Research report

# INSECT DECLINE AND PESTICIDE CONTAMINATION IN NATURE CONSERVATION AREAS

## in North Rhine-Westphalia and Rhineland-Palatinate

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for a Common Future

# COLOFON

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# Content

# Foreword

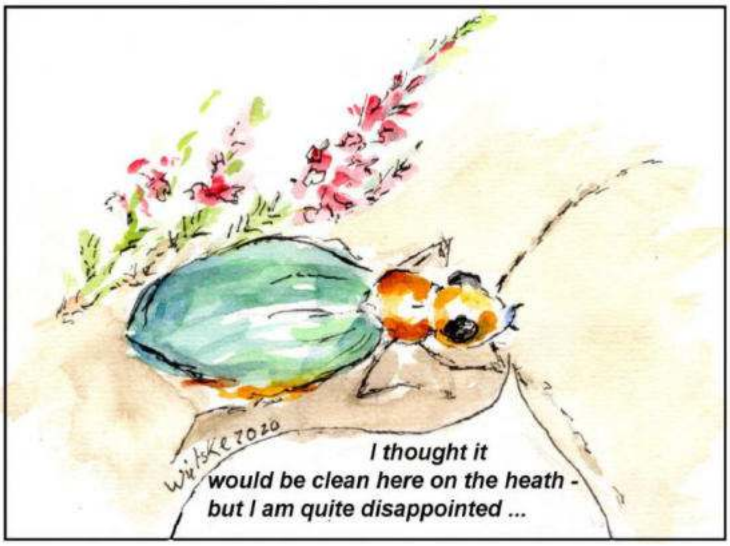
The decline of insect populations has been blamed on several factors, including on pesticides, but few focused studies have been carried out regarding the correlation between pesticides and insect decline.

The authors of this study have earlier carried out an extensive investigation into the contamination with harmful chemicals of animal husbandry farms in the Netherlands. That study formed a good preparation for the current study presented here. We hope that this study on the pesticide contamination of German nature conservation areas, will shed (some) light on the presence and effects of pesticides in our environment. In fact, the contamination of our natural environments might even be a threat to the agricultural production system itself, as well as for human health and for the health of biodiversity and ecosystems. In this study, we focus on the health of the ecosystem.

We note that research such as this depends on funding. And funding depends on priorities set by public or private organisations. Funding organisations often have influence on the choice of subjects and methodologies of research. To date, we note that little research has been carried out on the effects of pesticides on ecosystem wellbeing, which might be explained by the strong political position of industrial agricultural interests in the EU. Nevertheless, few scientists whom we have interviewed expect that pesticides would not play an important role in the ongoing ecological degradation that is currently taking place.

To stimulate other scientists to carry on this research, we have published all original measurement data in the appendices.

We hope that this research will contribute to strengthening the discussion about the role of pesticides in the decline of biodiversity. We let the facts speak for themselves.



# Acknowledgements

We would like to thank Mrs. Eline Platwel and her staff for analyses of all the samples and the elaboration of a new reporting protocol for these measurements. We are grateful for getting comments on different sections of this report from Professor Francisco Sanchez-Bayo (University of Sydney) and professor Weisser. We also thank Dr. Martin Sorg (of the Entomological Society Krefeld) for his support to this study by sharing his knowledge with us about the (former and present) locations of insect traps. We thank the German Postcode Lottery for their financial support. We thank the authorities and organisations from North Rhine-Westphalia and Rhineland-Palatinate for giving permission for sampling the areas under their responsibility. We also would like to thank Dr. Henk Tennekes for his insights that have helped us in conducting this study. It is with great sadness that we have to mention that Dr. Tennekes has passed away in the same period as that this investigation was being conducted, so that we could not share the results with him.

# Disclaimer

For this report, available information from assessment reports from the European Food Safety Authority (EFSA), EU Pesticide Database, The German Federal Office of Consumer Protection and Food Safety (BVL) and other databases such as the University of Hertfordshire's Pesticide Property Database, and the PAN Pesticides Database – Chemicals, have been used as the basis for the interpretations, assessments, advice, and conclusions. We note that a lot of information in these databases has been supplied by the industry. We have also used independent scientific sources, but for many pesticides the information about their ecotoxicological properties is still scarce, and not seldom contradictory. We therefore cannot guarantee the correctness of all the secondary data used in this report.

# Summary

In 2017, the Entomological Society of Krefeld (EVK) in Germany published their study together with the Radboud University of Nijmegen about the results of insect biomass measurements with the help of standardized Malaise insect traps in German nature reserves. They concluded that insect biomass of flying insects declined by about 76% in 27 years from 1989 until 2016. In that study the main causes for this decline could not be designated. Due to a lack of data, the analysis of the causal relationships was not able to include a number of potential factors, such as pesticides. In general, some potential causes were mentioned, like 'intensive agriculture' in the vicinity of the study sites. In intensive conventional farming the use of pesticides is a common practice, allowed by law.

This research study set out to test the following two hypotheses:

- pesticides can be found in vegetation and soil inside nature reserves
- pesticides in the environment have influence on insect declines inside nature reserves

The objectives of the study were therefore:

- to get understanding of the presence of pesticides in nature reserves
- to get understanding of influence of pesticides on insect populations by evaluation of the properties of the found pesticides

In our study we investigated the presence of 661 pesticides (including biocides and metabolites) in the vegetation and 664 pesticides in the soil in 15 nature reserves, where the EVK had operated "Malaise-Fallen" (MF) insect traps. In addition, we looked for the same pesticides in 3 buffer areas (belonging to, or bordering, nature reserves) where agricultural activities are allowed, and 5 reference areas, located more than 2 km from arable farming fields. The reference areas were selected on basis of their larger distance to arable farming fields. In the reference areas no MF insect traps were present. The buffer areas were locations with insect traps, but outside nature reserves, or within nature reserves but under agricultural management. All samples were taken in the autumn of the year 2019 from 5/11/2019 until 4/12/2019.

In total we found 53 different pesticides, including biocides and metabolites, in the vegetation and soil inside the nature reserves at the locations of the Malaise insect traps (called MF in the text), 15 in reference areas and 66 in buffer areas. Since many pesticides were found in all areas, the total number of different pesticides amounted to only 94, of which (at 1/12/2019) 60 are admitted for use by law. Inside the nature reserves in total 15 insecticides (including metabolites and isomers) were found, in the reference areas 5 and in the buffer areas also

15. In the vegetation of the reference areas the average total concentration of pesticides was 44.4% lower (28.41 µg/kg dry matter instead of 51.13 inside the nature reserves) and the number of found pesticides per sample was 34.3% lower than in the samples of nature reserves (5.0 instead of 7.6 pesticides per sample). A handful of them may originate from non-agricultural sources, such as industry, households and exhaustion gases (diphenyl, anthraquinone, phenylphenol-2 and diphenylamine). All the other 90 compounds are exclusively used in agriculture, or are metabolites, or isomers from pesticides used in agriculture. It will be useful to determine the origin of diphenyl and anthraquinone, which are in this study responsible for 33.3% of the amount of pesticides in wild plants and for 61.2% of pesticides in the soil. The amount of these compounds from non-agricultural origin represent 44.7% of the quantity found in the vegetation of nature reserves. However, due to a large variation of measured values and a relative low number of the investigated reference locations, the differences between the found pesticides in the reference areas and the nature reserves are not statistically significant.

Since only the pesticide load of selected substrates was determined at one point in time - no direct correlation is possible with the measured decline of the insect biomass in the time-line of the data in Hallmann et al. (2017). Because no historical data are available on the pesticide contamination of these insect trapping locations, our measured values provide first indications of the potential contribution of pesticides to the proven decline of insects inside of nature protected areas in Germany. Due to the large number of 53 different pesticides found in different nature reserves, with a wide range of various properties, it is in any case very complicated to link the effects of all these different compounds with the development of the entomofauna.

In this research a toxicological literature investigation has been made of the compounds that have been found, i.e. their mode of action, the time dependency of their effects and various other aspects that play a role in nature. The conclusion is that the integral assessment of the effects of pesticides on the entomofauna is at present not possible. Many official data are likely to underestimate the potential effects, because of 12 reasons, which are discussed in this study (Chapter 5.8). The underestimations of toxicity in case of pesticides with dose-time dependent action can easily amount to thousands of times. Examples are neonicotinoids and some pyrethroid insecticides but can be extended to fungicides and herbicides found often in this research. The effects of neonicotinoids are even reinforced by time. In the present admission procedures for pesticides in the EU, determination of time dependency is not required, so the information about this aspect is rare. The relative impact (harmfulness) of all the

94 pesticides found in this study for the entomofauna is so far completely unknown. It might even be that each of them has only a small effect and that the major effect is related to the whole of the cocktails found. In this context it needs to be noticed that although in this research the presence of many pesticides (and some metabolites) has been tested, there are still many pesticides that were not included in this research. Finally, pesticides and metabolites that were in the nature reserves but, due to limitations in the analysis technique, could not be measured might also contribute to the toxic effects on the entomofauna.

In short, there can be no certainty that the 94 pesticides found do not harm nature and its biodiversity. The ecotoxicological threshold value LR50 is known for only four out of the found 22 insecticides. The four insecticides of which the LR50 is available, almost certainly have (in the concentrations in which they were found) a serious impact on the entomofauna. Therefore, there can be no certainty that the other 18 insecticides found have less impact. There are sufficient reasons to assume that all insecticides (and other pesticides found) play an important role in the insect decline. Therefore, steps should be taken to prevent them from contaminating nature reserves even further. Although in this research the compounds from non-agricultural origin contribute substantially to the quantity found in the vegetation in nature reserves, in terms of toxic potential the few data available about the toxicity of these compounds indicate that they are probably less toxic than most of the other pesticides found. More research can help to solve various urgent questions, but research should not be a pretext in order to postpone measures against contamination of nature reserves with all the 94 pesticides found. A number of recommendations for policy makers have been presented in this study.

The primary aim of this study was to investigate the presence of pesticides in nature reserves, buffer areas and reference areas. It was not the aim to determine the spatial origin of the pesticides found, although it is a very important question. The methodology of this study did not allow us to establish correlations between on one hand the pesticides found, their concentrations in soil and vegetation and on the other hand the insect decline. Further research of causal relationships between insect decline and presence of pesticides should be an important next step.

# List of abbreviations and terms

| Abbreviation or term | Meaning |
|---|---|
| AA-EQS | Average annual environmental quality standard for surface water |
| Accumulating effect of compounds | Compounds that cause irreversible accumulating damage in living organisms (also at very low concentrations) |
| Accumulating compounds | Compounds that are accumulating in living organism by metabolic processes |
| ADI | Acceptable Daily Intake |
| AMPA | Abbreviation of name of metabolite of glyphosate (aminomethylphosphonic acid) |
| Ar | *Aphidus rhopalosiphi* (parasitic wasp) |
| Buffer zone | Areas without status of nature reserve or agriculturally used soils within nature reserves |
| BVL | German Federal Office of Consumer Protection and Food Safety |
| CAS number | Unique numerical identifier assigned by the Chemical Abstracts Service (CAS) to every chemical substance described in the open scientific literature |
| cm | Centimetre |
| CTGB | Dutch Board for the Authorisation of Plant Protection Products and Biocides |
| DDD | Dichlorodiphenyldichloroethane |
| DDE | Dichlorodiphenyldichloroethylene |
| DDT | Dichlorodiphenyltrichloroethane |
| DM | Dry matter |
| Dose-time-effect relationship | Relation between the combination of dose, exposure time and effect of compounds on living organisms |
| DT | Degradation time (time in which pesticides under defined conditions are converted into metabolites) |
| DT50 | Degradation time in which under defined conditions half of the original compound has turned into metabolites |

| Abbreviation or term | Meaning |
|---|---|
| DT90 | Degradation time in which under defined conditions 90% of the original compound has turned into metabolites |
| EFSA | European Food Safety Authority |
| EPA | Environmental Protection Agency (US) |
| EQS | Environmental Quality Standard |
| EU | European Union |
| EVK | Entomological Society Krefeld (Entomologischer Verein Krefeld) |
| Exposure time | Duration of the exposure of an organism to a certain chemical |
| g | Gram |
| GC | Gas chromatography |
| GPS | Global Positioning System |
| ha | Hectares |
| HCH | Hexachlorocyclohexane |
| HQ | Hazard quotient; compares measured values with an environmental quality standard/toxicological threshold value |
| Isomer | One of two or more compounds, radicals, or ions that contain the same number of atoms of the same elements but differ in structural arrangement and properties |
| IUPAC | International Union of Pure and Applied Chemistry |
| kg | Kilogram |
| km | Kilometre |
| l | Litre |
| LC | Liquid chromatography |
| LC50 | Lethal concentration: Concentration of a substance in soil, water or air killing 50% of the population of test organisms within 496 hours in mg/kg, mg/l or mg/m$^3$ |
| LD50 | Lethal dose: Dose of a substance killing 50% of the population of test organisms within 4-96 hours in mg/kg bodyweight |
| LOD | Limit of detection |
| LR50 | Lethal rate of a substance (in g/ha) that causes 50% mortality of terrestrial test organisms within 48 or 72 hours |
| Metabolite | Conversion product of pesticides or other chemicals |

| Abbreviation or term | Meaning |
|---|---|
| MF | Malaise-Fallen (Malaise insect traps for catching flying insects) |
| µg | Microgram; one millionth part of a gram |
| mg | Milligram |
| ml | Millilitre |
| mm | Millimetre |
| Mode of action (MOA) | Mechanism by which a substance performs its main function |
| mPa | Millipascal; one thousandth part of one Pascal, which is the SI unit of pressure, equal to one newton per square metre |
| MS | Mass spectrophotometry |
| MRL | Maximum residue limit |
| ng | Nanogram |
| NOAEL | No observed adverse effect concentration |
| NOEC | No observed effect concentration |
| PAN | Pesticide Action Network |
| Pesticide | Active ingredient of a crop protection agent, biocides, and their metabolites |
| pg | Picogram |
| Receptor binding | Binding to a functional organic macromolecule referred to as a specific receptor, in a bimolecular reaction |
| Reference zone | Areas located relatively far from arable farming |
| SFD | Soil Framework Directive |
| Tp | *Typhlodromus pyri* (predatory mite) |
| TU | Toxic unit |
| Vapour pressure | Pressure exerted by a vapor |
| WFD | Water Framework Directive |
| WHO | World Health Organisation |

# INTRODUCTION

## CHAPTER 1

# Introduction

In recent years, several studies have been published about unprecedented declines of insect populations and bird populations in Europe. From 1989 until 2016 a severe decline of flying insects by 76% was measured in 63 nature conservation areas in Germany (Hallmann, 2019; Hallmann et al., 2018). The decline of many insect and bird species has a yearly rate of several percent per year (either measured as biomass, or as population densities) and can be characterized, not only as decline of two important groups of organisms, but as a gradual degradation of the whole ecosystem. This is also demonstrated by the decline of plant species that are dependent on insect pollinators (Biesmeijer et al., 2006).

Pesticide contamination is widely discussed in society in general and in nature protection groups in particular. The contamination of nature is, as a rule, denied especially for nature protected areas and if the contamination is proven, its effects are trivialized. Therefore, we hope that the associated stakeholders (authorities, scientists, conservationists, and industry) will show a joint interest in establishing the hard facts in this sphere. Many factors (like climate change, exhaustion gases, industrial chemicals, etc.) can be blamed for the insect decline. Geiger et al. (2010) identified by statistical analyses that fungicides and insecticides were the strongest factors in biodiversity decline. In the context of this study only the potential relation with pesticide contamination will be elaborated.

It needs to be said that the measuring accuracy of the chemical analyses used in this research is higher than usual in current research, but are still not high enough to measure for insects potentially negatively influencing low concentrations (less than 1 µg/kg) of certain pesticides in the field. In the case of such pesticides (like pyrethroids, neonicotinoids, etc.) nature might be negatively influenced with respect to certain insect taxa, without us being able to measure anything with standard measuring protocols. More sensitive measuring methods for the affordable screening of large packages of pesticides were, however, not available to us during this research.

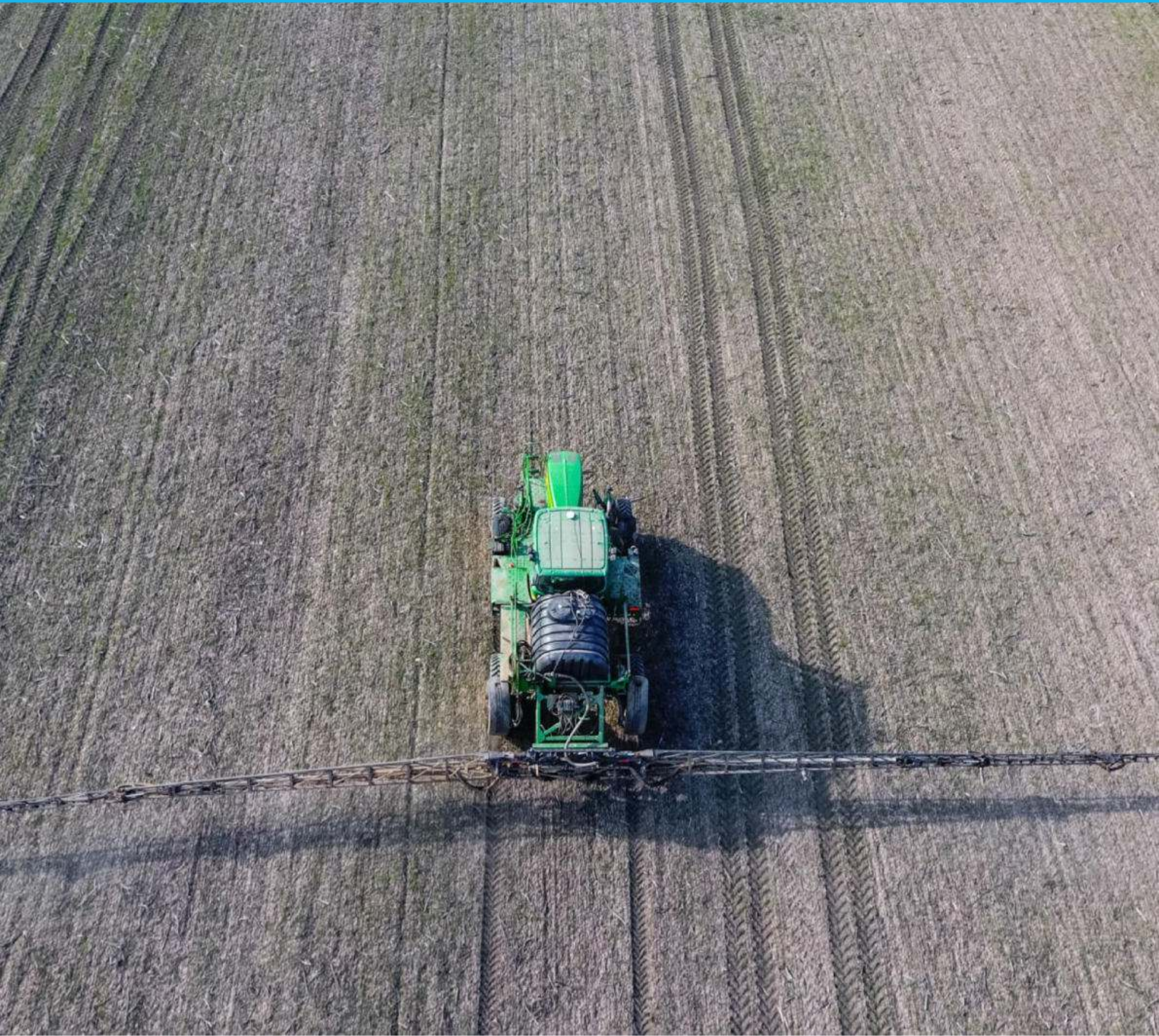
Due to the worrying results of Malaise insect traps measurements in German nature reserves, this research was started to establish the insecticide (and other pesticides) contamination of the nature reserves. In this context it needs to be said that pesticides are not the only chemicals that might influence insect populations, but they are good candidates because they are specifically designed to kill insects (i.e. insecticides) or their host plants (i.e. herbicides).

There is little information about the distribution of pesticides in nature reserves because there is no regular monitoring of the soil, vegetation, or animals. Regular monitoring of pesticides only occurs in surface water. Therefore, it was decided to investigate the pesticide contamination of nature reserves by analyses of plant and soil samples from those nature reserves. Ideally spoken, in such a research insect biomass measurements and sample taking of soil and vegetation should be done in the same year and during different seasons. In this research that was not possible, because the MF biomass measurements had been done during the past for 27 years. A similar research was conducted simultaneously in nature reserves in the province of Gelderland (in the Netherlands). This province is bordering North Rhine-Westphalia. The results can be found in Buijs & Mantingh (2020).

After obtaining data of the pesticide contamination of nature reserves, it will be a logical step to design experiments in order to determine the origin of all pesticides and the potential causal relationships between the cocktails of pesticides found in nature reserves and the effects on insect populations. In this research it was for practical reasons not possible to carry out research into causal relationships, but indications are given which factors should be focused on in such future research. Of special interest in that context are the pesticides with irreversible receptor binding in the target organism. Those compounds have an accumulative effect on living organisms but do not necessarily accumulate themselves in the tissues (as was the case with DDT). It is now generally accepted that neonicotinoid insecticides have irreversible receptor binding, whereas most researchers do not understand their cumulative effects. Strikingly enough, the property of (ir)reversibility of receptor binding is unknown for almost all pesticides, since determination of this property is not part of the admission procedures of new pesticides in the EU, or anywhere else on earth (Tennekes & Sanchez-Bayo 2020). In addition, the cocktail effect of more than one pesticide in the same organism is poorly understood. After obtaining data about the contamination of nature with pesticides, it is of utmost importance to carry out in vitro and in vivo experiments to establish causal relationships and time dependency of the effects. Testing toxicological effects with computer models doesn’t replace empirical testing, because no computer can predict the toxicological behaviour of chemicals in thousands of organisms present in the biosphere at a defined point. According to the results of Malaise insect traps, we now know, that the number of species of flying insects in one season reach several thousand species in a single Malaise insect trap result (Sorg et al. 2019).

# OBJECTIVES, TIME PERIOD & HYPOTHESIS

## of the research



## CHAPTER 2

# Objectives of the research and period in which it was carried out

The objectives of the research were:

- to get understanding of the presence of pesticides in nature reserves
- to get understanding of influence of pesticides on insect populations by evaluation of the properties of the found pesticides.

The research was carried out from 20/9/2019 until 1/12/2020.

## CHAPTER 3

# Hypothesis of the research

The hypothesis of this research is that:

- pesticides can be found in vegetation and soil inside nature reserves
- pesticides in the environment have influence on insect declines inside nature reserves.

# METHODOLOGY

## of the research

## CHAPTER 4

# Methodology

## 4.1 Selection of nature reserves and reference areas

For the analysis of the potential pesticide contamination three types of sampling locations were identified:

1. **Nature reserves**: Protected areas with no agricultural activities at the sampling locations and where measurements of Malaise insect traps (abbreviated as MF) would be (or become) available
2. **Buffer areas**: Locations classified as nature reserves, or bordering nature reserves, with Malaise insect traps, but with agricultural activities
3. **Reference or control areas**: Forested areas located at least at 2 km distance from arable fields, without Malaise insect traps installed

In order to take samples of vegetation and soil, 12 locations were selected from the earlier MF biomass measurements, as published in Hallmann (2019). Eight additional locations were chosen from more recently (after 2016) started MF locations of the EVK, in order to get newer biomass measurement data, that would better correspond with the 2019 chemical analyses of the soil and vegetation. These 22 selected locations belonged to 15 different nature reserves. In five nature reserves two locations were sampled and in one reserve three. Permissions to sample all the areas were requested and obtained from the local nature conservation authority ‘Untere Naturschutzbehörde’, or other responsible authorities and organisations, in written form in the autumn of 2019.

In the second category of areas, the buffer areas, five sampling points (located in, or near to, three different nature reserves) were selected. In, or near them, agricultural activities took place. Prior analyses indicated that the average distance from arable farming fields of the locations as published in Hallmann (2019) was less than 200 m. That relatively small distance implies that all those nature reserves are substantially exposed to pesticides’ drift coming from arable farming and that this distance is within the daily activity radius of many flying insects. In order to understand the ‘background’ exposure of more isolated areas to pesticides, 5 reference locations at 2-5 km distance from the nearest arable fields were chosen as well. They were covered by forest. The consequence of this choice was however that no MF measurements were available of those locations. In Table 1 the numbers and types of selected areas are indicated.

Table 1. Types of areas chosen for sampling of soil and vegetation for pesticides analysis

| Number and type of selected reserves | Number of selected locations for sampling | MF biomass measurements done or ongoing |
|---|---|---|
| 15 nature reserves | 22 | Yes |
| 3 buffer areas with agricultural activities | 5 | Yes |
| 5 reference sites in > 2 km distance from arable fields | 5 | No |
| **Total** | **32** | |

All locations of the selected areas are indicated in Figure 1.

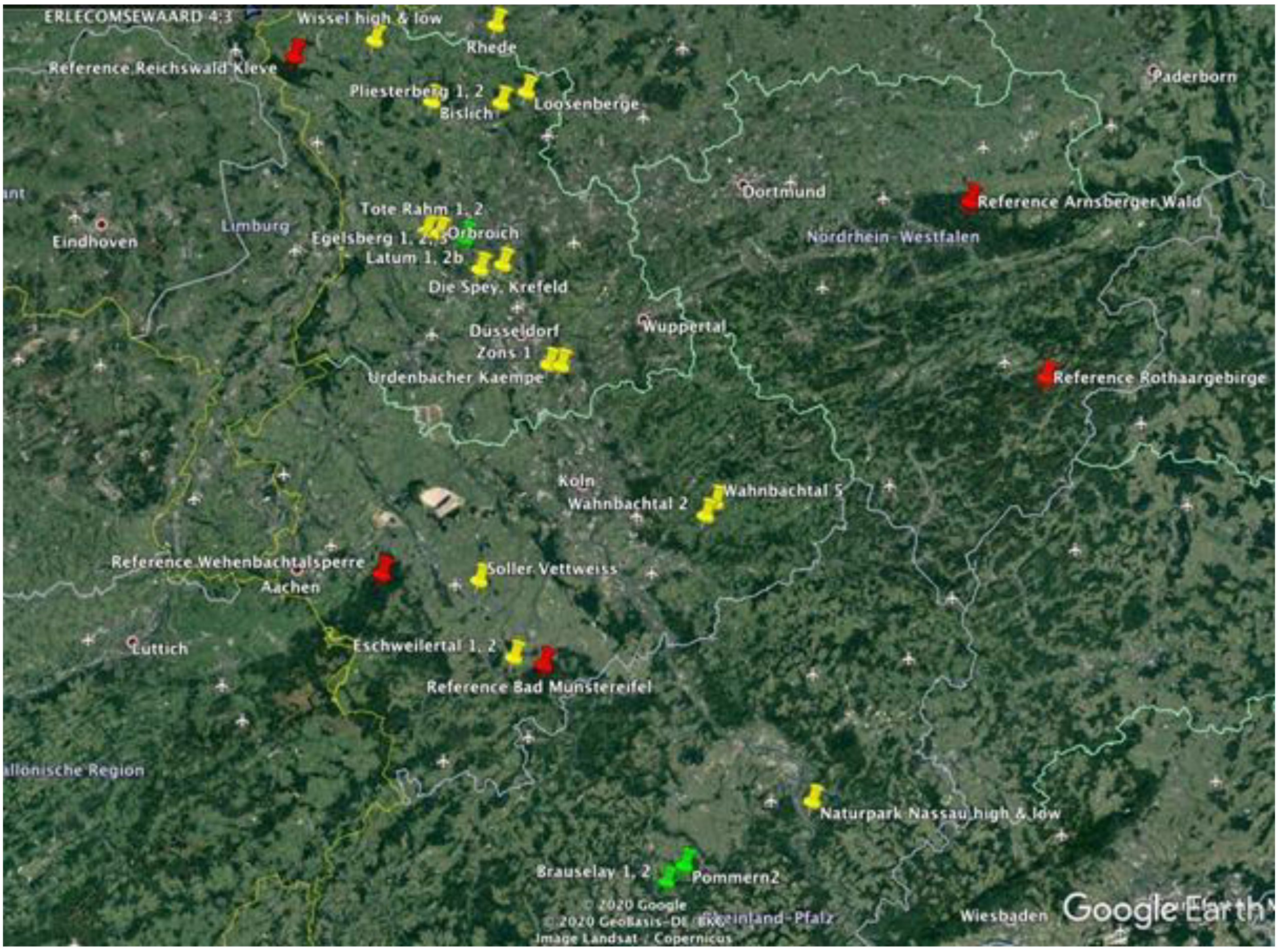


Figure 1. Locations of sampled nature reserves (yellow), buffer areas (green) and reference areas (red) in North Rhine-Westphalia and Rhineland Palatinate, Germany

Locations in nature reserves are located in the Rhine valley, the reference areas in larger units of forest and the buffer areas in the Mosel valley and near Krefeld. Exact locations (as GPS coordinates) are given in Appendix 7.

## 4.2 Selection of matrices to be sampled

To understand the contamination of nature with pesticides, there were several options for matrices to be sampled.

- Soil
- Vegetation
- Water
- Animal excrements

It was foreseen that the focus of sample taking would be on soil and vegetation because these are available everywhere. Water composition in the neighbourhood of sampling sites does not necessarily reflect long-term tendencies in the environment and bodies of water are not present in every location. Therefore, it was decided not to take surface water samples. In addition, the presence of animal excrements within the planned distance of 20 m from sampling sites is logically spoken dependent on sheer chance. It was decided to take samples in case they would be present.

## 4.3 Navigation

The coordinates of the MF were obtained from the EVK in digital form. These areas were visited and with help of a Garmin Etrex30 navigator the locations where the MF were standing, or had been standing, were found. In case of the Reference areas, open spots that had been earlier identified were also found in the same way. The sampling spot was then stored in the memory of the Garmin navigator.

## 4.4 Sampling protocol

At the 32 chosen locations (see Table 1) 43 samples were taken manually from the vegetation and 32 from the soil. In total 7 samples were taken from animal excrements. The full protocol can be found in Appendix 3.

### 4.4.1 Soil

The soil samples were taken with a metal auger of 50 mm diameter and sampling section of 18 cm. The auger is shown in Figure 2. This was done in the following way: With a measuring tape a distance of 20 m was indicated from the MF spot. Within this distance, around the MF spot 25 sub-samples were taken onto a depth of 18 cm. The samples were evenly spread across this circle of 20 m from the MF, as far as possible. On some places within this circle there were inaccessible places, like water, rocks, and dense bushes. The 25 sub-samples were put into a galvanized bucket and thoroughly mixed with a galvanized small spade. With the mixed sample two plasticised paper bags (provided by the laboratory) were filled with around 1 kg of soil. The small remaining part (as a rule less than 500 g) was not used.

Figure 2. Sampling auger used to take soil samples

### 4.4.2 Vegetation

Within the earlier mentioned distance of 20 m from all MF locations also vegetation samples were taken. Within this circle 25 sub-samples of the vegetation were taken with garden sheers and put into a transparent plastic bag of 30 litres (that were as well provided by the laboratory). At all MF locations the vegetation was different. Therefore, there was no option to choose one and the same plant for sample taking. For each location one of the dominant plant/vegetation types was chosen. For the matter of comparability, identical plants were, as far as possible, sampled at more than one location. In some locations twigs of trees were sampled with clean pruning shears. The total fresh weight of the plant/vegetation samples varied from 500 g to 1000 g. Due to the susceptibility of the chemical LC/GC analyses no use was made of any synthetic tools for handling the samples. No gloves were used either, in order to avoid contamination with unknown chemical compounds. After taking samples hands and tools were cleaned only with tap water from Bennekom (in the Netherlands).

### 4.4.3 Animal excrements

At 7 MF locations, animal excrements were found. Since the research team has extensive experience with manure analyses of farm animals, it was decided to take samples of that manure as well. Grazing animals collect specific parts of the vegetation thus showing the general contamination of the vegetation, possibly reflecting the state of the environment (the content of specific pesticides) better than individual plants. However, certain pesticides are inside organisms converted into metabolites of which the majority is not measured. Many pesticides and their metabolites can also be excreted via urine. So far available, the droppings of rabbits were collected from at least 20 spots, the excrements of roe deer and red deer were collected so far available from more than 10 spots. The samples of the animal excrements were put into plasticised paper bags (provided by the laboratory).

## 4.5 Storage of samples

Straight after taking the samples, they were stored for 1-3 days in a ski box on top of the car. Due to modest autumn temperatures, the condition of the samples stayed good. The maximum day temperature varied from 5 till 16°C and the minimal night temperature from +9°C till -4°C. After each field trip, the soil samples were all placed in the freezer (BEKO freezer) at -18°C and the vegetation samples were stored at +5°C. The next day they were brought to the storage of the laboratory and put into a storage room at -18°C. Freeze-dried and milled plant samples that were not needed for chemical analysis were stored for eventual later genetic research of their composition. During sampling there was not sufficient time to determine the exact botanic composition of the vegetation. Unprocessed duplicate soil samples were stored at -18°C for eventual future use in case this would become important for the interpretation of the research results and for eventual second measurements of the same sample.

## 4.6 Preparation and analyses of samples by the laboratory

All samples (vegetation, soil, and animal excrements) were freeze-dried and milled, and with the obtained data the moisture content could be determined. All vegetation samples were analysed according a fixed multi-test protocol (Appendix 1) for 661 different pesticides, including some biocides and metabolites (see Appendix 2), making use of the GC + MSMS of Agilent and LC of Agilent combined with the MSMS of Sciex. In addition, the soil samples were also analysed for glyphosate, AMPA and glufosinate. In case of the soil, therefore the total number of analysed compounds amounted 664 (661+3). The freeze-dried and milled samples were extracted with a mixture of three solvents: Acetone, petroleum-ether and dichloromethane. Four salts were used in the extraction: Sodium citrate (15.4%[1]), Sodium hydrogen citrate sesquihydrate (7.7%[1]), Magnesium sulphate (61.5%[1]) and Sodium chloride (15.4%[1]). Extraction was executed for 15 minutes while being mixed at 640 RPM and 10 minutes centrifugation at a Relative Centrifugal Force (RCF) of 17.105xg. Depending on the substance and matrix the Limit Of Quantification (LOQ) ranged from 0.6 µg/kg fresh sample to 2.4 µg/kg. The LOQ of the measurements of fresh vegetation varied from 0.6-3.0 µg/kg. Lower concentrations, above the limit of detection, were also detected, but with a non-specified probability interval of confidence. The 90% confidence interval of all measurements above the LOQ was 0.5 times the measured value up to 1.5 times the % measured value. The list of all pesticides, biocides, and metabolites, analysed by GC/MSMS and LC/MSMS, can be found in Appendix 2 of this report. In Appendix 5 the LOQ of the found pesticides in each sample is indicated. The list of analysed pesticides contains pesticides that can be extracted with the same extraction procedure and the same solvents. Those that require other procedures were not included in this research. In addition, the large majority of metabolites are not included in routine

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[1] weight percentages

multi-test protocols. That is the reason why in this study only few metabolites were tested for.

The analyses were performed under the conditions available to the certified laboratory and according to the techniques and methods developed by the laboratory at the time of execution. Although many compounds (661) were measured in this study, various widely used pesticides could not be included in the measuring program. This was decided on the basis of cost grounds. Also, due to the nature of the samples (soil / vegetation / manure), and the concentration step for achieving the intended limit of quantification (LOQ) in this project, there is a possibility of various disturbances being recorded. As a result, the quality cannot be guaranteed for certain compounds and depends on the matrix. As a result, there is an increased limit of quantification (LOQ) for those compounds. There are also numerous conversion products (degradation products, esters, conjugates, etc.) for each of the measured pesticides, for which no standard measuring procedures exist. As a rule, these conversion products have not been analysed either. Measurements of most of these conversion products are not offered by any laboratory.

## 4.7 Botanic composition of vegetation

Ideally spoken it would have been desirable to determine the botanic composition of the samples taken. This is however quite complicated for vegetative grasses and in addition there is always the risk of contamination (with pesticides or biocides) while doing this. To identify plant species, the vegetation samples have to be spread out and the use of synthetic surfaces unavoidably leads to contamination with compounds from the plastics and possibly from the air. It was decided to store a part of the freeze-dried samples for DNA analyses for future use, in case it will be required for later species identification.

## 4.8 Investigation of pesticide properties

In the literature countless properties and effects of every pesticide can be found. Within the limited scope of this research, it was not possible to investigate in literature properties of every pesticide found individually. Therefore, use was made of the Pesticide Properties database of IUPAC and PAN Pesticide Database-Chemicals, which contain information about all the active ingredients on the European market and contains also information about active ingredients that have been used in the past on the European market. In this and other databases pesticides are classified into insecticides, herbicides, fungicides, acaricides etc. Also, this classification is widely used by the general public. Selected relevant information about the found pesticides has been summarized into Appendix 4. In that table the following information can be found:

- Name of compound (in English)
- Type and compound group of pesticides to which it belongs
- International identification number (CAS)
- Vapor pressure (as measure of the sublimation/evaporation tendency)
- DT50 or DT90 as measure of the time needed to convert 50, or 90% of the parent substance into metabolites
- LR50 lethal rate per hectare (expressed in g/ha) for certain organisms at which 50% of the test organisms die
- Human health issues according to IUPAC and according to PAN, such as genotoxicity, carcinogenicity, reproduction and development effects, neurotoxicity, or endocrine disrupting properties
- Environmental quality standard (EQS) for surface water

## 4.9 Interpretation of insect biomass measurements

For the interpretation of insect biomass measurements, it would be important to understand whether areas that are more contaminated with pesticides show a greater decline of insect biomass or diversity. Because of methodological reasons for such an investigation a large number of relatively homogeneous nature conservation areas with comparable vegetation and conditions should have been selected. In addition, measurements during longer periods of time might have provided useful information. In this research however it was only possible to investigate a variety of different nature protected areas within one-month time to get a more general impression of pesticide contamination. That is one of the reasons why we could not investigate the influence of the found pesticide contamination on the insect biomass data.

## 4.10 Toxicological parameters used

For the investigation of effects of mixtures of pesticides, it is general practice in toxicology to add up toxic effects of different compounds by using so called ‘Toxic Units’ (TU’s). In ecotoxicology the No Observed Effect Concentration (NOEC), the median Lethal Dose (LD50) or median Lethal Concentration (LC50) are the standard toxicity measurements derived from laboratory experiments. Any of these values can be used as TU to calculate and compare toxic effects of mixtures. This sounds logic, but there are many reasons for not following this approach:

- The synergistic and antagonistic effects of the different pesticides in the found cocktails cannot be accurately predicted on the basis of present theory (Zhu et al., 2014)
- The LD50 or LC50 for non-target invertebrate terrestrial organisms is mostly limited to the pollinators (honeybees and bumblebees) and earthworms (*Eisenia fetida*) and in IUPAC not available for other non-target insects
- The toxicity of all compounds found for the specific insect taxa caught in the MF is completely unknown
- Various researches show that stress factors can increase in vivo susceptibility of organisms by a factor varying between 10 and 1000, especially in case of nutrient stress (Barmentlo et al., 2019)
- Time dependence of the effect of almost all pesticides is unknown. The LD50 and LC50 values are calculated after an exposure time of at maximum 72 hours, depending on the species. Hence chronic effects of the active substance on the life cycle /reproduction have been neglected until very recently. Published toxicity data in databases do not contain information about chronic effects or time dependency of toxic effects. This information is available only for a few compounds in the current literature (Tennekes & Sanchez-Bayo, 2013). For example, for imidacloprid the toxic effect of a 1000 times lower concentration on arthropods can be exactly the same after a few more days exposure to this chemical (Tennekes, 2010). This means that the toxic effect of a very low concentration after a longer exposure can be the same as the effect of a high concentration after a short exposure

In addition to the earlier mentioned toxicological parameters, the toxicity parameter LR50 can be used as a measure for toxicity for terrestrial arthropods, which is the quantity of a substance in g/ha by which half of the exposed population dies. Although the LR50 offers at least a connection with one or two species of terrestrial arthropods, it does not give any information about sub-lethal effects nor about the effects of long-term exposure. In addition to the LR50, the Environmental Quality Standard (AA-EQS) for aquatic organisms could be used as a measure of toxicity to insects that live a part of their life cycle in water. In this research, however, no pesticide concentrations were measured in water. The AA-EQS is based on the EU Water Framework Directive and on national regulations. The AA-EQS is supposed to protect all sections of the aquatic food chain. Generally accepted comparable toxicity parameters for insects on plants do not exist.

In this research the found pesticides were divided into the earlier mentioned categories of fungicides, herbicides, and insecticides, of which insecticides are the most likely compounds to affect non-target insects. Since the absence of trustworthy real-life data about individual active ingredients and cocktail toxicity, we choose the option to add up the concentrations of the pesticides found, expressed just as µg/kg dry matter. It would have been more correct to add them up taking into account their individual contribution to cocktail toxicity for relevant insects. Such an approach was however not possible.

## 4.11 Statistical analyses

Statistical analysis was conducted with the two-tailed non-parametric Mann–Whitney–Wilcoxon U Test for testing whether two groups of observations differ statistically significant from each other.

# RESULTS

## of the research

## CHAPTER 5

# Results

## 5.1 Characteristics of the 32 sampled locations

### 5.1.1 Location in relation to agricultural fields

The majority of the MF was placed in nature reserves and a few near to nature reserves. The sizes of the nature reserves differed from 0.5 ha up to 500 ha or more. In some of the larger nature reserves more than one MF had been placed by the EVK to study the influence of neighbouring agricultural fields. In eight reserves samples were taken at more than one location. The other investigated areas with MF are the buffer areas, located near to nature reserves. Formally two locations in the Egelsberg reserve are located inside the nature conservation area of Egelsberg but planted with agricultural crops (winter wheat sown with seeds treated with fungicides). The other buffer zone locations are Brauselay1, Brauselay2 and Pommern2, located along the Mosel river. Due to the agricultural management (including fungicides and manure applications), and their close proximity to protected nature reserves, they were put into the category of buffer areas. The reference sites were located at 3-5 km distance from the nearest arable fields. In Table 2 the number of locations of the various areas is given and their distance to arable farming fields.

Table 2. Number of locations of different categories of areas and their estimated distance to closest arable farming fields

| Type of location | Number of selected locations for sampling | Estimated distance to nearest arable field (in m)** |
|---|---|---|
| Nature reserves with MF | 22 | 143 |
| Buffer areas* with MF | 5 | 54 |
| Reference sites without MF | 5 | 3268 |
| **Total** | **32** | |

* including Egelsberg1 and Egelsberg2

** according to Google Earth Maps of 2018

The largest distance between two locations was 190 km between nature reserve Wissel (in the north of Nordrhein-Westfalen) and the buffer zone Brauselay (in the Mosel valley of Rheinland Palatinate).

### 5.1.2 Vegetation

The vegetation of all sampled locations in nature reserves, buffer areas and reference areas has been characterized in Table 3.

Table 3. The dominant type of vegetation of sampled locations

| Dominating vegetation | Number of locations | Code of location (see Figure 1 for location) |
|---|---|---|
| Bushes, trees | 7 | Pliesterberg1, Pliesterberg2, Eschweiler1, Eschweiler2, Arnsberger Wald, Soller-Vettweiß, Orbroich |
| Grass and/or herbs | 20 | Reichswald Kleve, Rothaargebirge, Egelsberg3, Zons, Tote Rahm1, Tote Rahm2, Latum1, Latum2b, Urdenbacher Kaempe, Wehenbachtalsperre, Bad Muenstereifel, Brauselay1, Brauselay2, Pommern, Wissel up-hill, Naturpark Nassau down-hill, Wahnbachtal2, Spey Krefeld, Loosenberge, Bislich |
| Grass | 3 | Naturpark Nassau up-hill, Wissel down-hill, Wahnbachtal5 |
| Agricultural crop | 2 | Egelsberg1, Egelsberg2 |
| **Total** | **32** | |

It was the aim to take samples of a component of the dominating vegetation, because in that case the measured values have a clear relation to a specific plant species. In pastures without a clear dominating component, the whole vegetation was sampled. Information about the type of vegetation sampled in the locations can be found in Appendix 7. Freeze-dried and milled plant samples were stored for eventual later genetic research of their composition.

Figure 3. Arnsberger Wald (Kreis Soest) forested reference area sampled at 21/11/2019 (beech leaves and soil)

### 5.1.3 Soil type

In Table 4, the dominant soil type is indicated for different locations. If in the future, soil properties will become of decisive importance for the interpretation of the research results, stored duplicated samples at -18°C can be used to determine additional parameters (as mentioned under 4.5).

Table 4. The dominant type of soil of all sampled (MF, buffer zone and reference) locations

| Soil type | Number of locations | Code of location |
|---|---|---|
| Sand | 9 | Loosenberge, Pliesterberg1, Pliesterberg2, Egelsberg1, Egelsberg2, Egelsberg3, Zons, Wissel up-hill, Wissel down-hill |
| Loam | 16 | Reichswald Kleve, Latumer Bruch Nr1, Soller Vettweiß, Eschweiler1, Eschweiler2, Bad Münstereifel, Wahnbachtal5, Brauselay1, Brauselay2, Pommern, Naturpark Nassau up-hill, Naturpark Nassau down-hill, Orbroich, Arnsberger Wald, Rothaarkamm (Latrop), Wehenbachtalsperre |
| Swamp | 4 | Tote Rahm1, Tote Rahm2, Wahnbachtal2, Latumer Bruch2b |
| Clay | 3 | Krefeld Spey, Bislich, Urdenbacher Kämpe |
| **Total** | **32** | |

Most of the locations (16) had loam soil, 9 sand soil, 3 river clay and 4 swampy soils with peat.

Figure 4. Transect of Malaise insect traps at Egelsberg (Kreis Krefeld) at 7/11/2019 with in front natural vegetation and on the background winter wheat fields located inside nature reserve on pure sand soil with gravel

### 5.1.4 Sampling dates

All samples were taken from 5/11/2019 until 4/12/2019. All sampling dates can be found in Appendix 5 as last part of the code of each sample.

### 5.1.5 Weather during sampling

Dry weather dominated during sampling. Even the swamps were relatively dry at the moment of sampling. No strong storms occurred in the autumn of 2019. Weather data have not been collected in the context of this study, but without doubt have influence on sublimation/evaporation and transport of pesticides through the atmosphere and runoff into neighbouring areas.

### 5.1.6 Other human activities than agriculture in the neighbourhood

Close to many nature reserves there are often industrial activities and always roads within a few kilometres distance. In certain cases, industries also use certain chemicals belonging to the category of pesticides for their production processes, for instance biocides, fungicides and insecticides used to preserve food stuffs in storage facilities, or herbicides in weed control in gardens and parks. Also, these can be transported to nature reserves, by the wind or by water. In addition, most nature reserves are accessible to walkers and bikers with dogs. Dogs are often treated with insecticides, like permethrin, fipronil or imidacloprid against ticks and flees. Pesticides were (and are) used in forestry of which residues may remain. Today, specific insecticides are still allowed for use in forestry, for instance in order to control *Ips typographus* (a bark beetle) in spruce trees. In river flood plains pesticides can be deposited during periods of flooding, together with the sediments. Some nature reserves are grazed by sheep or cows that may be treated with insecticides against insects.

### 5.1.7 General observations during sampling

In general, we have seen in many nature reserves stinging nettles and blackberry, presumably a sign of high nitrogen deposition from the neighbouring communities. In addition, it was observed that almost no beard mosses (lichen) were present on the trees in the reserves, which are considered as indicators of good air quality. In many areas recreating people are allowed access with pets, or without pets. The general attitude towards nature seems positive and very little waste was met during the visits. Most local people were aware of the problems with declining insect populations and are concerned about it.

## 5.2 Results of the pesticide analysis

In this research in total 94 different pesticides (including biocides and metabolites) have been found in the three types of areas investigated. Inside the 15 nature reserves (within 20 meters from the Malaise insect traps) 53 different pesticides were found, 15 in the 5 reference areas and 66 in the 3 buffer areas.

For processing of the analysis data obtained, the found pesticides have been subdivided into their functional groups. In the databases most pesticides have been subdivided into one (or more) of those groups (this means that a substance has been defined as insecticide, fungicide, herbicide, or others). However, there are compounds that are difficult to classify. Some compounds have multi-acting properties for example the found substance diphenylamine is acting as a fungicide, plant growth regulator, and as an insecticide. In this report diphenylamine was considered as an insecticide. Because the target organisms of acaricides are more or less comparable with those of insecticides, the two found acaricides were considered as insecticides. According to the databases, the compound anthraquinone is a repellent (against birds). It has been reported as a separate category of repellents. The results can be summarized as follows, as shown in Table 5.

