently in soil samples. On the other hand, Chlorpyrifos is found in both of the sediment samples where it was tested for, whereas it is found in only one of the soil samples (see table 5). Neither of the other compounds infrequently found in soil (Ethion and THPI) were found in the sediment.

The prefixes P4 and P5 before the sample number in Table 14 represent two different acequias. While both acequias are in a geographically small area (around the Cc fields), they are not connected. Values for AMPA, glyphosate and oxyfluorfen appear much higher in P4 than in P5.

Table 14: Concentration of pesticides (ppb) in each sediment sample. Cells filled with a hash were not tested for the given compound.

	AMPA	Chlorpyrifos	Glyphosate	Oxyfluorfen
P4-1	2441	72	7791	1550
P4-2	961	17	1460	515
P5-1	95	-	90	278
P5-2	101	-	100	0
P5-3	83	-	120	148

The concentrations of the other compounds present are notably higher in the sediment than in the soil. For example, the highest concentration of oxyfluorfen found in the soil was found in a clay topsoil sample from one of the spatial distribution sites (therefore not included in Table 4) was 85ppb. The lowest positive concentration of oxyfluorfen in the sediment is almost double that value. Similarly, the highest concentration of glyphosate in the soil was also in a spatial distribution site in clay topsoil (180ppb). In many cases the concentration of residues found in the sediment exceeds the maximum value found in the soil.

The sediment contains more fine particles than the soil samples from Spain. The pH is slightly lower and the OM% higher than the soil samples.

3.4 Associated Risk

A wealth of acceptable risk limits exists for pesticides, especially in food and water. And where limits exist, there is often little agreement between different countries (Borggaard & Gimsing, 2008). There are few official values for benchmark levels of pesticides in soil.

The Dutch Intervention Soil Screening value represents the concentration at which 50% of the species in the ecosystem are at risk for harm (Rijkswaterstaat, 2011). Any sample below the Dutch Target level is considered negligible for risk (VROM, 2000). Values in between the Target and intervention levels merit further screening and monitoring.

The Canadian Council of Ministers of the Environment has established limits for different pollutants (both agricultural and industrial) in freshwater sediment for the preservation of aquatic life (CCME, 2001). Similar to the Soil Screening

Benchmark, they represent target levels- any place where compounds are detected below the values listed below are considered to have negligible effects on the target freshwater organisms. Table 11 presents two values for each compound, one representing the acute risk for short-term exposure and the other representing risk for chronic exposure over a long term.

The USEPA Eco-SSL levels are set based on the direct dietary intake of soil by plant, avian and mammalian populations. They are set primarily for metals, but also exist for four types of pesticides (USEPA, 2007). Similarly, the US Resource Conservation and Recovery Act levels published by the USEPA (USEPA, 2003) include pages of limits in water, sediment, soil and air for pesticides among other pollutants. But there is little correspondence between established limits and what is present.

The USEPA Region 3 values are high as they focus on risk from the soil for cancer in humans (USEPA, n.d.). The list published is extensive- with hundreds of compounds, but as evidenced in Table 7, there is little correlation between the list of the USEPA and those compounds found in the Netherlands and Spain. The World Health Organization (WHO) publishes a classification of many pesticide products by their acute risk for a range of effects. The levels do not directly have to do with the soil, but are widely referenced as a broad assessment of risk of exposure to a compound for human health (WHO, 2010).

Compounds are classified as follows:

Ia= Extremely hazardous
Ib= Highly hazardous
II= Moderately hazardous
III= Slightly hazardous
U= Unlikely to present acute hazard

Table 15: Compiled benchmark levels for soil and sediment. n.d. indicates that the compound is not present on the given list.

	General Assessment Levels				Eco Levels			Human Health Risk	
Compound	Dutch Soil Screening Benchmarks (ppb)		Canadian Sediment Limits (ppb)		USEPA ECO-SSL (ppb)	USEPA Region 5 Ecological Screening (ppb)		USEPA Region 3 Residential Soil Screening Levels	WHO Pesticide Hazard Value
	Target Level	Intervention Level	Acute Risk	Chronic Risk		Sediment	Soil		
AMPA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	III
Azoxystrobin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	U
Bixafen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Boscalid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	U
Chlorpyrifos	n.d.	n.d.	0.02	0.002	n.d.	n.d.	n.d.	6300	II
Cyproconazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	II
DDT	10	4000	1.19	4.77	21 (mammals)-91 (birds	3.16	596	1900	II
Difenoconazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	II
Diflufenican	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	III
Epoxiconazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ethion	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	3200	II
Fluopicolide	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fluoxastrobin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Glyphosate	n.d.	n.d.	27,000	800	n.d.	n.d.	n.d.	630,000	III
Linuron	n.d.	n.d.	n.d.	7	n.d.	n.d.	n.d.	13,000	III
Mandipropamid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	U
Metolachlor	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	950,000	III
Oxyfluorfen	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	U
Pencycuron	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	U
Prosulfocarb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	II
Terbuthylazine	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	III
THPI	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	U

4 Discussion

4.1 Occurrence of residues

With regards to the occurrence of residues in soil, a few major generalizations of compounds present in the soil can be made. There are differences in the presence of compounds from different functional groups; modern pesticides occur on organic fields; and banned compounds occur frequently. Finally, residues are found in high concentrations in the sediment and are able to be transported to nearby fields.

4.1.1 Functional groups

There are by far fewer fungicides found in Spain than in the Netherlands. While in the Netherlands fungicides were found as abundantly as herbicides, in Spain the only fungicide detected, and in only one sample, was THPI, a metabolite of Captan, a substance that has not been used in Carcaixent for thirty years (Appendix III). Chlorpyrifos is the only modern insecticide detected in Spain, again in only one soil sample. Considering that Spain accounts for 26% of insecticide use Europe-wide, this was a surprise (Eurostat, 2007). Why would it be that a compound that is currently being used with such a high log KoW (4.7) only be found in one sample?

I believe that this is due to the method of pesticide application. There are two major routes for pesticides to arrive in the soil: the first is through drift of the spray from the target and onto the soil; the second is that the residues run off from the plant and onto the soil following a rainfall event (Rial-Otero et al., 2003). In Spanish orchards, insecticides are sprayed upwards to treat the leaves of the plant, not downwards on the soil, as would be the case for the root crops and cereals commonly grown in the Netherlands. Therefore, unless it rained soon after application, or some chemical dripped onto the soil, it is not likely that much pesticide would be available to adsorb to the soil. Knowing the irregularity of rainfall in Carcaixent, I believe that the absence of fungicides and insecticides in the Spanish sample is because little of the original compound arrived at the soil in the first place.

Further supporting the theory that mode of application explains which pesticides are detected back in the soil is a recent study conducted on the spatial-temporal variation of pesticide residues in vineyards in La Rioja, Spain, 500km NW of Carcaixent (Pose-Juan et al., 2015). Pose-Juan et al. found concentrations of residues of a different nature than those found here despite similar climatic conditions. High concentrations of fungicides were present in the vineyards. Consider the angle required for a farmer to spray a fungicide on a vine relative to an orange tree. A fungicide being sprayed downwards is much more likely to arrive on the soil than one being sprayed upwards.

DDT is present in many samples, indeed, but I have no evidence to support one way or another if the fields presently studied were in orange production at the time of DDT application. So I have no indication of how DDT may have been applied forty years ago. The relative absence of fungicides and insecticides in Spain is very likely due to the method of application.

4.1.2 Occurrence of glyphosate and AMPA on organic fields

I did not expect to find residues of modern pesticides on organic fields. However, I can propose two mechanisms for these residues to be present in isolated spots on organic fields: through transport by sediment and through spray drift (Rial-Otero et al., 2003; Borggaard & Gimsing, 2008). It is possible, given that AMPA and glyphosate residues are found in such high concentrations in the sediment (to be later discussed in depth), that the presence of glyphosate and AMPA on the organic fields is due to overland transport of the sediment. This is further supported by a geographical study of the area, which describes large amounts of sediment deposited by flooding from the river (Ferrer Pérez, 1985).

This, however does not explain the presence of pesticide residues on organic fields in the sandy region. The glyphosate and AMPA found here was on two fields, both managed by the same farmer. These fields are directly adjacent (separated by an ~3m wide dirt path) to conventionally managed fields. Organic farmers in Carcaixent are encouraged by buyers to protect from spray-drift through planting of natural fences, often of bamboo, around fields adjacent to conventional fields. However, these two fields are not surrounded by natural fencing. The organic farm in the sandy region where no glyphosate was detected was surrounded on all sides by either a road or a natural fence, as are all of the organically managed sites in the clay-rich region. So although I treat sites of the four principle soil groups the same for statistical analysis, I must return to site-specific observations to try to account for unexpected results.

The glyphosate and AMPA found on organic fields in the clay-rich region is likely to have been transported via sediment following a flood event. The same residues on sandy fields are likely to have come via spray drift from adjacent fields. The natural fences may be an effective protective measure for organic farms in the sandy region, but does not prevent overland transport via sediment in the flood-prone region.

4.1.3 Occurrence of residues of banned compounds

Of all of the pesticides found between the Netherlands and Spain, only two are completely banned in the EU, Ethion and DDT (Pesticide Action Network UK, 2008). According to experts in Carcaixent, Captan has not been used since the 90s, but it is currently permitted under EU regulation and is listed in an encyclopedia of permitted pesticides in Spain in 2012, but is not recommended for citrus (Eurostat, 2007; De Liñán & De Liñán, 2012). So while this is not officially banned from use, it has effectively been absent on the sites studied for about 20 years.

4.1.4 Occurrence of residues in sediment from canals

As hypothesized, the residues found in the sediment in Spain and sediment-enriched compost in the Netherlands are often at higher concentrations than the highest contamination levels found in the soil. Given that pesticide residence time is known to increase under anaerobic conditions (Warren et al., 2003). If the sediment portion of the compost were not exposed to oxygen in the drainage ditches, degradation would be limited.

Agricultural systems produce higher rates of erosion and soil degradation than other land use types (EEA, 2010). Once the eroded soil arrives into canals as sediment, the anaerobic conditions underwater can precipitate significantly higher concentrations of pesticide residues in the sediment than in surrounding soil (Warren et al., 2003). I have seen in the Netherlands that residues from sediment are transported with management practices of farmers and in Spain that residues move with flooding. Thus, sediment can be both a more potent sink for residue accumulation as well as a source for diffuse pollution as sediment is re-distributed through application as compost or as accumulating in larger water bodies.

4.2 Historical Application

We expected that a detailed understanding of past pesticide application rates would explain actual degradation rates of various compounds in the field. However, many discrepancies are found between the record and the compounds in the soil. This is not to say that farmers are lying or do not keep adequate records, but that dynamics of drift, sediment transport and non-uniform degradation rates are certainly relevant.

I hoped to find back only compounds that I knew were applied, and explain relative quantities of residues by the half-life and the length of time since application. Fields 1, 2, and 3 as listed in Table 8 are conventionally managed fields in Gelderland. The field where compost is applied is also conventionally managed, so in addition to application of pesticides, the field is also supplemented by compost. The compost is made of sediment dredged from nearby canals mixed with discarded green waste from other conventional and organically managed fields. When I try to link the historical data in Appendix II to the results of Table 8 I see some discrepancies.

There are grounds to make some assumptions for the presence of some unexpected compounds in Table 8. For example, prosulfocarb was introduced in Belgium in 1988, but has not been used in Gelderland since 1995 (Tomlin, 2009). If prosulfocarb was uniformly applied on fields 1,2 and 3 in rotation, since 1988, it is likely I would have found it on at least one other field, but this is not the case. It is only present in the compost. Therefore, it is logical to assume that this compound was carried to the field in the compost itself- either from the sediment or from crop residue.

Diflufenican was introduced to the market in 1985 (Tomlin, 2009). It is present on three of the fields, but is absent from the historical record. It is known to have very high sorption and accumulation rates in field studies (EFSA, 2008). This leads to the conclusion that this was regularly applied at the farm in Gelderland in the past, but prior to 1995.

Boscalid was only introduced to the (US) market in 2003 (Tomlin, 2009). That is during the period for which data is available. If I assume that the records are correct, then I must assume that the Boscalid has drifted over from adjacent fields. Fluopicolide was found on Field 2 at the detection limit, but is known to have been applied on its neighbor, Field 1. Given that it is found in such a low concentration, it is probably found due to drift, but I cannot be certain.

Not only is it important what occurs in the soil, but also what is absent. Linuron, for example, was applied on the Field 2 in 2014, but was not found back in the sample. At the same time, Linuron was applied last in 2013 on Field 3 and on the field with compost, but it was still detected in the samples. I have detected residues two years after application, but not on a field where it was applied last year. Thus, even within a small geographic area where conditions are managed in the same way, there is little uniformity in degradation rates.

Taking all of this together we learn that even with a historical record as comprehensive as one could hope for, there are still detectable residues that are unaccounted for. For future studies, it may be more economizing on effort to have a general understanding on common practices on a regional scale through interviews than focus on field-specific application rates.

4.3 Distribution of residues

The theory suggests that organic matter and clay content will positively correlate with the amount of adsorbed residues in the soil. I found that when considering averages across groups, residues appear to increase with clay content. Organic matter correlated in unexpected ways for some of the compounds while pH showed no relationship to residue concentration. Overall, none of the correlations between pH, organic matter or clay content were significant due to low sample sizes, but inferences can be made for patterns to expect with future study. Finally, although there are too many factors to make a comparison between the Dutch and Spanish results, major differences are discussed.

4.3.1 Distribution with respect to soil pH, organic matter and clay content

The presence of Oxyfluorfen and DDT in more frequent concentrations in the sand than in the clay disagrees with much of the theory on how residues correlate to soil physical characteristics. This is further emphasized by the negative relationship between the concentrations of these compounds and organic matter in Fig. 10. The four major soil category divisions made in this study were chosen with the theory that residues increase with soil matter and organic matter content. I found that indeed organic matter concentration differs significantly between groups, so may explain some of the variation in pesticide concentration. I see that this is probably the case, but not always as suggested by the theory. Figure 10 at least for DDT seems to show the opposite. When considering the averages of all pesticides between groups with clay content, an overall positive correlation seems evident. Trends are more evident when considered in the aggregate. Perhaps clay content is a more robust predictor of pesticide concentration in this case than organic matter or pH, but the statistical tests were insignificant, likely due to the low sample size.

An alternate theory is that high levels of organic matter and clay content are thought to correlate positively with microbial activity. So essentially organic matter and clay content are proxies for quantifying microbial activity (Penn State Extension, 2001; Kah et al., 2007; Barriuso et al., 2008). Perhaps in Carcaixent microbial activity does not correlate to organic matter and clay content. But I did not measure microbial activity, and physical data overall is limited for this study.

Furthermore, perhaps the apparent decrease in residues is supported by the concept of Non-extractable residues as described by Barriuso et al. (2008). Perhaps there are some residues so bound to the soil that I cannot extract them. However, I cannot guess at the presence of something that I did not measure. There is the possibility that DDT and Oxyfluorfen residues exist in the soil that are simply non-detectable using the methodologies selected.

Nevertheless, from Figures 10 and 11 I see that different compounds behave differently in response to physical conditions.

4.3.2 Distribution of residues by first-level factors

In Spain, I expected to find higher residue concentration in the rows of trees as opposed to in the inter-row areas. I learned through interviews that pesticides are applied using hoses with a spraying head fixture attached to a barrel of the active substance in the back of a tractor meaning that pesticides are applied by focusing on the trees themselves. However, none of the statistical tests performed suggest that pesticide concentrations are higher in the row. This probably has to do with the type of pesticide I found most frequently.