Table 5. Total number of pesticides found in the three different types of areas of this study (subdivided into fungicides, herbicides and insecticides) in vegetation, soil and animal excretions

| Type of area | Number of sampled locations | Number of pesticides* found | Number of fungicides* found | Number of herbicides* found | Number of insecticides* found | Number of repellents found |
|---|---|---|---|---|---|---|
| 15 nature reserves with MF | 22 | 53 | 23 | 14 | 15 | 1 |
| 5 reference areas | 5 | 15 | 5 | 4 | 5 | 1 |
| 3 buffer areas with MF | 5 | 66 | 41 | 9 | 15 | 1 |
| **Total** | **32** | **94**** | **49**** | **17**** | **28**** | **1** |

* including metabolites of those group*   s

** in the 3 types of areas partly the same compounds were found, therefore the total is less than the sum of compounds found in each type of area

As in Table 5 can be seen, significant numbers of different pesticides were found in all types of areas. The highest numbers of different pesticides (in particular fungicides) were found in 3 buffer areas, which consisted of a wine growing area in the Mosel valley and of Krefeld winter wheat fields inside the nature protection area. In all three areas the fungicides were the most frequent type of pesticide found and to a lesser extent herbicides and insecticides. In Appendix 6 the presence and concentrations of all pesticides in all samples are summarized in diagrams.

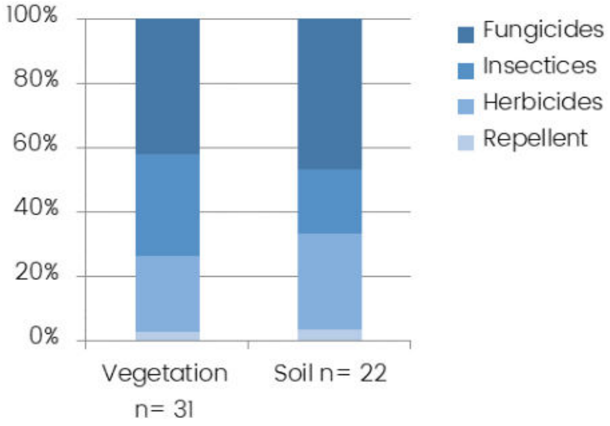

Figure 5. Average subdivision (in %) of different types of pesticides found in soil and vegetation samples from protected nature reserves

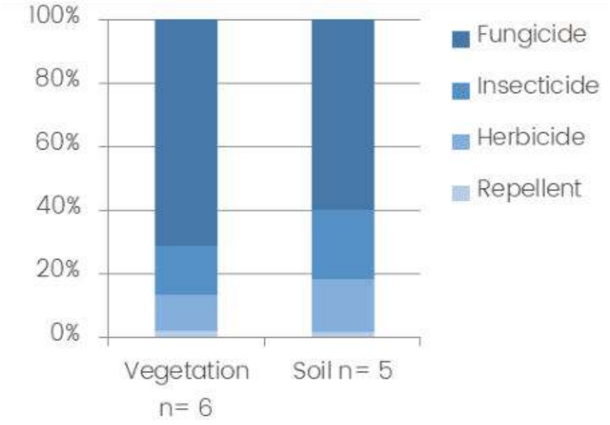

Figure 6. Average subdivision (in %) of different types of pesticides found in soil and vegetation samples from buffer areas

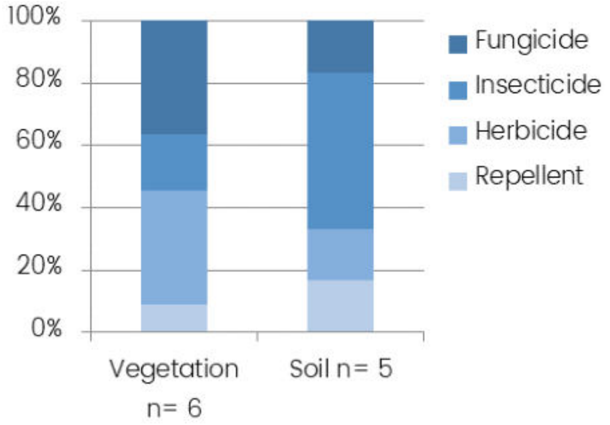

Figure 7. Average subdivision (in %) of different categories of pesticides in reference areas

The subdivisions of the found pesticides in soil and vegetation samples from the nature reserves, as given in Table 5, are illustrated in Figure 5. 50% of the number of pesticides found in soil and a bit less in vegetation are fungicides. In soil 20% of the number of pesticides found are insecticides and in vegetation 30%.

In Figure 6, the average subdivision of different types of pesticides found in soil and vegetation samples from buffer areas is indicated. It can be seen that in buffer areas, the large majority of pesticides (>60%) in soil and vegetation were fungicides, and insecticides represented 16% of the pesticides in the soil and 22% in the vegetation.

In Figure 7, the average subdivision of different types of pesticides found in soil and vegetation samples from reference areas is indicated. It can be seen, that although the total numbers of pesticides found are much lower in reference areas, the percentage of insecticides among those compounds was in the soil of reference areas higher than in the soil of nature reserves.

Except the total number of different pesticides in the different types of areas, the average number of pesticides per sample of vegetation, soil and animal excretions is also an important parameter. They are indicated in Table 6.

Table 6. Average number of pesticides in different matrices in the three types of areas included in this research

| | | Average number of pesticides per sample* | | |
|---|---|---|---|---|
| Category of area | Number of sampled locations | Vegetation | Soil | Animal excretions |
| 15 nature reserves | 22 | $7.6^{a}$ | $4.2^{b}$ | $5.0^{ab}$ |
| 5 reference areas | 5 | $5.0^{ab}$ | $3.5^{ab}$ | $5.0^{ab}$ |
| 3 buffer areas | 5 | $16.0^{c}$ | $23.4^{abc}$ | No samples taken |

* Different letters in upper-case represent significant differences at $p < 0.01$ probability level

All 89 samples contained one or more pesticides. The reference areas contained 34% lower numbers of pesticides than that were found in the nature reserves with MF. The nature reserves contained 52% less different pesticides than the buffer areas.

In case of the soil, the difference between nature reserves and reference areas was relatively small (17%), but the difference between these categories and the soil of buffer areas was much larger. The buffer zone soils contained respectively 5.4- and 6.5-times higher number of pesticides than the nature reserve soils and the reference areas. In this context it needs to be noticed that the differences between the different buffer areas were very also high. The locations of Brauselay and Pommern (in the wine Mosel Area) are extremely polluted with old pesticides (like DDT, Dieldrin) and more recently introduced pesticides. The contents of DDT (including metabolites) and dieldrin in wild plants growing there was relatively to the soil low (below 15 µg/kg dry matter), but in the grape leaves significantly higher (above 100 µg/kg dry matter, as indicated in Appendix 5). The soil of buffer areas contained a significantly higher number of pesticides than the soil of nature reserves and reference areas.

In the vegetation of nature reserves the number of pesticides was higher than in the reference areas, but the difference was not significant at $p < 0.05$ probability level. The difference with the number of pesticides in the vegetation of buffer areas was significant at $p < 0.055$.

Except numbers of different pesticides, their concentrations and properties are of major importance. The average total concentrations found in all matrices are indicated in Table 7.

Table 7. Average total concentration of pesticides (in µg/kg dry matter) in vegetation, soil and animal excretions in the three types of investigated areas

| | | Average total concentration of pesticides per sample (µg/kg DM) with standard deviation (sd)* | | | | | |
|---|---|---|---|---|---|---|---|
| Category of area | Number of sampled locations | Vegetation | sd | Soil | sd | Animal excretions | sd |
| 15 nature reserves | 22 | $51.13^{a}$ | 35.0 | $25.43^{a}$ | 28.0 | $29.46^{a}$ | 27.8 |
| 5 reference areas | 5 | $28.41^{a}$ | 5.2 | $13.86^{a}$ | 10.2 | $20.98^{a}$ | 12.7 |
| 3 buffer areas | 5 | $27230.06^{*b}$ | 65189 | $2132.8^{b}$ | 2771.1 | No samples taken | - |

* Different letters in upper-case represent significant differences at $p < 0.01$ probability level

In Table 7, it can be seen that the average total concentration of pesticides in the vegetation and soil in buffer areas was 532 and 958 times higher than in the nature reserves and reference areas, respectively. If Table 7 is compared with Table 6, it can be seen that though the buffer areas samples contained many times higher quantities of different pesticides, the numbers of different pesticides differed only a factor 2-5. The contamination is thus mainly expressed by the concentrations and not so much by the number of different pesticides.

Except the total number of pesticides found and the average number of pesticides in each sample, the composition of the pesticide contamination plays an important role. The compounds with the highest average concentrations in the vegetation are given in Table 8 together with the type of pesticide and their legal status.

Table 8. Top-10 of pesticides found in vegetation of 15 Nature reserves, their average concentration, the percentage of the total amount of pesticides, the category of the compound and their legal status in Germany

| **Pesticide** | **Average concentration found (µg/kg DM)** | **Percentage of total pesticides concentration found in all vegetation samples** | **Type of pesticide** | **Permitted in Germany[1] in agriculture or in industry** |
|---|---|---|---|---|
| Ametoctradin | 1.07 | 2.1 | Fungicide | Yes |
| Anthraquinone | 3.83 | 7.4 | Repellent | No approval since 2008 |
| Chlorpropham | 2.79 | 5.5 | Herbicide | No approval since 31.07.2019; Sale allowed until 31.01.2020. Use allowed until 08.10. 2020 |
| Diphenyl | 13.21[2] | 25.8 | Fungicide | No approval since 2013 |
| Diphenylamine | 4.18 | 8.2 | Insecticide | No approval since 2010 |
| Phenylphenol-2 | 1.69 | 3.3 | Fungicide | Not allowed in agriculture, but allowed in five southern EU member states as post-harvest treatment of citrus fruit (orthophenylphenol) |
| Phthalimide | 3.42 | 6.7 | Fungicide metabolite | Yes |
| Pendimethalin | 8.77 | 17.2 | Herbicide | Yes |
| Permethrin cis and trans | 2.52 | 5.0 | Insecticide | Yes |
| Prosulfocarb | 4.16 | 8.2 | Herbicide | Yes |
| All other 29 compounds | 5.49 | 10.6 | Fungicides, herbicides, insecticides | Some of them |
| **Total** | **51.13** | **100** | | |

[1] According to https://apps2.bvl.bund.de/psm/jsp/index.jsp

[2] In reality, the average content is higher due to 8 measurements where this substance was present but could not be quantified.

In Table 8, it can be seen that 10 compounds are responsible for 89.4% of the pesticide quantity found in the average vegetation sample and that the remaining 29 compounds found are responsible for 10.6% of the pesticide quantity found. Anthraquinone and diphenyl contribute together 33.2% to the pesticide contamination of the vegetation.

In Table 9 the pesticides with the highest average concentration in the soil of the nature reserves are given. In addition, the percentage of the total concentration of pesticides found in soil is given, the type of the pesticide and its legal status.

Table 9. Average concentration of top-10 pesticides found in soil of nature reserves with MF, their percentage of the total amount of pesticides, the category of the pesticide and their legal status in Germany

| Pesticide | Average concentration found (µg/kg DM) | Percentage of total pesticides concentration found in soil | Type of pesticide | Permitted in Germany |
|---|---|---|---|---|
| Anthraquinone | 8.95 | 35.4 | Repellent | No approval since 2008 |
| Boscalid | 0.91 | 3.5 | Fungicide | Yes |
| Chlorpropham | 0.50 | 2.0 | Herbicide | No approval since 31.07.2019. Sale allowed until 31.01.2020; use allowed until 08.10.2020 |
| Diphenyl | 6.62 | 26.0 | Fungicide | No approval since 2013 |
| Epoxiconazole | 1.32 | 5.1 | Fungicide | Yes |
| Fluxapyroxad | 0.84 | 3.1 | Fungicide | Yes |
| Phthalimide (Folpet) | 0.49 | 2.0 | Fungicide metabolite | Folpet is permitted |
| Hexachlorobenzene | 0.45 | 1.8 | Fungicide | No approval since 1974 |
| p,p DDT | 2.36 | 9.4 | Insecticide | No approval since 1974 |
| Prochloraz desmimidazole-amino (metabolite of prochloraz) | 1.13 | 4.3 | Fungicide metabolite | Prochloraz is permitted |
| All other 12 compounds | 1.86 | 7.4 | Fungicides, herbicides, insecticides | Some of them |
| **Total** | **25.43** | **100** | | |

In Table 8, it can be seen that the herbicide pendimethalin contributes 17.2% to the contamination of the vegetation, but in the soil it has been found only once (see original measurements in Appendix 5). The presence and concentration of many compounds shows significant differences between soil and vegetation.

Of the concentrations of all pesticides found in animal excrements in nature reserves no average has been calculated, because the samples were taken from excrements of different animals. The 7 pesticides found, and the probable animal species are indicated in Table 10.

Table 10. Pesticides found in animal excrements from nature reserves and reference areas, their highest concentration, and the legal status of the pesticide

| Pesticide | Animal species | Highest concentration found (µg/kg DM) | Permitted in Germany |
|---|---|---|---|
| Prosulfocarb | Rabbit, roe deer, cow | 3 | Yes |
| Anthraquinone | Roe deer, cow | 4 | No approval since 2008 |
| Chlorpropham | Roe deer | 1 | No approval since 31.07.2019; sale allowed until 31.01.2020; use allowed until 08.10.2020 |
| Deltamethrin | Cow | Could not be quantified | Permitted as veterinary medicine |
| Diphenyl | Cow, roe deer | 10.9 | No approval since 2013 |
| Diphenylamine | Roe deer, rabbit | 2 | No approval since 2010 |
| Metoxuron | Roe deer, cow | 63 | No approval since 1992 |

The data in Table 10 show that a part of the pesticides consumed by the animals with their food ends up in their excrements. Those pesticides that are most common in the vegetation and soil are also present in the excrements. The fact that metoxuron has such a high concentration in roe deer excrements might indicate that it has been used in this neighbourhood illegally, since the herbicide is forbidden since many years. As a matter of fact, barley fields inside this nature reserve (at less than 50 m distance) were sprayed with herbicides very recently. However, no samples of that barley were taken. In Appendix 5 all original measurements of animal excrements can be found and in the last diagrams of Appendix 6 those data have been summarized and visualized.

The results of the analyses of all individual samples of vegetation, soil, and animal excrements of all the 3 different investigated areas can be found in Appendix 5. Only those measurements are given where pesticides have been really found. All negative measurements, where nothing was found above the LOQ, are not indicated.

Figure 8. Sampling (at 21/11/19) of relatively clean Reference area Rothaarkamm (Kreis Siegen-Wittgenstein in Hochsauerland) where in vegetation, soil and animal excrements in total 8 pesticides were found (among which 3 from possible non-agricultural origin)

Figure 9. Close to vineyards along the river Mosel (sampled at 20/11/19 in Kreis Cochem) the vegetation and soil contain 532 and 958 times more pesticides (in particular fungicides and DDT) than in the respective reference areas. Blackberry leaves contained on this location 24 different pesticides, among which 3 insecticides

## 5.3 The share of compounds from non-agricultural origin

Most likely a small group of the 94 found pesticides in the vegetation and soil samples doesn´t originate from crop protection agents. These compounds are: Anthraquinone, diphenyl/biphenyl, diphenylamine, and phenylphenol-2, which in the past had approval as pesticide or as biocide.

Until 2008 anthraquinone was in the EU approved as a bird repellent and used as seed coating. Since 2002 the fungicide diphenyl has in the EU no approval as a biocide as food preservative. Until 2009 diphenylamine had an approval as fungicide, insecticide, and growth regulator. In Germany Phenylphenol-2 is not approved as a pesticide, but in five EU Member States (Cyprus, Greece, Spain, Croatia, Portugal) the compound is allowed for the post-harvest treatment of citrus fruit.

These compounds can spread into the environment from other sources than agriculture, such as traffic, industry, and households. In Table 11 the amounts of those non-agricultural compounds are given and the percentage of the total concentration of pesticides found.

Table 11. The share of four pesticides/biocides (anthraquinone, diphenyl/biphenyl, diphenylamine, phenylphenol-2) from non-agricultural origin as percentage of the total found quantity in soil and vegetation

| Category of area | Vegetation: average total pesticide content (in µg/kg DM) | Vegetation: average content of non-agricultural compounds (in µg/kg DM) | Vegetation: percentage of compounds from non-agricultural origin | Soil: average total pesticide content (in µg/kg DM) | Soil: average content of non-agricultural compounds (in µg/kg DM) | Soil: percentage of compounds from non-agricultural origin |
|---|---|---|---|---|---|---|
| 15 nature reserves | 51.1 | 22.9 | 44.7% | 25.4 | 15.6 | 61.4% |
| 5 reference areas | 28.4 | 15.3 | 52.9% | 13.9 | 12.9 | 81.6% |
| 3 buffer areas | 27230 | 17.5 | 0.06% | 2133 | 36.6 | 1.7% |

Table 11 shows, that in the vegetation samples of the nature reserves and the reference areas these four compounds contribute with respectively 44.7% and 52.9% to the total average mass of the found compounds. In the soil even 61.4% and 81.6% respectively.

In the buffer areas the percentage of the 4 non-agriculture compounds of the total mass of found pesticides is very small because the total concentration of pesticides is very high. The total concentrations of the compounds from non-agricultural origin (in µg/kg of soil) is however comparable.

## 5.4 Comparison of risks from pesticides from agricultural and non-agricultural origin

In toxicology, the so-called hazard quotient (HQ) – that is the concentration of individual compounds divided by the LC50 to individual organisms – is used (Campbell et al., 2000) as an indication of risks. In case of this study the LC50 should be taken for terrestrial invertebrates that feed on the vegetation (plant tissue), in the soil or feed on other invertebrates living on/in them. Unfortunately, the LC50 is available for very few relevant terrestrial arthropods. It was therefore not possible to compare the total toxicity of pesticides from agricultural and non-agricultural origins. The compounds from non-agricultural origin diphenyl and diphenylamine are in aquatic toxicology considered as less toxic for aquatic organisms than the other compounds phenylphenol-2 and anthraquinone from non-agricultural origin (see Appendix 4). It cannot be not excluded that compounds such as anthraquinone or phenyl-phenol-2 may also have a negative impact on the terrestrial entomofauna. However, it is expected that especially insecticides, from agricultural origin have a higher impact on the terrestrial entomofauna. It needs to be kept in mind that the difference in toxicity of all 94 pesticides found to organisms are magnitudes larger than the differences between their measured concentrations, so concentrations play only a limited role.

## 5.5 Pesticide contamination and distance to agricultural fields

As has been indicated in chapter 5.3, no statistically significant difference has been found between pesticide contamination of nature reserves (at an average distance of 143 m from arable farming fields) and reference areas (at an average distance of 3268 m), although the average concentrations found in reference areas were lower. It can also be concluded that the average concentration of chlorpropham and diphenyl in reference areas are more than 80% of those in nature reserves. The concentrations of other pesticides in reference areas were lower and of anthraquinone and phenylphenol-2 amounted only to 15.67% and 24.65% of the values in the nature reserves. All these differences were, however, not statistically significant with the Mann–Whitney–Wilcoxon U Test (at $p < 0.05$ probability level).

The EVK had in 2019 several nature reserves with more than one MF insect trap in order to get an indication of the influence of nearby arable fields. However, in those locations (Wissel and Naturpark Nassau) no significant differences were observed in total pesticide contamination of the vegetation (see original data in Appendix 5 and Appendix 7 with results and discussions of measurements in individual Nature reserves). Only the soil of the two locations in Naturpark Nassau showed a large difference. The soil of the higher location (under agricultural management) contained 9 pesticides and of the lower location without agricultural management only 4. The total concentration of pesticides of the lower location was only 7.6 µg/kg compared to 56.8 µg/kg DM of the higher location on the edge of the agricultural field.

In the buffer zones of Brauselay and Egelsberg, several MF were operational in 2019 and at those sites soil and vegetation were sampled and analysed. Those sites that were located inside the agricultural zones showed higher numbers and concentrations of pesticides, but because of the low number of sites, the difference could not be tested statistically. In Brauselay the blackberry leaves down-hill near the wine yard showed a 26 times higher pesticide content than the location up-hill (34 m higher at a distance of 50 m). In Egelsberg the vegetation of the wheat field had a 10 times higher pesticide content than the heather from the Egelsberg reserve.

## 5.6 Status of the found pesticides

In this research in total 94 different pesticides were found in the samples of soil, vegetation and animal excrements. Out of the 94 found pesticides were 4 (anthraquinone, diphenyl/biphenyl, diphenylamine and phenylphenol-2) from other than from actual or historical agricultural sources. Among the 94 different pesticides were **28 insecticides, acaricides and their metabolites**. These 28 compounds can be subdivided into:

- 2 acaricides (dicofol and tetradifon). These are no longer admitted for use.
- 6 metabolites (endosulfan-sulphate, fenamiphos-sulfoxide, o.p-DDE, o.pDDD, pp-DDE and p,p-DDD) of insecticides that are not allowed for use.
- 10 insecticides were at the date of sampling not approved in Germany (alpha-HCH, gamma HCH, aldrin, dieldrin, diphenylamine, betaendosulfan, heptenophos, p,p-DDT, picadin/icardin, thiofanox).
- Allowed for use are 10 insecticides.

Out of the **48 found compounds with fungicide properties** were:

- 2 metabolites (phthalamide, prochloraz-desmimidazole) of admitted fungicides.

- 11 fungicides were at the date of sampling not approved in Germany (diphenyl, diphenylphenol-2, fenarimol, flusilazole, hexachlorobenzene, Iprodione, procymidone, pyrifenox, quinoxyfen, tolyfluanid, vinclozolin).
- 35 fungicides (parent compounds) that are allowed to be used.

The **compound anthraquinone** is a bird repellent and in the table separated listed. In other summaries in this report the compounds anthraquinone was mostly counted as a fungicide.

Out of the **17 found compounds with herbicide properties** were:

- 1 metabolite (AMPA) of the herbicide glyphosate (that is still on the market)
- 4 herbicides (hexazinone, methabenzthiozuron, metoxuron, norflurazon) were at the date of sampling not approved in Germany.
- 12 herbicides are presently allowed for use.
- The above-mentioned information has been summarized in Table 12.

Table 12. Present legal status* (1/12/2019) in Germany of all found 94 pesticides, metabolites and isomers that were found in all samples of vegetation, soil, and excrements

| Type | Found number | Approved, including metabolites of approved parent compounds | Number of compounds not approved as pesticide or biocide, including metabolites of non-approved parent compounds | Total number of found metabolites |
|---|---|---|---|---|
| Insecticides, incl. metabolites, isomers and 2 acaricides | 28 | 10 | 18 | 6 |
| Fungicides, incl. metabolites | 48 | 37 | 11 | 2 |
| Herbicides, incl. metabolites | 17 | 13 | 4 | 1 |
| Anthraquinone | 1 | | 1 | |
| **Total** | **94** | **60** | **34** | **9** |

* Source: Bundesamt für Verbraucherschutz und Lebensmittelsicherheit

In Table 12, roughly 2/3 of all pesticides found are still on the market. From the total number of 94 pesticides found there are 9 metabolites. The legal status of the found pesticides has been visualized in Figure 10 and in Figure 11.

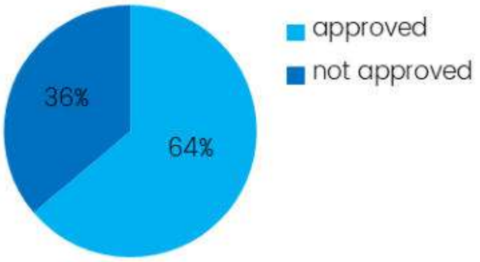

Figure 10. Legal status of the 94 found compounds, including parent compounds of the metabolites

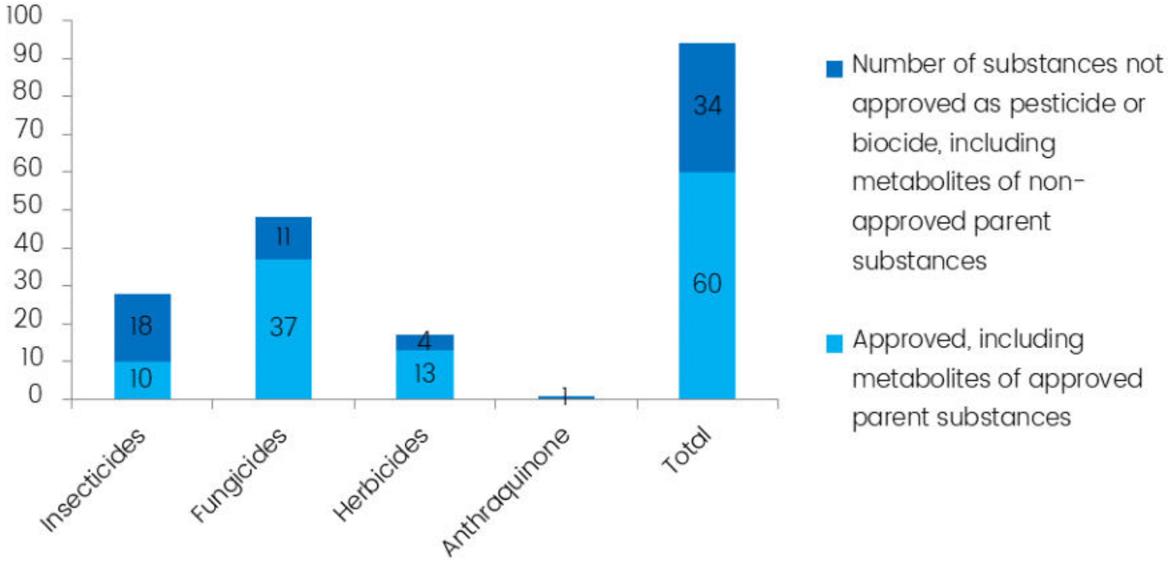

Figure 11. Legal status of all found pesticides subdivided into insecticides, fungicides, herbicides and anthraquinone

## 5.7 Relation of pesticide contamination with measured biomasses

In the context of this investigation, no insect traps were actively operated by us to determine the insect biomass. Our investigations were carried out at measuring points where standardized Malaise insect traps were operated by the EVK in the present, or in the past. As it has been said in the introduction of this report, in the context of this study the possible causal relationships of insect decline with pesticides could not be investigated. In this context it needs to be said that ideally spoken for such an investigation, the MF insect catches of the same year should be used as the year in which the soil and vegetation samples were taken for chemical analysis with the same intervals. This was however not possible in this research, because the MF do not stand every year at every location and sampling for chemical analysis was conducted only once. In this research, the effects of pesticide contamination on the MF insect catches might be expressed by:

- a small number of compounds that are present everywhere (like diphenyl and anthraquinone)
- a quite unique combination of other pesticides in every individual nature reserve.

In addition, there are other factors influencing the entomofauna, like climate change, management measures of the reserves, etc. To unravel the interactions of so many chemicals with insect decline is requires most likely a major research effort. It would be easier with a large number of relative homogeneous type of nature reserves. In case that the substances predominantly responsible for insect decline would have been found in all nature reserves a relative uniform insect decline could be expected. In case that the unique mixtures (that have been found in every single nature reserve) would be responsible for the insect decline, increasing variation between the nature reserves in insect biomass could be expected. The mixtures present in the vegetation of nature reserves might even fluctuate in time, in dependence of various factors. This could make it even more complicated to understand the exact impact of pesticides on the entomofauna.

Figure 12. Nature conservation area Bislicher Insel (Kreis Wesel). Here the largest pesticide content was measured in soil of all nature conservation areas (121.8 µg/kg soil DM). The pesticide content of stinging nettle (Urtica dioica) and reed (Phragmites australis) was not higher than at other locations

## 5.8 Genotoxicity, carcinogenicity, LR50 and EQS of found pesticides

In chapter 4.10, different limitations of the Toxic Unit approach were mentioned. Even if such an approach would be adopted, there are many strong constraints in its use. The properties of individual pesticides play an important role. Many pesticide properties can be found in databases. However, 12 serious shortcomings of the available information have been identified, among which some have been discussed already in chapter 4.10:

- Databases only contain information about the so called ‘active ingredients’. In agricultural practice only commercially, available formulations are used that also contain lots of other synthetic compounds that should improve the effect of the active ingredient. Databases give absolutely no information about the properties of the commercial formulations to which those other compounds are added. Even the admission tests are carried out with the pure active ingredient only.
- Databases contain large amounts of parameters of every single pesticide that have not been determined in particular of ecotoxicological parameters.
- Databases do not contain any information about possible synergistic effects of the simultaneous presence of more than one pesticide. These have been determined only for very few combinations of pesticides (Jansen et al., 2017; Gilbert et al., 2019). Carcinogenicity and genotoxicity can also be due to mixtures of certain compounds, while the single components might not have such a property.
- Databases do never contain any information about the time dependency of the effects of compounds and about the (ir)reversibility of the receptor binding in test organisms, although this property is of decisive importance for the long-term effects of pesticides in the environment (and in our own bodies).
- Although databases contain, as a rule, the names of the main metabolites of the active ingredient, the information about the toxic properties of those metabolites is close to zero.
- The information in the databases is mostly obtained from testing by the industry (producers). The reliability of this information cannot be guaranteed, as in the case of for instance glyphosate, where testing was corrupted because of commercial pressure.
- Toxicity facts are given without ecological context. It has been proven that stress factors can increase susceptibility of organisms for certain

chemicals thousands of times (Barmentlo et al., 2019). Since ecological stress is not used in laboratory situations, this information is not included in databases.

- In the natural food web, all organisms depend on other organisms for their food. Even very selective pesticides that do not affect a certain organism directly, can still wipe them out, if they affect their preys, or hosts. One example about the pesticide effects on skylarks is given by Boatman, 2004.
- Information given on ecotoxicity covers only a few selected organisms (out of the millions that are exposed in nature) and don't include the recovery of test organisms after exposure and seldom information about effects on reproduction and development.
- Safe threshold levels for toxic compounds are often derived by linear deduction from experiments with higher concentrations. This is however not correct since dose-response relations are in general logarithmic (Waddell, 2004).
- Endocrine disrupting chemicals can affect organisms at very low doses
- (less than 1 µg/l) which are not predicted by the traditional concepts in toxicology such as "the dose makes the poison (Vandenberg et al., 2012).
- Information about reproduction bioassays of the non-target organisms is seldom available. As shown in the research of Gols (2020) exposure of the farmland butterfly (Pieris brassicae) to low concentrations (until 1 µg/kg fresh plants) of fipronil during larval development already affects the adult stage.

In Appendix 4 a part of the information that is available has been summarized. An overview of genotoxicity, carcinogenicity and endocrine disruptive properties of the 94 pesticides found in this research are given in Table 13.

Table 13. Number of pesticides found in this research having genotoxic, carcinogen and endocrine disruptive properties (out of the total 94 pesticides found in this research)

| Property | Number of found pesticides having the given property* | Source of data | Group(s) of pesticide(s) |
|---|---|---|---|
| Genotoxic | 7 | IUPAC | Insecticides, fungicides, herbicides |
| Possibly genotoxic | 8 | IUPAC | Insecticides, fungicides, herbicides |
| Incomplete or no data of genotoxicity | 77 | IUPAC | Most insecticides, fungicides, herbicides |
| Proven absence of genotoxicity | 0 | IUPAC | Not applicable |
| Carcinogenic | 17 | IUPAC/ PAN | Many insecticides, fungicides, herbicides |
| Possible carcinogenic | 15 | IUPAC/ PAN | Many insecticides, fungicides, herbicides |
| Possible carcinogenic, cancerogenic, genotoxic & possible genotoxic | 46 | IUPAC/ PAN | Many insecticides, fungicides, herbicides |
| Endocrine disrupting or possible endocrine disrupting | 30 | IUPAC/ PAN | Many insecticides, fungicides, some herbicides |

* see Appendix 4

In Table 13, it can be seen that out of the 94 pesticides that have been found in this study genotoxicity of 77 pesticides (82%) could not be determined, because of lacking data. Further among the 94 pesticides there were no pesticides of which it has been proven that they are not genotoxic. In addition, there are 32 pesticides (34%) that are carcinogen or suspected carcinogen, and 30 pesticides (33%) that are endocrine disrupting, or possible endocrine disrupting. In total half of the 94 pesticides found are proven or suspected cancerogenic or proven or suspected genotoxic.

Unfortunately, the properties of genotoxicity, carcinogenicity and endocrine disruption are strong indicators for the fact that many of those 94 pesticides found are likely to have irreversible receptor binding in the test organisms or to have, through other mechanisms, chronic effects on organisms. Those tests are often done with test animals (mammals) in order to collect information for toxicity to humans, so it needs to be concluded that the risks for other organisms might be comparable (!). This means that it is possible that at least half of these 94 pesticides have irreversible receptor binding and as a consequence cumulative time dependent effects on affected organisms.

The specific properties of pesticides are important indicators for their ecologic effects. In Table 14 some relevant toxicological figures of pesticides found in this research are given.

Table 14. Toxicological relevant data of specific pesticides found in this research

| **Specified properties and ecotoxicological endpoints of pesticides with unit** | **Value** | **Name of pesticide(s)** | **Source of data** | **Category of pesticide** |
|---|---|---|---|---|
| Minimal LR50 (g/ha) with Typhlodromus pyri | 0.0029 | Cypermethrin | IUPAC | Insecticide |
| Maximum LR50 (g/ha) with Typhlodromus pyri | 7130 | Fluopicolide | IUPAC | Fungicide |
| AA-EQS (surface water) minimum value (µg/l) | 3.1 x $10^{-6}$ (which is 3.1 pg/l) | Deltamethrin | Dutch Atlas of pesticides in surface water* | Insecticide/veterinary medicine |
| AA-EQS (surface water) maximum value (µg/l) | 79 | AMPA | Dutch Atlas of pesticides in surface water* | Metabolite of glyphosate |
| Degradation (conversion) time minimal value (days) | 1.4 | Heptenophos | IUPAC | Insecticide |
| Degradation (conversion) time, maximum value (days) | Up to 9585 | Fluquinconazole | IUPAC | Fungicide |
| Vapor pressure (minimal) | 1.24 x $10^{-6}$ | Deltamethrin | IUAPAC | Insecticide |
| Vapor pressure (mPa) | >1 | Heptenophos, chlorpropham, pendimethalin, tri-allate, hexachlorobenzene, diphenyl, phenylphenol-2, HCH, Aldrin, Thiofanox, pyrimethanil, metoxuron | IUPAC | Various fungicides, herbicides, insecticides |

*http://www.bestrijdingsmiddelenatlas.nl

Table 14 shows that the pesticides found have a wide variety of toxicological relevant properties. The acute toxicity for terrestrial non-target arthropods is often expressed by the LR50 value, expressing the amount of a compound (in g/ha) required to kill 50% of test organisms (arthropods) within 2 or 3 days (see 4.8 and 4.10). Normally this test is conducted for two reference test organisms only: a predatory mite and a parasitic wasp (Braconidae). It is of interest to understand whether certain amounts of a compound (under laboratory conditions) have the potential to kill beneficial terrestrial organisms.

Unfortunately, this value is unknown for many compounds and if it is determined, it is determined only after 24 or 48 hours exposure. Time dependency would only be visible if effects after longer periods would be investigated. In Table 14 it can also be seen that cypermethrin is the compound with the lowest LR50 value which means that it is most toxic (of the 94 pesticides found) for the test organism used (*Typhlodromus pyri*) and fluopicolide the least toxic for the specific test organisms used. The difference between both compounds amounts to a factor 2.45 million. The insecticides cyfluthrin and etofenprox that have been found in vegetation (of Tote Rahm and Rothaarkamm near Latrop), both have a LR50 of 0.42 gram per ha and the insecticide imidacloprid 0.022 gram per ha (see appendix 4). In Egelsberg1 the insecticide cypermethrin has been found in the vegetation (winter wheat) with a LR50 of 0.0029 gram per ha. The concentrations of those insecticides in the biomass can be used in order to calculate the amounts of insecticides present per ha, if the biomass of the vegetation per ha would be known. The biomass of the investigated areas has not been measured. If the biomass of the vegetation is supposed to be between 500-5000 kg of dry matter per ha, it is likely that the amount of insecticides present is under the LR50 value for acute lethal effects. However, at the same time chronic effects on the entomofauna seem unavoidable.

In the past, a lot of attention has been paid by authorities to toxic properties of pesticides in aquatic environments. For the aquatic ecosystem, the Annual Average Environmental Quality Standard (AA-EQS) has been introduced as threshold level. To assess the surface water quality mostly the AA-EQS is used. The AA-EQS values in the appendix are obtained from 5 sources, as explained in Appendix 4. They vary from 3.1 pg/l water (for deltamethrin) to 79 µg/l (for AMPA), which is roughly 25 million times more. In spite of the 'harmless' value for AMPA there are many publications indicating that it has a strong impact on various organisms. The concentrations in the environment of this compound are after many years of widespread use also accordingly high, up to many mg/kg of agricultural soil.

In Table 14 it can also be seen that the differences between pesticides are huge. Deltamethrin is unprecedented toxic for aquatic organisms and fluquinconazole is extremely persistent almost not converted into metabolites. Deltamethrin has however a low vapor pressure. Many compounds have a vapor pressure that is a million times higher than that of deltamethrin.

In the Appendix 4 also the vapor pressure of all compounds is indicated, which influences the evaporation (or sublimation) of pesticides in the field. It is striking that 4 out of the 12 compounds with a vapor pressure more than 1 mPa belong to the top 10 of compounds found in nature reserves. It is also evident that two compounds are absent in the list of compounds with a high vapor pressure (Table 14), namely diphenylamine and anthraquinone. Diphenylamine has a vapor pressure of 0.852 mPa, so it can also be easily transported through the atmosphere. Anthraquinone has on the contrary a low vapor pressure of 5 x 10-3 mPa, so it seems that it must have another way of transport than evaporation or sublimation. Anthraquinone contributes 35.4% to the total concentration of pesticides found in the average soil and 7.4% in the average vegetation of the nature reserves with MF.

Also, the often-debated DT 'Degradation Time' is given. This parameter (expressed in days) does not indicate that a compound has disappeared, but that the parent compound has turned into metabolites, or conjugates, which are as a rule not measured. In the case of some compounds there can be dozens of metabolites of one pesticide with various properties. These metabolites can be less toxic than the parent pesticide, but also more toxic. Because the degradation of a compound depends on many factors like temperature, pH, type of soil, and microbial activity, databases contain as a rule very different values for the DT. Many compounds, once absorbed by the soil, show hardly any degradation, or conversion, even after many years.

In the context of this study the properties of the most frequent occurring pesticides are of special importance.

- Anthraquinone (repellent)
- Diphenyl (fungicide)
- Chlorpropham (herbicide)
- Diphenylamine (insecticide)
- Phthalimide (metabolite of folpet fungicide)
- Pendimethalin (herbicide)
- Prosulfocarb (herbicide)

Some properties of those pesticides are given in Table 15.

Table 15. Selected relevant properties of specific pesticides found in this research

| Name | AA-EQS aquatic (µg/l) | Average concentration found in soil (µg/kg DM) | Average concentration found in vegetation (µg/kg DM) | Presence in vegetation samples (%) | LR50 terrestrial arthropods | Genotoxic | Cancerogenic |
|---|---|---|---|---|---|---|---|
| Anthraquinone | 0.075 | 8.95 | 3.83 | 67.7 | No data | Unknown | IUPAC: possible;<br>PAN: Yes |
| Diphenyl | 1.5 | 6.62 | 13.2 | 100 | No data | Unknown | Not listed |
| Chlorpropham | 4 | 0.5 | 2.79 | 83.9 | No data | Unknown | Unknown |
| Diphenylamine | 1.2 | 0.07 | 4.18 | 71.0 | No data | Unknown | Unknown |
| Phthalimide | 16.5 | 0.49 | 3.42 | 61.3 | No data | Not listed | Unknown |
| Pendimethalin | 0.018 | 0.05 | 8.77 | 74.2 | 3800 (38% dead) | Unknown | PAN: Possible carcinogen |
| Prosulfocarb | 0.34 | 0.09 | 4.16 | 80.6 | 41.8 | Unknown | No |

Taken into account that the largest part of the entomofauna feeds on plants, pesticide threshold levels should be used for the vegetation in order to understand ecological effects of pesticide contamination. However, such threshold levels for vegetation are not given by the databases used. The only alternative would be to compare measured concentrations in (fresh) plants with the aquatic AA-EQS. The average concentrations found in the vegetation are higher than the AA-EQS for all compounds, except for chlorpropham. For anthraquinone the difference is a factor 51 and for pendimethalin even a factor 487. It needs to be noticed that aquatic EQS are in toxicology never applied on terrestrial substrates, like plants. It has been explained earlier that any data should be handled carefully, since toxicological data have a high degree of uncertainty, because of various reasons (see earlier in this chapter).

In daily life it is often assumed that only insecticides would be able to affect insects and fungicides only fungi. In toxicological reality, this fact is however not correct. Pesticides have different modes of actions. Some fungicides are designed to block certain enzymes, or metabolic processes that are crucial for insects, mammals, and plants as well. The modes of action will be discussed in more detail in 5.9. In addition, all organisms living in, or above, the soil are part of the food chain. If one section of the food chain is disrupted, the other organisms can disappear as well. Due to the enormous complexity of the food chain and the astronomic number of interactions of all organisms, the effects of the 94 found pesticides on the food chain in general, and on the insect populations in particular, cannot be calculated with any certainty, but only assessed on the limited ecotoxicological data available. By using the modes of action and the time-dosis-effect relationships of each pesticide separate however, the likelihood of effects can be made more evident.

## 5.9 Mode of action

The term 'mode of action' is used to describe the mechanism by which a pesticide performs its main function (IUPAC, 2020). In Table 16, the mode of action of a number of frequently found pesticides is given.

Table 16. Mode of action (MOA) of the most frequently found pesticides in vegetation samples (data from IUPAC)

| Name | Pesticide type | Mode of Action | Examples of concerned organisms |
|---|---|---|---|
| Anthraquinone | Repellent | Induces retching in birds and so deters attack and is possibly carcinogen | Its possible carcinogenicity concerns all animals |
| Diphenyl | Fungicide | Inhibits sporulation, lipid peroxidation | Lipid peroxidation is crucial for all fungi and for animals and humans |
| Chlorpropham | Herbicide, plant growth regulator | Mitosis inhibitor, absorbed predominately by roots | Mitosis is a type of cell division and a crucial process to all plants and animals |
| Diphenylamine | Insecticide, fungicide, plant growth regulator | An inhibitor of polyene and isoprene biosynthesis | Plants, bacteria, cyanobacteria, algae, insects |
| Phthalimide (metabolite of folpet) | Metabolite/ Fungicide | Folpet (the parent compound) acts by inhibiting normal cell division of many microorganisms. Multi-site activity | Chemical essence of cell division in living organisms is identical, or similar |
| Pendimethalin | Herbicide | Selective, absorbed by roots and leaves. Inhibition of mitosis and cell division. Microtubule assembly inhibition. | Mitosis is a crucial process to all plants and animals |
| Prosulfocarb | Herbicide | Selective, absorbed by leaves and roots. Lipid synthesis inhibitor. | Lipids (fats) are an essential component of all living organisms |

In Table 16 it can be seen that the mode of action of all compounds is not exclusively selective for the target group of organisms. It is though logical that farmers do not want to kill their crop with a fungicide that also affects the plants. The selective properties of commercially available formulations can be based on timing, exposure, penetration, and other factors. The table indicates that effects of fungicides and herbicides on the entomofauna can very well be expected. This fact is confirmed by the low value of the earlier mentioned LR50 for many fungicides and herbicides. For prosulfocarb this value is only 41.8 g/ha. Table 16 shows only a small part of potential mode of actions of a number of pesticides. Like other parameter such as LR50, is the mode of action an indication rather than a prediction of effects on insects caused by the exposure of a compound. Organisms can be exposed to constant concentrations of chemicals, or to fluctuating concentrations, or intermitted and variable concentrations with time. In the environment different patterns of exposures and time-fluctuating concentrations are frequently found. And in the ecotoxicology, there are strong indications that for toxicants the dose-time relations and stress factors play an important role for the effects on organisms.

## 5.10 Dose-time-effect relations

Current pesticide admission procedures and standards assume that an Acceptable Daily Intake (ADI) exists for each compound. The ADI is an estimate of the amount of a compound that a person can take during his/her life on a daily basis without any significant adverse effect (WHO, 1987).

This approach assumes a similar dose-effect relationship for all compounds.

Unfortunately, this is incorrect, but for the sake of commercial interests, fundamental toxicological laws are ignored by the legislators and regulators (Samwel-Mantingh, Tennekes & Buijs, 2018).

The dose- and time-dependent effects of the neonicotinoid insecticides imidacloprid and thiacloprid were described in 2009 by Francisco Sánchez-Bayo for arthropods (Sanchez-Bayo, 2009).

This was not only dependent on the dose, but also on the duration of exposure. It was also shown that the lower the exposure concentration, the lower the total dose needed for the harmful effect (see Table 17).

Table 17. Mortality of arthropods due to exposure to neonicotinoid insecticides (Sanchez-Bayo, 2009)

| Model organism | Test compound | Concentration (C) in µg/l | Time up to 50% mortality (T) in days | C x T product in µg/l *days |
|---|---|---|---|---|
| *Cypridopsis vidua* | Imidacloprid | 4 | 5.2 | 20.8 |
| | | 16 | 3.0 | 48 |
| | | 64 | 3.3 | 211.2 |
| | | 250 | 2.3 | 575 |
| | | 1000 | 2.0 | 2000 |
| | | 4000 | 0.9 | 3600 |
| *Daphnia magna* | Imidacloprid | 750 | 69.7 | 52275 |
| | | 2220 | 18.6 | 41292 |
| | | 6700 | 15.0 | 100500 |
| | | 20.000 | 18.4 | 368000 |
| | | 60.000 | 3.0 | 180000 |
| *Sympetrum striolatum* | Thiacloprid | 7.2 | 20.6 | 148.3 |
| | | 8.0 | 17.2 | 137.6 |
| | | 12.7 | 13.0 | 165.1 |
| | | 113.3 | 3.2 | 362.6 |

This phenomenon implies that even exposure of the smallest concentration of a compound having this property (such as the neonicotinoid insecticides, dieldrin and boscalid that were found in this research) will cause with time harmful effects on insects. The dose / time effect relationship of most pesticides has not been clarified because the current toxicological research only aims at establishing a No-Observed Adverse Effect Level (NOAEL) as the basis for the calculation of the Acceptable Daily Intake (ADI) for humans. Dose-time-effect relationships are almost always left out of consideration. Unfortunately, this means that for compounds that have a time dependent action, the official ADI and NOEL don't provide any safety on the long term for human beings.

Dose-effect relationships can be classified in the following way (Samwel-Mantingh et al., 2018):

A. Compounds with a dose-dependent action and a threshold value that do not irreversibly interact with components of the body (called receptors) and for which an ADI can be established. There will be no damage under the ADI, even under long exposure times. **Admission can be justified if the other conditions of admission can also be met, such as degradability and absence of accumulation in the food chain**.
B. Compounds with a dose- and time-dependent action without threshold, which enter into irreversible interactions with components of the body leading to accumulating adverse effects. The product of the daily dose **d** and exposure duration (until the occurrence of a harmful effect) **t** is

constant: **d.t=constant**. This dose-effect relationship is called Haber's rule. These compounds show cumulative toxicity and it is completely impossible to calculate an ADI for this. Accumulating effects do not necessarily mean that the compound itself is accumulating. Compounds are likely to lead to chronic disruption of the ecosystem. An example from the 94 pesticides found in our research is permethrin.

C. Compounds with a dose- and time-dependent action without a threshold value, which enter into irreversible interactions with components of the body whose harmful effect not only accumulates but is also strengthened by time. This dose-action relationship is now known as the DruckreyKüpfmüller equation and can be mathematically represented by the equation; d. t n = constant, where n> 1. The equation explains the harmful effects of very low exposure concentrations (d) of a poison after long exposure times (t). Since the factor n is an exponential factor, at long exposure times the required dose for effect becomes very small. These compounds show cumulative toxicity and it is completely impossible to calculate an ADI for this. Compounds are likely to lead to chronic disruptions of the ecosystem. Examples among the 94 compounds found in this research are imidacloprid and boscalid.

D. Compounds with an unclarified (or unpublished) dose-effect relationship. If these compounds are allowed on the market, we may expect anything. With some exceptions, it is the case for almost all 94 compounds found in this study.

Understanding the dose/time effect relationships is essential for establishing standards for permissible concentrations of pesticides. Given the fact that dose/time effect relationships in the preparation of NOAEL, LC50, LD50 or LR50 have been completely ignored, there can be no question of any confidence in the harmlessness of compounds for insects, which belong to categories B, C and D, even in concentrations far below the LR50 for terrestrial insects. In particular because of the time dependent expression of pesticide effects, this issue is of crucial importance for understanding chronic changes in our ecosystem. A video about this complicated subject is available (Tennekes, 2020).

# DISCUSSION

## of the research

## CHAPTER 6

# Discussion

## 6.1 Judgement of hypothesis

- The first of the two hypotheses of this research is that pesticides can be found in vegetation and soil of nature reserves. This hypothesis is confirmed with all the measurement results presented in Appendix 5. There was not one single nature reserve, reference area, or buffer area where pesticides were not found.
- The second part of our hypothesis is that "pesticides in the environment have influence on insect declines inside nature reserves" could not be judged for all areas (see 5.7). On basis of the LR50 values of 4 found insecticides, the vegetation in four areas was likely to have toxic effects on insects. For all other areas the effects could not be judged because of the lack of LR50 values for most pesticides found.

For future research, it might be considered to use instead of concentrations, the chronic toxicity of the different pesticides found for better evaluation of their impact on biodiversity. In that case a source of reliable toxicity data for insects living on vegetation should be identified. The databases that we used do not contain such data for the majority of non-target terrestrial insects. More or less complete toxicity data are only available for aquatic environments. It can be investigated to what extent those aquatic toxicity data are suitable for use of the evaluation of toxicity of contaminated plants to insects.

In total, 94 different pesticides were found in the three types of researched areas. In the nature reserves with MF 53 pesticides were found (Table 5). In Figure 5 it can be seen that 45-50% of the pesticides found in nature reserves with MF were fungicides, like diphenyl, phthalimide, phenylphonol-2. Also, the repellent anthraquinone has been detected in the majority of vegetation and soil samples (Appendix 6). The individual concentrations of pesticides in the vegetation amounted to 1.43-51.72 μg/kg dry matter and in the soil to 1-24 μg/kg of soil (Appendix 5). Geiger et al. (2010) analysed by statistical analyses the role of insecticides, herbicides, and fungicides in biodiversity decline. Out of the 13 studied components of agricultural intensification, use of pesticides, especially insecticides and fungicides, had the most consistent (statistically significant) negative effects on the species diversity of plants, carabids and ground-nesting farmland birds, and on the potential for biological pest control.

If the LR50 value of fungicides is considered, 13 of them have a value of less than 100 g/ha and only one herbicide (prosulfocarb) has such a high toxicity to LR50 test organisms (see Appendix 4). One of the fungicides fluxapyroxad has even a LR50 value of 0.128 g/ha (on the predatory mite Typhlodromus pyri). Fluxapyroxad has been found in two nature reserves (see Appendix 6). Prosulfocarb has been found in 80% of the vegetation samples in nature reserves with MF.

In the vegetation of nature reserves, 29% of the total number of pesticides found were herbicides and in the soil 40.9%. Of the pesticides found in the vegetation, 38.7% were insecticides and in the soil 27.3%. If these results are compared with the results of Hofmann et al. (2019) of their research of tree bark in Germany it is striking that the top ten contains two of the same compounds, namely pendimethalin and prosulfocarb, but that they found also DDT, lindane, glyphosate, prothioconazole-desthio in more than 50% of the samples. In our research the frequencies of those compounds in the vegetation samples were much lower and also their concentrations, while the LOQ was comparable. Possibly tree bark accumulates pesticides much more than herbal plants. The total concentration of all pesticides in tree bark in their research ranged from 6-1748 µg/kg dry matter and was on average a factor 7 higher (364 µg/kg) than what we found in our study (51.6 µg/kg) . In our study more pesticides were analysed (664 instead of >500 pesticides in Hofmann et al.). The 8 samples that were taken in our research of trees (small branches with leaves) contained a 49.4% higher content of pesticides than the herbs. It seems that trees absorb more pesticides than herbs and that tree bark has special properties in this context.

Concentrations of pesticides in the vegetation may fluctuate from day to day, dependent on the field operations that are carried out nearby and the weather conditions. In this study it was not possible to monitor during the whole year the contamination of the vegetation and soil. It cannot be excluded that pesticides concentrations fluctuate during the year. In our research we did also not analyse for glyphosate and AMPA in the vegetation, because of financial reasons. An evaluation has been made of all locations that were investigated in this research. This 'site evaluation' is mainly relevant to the responsible managers of the individual nature reserves and less to the general public. Therefore, this site evaluation has been included as appendix (Appendix 7).

## 6.2 Dose-time-effect relationships

Among the rather heterogenic buffers areas there is the Mosel valley with wine production. The soils contain around twice more different compounds than in the nature reserves (Table 6), but the concentrations are a dramatic factor 532 higher for the vegetation and 958 for the soil. The effect of insect decline should be more pronounced in these buffer areas, although in toxicology linear relations between dose and effect are rare. For compounds with a dose- and time-dependent action without threshold and which enter into irreversible interactions, the time to the same effect might be just a few days shorter in case of a concentration that is 1000 times higher (Tennekes & Sanchez-Bayo, 2011). In their publication it is explained what mechanism causes a concentration of 1000 times lower gives the same lethal effect on *Cypridopsis vidua* (seed shrimp) in 5.2 days instead of 0.9 day due to permanent exposure to imidacloprid. Liess, Carsten and von der Ohe (2005) published data that concentrations up to 10.000 times below the LC50 caused a delay in development of the caddisfly L. lunatus after 1-hour exposure to fenvalerate insecticide, which is a pyrethroid. This observation confirms irreversible receptor binding of this pyrethroid insecticide.

In Table 13, it can be read that the genotoxicity and the carcinogenicity, as the indicative properties for irreversible receptor binding by pesticides, is unknown for the majority of the 94 compounds found in this research. Taking into consideration that of half of the 94 compounds found in this research are cancerogenic/genotoxic, or possible cancerogenic/genotoxic, and of the majority of other compounds these properties are unknown, it is likely that many of the compounds found everywhere in nature conservation areas might have irreversible receptor binding and thus have accumulative properties on the ecosystem, which is in line with the observed gradual decline of biodiversity in and outside nature conservation areas. The accumulative damage to nature should not be confused with accumulation of fat-soluble compounds in wild organisms. The accumulation of pesticides took place with DDT, Dieldrin and certain other compounds. The ‘advantage’ of that effect was that it was easy to measure in organisms by chemical analysis. Now in cases of the accumulating damage, by possibly hundreds of pesticides that are on the market, totally different approaches are needed to unravel the exact (direct and indirect) relationships.

For several compounds, the concentration may fluctuate from day to day, dependent on the field operations that are carried out nearby and the weather conditions. As earlier mentioned, in this study it was not possible to monitor during the whole year the contamination of the vegetation and soil. It cannot be excluded that certain pesticides appear in much higher concentrations in soil and vegetation during the summer, resulting in acute damage (or stress). In certain cases, the damage on insect species might be reversible. In that context the nature of the receptor binding in combination with the recovery capacity of the exposed insect species will be of decisive importance for the authorisation of active ingredients.

## 6.3 Relation of insect decline with measured pesticides in plants and soil

In the framework of this study, it was not possible to research correlations between insect decline and pesticide contamination of soil and vegetation, because of methodological reasons and missing data. However, the fact that pesticides were found everywhere inside nature reserves and their modes of action and various chemical and physical properties of the pesticides found make it likely that such a relation exists. The measurements conducted show that at present the level of our understanding of the behaviour of pesticides in ecosystems is very limited. Which wild plants absorb which pesticides, when, how and why? Very little is known about these subjects. The Malaise insect traps are known to cover a broad section of the local species diversity with up to more than three thousand different insect species per single trap and yearly season (Sorg et al., 2019). Some of these insects may have life cycles that may partly depend on the quality (including pesticide contamination) of aquatic environments, and others on the quality of the soil, or vegetation. That might be a reason for a totally different reaction on pesticide contamination.

Due to the standardization of the complete sampling design over decades, the decline trends of insect biomass of these highly diverse composed samples were detectable (Hallmann et al., 2017). Since no historical data were available on the pesticide contamination of these insect trapping locations, our measured values provide first indications of the potential contribution of pesticides to the proven decline of insects inside of nature protected areas in Germany.

Hallmann et al. (2017) discussed a potential source-sink dynamic as one of the potential drivers of the declines and did not comment on direct pollution of the protected area areas themselves, as no data were available for this. In their statistical analysis, the main driver(s) of the negative development are pragmatically declared as "unknown".

The measured values of our results presented here prove that many of these measuring points with Malaise insect traps of the EVK were exposed to substantial pesticide loads for 2019 inside the protected areas and adjacent buffer areas. This reinforces the well-founded suspicion of a significant influence of conventional land management, including the use of pesticides, as one of the key drivers of creeping damage to biodiversity.

Since only the pesticide load of selected substrates was determined at one point in time - no direct correlation is possible with the measured decline results in the timeline of the data in Hallmann et al. (2017). Measured values of Malaise insect traps are also highly dependent on the habitat. They differ with certain variation between naturally insect-rich and insect-poor habitats due to nutrient availability, different soils, dryness and characteristics of the vegetation and other habitat features (Figure 13).

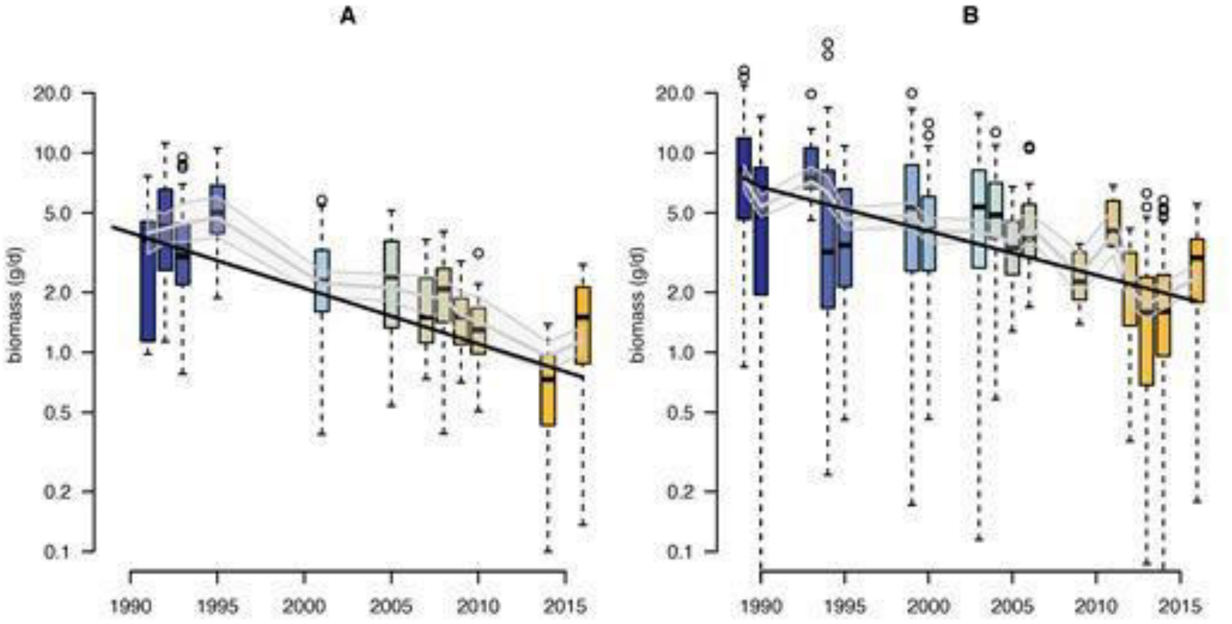

Figure 13. MF biomass difference and decline between naturally insect-rich and insect-poor habitats due to different soils, dryness and characteristics of the vegetation (Hallmann et al., 2017: Supplementary Figure B7)

*Supplementary information to Figure B7: Daily biomass of insects over time for two habitat clusters. Boxplots depict the distribution of insect biomass pooled over all traps and catches in each year at trap locations in nutrient-poor heathland, sandy grassland, and dunes (A), and in nutrient-rich grasslands, margins, and wasteland (B). Grey lines depict the fitted mean (+95% posterior credible intervals), while the black lines the mean estimated trend. Estimated annual decline amounts to 7.5% (6.6±8.4) for habitat cluster 1, as compared to 5.2% (4.8±5.5) habitat cluster 2. Models fitted independently for each habitat location. Color gradient in all panels range from 1989 (blue) to 2016 (orange).*

It needs to be said that the composition of the pesticides found at all locations investigated is quite different. That might be another reason that all potential effects on the entomofauna might be very different at different locations. Another reason might be the type of soil and habitat of those locations and other local factors. Clay and humus are to a certain extent able to bind pesticides strongly.

The Malaise insect trap data of 11 sites will still become available in the near future. Those sites are of great interest, because the soil of two sites has a pesticide content higher than 1000 µg/kg and one of almost 7000 µg/kg. It should be mentioned that the Bislicher Insel site (Figure 12), where the largest pesticide content was measured in soil of all nature conservation areas (121.8 µg/kg soil DM), is one of the sites with extremely high biomass losses in a relatively short period of time (Hallmann et al., 2017).

The detection of pesticides in plants as part of this investigation - inside of the protected areas - is of particular importance. This is the site-typical vegetation of the protected areas, in part within strictly protected habitat types according to FFH annex I (http://www.ffh-gebiete.de/natura2000/ffhanhang-i/), which is in direct contact with main parts of the entomofauna. Hence the indication that the characteristic insect species are subject to the strict protection of FFH annex I habitat types.

Measured plant pesticide loads results in food intake of these pesticides by leaf eaters, leaf miners, sap suckers, gall-forming and all other insects that interact with these plants. As a consequence, these pesticide loads will affect the subsequent invertebrate links in the food chain, the predatory and parasitoid species and finally also the vertebrate animals.

The fact that measured pesticide values in plants are higher than in soil substrates are therefore all the more frightening (Table 6, Table 7, Table 8, Table 9, Table 11). Our data show a relatively large variation of pesticide contents of the vegetation. In some cases where more than one plant species per location was sampled, the total pesticide contents and the composition were very different (for instance Krefeld Spey, see Appendix 5). In other locations (like Naturpark Nassau and Soller-Vettweiss) the composition was quite similar.

Therefore, in order to further elucidate the more accurate relationships between insect decline and pesticides, a considerably more intense investigation effort is needed. It should consist of experimental (in vivo and in vitro) studies and measurements of pesticide contamination in the timeline with simultaneous measurements of insect biomasses in different habitats. The measurements in this study also provide evidence that it is necessary to conduct measurements with an LOQ of less than 10 µg/kg, otherwise many of the important pesticides will not be detected.

In the context of this study, it needs to be said that the total pesticide concentration is, as such, not used normally in pesticide research, so we broke in this respect this convention. The advantage of using the total content is that it at least in some way it reflects the integrated total contamination of every location. To investigate potential correlations between insect-decline and pesticide contamination in the future, toxicity factors need to be taken into consideration for all pesticides found. As earlier mentioned, the databases used did not contain realistic ecotoxicological threshold values for non-target arthropod species in wild vegetation or in soil.

## 6.4 Role of compounds from non-agricultural origin

Two compounds found in almost all soil samples and a large fraction of the vegetation samples are anthraquinone and diphenyl. They are together responsible for 7.5 and 25.8% of the total pesticide load in the vegetation and 35.2% and 26% in the soil, respectively. Anthraquinone has in the past been used as deterrent on seeds against birds. It is not volatile with a vapour pressure of 0.005 mPa at 20°C. Diphenyl has in the past been used as wax on citrus fruit but has been banned for years. It has one of the highest vapour pressures of all the pesticides found, namely 1238 mPa (Appendix 4). Literature indicates that both compounds are also emitted by combustion engines (Zielinska et al., 2012) at a rate of respectively 60 and 6 µg/km. Another source may be the microplastics that are today present everywhere. Diphenylamine might have an industrial origin. Since 2012 diphenylamine has been banned in the EU as pesticide or biocide. The compound is active as fungicide, insecticide, and growth regulator. It needs to be determined where it comes from. In 5.4 it has been mentioned that the aquatic toxicity of the pesticides from non-agricultural origin is relatively low. This needs to be confirmed however for terrestrial organisms.

## 6.5 Role of compounds that have not or seldom been found

The type of compounds which were not found is also of high interest. The neonicotinoid imidacloprid was found in the vegetation of only one nature reserve with MF (Wissel) and the pyrethroids cyfluthrin and permethrin were found in the vegetation of six areas in concentrations between 1.7-18.4 µg/kg dry matter. In the research of Humann-Guillenot et al. (2019) neonicotinoids were found on Swiss organic (and conventional) farms almost everywhere, but in concentrations lower than 1 µg/kg. There is little reason to assume that these compounds are not present in German nature reserves, so they are a likely additional cause for insect decline. If you cannot measure compounds, it does not mean that they are not there and act. The research of Humann-Guillenot et al. had an extremely low LOQ ranging from 0.9-20 ng/kg of fresh samples.

Because of the large number of pesticides in our research, we were not able to achieve such an extraordinary low LOQ. Remarkably, in the research of Humann-Guillemot et al. plant samples from organic farms showed the highest percentage of contamination by neonicotinoids with 96% of all samples containing at least one neonicotinoid above the LOQ. The researchers concluded that a large part of the beneficial invertebrates may be exposed to detrimental concentrations of imidacloprid or clothianidin, measured by them. Although their research focused on agricultural fields, it is not unlikely that residues in nature reserves are comparable with those in the organic fields.

Since pyrethroids and neonicotinoids are seldom used alone, their presence will be correlated to the presence of other pesticides, which were found in our research. Insect decline might be caused by all of those pesticides together. Those found and those that could not be found, due to technical reasons. Three neonicotinoids have recently been banned from the EU. However, their use is partially replaced by pyrethroids, which have a different mode of action. They are nevertheless nerve poisons and may have the same adverse effect on biodiversity.

## 6.6 Distance to arable farming fields

As can be seen in Table 2, the average distance of the reference fields to arable farming fields amounted to 3268 m and the number of different pesticides in those areas was on average in the vegetation 3.5 compared with 4.2 in the nature reserves at an average distance of 143 m from arable fields. The number of pesticides in the soil of reference areas was 5 compared to 7.6 in the nature reserves with MF (Table 6).

The concentrations of pesticides in vegetation, soil and animal excrements showed a slightly bigger difference. The vegetation of the reference areas contained 28.41 µg pesticides/kg dry matter and of the nature reserves 51.13 µg/kg dry matter. The soil of reference areas showed at 3268 m distance from arable fields an average content of 13.86 µg/kg dry matter and in the nature reserves with MF 25.43 µg/kg dry matter. The animal excrements in the reference areas contained 20.98 µg of pesticides/kg dry matter and of the nature reserves with MF 29.46 µg/kg dry matter.

In the vegetation samples from nature reserves the herbicides pendimethalin, prosulfocarb and chlorpropham were found with a frequency of respectively 74%, 81% and 84%. In the vegetation of the reference areas these three compounds were found in 67%, 50% and 83% of the samples. The widespread occurrence of pendimethalin and prosulfocarb in German nature are confirmed by Hofmann et al. (2019), who found a presence of 87% and 66% in tree bark.

In all three matrices the reference areas were cleaner in terms of total pesticide content. However, for some individual pesticides this was not the case. The concentration of chlorpropham in the vegetation of the reference areas was 97.9% of the concentration in the nature reserves with MF. The percentage for diphenyl was 83.36% and for prosulfocarb, phthalimide and diphenylamine around 70%. These percentages amounted for anthraquinone, pendimethalin and phenylphenol-2 respectively 15.67%, 39.65% and 24.65%. The differences between the nature reserves and the reference areas are not statistically significant (Mann–Whitney–Wilcoxon U Test at $p < 0.05$ probability level) due to the large variation in measured values. Although these differences are substantial in absolute terms, due to the logarithmic nature of toxicological dose response relations it may be expected that the toxicological meaning of these differences in the field is small (chapter 5.8) and that the potential impact of pesticides through the landscape should be very evenly distributed. This coincides with the conclusion of Hallmann (2019) on basis of his insect trap biomass data. Current research of the EVK uses around 200 MF throughout Germany. That research will most likely provide more detailed information about the spatial component of insect decline.

The relative distance of the locations of the MF insect traps to arable fields is especially small because inside the nature conservation areas there are often also arable fields, where pesticides are used. Concerning the locations of this study, that was the case in the Egelsberg reserve near Krefeld (where fungicide treated seeds had been sown), in Eschweiler (treated seeds and herbicide application) and possibly in other locations as well. Sample taking took place late in the year and at that moment it was already difficult to recognize the recent field operations on nearby fields.

## 6.7 Effects of found insecticides on the entomofauna

A central question after determination of the presence of various pesticides in the different nature reserves is whether the found concentrations have influence on insect populations. If the number of locations is considered where one or more insecticides have been found, the following Table 18 is obtained.

Table 18. The number of locations where insecticides were found in vegetation and soil

| Matrix | Number of nature reserves where insecticides have been found (n=22) | Number of reference areas where insecticides have been found (n=5) | Number of buffer zones where insecticides have been found (n=5) | Total number of locations where insecticides have been found (n=32) |
|---|---|---|---|---|
| Vegetation | 20 | 4 | 5 | 29 |
| Soil | 7 | 3 | 3 | 13 |

From the table it can be concluded, that

- in the vegetation of almost all locations (90%) insecticides were found,
- in the soil ‘only’ in 31.8% of the locations insecticides were found.

The earlier mentioned threshold value LR50 (chapter 5.8) is available only for imidacloprid (0.022 gram per ha for *Aphidius rhopalosiphi*), for cypermethrin (0.0029 gram per ha for *Typhlodromus pyri*) and for cyfluthrin and etofenprox for the which this value is both 0.42 gram per ha. For the other 18 insecticides no LR50 values are available. On basis of those LR50 values it can be concluded that an assumed vegetation biomass of 5000 kg per ha in Tote Rahm, Latrop Reference area and Wissel uphill contained respectively 40, 15 and 31.7 milligram cyfluthrin, etofenprox and imidacloprid per ha. In case of Wissel uphill this amount is 14 times higher than the LR50 for acute damage. In the location EBK1 the amount of cypermethrin per ha was difficult to calculate, because the wheat crop on that site had just emerged. Tote Rahm and Latrop are exposed to concentrations of insecticides that are lower than the acute lethal concentration LR50.

Concentrations of cyfluthrin, etofenprox and cypermethrin may be considered sub-lethal within two days. However, they are likely to be lethal after a longer time interval (see chapters 5.10 & 6.2). Cyfluthrin and etofenprox are both pyrethroids that have the same mode of action as permethrin that follows Haber’s rule (see chapter 5.10). Based on the LR50 values the found insecticides predicts serious negative impacts on insect populations for those four locations. In addition, the vegetation of Tote Rahm contained a staggering amount of 44.7 micrograms of permethrin and 1.7 micrograms of picaridin.

For the other 29 locations no based interpretations can be made, because the LR50 values are not available. The general presence (in 29 out of 32 locations) of insecticides with all the other pesticides in the vegetation offers very grave living conditions for the entomofauna. Direct, or indirect, all insects live from plants. Short term sub-lethal effects (expressed by the LR50, that is often not available) are in the case of many insecticides likely to turn into lethal effects after longer periods of time. As indicated in chapter 5.10 the effect of a concentration of 1000 times lower than the acute lethal concentration can be exactly the same after a week (as shown in Table 17).

In the research that was conducted in the Dutch province of Gelderland, the conclusions are almost identical. In that research (Buijs & Mantingh, 2020) a statistically significant negative correlation has been found between the total pesticide content and dungbeetle counts in manure from nature conservation areas. In addition, the LR50 values of various insecticides made it obvious that they affect the entomofauna of different nature conservation areas. In that research though, the majority of the LR50 values of the 34 pesticides found were also not available.

## 6.8 Soil protection

Since 2000 there is in the EU a Water Framework Directive (WFD) protecting European surface and ground water against pollution by chemicals, but there is no Soil Framework Directive (SFD). The soil is outlawed and can be contaminated with most pesticides without legal or financial consequences. For only very few pesticides there are legally binding intervention values. There have been efforts to come to a Soil Framework Directive (Commission of the European Communities, 2006), but several countries, among which Germany and the Netherlands blocked the adoption of a draft SFD.

# CONCLUSION

## of the research

## CHAPTER 7

# Conclusions

- In the nature reserves, 53 different pesticides were found (see Table 5 for summarized results and Appendix 5 for original measurements).
- Pesticides are present in all the nature reserves in the soil and in the vegetation in concentrations ranging from 1-61 µg/kg dry matter for every single compound in vegetation and 1-50 µg/kg dry matter in soils (see Appendix 5).
- The higher number (statistically significant at $p<0.05$) of pesticides in vegetation than in soils may indicate that the vegetation functions as a catch mechanism for currently used pesticides from the air and/or accumulate pesticides taken up from soil (see Table 7). The presence of pesticides in the air in Germany has been firmly confirmed by the measurements of Kruse-Plaß (2020).
- The range of concentrations of the 94 compounds found in the three types of investigated areas are in principle enough to have a strong negative impact on the entomofauna (see 5.9, 5.10, 6.5 and 6.7). This should urgently be confirmed by extensive ecotoxicological research.
- Only of 4 insecticides (out of 22 found) the threshold value LR50 is known. In Wissel uphill acute damage (within 2 days) to the entomofauna is evident and in Tote Rahm, Egelsberg1 (EBK1) and in Latrop reference area such damage is likely to occur after 2 days because of chronic (time dependent) action of pyrethroid's presence. Of all other 18 insecticides found the LR50 and dose-time-effect relationships are unknown. Most of these insecticides have been specially developed to kill insects and many of them are very persistent.
- The second part of the hypothesis of this study that pesticides have influence on insect decline inside nature reserves" could not yet be proven empirically (see 5.7). There are three reasons for this namely: 1) the methodology used 2) the complexity of the issue, and 3) lacking relevant terrestrial ecotoxicological threshold values.
- The exposure of nature reserves to pesticides (expressed as total of all compounds) is rather evenly distributed across the landscape. The distance to agricultural fields seems to play no major role. The average contamination of reference areas (at an average distance to arable fields of 3268 m) was less than in the areas of Hallmann (2019) at an average distance of 143 m, but the difference was not statistically significant (Table

6, Table 7). Because of the special nature of dose-time-effect relations of pesticides, the effects of different concentrations of pesticides on entomofauna in all investigated locations might be very similar (see 6.6).

- The average concentration of some pesticides (like anthraquinone and phenylphenol-2) in reference areas was much (60-75%) lower, but the differences were not statistically significant, due to a large variation of measured values and a relative low number of locations (see 5.5)
- There are at least 12 reasons why current theoretical ecotoxicological values can be a strong underestimation of real in-vivo toxicity of pesticides (see 4.10)
- Further research is required to unravel causal relationships between insect decline and pesticide contamination (see 1 & 5.7). In such research attention should be paid to individual pesticides, but also to their mixtures.
- Taken into consideration the fact that dose-time-effect relations of most pesticides is unknown, it is necessary to investigate them urgently.
- The use of combustion engines may be an important source of two compounds, namely anthraquinone and diphenyl (see 6.4). The electrification of transport may strongly reduce these emissions together with all other compounds from exhaustion gases.
- Taken into consideration their aquatic toxicity threshold values, the toxicological role of the found compounds with an industrial origin might be limited, if compared with the pesticides originating from agriculture (see 5.4). This has to be confirmed by entomological research.
- In this research the origin of the pesticides found was not determined. A part can originate from agricultural fields inside the nature conservation areas, where they are sometimes allowed to be used (see 6.6). Partly they can originate from regional, national, and international sources.
- There are no legally binding threshold values of pesticide contents in soils (see 6.7) and wild plants in nature conservation areas, and not for agricultural soils.
- The established widespread contamination of nature reserves with pesticides shows that the fate of nature reserves is also closely linked with the agricultural policies. Our attitude to nature should be based on the precautionary principle. Let science do their task and explore the effect of chemical cocktails on the environment intensively. In a matter of a few years, it could become fully clear what role the found pesticide mixtures play in the insect decline.

# ADVICE

## for researchers, politicians, nature conservation organisations & farmers

## CHAPTER 8

# Advice

## 8.1 For research

- In order to research the correlation between pesticide contents of soil and vegetation and the biomass catches, there is a unique possibility now, because Germany wide around 200 MF are operational in 2020 and 2021. These locations can be used for a countrywide investigation of pesticide contamination in all those nature reserves, where in 2021 also the insect biomass will be established.
- In order to prove causal relations between the pesticides found most frequently and the population development of insects, it is necessary to do field tests and bioassays with those pesticides and certain species of insects. Such tests should also be done with the cocktails and not only with the individual pesticides. They should be done through at least several generations of the chosen species in order to include potential long-term effects of irreversible receptor binding. In order to get distinct results, the controls must be fully free from pesticides (which is not easy today), otherwise no difference may be observed between the controls and the treated variants.
- In order to unravel possible relations between insect development and pesticide contents of soil and vegetation, entomologists should analyse the relations of the different categories of insects caught in MF with the soil and the plants.
- In order to know more about the contamination of vegetation during the high season of insects, additional seasonal investigations on pesticides in nature reserves are needed in order to create timelines. These timelines can be made for different important wild plant species, not only within the season, but also through different years.
- It should be investigated which role very effective insecticides (that could not be measured in this research, because of their low concentrations), like neonicotinoids and pyrethroids could play next to the role of the compounds found.
- If it is the case that the vegetation in nature conservation areas accumulates pesticides from the air, the urgent question is how this process takes place on the physical and molecular levels

- In order to get predictions of the behaviour of anthraquinone and diphenyl, the degradation and accumulation of those compounds in nature must be investigated.
- The origin and effects of diphenylamine deserve more attention.
- Are pesticides thinkable which are not genotoxic or cancerogenic and do not lead to irreversible receptor binding and accumulative destruction of biodiversity?
- Is it realistic to expect that the ecological balance of organic farms will stay intact in spite of ongoing biodiversity decline, and that their farming system may not become impossible at longer term, because of this biodiversity decline?
- Are the rules of organic farming tight enough to: a) keep out pesticides from those farms in spite of the fact that they are scattered through a huge landscape with conventional farms b) keep out pesticides that they acquire themselves by using conventional manure, conventional straw, fly repellents, disinfecting agents, contaminated irrigation water, etc.?
- Work on causal relationships between pesticides exposure and insect decline must be accelerated in order to get hard facts within a few years.
- The dose-time-effect relations of all pesticides must be identified within a few years.

## 8.2 For policy

- A strong reduction in the use of chemical pesticides seems to be unavoidable, taken into consideration the 53 pesticides found inside nature reserves. It would be logical to start with the elimination of the compounds that were found most frequently in nature reserves from the market, including those compounds that cannot be measured with standard measuring protocols, like pyrethroids and neonicotinoids. Such compounds are lethal to most insects at concentrations below 1 µg/kg fresh material, so the effect of those compounds in protected nature reserves is uncontrollable.
- Directive 2009/128/EC of the European Parliament and of the Council of 21 October 2009 (article 12) mentions that environmental risk assessments should be carried out in order to minimize the use of pesticides in protected areas. With the data available from this study, there is solid reason to start with those assessments (European Parliament, 2009).
- Volatile and persistent pesticides whose spreading into the environment is unavoidable due to their physical properties, should be banned.
- Politicians should put pressure on the relevant authorities involved in the authorization of pesticides for a stringent and producer-independent

toxicology tests which covers also the dose-time-effect relations of the compounds and their potential to spread around in the countryside.

- Politicians should become aware that even 50% organic agriculture might not be enough to dilute the pesticides originating from 50% conventional farms.
- A Soil Protection Directive must be adopted on European scale with legally binding threshold values for all separate pesticides and for the whole of the pesticide concentrations in soils because soils are now predominantly outside the protection of the law (see 6.8) regarding pesticide contamination.
- Society as a whole should become aware that potential financial losses due to biodiversity decline are unimaginable high.
- Soils that have been contaminated strongly in the past (like those met in the Mosel valley) need to be depreciated. Lower quality must mean lower price. That is the way the economy is supposed to work. Depreciation of contaminated soils will be an incentive to keep soils clean and not to purchase the latest developed weed killer, fungicide, or insecticide (even though they might have been approved by admission authorities).

## 8.3 For nature conservation organisations

- Nature conservation has to adopt a more active approach in the debates about pesticides that are found inside nature reserves. After taking the results of this research into consideration, a new approach should be developed in favour of totally different agricultural and industrial policies.
- Seek close cooperation with agricultural organizations, based on the principle that agriculture, above anything, needs also a healthy ecological balance for the production of healthy food.
- Put pressure on policy-makers in order to convince governments that the present contamination of nature reserves is against the letter and the spirit of current nature conservation legislation at national, EU and international levels.
- Advocate for the phasing-out of all pesticides that have been found in nature reserves.
- Advocate for totally different admission rules for new pesticides that prevent compounds with irreversible receptor binding, high vapor pressure, toxicity at concentrations that cannot be measured, and other unacceptable properties from being admitted for use.
- Support actively further pesticide research and investigations of nature reserves and sue those that contaminate them, or those that allow them to be contaminated.

## 8.4 For agriculture

- In order to facilitate an objective discussion in society about the role that agriculture plays in the contamination of nature conservation areas, collect proper data about the pesticide emissions from farms to air, soil, surface water and groundwater.
- Let measurements be done by reliable independent organizations, not connected with the suppliers of pesticides.
- Measurements should be done on crops, manure, soils, drainage water and all relevant other matrices that may have influence on the environment.
- Qualify and quantify not only the advantages of chemical crop protection but also their disadvantages for farming (in terms of soil health, yield, vulnerability to pests and diseases, occupational health risks, etc), in order to create objective balanced information.
- Raise awareness of the fact that the current level of pesticides found in soil and vegetation in nature reserves, in buffer zones and in reference areas cannot be called a ‘normal’ situation.
- Support advocacy for a Soil Framework Directive legislation in order to start legal protection of agricultural soils (among others against contamination by pesticides) and to create a fair playing field for agricultural producers throughout the EU.

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# APPENDIX

# Appendix 1. Analysis protocol of the laboratory

A representative sub-sample of each sample (vegetation, soil and animal excrements), between 100 and 200 g, was taken before pre-treatment. Afterwards the sub-samples were freeze-dried and milled, and with the obtained data the moisture content could be determined. All vegetation samples were analysed according to a fixed protocol (Appendix 1) for 661 different pesticides, biocides and metabolites (see Appendix 2) making use of the GC + MSMS of Agilent and LC of Agilent combined with the MSMS of Sciex. The soil samples were also tested on presence of glyphosate, AMPA and glufosinate. In case of the soil, therefore the total number of analysed compounds amounted 664 (661+3). After freeze-drying and milling the samples 7 ml of water was added. The tubes were then stirred in a multivortex at 2000 RPM for one minute. Afterwards the samples were soaked for two hours. The freezedried, milled and soaked samples were extracted with a mixture of three solvents: Acetone, petroleumether dichloromethane. Four salts were used in the extraction: Sodium citrate (15.4%), Sodium hydrogen citrate sesquihydrate (7.7%), Magnesium sulphate (61.5%) and Sodium chloride (15.4%) [1]. Extraction was executed while being stirred in a Collomix at 690 RPM for one minute, stirred in a multivortex at 2000 RPM for five minutes and centrifuged at 10.000 RPM for ten minutes. Depending on the compound and matrix the Limit Of Quantification (LOQ) ranged from 0.5 µg/kg fresh sample (in case of manure) to 2.4 µg/kg. Lower concentrations, above the limit of detection, were also detected, but with a non-specified probability interval of confidence. The 90% confidence interval of all measurements above the LOQ was 0.5 x measured value up to 1.5 measured value. The list of all pesticides, biocides and metabolites measured analysed by GC/MSMS and LC/MSMS can be found in Appendix 2 of this report. Before and after analysis all sub-samples were stored at a temperature of -18°C. In certain cases, pesticides were only qualitatively measured, since due to interference with other compounds in the samples their concentration could not be determined. In such cases these pesticides were reported as ‘detected qualitatively’.

# Appendix 2. Analysed compounds

## Analysis 1: Pesticides GC-MSMS (GC-MS-Triplequad WVS-092)

### Pesticide (active compound)

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| (3- + 4-) Chloroaniline* | Bromophos-methyl $^{Q}$ |
| 1-Naphthylacetamide | Bromopropylate $^{Q}$ |
| 1-Naphtol (degradation Carbaryl) $^{Q}$* | Bromoxynil-octanoate |
| 1,4-Dimethylnaphthalene | Bromuconazole $^{Q}$ |
| 2,4,6-Trichlorophenol* | Bupirimate $^{Q}$ |
| 2,6-Dichlorobenzamide (degradation Dichlobenil) $^{Q}$* | Buprofezin $^{Q}$ |
| 3,4-Dichloroaniline* | Butralin |
| 3,5-Dichloroaniline (degradation Iprodion)* | Cadusafos $^{Q}$ |
| 4,4-Dichlorobenzophenon (degradation Dicofol)* | Captafol (ECD) |
| Acibenzolar-S-methyl | Captan (ECD) |
| Aclonifen $^{Q}$ | Carbaryl $^{Q}$ |
| Acrinathrin $^{Q}$ | Carbofuran $^{Q}$ |
| Alachlor $^{Q}$ | Carbofuran-phenol $^{Q}$* |
| Aldrin $^{Q}$ | Carbophenothion |
| Allethrin $^{Q}$ | Carbophenothion-methyl** |
| Ametryn $^{Q}$ | Chinomethionat |
| Aminocarb | Chlorbufam |
| Amitraz | Chlordane-cis $^{Q}$ |
| Anthraquinone $^{Q}$ | Chlordane-trans $^{Q}$ |
| Azinphos-ethyl | Chlorfenapyr $^{Q}$ (ECD) |
| Azoxystrobin $^{Q}$ | Chlorfenson $^{Q}$ |
| Benalaxyl $^{Q}$ | Chlorfenvinphos-cis $^{Q}$ |
| Bendiocarb | Chlorfenvinphos-trans $^{Q}$ |
| Benfluralin | Chloridazon |
| Benfuracarb as carbofuran | Chlorobenzilate (degradation Dicofol) $^{Q}$ |
| Bifenazate | Chloroneb |
| Bifenox $^{Q}$ | Chlorothalonil $^{Q}$ |
| Bifenthrin $^{Q}$ | Chlorpropham $^{Q}$ |
| Biphenyl $^{Q}$ | Chlorpyrifos $^{Q}$ |
| Bitertanol $^{Q}$ | Chlorpyrifos-methyl $^{Q}$ |
| Bromacil (ECD) | Chlorthal-dimethyl $^{Q}$ |
| Bromocyclen | Chlorthiamid (ECD) |
| Bromophos-ethyl $^{Q}$ | Chlozolinate $^{Q}$ |
| Clodinafop-propargyl | Dioxabenzofos |
| Clomazone $^{Q}$ | Diphenamide |
| Cloquintocet-mexyl | Diphenyl $^{Q}$ |
| Coumafos | Diphenylamine $^{Q}$ |
| Cyanazine | Disulfoton $^{Q}$ |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Cyanofenphos | Disulfoton sulfone [Q] |
| Cyanophos | Disulfoton sulfoxide |
| Cycloate | Ditalimfos [Q] |
| Cyfenothrin [Q] | Endosulfan (alpha-) [Q] |
| Cyfluthrin [Q] | Endosulfan (beta-) [Q] |
| Cyhalothrin | Endosulfan-sulphate [Q] |
| Cypermethrin [Q] | Endrin (ECD) |
| Cyproconazole [Q] | EPN [Q] |
| Cyprodinil [Q] | Epoxiconazole [Q] |
| Deltamethrin [Q] | EPTC |
| Demeton-O [Q] | Etaconazole |
| Demeton-S [Q] | Ethion [Q] |
| Demeton-S-methyl | Ethofumesate [Q] |
| Desmetryn | Ethoprophos [Q] |
| Diazinon [Q] | Ethoxyquin |
| Dichlobenil (degradation Chlorthiamid) | Etofenprox [Q] |
| Dichlofenthion [Q] | Etridiazole (ECD) |
| Dicloran [Q] | Etrimfos [Q] |
| Dicofol | Famoxadone |
| Dieldrin [Q] | Fenarimol [Q] |
| Diethofencarb [Q] | Fenazaquin [Q] |
| Difenoconazole [Q] | Fenchlorphos |
| Diflufenican [Q] | Fenfluthrin |
| Dimethipin | Fenitrothion [Q] |
| Dimethoate [Q] | Fenkapton |
| Dimethylaminosulfotoluidide (DMST) [Q] | Fenobucarb [Q] |
| Dimethylvinphos | Fenoxycarb [Q] |
| Diniconazole [Q] | Fenpiclonil [Q] |
| Clodinafop-propargyl | Dioxabenzofos |
| Clomazone [Q] | Diphenamide |
| Cloquintocet-mexyl | Diphenyl [Q] |
| Coumafos | Diphenylamine [Q] |
| Cyanazine | Disulfoton [Q] |
| Cyanofenphos | Disulfoton sulfone [Q] |
| Fenpropathrin [Q] | HCH (gamma-) (= Lindane) |
| Fenpropidin [Q] | Heptachlor [Q] (ECD) |
| Fenpropimorph [Q] | Heptachlor-endo-epoxide (trans) |
| Fenpyroximate [Q] | Heptachlor-exo-epoxide (cis) |
| Fenson | Heptenophos [Q] |
| Fensulfothion [Q] | Hexachlorobenzene [Q] |
| Fenthion [Q] | Hexachlorobutadiene [Q] ** |
| Fenthion sulfoxide [Q] | Hexaconazole [Q] |
| Fenvalerate + Esfenvalerate [Q] | Hexazinone |
| Fipronil [Q] | Imazethapyr |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Fipronil sulfone | Iodofenphos |
| Fluazifop-butyl $^{Q}$ | Iprobenfos |
| Flubenzimine | Iprodione $^{Q}$ |
| Fluchloralin | Isazofos |
| Flucythrinate $^{Q}$ | Isocarbophos $^{Q}$ |
| Fludioxonil $^{Q}$ | Isodrin $^{Q}$ |
| Fluquinconazole $^{Q}$ | Isofenphos $^{Q}$ |
| Flurprimidole | Isofenphos-methyl $^{Q}$ |
| Flusilazole $^{Q}$ | Isofenphos-oxon (degradation Isofenphos)* |
| Flutolanil $^{Q}$ | Isoprocarb |
| Fluvalinate $^{Q}$ | Isoproturon $^{Q}$ |
| Folpet (ECD) | Isoxadifen-ethyl |
| Fonofos | Kresoxim-methyl $^{Q}$ |
| Formothion $^{Q}$ | Lambda-Cyhalothrin $^{Q}$ |
| Phthalimide (degradation Folpet) | Lenacil $^{Q}$ |
| Fosthietan | Leptofos |
| Fuberidazole | Malaoxon (degradation Malathion ) |
| Furalaxyl $^{Q}$ | Malathion $^{Q}$ |
| Halfenprox | Mecarbam $^{Q}$ |
| Haloxyfop-ethoxyethyl $^{Q}$ | Mephosfolan $^{Q}$ |
| HCH (alpha-) $^{Q}$ | Mepanipyrim $^{Q}$ |
| HCH (beta-) | Mepronil $^{Q}$ |
| HCH (delta-) $^{Q}$ | Metalaxyl $^{Q}$ |
| Fenpropathrin $^{Q}$ | HCH (gamma-) (= Lindane) |
| Fenpropidin $^{Q}$ | Heptachlor $^{Q}$ (ECD) |
| Fenpropimorph $^{Q}$ | Heptachlor-endo-epoxide (trans) |
| Fenpyroximate $^{Q}$ | Heptachlor-exo-epoxide (cis) |
| Fenson | Heptenophos $^{Q}$ |
| Fensulfothion $^{Q}$ | Hexachlorobenzene $^{Q}$ |
| Metazachlor $^{Q}$ | Parathion $^{Q}$ |
| Methabenzthiazuron $^{Q}$ | Parathion-methyl $^{Q}$ |
| Methacrifos | Penconazole $^{Q}$ |
| Methidathion $^{Q}$ | Pencycuron |
| Methiocarb $^{Q}$ | Pendimethalin $^{Q}$ |
| Methoxychlor | Pentachloroaniline $^{Q}$ |
| Metobromuron | Pentachloroanisol $^{Q}$ |
| Metolachlor-S $^{Q}$ | Pentachlorobenzene $^{Q}$ |
| Metolcarb | Pentachlorophenol |
| Metoprotryn | Permethrin-cis $^{Q}$ |
| Metrafenone $^{Q}$ | Permethrin-trans $^{Q}$ |
| Metribuzin $^{Q}$ | Perthaan |
| Mevinphos $^{Q}$ | Phenothrin $^{Q}$ |
| Mirex | Phenthoate $^{Q}$ |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Molinate | Phenylphenol-2 $^{Q}$ |
| Myclobutanil $^{Q}$ | Phosalone $^{Q}$ |
| Napropamide $^{Q}$ | Phospholan |
| Nitrofen | Phosmet $^{Q}$ |
| Nitropyrin | Picoxystrobin $^{Q}$ |
| Nitrothal-Isopropyl | Piperonyl butoxide $^{Q}$ |
| Norflurazon | Pirimicarb $^{Q}$ |
| o,p'-DDD $^{Q}$ * | Pirimicarb-desmethyl $^{Q}$ * |
| o,p'-DDE $^{Q}$ * | Pirimicarb-desmethylformamido* |
| Ofurace $^{Q}$ | Pirimiphos-ethyl $^{Q}$ |
| Oxadiazon $^{Q}$ | Pirimiphos-methyl $^{Q}$ |
| Oxadixyl $^{Q}$ | Procymidone $^{Q}$ |
| Oxychlordane* | Profenofos $^{Q}$ |
| Oxyfluorfen | Profluralin $^{Q}$ |
| p,p'-DDD + o,p'-DDT $^{Q}$ | Profoxydim |
| p,p'-DDE $^{Q}$ | Promecarb $^{Q}$ |
| p,p'-DDT | Prometryn $^{Q}$ |
| Paraoxon* | Propachlor $^{Q}$ |
| Paraoxon-methyl | Propanil $^{Q}$ |
| Metazachlor $^{Q}$ | Parathion $^{Q}$ |
| Methabenzthiazuron $^{Q}$ | Parathion-methyl $^{Q}$ |
| Methacrifos | Penconazole $^{Q}$ |
| Methidathion $^{Q}$ | Pencycuron |
| Methiocarb $^{Q}$ | Pendimethalin $^{Q}$ |
| Methoxychlor | Pentachloroaniline $^{Q}$ |
| Propargite $^{Q}$ | Sulprofos |
| Propazine $^{Q}$ | Tebuconazole $^{Q}$ |
| Propetamphos | Tebufenpyrad $^{Q}$ |
| Propham $^{Q}$ | Tecnazene $^{Q}$ |
| Propiconazole $^{Q}$ | Tefluthrin $^{Q}$ |
| Propoxur $^{Q}$ | Telodrin $^{Q}$ |
| Propoxycarbazone | Terbacil |
| Propyzamide $^{Q}$ | Terbumeton |
| Prosulfocarb $^{Q}$ | Terbutryn $^{Q}$ |
| Prothioconazole** | Terbutylazine $^{Q}$ |
| Prothioconazole-desthio | Terbutylazine-desethyl* |
| Prothiofos $^{Q}$ | Tetrachlorovinphos (Z-) $^{Q}$ |
| Pyraflufen-ethyl | Tetraconazole $^{Q}$ |
| Pyrazophos $^{Q}$ | Tetradifon $^{Q}$ |
| Pyridaben $^{Q}$ | Tetrahydrofthalimide (degradation captan/captafol) |
| Pyridaphenthion $^{Q}$ | Tetramethrin $^{Q}$ |
| Pyrifenox | Tetrasul |
| Pyrimethanil $^{Q}$ | Tolclofos-methyl $^{Q}$ |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Pyriproxyfen Q | Transfluthrin Q |
| Quinalphos Q | Triadimefon Q |
| Quinoxyfen Q | Triadimenol Q |
| Quintozene Q | Tri-allate Q |
| Quizalofop-ethyl | Triazamate Q |
| S 421 | Triazophos Q |
| Silthiofam | Trichloronat |
| Simazine Q | Trifloxystrobin Q |
| Spiromesifen Q | Triflumizole Q |
| Spiroxamine Q | Trifluralin Q |
| Sulfotep | Trinexapac-ethyl |
| Sulphur ** | Vinclozolin Q |

The reporting limits mentioned are indicative and can change depending on the matrix and the circumstances of the analysis.

Q: Accreditated by the Raad voor Accreditatie (registration number L201).

* These metabolites according to EU regulation 396/2005 will not be reported with an MRL. Only on request this will be reported.

** Only on request these analytes will be reported.

Exceptions of the GC-MSMS analysis concerning the reporting

If a pesticide cannot be detected for example due to matrix interference, this will be mentioned on the analysis report with a remark.