First, glyphosate/ AMPA, is found most frequently of all of the compounds in Spain. A farmer aiming to rid his field of weeds would want to rid his entire field of weeds, not just within the row of trees. He or she would aim to apply the herbicide evenly. In fact, it is recommended that a farmer avoid spraying the base of his trees, especially if the tree is young (De Liñán & De Liñán, 2012). So our hypothesis was not supported, but upon reflection, the results agree with the management aims of a farmer.

The next most frequent residue found in Spain is DDT, an insecticide with an especially long residence time. Similarly, it makes sense that I find no row/ inter-row patterning. DDT was prohibited from use in Spain in the late 1970s

(Zumbado et al., 2005), well before any of the plantations analyzed in this study were planted. I cannot assume that the fields I analyzed were in citrus production at that time, let alone that the existing rows are in the same location as those observed today. Farmers probably also tilled the soil between the death of old plantations and the establishment of new ones. If I had found trends in the spatial distribution of DDT, it would be due to chance alone.

4.3.3 Major differences between the Netherlands and Spain

4.3.3.A Differences in distribution of banned compounds

DDT residues were found much more frequently in Spain than in the Netherlands. DDT was found at least twice as frequently in Spain as in the Netherlands. Perhaps this discrepancy has to do with differences in original application rates- especially given that DDT was only found on one farm in the Netherlands. But without concrete historical data, I cannot be sure.

Despite the high frequency of DDT found in Spain, I can be confident that the residues are old and do not indicate that farmers have been applying pesticides after they have been banned. A low ratio of DDT to DDE indicates old, microbally degraded DDT (Harner et al., 1999). The lower the value, the longer it has been since application. 25 years after the most recent application, the ratio of DDT:DDE was found to be 1.3 in the northeastern US (Dimond & Owen, 1996). The average DDT:DDE ratio found in Spanish samples was 0.05. No DDT itself was ever found in conventionally managed Spanish samples, only its metabolite DDE. The average ratio for all organic samples was 0.09. For Oc samples the ratio was 0.07, and for Os 0.09. This tells us that indeed in Spain the DDT found is old and degraded, if at a slightly slower rate in the organically managed fields.

This contrasts to the average ratio for the Dutch fields, which is 4.5. This value is closest to the level found in the U.S. 15 years after application (Dimond & Owen, 1996). However, I cannot use this value alone as evidence of malpractice. There is evidence that at northern latitudes, the conversion of DDT into DDE is slowed (Dimond & Owen, 1996; Harris et al., 2000). Proposed factors for this phenomenon that correlate with northern latitudes include the fact that low pH, high % OM, and low temperatures. All of which precipitate lower microbial activity (Dimond & Owen, 1996). Each of these conditions is true in the Netherlands versus Spain. Furthermore, the Netherlands is at even higher latitude than the study in the U.S. Thus, I have reason to expect inhibited degradation rates of DDT in the Netherlands. So I am confident to conclude that the residues of DDT found in Spain are indeed old, and those in the Netherlands are likely to be old given the trustworthiness of the managers and the low total concentrations found despite a high DDT:DDE ratio.

Other old compounds found in Spain were found at such low frequency with so many samples that it is possible that further work in the Netherlands would detect greater variety in the residues of banned or old pesticides found.

The presence of DDT in organic fields at as high, if not higher concentrations than conventionally managed fields poses an interesting dilemma to the consumer. The consumer pays a premium for a product she considers safer, with low potential damage to the environment. At least when it comes to DDT, there may be no difference in the quality of ‘cleanliness’ of a crop grown organically or conventionally.

4.3.3.B Differences in patterning of modern compounds

The general trend is that although fewer compounds were detected in Spain, they tend to be in a greater proportion of compounds than that found in the Netherlands.

Interestingly, I was told by experts in Spain that linuron is commonly applied to fields in the area as an herbicide along with glyphosate and oxyfluorfen. However, no linuron was detected in any sample. Meanwhile, two years after application, linuron is detected in the Netherlands.

In general, increased pH slows chemical and microbial breakdown of pesticides. However, high pH also prevents sorption in the first place. So it is more difficult for a compound to adsorb to alkaline soil, but when it does adsorb, it breaks down more slowly (Penn State Extension, 2001).

4.3.3.C Comparing frequency of application

I hypothesized that I would find lower residues in Spain due to the theory described that repeated application of the same pesticide over time would decrease its ability to adsorb to the soil. I thought that in Spain I may see lower residues than expected of the same fungicide applied year after year when compared to the fungicides applied on a rotating basis in the Netherlands (Osborn et al., 2010). However, I found that mode of application makes it unlikely for fungicides to be found in orchards. Therefore, the only comparison with regards to repeat application I can make between the Netherlands and Spain is with glyphosate. According to the historical data collected in the Netherlands, glyphosate is applied about every third year (Appendix II), and in Spain on an annual basis (Appendix III). Meanwhile, the recommended dose for Roundup, one of the most recognized products containing glyphosate is higher for citrus plantations in Spain (4L/ha) than for field crops in the Netherlands (3L/ha) (De Liñán & De Liñán, 2012; Monsanto Europe nv, 2015).

So glyphosate is typically applied at a higher dosage three times as often in Spain than in the Netherlands. This resulted in a much higher frequency of occurrence for AMPA (50% vs. 72%) and higher mean concentrations of the sum of glyphosate and AMPA for positive samples (154 ppb vs. 506 ppb) in Spain than in the Netherlands. Glyphosate was found more frequently in the Netherlands, but at lower concentrations.

4.4 Associated Risk

We aimed to make a thorough assessment of risks associated with the pesticides present in the soil. Upon comparing existing limits, there is little overlap between what is found and what known risk levels are. The fact that there are no established limits for most of the compounds found in soil and sediment shows that there is still more work to be done in establishing regulatory limits for the compounds actually found in the soil.

Analysis of existing quantifications of hazard associated with pesticides in the soil was disappointing. Regulations for residues in soil are rare. When they do exist they are often for highly persistent, old compounds, like those listed in the Stockholm convention of Persistent Organic Pollutants. Essentially the Dutch target value is exceeded anywhere where DDT was detected, but never was the intervention value reached. Of the 22 sites in Spain that tested positive for DDT, 17 exceed limits established to protect mammals, and 10 exceed limits to protect birds. Two of these sites exceed the USEPA's ECOSSL level (USEPA, 2007). Potentially troubling is the fact that of the sites that pose ecological risk to mammals, only two are conventionally managed. Organic sites pose as much, if not more risk to wildlife as conventional sites.

A direct food chain link has been established between DDT values in the soil to young robins via earthworms and adult robins (Harris et al., 2000). Concentrations as low as 40ppb in the soil can accumulate in the tissue of earthworms and transfer into the robin. There is a direct link establishing (low) DDT levels in the soil with bioaccumulation into common species.

The levels of DDT metabolites found in Spain would also likely be able to translocate from the soil into the plants of certain crops, Lunney et al. (2004) found DDT residues in winter squash grown under laboratory conditions with only 150ppb of DDT metabolites in the soil. Given that I found DDT in Spanish soil up to four times that amount, it is not impossible that residues would transfer to the fruit.

We must not, however, be alarmist, I do not know certainly if DDT would translocate from the soil into the oranges as it does in the squash, and if so, how much over the long term a person can safely eat without having negative effects. If ingested in excess, these classes of pesticides have potentially devastating effects. Organochlorines and Organophosphates, notably toxic members found in the present study include DDT and chlorpyrifos are neurotoxic to humans-leading to involuntary convulsions (Roberts & Reigart, 2013). But again, I do not know the concentration of these compounds in oranges, nor how many oranges a person would have to eat before any negative consequences are observed. Concentrations in the fruit are likely to be low, and any risk would likely come from chronic exposure to the toxin.