ECD: This pesticide is qualified with GC-MSMS. The quantification and confirmation is determined with GC-MSMS.

The GC-MSMS analysis 1 consists of a total number of 323 pesticides.

The accreditation other than fruit and vegetables, will be shown on DRF-260 Flexible scope.

## Analysis 3: Pesticides LC-MSMS standard (method WVS-040). Pesticide (active compound)

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| 4-Bromophenylurea | Carbaryl $^{Q}$ |
| 6-Benzyladenine | Carbendazim $^{Q}$ |
| Abamectine $^{Q}$ | Carbetamide |
| Acephate $^{Q}$ | Carbofuran $^{Q}$ |
| Acequinocyl | Carbofuran-3-hydroxy $^{Q}$ |
| Acetamiprid $^{Q}$ | Carbofuran-3-keto $^{Q}$ * |
| Alanycarb | Carbosulfan |
| Aldicarb $^{Q}$ | Carboxin |
| Aldicarb sulfone $^{Q}$ | Carfentrazone-ethyl |
| Aldicarb sulfoxide $^{Q}$ | Carpropamide $^{Q}$ |
| Ametoctradin | Chlorantraniliprole $^{Q}$ (Rynaxypyr) |
| Aminopyralid | Chlorbromuron $^{Q}$ |
| Amisulbrom | Chlordimeform |
| Amitraz *** | Chlorfluazuron |
| Amitraz DMA *** | Chlorotoluron |
| Amitraz DMF *** | Chloroxuron |
| Amitraz DMPF *** | Chlorthiophos $^{Q}$ |
| Amitrole | Chlorthiophos sulfone $^{Q}$ * |
| Anilazine | Cinnerin |
| Asulam $^{Q}$ | Clethodim $^{Q}$ |
| Atrazine $^{Q}$ | Climbazol $^{Q}$ |
| Azaconazole $^{Q}$ | Clofentezine $^{Q}$ |
| Azadirachtin | Clopyralid |
| Azamethiphos $^{Q}$ | Clothianidin $^{Q}$ |
| Azimsulfuron $^{Q}$ | Crimidine $^{Q}$ |
| Azinphos-methyl $^{Q}$ | Cyantraniliprole (Cyazypyr) |
| Azoprotryne | Cyazofamid |
| Azoxystrobin $^{Q}$ | Cycloxydim $^{Q}$ |
| Barban | Cyflufenamid $^{Q}$ |
| Beflubutamid | Cyflumetofen |
| Benfuracarb $^{Q}$ as carbofuran | Cymoxanil $^{Q}$ |
| Benomyl $^{Q}$ as carbendazim | Cyproconazole $^{Q}$ |
| Benoxacor $^{Q}$ | Cyprodinil $^{Q}$ |
| Benthiavalicarb-isopropyl $^{Q}$ | Cyromazine $^{Q}$ *** |
| Benzoximate | Cythioate $^{Q}$ |
| Bitertanol $^{Q}$ | Daminozide *** |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Bixafen | DEET Q |
| Boscalid Q | Demeton-S-methyl sulfone Q |
| Bromuconazole Q | Demeton-S-methyl sulfoxide(=oxydemeton-ethyl) Q |
| Bupirimate Q | Desmedipham Q |
| Buprofezin Q | Diafenthiuron Q |
| Butafenacil Q | Dichlofluanid Q |
| Butocarboxim | Dichlorvos |
| Butocarboxim sulfoxide Q* | Diclobutrazol |
| Butoxycarboxim Q | Dicrotophos Q |
| Buturon Q | Diethofencarb Q |
| Caffeine ** | Difenoconazole Q |
| Diflubenzuron Q | Florasulam Q |
| Dimethenamid Q | Fluazifop-P-butyl Q |
| Dimethirimol Q | Flubendiamide Q |
| Dimethoate Q | Flucycloxuron Q |
| Dimethomorph Q | Flufenacet Q |
| Dimethylaminosulfotoluidide (DMST) Q | Flufenoxuron Q |
| Dimoxystrobin Q | Flumioxazine Q |
| Diniconazole Q | Fluopicolide Q |
| Dinotefuran Q | Fluopyram Q |
| Dipropetryn Q | Fluotrimazol Q |
| Diuron Q | Fluoxastrobin Q |
| DMSA Q * | Fluquinconazole Q |
| Dodemorph Q | Flurochloridone |
| Dodine Q | Fluroxypyr |
| Emamectin (benzoate B1a) Q | Fluroxypyr-1-methylheptylester Q |
| Epoxiconazole Q | Flurpyridafurone |
| Ethiofencarb Q | Flupyrsulfuron-methyl |
| Ethiofencarb sulfone Q * | Flusilazole Q |
| Ethiofencarb sulfoxide Q* | Fluthiacet-methyl |
| Ethiprole | Flutolanil Q |
| Ethirimol Q | Flutriafol Q |
| Ethoxysulfuron | Fluxapyroxad |
| Etofenprox Q | Foramsulfuron |
| Etoxazole Q | Forchlorfenuron |
| ETU | Formetanate hydrochloride Q |
| Famophos (= Famphur) Q | Fosetyl-Al*** |
| Famoxadone Q | Fosthiazate Q |
| Fenamidone Q | Furalaxyl Q |
| Fenamiphos Q | Furathiocarb Q |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Fenamiphos sulfone | Furmecyclox [Q] |
| Fenamiphos sulfoxide | Halofenozide |
| Fenarimol [Q] | Haloxyfop [Q] |
| Fenazaquin [Q] | Hexaconazole [Q] |
| Fenbuconazole [Q] | Hexaflumuron [Q] |
| Fenbutatin oxide*** | Hexythiazox [Q] |
| Fenhexamid [Q] | Hymexazol [Q] |
| Fenoxycarb [Q] | Imazamethabenz-methyl |
| Fenpropidin [Q] | Imazalil [Q] |
| Fenpropimorph | Imazamox |
| Fenpyrazamine | Imazaquin [Q] |
| Fenpyroximate [Q] | Imibenconazole [Q] |
| Fenthion [Q] | Imidacloprid [Q] |
| Fenthion-oxon | Indoxacarb [Q] |
| Fenthion-oxon sulfone | Iodosulforon-methyl |
| Fenthion-oxon sulfoxide | Iprovalicarb [Q] |
| Fenthion sulfone | Isocarbophos [Q] |
| Fenthion sulfoxide [Q] | Isoprothiolane [Q] |
| Fenuron | Isopyrazam [Q] |
| Flazasulfuron | Isouron [Q] |
| Isoxaflutole [Q] | Oxasulfuron |
| Isoxathion [Q] | Oxycarboxin [Q] |
| Jasmolin | Paclobutrazol [Q] |
| Kresoxim-methyl | Paraoxon-ethyl [Q]* |
| Lenacil [Q] | Paraoxon-methyl |
| Linuron [Q] | Pebulate |
| Lufenuron [Q] | Penconazole [Q] |
| Malathion [Q] | Pencycuron [Q] |
| Maleic hydrazide [Q]*** | Penflufen |
| Mandipropamid | Penthiopyrad |
| Mefenacet [Q] | Phenisopham |
| Mefenpyr-diethyl [Q]** | Phenmedipham [Q] |
| Mepanipyrim [Q] | Phorate |
| Mephosfolan [Q] | Phorate sulfone |
| Mepronil | Phorate sulfoxide* |
| Mesosulfuron-methyl | Phosalone [Q] |
| Mesotrione [Q] | Phosmet [Q] |
| Metaflumizone | Phosmet-oxon [Q] |
| Metalaxyl [Q] | Phosphamidon [Q] |
| Metaldehyde | Phoxim |
| Metamitron [Q] | Picaridin (= Icaridin)** |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Metconazole Q | Picolinafen Q |
| Methamidophos Q | Picoxystrobin Q |
| Methidathion Q | Pinoxaden |
| Methiocarb (=mercaptodimethur) Q | Piperonyl butoxide Q |
| Methiocarb sulfone Q | Pirimicarb Q |
| Methiocarb sulfoxide Q | Pirimicarb-desmethyl Q * |
| Methomyl Q | Prochloraz Q |
| Methoxyfenozide Q | Prochloraz-desimidazole-amino |
| Metobromuron Q | Prochloraz-desimidazoleformylamino |
| Metosulam | Profenofos Q |
| Metoxuron Q | Propamocarb hydrochloride Q*** |
| Metsulfuron-methyl | Propaquizafop Q |
| Milbemectin | Propiconazole Q |
| Monocrotophos Q | Propoxur Q |
| Monolinuron Q | Propyzamide Q |
| Monuron Q | Proquinazid Q |
| Myclobutanil Q | Prosulfocarb |
| Naled | Prosulfuron |
| Neburon | Prothiocarb |
| Nicosulfuron | Prothiocarb hydrochloride Q |
| Nitenpyram Q | Prothioconazole** |
| Nitralin | Prothioconazole-desthio |
| Novaluron | Pymetrozine Q |
| Nuarimol Q | Pyracarbolid |
| Omethoate Q | Pyraclofos |
| Oxadixyl Q | Pyrazophos Q |
| Oxamyl Q | Pyrethrin |
| Oxamyl-Oxime Q* | Pyridaben Q |
| Pyridaphenthion Q | Thidiazuron Q |
| Pyridalyl Q | Thiencarbazone-methyl |
| Pyridate Q | Thifensulfuron-methyl |
| Pyridate (metabolite) (=6-chloro4-hydroxy-3-phenylpyridazin) Q CL9673 | Thiobencarb Q |
| Pyrifenox Q | Thiocyclam Q |
| Pyrimethanil Q | Thiodicarb Q |
| Pyrimidifen | Thiofanox |
| Pyriproxyfen Q | Thiofanox sulfone Q* |
| Pyroxsulam | Thiofanox sulfoxide Q* |
| Quinclorac Q | Thiophanate-methyl Q |
| Quinmerac | Thiometon |

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| Quizalofop | Tolclofos-methyl |
| Rimsulfuron | Tolfenpyrad |
| Rotenone [Q] | Tolylfluanid [Q] |
| Saflufenacil | Tralkoxydim [Q] |
| Sethoxydim [Q] | Triadimefon [Q] |
| Silafluofen [Q] | Triadimenol [Q] |
| Simazine [Q] | Triapenthenol [Q] |
| Spinetoram | Triazophos [Q] |
| Spinosad (A and D) [Q] | Triazoxide |
| Spirodiclofen [Q] | Tribenuron-methyl |
| Spirotetramat [Q] | Trichlorfon [Q] |
| Spirotetramat cis-enol [Q] | Tricyclazole [Q] |
| Spirotetramat cis-keto-hydroxy [Q] | Tridemorph [Q] |
| Spirotetramat enol-glucoside | Trifloxystrobin |
| Spirotetramat mono-hydroxy [Q] | Triflumizole [Q] |
| Spiroxamine [Q] | Triflumizole-FM-6-1 |
| Sulcotrione [Q] | Triflumuron [Q] |
| Sulfentrazone [Q] | Triflusulfuron-methyl |
| Sulfoxaflor | Triforine [Q] |
| Tebuconazole [Q] | Trimethacarb-3,4,5 (=Landrin) [Q] |
| Tebufenozide [Q] | Trinexapac-ethyl [Q] |
| Tebufenpyrad [Q] | Triticonazole [Q] |
| Teflubenzuron [Q] | Tritosulfuron |
| Tembotrione | Uniconazole |
| Tepraloxydim [Q] | Valifenalate |
| Terbufos | Vamidothion [Q] |
| Terbufos sulfone * | Warfarin |
| Terbufos sulfoxide * | XMC |
| Terbutylazine | Zoxamide [Q] |
| Terbutylazine-desethyl | |
| Tetraconazole [Q] | |
| Thiabendazole [Q] | |
| Thiacloprid [Q] | |
| Thiametoxam [Q] | |

## Analysis 4: Pesticides LC-MSMS (method WVS-040) Pesticide (active compound)

| Pesticide (active ingredient) | Pesticide (active ingredient) |
|---|---|
| 1-Naphthylacetic acid | Fipronil-sulfone |
| 1,2,4-Triazole* | Flonicamid TFNA-AM * |
| 2-Naphtyloxyacetic acid | Flonicamid-TFNA |
| 2,4-D $^{Q}$ | Flonicamid-TFNG |
| 2,4-DB | Fluazifop (free acid) |
| 2,4,5-T | Fluazinam $^{Q}$ |
| 2,4,6-Trichlorophenoxy acetic acid* | Imazamox |
| 4-CPA (4-chlorophenoxyacetic acid =PCPA) | Ioxynil |
| Bentazone $^{Q}$ | MCPA $^{Q}$ |
| Benzovindiflupyr | MCPB |
| Bromoxynil | Mecoprop $^{Q}$ |
| Chloramben | Meptyldinocap |
| Chlordecone hydrate | Picloram |
| Chlorothalonil-4-hydroxy**** | Prohexadione-calcium |
| Chlorthion | Triclopyr |
| Cyclanilide | |
| Cyenopyrafen | |
| Dicamba | |
| Dichlorophen | |
| Dichlorprop | |
| Dinocap $^{Q}$ | |
| Dithianon $^{Q}$ | |
| Fenoprop (2,4,5-TP) | |
| Fipronil | |

The reporting limits mentioned are indicative and can change depending on the matrix and the circumstances of the analysis.

$^{Q}$: Accreditated by the Raad voor Accreditatie (registration number L201).

* These metabolites according to EU regulation 396/2005 will not be reported with an MRL.

Only on request this will be reported.

** Only on request these analytes will be reported.

*** quantification take place by separate provision with a single residue method.

By request we can report this analyte.

**** Chlorothalonil-4-hydroxy is a metabolite of Chlorothalonil. This metabolite will be according to EU regulation 396/2005 reported for food of animal origin except honey.

***** Caffeine is no pesticide and will be only reported by request.

****** 2,4,6-Trichlorophenoxy acetic acid is a metabolite of Prochloraz. This metabolite according to EU regulation 396/2005 will not be reported. On request we can report this metabolite.

Exceptions reporting the LC-MSMS standard analysis.

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If a pesticide cannot be detected, for example due to matrix interference, this will be mentioned on the analysis report with a remark.

The LC-MSMS analysis 3 and 4 consists of a total number of 415 pesticides.

The accreditation other than fruit and vegetables, will be shown on DRF-260 Flexible scope.

### Glyphosate (WVS-145) Q LC-MSMS

| Pesticide (active ingredient) |
|---|
| Glyphosate |
| Glufosinate-ammonium (Glufosinate, N-AcetylGlufosinate en 3-MPPA) |
| AMPA |

## Appendix 3. Sampling protocol

1) Finding of correct MF locations: by using obtained GPS coordinates with Garmin E-trex 30 the correct locations can be found with around one-meter precision. At most locations either the MF of the 2019 season was still there, or the poles were left behind, which eased orientation.
2) Finding of locations without MF traps: similar with Garmin E-trex 30 but without support of MF remains.
3) At the site measuring tape of 50 m length was used in order to show in the field a distance of 20 m into different directions. Within the radius of 20 m 25 samples of soil and vegetation were taken, evenly distributed across the surface within the 20 m radius (as far as the territory within this radius was accessible).
4) 25 Soil samples were taken and put into a galvanized bucket of 12 litres, 5 minutes thoroughly mixed with a galvanized garden spade and filled into 2 laboratory sample bags.
5) At arrival of the sampling site, the vegetation was observed, and a wild plant was chosen that was sufficiently present in order to get a sample of 1 kg within the circle with a radius of 20 m from the MF. It was preferred to take a sample of one plant species, but in cases where this was impossible, a sample of the mixed vegetation was taken. For reasons of comparability species which had been sampled already at other locations, were preferred. Samples of grass were taken with garden-shears and samples of branches were taken with hedge shears. Vegetation samples were stored in large transparent PE plastic bags obtained from the laboratory.
6) No samples were taken in the direct neighbourhood (within 50 cm) of the MF traps, since the wood of the poles was in many cases impregnated wood, which could leak pesticides into the soil and vegetation.
7) In cases where the territory within 20 m from the MF was not accessible (due to the presence of water or slopes, that territory was excluded from sampling.
8) In some cases, the soil was too shallow in order to take samples at 18 cm depth. In those cases, samples were only taken from the layer that could be penetrated with the sampling auger.

9) In case of presence of sufficient amounts of animal excrements within the 20-m radius, those were also sampled.
10) At all sampling bags a unique code was written with a permanent marker. The code included the date of sampling.
11) All (soil and vegetation) samples were stored in a ski-box on top of the car or in the luggage compartment of the car during maximum two days. After arrival in the Netherlands, the soil samples were stored at -18°C and the vegetation samples at +5°C for at maximum 3 days. Then they were brought to the laboratory storage room, where they were all stored at -18°C.
12) During handling of the samples no polymer tools (or gloves) were used, in order to prevent contamination with components of those materials.
13) After sampling of a site, hands, buckets, garden spades, garden-shears and the hedge shears were cleaned with pure tap water (from Bennekom).

# Appendix 4. Pesticide properties

## Abbreviations table pesticide properties

Key: Genotoxicity
A: Chromosome aberration (EFSA database)
B: DNA damage/repair (EFSA database)
C: Gene mutation (EFSA database)
D: Genome mutation (EFSA database)
E: Unspecified genotoxicity type (miscellaneous data source)
0: No data
1: Positive
2: Mixed/ambiguous results
3: Negative

### Compounds*

| | |
|---|---|
| A | Acaricide |
| B | Biocide |
| F | Fungicide |
| I | Insecticide |
| H | Herbicide |
| M | Metabolite |
| N | Nematocide |
| Pgr | Plant growth regulator |
| Rep | Repellent |
| V.s. | Veterinary compound |
| ?: | Indicates no available weight-of-the-evidence summary assessment, or insufficient data are available for review |

### Environmental issues

LR 50*: lethal Rate expressed in gram per hectare whereas 50% of the test organism dies.

AA-EQS[1, 2, 3]: Annual Average Environmental quality standard for surface water, expressed in microgram per litre water.

MTR[4]: Maximal Tolerable Risk for surface water, expressed in microgram per litre water

### Test organism*

| | |
|---|---|
| Ar | *Aphidius rhopalosiphi* |
| Cc | *Chrysoperla carnea* |
| Cs | *Coccinella septempunctata* |
| Tc | *Trichogramma cacoeciae* |
| Tp | *Typhlodromus pyri* |

## Sources of the presented data

***: Pesticide Properties Database (PPPB), University of Hertfordshire (IUPAC)**
**Website: [https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm](https://sitem.herts.ac.uk/aeru/ppdb/en/atoz.htm)**
**2) Pesticide Action Network (PAN) Pesticides Database – Chemicals**

Website: http://www.pesticideinfo.org/Search_Chemicals.jsp

[1]: Directive 2000/60/EC of the European Parliament and of the Council establishing a framework for Community action in the field of water policy

[2]: Verordnung zum Schutz der Oberflächengewässer (Oberflächengewässerverordnung – OGewV, 2016)/ the Directive for the protection of surface waters

[3, 4]: Atlas Bestrijdingsmiddelen in Oppervlaktewater (Atlas of pesticides in surface water) Website: http://www.bestrijdingsmiddelenatlas.nl/

[5] National Institute for Public Health and the Environment | RIVM the Netherlands

Selection of properties

Besides the basic information about an active ingredient, such as pesticide type, chemical group of the compound and the CAS registration number (RN), specific properties of the active ingredients were selected which may support the assessment of appearance of the compound in the environment and their possible effects on the insect fauna.

Vapour pressure and degradation time

Regarding the appearance of the found pesticides in the environment the vapour pressure and the degradation time into metabolites may be useful properties of a compound to understand their occurrence in respectively the vegetation and soil.

In the table the vapour pressure at 20°C is expressed in mPa. It is a measure of the tendency of a material to vaporise. The higher the vapour pressure the greater the potential to spread into the environment by evaporation or sublimation.

The degradation time or DT50 or DT90 is the time required for the chemical concentration to decline respectively to 50% or to 90% of the amount of application. The degradation time for a compound in soil may be estimated in laboratory or field studies. Pesticides with a DT50 less than 30 days are considered as non-persistent. However, it does not mean that the active ingredient has been completely converted into harmless compounds (metabolites). The mass of potential metabolites, their properties and the effects are mostly not assessed and not known. Persistent pesticides and metabolites can be found in the environment decades after their application and affect the biodiversity and human health negatively. In addition, pesticides with a short degradation (conversion) time into metabolites can form metabolites that are very stable and stay decades (or centuries) in the environment.

### Lethal Rate in g/ha

For the approval of an active ingredient certain tests for the assessment of the properties of the compound have to be conducted. For the assessment of the ecotoxicology of an active ingredient the basis is the greatest concentration or level of a compound, found by observation or experiment, which cause no effects. Other parameter to be tested is the concentration of a chemical that can be expected to cause non-lethal (EC50) or a lethal effect (LC50) in 50% of the tested population. The species used for toxicological studies are mammals for human health studies (rat, mice, dog), for ecotoxicological studies birds, fishes and aquatic organism. Furthermore, for pollinators (honeybees or bumblebees) the acute LC50 may be estimated. Studies on chronic effects on the life cycle and development of the pollinators are not or seldom conducted.

The requirements for determining the toxicity of a compound to non-target terrestrial insects other than pollinators are weak. Very few ecotoxicological data on the toxicity of an active ingredient to non-target insects (arthropods) are in the databases available.

For our investigation we identified the lethal rate (LR50) as the best available parameter for non-target arthropods. The LR50 is the concentration of a pesticide applied on one hectare that can be expected to cause a lethal effect in 50% of the tested population. The LR50 of a pesticide is expressed in g/ha. Frequently the tested insect population is *Aphidius rhopalosiphi* and/or *Typhlodromus pyri.* Usually, the LR50 value is estimated for insecticides, however less frequently for fungicides and even less often for herbicides.

Moreover, for several fungicides the databases don’t provide the LR50 values, but the percentage of effect on the test-specie at a certain concentration of an active ingredient applied on one hectare. Information about the duration of exposure time is usually missing.

Both ecotoxicological parameters should only be considered as an indication of the rate of toxicity of a compound.

### Environmental Quality Standard for surface water

Although this research targets a possible relation between pesticides and terrestrial insects, we approached the annual average Environmental Quality

Standard (AA-EQS) for surface water as an optional indicator for the toxicity of a compound to terrestrial insects.

For the European EQS in general, three aspects are considered: direct ecotoxicity of aquatic organisms, secondary poisoning of predatory birds and mammals and exposure of humans via consumption of fish or fishery products. The decision to include the EQS in the table with the properties of the found active compounds is taken, because the EQS values for surface water are often related to the toxicity of the compound to the aquatic specie daphnia, belonging to the arthropods.

Not for all active ingredients individual EQS are established and the number of compounds can differ from country to country.

The European Water Framework Directive (WFD) provides basic (AA-)EQS for priority compounds and certain other pollutants. The German Directive for the protection of surface waters presents (AA-)EQS for additional selected hazardous pesticides. Further the Dutch government handles for those active ingredients without an established (AA-)EQS the so-called MTR, the Maximal Tolerable Risk. The MTR presents the annual tolerable average of a compound in surface water for the most sensible tested water organism, being in particular for insecticides mostly the daphnia. For herbicides, the MTR may be linked to algae as the most sensitive to the compound.

The presented MTR and the EQS-AA values express both the maximal tolerable annual average of an active compound in surface water. We considered the two parameters as comparable for indicating the toxicity of the compound to water organism.

*Italic compounds*: not approved

Source: EU Pesticide database, https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activecompound.selection&language=EN

| INSECTIDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Health issues Known toxicity (PAN Pesticides database) | AA- EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| *Alpha Hexachlorocyclohexane (HCH) (α-Lindane)* | I | Organochlorine | 319-84-6 | Not Listed | Not Listed | Not Listed | Not Listed | Carcinogen | Not Listed |
| *Gamma Hexachlorocyclohexane (HCH) (γ-Lindane)* | i, A, V.s. | Organochlorine | 58-89-9 | 4.4 | 75-971 (dt90) | Not Listed (honeybees highly toxic) | Genotoxic A0, B0,C0,D0,E3 Neurotoxicant, carcinogenic, highly toxic. Endocrine issues: reduction of oestrous cycles | Carcinogen, suspected endocrine disruptor | 0.02[1] |
| *Aldrin* | I | Organochlorine | 309-00-2 | 8.6 | 365 (dt50) | Not Listed (honeybees highly toxic) | Genotoxic A0, B0,C0,D0,E0 Neurotoxicant, carcinogen. Endocrine issues: competitive binding to androgen receptors | Carcinogen, suspected endocrine disruptor | Cyclodien pesticides (aldrin, Dieldrin, Endrin, Isodrin Σ 0.01[1] |
| Cyfluthrin | I | Pyrethroid | 68359-375 | 0.0003 | 133 (dt90) | 1.63g/ha (Ar 48h) 0.42 g/ha (Tp 7d) | Genotoxic A0, B0,C0,D0,E3 Neurotoxicant, highly toxic, possible liver or kidney toxicant | ? | 0.0002[4] |
| Cypermethrin | I, M, V.s. | Pyrethroid | 52315-078 | 0.00678 | 28-365 (dt90) | 0.0029g/ha (Tp) 0.822 g/ha (Ar) | Genotoxic A2,B3,C3,D3,E3, Possible carcinogen, possible liver & kidney | Possible carcinogen, suspected | 0.00008[3] |

| INSECTIDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Health issues Known toxicity (PAN Pesticides database) | AA- EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | toxicant. Endocrine issues: estrogenic effect | endocrine disruptor | |
| Deltamethrin | I, M, V.s | Pyrethroid | 52918-635 | 0.0000124 | 30-365 (dt90) | 13.5 g/ha (Cs, Tc 100% effect) | Genotoxic A0,B0,C0,E3 Endocrine disrupter, neurotoxicant, weak estrogenic activity | ? | 0.0000031[3] |
| *Dieldrin* | I, M | Chlorinated Hydrocarbon | 60-57-1 | 0.024 | 2000 (dt50 lab) | Not Listed (honeybees highly toxic) | Genotoxic A3,B0,C0,D0,E1 Carcinogen, reproduction/development effects, neurotoxicant, extreem hazardous, competitive binding to androgen receptors, estrogenic effect | Possible carcinogen, suspected endocrine disruptor | Cyclodien pesticides (aldrin, Dieldrin, Endrin, Isodrin Σ 0.01[1] |
| *Diphenylamine* | I, F, pg | Amine | 122-39-4 | 0.852 | Not Listed | Not Listed | Genotoxic A3,B3,C3,D0,E3 Reproduction/development effects, gastrointestinal, cardiovascular, kidney and liver toxicant | ? | 1.2[4] |
| *Beta-Endosulfan* | I,A | Organochlorine | 115-29-7 | 0.83 | 60-88 (dt50) | Not Listed | Genotoxic A3,B0,C0,D0,E1 Reproduction/development effects, neurotoxicant, mutagenic potential, highly toxic. Endocrine issues: competitive binding to androgen receptors | Suspected endocrine disruptor | Not Listed |

| INSECTIDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Health issues Known toxicity (PAN Pesticides database) | AA- EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| Endosulfan sulfate | M | Organophosphate | 31972-437 | Not Listed | Not Listed | Not Listed | Not Listed | Cholinesterase inhibitor | Not Listed |
| Etofenprox | I | Pyrethroide | 80844-071 | 0.000813 | 22 - 84 (dt90) | 0.42g/ha (Ar) 0.70 g/ha (Tp) | Genotoxic A3,B3,C3,D0,E0 Reproduction/development effects, thyroid toxicant | Carcinogen, suspected endocrine disruptor | 0.00054 [4] |
| *Fenamiphos-sulfoxide* | M | Unclassified | 31972-437 | Not Listed | 9.4-14.1 (dt50) | Not Listed | Genotoxic A0,B0,C0,D0,E3 No further information available | Cholinesterase inhibitor | Not Listed |
| *Heptenophos* | I, V.s. | Organophosphate | 23560-590 | 65 | 1.4 (Dt50) | Not Listed | Genotoxic A0,B0,C0,D0,E3 Cholesterase inhibitor, neurotoxicant. No further information available | Cholinesterase inhibitor | 0.002 [3] |
| *Imidacloprid* | I | Neonicotinoid | 138261-41-3 | 4 x $10^{-7}$ | 104-228 (Dt50 field) | 0.022 g/ha (Ar) 4.23 g/ha (Tp) | Genotoxic A3,B3,C3,D3,E0 Reproduction/development effects. Potential liver, kidney, thyroid, heart and spleen toxicant | ? | 0.002[2] |
| *p,p DDD+o,p DDT* | I,M | Organochlorine | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed |
| *p,p DDE* | I,M | Organochlorine | 72-55-9 | Not Listed | Not Listed | Not Listed | Not Listed | Carcinogen, suspected endocine disruptor | 0.0004 [3] |
| *p,p DDT* | I | Organochlorine | 50-29-3 | 0.025 | 6200 (dt50). | moderately harmful(Tp) | Genotoxic A3,B0,C0,D0,E2 Carcinogen, endocrine disruptor, reproduction | Carcinogen, Developmental or Reproductive | DDT Σ of isomers 0.025 [1] |

| INSECTIDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Health issues Known toxicity (PAN Pesticides database) | AA- EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | (honeybees highly toxic) | /development effects, neurotoxicant. Strong links with breast and womb cancer. Endocrine issues: competitive binding to androgen receptors | Toxin, suspected endocine disruptor | |
| Permethrin-cis | I, V.s | Pyrethroid | 61949-766 | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed |
| Permethrin-trans | I | Pyrethroid | 52341-329 | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed | Not Listed |
| Permethrin (-cis and trans) | I, V.s | Pyrethroid | 52645-531 | 0.007 | 42 | harmful (Tp and parasitoids) | Genotoxic A3,B0,C0,D0,E3 Carcinogen, endocrine disruptor, reproduction /development effects, neurotoxicant, estrogenic, Endocrine issues: Inhibition of estrogen-sensitive cells proliferation | Carcinogen, suspected endocine disruptor | 0.0002 [3] |
| *Picaridin (or Icardin)* | I, Rep, V.s | Piperdine | 119515-38-7 | 0.034 | Not Listed | Not Listed | Not Listed | ? | Not Listed |
| Spinosad a | I | Spinosoid/Spinosyn | 168316-95-8 | Not Listed | Not Listed | Not Listed | Not Listed | ? | 0.024 [4] |
| *Thiofanox* | I, A | Carbamate | 39196-184 | 22.6 | 2-6 (dt50) | Not Listed | Genotoxic A0, B0,C0,D0, E0 Cholinesterase inhibitor, neurotoxicant. No further information available | Cholinesterase inhibitor | 0.13 [4] |

| HERBICIDE Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| AMPA | M | Unclassified | 1066- 51-9 | Not listed | Not listed | Not listed | Not listed | ? | 79.7[4] |
| *Chlorpropham* | H, pg | Carbamate | 101-213 | 24 | 53.2 (dt90 lab) | Not listed | Genotoxic A0,B0,C0,D0,E3 Possible spleen, bone-marrow & red blood cell toxicant. | ? | 4[3] |
| Chlorotoluron | H | Urea | 15545-48-9 | 0.005 | 173-218 (dt90) | 2450g/ha, no adverse effects (Tp, Ar) | Genotoxic A3,B0,C0,D0,E0 Carcinogen | ? | 0.4[2] |
| Dichlobenyl | H, M | Benzotrillen | 1194-65-6 | 0.00014 | 105-123 (dt90) | Not listed | Genotoxic A0,B0,C0,D0,E3 Reproduction(development effects, possible liver, kidney, stomach and parathyroid toxicant, possible carcinogen | Possible carcinogen | 0.63[3] |
| Diflufenican | H | Carboxamide | 83164-33-4 | 4.25 X $10^{-3}$ | 127-1900(dt90) | Not listed | Genotoxic A3,B3,C3,D0,E3 No further information available | ? | 0.009[2] |
| Flufenacet | H | Oxyacetamide | 142459-58-3 | 0.09 | 53-132 (dt90) | 60g/ha, 100% effect mortality, reproduction (Tp) | Genotoxic A3,B0,C0,D0,E3 Potential liver, spleen and thyroid toxicant | ? | 0.04[2] |

| HERBICIDE Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| Glyphosate | H | phosphonoglycine | 1071-83-6 | 0.0131 | 66.9-386.6 (dt90) | 5769g(ha (Ar), 4320 g/ha (Tp) | "Genotoxic A3,B1,C3,D0,E3 Possible bladder and liver toxicant, Endocrine issues - Disruption of aromatase activity | Carcinogen | 77[4] |
| *Hexazinone* | H | Triazinone | 51235-04-2 | 0.03 | 30-180(dt50 lab) | Not listed | Genotoxic A3,B0,C0,D0,E3 Highly toxic | Highly acute toxicity | 0.56[4] |
| *Methabenzthiazuron* | H | Urea | 18691-97-9 | 5.90 X $10^{-3}$ | 135(dt50 lab) | Not listed | Genotoxic A0,B0,C0,D0,E0. No further information available | ? | 1.8[3] |
| *Metoxuron* | H | Ura | 19937-59-8 | 4.3 | 18.5 (dt50) | Not listed | Genotoxic A0,B0,C0,D0,E1. No further information available | ? | 19 4 |
| *Norflurazon* | H | Pyridazinone | 27314-13-2 | 3.86 X $10^{-3}$ | 225(dt50) | Not listed | Genotoxic A3,B0,C0,D0,E0 Possible liver toxicant, possible carcinogen | Possible carcinogen | Not listed |
| Pendimethalin | H | Dinitroaniline | 40487-42-1 | 3.34 | 144-582 (dt90) | 3200g/ha 38% mortality(Tp) | Genotoxic A0,B0,C0,D0,E3 Reproduction/development effects, thyroid & liver toxicant, bioaccumulates, possible carcinogen | Possible carcinogen, suspected endocrine disruptor | 0.018[3] |
| Propyzamide | H | Benzamide | 23950-58-5 | 0.058 | 59-648 (dt90) | Not listed | Genotoxic A0,B0,C0,D0,E3 Possible liver, kidney & spleen toxicant Associated with thyroid follicular cell | Carcinogen, possible endocrine disruptor | 11[4] |

| HERBICIDE Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | adenomas and Leydig cell benign tumours | | |
| Prosulfocarb | H | Thiocarbamate | 52888-80-9 | 0.79 | 22-48 (dt90) | 524g/ha (Tp)<br>41.8g/ha (Ar) | Genotoxic A3,B3,C3,D0,E0<br>Moderately toxic | Cholinesterase inhibitor | 0.34[3] |
| Tembotrione | H | Triketone | 335104-84-2 | 1.1 X $10^{-5}$ | 27.8-262 (dt90) | 1.301 (Tp)<br>0.256 (Ar) | Genotoxic A3,B3,C3,D0,E0<br>USEPA - some evidence to suggest possible human carcinogen | Possible carcinogen | 0.32[3] |
| Terbuthylazine | H, Microbiocide, Algicide | Triazine | 5915-41-3 | 0.152 | 33-119 (dt90) | 750g/ha(Tp and Ar) >mortality | Genotoxic A3,B0,C0,D0,E0<br>Health effects may be delayed | ? | 0.32[3] |
| Tri-allate | H | Thiocarbamate | 2303-17-5 | 12 | 27-682 (dt90) | Not listed | Genotoxic A3,B2,C2,D0,30<br>Liver, spleen and kidney toxicant, possible carcinogen | Cholinesterase inhibitor, possible carcinogen | 1.9 4 |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| Ametoctradin | F | Triazolopyrimidine | 865318-97-4 | 2.1 X $10^{-7}$ | 48.8-420 (dt90) | 3.2 g/ha (Tp, Ar) | Genotoxic A3,B0,C0,D0,E3 | ? | Not listed |
| Azoxystrobin | F | Strobilurin | 131860-33-8 | 1.10 X $10^{-7}$ | 402-870 (dt90) | 1000 g/ha (Ar) 250g/ha (23% effect Ar) | Genotoxic A2,B0,C3,D0,E2 Minor effects on reproduction/development observed, liver toxicant. | ? | 0.2 [3] |
| *Biphenyl (Diphenyl)* | F | Aromatic Hydrocarbon | 92-52-4 | 1238 | 1.5-7 (dt50) | Not listed | Genotoxic A3,B0,C0,D0,E0 Neurotoxicant, exerts toxic effects on the central nervous system and liver, may cause skin sensitization or dermatitis | Suspected endocrine disruptor | 1.45 |
| Bixafen | F | Pyrazolium | 581809-46-3 | 146.6 | >1000 (dt90) | 116 g/ha (Tp), 35.5 g/ha (Ar) | Genotoxic A3,B0,C0,D0,E3 Reproduction/development effects, possible thyroid and liver toxicant | ? | 0.44 [3] |
| Boscalid | F | Carboxamide | 188425-85-6 | 0.00072 | >1000 (dt90) | 3600g/ha, effect 0% mortality Tp, 11% mortality Ar | Genotoxic A3,B0,C0,D0,E3 Liver and thyroid toxicant, possible carcinogen | Possible carcinogen | 0.55 [4] |
| Carbendazim | F, M | Benzimidazole | 10605-217 | 0.09 | 36-257 (dt90) | 30g/ha(Tp), 30g/ha, effect 100% mortality Tp Protonymf | Genotoxic A2,B3,C3,D0,E1 Reproduction/development effects, evidence of liver enzyme induction, possible liver toxicant and human carcinogen, Increase of | Possible carcinogen, suspected endocrine disruptor | 0.7 [2] |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | estrogen production and aromatase activity | | |
| Cyazofamid | F | Cyanoimidazole | 120116-88-3 | 0.0133 | 16.8-37 (lab dt90) | 210 g/ha , effect 2.5% mortality Ar, Tp | Genotoxic A0,B0,C0,D0,E3 Possible kidney & liver toxicant | ? | 0.13 [4] |
| Cyflufenamid | F | Amidoxine | 180409-60-3 | 0.0354 | 35-301 (dt90) | 50g/ha (Ar-48h; Tp 7d) | Genotoxic A3,B3,C3,D0,E0 Kidney and liver toxicant, possible carcinogen | ? | 2.4 [3] |
| Cyprodinil | F | Anilinopyrimidine | 121552-61-2 | 6.60 X $10^{-3}$ | 103-135 (dt90 lab) | 750g/ha, effect 46% mortality Ar, 10% mortality Tpprotonymf | Genotoxic A3,B3,C0,D0,E3 No further information available | ? | 0.16 [3] |
| Difenoconazole | F | Azole | 119446-68-3 | 3.33 X $10^{-5}$ | 68 -879 (dt90) | 178 g/ha (Ar 48h) 112 g/ha (Tp 7d) | Genotoxic A2,B3,C3,D0, E0 Liver, heart, thyroid and kidney toxicant, possible carcinogen | Possible carcinogen, suspected endocrine disruptor | 0.76 [3] |
| Dimethomorph | F | Morpholine | 110488-70-5 | 9.7 X $10^{-4}$ | 34-92 (dt50) | Not listed | Genotoxic A2,B3,C3,D0,E3 Possible liver & prostate toxicant | ? | 10 [3] |
| Dithianon | F | Quinone | 3347-22-6 | 1.0 X $10^{-7}$ | 35 (dt50) | 960g/ha (Tp) | Genotoxic A2,B2,C3,D0,E0 Possible liver and kidney toxicant, possible carcinogen | Possible carcinogen | 0.097 [3] |
| Epoxiconazole | F | Triazool | 133855-98-8 | 3.5 X $10^{-4}$ | 52-226 (dt50) | 3.58 g/ha (48h Ar), | Genotoxic A3,B0,C0,D0,E0 Carcinogen, reproduction | Carcinogen, Suspected | 0.2 [2] |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | 0.057 g/ha (7d. Tp mortality) | /development effects, possible liver toxicant, endocrine issues - Inhibition of aromatase activity, decrease of estrogen production | endocrine disruptor | |
| *Etaconazole* | F | Conazole | 60207-934 | 0.031 | Not listed | Not listed | Genotoxic A0,B0,C0,D0,E0 No further information available | ? | 0.25 [4] |
| *Fenarimol* | F | Pyrimidine | 60168-889 | 0.065 | 14-130 (dt50) | 32g/ha, effect Ar 100% mortality, Tp 30% mortality | Genotoxic A0,B0,C0,D0,E0 Endocrine disruptor | Suspected endocrine disruptor | 1.1 [4] |
| Fenpyrazamine | F | Pyrazolium | 473798-59-3 | 0.01 | 7.7-39.8 (dt90) | 1200 g/ha (>, Ar, Tp) | Genotoxic A3,B3,C3,D0,E3 Possible liver toxicant | ? | 19 [3] |
| Phenylphenol-2 | F, disinfectant, preservative | Phenol | 90-43-7 | 474 | non persistent | Not listed | Genotoxic A3,B1,C3,D0,E0 Carcinogen, neurotoxicant, bladder, kidney and liver toxicant, estrogen agonist | Carcinogen, developmental or reproductive toxin, suspected endocrine disruptor | 0.036 [4] |
| Fluazinam | F, A | Phenylpyridinamine | 79622-596 | 0.0172 | 44.8-145(dt90) | 2500 g/ha (Ar), 34.3g/ha (Tp) | Genotoxic A3,B3,C3,D0,E3 Potential liver toxicant, possible carcinogen | Possible carcinogen | 0.55 [4] |
| Fludioxonil | F | Phenylpyrrole | 131341-86-1 | 3.90 X $10^{-4}$ | 10-25 (dt50) | 112 g/ha, effect 14% mortality Ar, 1 kg/ha 2% mortality Tp | Genotoxic A2,B2,C3,D0,E0 Liver and kidney toxicant | ? | 0.98 [4] |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| Fluopicolide | F | Benzamide | 239110-15-7 | 3.03 X 10$^{-4}$ | 863-1184 (dt90) | 8230 g/ha (Ar48 h) 7130 g/ha (Tp 7d) | Genotoxic A2,B0,C3,D0,E0 Possible liver, kidney and spleen toxicant | ? | 0.71 [3] |
| Fluopyram | F, N | Benzamide Pyramide | 658066-35-4 | 1.2 X 10$^{-3}$ | 487->1000 (dt90) | 2000 g/ha (>Tp and Ar) | Genotoxic A3,B0,C3,D0,E0 Possible liver, thyroid and blood toxicant | Carcinogen | 2.7 [3] |
| Fluoxastrobin | F | Strobilurin | 361377-29-9 | 5.60 X 10$^{-7}$ | 94-553(dt90) | 34.1 g/ha (Ar) 122.2 g/ha (Tp) | Genotoxic A3,B0,C3,D0,E3 Possible liver & kidney toxicant | ? | 0.012 [3] |
| Fluquinconazole | F | Triazole | 136426-54-5 | 6.40 X 10$^{-6}$ | 261-9585 (dt90) | 149.4g/ha <, mortlity TP and Ar) | Genotoxic A3,B3,C3,D0,E0, possible liver & kidney toxicant | ? | 0.032 [4] |
| *Flusilazole* | F | Triazole | 85509-199 | 0.0387 | 63-240 (dt50) | 38g/ha, effect (Tp) 100% mortality | Genotoxic A0,B0,C0,D0,E0 Reproduction/development effects | ? | 0.066 [4] |
| Fluxapyroxad | F, B | Pyrazolium | 907204-31-3 | 2.7 X 10$^{-6}$ | 299->1000 (lab dt90) | 0.128g/ha (Tp), 4.70g/ha (Ar) | Genotoxic A3,B3,C3,D0,E0 Possible liver, prostrate and thyroid toxicant | ? | 3.6 [3] |
| Phthalimide | M | Imide | 85-41-6 | Not listed | Not listed | Not listed | Not listed | ? | 16.5 [4] |
| *Hexachlorobenzene* | F, B, M, wood preservative | Chlorinated Hydrocarbon | 118-74-1 | 1.45 | 1000 -2700 (dt50) | Not listed | Genotoxic A0,B0,C0,D0,E3 Carcinogen, severely disruption of thyroid hormone production | Carcinogen, developmental or reproductive toxin, suspected endocrine disruptor | 0.000026 [3] |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| Imazalil | F, V.s. | Imidazole | 35554-440 | 0.158 | 54-68 (dt90) | Not listed | Genotoxic A3,B1,C3,D0,E3 Reproduction/development effects, possible liver, kidney toxicant | Carcinogen, developmental or reproductive toxin | 0.87 [4] |
| *Iprodione* | F | Dicarboximide | 36734-197 | 0.0005 | 29-197 (dt90= | Not listed | Genotoxic A3,B0,C0,D0,E2 Reproduction/development effects, probable human carcinogen | Carcinogen, suspected endocrine disruptor | 0.5 [4] |
| Metalaxyl | F | Phenylamide | 57837-191 | 0.75 | 19.5 -113 (dt50) | 630 g/ha (Tp)<br>380g/ha (Ar) | Genotoxic A3,B0,C0,D0,E3 Liver toxicant, a weak inducer of cytochrome P450 | ? | 9.7 [4] |
| Metrafenone | F | Benzophenone | 220899-03-6 | 0.153 | 784-1141 (dt90) | 300g/ha (Ar48h), 500g/ha (Tp 7d) | Genotoxic A3,B0,C3,D0,E3 Reproduction/development effects, Liver &kidney toxicant | ? | 0.142 [4] |
| Myclobutanil | F | Triazole | 88671-890 | 0.198 | > 1year (DT90) | 36g/ha, effect 67% mortality Tp protonymf, -43% reproductory effect Ar | Genotoxic A3,B3,C3,D0,E3 Liver toxicant, weak estrogen and androgen inhibitor | Developmental or reproductive toxin, suspected endocrine disruptor | 55 [4] |
| Penconazole | F | Triazole | 66246-886 | 0.366 | 22-115 (dt50) | 100g/ha, effect 59% mortality Ar and 79% mortality Tp | Genotoxic A3,B3,C3,D0,E0 Reproduction/development effects, Potential liver toxicant, weak estrogen effects | Suspected endocrine disruptor | 1.7 [4] |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| Pencycuron | F | Phenylurea | 66063-056 | $4.1 X 10^{-4}$ | 108-11715 (dt90) | 6200g/ha (Tp), 685 g/ha (Ar) | Genotoxic A3,B3,C3,D3,E0 No further information available | ? | 2.7 [4] |
| Prochloraz | F | Imidazole | 67747-095 | 0.15 | 55-7545 (dt90) | 85.1 g/ha (48h Ar) 44.3 g/ha (7d Tp) | Genotoxic A3,B2,C3,D3,E0 Reproduction/development effects, possible liver toxicant and carcinogen | Possible cancerogenic, suspected endocrine disruptor | 1.3 [4] |
| Prochloraz desmimidazoleamino | M | Not Listed | 139520-94-8 | Not listed | Not listed | Not listed | Not listed | Not listed | Not listed |
| *Procymidone* | F | Dicarboximide | 32809-168 | 0.023 | 56-525 (dt90) | 150g/ha, effect 29.7% mortalityTP, 664g/ha 10.5% mortaiity Cc | Genotoxic A0,B0,C0,D0,E0 Reproduction/development effects, carcinogen, endocrine disruptor, possible liver and testes toxicant | Carcinogen, suspected endocrine disruptor | 370 [4] |
| Propiconazole | F | Triazole | 60207-901 | 0.056 | 108-525 (dt90) | 250 g/ha, effect 100% mortality Ar, 125 g/ha 100% beneficial capacity Tp | Genotoxic A3,B0,C0,D0,E3 Possible carcinogen, possible liver toxicant, weak estrogen and aromatase activity inhibition | Possible carcinogen, developmental or reproductive toxin, suspected endocrine disruptor | 1 [2] |
| Proquinazid | F | Quinazolinone | 189278-12-4 | 0.09 | 18-231 (dt90) | 131.4g/ha (Ar), 47.85g/ha(Tp) | Genotoxic A3, B3,C3,D0,E0 Reproduction/development effects, possible liver and | ? | Not listed |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | thyroid toxicant, may cause hormonal changes | | |
| PropiconazoleDesthio | M | Azole | 120983-64-4 | Not listed | Not listed | Not listed | Not listed | ? | Not listed |
| *Pyrifenox* | F | Pyridine | 88283-414 | 1.7 | 50-120 (dt50) | Not listed | Genotoxic A3, B0,C0,D0,E0 Weak estrogen inhibition | ? | 0.95 [4] |
| Pyrimethanil | F | Anilinopyrimidine | 53112-280 | 1.1 | 59.4-143.9 (dt90) | 1000g/ha, effect 38% mortality Ar, 1040g/ha 38% mortality Tp | Genotoxic A3, B3,C3,D0,E3 Possible liver, kidney, adrenals, bladder and thyroid toxicant and carcinogen | Possible carcinogen, suspected endocrine disruptor | 7 [3] |
| *Quinoxyfen* | F | Quinoline | 124495-18-7 | 0.012 | 380-750 (dt90) | Not listed | Genotoxic A0,B0,C0,D0,E0 Possible liver, kidney and blood toxicant | ? | 0.15 [3] |
| Tebuconazole | F | Triazole | 107534-96-3 | 1.3 x $10^{-3}$ | 453-5606 (dt90) | 62.5 g/ha (Ar) 58 g/ha (Tp) | Genotoxic A3,B3,C3,D0,E3, targets liver/blood system, possible carcinogen | Possible carcinogen, suspected endocrine disruptor | 0.63 [3] |
| Tetraconazole | F | Triazole | 112281-77-3 | 0.18 | 453-5606 (dt90) | 40g/ha harmless (Ar) and harmful (Tp) | Genotoxic A3, B3,C3,D0,E3 Liver toxicant, possible carcinogen | Carcinogen | Not listed |
| *Tolyfluanid* | *F, wood preservative,* | Sulphamide | 731-27-1 | 0.2 | 1.7-8.6 (dt90 lab) | 912 (Ar 48h), 247g/ha | Genotoxic A2, B3,C3,D0,E0 Liver and thyroid toxicant, linked to | Carcinogen | 0.5 [4] |

| FUNGICDES Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT Degradation time into metabolites in days (field) | Ecotoxicology LR50 Lethal Rate or % effect (g/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| | *antifouling agent* | | | | | (reproduction Tp) | insulin resistance, probably carcinogen | | |
| Trifloxystrobin | F | Strobilurin | 141517-21-7 | 3.40 X 10$^{-3}$ | 10.4-35.6 (dt90) | 10g/ha, effect 29% mortality Ar, 500g/ha mortality 93% Tp | Genotoxic A0, B0,C0,D0,E0 Reproduction/development effects, probably liver and teste toxicant | ? | 0.27[3] |
| *Vinclozolin* | F | Oxazole | 50471-448 | 0.016 | 34-94 (dt50) | Not listed | Genotoxic A3,B0,C0,D0,E3 Reproduction/development effects, renal and prostate gland toxicant- androgen, possible carcinogen | Carcinogen, developmental or reproductive toxin, suspected endocrine disruptor | 1.6[4] |

| ACARICIDES and Others Compound | Pesticide type | Compound group | CAS RN | Vapour pressure at 20°C (mPa) | DT (Degradation time into metabolites) in days (field) | LR50 Lethal Rate or % effect (gr/ha) | Health issues Known toxic properties (IUPAC database) | Known toxicity (PAN Pesticides database) | EQS as annual average for surface water (ug/L) |
|---|---|---|---|---|---|---|---|---|---|
| ACARICIDES | | | | | | | | | |
| *Dicofol* | A | Organochlorine | 115-32-2 | 2.45 X $10^{-2}$ | 40-80 (dt50) | Not listed | Genotoxic A3,B3,C3,D0,E3 Neurotoxic, possible carcinogen, Endocrine issues: Inhibition of androgen synthesis | Possible carcinogen, suspected endocrine disruptor | 0.0013 [3] |
| *Tetradifon* | A, I | Bridged diphenyl | 116-29-0 | 3.20 X $10^{-5}$ | 112 (dt50) | Not listed | Genotoxic A0,B0,C0,D0,E3 Possible liver and kidney toxicant | ? | 0.1 [3] |
| OTHER COMPOUNDS | | | | | | | | | |
| *Anthraquinone* | Repellent | Unclassified | 84-65-1 | 5.00 X $10^{-3}$ | 8 (dt50) | Not listed | Genotoxic A0,B0,C0,D0,E0 Possible carcinogen | Carcinogen | 0.075 [4] |

?: Indicates no available weight-of-the-evidence summary assessment.