When it comes to human health risk, more work needs to be done to establish the link between pesticides in the soil to food or water contamination. Limits are established EU wide and on a national level in both the Netherlands and Spain for pesticide residues in food and water, but the degree to which pesticides bound to the soil may transport into food is unknown. The Codex Alimentarius is the FAO's database of acceptable risk levels for pesticide residues in food while the EU publishes Maximum Residue Levels (MRLs) on the European Commission's website. But the relationship between residue levels in soil and contamination in food is another unknown. Compounds such as difenoconazole, prosulfocarb, and cyproconazole were all found in this study are classified as 'moderately hazardous' by the WHO, but no limits associated with the soil were found. Just because no limits in the soil are established, I cannot assume that the compounds are irrelevant to public health concerns.

Furthermore, there is debate as to the toxicity of some of the compounds found. Notably, glyphosate has historically been considered nontoxic as it inhibits a metabolic pathway only found in plants, and international target levels for residues in food and water have been set accordingly (Borggaard & Gimsing, 2008). However, this year a study was published that proposes glyphosate as a human carcinogen (Fritschi et al., 2015). Studies that link glyphosate to environmental risks are often highly controversial (Borggaard & Gimsing, 2008). It is no wonder that ecological limits are poorly established if I do not even know the human and ecological risk associated with many compounds.

4.5 General Discussion

It is important to recognize that not all of the residues detected are necessarily bioavailable. Remember, the methodology involves shaking the soil in a series of extractants in such a way that would not occur in nature. Attempts have been made to describe what portion of extractable residues are actually bioavailable, but the results range from no correlation to almost perfect (Arias-Estévez et al., 2008). Again, this relationship is unpredictable and likely to be specific to each compound.

Another point for discussion is that the present study focused in the grand majority on identifying the parent pesticide itself, rather than its metabolites. The notable exceptions are well-known DDT metabolites (DDE, DDMU, DDD), AMPA and THPI. However, metabolites are frequently found in the environment in concentrations higher than its parent compound (Sinclair & Boxall, 2003), but often this determination is made difficult due to a lack of understanding of the nature of the metabolites. Lerch et al., (2003) describe the presence of 28 different metabolites of the single parent herbicide, trifluralin in soil, and only 6 of these metabolites have available standards for quantification using GC-MS/MS. It would be very difficult in a broad-spectrum analysis to include all metabolites of all compounds applied, even if standards were available. While most of these metabolites are less toxic than their parent, up to 30% of metabolites are more toxic than the original compound applied (Sinclair & Boxall, 2003). It is worth noting that the metabolite most frequently found in this study, AMPA, is considered no more toxic than its parent compound, glyphosate (JMPR, 2005). I can reasonably suppose that looking at the parent compounds alone does not mean that that compound is fully absent from the system, and metabolites may be present.

Some compounds that may be of interest for future research were not included in this study. This is due to limitations of the extraction methodology. Notably absent compounds from the methodology described are dithiocarbamate fungicides such as maneb, mancozeb and zineb, as well as dipyridil herbicides such as paraquat and diquat. I know that some of these compounds were indeed applied in Carcaixent, and may be found in the soil using other methodologies.

We also must recognize potential limits to the methodology. The extraction technique used here was primarily designed for extraction of residues from food, not soil. So perhaps future studies may find a more optimal extraction method. Perhaps a stronger acid or longer period of agitation would extract more residues. Also, in the integration of the peak areas, there is room for human misjudgment as to the selection of the proper area. Of course mechanical error in pipetting of solvents is also a possibility. I trust though, that the general relationships between factors observed in this study would not be dramatically changed by minor changes or improvements of the methodology.

4.6 Implications for future experiments

4.6.1 Pre-selection of compounds

There is value to applying this broad-screening method to assess the distribution of pesticide residues in the soil. But it is important that a researcher make a pre-selection of likely compounds to save resources. In making a pre-selection it is useful to talk to local experts. All of the compounds found present in Spanish soil were on the original list of compounds mentioned by local experts, and none present were exclusively on the EU's list of pesticides likely to have been applied on Spanish orange plantations (Eurostat, 2007). At the same time had I only looked for compounds mentioned in the specific record of pesticides applied per field in the Netherlands, I would have missed about one-third of the true occurrence of residues (see Table 8). Future researchers would also do well to consider mode of application while screening.

We were alarmed at first to find essentially an absence of modern fungicides and insecticides in Spain because I were not considering how a farmer originally applies these compounds. Such compounds that are sprayed upwards should not be excluded from the pre-selection, but researchers should not be alarmed if some compounds with high log KoW values are absent from the soil if they may be applied far from the soil.

4.6.2 Analysis on a regional scale

This leads to the second point: site-specific detailed analysis will not yield as much insight as a regional assessment. Where I tried to understand the details by taking the spatial distribution samples or linking residues to exact historical data, I was left with many further questions. For an accurate characterization of the sorts of residues of modern pesticides at a site, there appears to be little that we learn from analysis at a regional level. I see in the historical data from the Netherlands that there isn't a linear relationship between time since application and quantity of residues. I see in the spatial distribution of AMPA that patterns are hard to distinguish based on the quantity. Data on a small scale is so variable that interpretation is difficult. On the other hand, the Chi-Square, Kruskal-Wallis and Mann-Whitney U tests demonstrate patterns that are easy to interpret. I understand more about potential risks associated with pesticide residues when considering all twelve fields together. If future researchers wanted to better understand the fate and distribution of residues in the soil and only were able to analyze fifty samples, it would be better that these be distributed across many fields in a region than densely focused on one field.

5 Conclusion

From this study we can draw six major conclusions:

1. *Heterogeneity of residue occurrence within and between fields is great*

In the field I found that residues degrade without much uniformity, as in previous laboratory studies. Taking a sample every meter does not tell us anything more about the site. Also from the Dutch results we see that fields with management from exactly the same farmers with nearly identical crop rotation patterns have a range of frequencies and concentrations of residues present.

So, an in-depth study of a single farm may show as many outliers as samples following the trend. Perhaps gaining understanding of trends on a macro/ regional level will yield more useful conclusions.

2. *Different compounds exhibit different patterns*

Individual compounds do appear at different frequencies across groups. However given that the frequency of occurrence for some compounds was low and correlations with physical characteristics of the soil was not the primary aim of the study, I cannot propose mechanisms as to why these compounds behave as they do. There is indication, especially with oxyfluorfen and DDT that they behave contrary to what laboratory studies would predict.

3. *Frequency of detection is a robust measure for quickly characterizing a given region*

Most of the trends observed in the Spanish data were apparent just as readily in the results from the Chi-Square test as in more detailed analyses. Furthermore, given that many compounds from both the Netherlands and Spain occur less than five times, all I need to know about these compounds is their presence in the study area.

On the other hand, knowing the quantity AMPA showed us that while the AMPA is found more frequently in the subsoil, it is in higher concentrations in the topsoil than in the bottom. And while I did not see a row/inter row correlation in the aggregate, I do see a pattern in the quantity in a paired t-test. For banned compounds, indeed patterns are only visible when considering quantity. Because of the age of the compounds, they are uniformly present in the soil, but exhibit patterns in concentration of residues.

4. *Mode of application is an important factor to consider when predicting what residues you may detect back on a site*

Mode of application was not mentioned in the literature as an important factor in the fate of pesticide residues. When I compare the results from the Netherlands to those of Spain and partner these findings with other studies we see that this is indeed an important factor. This is relevant if, for example, policymakers were concerned about environmental impacts of fungicides on a regional or national level. Where fruit trees are a dominant crop, more risk would be associated with volatilization or inhalation of the compound whereas a region where vegetables are grown has more risk for soil and groundwater contamination.

5. *Some banned compounds are detectable up to four decades following last application*

DDT and Ethion have been banned in Europe for decades. DDT is found, in degraded form, at a very high frequency, especially in Spain. DDT is widespread in the soil. However, it was absent from the sediment despite being found just as frequently in the topsoil as in the bottom, and just as frequently in the flood-zone. DDT often exceeds target levels and is present at concentrations great enough to translocate to some crops. Other compounds that have not been banned, but have not been used onsite for at least 20 years were found. Prosulfocarb was found in the Netherlands and THPI was found in Spain. Indeed banned compounds still persist in the environment at levels that pose potential human and environmental health risks.