# Appendix 5. Original measurements of all matrices (in microgram per kilogram fresh sample and per kilogram dry matter)

## KREFELD SPEY

### KS-5/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN933P* | *Soil* | *DIPHENYL* | *8.14* | *10.2* | |
| Dry matter % | | *HEPTENOPHOS* | *Detected qualitatively* | | |
| 79.8% | | *HEXACHLORBENZENE* | *3.89* | *4.9* | |
| | | *ANTHRAQUINONE* | *15.96* | *20.0* | |
| LOQ | | *p,p'-DDE* | *0.80* | *1.0* | *< 1.5 µg/kg* |
| 1.5 | | *p,p'-DDD + o,p'-DDT* | *0.80* | *1.0* | *< 1.5 µg/kg* |
| µg/kg | | *p,p'-DDT* | *0.32* | *0.4* | *< 1.5 µg/kg* |
| | | | *Total* | *37.5* | |

### KS-5/11/19-STINGING NETTLE (URTICA DIOICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN934P* | *stalks and leaves* | *DIPHENYL* | *Detected qualitatively* | | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *0.52* | *3.2* | *< 0.6 µg/kg* |
| 16.4% | | *PHENYLPHENOL-2* | *0.34* | *2.1* | *< 0.6 µg/kg* |
| | | *CHLORPROPHAM* | *0.89* | *5.5* | |
| LOQ | | *PROSULFOCARB* | *0.47* | *2.9* | *< 0.6 µg/kg* |
| 0.6 | | | *Total* | *13.6* | |
| µg/kg | | | | | |

## KS-5/11/19-KNOTGRASS (POLYGONUM AVICULARE)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN935P* | *Dead plants* | *Flufenacet 1* | *1.15* | *3.6* | *< 1.2 µg/kg* |
| Dry matter % | | *Prosulfocarb 1* | *3.16* | *9.8* | |
| 32.1% | | *DIPHENYL* | *Detected qualitatively* | | |
| | | *PHTHALIMIDE (metabolite of folpet)* | *1.93* | *6.0* | |
| LOQ | | *CHLORPROPHAM* | *0.66* | *2.0* | *< 1.2 µg/kg* |
| 1.2 | | *ALFA-HCH* | *1.04* | *3.2* | *< 1.2 µg/kg* |
| µg/kg | | *GAMMA-HCH (LINDANE)* | *7.32* | *22.8* | |
| | | *ANTHRAQUINONE* | *Detected qualitatively* | | |
| | | *PENDIMETHALIN* | *0.97* | *3.0* | *< 1.2 µg/kg* |
| | | *PERMETHRIN-CIS* | *4.82* | *15.0* | |
| | | *PERMETHRIN-TRANS* | *5.91* | *18.4* | |
| | | | *Total* | *83.9* | |

## LATUMER BRUCH 1b

## LB-5/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN936P* | *Soil* | *DIPHENYL* | *3.06* | *4.1* | |
| Dry matter % | | *ANTHRAQUINONE* | *3.75* | *5.0* | |
| 74.9% | | | *Total* | *9.1* | |
| | | | | | |
| LOQ | | | | | |
| 1.4 | | | | | |
| µg/kg | | | | | |

## LB-5/11/19 GREAT BURNET (SANGUISORBA OFFICINALIS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN937P* | *stalks and leaves* | *Prosulfocarb 1* | *1.03* | *3.2* | *< 1.2 µg/kg* |
| Dry matter % | | *DIPHENYL* | *Detected qualitatively* | | |
| 31.9% | | *PHTHALIMIDE (metabolite of folpet)* | *1.52* | *4.8* | |
| | | *DIPHENYLAMINE* | *1.10* | *3.4* | *< 1.2 µg/kg* |
| LOQ | | | *Total* | *11.4* | |
| 1.2 | | | | | |
| µg/kg | | | | | |

## LB-5/11/19-POTTING SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN938P* | *Potting soil* | *Boscalid 1* | *10.33* | *32.9* | |
| Dry matter % | | *Fluopyram 1* | *1.98* | *6.3* | |
| 31.4% | | *Spinosad A 1* | *0.93* | *2.9* | |
| | | *Metoxuron nl* | *1.58* | *5.0* | |
| LOQ | | *DIPHENYL* | *1.92* | *6.1* | |
| 0.6 | | *PHTHALIMIDE (metabolite of folpet)* | *Detected qualitatively* | | |
| µg/kg | | *CHLORPROPHAM* | *0.31* | *1.0* | *< 0.6 µg/kg* |
| | | *ANTHRAQUINONE* | *1.57* | *5.0* | |
| | | *CYPRODINIL* | *0.31* | *1.0* | *< 0.6 µg/kg* |
| | | *FLUDIOXONIL* | *0.63* | *2.0* | |
| | | *p.p'-DDE* | *0.31* | *1.0* | *< 0.6 µg/kg* |
| | | | *Total* | *63.3* | |

## LATUMER BRUCH. SUMPF

## LBS-5/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN939P* | *Soil* | *DIPHENYL* | *4.87* | *8.2* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *Detected qualitatively* | | |
| 59.7% | | *ANTHRAQUINONE* | *5.97* | *10.0* | |
| | | | *Total* | *18.2* | |
| LOQ | | | | | |
| 1.1 | | | | | |
| µg/kg | | | | | |

## LBS-5/11/19 STINGING NETTLE (URTICA DIOICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN940P* | *Stalks and leaves* | *Thiofanox 1* | *Detected qualitatively* | | |
| Dry matter % | | *DIPHENYL* | *Detected qualitatively* | | |
| 21.8% | | *PHTHALIMIDE (metabolite of folpet)* | *1.38* | *6.3* | |
| | | *DIPHENYLAMINE* | *0.75* | *3.4* | *< 0.8 µg/kg* |
| LOQ | | *CHLORPROPHAM* | *0.40* | *1.8* | *< 0.8 µg/kg* |
| 0.8 | | *PROSULFOCARB* | *0.62* | *2.9* | *< 0.8 µg/kg* |
| µg/kg | | | *Total* | *14.5* | |

## LBS-5/11/19-WILLOW TREE

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN941P* | *Branches and leaves* | *Picaridin 1* | *1.01* | *2.2* | *< 1.7 µg/kg* |
| Dry matter % | | *Prosulfocarb 1* | *6.98* | *15.4* | |
| 45.2% | | *DIPHENYL* | *Detected qualitatively* | | |
| | | *PHENYLPHENOL-2* | *3.77* | *8.3* | |
| LOQ | | *CHLORPROPHAM* | *1.64* | *3.6* | *< 1.7 µg/kg* |
| 1.7 | | *ANTHRAQUINONE* | *2.38* | *5.3* | |
| µg/kg | | *PENDIMETHALIN* | *5.48* | *12.1* | |
| | | | *Total* | *47.0* | |

## PLIESTERBERG 2

## PB2-6/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN942P* | *Soil* | *DIPHENYL* | *6.87* | *8.2* | |
| Dry matter % | | *ANTHRAQUINONE* | *14.30* | *17.0* | |
| 84.1% | | | *Total* | *25.2* | |
| | | | | | |
| LOQ | | | | | |
| 1.6 | | | | | |
| µg/kg | | | | | |

## PB2-6/11/19-OAK LEAVES (QUERCUS ROBUR LEAVES)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN943P* | *Branches and leaves* | *DIPHENYL* | *Detected qualitatively* | | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *2.14* | *4.8* | |
| 45.0% | | *PHENYLPHENOL-2* | *1.88* | *4.2* | |
| | | *DIPHENYLAMINE* | *18.62* | *41.4* | |
| LOQ | | *CHLORPROPHAM* | *0.82* | *1.8* | *< 1.7 µg/kg* |
| 1.7 | | *PROSULFOCARB* | *2.57* | *5.7* | |
| µg/kg | | *ANTHRAQUINONE* | *2.37* | *5.3* | |
| | | *PENDIMETHALIN* | *5.45* | *12.1* | |
| | | | *Total* | *75.2* | |

## PB2-6/11/19-MEAT COW MANURE

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN944P* | *Manure* | *Prosulfocarb* | *0.35* | *1.6* | *< 0.8 µg/kg* |
| Dry matter % | | *Metoxuron* | *2.51* | *11.4* | |
| 22.0% | | *DIPHENYL* | *Detected qualitatively* | | |
| | | *ANTHRAQUINONE* | *Detected qualitatively* | | |
| LOQ | | *DELTAMETHRIN* | *Detected qualitatively* | | |
| 0.8 | | | *Total* | *13.0* | |
| µg/kg | | | | | |

## PLIESTERBERG 1

## PB1-6/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN945P* | *Soil* | *DIPHENYL* | *1.91* | *2.0* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *1.87* | *2.0* | |
| 95.3% | | *CHLORPROPHAM* | *0.95* | *1.0* | *< 1.8 µg/kg* |
| | | *ANTHRAQUINONE* | *0.95* | *1.0* | *< 1.8 µg/kg* |
| LOQ | | | *Total* | *6.0* | |
| 1.8 | | | | | |
| µg/kg | | | | | |

## PB1-6/11/19-OAK LEAVES (QUERCUS ROBUR LEAVES)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN946P* | *Branches and leaves* | *Prosulfocarb* | *0.81* | *1.9* | *< 1.6 µg/kg* |
| Dry matter % | | *DIPHENYL* | *4.24* | *9.8* | |
| 43.5% | | *PHTHALIMIDE (metabolite of folpet)* | *1.74* | *4.0* | |
| | | *PHENYLPHENOL-2* | *0.44* | *1.0* | *< 1.6 µg/kg* |
| LOQ | | *DIPHENYLAMINE* | *0.68* | *1.6* | *< 1.6 µg/kg* |
| 1.6 | | *CHLORPROPHAM* | *1.31* | *3.0* | *< 1.6 µg/kg* |
| µg/kg | | *ANTHRAQUINONE* | *1.38* | *3.2* | *< 1.6 µg/kg* |
| | | *PENDIMETHALIN* | *3.11* | *7.1* | |
| | | | *Total* | 31.5 | |

## PB1-6/11/19-WILD BLACK CHERRY (PRUNUS SEROTINA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN947P* | *Branches and leaves* | *Picaridin* | *1.71* | *4.9* | |
| Dry matter % | | *Prosulfocarb* | *1.27* | *3.6* | |
| 35.1% | | *DIPHENYL* | *3.42* | *9.8* | |
| | | *PHENYLPHENOL-2* | *0.70* | *2.0* | *< 1.08 µg/kg* |
| LOQ | | *DIPHENYLAMINE* | *0.55* | *1.6* | *< 1.08 µg/kg* |
| 1.1 | | *CHLORPROPHAM* | *0.70* | *2.0* | *< 1.08 µg/kg* |
| µg/kg | | *ANTHRAQUINONE* | *2.79* | *7.9* | |
| | | *PENDIMETHALIN* | *2.51* | *7.1* | |
| | | *TRIFLOXYSTROBIN* | *1.28* | *3.6* | |
| | | | *Total* | *42.5* | |

## TOTE RAHM 1

## TR1-6/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN948P* | *Soil* | *DICHLOBENIL* | *1.60* | *4.5* | |
| Dry matter % | | *DIPHENYL* | *4.22* | *12.0* | |
| 35.2% | | *PHTHALIMIDE (metabolite of folpet)* | *1.38* | *3.9* | |
| | | *PHENYLPHENOL-2* | *0.63* | *1.8* | *< 1.1 µg/kg* |
| LOQ | | *DIPHENYLAMINE* | *0.58* | *1.6* | *< 1.1 µg/kg* |
| 1.1 | | *CHLORPROPHAM* | *2.11* | *6.0* | |
| µg/kg | | *PROSULFOCARB* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *ANTHRAQUINONE* | *10.21* | *29.0* | |
| | | *PENDIMETHALIN* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *p.p'-DDE* | *1.06* | *3.0* | *< 1.1 µg/kg* |
| | | *DIELDRIN* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *TEBUCONAZOLE* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *PROTHIOCONAZOLEDESTHIO* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *ETACONAZOLE* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *NORFLURAZON* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | *HEXAZINON* | *0.35* | *1.0* | *< 1.1 µg/kg* |
| | | | *Total* | *69.9* | |

## TR1-6/11/19-WATER MINT (MENTHA AQUATICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN949P* | *Stalks and leaves* | *Prosulfocarb* | *0.47* | *3.0* | *< 0.72 µg/kg* |
| Dry matter % | | *DIPHENYL* | *1.90* | *12.2* | |
| 15.6% | | *PHTHALIMIDE (metabolite of folpet)* | *0.94* | *6.0* | |
| | | *CHLORPROPHAM* | *0.47* | *3.0* | *< 0.72 µg/kg* |
| LOQ | | *ANTHRAQUINONE* | *0.25* | *1.6* | *< 0.72 µg/kg* |
| 0.7 | | *PENDIMETHALIN* | *0.45* | *2.9* | *< 0.72 µg/kg* |
| µg/kg | | *CYFLUTHRIN* | *1.26* | *8.1* | |
| | | *DIFENOCONAZOLE* | *0.16* | *1.0* | *< 0.72 µg/kg* |
| | | | *Total* | *37.7* | |

## TR1-6/11/19-ALDER TREE (ALNUS GLUTINOSA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN950P* | *Leaves only* | *Boscalid 1* | *1.49* | *4.7* | |
| Dry matter % | | *Picaridin 1* | *0.54* | *1.7* | *< 1.2 µg/kg* |
| 31.6% | | *Propyzamide 1* | *0.34* | *1.1* | *< 1.2 µg/kg* |
| | | *Prosulfocarb 1* | *2.12* | *6.7* | |
| LOQ | | *Fluazinam 1* | *0.67* | *2.1* | *< 1.2 µg/kg* |
| 1.2 | | *DIPHENYL* | *4.62* | *14.6* | |
| µg/kg | | *PHTHALIMIDE (metabolite of folpet)* | *1.58* | *5.0* | |
| | | *PHENYLPHENOL-2* | *0.95* | *3.0* | *< 1.2 µg/kg* |
| | | *CHLORPROPHAM* | *0.95* | *3.0* | *< 1.2 µg/kg* |
| | | *TRIALLAAT* | *1.29* | *4.1* | |
| | | *ANTHRAQUINONE* | *2.01* | *6.3* | |
| | | *PENDIMETHALIN* | *6.32* | *20.0* | |
| | | *p.p'-DDE* | *0.54* | *1.7* | *< 1.2 µg/kg* |
| | | | *Total* | *74.1* | |

## TOTE RAHM 2

### TR2-6/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN951P* | *Soil* | *DIPHENYL* | *3.55* | *6.0* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *2.32* | *3.9* | |
| 59.1% | | *CHLORPROPHAM* | *1.77* | *3.0* | |
| | | *PROSULFOCARB* | *0.59* | *1.0* | *< 1.1 µg/kg* |
| LOQ | | *ANTHRAQUINONE* | *4.73* | *8.0* | |
| 1.1 | | *p.p'-DDE* | *0.59* | *1.0* | *< 1.1 µg/kg* |
| µg/kg | | | *Total* | *22.9* | |

### TR2-6/11/19-FIELD THISTLE (CIRSIUM ARVENSE)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN952P* | *Stalks and leaves* | *Propyzamide* | *0.41* | *0.9* | *< 2.1 µg/kg* |
| Dry matter % | | *Prosulfocarb* | *2.09* | *4.7* | *< 2.1 µg/kg* |
| 44.6% | | *DIPHENYL* | *5.44* | *12.2* | |
| | | *PHTHALIMIDE (metabolite of folpet)* | *1.34* | *3.0* | *< 2.1 µg/kg* |
| LOQ | | *PHENYLPHENOL-2* | *0.45* | *1.0* | *< 2.1 µg/kg* |
| 2.1 | | *DIPHENYLAMINE* | *0.70* | *1.6* | *< 2.1 µg/kg* |
| µg/kg | | *CHLORPROPHAM* | *1.78* | *4.0* | *< 2.1 µg/kg* |
| | | *TRIALLAAT* | *0.91* | *2.0* | *< 2.1 µg/kg* |
| | | *ANTHRAQUINONE* | *0.71* | *1.6* | *< 2.1 µg/kg* |
| | | *PENDIMETHALIN* | *1.91* | *4.3* | *< 2.1 µg/kg* |
| | | | *Total* | *35.3* | |

### TR2-6/11/19-REED (PHRAGMITES AUSTRALIS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN953P* | *Stalks and leaves* | *Ametoctradin* | *11.75* | *33.1* | |
| Dry matter % | | *Prosulfocarb* | *1.13* | *3.2* | *< 1.6 µg/kg* |
| 35.5% | | *DIPHENYL* | *4.33* | *12.2* | |
| | | *PHTHALIMIDE (metabolite of folpet)* | *0.71* | *2.0* | *< 1.6 µg/kg* |
| LOQ | | *DIPHENYLAMINE* | *0.55* | *1.6* | *< 1.6 µg/kg* |
| 1.6 | | *CHLORPROPHAM* | *0.71* | *2.0* | *< 1.6 µg/kg* |
| µg/kg | | *TRIALLAAT* | *0.72* | *2.0* | *< 1.6 µg/kg* |
| | | *ANTHRAQUINONE* | *0.56* | *1.6* | *< 1.6 µg/kg* |
| | | *PENDIMETHALIN* | *1.01* | *2.9* | *< 1.6 µg/kg* |
| | | | *Total* | *60.5* | |

## EGELSBERG 1

### EBK1-7/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN954P* | *Soil* | *DIPHENYL* | *3.31* | *4.0* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *1.62* | *2.0* | |
| 82.8% | | *CHLORPROPHAM* | *0.83* | *1.0* | *< 1.5 µg/kg* |
| | | *METHABENZTHIAZURON* | *5.18* | *6.3* | |
| LOQ | | *ANTHRAQUINONE* | *8.28* | *10.0* | |
| 1.5 | | *PENDIMETHALIN* | *1.66* | *2.0* | |
| µg/kg | | *FLUDIOXONIL* | *0.83* | *1.0* | *< 1.5 µg/kg* |
| | | *DIFLUFENICAN* | *1.66* | *2.0* | |
| | | | *Total* | *28.2* | |

### EBK1-7/11/19-WINTER WHEAT (TRITICUM AESTIVUM)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN955P* | *Winterwheat* | *Difenoconazole* | *20.85* | *57.8* | |
| Dry matter % | | *Fluoxastrobin* | *242.95* | *673.0* | |
| 36.1% | | *Prochloraz* | *1.11* | *3.1* | |
| | | *Pyrimethanil* | *1.04* | *2.9* | |
| LOQ | | *DIPHENYL* | *2.41* | *6.7* | |
| 0.7 | | *PHTHALIMIDE (metabolite of folpet)* | *Detected qualitatively* | | |
| µg/kg | | *DIPHENYLAMINE* | *0.36* | *1.0* | *< 0.66 µg/kg* |
| | | *METHABENZTHIAZURON* | *2.17* | *6.0* | |
| | | *HEXACHLORBENZENE* | *0.72* | *2.0* | |
| | | *PROSULFOCARB* | *0.36* | *1.0* | *< 0.66 µg/kg* |
| | | *ANTHRAQUINONE* | *4.69* | *13.0* | |
| | | *PENDIMETHALIN* | *1.08* | *3.0* | |
| | | *FLUDIOXONIL* | *103.97* | *288.0* | |
| | | *TEBUCONAZOLE* | *0.36* | *1.0* | *< 0.66 µg/kg* |
| | | *DIFLUFENICAN* | *0.72* | *2.0* | |
| | | *CYPERMETHRIN* | *1.37* | *3.8* | |
| | | *PROTHIOCONAZOLEDESTHIO* | *7.96* | *22.1* | |
| | | | *Total* | *1086.2* | |

## EGELSBERG 2

### EBK2-7/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN956P* | *Soil* | *CHLOROTOLURON* | *1.67* | *2.0* | |
| Dry matter % | | *DICHLOBENIL* | *1.28* | *1.5* | *< 1.6 µg/kg* |
| 84.7% | | *DIPHENYL* | *3.39* | *4.0* | |
| | | *CHLORPROPHAM* | *0.85* | *1.0* | *< 1.6 µg/kg* |
| LOQ | | *PENCYCURON* | *0.85* | *1.0* | *< 1.6 µg/kg* |
| 1.6 | | *HEXACHLORBENZENE* | *1.97* | *2.3* | |
| µg/kg | | *ANTHRAQUINONE* | *6.78* | *8.0* | |
| | | *PENDIMETHALIN* | *2.54* | *3.0* | |
| | | *FLUDIOXONIL* | *0.85* | *1.0* | *< 1.6 µg/kg* |
| | | *FLUSILAZOLE* | *0.85* | *1.0* | *< 1.6 µg/kg* |
| | | *DIFLUFENICAN* | *2.54* | *3.0* | |
| | | *EPOXICONAZOLE* | *0.66* | *0.8* | *< 1.6 µg/kg* |
| | | | *Total* | *28.6* | |

### EBK2-7/11/19-RABBIT PELLETS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN958P* | *Rabbit manure* | *Fluoxastrobin* | *0.85* | *3.8* | *< 1.03 µg/kg* |
| Dry matter % | | *Prosulfocarb* | *0.97* | *4.3* | *< 1.03 µg/kg* |
| 22.4% | | *DIPHENYL* | *3.93* | *17.5* | |
| | | *CHLORPROPHAM* | *0.63* | *2.8* | *< 1.03 µg/kg* |
| LOQ | | *ANTHRAQUINONE* | *1.46* | *6.5* | |
| 1.0 | | *PENDIMETHALIN* | *0.37* | *1.6* | *< 1.03 µg/kg* |
| µg/kg | | *FLUDIOXONIL* | *0.77* | *3.4* | *< 1.03 µg/kg* |
| | | *DIFLUFENICAN* | *0.35* | *1.6* | *< 1.03 µg/kg* |
| | | | *Total* | *41.6* | |

## EBK2-7/11/19-WINTER WHEAT (TRITICUM AESTIVUM)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN957P* | *Winterwheat* | *DIPHENYL* | *3.41* | *8.9* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *Detected qualitatively* | | |
| 38.4% | | *DIPHENYLAMINE* | *0.38* | *1.0* | *< 0.71 µg/kg* |
| | | *HEXACHLORBENZENE* | *0.77* | *2.0* | |
| LOQ | | *METALAXYL* | *3.46* | *9.0* | |
| 0.7 | | *ANTHRAQUINONE* | *3.84* | *10.0* | |
| µg/kg | | *PENDIMETHALIN* | *1.15* | *3.0* | |
| | | *FLUDIOXONIL* | *303.74* | *791.0* | |
| | | *FLUSILAZOLE* | *0.38* | *1.0* | *< 0.71 µg/kg* |
| | | *TEBUCONAZOLE* | *0.38* | *1.0* | *< 0.71 µg/kg* |
| | | *DIFLUFENICAN* | *1.54* | *4.0* | |
| | | *EPOXICONAZOLE* | *0.31* | *0.8* | *< 0.71 µg/kg* |
| | | *DIFENOCONAZOLE* | *0.38* | *1.0* | *< 0.71 µg/kg* |
| | | | *Total* | *832.7* | |

## EGELSBERG 3

### EBK3-7/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN959P* | *Soil* | *DIPHENYL* | *3.18* | *4.0* | |
| Dry matter % | | *ANTHRAQUINONE* | *13.52* | *17.0* | |
| 79.5% | | | *Total* | *21.0* | |
| | | | | | |
| LOQ | | | | | |
| 1.5 | | | | | |
| µg/kg | | | | | |

## EBK3-7/11/19-HEIDE (Calluna vulgaris)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN960P* | *Branches and leaves* | *Boscalid* | *1.65* | *8.2* | |
| Dry matter % | | *Flufenacet* | *0.84* | *4.1* | |
| 20.2% | | *Fluopyram* | *0.46* | *2.3* | *< 0.62 µg/kg* |
| | | *Propyzamide* | *0.47* | *2.3* | *< 0.62 µg/kg* |
| LOQ | | *Prosulfocarb* | *3.37* | *16.7* | |
| 0.6 | | *Fluazinam* | *0.57* | *2.8* | *< 0.62 µg/kg* |
| µg/kg | | *DIPHENYL* | *2.96* | *14.6* | |
| | | *DIPHENYLAMINE* | *2.53* | *12.5* | |
| | | *CHLORPROPHAM* | *1.21* | *6.0* | |
| | | *TERBUTYLAZIN* | *0.40* | *2.0* | *< 0.62 µg/kg* |
| | | *TRIALLAAT* | *0.82* | *4.1* | |
| | | *ANTHRAQUINONE* | *1.60* | *7.9* | |
| | | *CYPRODINIL* | *0.40* | *2.0* | *< 0.62 µg/kg* |
| | | *PENDIMETHALIN* | *2.89* | *14.3* | |
| | | *p.p'-DDE* | *0.35* | *1.7* | *< 0.62 µg/kg* |
| | | *TEBUCONAZOLE* | *0.35* | *1.8* | *< 0.62 µg/kg* |
| | | *DIFLUFENICAN* | *0.34* | *1.7* | *< 0.62 µg/kg* |
| | | *DIFENOCONAZOLE* | *0.20* | *1.0* | *< 0.62 µg/kg* |
| | | *PROTHIOCONAZOLEDESTHIO* | *0.61* | *3.0* | *< 0.62 µg/kg* |
| | | | *Total* | 109.0 | |

## BISLICH

## BL-12/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN910P* | *Soil* | *DIPHENYL* | *13.53* | *24.1* | |
| Dry matter % | Boden | *HEXACHLORBENZENE* | *1.41* | *2.5* | |
| 56.2% | | *ANTHRAQUINONE* | *22.48* | *40.0* | |
| | | *p.p'-DDE* | *0.56* | *1.0* | *< 1 µg/kg* |
| LOQ | | *p.p'-DDT* | *28.63* | *50.9* | |
| 1.0 | | | *Total* | *118.5* | |
| µg/kg | | | | | |

| Soil | | | |
|---|---|---|---|
| | µg/kg | | |
| Glyphosate | 0.0000 | < 0.5 µg/kg | LOQ Glyphosate method |
| AMPA | 3.3100 | | 0.50 |
| Glufosinate | 0.0000 | < 0.5 µg/kg | µg/kg |

## BL-12/11/19-REED (PHRAGMITES AUSTRALIS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN911P* | *Whole plant* | *DIPHENYL* | *12.41* | *20.7* | |
| Dry matter % | | *DIPHENYLAMINE* | *2.07* | *3.4* | *< 2.4 µg/kg* |
| 60.0% | | *PROSULFOCARB* | *1.94* | *3.2* | *< 2.4 µg/kg* |
| | | *ANTHRAQUINONE* | *2.31* | *3.8* | *< 2.4 µg/kg* |
| LOQ | | | *Total* | *31.2* | |
| 2.4 | | | | | |
| µg/kg | | | | | |

## BL-12/11/19-STINGING NETTLE (URTICA DIOICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO266P* | *Stalks and leaves* | *Fenamiphos-sulfoxide* | *1.37* | *2.1* | *< 2.4 µg/kg* |
| Dry matter % | | *Prosulfocarb* | *0.93* | *1.4* | *< 2.4 µg/kg* |
| 64.8% | | *DIPHENYL* | *11.06* | *17.1* | |
| | | *PHTHALIMIDE (metabolite of folpet)* | *3.89* | *6.0* | |
| LOQ | | *PHENYLPHENOL-2* | *0.65* | *1.0* | *< 2.4 µg/kg* |
| 2.4 | | *DIPHENYLAMINE* | *1.01* | *1.6* | *< 2.4 µg/kg* |
| µg/kg | | *CHLORPROPHAM* | *1.94* | *3.0* | *< 2.4 µg/kg* |
| | | *ANTHRAQUINONE* | *2.06* | *3.2* | *< 2.4 µg/kg* |
| | | *PENDIMETHALIN* | *0.93* | *1.4* | *< 2.4 µg/kg* |
| | | *FLUDIOXONIL* | *1.30* | *2.0* | *< 2.4 µg/kg* |
| | | | *Total* | *38.8* | |

## LOOSENBERGE

## LB-12/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN912P* | *Soil* | *ANTHRAQUINONE* | *11.60* | *13.0* | |
| Dry matter % | | | *Total* | *13.0* | |
| 89.2% | | | | | |
| | | | | | |
| LOQ | | | | | |
| 1.6 | | | | | |
| µg/kg | | | | | |

## LB-12/11/19-HEATHER (CALLUNA VULGARIS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN913P* | *Whole plant* | *DIPHENYL* | *26.79* | *51.7* | |
| Dry matter % | | *PHENYLPHENOL-2* | *5.01* | *9.7* | |
| 51.8% | | *DIPHENYLAMINE* | *5.36* | *10.3* | |
| | | *CHLORPROPHAM* | *2.93* | *5.7* | |
| LOQ | | *PROSULFOCARB* | *10.86* | *21.0* | |
| 1.6 | | *ANTHRAQUINONE* | *7.97* | *15.4* | |
| µg/kg | | *CYPRODINIL* | *0.88* | *1.7* | *< 1.6 µg/kg* |
| | | *PENDIMETHALIN* | *9.64* | *18.6* | |
| | | | *Total* | *134.1* | |

## LB-12/11/19-SOIL (0-6 CM)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO267P* | *Soil 0-6 cm* | *DIPHENYL* | *1.39* | *1.8* | *< 1.4 µg/kg* |
| Dry matter % | | *CHLORPROPHAM* | *0.77* | *1.0* | *< 1.4 µg/kg* |
| 76.6% | | *ANTHRAQUINONE* | *5.36* | *7.0* | |
| | | | *Total* | *9.8* | |
| LOQ | | | | | |
| 1.4 | | | | | |
| µg/kg | | | | | |

## URDENBACHER KAEMPEN

## UK-13/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN914P* | *Soil* | *DIPHENYL* | *7.53* | *11.1* | |
| Dry matter % | | *HEXACHLORBENZENE* | *1.70* | *2.5* | |
| 67.8% | | *ANTHRAQUINONE* | *11.53* | *17.0* | |
| | | | *Total* | *30.6* | |
| LOQ | | | | | |
| 1.3 | | | | | |
| µg/kg | | | | | |

## UK-13/11/19-STINGING NETTLE (URTICA DIOICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN915P* | *Whole plant* | *DIPHENYL* | *3.81* | *13.8* | |
| Dry matter % | | | *Total* | *13.8* | |
| 27.6% | | | | | |
| | | | | | |
| LOQ | | | | | |
| 1.1 | | | | | |
| µg/kg | | | | | |

## UK-13/11/19-GREAT BURNET (SANGUISORBA OFFICINALIS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN916P* | *Leaves* | *DIPHENYL* | *8.09* | *37.0* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *1.31* | *6.0* | |
| 21.9% | | *PHENYLPHENOL-2* | *0.44* | *2.0* | *< 1 µg/kg* |
| | | *DIPHENYLAMINE* | *0.44* | *2.0* | *< 1 µg/kg* |
| LOQ | | *CHLORPROPHAM* | *0.22* | *1.0* | *< 1 µg/kg* |
| 1.0 | | *PENDIMETHALIN* | *0.39* | *1.8* | *< 1 µg/kg* |
| µg/kg | | | *Total* | *49.7* | |

## ZONS

## ZO-13/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN917P* | *Soil* | *DIPHENYL* | *3.04* | *3.7* | |
| Dry matter % | | *ANTHRAQUINONE* | *4.10* | *5.0* | |
| 82.0% | | | *Total* | *8.7* | |
| | | | | | |
| LOQ | | | | | |
| 1.5 | | | | | |
| µg/kg | | | | | |

## ZO-13/11/19-GREAT BURNET (SANGUISORBA MINOR)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN918P* | *Leaves* | *DIPHENYL* | *8.42* | *34.8* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *0.97* | *4.0* | |
| 24.2% | | *PHENYLPHENOL-2* | *0.97* | *4.0* | |
| | | *DIPHENYLAMINE* | *1.21* | *5.0* | |
| LOQ | | *CHLORPROPHAM* | *0.73* | *3.0* | *< 0.77 µg/kg* |
| 0.8 | | *PROSULFOCARB* | *0.97* | *4.0* | |
| µg/kg | | *PENDIMETHALIN* | *1.30* | *5.4* | |
| | | | *Total* | *60.1* | |

## SOLLER VETTWEISS

## SV-13/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN919P* | *Soil* | *DIPHENYL* | *5.62* | *7.4* | |
| Dry matter % | | *ANTHRAQUINONE* | *3.04* | *4.0* | |
| 75.9% | | *p.p'-DDE* | *0.76* | *1.0* | *< 1.4 µg/kg* |
| | | | *Total* | *12.4* | |
| LOQ | | | | | |
| 1.4 | | | | | |
| µg/kg | | | | | |

## SV-13/11/19-STINGING NETTLE (URTICA DIOICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN920P* | *Whole plant* | *DIPHENYL* | *6.81* | *27.6* | |
| Dry matter % | | *PHENYLPHENOL-2* | *0.80* | *3.2* | *< 0.91 µg/kg* |
| 24.7% | | *DIPHENYLAMINE* | *1.70* | *6.9* | |
| | | *CHLORPROPHAM* | *0.47* | *1.9* | *< 0.91 µg/kg* |
| LOQ | | *PENDIMETHALIN* | *13.21* | *53.5* | |
| 0.9 | | *DIFLUFENICAN* | *1.43* | *5.8* | |
| µg/kg | | | *Total* | *98.9* | |

## SV-13/11/19-MIXED GRASSES

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO268P | Whole plants | CHLOROTOLURON | 1.00 | 5.1 | |
| Dry matter % | | Flufenacet | 0.45 | 2.3 | < 0.9 µg/kg |
| 19.5% | | Prosulfocarb | 0.31 | 1.6 | < 0.9 µg/kg |
| | | DIPHENYL | 3.08 | 15.8 | |
| LOQ | | DIPHENYLAMINE | 0.39 | 2.0 | < 0.9 µg/kg |
| 0.9 | | CHLORPROPHAM | 0.63 | 3.3 | < 0.9 µg/kg |
| µg/kg | | ANTHRAQUINONE | 0.59 | 3.0 | < 0.9 µg/kg |
| | | PENDIMETHALIN | 11.90 | 61.0 | |
| | | DIFLUFENICAN | 1.56 | 8.0 | |
| | | EPOXICONAZOLE | 0.12 | 0.6 | < 0.9 µg/kg |
| | | | Total | 102.7 | |

## ESCHWEILER 1

## EW1-14/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CN921P | Soil | Epoxiconazole | 3.47 | 5.1 | |
| Dry matter % | | Prochloraz desimidazoleamino | 15.46 | 22.8 | |
| 67.9% | | DIPHENYL | 3.77 | 5.6 | |
| | | ANTHRAQUINONE | 0.68 | 1.0 | < 1.3 µg/kg |
| LOQ | | PROPICONAZOLE | 0.68 | 1.0 | < 1.3 µg/kg |
| 1.3 | | | Total | 35.4 | |
| µg/kg | | | | | |

## EW1-14/11/19-HASELNUT (CORYLUS AVELLANA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CN922P | Branches with leaves | DIPHENYL | 11.26 | 20.7 | |
| Dry matter % | | PHENYLPHENOL-2 | 1.75 | 3.2 | |
| 54.4% | | DIPHENYLAMINE | 1.88 | 3.4 | |
| | | CHLORPROPHAM | 1.03 | 1.9 | < 1.5 µg/kg |
| LOQ | | PROSULFOCARB | 1.75 | 3.2 | |
| 1.5 | | PENDIMETHALIN | 6.33 | 11.6 | |
| µg/kg | | TEBUCONAZOLE | 0.97 | 1.8 | < 1.5 µg/kg |
| | | DIFLUFENICAN | 1.05 | 1.9 | < 1.5 µg/kg |
| | | PROTHIOCONAZOLEDESTHIO | 0.84 | 1.5 | < 1.5 µg/kg |
| | | | Total | 49.4 | |

### EW1-14/11/19-ROE DEER DROPPINGS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN923P* | *Manure roe deer* | *Metoxuron* | *32.82* | *63.0* | |
| Dry matter % | | *DIPHENYLAMINE* | *1.04* | *2.0* | *< 2.4 µg/kg* |
| 52.1% | | *CHLORPROPHAM* | *0.52* | *1.0* | *< 2.4 µg/kg* |
| | | *PROSULFOCARB* | *1.56* | *3.0* | *< 2.4 µg/kg* |
| LOQ | | *ANTHRAQUINONE* | *1.04* | *2.0* | *< 2.4 µg/kg* |
| 2.4 | | | *Total* | *71.0* | |
| µg/kg | | | | | |

## ESCHWEILER 2

### EW2-14/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN924P* | *Soil* | *Prochloraz 1* | *Detected qualitatively* | | |
| Dry matter % | | *DIPHENYL* | *3.94* | *5.6* | |
| 70.9% | | *ANTHRAQUINONE* | *1.42* | *2.0* | |
| | | *EPOXICONAZOLE (piek 1 + 2)* | *6.38* | *9.0* | |
| LOQ | | | *Total* | *16.6* | |
| 1.3 | | | | | |
| µg/kg | | | | | |

### EW2-14/11/19 HASELNUT (CORYLUS AVELLANA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN925P* | *Branches with leaves* | *DIPHENYL* | *Detected qualitatively* | | |
| Dry matter % | | *PHTHALIMIDE (metabolite folpet)* | *3.58* | *7.9* | |
| 45.1% | | *PROSULFOCARB* | *1.29* | *2.9* | *< 1.7 µg/kg* |
| | | *PENDIMETHALIN* | *4.10* | *9.1* | |
| LOQ | | *DIFLUFENICAN* | *2.91* | *6.5* | |
| 1.7 | | | *Total* | *26.3* | |
| µg/kg | | | | | |

## BAD MUENSTEREIFEL (REFERENCE AREA)

### RBME-14/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN926P* | *Soil* | *DIPHENYL* | *3.04* | *4.1* | |
| Dry matter % | | *ANTHRAQUINONE* | *1.49* | *2.0* | |
| 74.4% | | | *Total* | *6.1* | |
| | | | | | |
| LOQ | | | | | |
| 1.4 | | | | | |
| µg/kg | | | | | |

### RBME-14/11-GRASSES AND HERBS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN927P* | *Whole plant* | *DIPHENYL* | *Detected qualitatively* | | |
| Dry matter % | | *PHTHALIMIDE (metabolite folpet)* | *3.70* | *12.7* | |
| 29.1% | | *PHENYLPHENOL-2* | *0.61* | *2.1* | *< 1.1 µg/kg* |
| | | *CHLORPROPHAM* | *1.06* | *3.6* | *< 1.1 µg/kg* |
| LOQ | | *PROSULFOCARB* | *2.49* | *8.6* | |
| 1.1 | | *PENDIMETHALIN* | *0.88* | *3.0* | *< 1.1 µg/kg* |
| µg/kg | | | *Total* | *30.0* | |

### RBME-14/11/19-RED DEER DROPPINGS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN928P* | *Manure Red deer* | *DIPHENYL* | *6.78* | *25.0* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *0.81* | *3.0* | *< 1 µg/kg* |
| 27.1% | | *PHENYLPHENOL-2* | *0.27* | *1.0* | *< 1 µg/kg* |
| | | *CHLORPROPHAM* | *0.54* | *2.0* | *< 1 µg/kg* |
| LOQ | | *PROSULFOCARB* | *0.27* | *1.0* | *< 1 µg/kg* |
| 1.0 | | *ANTHRAQUINONE* | *0.81* | *3.0* | *< 1 µg/kg* |
| µg/kg | | | *Total* | *35.0* | |

## WAHNBACHTAL 2

### WBT2-14/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN929P* | *Soil* | *DIPHENYL* | *2.62* | *4.1* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *0.64* | *1.0* | *< 1.2 µg/kg* |
| 64.3% | | *ANTHRAQUINONE* | *1.93* | *3.0* | |
| | | | *Total* | *8.1* | |
| LOQ | | | | | |
| 1.2 | | | | | |
| µg/kg | | | | | |

### WBT2-14/11/19-GRASSES

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN930P* | *Whole plant* | *DIPHENYL* | *Detected qualitatively* | | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *2.26* | *12.7* | |
| 17.8% | | *PHENYLPHENOL-2* | *0.74* | *4.2* | |
| | | *DIPHENYLAMINE* | *1.84* | *10.3* | |
| LOQ | | *CHLORPROPHAM* | *1.29* | *7.3* | |
| 0.7 | | *ANTHRAQUINONE* | *0.47* | *2.6* | *< 0.65 µg/kg* |
| µg/kg | | | *Total* | *37.1* | |

## WAHNBACHTAL 5

### WBT5-14/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN931P* | *Soil* | *DIPHENYL* | *7.04* | *10.2* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *Detected qualitatively* | | |
| 69.0% | | *DIPHENYLAMINE* | *Detected qualitatively* | | |
| | | *ANTHRAQUINONE* | *1.38* | *2.0* | |
| LOQ | | | *Total* | *12.2* | |
| 1.3 | | | | | |
| µg/kg | | | | | |

## WBT5-14/11/19-GRASSES WITH DENDELION (TARAXACUM OFFICINALE)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CN932P* | *Whole plant* | *DIPHENYL* | *Detected qualitatively* | | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *2.47* | *14.3* | |
| 17.3% | | *PHENYLPHENOL-2* | *0.36* | *2.1* | *< 0.64 µg/kg* |
| | | *CHLORPROPHAM* | *0.63* | *3.6* | *< 0.64 µg/kg* |
| LOQ | | | *Total* | *20.0* | |
| 0.6 | | | | | |
| µg/kg | | | | | |

## BRAUSELAY 1 (DOWN-HILL)

### BL-20/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO269P* | *Soil* | *Ametoctradin* | *3.72* | *4.5* | |
| Dry matter % | | *Boscalid* | *599.98* | *722.0* | |
| 83.1% | | *Cyflufenamid* | *1.42* | *1.7* | |
| | | *Dimethomorph* | *108.86* | *131.0* | |
| LOQ | | *Fenpyrazamine* | *1.47* | *1.8* | *< 1.5 µg/kg* |
| 1.5 | | *Fluopicolide* | *67.16* | *80.8* | |
| µg/kg | | *Fluopyram* | *70.97* | *85.4* | |
| | | *Fluquinconazole* | *1.27* | *1.5* | *< 1.5 µg/kg* |
| | | *Fluxapyroxad* | *41.38* | *49.8* | |
| | | *Tetraconazole* | *19.36* | *23.3* | |
| | | *DICHLOBENIL* | *6.78* | *8.2* | |
| | | *DIPHENYL* | *3.02* | *3.6* | |
| | | *CHLORPROPHAM* | *0.83* | *1.0* | *< 1.5 µg/kg* |
| | | *ALDRIN* | *3.32* | *4.0* | |
| | | *ANTHRAQUINONE* | *18.28* | *22.0* | |
| | | *CYPRODINIL* | *4.16* | *5.0* | |
| | | *PENCONAZOLE* | *10.73* | *12.9* | |
| | | *PROCYMIDON* | *2.75* | *3.3* | |
| | | *o.p'-DDE* | *4.99* | *6.0* | |
| | | *FLUDIOXONIL* | *19.94* | *24.0* | |
| | | *p.p'-DDE* | *543.47* | *654.0* | |
| | | *DIELDRIN* | *110.52* | *133.0* | |
| | | *MYCLOBUTANIL* | *17.45* | *21.0* | |
| | | *o.p'-DDD* | *28.25* | *34.0* | |
| | | *p.p'-DDD + o.p'-DDT* | *164.87* | *198.4* | |
| | | *QUINOXYFEN* | *28.25* | *34.0* | |
| | | *p.p'-DDT* | *41.88* | *50.4* | |
| | | *DICOFOL* | *5.82* | *7.0* | |

| | | | |
|---|---|---|---|
| TEBUCONAZOLE | 25.76 | 31.0 | |
| TETRADIFON | 1.66 | 2.0 | |
| FENARIMOL | 4.16 | 5.0 | |
| METRAFENONE | 59.88 | 72.1 | |
| DIFENOCONAZOLE | 4.16 | 5.0 | |
| AZOXYSTROBIN | 2.49 | 3.0 | |
| | Total | 2441.7 | |

| Soil (BL-20/11/19-SOIL) | | | |
|---|---|---|---|
| | µg/kg | | |
| Glyphosate | 0.4290 | < 0.5 µg/kg | LOQ Glyphosate method |
| AMPA | 7.1800 | | 0.50 |
| Glufosinate | 0.0000 | < 0.5 µg/kg | µg/kg |

## BL-20/11/19-WILD BRAMBLE (RUBUS FRUTICOSUS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO270P | leaves and stalks | Ametoctradin | 184.42 | 414.4 | |
| Dry matter % | | Cyazofamid | 2.38 | 5.4 | |
| 44.5% | | Cyflufenamid | 1.81 | 4.1 | |
| | | Difenoconazole | 2.45 | 5.5 | |
| LOQ | | Dimethomorph | 24.48 | 55.0 | |
| 1.6 | | Fluopicolide | 1.60 | 3.6 | |
| µg/kg | | Fluopyram | 1.35 | 3.0 | < 1.6 µg/kg |
| | | Fluxapyroxad | 3.25 | 7.3 | |
| | | Proquinazid | 2.17 | 4.9 | |
| | | Prosulfocarb | 0.52 | 1.2 | < 1.6 µg/kg |
| | | Tebuconazole | 0.63 | 1.4 | < 1.6 µg/kg |
| | | Tetraconazole | 0.90 | 2.0 | < 1.6 µg/kg |
| | | Dithianon | 224.39 | 504.3 | |
| | | DIPHENYL | 6.36 | 14.3 | |
| | | PHTHALIMIDE (metabolite of folpet) | 7.57 | 17.0 | |
| | | CHLORPROPHAM | 1.99 | 4.5 | |
| | | ANTHRAQUINONE | 0.93 | 2.1 | < 1.6 µg/kg |
| | | PENDIMETHALIN | 0.86 | 1.9 | < 1.6 µg/kg |
| | | PENCONAZOLE | 0.82 | 1.9 | < 1.6 µg/kg |
| | | PROCYMIDON | 1.44 | 3.2 | < 1.6 µg/kg |
| | | p.p'-DDE | 4.64 | 10.4 | |
| | | DIELDRIN | 0.97 | 2.2 | < 1.6 µg/kg |

| | | | | | |
|---|---|---|---|---|---|
| | | p.p'-DDD + o.p'-DDT | 0.82 | 1.9 | < 1.6 µg/kg |
| | | METRAFENON | 4.85 | 10.9 | |
| | | | Total | 1082.2 | |

## BL1-20/11/19-GRAPE LEAVES (VITIS VINIFERA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO271P | Leaves | Ametoctradin | 38640.00 | 140000.0 | |
| Dry matter % | | Boscalid | 36.64 | 132.8 | |
| 27.6% | | Cyazofamid | 102.01 | 369.6 | |
| | | Cyflufenamid | 19.34 | 70.1 | |
| LOQ | | Dimethomorph | 3367.20 | 12200.0 | |
| 1.0 | | Fluopicolide | 267.44 | 969.0 | |
| µg/kg | | Fluopyram | 367.08 | 1330.0 | |
| | | Fluxapyroxad | 750.72 | 2720.0 | |
| | | Proquinazid | 5.13 | 18.6 | |
| | | Prosulfocarb | 0.47 | 1.7 | < 1 µg/kg |
| | | DIPHENYL | 3.37 | 12.2 | |
| | | PHTHALIMIDE (metabolite of folpet) | 208.93 | 757.0 | |
| | | CHLORPROPHAM | 0.55 | 2.0 | < 1 µg/kg |
| | | ANTHRAQUINONE | 2.19 | 7.9 | |
| | | TETRACONAZOLE | 97.85 | 354.5 | |
| | | CYPRODINIL | 1.93 | 7.0 | |
| | | PENDIMETHALIN | 0.79 | 2.9 | < 1 µg/kg |
| | | PENCONAZOLE | 10.76 | 39.0 | |
| | | PROCYMIDON | 2.09 | 7.6 | |
| | | FLUDIOXONIL | 1.66 | 6.0 | |
| | | p.p'-DDE | 15.23 | 55.2 | |
| | | DIELDRIN | 2.88 | 10.4 | |
| | | MYCLOBUTANIL | 0.47 | 1.7 | < 1 µg/kg |
| | | p.p'-DDD + o.p'-DDT | 1.78 | 6.5 | |
| | | QUINOXYFEN | 0.99 | 3.6 | < 1 µg/kg |
| | | p.p'-DDT | 17.40 | 63.0 | |
| | | TEBUCONAZOLE | 40.19 | 145.6 | |
| | | METRAFENON | 229.87 | 832.9 | |
| | | DIFENOCONAZOLE | 46.09 | 167.0 | |
| | | | Total | 160293.6 | |

# BRAUSELAY 3 (UP-HILL)

## BL3-20/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO272P* | *Soil* | *Ametoctradin* | *3.97* | *4.8* | |
| Dry matter % | | *Boscalid* | *1.05* | *1.3* | *< 1.5 µg/kg* |
| 82.6% | | *Carbendazim* | *1.33* | *1.6* | *< 1.5 µg/kg* |
| | | *DICHLOBENIL* | *5.06* | *6.1* | |
| LOQ | | *DIPHENYL* | *1.50* | *1.8* | |
| 1.5 | | *PHTHALIMIDE (metabolite of folpet)* | *0.45* | *0.5* | *< 1.5 µg/kg* |
| µg/kg | | *CHLORPROPHAM* | *0.83* | *1.0* | *< 1.5 µg/kg* |
| | | *ALDRIN* | *1.65* | *2.0* | |
| | | *ANTHRAQUINONE* | *9.91* | *12.0* | |
| | | *PROCYMIDON* | *2.73* | *3.3* | |
| | | *o.p'-DDE* | *2.48* | *3.0* | |
| | | *p.p'-DDE* | *320.49* | *388.0* | |
| | | *DIELDRIN* | *56.17* | *68.0* | |
| | | *o.p'-DDD* | *12.39* | *15.0* | |
| | | *p.p'-DDD + o.p'-DDT* | *92.88* | *112.4* | |
| | | *p.p'-DDT* | *649.66* | *786.5* | |
| | | *DICOFOL* | *4.96* | *6.0* | |
| | | *IPRODION* | *1.28* | *1.6* | *< 1.5 µg/kg* |
| | | *TETRADIFON* | *0.83* | *1.0* | *< 1.5 µg/kg* |
| | | | *Total* | *1416.0* | |

## BL3-20/11/19-WILD BRAMBLE (RUBUS FRUTICOSUS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO273P* | *Leaves and stalks* | *Ametoctradin* | *5.14* | *10.4* | |
| Dry matter % | | *Prosulfocarb* | *0.60* | *1.2* | *< 1.8 µg/kg* |
| 49.3% | | *DIPHENYL* | *5.63* | *11.4* | |
| | | *PHTHALIMIDE (metabolite of folpet)* | *2.96* | *6.0* | |
| LOQ | | *CHLORPROPHAM* | *1.47* | *3.0* | *< 1.8 µg/kg* |
| 1.8 | | *ANTHRAQUINONE* | *1.03* | *2.1* | *< 1.8 µg/kg* |
| µg/kg | | *PROCYMIDON* | *2.39* | *4.8* | |
| | | *p.p'-DDE* | *1.03* | *2.1* | *< 1.8 µg/kg* |
| | | | *Total* | 41.1 | |

## POMMERN 2

### PM2-20/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO274P | Soil | Ametoctradin | 1.64 | 2.1 | |
| Dry matter % | | Azoxystrobin | 1.07 | 1.3 | < 1.5 µg/kg |
| 79.7% | | Boscalid | 35.79 | 44.9 | |
| | | Carbendazim | 1.19 | 1.5 | < 1.5 µg/kg |
| LOQ | | Cyprodinil | 5.58 | 7.0 | |
| 1.5 | | Dimethomorph | 23.59 | 29.6 | |
| µg/kg | | Fluopicolide | 0.88 | 1.1 | < 1.5 µg/kg |
| | | Penconazole | 1.05 | 1.3 | < 1.5 µg/kg |
| | | Tolylfluanid | Detected qualitatively | | |
| | | DICHLOBENIL | 3.25 | 4.1 | |
| | | DIPHENYL | 7.25 | 9.1 | |
| | | PHTHALIMIDE (metabolite of folpet) | 1.31 | 1.6 | < 1.5 µg/kg |
| | | PHENYLPHENOL-2 | 1.16 | 1.4 | < 1.5 µg/kg |
| | | CHLORPROPHAM | 0.80 | 1.0 | < 1.5 µg/kg |
| | | METHABENZTHIAZURON | 0.80 | 1.0 | < 1.5 µg/kg |
| | | VINCHLOZOLIN | 0.80 | 1.0 | < 1.5 µg/kg |
| | | ALDRIN | 1.59 | 2.0 | |
| | | ANTHRAQUINONE | 85.28 | 107.0 | |
| | | PYRIFENOX | 1.59 | 2.0 | |
| | | PROCYMIDON | 9.88 | 12.4 | |
| | | o.p'-DDE | 3.99 | 5.0 | |
| | | FLUDIOXONIL | 5.58 | 7.0 | |
| | | p.p'-DDE | 329.96 | 414.0 | |
| | | DIELDRIN | 196.06 | 246.0 | |
| | | MYCLOBUTANIL | 19.13 | 24.0 | |
| | | o.p'-DDD | 17.53 | 22.0 | |
| | | BETA-ENDOSULFAN | 0.80 | 1.0 | < 1.5 µg/kg |
| | | p.p'-DDD + o.p'-DDT | 140.84 | 176.7 | |
| | | QUINOXYFEN | 16.74 | 21.0 | |
| | | ENDOSULFAN-SULPHATE | 3.99 | 5.0 | |
| | | p.p'-DDT | 4366.11 | 5478.2 | |
| | | DICOFOL | 10.36 | 13.0 | |
| | | TEBUCONAZOLE | 20.72 | 26.0 | |
| | | IPRODION | 2.47 | 3.1 | |
| | | TETRADIFON | 0.80 | 1.0 | < 1.5 µg/kg |
| | | LAMBDA-CYHALOTHRIN | 0.56 | 0.7 | < 1.5 µg/kg |
| | | FENARIMOL | 2.39 | 3.0 | |
| | | METRAFENONE | 11.72 | 14.7 | |

| | | | | | |
|---|---|---|---|---|---|
| | | *FLUQUINCONAZOLE* | *1.91* | *2.4* | |
| | | | *Total* | *6695.3* | |

| Soil PM2 | | | |
|---|---|---|---|
| | µg/kg | | |
| Glyphosate | 3.0700 | | LOQ Glyphosate method |
| AMPA | 43.7100 | | 0.50 |
| Glufosinate | 0.0000 | < 0.5 µg/kg | µg/kg |

## PM2-20/11/19-WILD BRAMBLE (RUBUS FRUTICOSUS)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO275P* | *Leaves and stalks* | *DIPHENYL* | *5.18* | *12.5* | |
| Dry matter % | | *PHTHALIMIDE* | *2.48* | *6.0* | |
| 41.4% | | *CHLORPROPHAM* | *0.83* | *2.0* | *< 1.5 µg/kg* |
| | | *ANTHRAQUINONE* | *0.83* | *2.0* | *< 1.5 µg/kg* |
| LOQ | | *CYPRODINIL* | *2.48* | *6.0* | |
| 1.5 | | *PENDIMETHALIN* | *1.24* | *3.0* | *< 1.5 µg/kg* |
| µg/kg | | *PROCYMIDON* | *2.07* | *5.0* | |
| | | *FLUDIOXONIL* | *1.24* | *3.0* | *< 1.5 µg/kg* |
| | | *p.p'-DDE* | *0.84* | *2.0* | *< 1.5 µg/kg* |
| | | *ETOFENPROX* | *1.24* | *3.0* | *< 1.5 µg/kg* |
| | | | *Total* | *44.5* | |

## PM2-20/11/19-MUSHROOM

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO276P* | *whole mushroom* | *Boscalid* | *Detected qualitatively* | | |
| Dry matter % | | *Dimethomorph* | *Detected qualitatively* | | |
| 4.0% | | *Myclobutanil* | *Detected qualitatively* | | |
| | | *DIELDRIN* | *Detected qualitatively* | | |
| LOQ | | *ENDOSULFAN SULPHATE* | *Detected qualitatively* | | |
| 0.2 | | *o.p'-DDD* | *Detected qualitatively* | | |
| µg/kg | | *p.p'-DDD DDT* | *Detected qualitatively* | | |
| | | *p.p'-DDE* | *Detected qualitatively* | | |
| | | *p.p'-DDT* | *Detected qualitatively* | | |
| | | *DICOFOL* | *Detected qualitatively* | | |
| | | | | | |
| | | *Of this sample the quantity was not sufficient to conduct quantitative analyses* | | | |

## NATUREPARK NASSAU (KOPPELSTEIN); UP-HILL

## NN-20/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO277P* | *Soil* | *Boscalid* | *16.28* | *20.0* | |
| Dry matter % | | *Epoxiconazole* | *9.85* | *12.1* | |
| 81.4% | | *Fluxapyroxad* | *12.45* | *15.3* | |
| | | *DIPHENYL* | *3.07* | *3.8* | |
| LOQ | | *ANTHRAQUINONE* | *1.63* | *2.0* | |
| 1.5 | | *p.p'-DDE* | *0.81* | *1.0* | *< 1.5 µg/kg* |
| µg/kg | | *p.p'-DDT* | *0.53* | *0.6* | *< 1.5 µg/kg* |
| | | *DIFLUFENICAN* | *0.81* | *1.0* | *< 1.5 µg/kg* |
| | | *FLUQUINCONAZOLE* | *0.81* | *1.0* | *< 1.5 µg/kg* |
| | | | *Total* | *56.8* | |

## NN-20/11/19-GRASSES AND HERBS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO278P* | *whole plant* | *DIPHENYL* | *4.41* | *17.1* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *0.77* | *3.0* | *< 1 µg/kg* |
| 25.7% | | *HEPTENOPHOS* | *0.26* | *1.0* | *< 1 µg/kg* |
| | | *CHLORPROPHAM* | *0.51* | *2.0* | *< 1 µg/kg* |
| LOQ | | *PROSULFOCARB* | *0.40* | *1.6* | *< 1 µg/kg* |
| 1.0 | | *ANTHRAQUINONE* | *1.29* | *5.0* | |
| µg/kg | | *PENDIMETHALIN* | *0.84* | *3.3* | *< 1 µg/kg* |
| | | | *Total* | *33.0* | |

## NATUREPARK NASSAU (KOPPELSTEIN); DOWN-HILL

## NN-20/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO279P* | *Soil* | *DICHLOBENIL* | *1.38* | *1.8* | *< 1.4 µg/kg* |
| Dry matter % | | *DIPHENYL* | *2.92* | *3.8* | |
| 77.5% | | *ANTHRAQUINONE* | *0.78* | *1.0* | *< 1.4 µg/kg* |
| | | *PROTHIOCONAZOLEDESTHIO* | *0.78* | *1.0* | *< 1.4 µg/kg* |
| LOQ | | | *Total* | *7.6* | |
| 1.4 | | | | | |
| µg/kg | | | | | |

## NN-20/11/19-GRASSES AND HERBS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO280P* | *whole plant* | *DIPHENYL* | *5.53* | *14.3* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *1.55* | *4.0* | *< 1.8 µg/kg* |
| 38.7% | | *PHENYLPHENOL-2* | *0.55* | *1.4* | *< 1.8 µg/kg* |
| | | *DIPHENYLAMINE* | *1.11* | *2.9* | *< 1.8 µg/kg* |
| LOQ | | *CHLORPROPHAM* | *1.55* | *4.0* | *< 1.8 µg/kg* |
| 1.8 | | *PROSULFOCARB* | *1.21* | *3.1* | *< 1.8 µg/kg* |
| µg/kg | | *ANTHRAQUINONE* | *2.32* | *6.0* | |
| | | *PENDIMETHALIN* | *1.90* | *4.9* | |
| | | | *Total* | *40.6* | |

## 20-nov NN-20/11/19-GREAT BURNET (SANGUISORBA MINOR)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO281P* | *whole plant* | *DIPHENYL* | *3.16* | *14.6* | |
| Dry matter % | | *PHTHALIMIDE (metabolite of folpet)* | *0.65* | *3.0* | *< 1 µg/kg* |
| 21.7% | | *DIPHENYLAMINE* | *1.09* | *5.0* | |
| | | *CHLORPROPHAM* | *0.43* | *2.0* | *< 1 µg/kg* |
| LOQ | | *PROSULFOCARB* | *0.22* | *1.0* | *< 1 µg/kg* |
| 1.0 | | *ANTHRAQUINONE* | *0.43* | *2.0* | *< 1 µg/kg* |
| µg/kg | | *PENDIMETHALIN* | *0.32* | *1.5* | *< 1 µg/kg* |
| | | | *Total* | *29.1* | |

## NN-20/11/19-DROPPINGS ROE DEER

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO282P* | *Manure roe dee* | *DIPHENYL* | *3.00* | *10.9* | |
| Dry matter % | | *DIPHENYLAMINE* | *0.55* | *2.0* | *< 1 µg/kg* |
| 27.5% | | *CHLORPROPHAM* | *0.28* | *1.0* | *< 1 µg/kg* |
| | | *PROSULFOCARB* | *0.28* | *1.0* | *< 1 µg/kg* |
| LOQ | | *ANTHRAQUINONE* | *1.10* | *4.0* | |
| 1.0 | | | *Total* | *18.9* | |
| µg/kg | | | | | |

## LATROP (HOCH SAUERLAND)

## LT-21/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO283P* | *Soil* | *DIPHENYL* | *4.02* | *5.7* | |
| Dry matter % | | *CHLORPROPHAM* | *0.71* | *1.0* | *< 1.3 µg/kg* |
| 71.0% | | *ANTHRAQUINONE* | *3.55* | *5.0* | |
| | | | *Total* | *11.7* | |
| LOQ | | | | | |
| 1.3 | | | | | |
| µg/kg | | | | | |

### LT-21/11/19-GRASSES

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO284P* | *Whole plant* | *DIPHENYL* | *2.66* | *17.1* | |
| Dry matter % | | *DIPHENYLAMINE* | *0.22* | *1.4* | *< 0.71 µg/kg* |
| 15.5% | | *CHLORPROPHAM* | *0.31* | *2.0* | *< 0.71 µg/kg* |
| | | *ANTHRAQUINONE* | *0.47* | *3.0* | *< 0.71 µg/kg* |
| LOQ | | *PENDIMETHALIN* | *0.76* | *4.9* | |
| 0.7 | | *ETOFENPROX* | *0.48* | *3.1* | *< 0.71 µg/kg* |
| µg/kg | | | *Total* | *31.6* | |

### LT-21/11/19-ROE DEER

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO285P* | *Manure roe deer* | *Indoxacarb* | *0.28* | *1.8* | *< 0.58 µg/kg* |
| Dry matter % | | *DIPHENYL* | *1.43* | *9.1* | |
| 15.7% | | *DIPHENYLAMINE* | *0.31* | *2.0* | *< 0.58 µg/kg* |
| | | *CHLORPROPHAM* | *0.16* | *1.0* | *< 0.58 µg/kg* |
| LOQ | | *PROSULFOCARB* | *0.16* | *1.0* | *< 0.58 µg/kg* |
| 0.6 | | *ANTHRAQUINONE* | *0.31* | *2.0* | *< 0.58 µg/kg* |
| µg/kg | | *PENDIMETHALIN* | *0.16* | *1.0* | *< 0.58 µg/kg* |
| | | | *Total* | *17.9* | |

## ARNSBERG

### AB-21/11/19-FOREST SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO287P* | *Soil* | *DIPHENYL* | *5.37* | *7.5* | |
| Dry matter % | | *CHLORPROPHAM* | *0.71* | *1.0* | *< 1.3 µg/kg* |
| 71.1% | | *ANTHRAQUINONE* | *6.40* | *9.0* | |
| | | *p.p'-DDE* | *0.71* | *1.0* | *< 1.3 µg/kg* |
| LOQ | | | *Total* | *18.5* | |
| 1.3 | | | | | |
| µg/kg | | | | | |

## AB-21/11/19-FOREST SOIL (0-5 CM)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO289P* | *Soil* | *DIPHENYL* | *4.24* | *7.5* | |
| Dry matter % | | *CHLORPROPHAM* | *0.56* | *1.0* | *< 1 µg/kg* |
| 56.2% | | *ANTHRAQUINONE* | *17.42* | *31.0* | |
| | | *p.p'-DDE* | *1.69* | *3.0* | |
| LOQ | | *p.p'-DDD + o.p'-DDT* | *0.56* | *1.0* | *< 1 µg/kg* |
| 1.0 | | | *Total* | *43.5* | |
| µg/kg | | | | | |

## AB-21/11/19-LEAVES OF EUROPEAN BEECH (FAGUS SYLVATICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO288P* | *leaves* | *Imazalil* | *Detected qualitatively* | | |
| Dry matter % | | *DIPHENYL* | *3.16* | *12.2* | |
| 25.9% | | *DIPHENYLAMINE* | *0.52* | *2.0* | *< 1.2 µg/kg* |
| | | *PENDIMETHALIN* | *1.06* | *4.1* | *< 1.2 µg/kg* |
| LOQ | | | *Total* | *18.3* | |
| 1.2 | | | | | |
| µg/kg | | | | | |

## WEHEBACHTALSPERRE

## WS-22/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO290P* | *Soil* | *DIPHENYL* | *3.52* | *5.7* | |
| Dry matter % | | *DIPHENYLAMINE* | *3.36* | *5.4* | |
| 62.2% | | *CHLORPROPHAM* | *0.62* | *1.0* | *< 1.2 µg/kg* |
| | | *ANTHRAQUINONE* | *8.71* | *14.0* | |
| LOQ | | *p.p'-DDE* | *0.62* | *1.0* | *< 1.2 µg/kg* |
| 1.2 | | *p.p'-DDD + o.p'-DDT* | *1.24* | *2.0* | |
| µg/kg | | | *Total* | *29.1* | |

## WS-22/11/19-ROE DEER DROPPINGS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO292P* | *Manure roe deer* | *DIPHENYL* | *2.54* | *9.1* | |
| Dry matter % | | *PENDIMETHALIN* | *0.28* | *1.0* | *< 1 µg/kg* |
| 27.9% | | | *Total* | *10.1* | |
| | | | | | |
| LOQ | | | | | |
| 1.0 | | | | | |
| µg/kg | | | | | |

## WS-22/11/19-GRASSES

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO291P | whole plant | Prosulfocarb | 0.78 | 2.6 | < 1.4 µg/kg |
| Dry matter % | | DIPHENYL | 4.23 | 14.3 | |
| 29.6% | | DIPHENYLAMINE | 2.54 | 8.6 | |
| | | CHLORPROPHAM | 1.78 | 6.0 | |
| LOQ | | | Total | 31.5 | |
| 1.4 | | | | | |
| µg/kg | | | | | |

## ORBROICH

## OB-22/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO293P | Soil | DIPHENYL | 2.69 | 3.8 | |
| Dry matter % | | | Total | 3.8 | |
| 71.2% | | | | | |
| | | | | | |
| LOQ | | | | | |
| 1.3 | | | | | |
| µg/kg | | | | | |

## OB-22/11/19-STINGING NETTLES (URTICA DIOICA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| 19CO294P | Stalks and leaves | DIPHENYL | 2.91 | 12.2 | |
| Dry matter % | | DIPHENYLAMINE | 0.48 | 2.0 | < 1.1 µg/kg |
| 23.9% | | CHLORPROPHAM | 0.72 | 3.0 | < 1.1 µg/kg |
| | | PENDIMETHALIN | 0.49 | 2.0 | < 1.1 µg/kg |
| LOQ | | | Total | 19.2 | |
| 1.1 | | | | | |
| µg/kg | | | | | |

## WISSEL (UP-HILL)

### WI-22/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO295P* | *Soil* | *DIPHENYL* | *2.88* | *3.2* | |
| Dry matter % | | | *Total* | *3.2* | |
| 89.3% | | | | | |
| | | | | | |
| LOQ | | | | | |
| 1.6 | | | | | |
| µg/kg | | | | | |

### WI-22/11/19-RED SORREL (DEAD PLANTS OF RUMEX ACETOSELLA)

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO296P* | *dead stalks and leaves* | *Boscalid* | *1.84* | *2.8* | *< 3 µg/kg* |
| Dry matter % | | *CHLOROTOLURON* | *2.95* | *4.5* | *< 3 µg/kg* |
| 65.8% | | *Flufenacet* | *2.90* | *4.4* | *< 3 µg/kg* |
| | | *Imidacloprid* | *4.18* | *6.4* | |
| LOQ | | *Prosulfocarb* | *3.21* | *4.9* | |
| 3.0 | | *DIPHENYL* | *8.23* | *12.5* | |
| µg/kg | | *DIPHENYLAMINE* | *1.32* | *2.0* | *< 3 µg/kg* |
| | | *CHLORPROPHAM* | *4.61* | *7.0* | |
| | | *ANTHRAQUINONE* | *20.40* | *31.0* | |
| | | *PENDIMETHALIN* | *7.86* | *11.9* | |
| | | *DIFLUFENICAN* | *2.09* | *3.2* | *< 3 µg/kg* |
| | | *PERMETHRIN-CIS* | *12.70* | *19.3* | |
| | | *PERMETHRIN-TRANS* | *16.73* | *25.4* | |
| | | *DIFENOCONAZOLE* | *1.32* | *2.0* | *< 3 µg/kg* |
| | | | *Total* | 137.3 | |

### WI-22/11/19-RABBIT PALLETS

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO297P* | *Manure rabbit* | *DIPHENYL* | *2.30* | *10.9* | |
| Dry matter % | | *DIPHENYLAMINE* | *0.42* | *2.0* | *< 0.78 µg/kg* |
| 21.1% | | *PROSULFOCARB* | *0.42* | *2.0* | *< 0.78 µg/kg* |
| | | | *Total* | *14.9* | |
| LOQ | | | | | |
| 0.8 | | | | | |
| µg/kg | | | | | |

## WISSEL (DOWN-HILL)

### WI-22/11/19-SOIL

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO298P* | *Soil* | *Bixafen* | *3.26* | *3.8* | |
| Dry matter % | | *Epoxiconazole* | *2.39* | *2.8* | |
| 86.6% | | *Fluxapyroxad* | *2.80* | *3.2* | |
| | | *Prochloraz desimidazoleamino* | *1.76* | *2.0* | |
| LOQ | | *Tembotrione* | *0.87* | *1.0* | *< 1.6 µg/kg* |
| 1.6 | | *DIPHENYL* | *4.19* | *4.8* | |
| µg/kg | | *CHLORPROPHAM* | *0.87* | *1.0* | *< 1.6 µg/kg* |
| | | *TEBUCONAZOLE* | *0.87* | *1.0* | *< 1.6 µg/kg* |
| | | | *Total* | *19.6* | |

### WI-22/11/19-GRASSES

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CO299P* | *Whole plant* | *DIPHENYL* | *3.26* | *14.3* | |
| Dry matter % | | *DIPHENYLAMINE* | *1.30* | *5.7* | |
| 22.8% | | *PROSULFOCARB* | *0.36* | *1.6* | *< 0.91 µg/kg* |
| | | *ANTHRAQUINONE* | *0.68* | *3.0* | *< 0.91 µg/kg* |
| LOQ | | | *Total* | *24.6* | |
| 0.9 | | | | | |
| µg/kg | | | | | |

## REICHSWALD (KREIS KLEVE)

### RW-4/12/19-BODEM

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CS946P* | *Bodem* | *DIPHENYL* | *3.23* | *3.9* | |
| Dry matter % | | | *Total* | *3.9* | |
| 82.3% | | | | | |
| | | | | | |
| LOQ | | | | | |
| 1.5 | | | | | |
| µg/kg | | | | | |

## RW-4/12/10-BEECH LEAVES

| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CS945P* | *Leaves* | *Fluopyram* | *0.45* | *1.4* | *< 1.5 µg/kg* |
| Dry matter % | | *Propyzamide* | *0.44* | *1.4* | *< 1.5 µg/kg* |
| 31.5% | | *DIPHENYL* | *3.60* | *11.4* | |
| | | *DIPHENYLAMINE* | *0.95* | *3.0* | *< 1.5 µg/kg* |
| LOQ | | *CHLORPROPHAM* | *0.63* | *2.0* | *< 1.5 µg/kg* |
| 1.5 | | *PROSULFOCARB* | *0.95* | *3.0* | *< 1.5 µg/kg* |
| µg/kg | | *PENDIMETHALIN* | *1.69* | *5.4* | |
| | | | *Total* | *27.6* | |

## RW-4/12/19-GRASSES AND HERBS

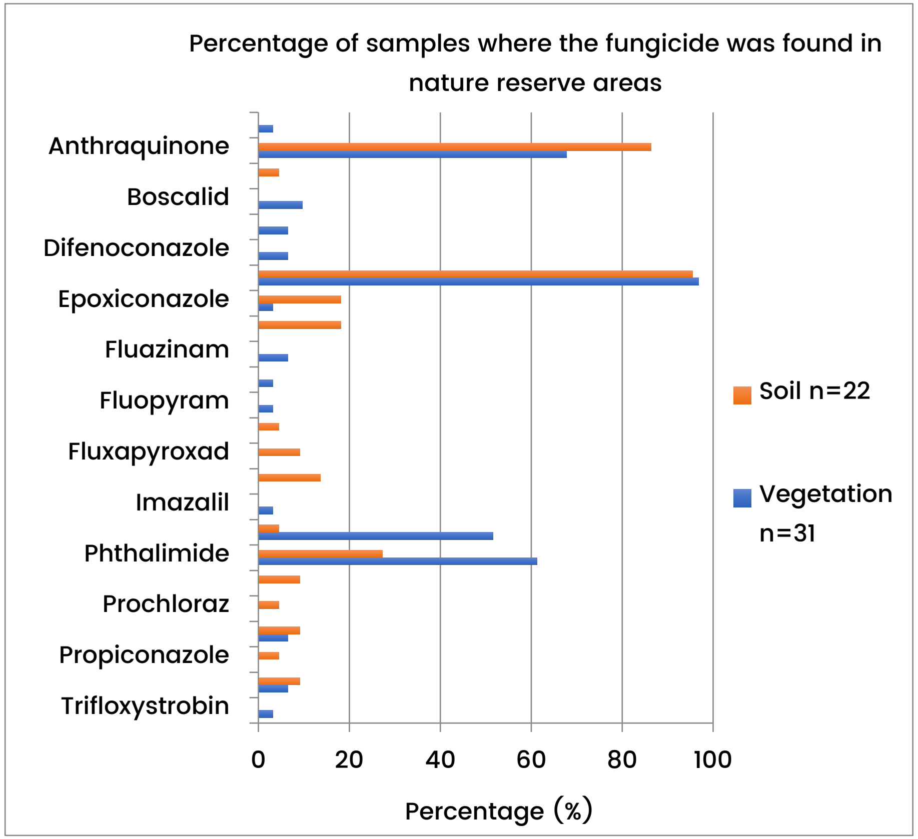
| Lab code | Sample | Compound | µg/kg | µg/Kg DM | Remark |
|---|---|---|---|---|---|
| *19CS947P* | *Whole plant* | *PHENYLPHENOL-2* | *0.61* | *3.4* | *< 0.71 µg/kg* |
| Dry matter % | | *DIPHENYLAMINE* | *4.45* | *25.0* | |
| 17.8% | | *CHLORPROPHAM* | *0.53* | *3.0* | *< 0.71 µg/kg* |
| | | | *Total* | *31.4* | |
| LOQ | | | | | |
| 0.7 | | | | | |
| µg/kg | | | | | |

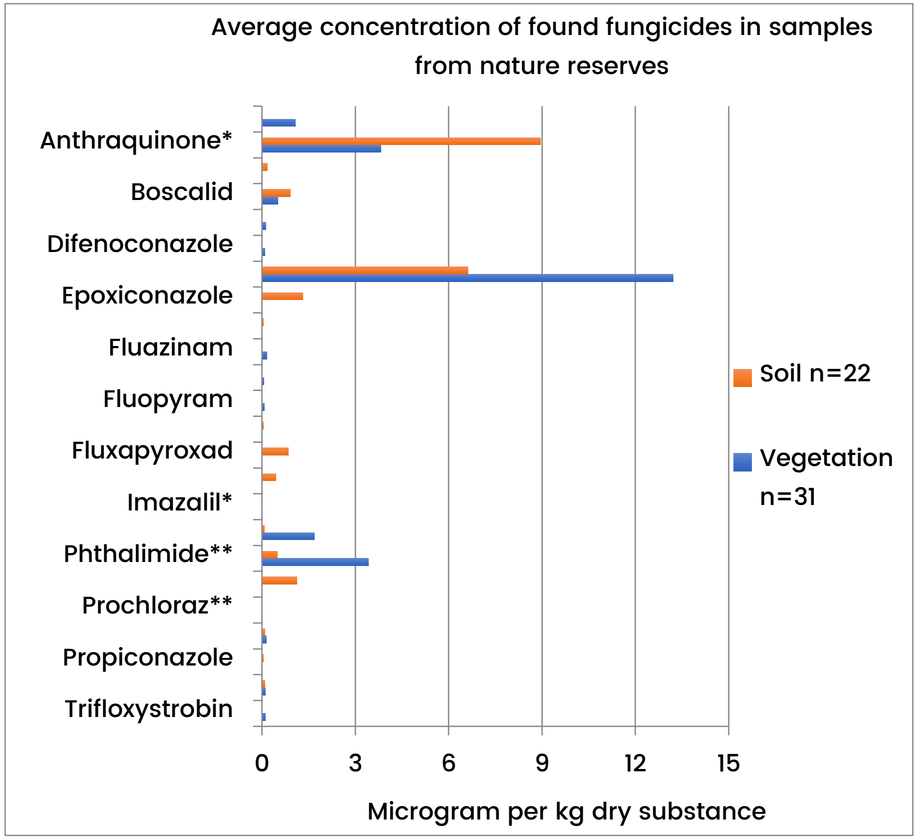
# Appendix 6. Presence and concentrations of pesticides in nature reserves with MF, buffer areas and reference areas in figures

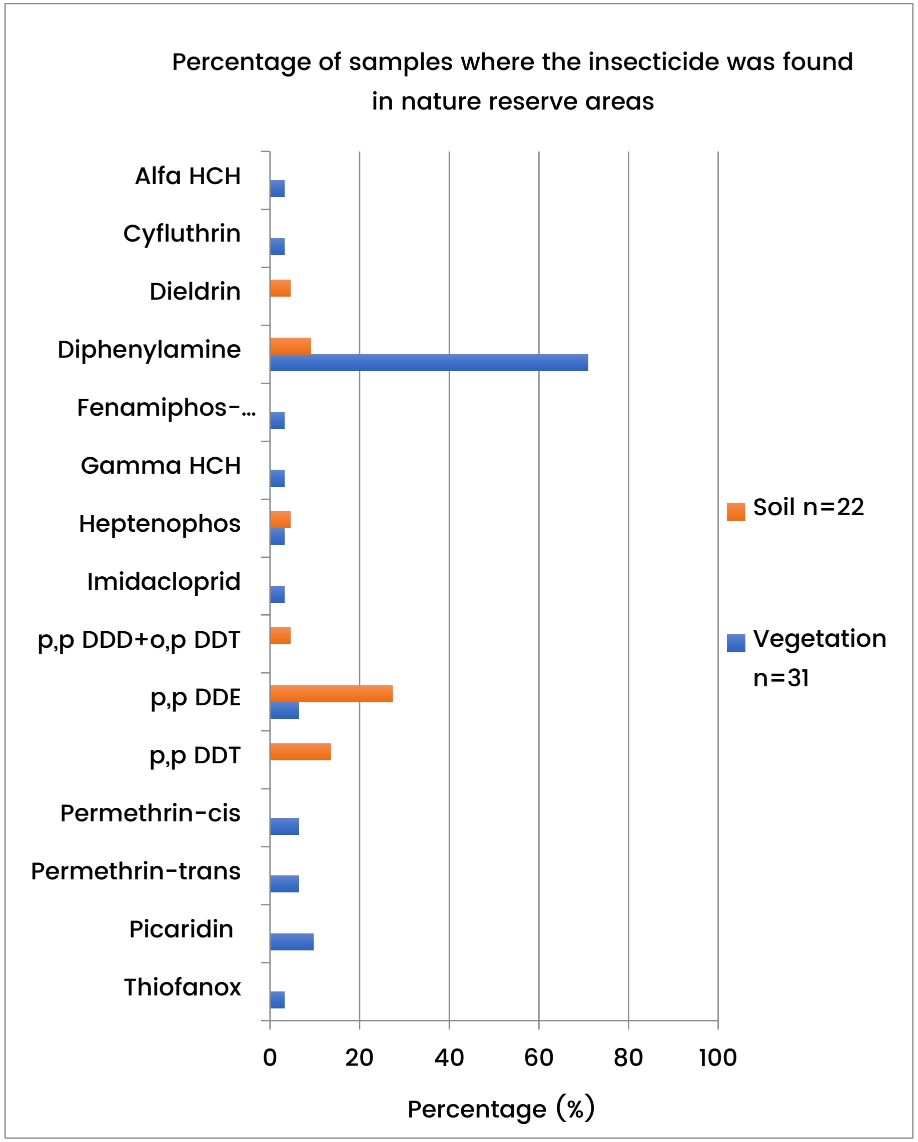
Additional information about compounds found (as indicated in tables):

* Additional vegetation sample(s) in which the compound was detected but due to interfering compounds not quantifiable

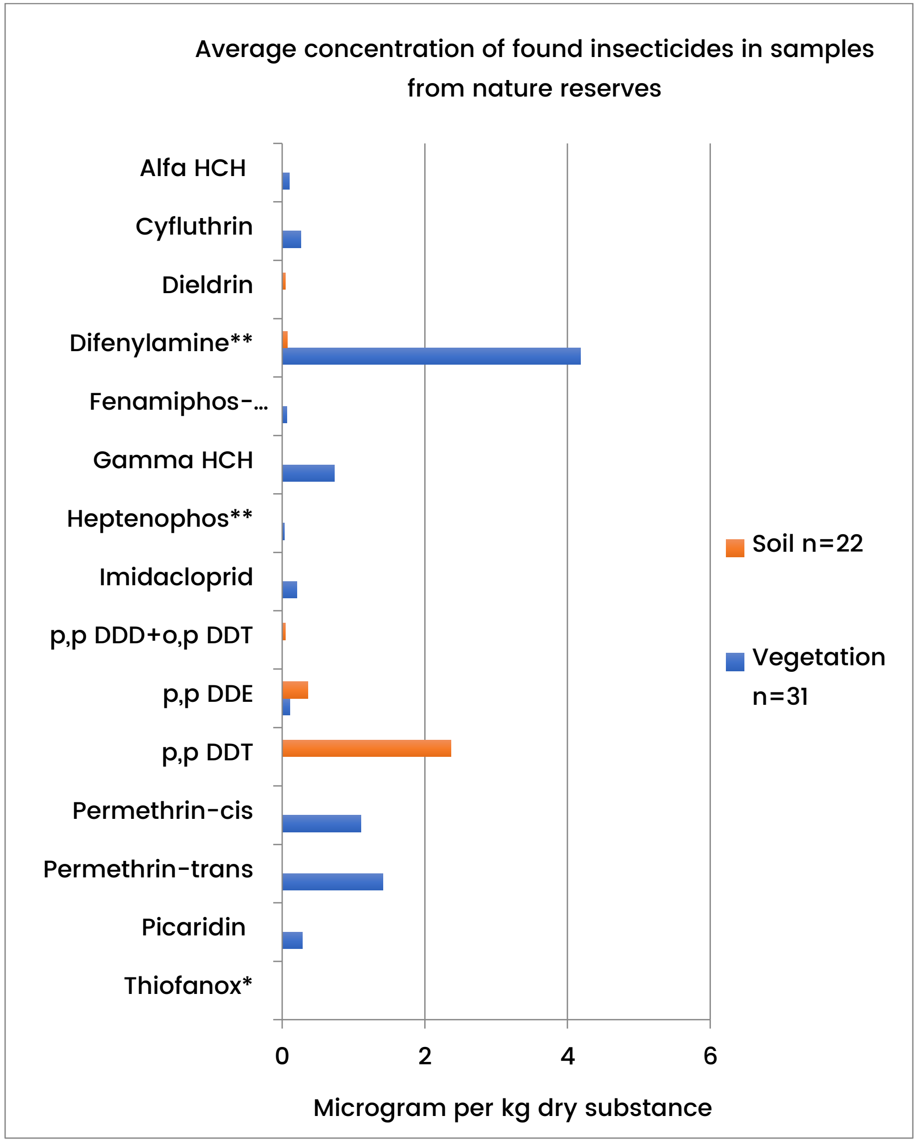
** Additional soil sample(s) in which the compound was detected but due to interfering compounds not quantifiable



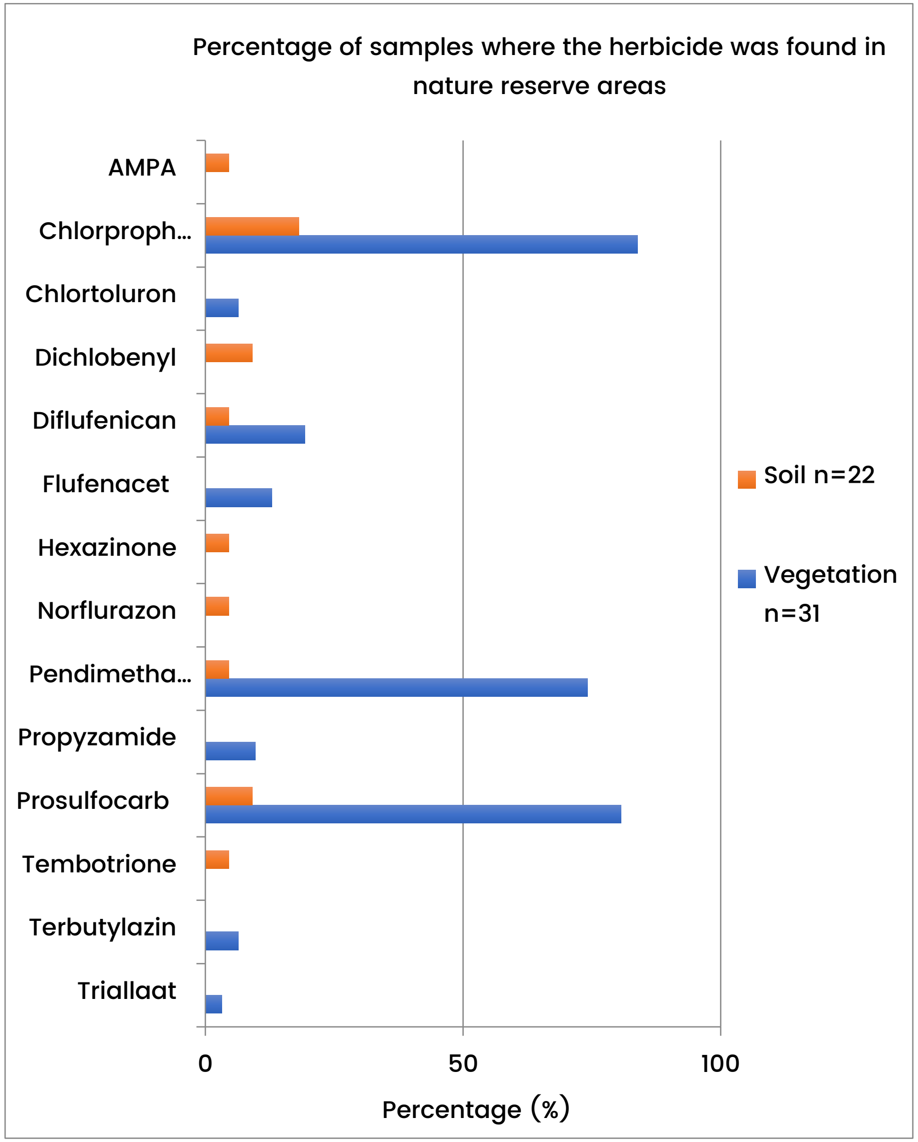


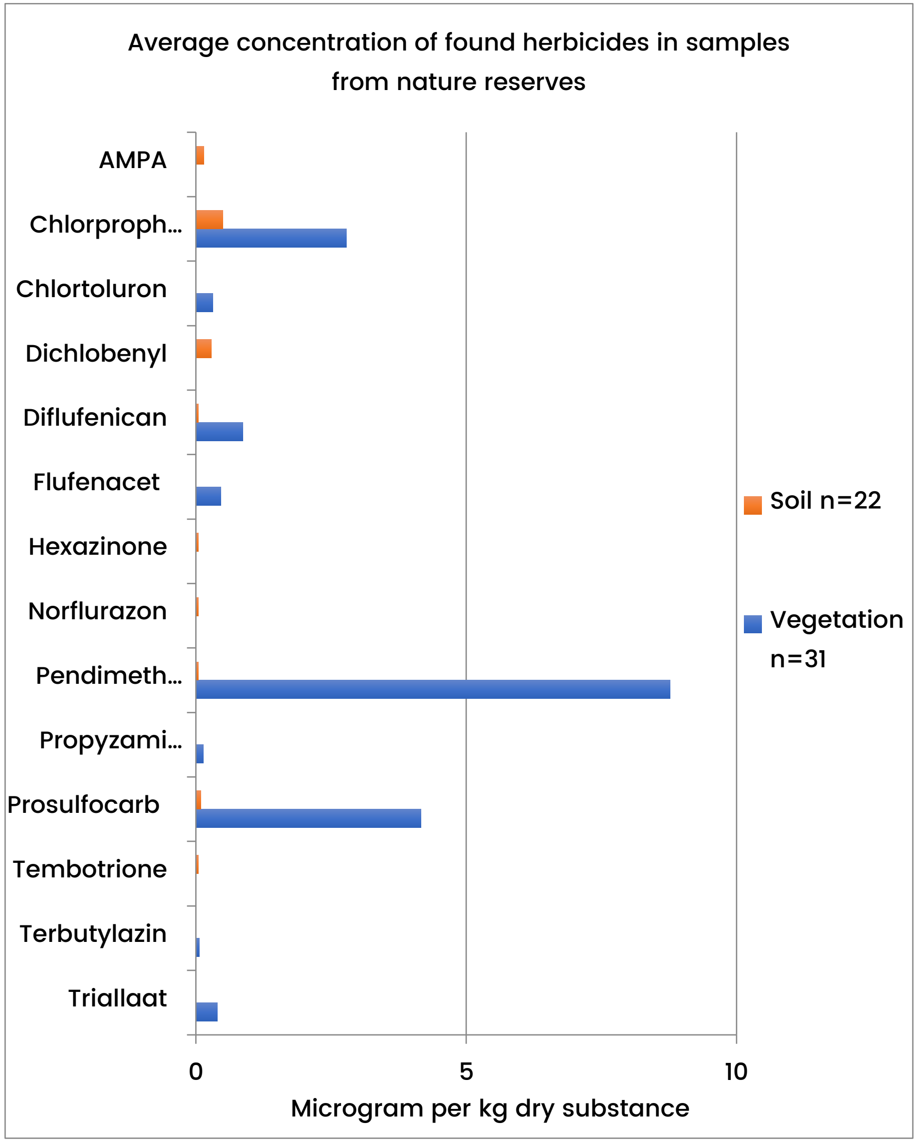


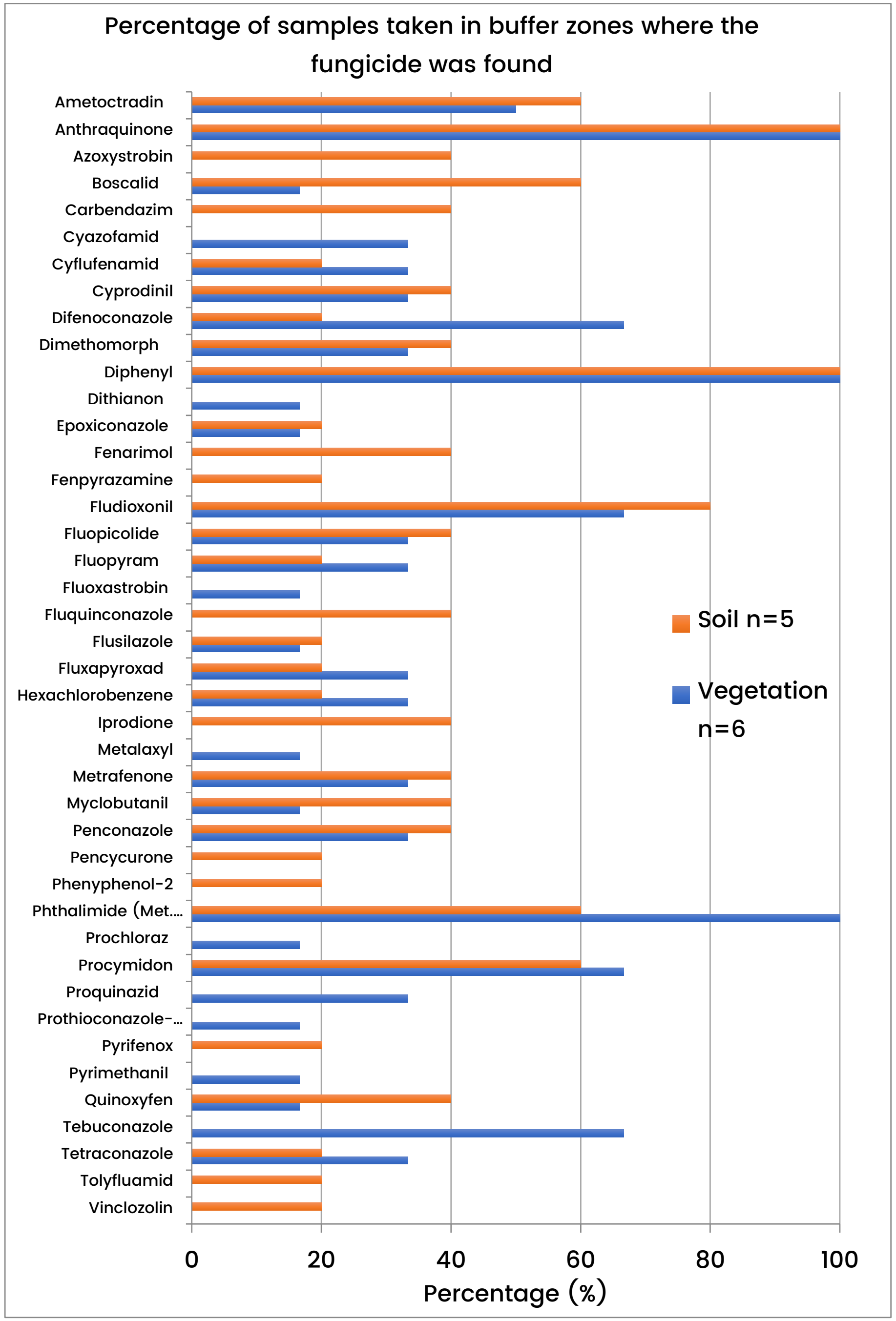
Percentage of samples where the insecticide was found in nature reserve areas