6. *Pesticide residues can accumulate in sediment of water bodies connected to farms*

Sediment in freshwater canals adjacent to sites is a relevant source and sink of pesticide residues. If this sediment is then transferred to another site, it is likely that the residues will transport with it. The theory that bound residues in the soil are completely immobile is not supported by these findings. However, risks associated with such diffuse pollution are unknown.

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7 Appendix I: List of Compounds Analyzed

Key:
(f)= fungicide (h)= herbicide (i)= insecticide
+= tested in Spain
**= those compounds used in Spain, as recommended by Spanish interviews*
S= listed on the Stockholm convention (Persistent Organic Pollutants)

Aliphatic Nitrogen							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Cymoxanil (f)	0.6	2 (1)	LC+	Dodine (f)	1.7	22 (1)	LC+
Amide							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Amisulbrom (f)	4.4	13	LC+	Flutolanil (f) +	3.2	320 (1)	LC+
Asulam (h)	0.05	14 (1)	LC+	Iprovalicarb (f)	3.2	17 (1)	LC+
Bixafen (f)	3.3	360 (3)	LC+	Isopyrazam (f)	4.4		LC+
Cyazofamid (f)	3.2	5	LC+	Mandipropamid (f)	3.2	24 (4)	LC+
Dichlofluanid (f) +	3.7	3.5 (2)	LC+	Metalaxyl (f) +*	1.8	70	GC
Diflufenican (h)	4.2	280 (1)	LC+	Metazachlor (h)	2.1	21 (1)	LC+
Fenhexamid (f)	3.5	1 (1)	LC+	Metolachlor (h)	2.9	90	LC+
Florasulam (h)	-1.2	5	LC+	Propyzamide (h)	3.4	392 (2)	GC
Flufenacet (h)	3.2	54 (1)	LC+	Tolylfluanid (f) +	3.9	11 (1)	LC+
Antibiotic							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Azoxystrobin (f)	2.5	70 (1)	LC+	Picoxystrobin (f)	3.6	35 (1)	LC+
Fluoxastrobin (f)	2.9	184 (2)	LC+	Pyraclostrobin (f)	4.0	55 (1)	LC+
Kresoxim-methyl (f)	3.4	1 (1)	LC+	Trifloxystrobin (f)	4.5	9.5 (1)	LC+
Aromatic Acid							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Chlorothalonil (f)	2.9	30	GC	Dicloran (f)	2.8	78 (1)	GC
Quinmerac (h)	-1.1	33 (1)	LC+				
Benzimidazole							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Carbendazim (f) +	1.4	120	LC+	Thiophanate-methyl (f)	1.5	28 (1)	LC+
Thiabendazole (f) +	2.4	403	LC+	Methabenzthiazuron (h) +	2.6	135 (2)	LC+
Benzoylcyclohexanedione							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Mesotrione (h)	0.1	7 (1)	LC+	Sulcotrione (h)	0.0	11 (1)	LC+
Botanical							

Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Azadirachtin (i)	0.6	25 (1)	LC+				
Bridged Diphenyl							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Bromopropylate (i)	5.4	70 (1)	GC	Chlorobenzilate (i)	4.7	20	GC
Tetradifon (i) +	4.6	112 (2)	GC				
Carbamate							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Aldicarb (i) +*	1.2	30	LC+	Methomyl (i) +	0.1	30	LC+
Bendiocarb (i)	1.7	5	LC+	Oxamyl (i) +	-0.4	4	LC+
Bifenazate (i)	3.4	1 (1)	LC+	Phenmedipham (h)	3.6	30	LC+
Carbaryl (i) +*	1.9	10	LC+	Pirimicarb (i)	1.7	10	LC+
Carbetamide (h)	1.8	30 (1)	LC+	Propamocarb (f)	0.8	30	LC+
Carbofuran (i)	1.5	60 (1)	LC+	Propham (h)	1.2	11 (2)	GC
Chlorpropham (h)	3.3	30	GC	Prosulfocarb (h)	4.7	49 (1)	LC+
Desmedipham (h)	3.4	30	LC+	Tri-allate (h)	4.6	82	LC+
Methiocarb (i)	3.1	30	LC+				
Conazole							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Cyproconazole (f)	3.1	40 (1)	LC+	Penconazole (f)	3.7	188 (1)	LC+
Difenoconazole (f)	4.4	318 (2)	LC+	Prochloraz (f) +	3.5	120	GC
Epoxiconazole (f)	3.3	90 (1)	LC+	Propiconazole (f)	3.7	110	GC
Imazalil (f)	3.8	150	LC+	Tebuconazole (f)	3.7	597 (2)	LC+
Isoxaflutole (h)	2.3	2.3 (1)	LC+	Tetraconazole (f)	3.6	364 (2)	LC+
Metconazole (f)	3.9	639 (2)	LC+	Triflumizole (f)	5.1	14	LC+
Myclobutanil (f)	2.9	66	GC				
Coumarin Rodenticide							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Brodifacoum (r)	8.5	84	LC+	Bromadiolone (r)	5.0	53 (2)	LC-
Dicarboxamide							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Captan (f) +*	2.8	2.5	GC	THPI (Captan Metabolite) (f) +*			GC
Famoxadone (f)	4.7	28 (1)	LC+	PTI (Folpet Metabolite) (f) +*	3.1		GC
Folpet (f) +*	3.1	4.3 (1)	GC	Vinclozolin (f)	3.0	20	GC
Procymidone (f)	3.1	7	GC				
Dinitroaniline/ Dinitrophenol							

Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Pendimethalin (h)	5.2	90	GC	DNOC (i)	4.4		LC-
Dinoterb (h) +	3.6	10 (2)	LC-				
Diphenyl Ether							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Aclonifen (h)	4.4	80	LC+	Oxyfluorfen (h) +*	4.5	35	LC+
Growth Regulators							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Buprofezin (i)	4.9	80 (1)	GC	Hexythiazox (i)	2.5	30	LC+
Clofentezine (i)	4.1	40	LC+	Lufenuron (i)	5.1	83 (1)	LC+
Diflubenzuron (i)	3.9	10	LC+	Methoxyfenozide (i)	3.7	173 (1)	LC+
Etoxazole (i) +*	5.6	19 (1)	LC+	Paclobutrazol (h)	3.2	200	LC+
Fenoxycarb (i)	4.1	1	LC+	Teflubenzuron (i)	4.3	84 (1)	LC+
Flucycloxuron (i)	4.0	208 (2)	LC+	Triflumuron (i)	4.9		LC+
Flufenoxuron (i)	4.0	42 (1)	LC+				
Macrocyclic Lactone							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Abamectin (i) +*	4.4	28	LC+	Emamectin (i)	5.0	211 (2)	LC+
Morpholine							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Dimethomorph (f)	2.6	96 (1)	GC	Fenpropimorph (f)	2.6	90 (1)	LC+
Dodemorph (f)	4.1	73 (1)	LC+				
Neonicitinoid							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Acetamiprid (i)	0.8	5 (1)	LC+	Thiacloprid (i)	0.7	21 (1)	LC+
Imidacloprid (i)	0.6	27 (2)	LC+				
Nitrile							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Bromoxynil (h)	1.0	7 (1)	LC-	Ioxynil (h)	2.5	10 (1)	LC-
Organochlorine							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Aldrin (i) +S	6.5	365	GC	Endosulfan beta- (i) +	4.8	50	GC
Chlordane (i) S	6.0	350	GC	Endosulfan sulphate (i) +	3.7	50	GC
DDD o,p'- (TDE) (i) +*S	6.1	30 (y) (1)	GC	Endrin (i) S	5.0	4300 (2)	GC
DDD p,p'- (TDE) (i) +*S	6.1	31 (y) (1)	GC	HCB (f) S	5.31	1000	GC
DDE o,p'- (i) +*S	6.8	32 (y) (1)	GC	HCH alpha-, beta-, delta-	3.8		GC