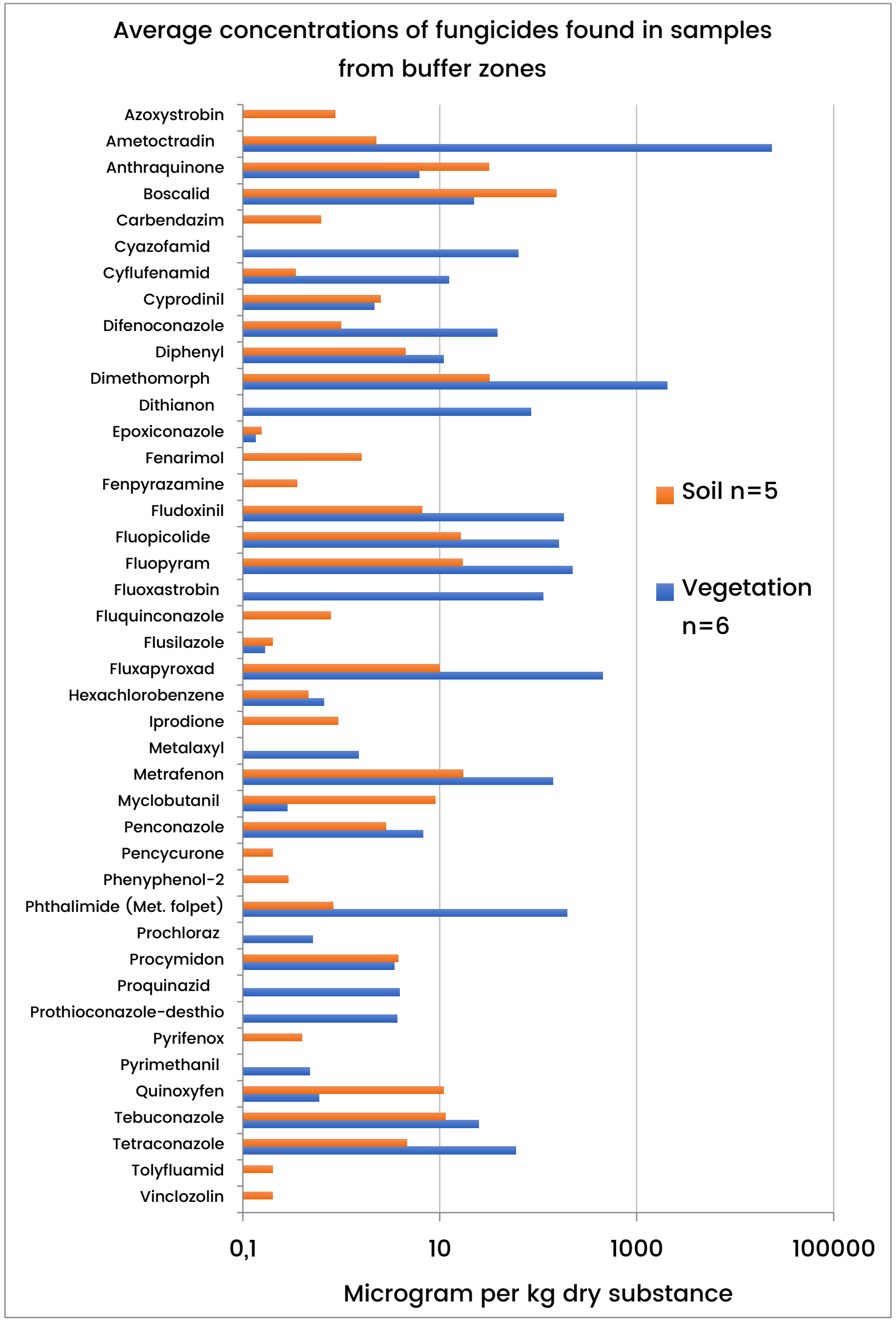


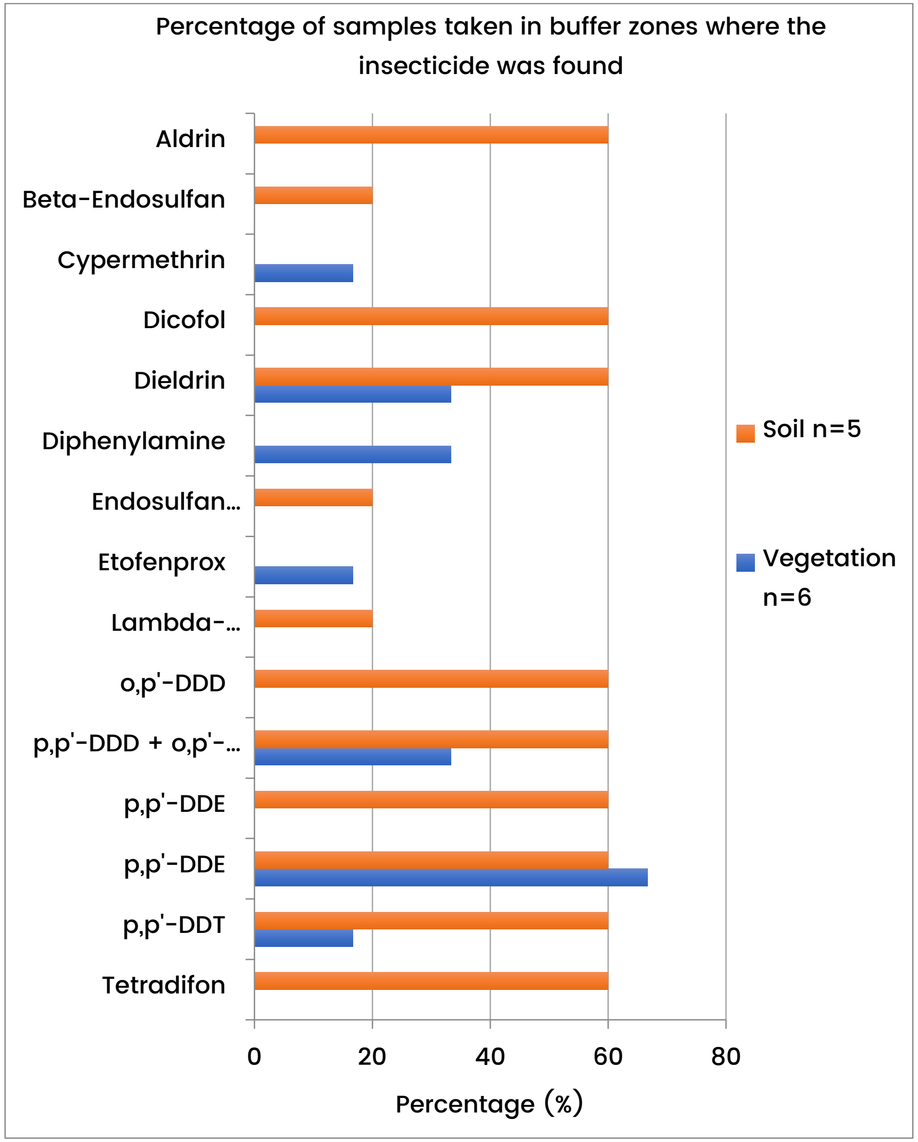
Average concentration of found insecticides in samples from nature reserves


Percentage of samples where the herbicide was found in nature reserve areas
AMPA
Chlorproph...
Chlortoluron
Dichlobenyl
Diflufenican
Flufenacet
Hexazinone
Norflurazon
Pendimetha...
Propyzamide
Prosulfocarb
Tembotrione
Terbutylazin
Triallaat
0
50
100
Percentage (%)
Soil n=22
Vegetation n=31

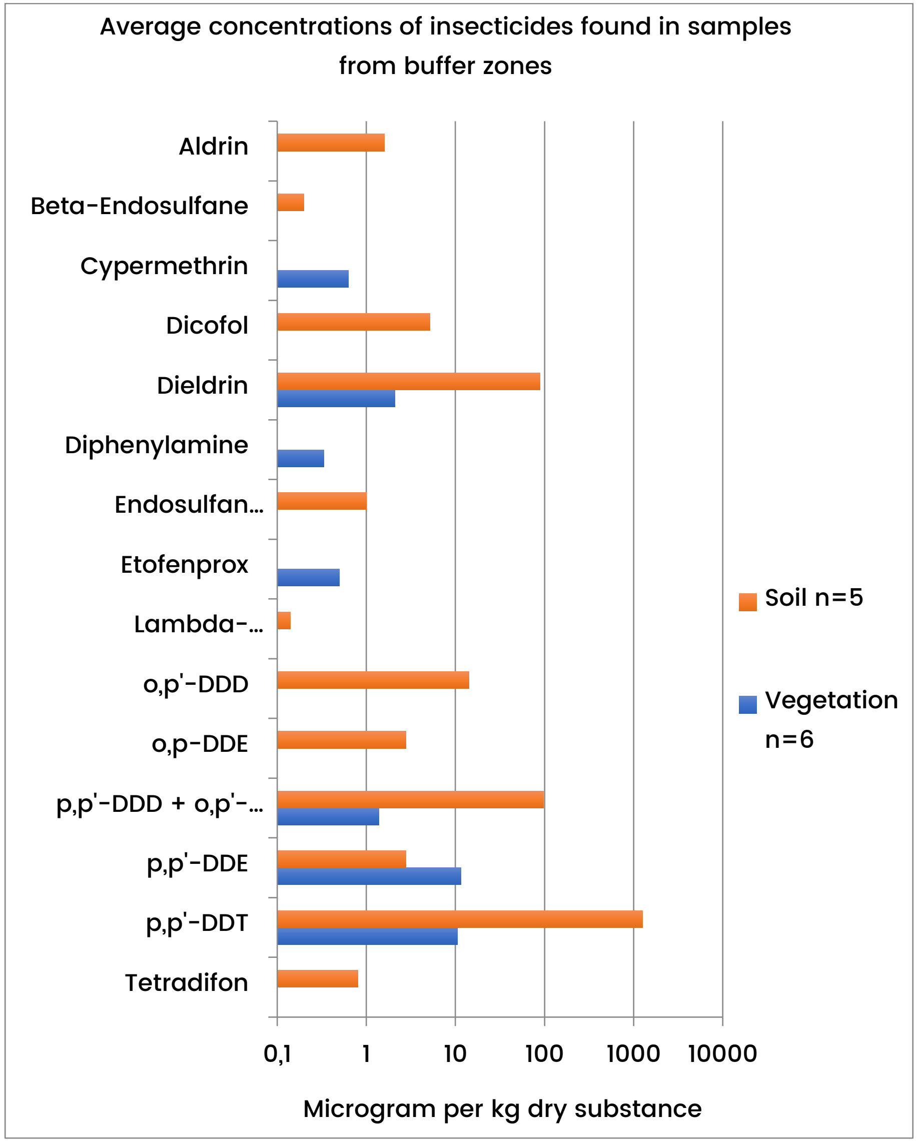

Average concentration of found herbicides in samples from nature reserves
AMPA
Chlorproph...
Chlortoluron
Dichlobenyl
Diflufenican
Flufenacet
Hexazinone
Norflurazon
Pendimeth...
Propyzami...
Prosulfocarb
Tembotrione
Terbutylazin
Triallaat
0
5
10
Microgram per kg dry substance
Soil n=22
Vegetation n=31


Percentage of samples taken in buffer zones where the fungicide was found

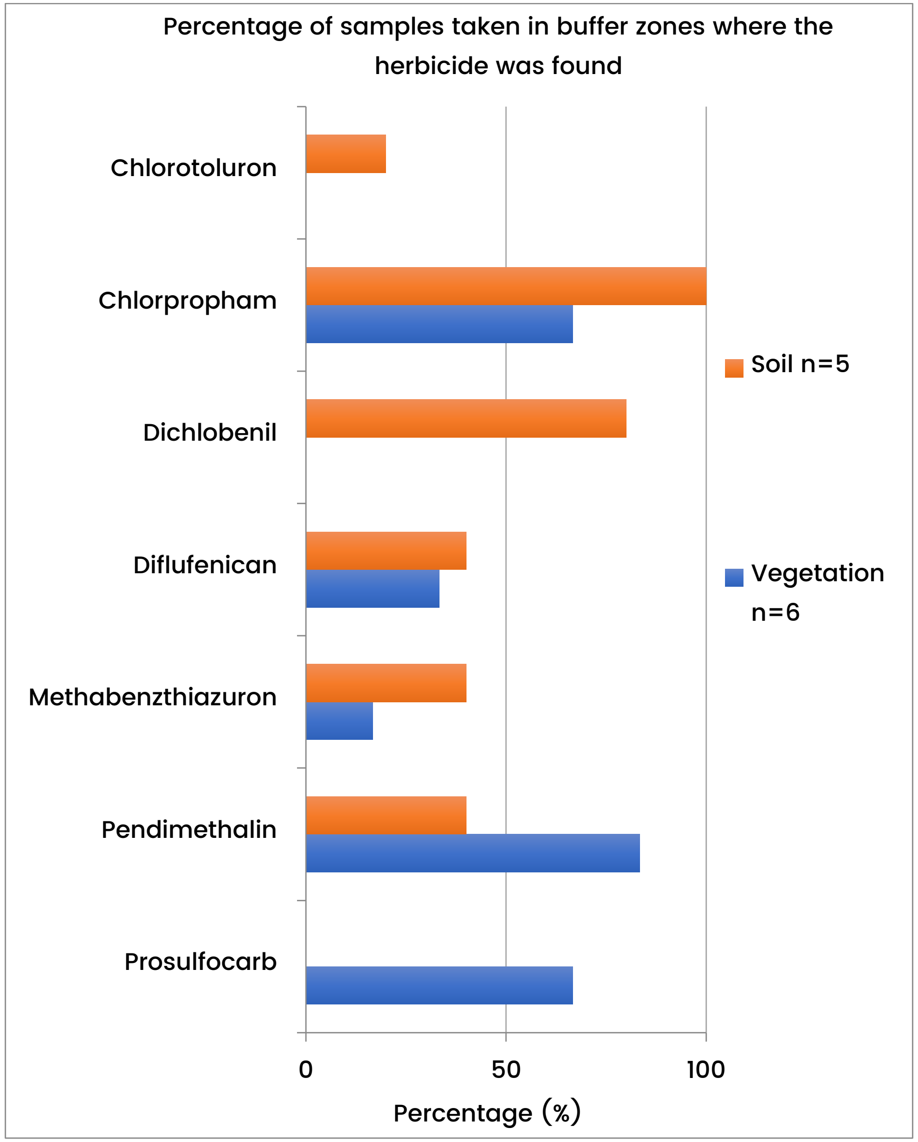

Average concentrations of fungicides found in samples from buffer zones



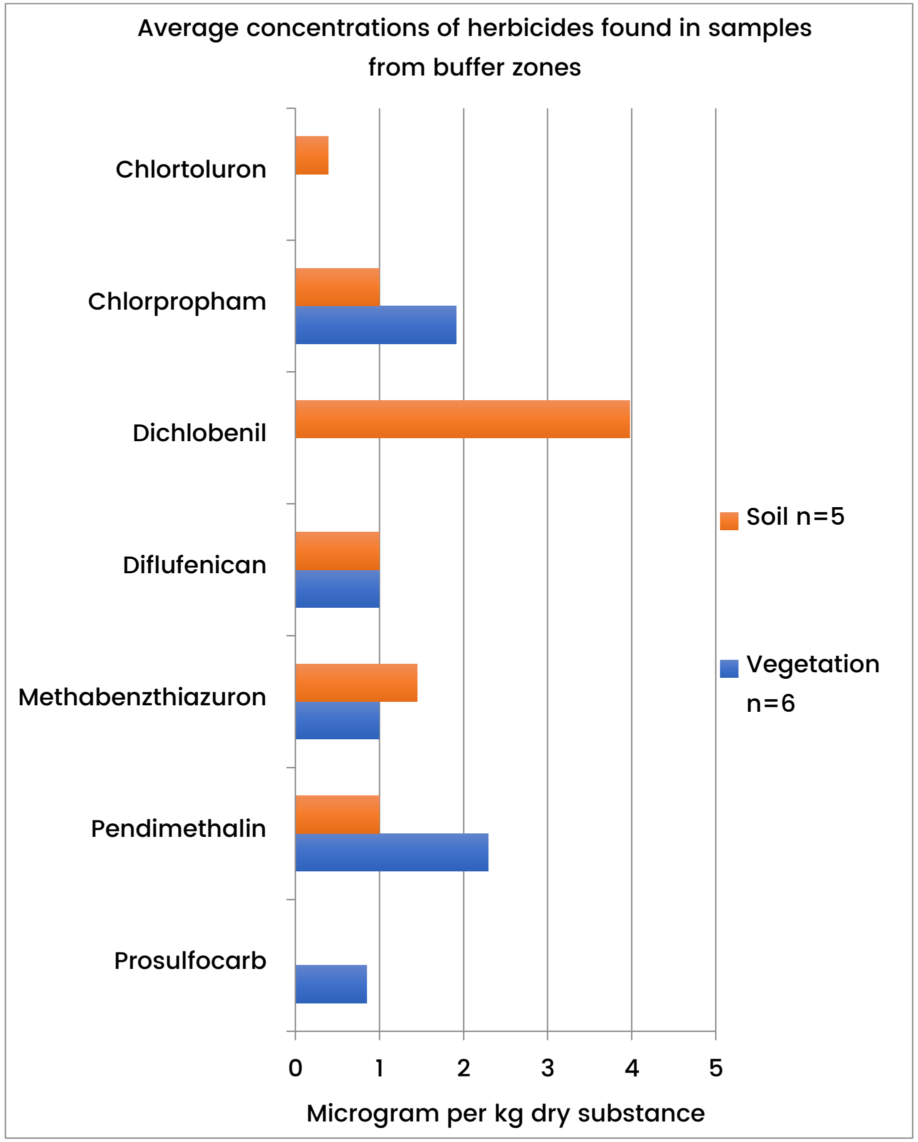
Percentage of samples taken in buffer zones where the insecticide was found



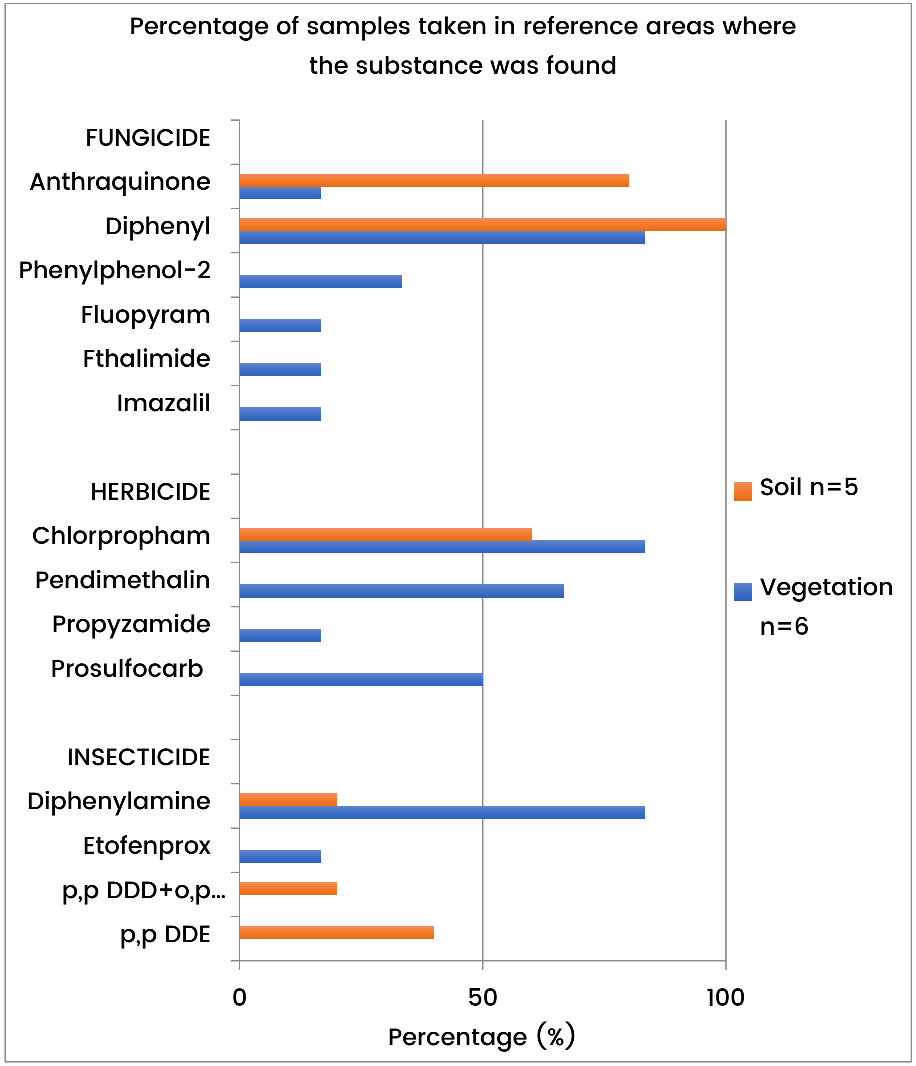
Average concentrations of insecticides found in samples from buffer zones



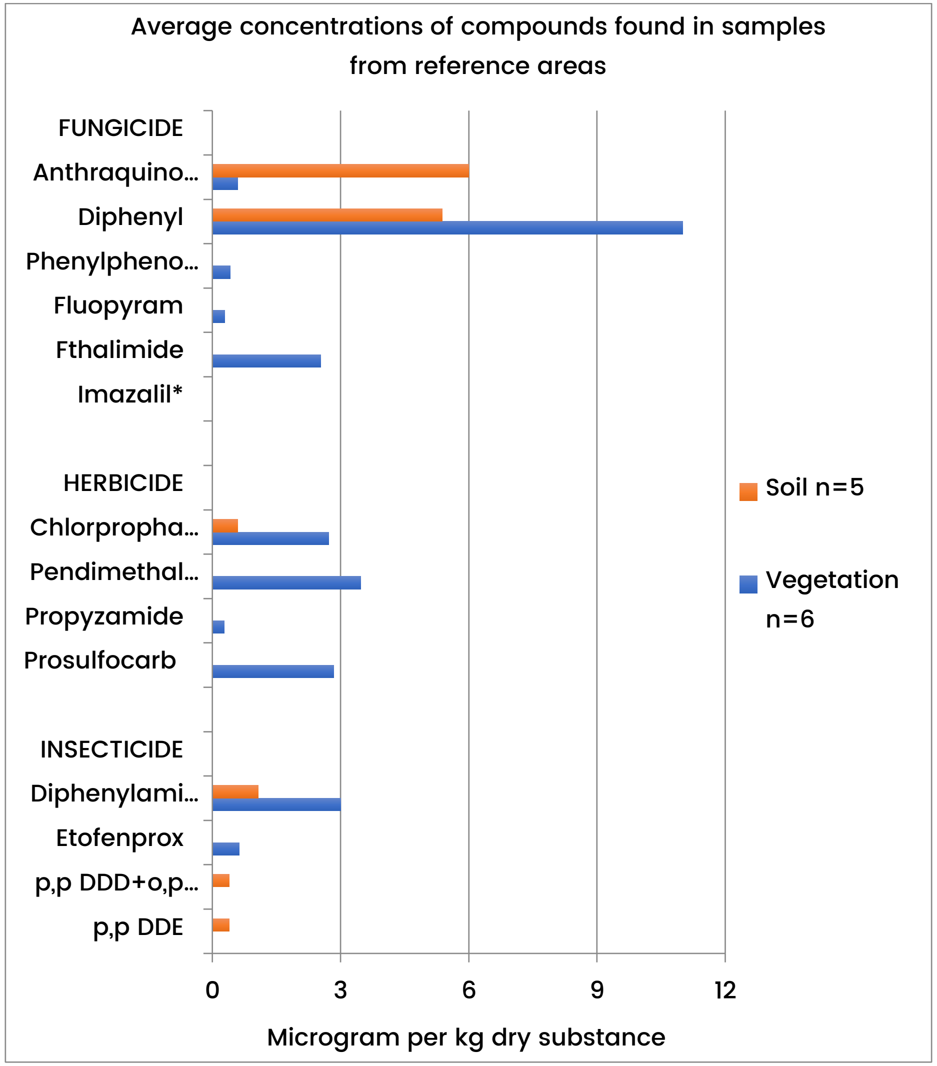
Percentage of samples taken in buffer zones where the herbicide was found



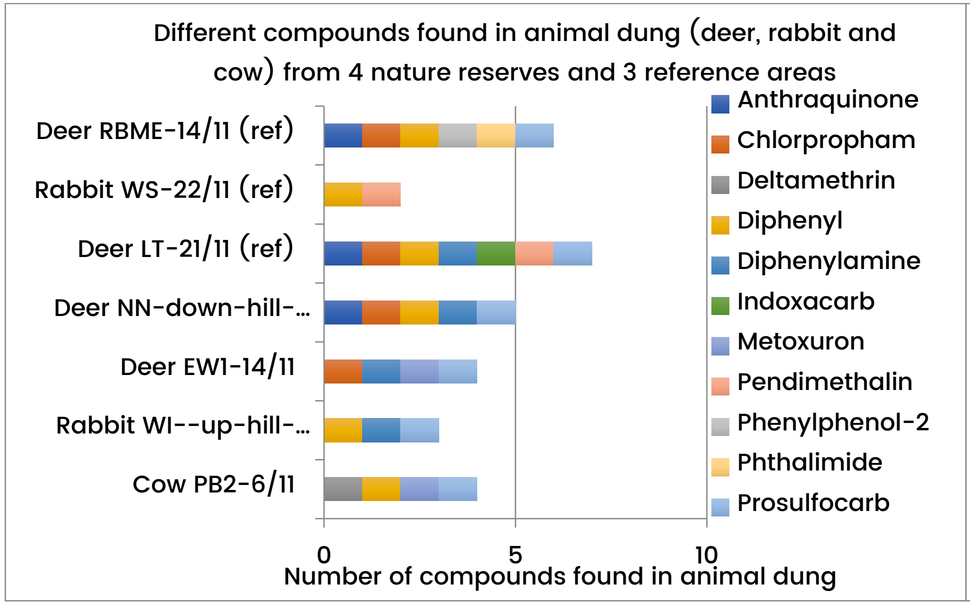
Average concentrations of herbicides found in samples from buffer zones

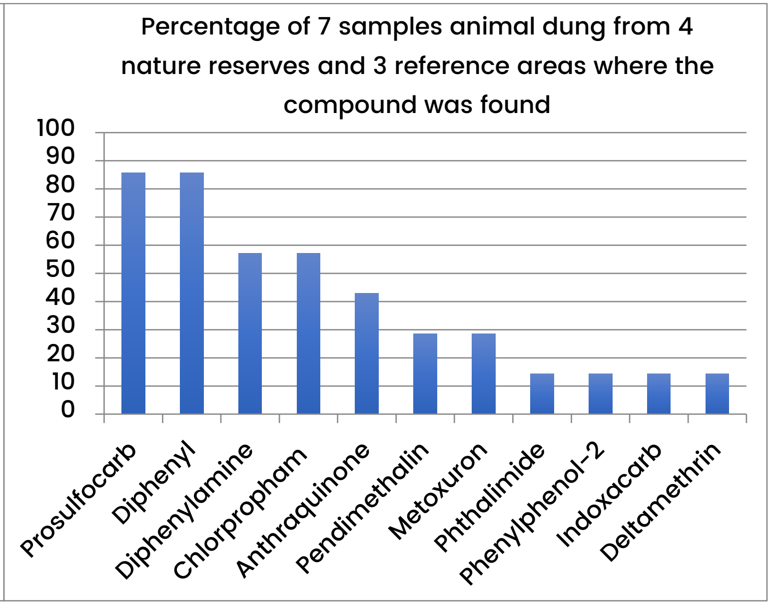


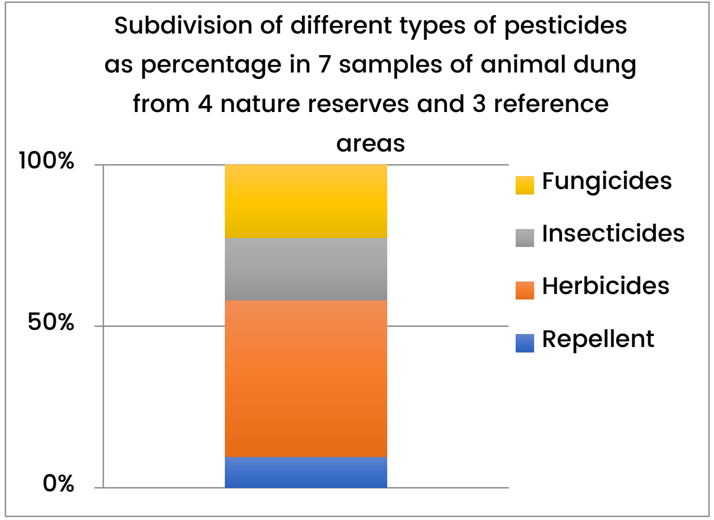
Percentage of samples taken in reference areas where the substance was found



Average concentrations of compounds found in samples from reference areas


Different compounds found in animal dung (deer, rabbit and cow) from 4 nature reserves and 3 reference areas


Percentage of 7 samples animal dung from 4 nature reserves and 3 reference areas where the compound was found


Subdivision of different types of pesticides as percentage in 7 samples of animal dung from 4 nature reserves and 3 reference areas

*deltamethrin was only detected qualitatively

For codes of areas: see Appendix 5

# Appendix 7. Discussion of all investigated locations

NOTE 1: All original chemical measurements can be found in Appendix 5
NOTE 2: in some areas the total biomass catches are mentioned of the MF traps. In this appendix the total measured biomass has been used, and not the corrected biomass for the standard period of May 1st– August 31st. In reality, the MF were operational from different dates and they were taken away also at different dates.

## RESULTS AND DISCUSSION OF MEASUREMENTS IN INDIVIDUAL NATURE RESERVES

### Die Spey, Krefeld, NRW

Coordinates: W 51.335.317 L 6.703.692
Code of location: KS-5/11/19

Die Spey is a floodplain, embedded between the river Rhine and industrial factories. In former times the floodplain was a botanical rich and diverse area.

The sampled location is partly used for hay production and is mown sometimes. The main vegetation is grass, separated from the river itself by willow trees with stinging nettles under the trees. On the access road knotweed (*Polygonum aviculare*) grows, which at the moment of sampling was dead. The distance to the most nearby agricultural field is 470m.

Type of soil: clay with sand.

The area is accessible to public, dogs, horses, and sheep

Samples were taken from soil, stinging nettle, and knotweed. The latter was selected because the dead plants draw our attention.

Results

As the table below shows, the most remarkable finding of this location are analyses results of the knotweed. A high number (11) of different pesticides and high concentrations of the very toxic insecticides alfa & gamma Hexachlorocyclohexane and (cis & trans) permethrin were found. In the soil traces of the very persistent insecticide DDT and its metabolites were detected. In comparison with the overall average concentration of anthraquinone in other soil samples, the found concentration in the soil sample is with 20 µg/kg DS rather high.

| Die Spey, Krefeld, NRW | Polygonum aviculare | Stinging nettle | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 83.9 | 13.6 | 37.5 |
| *Insecticides µg/kg DM* | 59.45 | 0 | 2.40 |
| *Fungicides µg/kg DM* | 12.80 | 8.31 | 15.08 |
| *Herbicides µg/kg DM* | 14.91 | 5.26 | 0 |
| *Repellent µg/kg DM* | detected | 0 | 20 |
| *Number of different pesticides* | 11 | 5 | 7 |

It was observed that three identical compounds were found in knotweed and in stinging nettle, but that the other compounds are very different in both plants. Only diphenyl has been found in the 2 samples of the plants and in the soil.

Overall contamination

It is remarkable that knotweed is much more contaminated than stinging nettle, which was growing nearby on the sand ridge along the river. The soil is contaminated with old pesticides (DDT and hexachlorocyclohexane) and with the more recently introduced heptenophos. The overall impression is that the soil concentrations of pesticides at this location are not very high, but they may have a serious impact on the food chain. The MF biomass catch in 2016 amounted to 455.6 g, which was around the average for that year. The concentrations of insecticides in the knotweed were very high. Permethrin might originate from treated sheep or dogs that graze or walk in this area.

## Latumer Bruch 2b, NRW

Coordinates: W 51.319.761 L 6.674.659

Code of location: LB-5/11/19

Latumer Bruch is located southeast from Krefeld and belongs to the Nature protection project Buersbach. The size of this area is exceptionally small with approximately 120 m$^2$ and the distance to agricultural fields is 10 m only. The aim of this nature reserve is to protect the butterfly Phengaris nausithous which reproduction depends on the plant Great burnet (Sanguisorba officinalis). Because nature conservationists observed that the number of Great burnet plants was low, they have placed purchased Great burnet plants in the nature reserve. These plants have been grown on potting soil. The dominant vegetation was grass. Also present were thistles, stinging nettle, willow trees, black berries and the great burnet. The area is not accessible to the public and no insect traps were installed. Samples were taken from the soil, the plant great burnet and from potting soil.

Results

In comparison with the overall average number and concentration of the found pesticides in other nature reserve areas, the found pesticides in soil and great burnet are rather low. Besides diphenyl, different compounds were found in the plant and in the soil. In the purchased potting soil 11 different pesticides with a total concentration of 63.3 µg/kg DM were found. The majority of the compounds consisted of fungicides. The highest concentration showed the fungicide boscalid with 32.9 µg/kg DM. It is known that this compound has in tests a time dependent toxic effect on bees. This means that the negative effects on bees increase with time.

| Latumer Bruch 2b, NRW | Great burnet | Soil | Potting soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 11.43 | 9.1 | 63.3 |
| *Insecticides µg/kg DM* | 3.45 | 0 | 3.9 |
| *Fungicides µg/kg DM* | 4.76 | 4.1 | 48.3 |
| *Herbicides µg/kg DM* | 3.22 | 0 | 6 |
| *Repellent µg/kg DM* | 0 | 5 | 5 |
| *Number of different pesticides* | 4 | 2 | 11 |

Overall contamination

The overall contamination of the soil and the plant Great burnet can be considered as rather low. Nevertheless, it should be stated, that the effects of the pesticides found in the Great burnet on the life cycle of the butterfly Phengaris nausithous are fully unknown. On basis of the total pesticides content, the potting soil can be considered as moderately polluted and may cause contamination of the Great burnet plants, for instance with boscalid. The sampled Great burnet plants were predominantly wild plants, so the low contamination of the sampled plants does not say anything about the composition of the purchased plants. It is evident that the pesticides (especially boscalid) in purchased potting soil may pose a risk for the protection of insects that are supposed to live on great burnet.

## Latumer Bruch 1, NRW

Coordinates: W 51.32673 L 6.63307

Code of location: LBS-5/11/19

In this nature reserve the samples were taken in a swampy area. Accordingly, the vegetation is dominated by reed, grass, stinging nettle and willow trees. The moisty soil consisted of a mixture of peat and sand. The location is audibly close to a highway and the distance to the closest agricultural field is 10 m. Samples were taken from soil, stinging nettle and a mix of leaves and twigs from willow trees.

### Results

In this location the found compounds indicated an influence of agricultural activities. In particular herbicides and fungicides and which are prone to evaporation and thus to spreading into the environment, are found in the vegetation samples. In the sample of the willow tree a total pesticide concentration of 47.0 µg/kg DM was found, to which mainly the herbicides prosulfocarb and pendimethalin contribute. The herbicides chlorpropham and prosulfocarb were found in both vegetation samples. Unfortunately, in the sample of the willow tree the insecticide picardin and in stinging nettle the insecticide thiofanox were found. In the soil out of the 3 found compounds anthraquinone showed with 10 µg/kg DM the highest concentration.

### Overall contamination

In comparison with the overall average pesticide concentrations and the number of compounds found in other nature reserves, the contamination of the soil and the willow tree sample can be considered as moderate. The found concentrations in stinging nettle are rather low, but therefore 6 different compounds were found of which two with insecticide properties (diphenylamine and thiofanox). It is possible, that the found insecticides and other compounds will impact the insect fauna. In this location it seems that the willow trees collect higher quantities of pesticides than stinging nettles.

| Latumer Bruch 1, NRW | Willow tree, leaves and twigs | Stinging nettle | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 47.03 | 14.47 | 18.16 |
| *Insecticides µg/kg DM* | 2.24 | 3.45 | 0 |
| *Fungicides µg/kg DM* | 8.34 | 6.35 | 8.16 |
| *Herbicides µg/kg DM* | 31.19 | 4.68 | 0 |
| *Repellent µg/kg DM* | 5.26 | 0 | 10 |
| *Number of different pesticides* | 4 | 6 | 3 |

In the table it can also be seen that willow trees absorbed predominantly herbicides and stinging nettle fungicides.

## Pliesterberg 2, NRW

Coordinates: W51.648454 L 6.700733

Code of location: PB2-6/11/19

The nature reserve Pliesterberg is located in the region of Wesel, nearby the river Lippe. The sampled area belongs to a sandy area with some heather and dry grassland. The main vegetation of the sampled location was sheep´s sorrel (Rumex acetosella), moss, some oak trees and black cherry (Prunus serotina). The soil is sandy with a thin layer of humus.

A meadow with grazing Scottish Highlander borders the area. Agricultural fields are at 200 m distance from the location. Samples were taken from the very poor sandy soil, oat leaves and twigs, and manure from the nearby meadow. For counting the number of beetles in the manure an additional sample was taken.

### Results

The total concentration (25.16 µg/kg DM) found in the soil sample is equal to the average concentration of soils in the other nature reserves. Anthraquinone was the main compound.

In the oak sample the total pesticide concentration was 75.2 µg/kg DM and the number of different pesticides found (8) was higher than the average values from other sampled nature reserves. The compound diphenylamine which has insecticide properties, showed with 41.36 µg/kg DM the highest concentration of the vegetation samples in NRW. Pesticides originated from agricultural activities such as phthalimide, pendimethalin or prosulfocarb were found as well. In the cattle manure two herbicides, metoxuron and prosulfocarb were quantitative detected. However, three pesticides were detectable but could not be quantified. Among them the insecticide deltamethrin, being extremely toxic for insects, even in much lower concentrations than the LOQ of this research.

### Overall contamination

The soil could be considered as rather clean, perhaps due to the lack of pesticide-binding humus or clay in the soil. Nevertheless, taking the contamination of the oak sample in consideration, this location is rather strong affected by the deposition of pesticides. The compound diphenylamine has no authorisation for agricultural use but is widely used as an industrial antioxidant. Approximately 900 m south of Pliesterberg2 the industrial complex Bucholtwelmen is located. This complex might be the source of the found diphenylamine. A negative impact of this pollution on insects seems to be plausible: the investigation of the EVK shows very low levels of insect masses in this area. Given the low number of counted beetles in the manure (only 5 beetles were found in one kg manure), the impact of the found pesticides (a.o. deltamethrin) in the manure becomes clear. Deltamethrin is used by many (conventional and also organic) farmers as veterinary medicine, or against flies and ticks.

| Pliesterberg 2, NRW | Oak tree, leaves and twigs | Soil | Manure Scottish Highlander |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 75.22 | 25.16 | 13 |
| *Insecticides µg/kg DM* | 41.38 | 0 | qualitative detected |
| *Fungicides µg/kg DM* | 9.93 | 8.16 | qualitative detected |
| *Herbicides µg/kg DM* | 19.65 | 0 | 13 |
| *Repellent µg/kg DM* | 5.26 | 17 | qualitative detected |
| *Number of different pesticides* | 8 | 2 | 5 |

### Pliesterberg 1, NRW

Coordinates: W51.65098 L 6.69863

Code of location: PB1-6/11/19

Similar to the location Pliesterberg 2, also this location has a sandy and a poor soil. On the sampled location no humus layer was visible. The vegetation consisted of some herbs, sheep´s sorrel (Rumex acetosella), grass (Nardus sticta), common broom (Cýtisus scopárius), black cherry (Prunus serotina), oak and birch trees. Agricultural fields are at 130 m distance from the sampled location and the area is accessible to people, dogs and horses. Samples were taken from poor sandy soil, leaves and twigs from oak and black cherry trees.

Results

In the black berry and oak samples the found concentrations and the number of pesticides did not differ much. In both samples diphenyl showed with 9.8 µg/kg DM the highest concentration. In both samples the herbicides pendimethalin, prosulfocarb, chlorpropham were found, as well as the fungicide phenylphenol-2. Diphenylamine, acting as an insecticide, was present in both samples,

In addition, the insecticide picardin was found in the black berry sample. The total concentration of pesticides in the soil sample was with 6 µg/kg DM rather low. Nevertheless, 4 different compounds in low concentrations were detected. Compared with Pliesterberg 1, in the samples of this location much less anthraquinone was found in the soil.

Overall contamination

The soil can be considered as rather clean, possibly due to the lack of pesticide-binding humus. Taking the contamination of the samples taken from oak and black cherry trees into consideration, the contamination of this location is partly similar to Pliesterberg 2. However, in the oak sample from Pliesterberg 1 a much lower concentration of diphenylamine was found than in the sample from Pliesterberg 2. May be the trees in between the two locations reduce the influx of diphenylamine.

| Pliesterberg 1, NRW | Black cherry tree, leaves and twigs | Oak tree, leaves and twigs | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 42.53 | 31.50 | 5.96 |
| *Insecticides µg/kg DM* | 6.44 | 1.56 | 0 |
| *Fungicides µg/kg DM* | 15.39 | 14.75 | 3.96 |
| *Herbicides µg/kg DM* | 12.76 | 12.00 | 1 |
| *Repellent µg/kg DM* | 7.94 | 3.17 | 1 |

## Tote Rahm 1, NRW

Coordinates: W51.40213 L 6.46813

Code of location: TR1-6/11/19

The Nature reserve Tote Rahm is characterized by moisty forests and belongs to the district Viersen. The sampled location was down hills, in a bowl with a swampy soil. Normally it contains water. The vegetation is dominated by water mint (*Mentha aquatica*), ferns and alder trees (*Alnus glutinosa*). Agricultural fields are at 260 m distance from the sampled location and the area is accessible to people and dogs. Samples were taken from the soil, water mint and leaves of the alder trees.

Results

As the table shows, the total concentration and the number of found pesticides was in all samples rather high. In the soil 15 pesticides were found, in the water mint 8 and in the alder trees 13. In water mint and soil samples fungicides dominated. In the alder leaves the total concentrations of herbicides and fungicides were similar (34.88 and 29.45 µg/kg DM respectively). The pesticides phthalimide, pendimethalin, prosulfocarb, diphenyl and anthraquinone were found in all samples. In the water mint the fungicide diphenyl showed the highest concentration (12.2 µg/kg DM), in the alder leaves the herbicide pendimethalin (20.0 µg/kg DM) and in soil the compound anthraquinone (29 µg/kg DM). In the water mint the insecticide cyfluthrin, in the soil the insecticides dieldrin, diphenylamine, p,p DDE were found. Dieldrin and DDE (metabolite of DDT) are very persistent and since 1973 their use has been banned. Therefore, the residues of these insecticides must result from applications long ago (>47 years). Where the cyfluthrin might come from is impossible to say. It is not particularly volatile, and it is also poorly soluble in water.

Overall contamination

The sampled location of this nature reserve is contaminated with many different pesticides and exceeded up to three times the average concentrations and number of pesticides found in other nature reserve areas. The majority of the found pesticides are still used in agriculture, however partly they stem from earlier use and partly the source of the compound is not clear, for example diphenyl, diphenylamine and anthraquinone. Out of the 15 pesticides found in the soil sample, 10 of them are authorised for application in agriculture. The overall conclusion can only be that this location is affected by mixtures of pesticides, which poses a serious risk for the protection of insect diversity.

| Tote Rahm 1, NRW | Water mint | Alder leaves | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 37.70 | 74.11 | 69.89 |
| *Insecticides µg/kg DM* | 8.06 | 3.43 | 5.64 |
| *Fungicides µg/kg DM* | 19.19 | 29.45 | 20.71 |
| *Herbicides µg/kg DM* | 8.85 | 34.88 | 14.55 |
| *Repellent µg/kg DM* | 1.59 | 6.35 | 29 |
| *Number of different pesticides* | 8 | 13 | 15 |

## Tote Rahm 2, NRW

Coordinates: W51.40305 L 6.48013

Code of location: TR2-6/11/19

In the sampled location Tote Rahm2 the dominating vegetation was reed (Phragmites australis), stinging nettle (Urtica dioica) and blackberries (Rubus fruticosus). The location has a boggy soil, which is normally under water. During sampling the soil was just moist, because of a dry spell. Agricultural fields are at 110 m distance from the sampled location. The area is accessible to people and dogs.

Samples were taken from, soil, reed (Phragmites australis) and creeping thistle (Cirsium arvense)

Results

The total found pesticide concentrations in the soil and vegetation samples don´t deviate much from the average concentrations found in the other nature reserves. Remarkable is the fact that a high number of different pesticides were detected. In the two vegetation samples the concentrations of the fungicides phthalimide, diphenyl, the herbicides pendimethalin and prosulfocarb, the insecticide diphenylamine, were similar or did not differ much from each other. In reed the fungicide ametocradin was found in high concentration of 33.09 µg/kg DM. This compound was neither detected in creeping thistle, nor in the soil. In soil anthraquinone showed the highest concentration (8 µg/kg DM), followed by diphenyl with 6 µg/kg DM. A trace of the metabolite of DDT was detectable.

Overall contamination

The types of pesticides found in the nature reserves indicate clearly a supply of compounds from the agriculture. Through this area there is a small river that may contaminate this nature reserve with all those compounds. More than half of the found pesticides are used either as fungicide: Phtalimide, a metabolite folpet, phenylphenol-2, ametocradin, or as herbicide such as chlorpropham, pendimethalin, prosulfocarb and propyzamide. The overall conclusion is that also the location Tote Rahm 2 is probably too much affected by a mixture of pesticides for the effective conservation of insects.

| Tote Rahm 2, NRW | Creeping thistle | Reed | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 35.28 | 60.53 | 22.92 |
| *Insecticides µg/kg DM* | 1.56 | 1.56 | 1 |
| *Fungicides µg/kg DM* | 18.61 | 47.70 | 9.92 |
| *Herbicides µg/kg DM* | 15.93 | 10.09 | 4 |
| *Repellent µg/kg DM* | 1.59 | 1.59 | 8 |
| *Number of different pesticides* | 10 | 9 | 6 |

## Egelsberg3, NRW

Coordinates: W51.38712 L 6.58626

Code of location: EBK3-7/11/19

The nature reserve area Egelsberg belongs to the district Krefeld. The sampled location with the code EBK3 is situated on the top of a hilly area. The soil is sandy with gravel. The variety of vegetation is rather poor. Some sheep´s sorrel (Rumex acetosella), moss and heather (Calluna vulgaris) are growing in the reserve, but significant sections with bare soil are also present. Possibly wild animals, like hares and rabbits are responsible for digging and in addition dogs that walk there often. The distance of this location to agricultural fields amounts to 190 m. Samples were taken from heather and soil.