				(i)			
DDE p,p'- (i) +*S	6.8	33 (y) (1)	GC	HCH gamma- (Lindane) (i)	3.5	400	GC
DDMU (i) +*S		34 (y) (1)	GC	Heptachlor (i) S	3.9	250	GC
DDT o,p'- (i) +*S	6.5	35 (y) (1)	GC	Isodrin (i)	6.8		GC
DDT p,p'- (i) +*S	6.5	36 (y) (1)	GC	Methoxychlor (i)	4.7	120	GC
Dieldrin (i) S	4.1	1000	GC	Oxychlordane (Chlordane Metabolite) (i)			GC
Endosulfan alpha- (i) +	4.7	50	GC				
Organophosphorus							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Acephate (i) +	-0.9	3	LC+	Fensulfothion (i)	2.2	30	GC
AMPA (Glyphosate Metabolite) (h) +*			LC-	Fosthiazate (i)	1.7	45 (1)	LC+
Azamethiphos (i)	1.1	0.25 (1)	LC+	Glyphosate (h) +*	-3.2	130 (1)	LC-
Chlorfenvinphos (i) +	3.9	161 (1)	GC	Malathion (i) +*	2.8	1	LC+
Chlorpyrifos (i) +*	4.7	30	GC	Methamidophos (i)	-0.8	6	LC+
Chlorpyrifos-methyl (i) +*	4.2	7	GC	Methidathion (i) +*	2.2	7	GC
Coumaphos (i)	4.1	23.8	GC	Mevinphos (i) +	0.1	3	LC+
Cythioate (i)			LC+	Omethoate (i) +	-0.7	14 (2)	LC+
Diazinon (i) +	3.3	21 (1)	GC	Oxydemeton-methyl (i) +	-0.1	10	LC+
Dichlorvos (i) +	1.9	0.5	GC	Parathion-ethyl (i) +*	3.8	14	GC
Dimethoate (i) +*	0.7	7	LC+	Parathion-methyl (i) +*	3.0	14	GC
Disulfoton (i) +	4.0	30	GC	Phorate (i) +	3.9	60	GC
Edifenphos (f)	3.8	21 (2)	GC	Pirimiphos-methyl (i) +	4.2	10	LC+
Ethion (i) +*	4.3	150	GC	Profenofos (i) +	4.5	8	LC+
Ethoprophos (i) +	3.6	28 (1)	LC+	Pyrazophos (f) +	3.8	21 (1)	GC
Fenamiphos (i) +	3.3	50	LC+	Pyridaphenthion (i)	3.2	35 (1)	GC
Fenitrothion (i) +*	3.4	4	GC	Triazophos (i)	3.3	12 (1)	GC
Oxazole							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Isoxaben (h)	3.9	100	LC+	Topramezone (h)	-0.8	81 (1)	LC+
Oxadixyl (f)	0.8	90 (1)	GC				
Phenoxy							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
2,4-D (h) +*	2.6	10	LC-	Fluazifop (h)	4.5	7	LC+
2,4,5- T (h) +*	3.9	30	LC-	MCPA (h) +*	2.8	25	LC-
Clodinafop-propargyl (h)	3.9	20	LC+	Quizalofop-Ethyl (h)	4.3	60	LC+
Fenoxaprop-ethyl (h)	1.8	9	LC+				
Pyrazole							

Compound	Log KoW	Soil Half-life (days)	Machine	Compound	Log KoW	Soil Half-life (days)	Machine
Fipronil (i)	4.0	366 (2)	LC+	Tebufenpyrad (i)	4.9	50 (1)	GC
Pinoxaden (h)	3.2	1 (1)	LC+				
Pyrethroid							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Bifenthrin (i)	6.0	26	GC	Flucythrinate (i)	4.7	60 (1)	GC
Cyhalothrin (i)	6.9	84 (1)	GC	Permethrin (i) +*	6.1	30	GC
Deltamethrin (i)	4.6	28 (1)	GC	Tetramethrin (i)	4.6	3 (2)	GC
Fenvalerate (i)	4.4	35	GC				
Pyridazine/ Pyridazinone/ Pyridine/ Pyrimidine							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Boscalid (f) +	3.0	200	LC+	Fluroxypyr (h)	-1.2	9 (1)	LC-
Bupirimate (f)	3.9	90 (1)	LC+	Mepanipyrim (f)	3.3	105 (1)	LC+
Chloridazon (h)	1.2	56 (1)	LC+	Pyridate (h)	4.0	1 (1)	LC+
Cyprodinil (f)	3.9	60 (1)	GC	Pyrimethanil (f)	2.8	54 (1)	GC
Ethirimol (f)	2.3	77 (2)	LC+	Pyroxsulam (h)	-1.0	13 (1)	LC+
Fluazinam (f)	4.0	26.5 (1)	LC-	Triclopyr (h)	0.4	46 (1)	LC-
Fluopicolide (f)	3.3	415 (2)	LC+				
Thiazole							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Clothianidin (i)	0.7	1155	LC+	Thiamethoxam (i)	-0.1	109 (1)	LC+
Triazine/ Triazinone/ Triazolopyrimidine							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Atrazine (h) +*	2.5	60	LC+	Terbutryn (h)	3.7	42	LC+
Cybutryne (h)			LC+	Metamitron (h)	0.8	30 (2)	LC+
Pymetrozine (i)	-0.2	69 (1)	LC+	Metribuzin (h)	1.6	40	LC+
Simazine (h) +*	2.1	60	LC+	Carfentrazone-ethyl (h)	3.4	50	LC+
Terbuthylazine (h)	3.4	149 (1)	LC+	Ametoctradin (f)			LC+
Uracil							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Bromacil (h) +*	1.9	60	LC+	Lenacil (h) +	2.3	90 (1)	LC+
Urea							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Chlorbromuron (h) +	2.9	40	LC+	Metoxuron (h) +	1.6	30 (1)	LC+
Diuron (h) +*	2.9	90	LC+	Metsulfuron-methyl (h)	0.0	30	LC+
Foramsulfuron (h)	1.4	12.7 (1)	LC+	Nicosulfuron (h)	-0.4	21	LC+
Haloxyfop (h)	4.3	55	LC+	Pencycuron (f)	4.7	64 (2)	LC+

Iodosulfuron-methyl (h)	1.1	10 (1)	LC-	Rimsulfuron (h)	0.3	20 (1)	LC+
Isoproturon (h) +	2.5	28 (1)	LC+	Tribenuron-methyl (h)	0.8	5.1 (1)	LC+
Linuron (h) +	3.0	60	LC+	Triflusulfuron-methyl (h)	1.0	3 (1)	LC+
Mesosulfuron-methyl (h)	1.4	68 (1)	LC+				
Other/ Unclassified							
Compound	**Log KoW**	**Soil Half-life (days)**	**Machine**	**Compound**	**Log KoW**	**Soil Half-life (days)**	**Machine**
Acequinocyl (i)	6.2	2	LC+	Propargite (i)	5.7	56	GC
Bentazone (h)	0.8	20	LC-	Pyridaben (i)	6.4	21 (1)	LC+
Chlorantraniliprole (i)	2.8	60 (1)	LC+	Pyriproxyfen (i) +*	5.4		LC+
Clomazone (h) +	2.5	24	LC+	Quinoclamine (h) +	1.6	28 (1)	LC+
Dimethenamid (h)	2.2	43 (1)	LC+	Quinoxyfen (f)	4.7	454 (1)	LC+
Fenamidone (f)	2.8	8.5 (1)	LC+	Silthiofam (f)	3.7	66 (1)	LC+
Fenpropidin (f)	2.9	95 (1)	LC+	Spinosad (i)	4.0	14 (2)	LC+
Flonicamid (i)	0.3	1.8 (1)	LC+	Spirodiclofen (i)	5.1	64 (1)	LC+
Fludioxonil (f)	4.1	54 (1)	LC+	Spiromesifen (i)	4.6	17.9	LC+
Indoxacarb (i)	4.7	23 (1)	LC+	Spirotetramat (i)	2.5	1 (1)	LC+
MCPP (h)		21	LC-	Spiroxamine (f)	1.3	64 (1)	LC+
Metrafenone (f)	4.3	124 (1)	LC+	Tembotrione (h)	-1.4	56 (1)	LC+
PCB 28, 52, 101, 118, 138, 153, 180 S			GC	Tepraloxydim (h)	1.5	14 (1)	LC+
Piperonyl butoxide (i)	4.8	14 (1)	GC				

Citations- All Kow values come from Pesticide Encyclopedia, Half life without number = npic.orst.edu/ingred/ppdmove.htm. Half Life (1)= Pesticide Encyclopedia, (2)= PAN database, (3)= VKM, 2013, (4)= USEPA, 2008

8 Appendix II: Historical Data- the Netherlands

Field 1

Discovered Compounds: Bixafen, Diflufenican, Fluopicolide

	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
Crop:	**Beets**	**Wheat**	**Potatoes**	**Barley**	**Beets**	**Wheat**	**Corn**	**Potatoes**	**Barley**	**Corn**	**Beets**	**Fallow**	**Potatoes**	**Barley**	**Beets**	**Wheat**	**Potatoes**	**Corn**	**Wheat**	**Corn**
	Ethofumesale (h)	Chloromequat Chloride (h)	Florasulam (h)	Deltamethrin (i)	Ethofumesale (h)	Chloromequat Chloride (h)	Bentazon (h)	Florasulam (h)	MCPA (h)	Bentazon (h)	Ethofumesale (h)		Florasulam (h)	Deltamethrin (i)	Ethofumesale (h)	Bacillus Thuringiensis (i)	Azoxystrobin (f)	Metolachlor (h)	Bacillus Thuringiensis (i)	Metolachlor (h)
	Metamitron (h)	Deltamethrin (i)	Fluazinam (f)	Fluoxastrobin (f)	Metamitron (h)	Deltamethrin (i)	Nicosulfuron (h)	Fluazinam (f)	Deltamethrin (i)	Nicosulfuron (h)	Metamitron (h)		Fluazinam (f)	Fluoxastrobin (f)	Metamitron (h)	Deltamethrin (i)	Boscalid (f)	Tembotrione (h)	Bixafen (f)	Tembotrione (h)
	Phenmedipham (h)	Epoxiconazole (f)	Linuron (h)	Fluoxypyr (h)	Phenmedipham (h)	Epoxiconazole (f)	Terbutylazin (h)	Linuron (h)	Prothioconazole (i)	Sulcotrione (h)	Phenmedipham (h)		Linuron (h)	MCPA (h)	Phenmedipham (h)	Fenpropidin (f)	Florasulam (h)	Terbutylazine (h)	Chloromequat Chloride (h)	Terbutylazine (h)
	Tri-allate (h)	Fenpropimorph (f)	Pirimicarb (i)	MCPA (h)	Tri-allate (h)	Fenpropimorph (f)		Pirimicarb (i)	Fluoxypyr (h)	Terbutylazin (h)	Tri-allate (h)		Pirimicarb (i)	Metsulfuron methyl (f)	Tri-allate (h)	Fluazinam (f)	Fluazinam (f)	Dicamba (h)	Deltamethrin (i)	
		Fluazinam (f)		Prothioconazole (i)		Fluazinam (f)				Dicamba (h)				Prothioconazole (i)		Iodosulfuron-methyl (h)	Fluopicolide (f)		MCPA (h)	
		Fluoxypyr (h)				Fluoxypyr (h)										Mesosulfuron methyl (h)	Mandipropamid (f)		Metsulfuron methyl (f)	
		Metsulfuron methyl (h)				Metsulfuron methyl (h)										Metsulfuron methyl (f)	Pyraclostrobin (f)		Prothioconazole (f)	
																Prothioconazole (f)	Rimsulfuron (h)		Tebuconazole (f)	
																Tebuconazole (f)	Thiacloprid (i)		Trinexapac-ethyl (h)	

Field 2

Discovered Compounds: AMPA, Diflufenican, Epoxiconazole, Fluopicolide

	1995	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Crop:	**Barley**	**Potatoes**	**Barley**	**Beets**	**Wheat**	**Corn**	**Potatoes**	**Grass**	**Grass**	**Beets**	**Barley**	**Potatoes**	**Fallow**	**Wheat**	**Beets**	**Potatoes**	**Barley**	**Corn**	**Wheat**	**Potatoes**
	Deltamethrin (i)	Deltamethrin (i)	Deltamethrin (i)	Ethofumesate (h)	Chloromequat Chloride (h)	Atrazine (h)	Deltamethrin (i)	MCPP (h)	MCPP (h)	Ethofumesate (h)	Deltamethrin (i)	Florasulam (h)		Chloromequat Chloride (h)	Ethofumesale (h)	Acetamiprid (i)	Deltamethrin (i)	Dicamba (h)	Prothioconazole (f)	Linuron (h)
	Flyoxypyr (h)	Florasulam (h)	Flyoxypyr (h)	Metamitron (h)	Deltamethrin (i)	Dicamba (h)	Florasulam (h)	MCPA (h)	MCPA (h)	Metamitron (h)	Fluoxypyr (h)	Glyphosate (h)		Deltamethrin (i)	Metamitron (h)	Florasulam (h)	Florasulam (h)	Metolachlor (h)	Tebuconazole (f)	Florasulam (h)
	MCPA (h)	Fluazinam (f)	MCPA (h)	Phenmedipham (h)	Epoxiconazole (f)	Nicosulfuron (h)	Fluazinam (f)	Flyoxypyr (h)	Flyoxypyr (h)	Phenmedipham (h)	MCPA (h)	Linuron (h)		Epoxiconazole (f)	Phenmedipham (h)	Glyphosate (h)	Fluoxastrobin (f)	Tembotrione (h)	Trinexapac-ethyl (h)	Glyphosate (h)
	Metolachlor (h)	Linuron (h)	Metolachlor (h)	Tri-allate (h)	Flyoxypyr (h)		Linuron (h)			Tri-allate (h)	Prothioconazole (i)			Fenpropimorph (f)	Tri-allate (h)	Linuron (h)	Fluroxypyr (h)	Terbutylazine (h)		Thiacloprid (i)
					Metsulfuron methyl (h)									Fluazinam (f)		Mancozeb (f)	MCPA (h)			
														Fluoxypyr (h)			Prothioconazole (f)			
														Metsulfuron methyl (h)						

Field 3

Discovered Compounds: AMPA, Boscalid, Diflufenican, Epoxiconazole, Fluopicolide, Linuron, Mandipropamid

	1995	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Crop:	**No Record**	**No Record**	**No Record**	**Potatoes**	**Barley**	**Corn**	**Fallow**	**Grass**	**Grass**	**Wheat**	**Potatoes**	**Barley**	**Beets**	**Wheat**	**Potatoes**	**Wheat**	**Beets**	**Corn**	**Potatoes**	**Wheat**
				Deltamethrin (i)	Deltamethrin (i)	Atrazine (h)		Flyoxypyr (h)	Flyoxypyr (h)	Chloromequat Chloride (h)	Florasulam (h)	Deltamethrin (i)	Ethofumesate (h)	Chloromequat Chloride (h)	Deltamethrin (i)	Bacillus Thuringiensis (i)	Ethofumesate (h)	Dicamba (h)	Cyazofamid (f)	Bacillus Thuringiensis (i)
				Florasulam (h)	Flyoxypyr (h)	Dicamba (h)		MCPA (h)	MCPA (h)	Deltamethrin (i)	Linuron (h)	Fluoxastrobin (f)	Metamitron (h)	Deltamethrin (i)	Florasulam (h)	Chloromequat Chloride (h)	Fluazifop-P (h)	Metolachlor (h)	Florasulam (h)	Bixafen (f)
				Fluazinam (f)	MCPA (h)	Nicosulfuron (h)		MCPP (h)	MCPP (h)	Epoxiconazole (f)	Glyphosate (h)	Flyoxypyr (h)	Phenmedipham (h)	Epoxiconazole (f)	Fluazinam (f)	Deltamethrin (i)	Metamitron (h)	Tembotrione (h)	Fluazinam (f)	Deltamethrin (i)
				Linuron (h)	Metolachlor (h)					Fluazinam (f)		MCPA (h)	Tri-allate (h)	Fluazinam (f)	Linuron (h)	Fenpropodin (f)	Phenmedipham (h)	Terbutylazine (h)	Fluopicolide (f)	Epoxiconazole (f)
										Flyoxypyr (h)		Prothioconazole (f)		Flyoxypyr (h)		Florasulam (h)	Tri-allate (h)		Linuron (h)	Fluroxypyr (h)
										Metsulfuron methyl (h)				Metsulfuron methyl (h)		Fluazinam (f)			Mandipropamid (f)	Mepiquat Chloride (h)
																Fluroxypyr (h)			Rimsulfuron (h)	Metsulfuron-methyl (h)
																MCPA (h)			Thiacloprid (i)	Tribenuron methyl (h)
																Prothioconazole (f)				
																Tebuconazole (f)				
																Trinexapac-ethyl (h)				

Compost

Discovered Compounds: Boscalid, Epoxiconazole, Fluopicolide, Glyphosate, Linuron, Mandipropamid, Prosulfocarb

	1995	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**
Crop:	**Wheat**	**Potatoes**	**Barley**	**Beets**	**Fallow**	**Potatoes**	**Barley**	**Beets**	**Wheat**	**Corn**	**Potatoes**	**Barley**	**Corn**	**Wheat**	**Potatoes**	**Wheat**	**Corn**	**Barley**	**Potatoes**	**Barley**
	Chloromequat Chloride (h)	Deltamethrin (i)	Deltamethrin (i)	Ethofumesate (h)		Florasulam (h)	Deltamethrin (i)	Ethofumesate (h)	Chloromequat Chloride (h)	Atrazine (h)	Deltamethrin (i)	Deltamethrin (i)	Dicamba (h)	Chloromequat Chloride (h)	Deltamethrin (i)	Bacillus Thuringiensis (i)	Metolachlor (h)	Glyphosate (h)	Cyazofamid (f)	Glyphosate (h)
	Deltamethrin (i)	Florasulam (h)	Fluoxastrobin (f)	Metamitron (h)		Fluazinam (f)	Fluoxastrobin (f)	Metamitron (h)	Deltamethrin (i)	Dicamba (h)	Florasulam (h)	Fluoxastrobin (f)	Metolachlor (h)	Deltamethrin (i)	Florasulam (h)	Chloromequat Chloride (h)	Nicosulfuron (h)	Bixafen (f)	Florasulam (h)	Deltamethrin (i)
	Epoxiconazole (f)	Fluazinam (f)	Flyoxypyr (h)	Phenmedipham (h)		Linuron (h)	Flyoxypyr (h)	Phenmedipham (h)	Epoxiconazole (f)	Nicosulfuron (h)	Fluazinam (f)	Flyoxypyr (h)	Nicosulfuron (h)	Epoxiconazole (f)	Fluazinam (f)	Deltamethrin (i)	Tembotrione (h)	Deltamethrin (i)	Fluazinam (f)	Fluoxastrobin (f)
	Fluazinam (f)	Linuron (h)	MCPA (h)	Tri-allate (h)		Pirimicarb (i)	MCPA (h)	Tri-allate (h)	Fluazinam (f)	Sulcotrione (h)	Linuron (h)	MCPA (h)	Sulcotrione (h)	Fluazinam (f)	Linuron (h)	Fenpropidin (f)	Terbutylazine (h)	Florasulam (h)	Fluopicolide (f)	Flyoxypyr (h)
	Flyoxypyr (h)		Prothioconazole (f)				Prothioconazole (f)		Flyoxypyr (h)			Prothioconazole (f)	Terbutylazine (h)	Flyoxypyr (h)		Fluazinam (f)		MCPA (h)	Linuron (h)	Metsulfuron-methyl (h)
	Metsulfuron methyl (h)								Metsulfuron methyl (h)					MCPA (h)		Prothioconazole (f)		Prothioconazole (f)	Mandipropamid (f)	Prothioconazole (f)
														Trinexapac - ethyl (h)		Tebuconazole (f)			Rimsulfuron (h)	Tribenuron methyl (h)
																Trinexapac-ethyl (h)			Thiacloprid (i)	

9 Appendix III: Historical Data- Spain

	1960-1969	1970-1979	1980-1989	1990-1999	2000-2009	2010- present
Herbicides	2,4-D	2,4-D	Atrazine	Atrazine	Glyphosate	Glyphosate
	MCPA	MCPA	Diuron	Diuron	Linuron	Linuron
	Paraquat	Paraquat	Simazine	Simazine	Oxyfluorfen	Oxyfluorfen
Insecticides	Carbaryl	Aldicarb	Methidathion	Abamectin	Abamectin	Abamectin
	DDT	DDT		Etoxathol	Etoxathol	Etoxathol
	Dimethoate	Fenitrothion		Chlorpyrifos	Chlorpyrifos	Chlorpyrifos
	Ethion	Malathion		Permethrin	Permethrin	Permethrin
	Parathion			Pyripoxyfen	Pyripoxyfen	Pyripoxyfen
				Pyrithines	Pyrithines	Pyrithines
Fungicides	Carbaryl	Aldicarb	Captan	Captan	Mancozeb	Copper-Oxychloride
	Dimethoate	Malathion	Mancozeb	Mancozeb	Maneb	Folpet
	Ethion	Sumithion	Maneb	Maneb	Sinep	Fosetyl Aluminum
	Parathion		Sinep	Sinep	Thiram	Metalaxyl
			Thiram	Thiram		

10 Appendix IV: Questionnaire for Spanish Farmers

Cuestionario: uso de agroquímicos

Fecha: Nombre del entrivisado(a): Puesto: Tiempo trabajando en el puesto:

Ubicación: Tipo de tierra:

1. Cuántas hectáreas maneja? ______________________ Ha
2. Quien provee el consejo que utiliza en decidir cuales productos usar en su tierra? Una universidad? Un agente privado?
3. Maneja un sistema de riego? De que tipo? Con que frecuencia? En que año empezó?
4. Cuales son las plagas principales/ cultivo para que usaría agroquímicos (excluso fertilizantes) en el cultivo de naranjas?
    - i. Problema 1:
    - ii. Problema 2:
    - iii. Problema 3:
5. Cual producto usaría Ud. para cada problema en cada década?

	Naranjas					
	Problema 1:					
	2010- Presente	*2000-2009*	*1990-1999*	*1980-1989*	*1970-1979*	*1960-1969*
Cual agroquímico/ producto habría usado para resolver este problema?						
Como lo habría aplicado?						
Cuanto habría usado en una aplicación?						
Cuantas veces al año habría aplicado este producto?						
Aplicó este producto antes o después que las plantas crecieran?						
	Problema 2:					

	2010- Presente	*2000-2009*	*1990-1999*	*1980-1989*	*1970-1979*	*1960-1969*
Cual agroquímico/ producto habría usado para resolver este problema?						
Como lo habría aplicado?						
Cuanto habría usado en una aplicación?						
Cuantas veces al año habría aplicado este producto?						
Aplicó este producto antes o después que las plantas crecieran?						
	Problema 3:					
	2010- Presente	*2000-2009*	*1990-1999*	*1980-1989*	*1970-1979*	*1960-1969*
Cual agroquímico/ producto habría usado para resolver este problema?						
Como lo habría aplicado?						
Cuanto habría usado en una aplicación?						
Cuantas veces al año habría aplicado este producto?						
Aplicó este producto antes o después que las plantas crecieran?						

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