Results

The sample of the heather shows a very high total content of pesticides. In total 19 different pesticides were found with a total concentration of 109.2 µg/kg dry matter. The herbicides showed the highest concentrations of respectively 16.69 and 14.29 µg/kg DM

The fungicide boscalid with an accumulative toxicity to bees was present with a concentration of

8.15 µg/kg DM. The other compounds found with insecticide properties were diphenylamine and p,p DDE. In contrary to the heather, the soil was much less contaminated; only 2 different compounds were found. Out of the total found pesticides of 21 µg/kg DM, anthraquinone contributed with 17.0 µg/kg DM. The sample of the heather shows a very high total content of pesticides of 109.2 µg/kg dry matter. With this content the Egelsberg3 heather belongs to the most contaminated vegetation samples that were met in this research.

| Egelsberg 3, NRW | Heather | Soil |
|---|---|---|
| | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 109.2 | 21 |
| *Insecticides µg/kg DM* | 14.22 | 0 |
| *Fungicides µg/kg DM* | 35.66 | 4 |
| *Herbicides µg/kg DM* | 51.20 | 0 |
| *Repellent µg/kg DM* | 7.94 | 17 |
| *Number of different pesticides* | 19 | 2 |

In the heather 14.2 µg of insecticides were found, 35.66 µg of fungicides and 51.2 µg of herbicides. It seems very unlikely that insects can flourish in such an environment on the long run. The soil contains relatively few pesticides. It is likely that this soil (pure sand with gravel) cannot bind pesticides and they may fast move to the groundwater as a result.

Overall contamination

The soil can be considered as rather clean, possibly due to the lack of pesticide-binding humus. However, with the content of found pesticides the Egelsberg3 heather belongs to the most contaminated samples that were met in this research. The type of the found pesticides indicates that this nature reserve is heavily affected by agricultural activities. Out of the 19 found compounds 15 of them stem with a high probability from agricultural use.

The sampled area is located more or less on a hill and possible sensitive to the deposition of pesticides spread by the wind. May be heather has the property to accumulate pesticides.

The overall conclusion is that also the nature reserve Ebersberg3 is probably too much affected by a mixture of pesticides for the effective conservation of insects.

## Bislich, NRW

Coordinates: W51.65176 L 6.48530

Code of location: BL-12/11/19

The nature reserve Bislich near Xanten on the Lower Rhine, belongs to the district Wesel. Nearby the sampled location several small ditches and tributaries can be found.

The soil consists of heavy clay with a thin layer of humus. Probably the area is sometimes flooded with Rhine water. The dominant vegetation was reed (Phragmites australis) and stinging nettle (Urtica dioica). For people the area is difficult to access. The distance of this location to agricultural fields amounts to 130 m.

Samples were taken from soil, reed and stinging nettle.

Results

The total concentration of the found pesticides in the vegetation exceeded slightly the average concentration from other investigated nature reserves. Nevertheless, remarkable were the many different compounds (10) found in the stinging nettle. In reed less compounds (4) were found. Possibly reed accumulates less pesticides than stinging nettles. Out of the 10 compounds found in stinging nettle were 3 fungicides (phenylphenol-2, fludioxonyl, phthalimide a metabolite of folpet), 3 herbicides (chlorpropham, pendimethalin and prosulfocarb) and a metabolite of the insecticide fenamiphos, of which we can assume that they originate from agricultural activities. The concentrations of the in nature reserves almost ubiquitously found compounds anthraquinone, diphenyl, diphenylamine and prosulfocarb were in the reed and stinging nettle sample comparable.

The analyse results of the soil showed a high contamination. The total amount of the found pesticides was 121.8 µg/kg DM and 6 different compounds were detected. The since 1973 banned insecticide DDT showed a remarkable high concentration of 51 µg/kg DM. DDT is an extremely persistent insecticide with an undefined conversion time. It was banned almost 50 years ago. Furthermore, rather high concentrations of the fungicide diphenyl (24.1 µg/kg DM) and the compound anthraquinone of 40 µg/kg DM were found in the soil.

| Bislich, NRW | Reed | Stinging nettle | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 31.21 | 38.78 | 121.83 |
| *Insecticides µg/kg DM* | 3.45 | 3.67 | 51.94 |
| *Fungicides µg/kg DM* | 20.69 | 26.08 | 29.88 |
| *Herbicides µg/kg DM* | 3.23 | 5.86 | 0 |
| *Repellent µg/kg DM* | 3.85 | 3.17 | 40 |
| *Number of different pesticides* | 4 | 10 | 6 |

Overall contamination

The location Bislich seems to be contaminated by agricultural and industrial activities, and by flooding by the Rhine. The soil could be considered as very polluted by the persistent insecticide DDT and by the compounds anthraquinone and diphenyl. The DDT residues in soil result possibly by from flooding by polluted water from the river. It is very likely that the insect fauna and soil organisms will be affected by this contamination. Taking the found pesticides in the stinging nettle into consideration, this location is also affected by pesticides from agriculture. The overall conclusion is that this location is too much affected by a mixture of pesticides for an effective conservation of insects. The low catches of insects with MF from this location in recent years seems to confirm that context.

## Loosenberge, NRW

Coordinates: W51.66938 L 6.77983

Code of location: LB-12/11/19

The nature reserve Loosenberge, belongs to the community Schermbech, district Wesel

It's a well-wooded area. According to the information boards, to obtain nutrient-poor soil the upper layer of the soil of the sampled location was removed. In the location grow different types of moss. The soil is sandy with a thin layer of humus.

The dominant vegetation was heather (Calluna vulgaris), moss, juniper (Juniperus communis) and holly (Ilex aquifolium). In the areas are hiking trails for people and horsemen.

The distance of this location to agricultural fields amounts to 160 m.

Samples were taken from heather and soil

Results

As the table shows, the total concentration and the number of found pesticides was in the heather sample rather high and in the soil sample low.

In the heather the fungicide diphenyl showed with 51.7 µg/kg DM the highest concentration, followed by the herbicides prosulfocarb and pendimethalin with respectively 21.0 µg/kg DM and 18.6 µg/kg DM. The concentration of the found compound diphenylamine, with insecticide properties, was 10.3 µg/kg DM. In the soil sample only the compound anthraquinone was found.

| Loosenberge, NRW | Heather | Soil |
|---|---|---|
| | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 134.06 | 13.0 |
| *Insecticides µg/kg DM* | 10.34 | 0 |
| *Fungicides µg/kg DM* | 63.18 | 0 |
| *Herbicides µg/kg DM* | 45.23 | 0 |
| *Repellent µg/kg DM* | 15.38 | 13 |
| *Number of different pesticides* | 8 | 1 |

Overall contamination

The types of pesticides found in the heather from this nature reserve indicate clearly a supply of compounds from agriculture. More than half of the found pesticides are used either as fungicide or as herbicide. From the analysed vegetation samples from other nature reserves, this heather sample was the most contaminated with pesticides. The soil sample was however approximately 50% less contaminated than the average soils from other nature reserves. An indication of this observation could be the fact that the upper soil layer of the sampled location had been removed. In addition, it is a very sandy humus-poor soil, with a low capacity to bind pesticides. The overall conclusion is, that the location Pliesterberg is probably too much affected by a mixture of pesticides for the effective conservation of insect diversity.

## Urdenbacher Kämpe, NRW

Coordinates: W51.13979 L 6.87993

Code of location: UK-13/11/19

The nature reserve Urdenbacher Kämpe is located in the south of Düsseldorf. The area is an old Lower Rhine cultural landscape. The sampled location consisted partly of a mown meadow with pollard willows and partly of a herb-rich meadow. The dominant vegetation in the mown meadow was blackberries (Rubus fruticosus), stinging nettle (Urtica Dioica), reed (Phragmites australis) and pollard willows (Salix alba). The dominant vegetation of the meadow was grass, ribwort plantain (Plantago lanceolata), Small burnet (Sanguisorba minor), Great burnet (Sanguisorba officinalis) and meadow buttercup (Ranunculus acris). Agricultural fields are at 80 m distance from the sampled location. The area is accessible to people and dogs.

Samples were taken from Stinging nettle, Great burnet and soil.

Results

As the table shows, the sample of stinging nettle is less contaminated than the Great burnet sample. In the stinging nettle only the pesticide diphenyl was found and in the Great burnet 6 different pesticides were detected with a total concentration of 45.0 µg/kg DM. This concentration exceeded the average concentrations found the other nature reserves. Diphenyl had the highest concentration (37.0 µg/kg DM), followed by phthalimide (6.0 µg/kg DM), a metabolite of the fungicide folpet. Besides the phthalimide other found compounds originating from agriculture were the fungicide Phenylphenol-2 and the herbicide pendimethalin. In the soil sample the banned compounds diphenyl, anthraquinone and the very persistent fungicide hexachlorobenzene were found.

| Urdenbacher Kämpe, NRW | Stinging nettle | Great Burnet | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 13.79 | 49.74 | 30.61 |
| *Insecticides µg/kg DM* | 0 | 2 | 0 |
| *Fungicides µg/kg DM* | 13.79 | 43.96 | 18.61 |
| *Herbicides µg/kg DM* | 0 | 2.79 | 0 |
| *Repellent µg/kg DM* | 0 | 1 | 12 |
| *Number of different pesticides* | 1 | 6 | 3 |

Overall contamination

The types of pesticides found in this nature reserve indicate a supply of compounds from the agriculture. The source of the dominant found fungicide diphenyl in the vegetation samples is unclear, as well as the in soil found anthraquinone and diphenyl. The very persistent fungicide hexachlorobenzene may be a rest of past use.

In the literature no data are available about the impact of a mixture of anthraquinone, diphenyl and other compounds on insects. The Great burnet (Sanguisorba officinalis) is a key component in the nutritional cycle of

Phengaris nausithous, a target species of nature conservation in the context of reintroduction programs.

## Zons, NRW

Coordinates: W51.14193 L 6.84330

Code of location: ZO-13/11/19

The sampled location is situated in the north of the city Zons on the west bank of the river Lower Rhine, district Neuss. The location, a herb-rich meadow, is not accessible to people or dogs. The dominant vegetation was grass with Small burnet (Sanguisorba minor), Primula, Yarrows (Achillea millefolium), and the soil was sandy with humus. Agricultural fields are at 290 m distance from the sampled location.

Samples were taken from the Small burnet and soil.

Results

The total concentration (60.1 µg/kg DM) and the number of different compounds (7) found in the Small burnet sample is almost equal to the average concentration of vegetation in other nature reserves. The fungicide diphenyl showed with 34.8 µg/kg DM the highest concentration, followed by pendimethalin with 5.4 µg/kg DM. Out of the 7 found compounds 5 (chlorpropham, phenylphenol-2, phthalimide, pendimethalin and prosulfocarb) originate from the use in agriculture. The compound with official insecticide status had a concentration of 5 µg/kg DM. As the table shows, the total concentration of the pesticides found in soil is rather low. The found compounds diphenyl and anthraquinone were almost ubiquitous in other investigated nature reserves.

| Zons, NRW | Small Burnet | Soil |
|---|---|---|
| | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 60.14 | 8.70 |
| *Insecticides µg/kg DM* | 5 | 0 |
| *Fungicides µg/kg DM* | 42.78 | 3.70 |
| *Herbicides µg/kg DM* | 12.36 | 0 |
| *Repellent µg/kg DM* | 0 | 5 |
| *Number of different pesticides* | 7 | 2 |

Overall contamination

The nature reserve Zons is affected by pesticides used in the agricultural. However, the found concentrations of the individual pesticides are not high compared to other locations, but the effects of the mixture of the 7 identified compounds on the insect fauna is up to now unknown. The same can be said of the compounds found in soil, diphenyl and anthraquinone.

## Soller-Vettweiß, NRW

Coordinates: W 50.72563 L 6.62577

Code of location: SV-13/11/19

The nature reserve Soller-Vetweiß belongs to the district Euskirchen. The location was surrounded by agricultural fields, where corn, cereals, canola (rape) and sugar beets are cultivated. In the nature reserve were fields with feed for wild animals (and high seats), bushes and trees. The dominant vegetation was grass, blackberries (Rubus fruticosus), stinging nettle (Urtica Dioica) and rainfarn (Tanacetum vulgare). The soil consists of sandy loam.

Agricultural fields are at 100 m distance from the sampled location in all directions. The area is accessible to people and dogs.

Samples were taken from Stinging nettle, mixed grass and soil.

Results

As the table shows, the total concentration and the number of found pesticides was in the two vegetation samples rather high and in the soil sample low. In the vegetation samples the concentrations were double of the average concentrations found the other nature reserves. The herbicide pendimethalin showed in both vegetation samples the highest concentration; in stinging nettle 53.5 µg/kg DM and in grass 61.0 µg/kg DM, followed by diphenyl with respectively 27.6 µg/kg DM and 15.8 µg/kg DM. Out of the 6 found compounds in the stinging nettle originated 4 pesticides from agricultural use and out of the 10 found compounds in grass 7 pesticides (chlorpropham, chlortoluron, diflufenican, epoxyconazole, flufenacet, pendimethalin, and prosulfocarb).

In contrast with the vegetation, the (sandy-loam) soil seems to have accumulated less pesticides than the vegetation. The three identified compounds anthraquinone, diphenyl, and DDT had rather low concentrations. DDT was found in five other nature reserves with MF just above the LOQ.

| Soller –Vettweiß, NRW | Stinging nettle | Grass | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 101.85 | 102.73 | 12.41 |
| *Insecticides µg/kg DM* | 6.90 | 2.00 | 1 |
| *Fungicides µg/kg DM* | 27.81 | 16.40 | 7.41 |
| *Herbicides µg/kg DM* | 61.14 | 81.33 | 0 |
| *Repellent µg/kg DM* | 3.0 | 3.0 | 4.0 |
| *Number of different pesticides* | 6 | 10 | 3 |

Overall contamination

This nature reserve is clearly affected by the surrounding agricultural fields. The found number of pesticides and the concentration of pendimethalin is in comparison with other investigated nature areas high. The soil contains relatively few pesticides. It is likely that this soil (sandy loam) cannot bind pesticides and they may move to the groundwater instead. The overall conclusion is, that the location Soller Vettweiß is probably too much affected by a mixture of pesticides for the effective conservation of insect diversity.

## Eschweiler1, NRW

Coordinates: W50.57668 L 6.73039

Code of location: EW1-14/11/19

This sampled location belongs to the nature reserve Eschweiler Tal, in the area of the city Bad Münstereifel, district Euskirchen. It is an area with forests, meadows and agricultural fields.

In the sampled location the dominant vegetation was grass, Small burnet (*Sanguisorba minor*), clover (*Trifolium*), hazelnut (*Corylus avellana*), beech (*Fagus sylvatica*), hawthorn (*Crataegus laevigata*). In between of Echweiler1 and the following Eschweiler2 is an agricultural field, the distance between the two locations is 57 m. The area is accessible to people, dogs and horses.

The soil is very gritty. A cereal field was at 10 m distance from the sampled location.

Samples were taken from the hazel tree (leaves and twigs), the soil and deer droppings.

Results

The total concentration (49.35 µg/kg DM) of the found pesticides in the sample of the hazel was similar to the average concentration from other investigated nature reserves. The total concentration (35.44 µg/kg DM)of the soil sample exceeded slightly the average concentration from other nature reserves. Out of the 9 different found compounds in the hazel 6 (3 fungicides and 3 herbicides) originated from agricultural applications of which the herbicide pendimethalin with 11.6 µg/kg DM showed the highest concentration. In the soil sample the metabolite of the fungicide prochloraz was found with the highest concentration of 22.8 µg/kg DM. In the hazel the compound diphenylamine with insecticide properties was found.

In the droppings of the deer 5 compounds (3 herbicides, 1 insecticide and 1 fungicide) were identified with a total concentration of 71 µg/kg DM. The herbicide metoxuron showed the highest concentration 63 µg/kg DM. This compound was not found in the soil or in the vegetation of this location, so the roe deer might have eaten contamination elsewhere.

| Eschweiler 1, NRW | Leaves and twigs from hazel | Soil | Roe deer droppings |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 49.35 | 35.44 | 71 |
| *Insecticides µg/kg DM* | 3.45 | 0 | 2 |
| *Fungicides µg/kg DM* | 27.24 | 34.44 | 0 |
| *Herbicides µg/kg DM* | 18.66 | 0 | 67 |
| *Repellent µg/kg DM* | 0 | 1 | 2 |
| *Number of different pesticides* | 9 | 5 | 5 |

Overall contamination

Taking the only 10 m distance between the agricultural field and the sampled location in consideration may be the found compounds are not surprising. The fungicide prochloraz is used in growing cereals. However, partly the influx of pesticides can be from applications many km far away. Surprisingly is the high concentration of the found herbicide metoxuron in the droppings of the roe deer. Since 1989 was in Germany the use of this herbicide in crop production banned, which is 31 years ago. Overall, the conclusion is, that a mix of several pesticides enter these nature reserves, of which the overall effects on the insect fauna are still unknown. The cereal fields nearby had been sprayed with an herbicide less than a few days before the sampling date. That could have been pendimethalin, because this herbicide has been found in the vegetation of both nearby locations. This is an herbicide which is widely used in cereals. However, metoxuron used to be applied also to cereal crops before 1989.

## Eschweiler2, NRW

Coordinates: W50.57625 L6.73079

Code of location: EW2-14/11/19

Eschweiler2 was located approximately 16 m from the agricultural field and 57 m southeast from Eschweiler1

The dominant vegetation was grass eaten short by wild animals, hazel (*Corylus avellana*), hawthorn (*Crataegus laevigata*) and beech (*Fagus sylvatica*). The adjacent field was sown with coated (pesticide dressed) winter barley. Further due to the tire tracks and the yellow discoloured vegetation, it looked like field was treated with pesticides. The nature reserve was accessible to people, dogs and horses. Soil was loam with gravel. The cereal field was at 20 m distance from the sampled location.

Samples were taken from hazel and soil

Results

As the table shows, in the vegetation and soil were respectively 5 and 3 different compounds found with a moderate total concentration. In the hazel 3 herbicides diflufenican, pendimethalin and prosulfocarb, and the two compounds diphenyl and the metabolite of the fungicide folpet were found. In the soil only fungicides were found, of which epoxiconazole showed the highest concentration (9 µg/kg DM). The fungicide prochloraz was present, but could not be quantified. So, the total concentration of the fungicides in soil is underestimated.

| Eschweiler2, NRW | Hazel, leaves and twigs | Soil |
|---|---|---|
| | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 26.34 | 16.56 |
| *Insecticides µg/kg DM* | 0 | 0 |
| *Fungicides µg/kg DM* | 7.94 | 14.56 |
| *Herbicides µg/kg DM* | 18.40 | 0 |
| *Repellent µg/kg DM* | 0 | 2 |
| *Number of different pesticides* | 5 | 4 |

In the next table the composition of the samples of the samples from Eschweiler1 (EW-1) and Eschweiler2 (EW-2) is compared.

| | Hazel, leaves and twigs | | Soil | |
|---|---|---|---|---|
| | EW-1 | EW-2 | EW-1 | EW-2 |
| Compound | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *ANTHRAQUINONE* | | | 1.0 | 2 |
| *DIPHENYL* | 20.7 | detected | 5.6 | 5.6 |
| *PHENYLPHENOL-2* | 3.2 | | | |
| *EPOXICONAZOLE* | | | 5.1 | 9 |
| *DIFLUFENICAN* | | 6.5 | | |
| *DIPHENYLAMINE* | 3.4 | | | |
| *CHLORPROPHAM* | 1.9 | | | |
| *PROCHLORAZ* | | | | detected |
| *PROCHLORAZ desimidazole-amino* | | | 22.8 | |
| *PROPICONAZOLE* | | | | |
| *PROSULFOCARB* | 3.2 | 2.9 | 1 | |
| *PENDIMETHALIN* | 11.6 | 9.1 | | |
| *TEBUCONAZOOL* | 1.8 | | | |
| *DIFLUFENICAN* | 1.9 | | | |
| *PHTHALIMIDE* | | 7.9 | | |
| *PROTHIOCONAZOLE-DESTHIO* | 1.5 | | | |
| *Total pesticides µg/kg DM* | 49.2 | 26.4 | 35.5 | 16.6 |
| *Number of different pesticides* | 9 | 5 | 5 | 4 |

### Overall contamination

The total found pesticide concentrations in the soil and vegetation samples from Eschweiler2 are around the average found in the other nature reserves. As visible in the joint tables of EW-1 and EW-2, in the two sampled locations the concentrations of some compounds are in soil similar, except for the prochloraz desimidazole-amino fungicide metabolite. The compounds detected in the hazelnut on both locations are partly identical (prosulfocarb and pendimethalin) and partly different (diflufenican and phthalimide). Diflufenican and pendimethalin are omnipresent in most locations. It seems pesticides are absorbed from the air by the vegetation, and once they reach the soil become diluted, or bound to other soil components and invisible. The overall conclusion is, that the nature reserve Eschweiler is affected by pesticides, originating mainly from agricultural activities. Negative effects on the protection of insect diversity should be clarified including the influence of the pollution of perennial plants and woody plants in a risk analysis.

## Wahnbachtal 2, NRW

Coordinates: W50.84714 L 7.31862
Code of location: WBT2-14/11/19

## Wahnbachtal 3, NRW

Coordinates: W50.87403 L 7.34734
Code of location: WBT5-14/11/19

The EVK had in the year 6 insect traps installed the nature reserve Wahnbachtal. For this investigation we sampled the location number 2 and because number 5 was not accessible the sample was taken 200 up to 240 m distance from the insect trap nr. 5. The site of Wahnbachtal belongs to the district Rhein-Sieg. The sampled location 2 was 900 m west of the city Neunkirchen. Between location 2 and 5 is the distance 3.5 km. Location 5 is northeast of location 2. The sampled location of Wahnbachtal 2 (WBT2) was rather swampy and so the dominant vegetation was grass, bog plants and dandelions.

The location Wahnbachtal 5 (WBT5) had a loamy soil with grass and dandelions. The area is sand witched between a busy traffic road and an uphill slope; no agricultural fields were visible. An arable field was at 310 m distance from the location WBT2 and at 130 m from location WBT5.

From both locations samples were taken from grass and soil. The grass sample of location number 5 contained a few dandelions.

### Results

As the table shows, in all samples the fungicide diphenyl and phthalimide, a metabolite of the fungicide folpet, were found. In all samples the numbers and the concentrations of the found compounds were lower than the averages from other investigated nature reserves.

Not all compounds were quantifiable but were present. So, the concentrations of those compounds are unknown and they are listed in the table as “detected”.

### Overall contamination

About the compounds phthalimide, phenyphenol, chlorpropham can be said, that they originate from agricultural activities. Chlorpropham is an anti-sprouting agent, used for the storage of potatoes and used as herbicide as well. The compounds diphenyl, diphenylamine, anthraquinone may stem from industry and/or traffic. Once these compounds were used as pesticides and/or biocides. Diphenylamine has insecticide properties. The overall impact of the mixtures of the found compounds on insects is unknown.

| | WBT2 | | WBT5 | |
|---|---|---|---|---|
| | Grass | Soil | Grass, dendelions | Soil |
| Compound | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *Diphenyl* | detected | 4.1 | detected | 10.2 |
| *Phthalimide (Met. Folpet)* | 12.7 | 1 | 14.3 | detected |
| *Phenylphenol-2* | 4.2 | | 2.1 | |
| *Diphenylamine* | 10.3 | | | detected |
| *Chlorpropham* | 7.3 | | 3.6 | |
| *Anthraquinone* | 2.6 | 3 | | 2 |
| | | | | |
| *Total pesticides µg/kg DM* | 37.1 | 8.1 | 20 | 12.2 |
| *Insecticides µg/kg DM* | 10.3 | 0 | 0 | detected |
| *Fungicides µg/kg DM* | 16.9 | 5.1 | 16.37 | 10.20 |
| *Herbicides µg/kg DM* | 7.27 | 0 | 3.64 | 0 |
| *Repellent µg/kg DM* | 2.6 | 3 | 0 | 2 |
| *Number of different pesticides* | 6 | 3 | 4 | 4 |

## Naturpark Nassau, Koppelstein – Helmestal, Rheinland-Pfalz

In this nature reserve two locations of the 4 in transect insect traps (MF) were sampled: one uphill and one downhill.

Coordinates: W50.29305 L 7.63071

Code of location: NN-20/11/19- hoch (uphill)

Coordinates: W50.29263 L 7.63149

Code of location: NN-20/11/19 – niedrig (downhill)

Within the Naturpark Nassau of the district Rheinland Pfalz there are several nature reserves. One of them the Koppelstein-Helmestal was sampled. The area is located approximately one km from the river Rhine. The distance between the two sampled locations is 80 m. The soil of both locations is loamy. The vegetation of the up-hill location is dominated by sown production grass and clover with some rainfarn (Tanacetum vulgare). The vegetation downhill is rich: Mainly grass with small burnet (Sanguisorba minor), oregano vulgare, milk thistle (Silybum marianum), rainfarn (Tanacetum vulgare) and gallium. An arable field was directly bordering the uphill location and at a distance of 80 m from the downhill location. The nature reserve is accessible to people, dogs and horses.

Samples were taken from grass (down- and uphill), small burnet (uphill), from soil and droppings from roe deer (down-hill).

### Results

As the tables show in all samples from the two locations the compounds diphenyl and anthraquinone were found in comparable quantities. In all vegetation the herbicides chlorpropham, prosulfocarb, pendimethalin and a metabolite of the fungicide folpet were found, and partly in the roe deer droppings as well. The number and the concentrations of the found pesticides in the three vegetation samples from the two locations did not differ much, and the total concentration was lower than the average concentration found in the other nature reserves,

In contrary in the soil sample from the location uphill considerably more pesticides and higher concentrations were found than in the sample from downhill. The number of different found pesticides was respectively 9 and 4 with total concentrations of 56.8 µg/kg DM and 7.6 µg/kg DM. In the soil sample from the location NN-hoch were fungicides the dominant compounds. It is evident that this location was treated with boscalid, epoxiconazole and fluxapyroxad, or that at this field organic manure has been applied with those fungicides.

### Overall contamination

The most remarkable finding in this nature reserve is the fact that apparently pesticides of which at least 3 different fungicides are applied on a field for growing grass. Further three herbicides (chlorpropham, pendimethalin, prosulfocarb) originate from agricultural activities, either on this field or on other fields. These herbicides contaminate the vegetation and are found in the roe deer droppings. In all samples traces of insecticides were found. The overall conclusion is that the location Nassau is probably too much affected by a mixture of pesticides for an effective conservation of insect diversity. MF have been placed on these locations for the first time in 2019, but very late in the season. The first reliable MF biomass catch (from a whole season) will become only available of 2020. In the next table the composition of the vegetation is compared on the low location and on the lower location.

| Naturpark Nassau, Koppelstein – Helmestal, RP | Grass | Grass | Small burnet | Deer droppings |
|---|---|---|---|---|
| | NN-uphill | NN-downhill | NN-downhill | NN-downhill |
| Compound | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *Diphenyl* | 17.1 | 14.3 | 14.6 | 10.9 |
| *Phthalimide (Met. Folpet)* | 3.0 | 4.0 | 3.0 | |
| *Fenylfenol-2* | | 1.4 | | |
| *Diphenylamine* | | 2.9 | 5 | 2.0 |
| *Heptenophos* | 1.0 | | | |
| *Chlorpropham* | 2.0 | 4.0 | 2.0 | 1.0 |
| *Prosulfocarb* | 1.6 | 3.1 | 1.0 | 1.0 |
| *Anthraquinone* | 5.0 | 6.0 | 2.0 | 4.0 |
| *Pendimethalin* | 3.3 | 4.9 | 1.5 | |
| | | | | |
| *Total pesticides µg/kg DM* | 33.0 | 40.6 | 29.08 | 18.9 |
| *Insecticides µg/kg DM* | 1.0 | 2.86 | 5.0 | 2.0 |
| *Fungicides µg/kg DM* | 20.14 | 17.71 | 12.58 | 8.9 |
| *Herbicides µg/kg DM* | 6.84 | 12.04 | 4.49 | 2.0 |
| *Repellent µg/kg DM* | 5.0 | 6.0 | 2.0 | 4.0 |
| *Number of different pesticides* | 7 | 8 | 7 | 6 |

In the table below such a comparison has also been made of the soil analyses of the locations NNup-hill and NN-down-hill.

| Naturpark Nassau, Koppelstein-Helmestal, RP | | |
|---|---|---|
| | Soil | Soil |
| | NN-uphill | NN-downhill |
| Compound | µg/kg DM | µg/kg DM |
| *Boscalid* | 20.0 | |
| *Epoxiconazole* | 12.1 | |
| *Fluxapyroxad* | 15.3 | |
| *Diphenyl* | 3.8 | 3.8 |
| *Anthraquinon* | 2.0 | 1.0 |
| *P,P'-DDE* | 1.0 | |
| *P,P'-DDT* | 0.6 | |
| *Diflufenican* | 1.0 | |
| *Dichlobenil* | | 1.8 |
| *Fluquinconazole* | 1.0 | |
| *Prothioconazole-Desthio* | | 1.0 |
| | | |
| *Total pesticides µg/kg DM* | 56.8 | 7.6 |
| *Insecticides µg/kg DM* | 1.65 | 0 |
| *Fungicides µg/kg DM* | 52.17 | 4.77 |
| *Herbicides µg/kg DM* | 1 | 1.79 |
| *Repellent µg/kg DM* | 2.0 | 1.0 |
| *Number of different pesticides* | 9 | 4 |

The identical values for diphenyl indicate that this compound is airborne. The same is likely for the other compounds that were not found in the soil of the uphill location.

## Orbroich, NRW

Coordinates: W51.39709 L 6.50641 Code of location: OB-22/11/19

The nature reserve Orbroich belongs to the district Krefeld. The sampled location was a pasture with sawn and mown grass. Several herbs were growing: ground-ivy (Glechoma hederacea), common Dandelion (Taraxacum officinale), sorrel (Rumex acetosa), Wisley Blue (Symphytum officinale), gypsywort (Lycopus europaeus), Mentha, yellowcress (Nasturtium officinale), stinging nettle (Urtica Dioica) and blackberry (Rubus). The soil was loam and an agricultural field was at 20 m distance from the sampled location.

Samples were taken from soil and stinging nettle.

Results

As the table shows the total number and concentrations of pesticides found in the two samples were modest and below the averages of the other investigated nature reserves.

In the stinging nettle the highest concentration was found of the fungicide diphenyl (12.2 µg/kg DM). In the soil only the compound anthraquinone was detected.

| Orbroich, NRW | Stinging nettle | Soil |
|---|---|---|
| | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 19.24 | 3.77 |
| *Insecticides µg/kg DM* | 2 | 0 |
| *Fungicides µg/kg DM* | 12.20 | 3.77 |
| *Herbicides µg/kg DM* | 5.04 | 0 |
| *Repellent µg/kg DM* | 0 | 0 |
| *Number of different pesticides* | 4 | 1 |

Overall contamination

The vegetation was slightly contaminated by two herbicides (pendimethalin and chlorpropham) originating from agriculture. The other found compounds such as diphenyl, anthraquinone, diphenylamine are in the EU and in Germany banned as pesticides and biocides and are likely to be released into the environment by the industry and/or traffic.

The effects of the mix of those compounds on the insect fauna is not investigated and thus unknown. In 2014 an insect MF biomass catch was registered of 377 g. Before the year 2000 this would have been at least 1000 g.

## Wissels, NRW

In the nature reserve Wissel in three locations insect traps had been installed by the EVK. For this research 2 locations were sampled.

Wissels-hoch (up-hill)

Coordinates: W51.76924 L 6.30493

Code of location: WI-22/11/19-hoch (up-hill)

Samples were taken from soil, sorrel (Rumex acetosella) and rabbit droppings

Wissels -unten (down-hill)

Coordinates: W51.76932 L 6.30564

Code of location: WI-22/11/19-unten (down-hill)

Samples were taken from soil and grass

The sampled location Wissels up-hill includes a last remnant of river dunes from the Rhine, so the area had a poor sandy soil with mainly moss and sorrel. There were many rabbit holes and rabbit droppings. The vegetation of Wissels down-hill differed fairly from the location Wissels up-hill. The sampled location of Wissels down-hill was culture grass for half and nature grass for the other half, since the MF was located exactly on the border of those two fields. Herbs were lacking. Also in this area there were many rabbit holes and droppings. The two areas are at 245 m distance from agricultural fields and are accessible to people and dogs; occasional sheep grazing is practiced here, and along the Wissels up-hill was a walking path.

### Results

As the table shows, the contamination of the two sampled locations differ significantly. In the soil of Wissels-up-hill only one compound was found, In Wissels-down-hill in total 8 different compounds. On the other hand, in Wissels-up-hill in the sorrel sample 15 different compounds were found, in contrast with the grass sample from Wissels-down-hill 4 compounds. In all samples the fungicide diphenyl was detected, further the compounds differed substantially between the two locations.

Remarkable are the found high concentrations of insecticides imidacloprid and Permethrin-cis and trans in sorrel. These insecticides have a high toxicity for all insects. Including the compound diphenylamine the total concentration of insecticides in sorrel was 53 µg/kg DM, which was except for one vegetation sample (Polygonum aviculare) in Krefeld Spey, the highest concentration found in any wild plant in a nature reserve. In the sorrel sample are out of the 15 compounds are 4 insecticides, 3 fungicides, the repellent anthraquinone and 6 herbicides.

In the soil sample out of the 8 found compounds are 6 fungicides and two herbicides.

In the rabbit droppings 3 compounds were found with diphenyl the highest concentration.

| Wissels, NRW | Wissels-Hoch (up-hill) | | | Wissels-niedrig (downhill) | |
|---|---|---|---|---|---|
| | Sorrel | Soil | Rabbit droppings | Grass | Soil |
| Compound | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *Bixafen* | | | | | 3.8 |
| *Epoxiconazole* | | | | | 2.8 |
| *Fluxapyroxad* | | | | | 3.2 |
| *Prochloraz desimidazole-amino* | | | | | 2.0 |
| *Tembotrione* | | | | | 1.0 |
| *Boscalid* | 2.8 | | | | |
| *Chlortoluron* | 4.5 | | | | |

| Wissels, NRW | Wissels-Hoch (up-hill) | | | Wissels-niedrig (downhill) | |
|---|---|---|---|---|---|
| | Sorrel | Soil | Rabbit droppings | Grass | Soil |
| Compound | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *Flufenacet* | 4.4 | | | | |
| *Imidacloprid* | 6.4 | | | | |
| *Prosulfocarb* | 4.9 | | 2 | | |
| *Diphenyl* | 12.5 | 3.23 | 10.9 | 14.3 | 4.8 |
| *Diphenylamine* | 2.0 | | 2 | 5.7 | |
| *Chlorpropham* | 7.0 | | | | 1 |
| *Anthraquinone* | 31.0 | | | 3 | |
| *Pendimethalin* | 11.9 | | | | |
| *Prosulfocarb* | | | | 1.6 | |
| *Diflufenican* | 3.2 | | | | |
| *Permethrin-Cis* | 19.3 | | | | |
| *Permethrin-Trans* | 25.4 | | | | |
| *Difenoconazole* | 2.0 | | | | |
| *Tebuconazole* | | | | | 1 |
| | | | | | |
| *Total pesticides µg/kg DM* | 137.3 | 3.23 | 14.9 | 24.6 | 19.63 |
| *Insecticides µg/kg DM* | 53.07 | 0 | 2 | 5.7 | 0 |
| *Fungicides µg/kg DM* | 17.3 | 3.23 | 10.9 | 14.3 | 17.63 |
| *Herbicides µg/kg DM* | 35.89 | 0 | 2 | 1.56 | 2.01 |
| *Repellent µg/kg DM* | 31.0 | 0 | 0 | 3 | 0 |
| *Number of different pesticides* | 14 | 1 | 3 | 4 | 8 |

### Overall contamination

The two locations are affected by too many pesticides. In particular the type and the concentrations of the found pesticides in Wissels-up-hill are very worrying and a very negative factor for the conservation of the insect diversity. It will be important to find out the sources of the insecticides.

The source could be dogs and /or sheep, which are treated against fleas and ticks with insecticides (veterinary compounds) based on imidacloprid or permethrin.

But also the found fungicides and herbicides mainly from agriculture are probably too many and in too high concentrations for an effective insect conservation.

## RESULTS AND DISCUSSION OF MEASUREMENTS IN REFERENCE AREAS

### Reference Bad Münstereifel, NRW

Code of location: RBME-14/11/19

Coordinates: W 50.56176 L 6.82089

The sampled location is 4 km east of the town Bad Münstereifel, district Euskirchen. The distance to the nearest arable field was 2900 m. The size of the area was approximately 1500 ha and used for hunting. The sampled location was a small open meadow in the middle of the forest with sown grass, and a loamy soil with some gravel. The meadow was used as feeding place for wild animals like red deer and wild boar. There were many droppings in the meadow. The animals were fed with organic hay and conventional grown cereals. The dominant vegetation was grass, moss, clover and dandelion.

Samples are taken from soil, red deer droppings and grass with some herbs (approx. 1%) An extra sample of the red deer droppings was reserved for counting dung beetles.

Results

As the table shows, in the vegetation 6 different compounds were found with a total concentration of 30.0 µg/kg DM. Because the fungicide diphenyl was not quantifiable, the total concentration was underestimated. Half of the compounds were herbicides and the other half fungicides. The found herbicides chlorpropham, pendimethalin and prosulfocarb, and the fungicide diphenyl were found in the vegetation of many other protected nature reserves and are present almost everywhere. The soil sample was rather clean. Only two compounds (diphenyl and anthraquinone) in relative low concentrations were found. In the droppings of the red deer 6 compounds with a total concentration of 35 µg/kg DM were found. Diphenyl showed the highest concentration of 25 µg/kg DM. The pesticides diphenyl, chlorpropham, phenylphenol-2, prosulfocarb and the metabolite phthalimide found in the vegetation, were also present in the droppings. In the droppings 8 beetles (Aphodius sphacelatus) per kg were counted.

| Reference area Bad Münstereifel, NRW | Grass and herbs | Soil | Red deer droppings |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 30.02 | 6.08 | 35 |
| *Insecticides µg/kg DM* | 0 | 0 | 0 |
| *Fungicides µg/kg DM* | 14.78 | 4.08 | 28 |
| *Herbicides µg/kg DM* | 15.24 | 0 | 1 |
| *Repellent µg/kg DM* | 0 | 2 | 3 |
| *Number of different pesticides* | 6 | 2 | 6 |

Overall contamination

The vegetation was mainly contaminated with pesticides used in arable farming. Many of those pesticides evaporate easily and are spread into the environment. So, the sources of those pesticides were not traceable. The detected compounds anthraquinone and diphenyl stem probably from industry and traffic. The conclusion is that even though arable farming fields are almost 3 km away, this reserve is not protected against the influx of pesticides. But, the overall contamination is lower than in the average found contamination in the other Nature Reserves of this study. However, the dose effect relations of many compounds are logarithmic, and the fact that the concentrations of pesticides in this reference area are a bit lower, might not have much meaning for insect populations. The dropping sample of the red deer shows that animals take in via the vegetation and excrete pesticide residues. The effects of such pesticides mixtures on the health of the animals and the biodiversity have so far not exactly been determined.

## Reference Rothaarkamm (Latrop), NRW

Code of location: LT 21/11/19

Coordinates: W 51.09962 L 8.37191

The reference area Rothaarkamm (und Wiesenthaler) belongs to the district Siegen-Wittgenstein and has the size of 1100 ha. The small city Bad Berleburg was 4.5 km south of the sampled location. The sampled location was in a production forestry, 50 m away from an unpaved forest road and at 3350 m distance from agricultural fields. The dominant trees were spruce and some larch. The vegetation was grass, foxglove (Digitalis purpurea) and plants of the family geraniaceae. The soil is loamy.

Samples were taken from the soil, grass, and a mix of boar and deer droppings.

An extra sample of the droppings was reserved for counting dung beetles.

Results

The number of different found compounds in the three samples varied from 3 up to 7 and the total concentrations from 11.66 µg/kg DM up to 31.61 µg/kg DM. The most remarkable of the found compounds were the presence of 2 different insecticides in the grass and in the animal droppings. In grass the insecticides diphenylamine and the for insects extremely toxic etofenprox were detected, and in the droppings the insecticide diphenylamine and the for insects very toxic indoxacarb. The compound diphenylamine act besides as insecticide also as fungicide, herbicide and growth regulator. In all samples the compound anthraquinone, the fungicide diphenyl and the herbicide chlorpropham were found. In the droppings 17 beetles (Aphodius larve, and Aphodius sphacelatus) per kg were counted.

| Reference area Rothaarkamm (Latrop), NRW | Grass | Soil | Red deer /boar droppings |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 31.61 | 11.66 | 17.86 |
| *Insecticides µg/kg DM* | 4.55 | 0 | 3.77 |
| *Fungicides µg/kg DM* | 17.14 | 5.7 | 11.09 |
| *Herbicides µg/kg DM* | 6.92 | 1 | 3 |
| *Repellent µg/kg DM* | 3 | 5 | 2 |
| *Number of different pesticides* | 6 | 3 | 7 |

Overall contamination

The overall contamination is lower than the average found contamination in the other selected nature Reserves with MF of this study. But also this reference area is not protected against the contamination with pesticides. The concentrations found are not high. Nevertheless, effects on the insect fauna are certainly not to be excluded. In particular the presence of various insecticides is worrying, which may be a result of insect control in forestry.

Similar as the frequently found compounds diphenyl and anthraquinone, diphenylamine is not currently used in agriculture. So, the source of these compounds may be the industry and/or traffic. The source of the other found pesticides such as pendimethalin, prosulfocarb and chlorpropham, is doubtlessly agriculture.

## Reference Arnsberger Wald, NRW

Code of location: AB 21/11/19

Coordinates: W 51.27705 L 8.12504

The Arnsberger Wald is a nature park and belongs to the district Soest. At the sampled location mainly spruce and some beech are growing. Forestry was carried out. The town Warstein is 13 km east of the sampled location and the town Arnsbach 7 km southwest. The sampled location was at a distance of 4770 m of arable fields. On the humus, rich soil little vegetation was growing:

Some grass, foxglove (*Digitalis purpurea*) and stinging nettle (*Urtica dioica*). Samples were taken from soil and beech leaves.

Results

As the table shows, the found number of different pesticides and the total concentrations were in comparison with other sampled nature areas fairly low. In the beech leaves diphenyl showed the highest concentration, followed by pendimethalin and diphenylamine. In the leaves was the fungicide imazalil present but not quantifiable. In the soil sample the compound anthraquinone showed with 9 µg/kg DM the highest concentration. In the soil traces of chlorpropham and DDT were found as well.

| Reference area Arnsberger Wald, NRW | Beech leaves | Soil |
|---|---|---|
| | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 18.28 | 18.55 |
| *Insecticides µg/kg DM* | 2 | 1 |
| *Fungicides µg/kg DM* | 12.2 | 7.55 |
| *Herbicides µg/kg DM* | 4.08 | 1 |
| *Repellent µg/kg DM* | 0 | 9 |
| *Number of different pesticides* | 4 | 4 |

Overall contamination

The reference area Arnsberger Wald belongs to the cleaner nature reserves but is not completely free of pesticides. The sources of the compounds are partly agriculture and partly industry and/or traffic.

## Wehenbachtalsperre, Reference Gressenich, NRW

Code of location: WS 22/11/19

Coordinates: W 50.73766 L 6.30851

The area of Wehenbachtalsperre is allocated as a water protection area and production forestry takes place. The area belongs to the Naturpark Nordeifel, district Euskirchen. The sampled location was 3.7 km southeast of the town Gressenich and at 2500 m distance of the nearest arable field. The dominant trees were spruce, beech, Norway spruce and larch. Further observed species of vegetation were holly, blueberry, hulk, grass and foxglove (Digitalis purpurea). The soil was humus rich.

Samples were taken from grass, soil and animal droppings

An extra sample of the droppings was reserved for counting the beetles.

Results

The total found concentration and compounds in the soil of this reference area exceeds the averages of the other investigated nature reserves and reference areas. The compound anthraquinone showed with 14 µg/kg DM the highest concentration, followed by the fungicide diphenyl and the insecticide diphenylamine with respectively 5.67 µg/kg DM and 5.41 µg/kg DM. Furthermore, in the soil traces of DDT and two metabolites of DDT were found. Also in the vegetation and dropping sample diphenyl had the highest concentration of the found compounds. In this area there was a clear influx of the in agriculture used herbicides chlorpropham and prosulfocarb.

| Wehenbachtalsperre, Reference area Gressenich, NRW | Grass | Soil | Red deer /boar droppings |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 31.5 | 29.07 | 10.09 |
| *Insecticides µg/kg DM* | 8.57 | 8.41 | 0 |
| *Fungicides µg/kg DM* | 14.29 | 5.66 | 9.09 |
| *Herbicides µg/kg DM* | 8.64 | 1 | 1 |
| *Repellent µg/kg DM* | 0 | 14 | 0 |
| *Number of different pesticides* | 4 | 6 | 2 |

Overall contamination

The fairly contaminated soil may be correlated with the large amount of humus in the soil. It is known, that humus has the capacity to bind pesticides and other chemical compounds. The physical properties of the in the vegetation herbicides (chlorpropham and prosulfocarb) cause a widespread distribution in the environment. It is not known what the effects of the found cocktails of pesticides on the insect fauna are. Nevertheless, it is assumable that the effects don´t contribute to a positive insect conservation.

## Reference Klever Reichswald, NRW

Code of location: RW 4/12/19

Coordinates: W 51.74532 L 6.055452

The forest Klever Reischswald of 5100 ha and belongs to the district Kleve. The dominant trees are beech (Fagus sylvatica), larix and firs. The soil is loamy sand almost without gravel.

Grass and herbs were growing, such as clover, plantain (Plantago lanceolata), sorrel (Rumex acetosa), Stinking willie (Jacobaea vulgaris), foxglove (Digitalis purpurea), yarrow (Achillea millefolium). The sampled location was at 1635 m distance of the nearest agricultural field.

Samples were taken from soil, beech leaves and a sample of 90% grass and 10% herbs.

### Results

As shown in the table, in the beech leaves and in the grass/herbs samples were found respectively 7 and 3 different compounds with a total concentration of 27.63 µg/kg DM and 31.45 µg/kg DM. In the soil only the fungicide diphenyl was found with a rather low concentration of 3.9 µg/kg DM. In the sample of grass with herbs diphenylamine was found in a relative high concentration of 25 µg/kg DM. Among the pesticides found in the vegetation samples and used in agriculture, we can mention the herbicides chlorpropham, pendimethalin, propyzamide and prosulfocarb, furthermore the fungicide phenylphenol-2 and fluopyram. The other found compounds diphenylamine, diphenyl and anthraquinone may be released by the industry and /or traffic.

| Reference area Klever Reichswald, NRW | Beech leaves | Grass and herbs | Soil |
|---|---|---|---|
| | µg/kg DM | µg/kg DM | µg/kg DM |
| *Total pesticides µg/kg DM* | 27.63 | 31.45 | 3.92 |
| Insecticides µg/kg DM | 3 | 25 | 0 |
| Fungicides µg/kg DM | 14.87 | 3.45 | 3.92 |
| Herbicides µg/kg DM | 8.36 | 3 | 0 |
| Repellent µg/kg DM | 0 | 0 | 0 |
| Number of different pesticides | 7 | 3 | 1 |

### Overall contamination

Although the soil is rather clean, the leaves are clearly contaminated with pesticides originating from agricultural and industrial activities. The found pesticides must be released into the environment from treated fields at larger distances. The found concentration of diphenylamine in grass and herbs is remarkable since the compound is banned as pesticide and biocide. Until 2012 diphenylamine was employed in the EU as insecticide, fungicide, antihelmintic and grow regulator. The compound is currently still used in the industry.

## RESULTS AND DISCUSSION OF MEASUREMENTS IN BUFFER AREAS

### Buffer area: Egelsberg1 and Egelberg2, NRW

In the nature reserve Egelsberg five insect traps were installed by EVK in transect. For this research 3 locations were sampled, but the analyses results are presented in different sections of this report, because locations where pesticides are applied cannot be compared with locations where they aren't applied. The location Egelsberg3, is situated in a protected area and those analyses results are presented in the section protected natures reserves (earlier in this appendix). Because the locations Egelsberg1 and 2 were sawn with coated winter wheat, those two locations were considered as buffer areas of the protected nature reserves.

Egelsberg1
Code of location: EBK1-7/11/19
Coordinates: W 51.38735 L 6.58819
Egelsberg2
Code of location: EBK2-7/11/19
Coordinates: W 51.38729 L 6.58734

The soil of these two locations was sandy. Winter wheat and some germinating herbs were growing. The adjacent field of EBK1 was under fallow. It was visible that rabbits and/or hares consume the young wheat.

Samples were taken from EBK1 parallel to the field edge, from soil and from the entire wheat plant (approximately 10 cm in the third leave stage, inclusive seed and roots).

Samples were taken from EBK2 from soil, from the entire wheat plant (approximately 10 cm in the third leave stage, inclusive seed and roots) and from rabbit droppings.

An extra sample of the droppings was taken for counting the beetles.

Results

In the wheat samples from the two sampled locations many pesticides and high concentrations were found: in EBK1 and EBK2 respectively 18 and 24 different compounds with a total concentration of 1079 µg/kg DM and 825 µg/kg DM. As the table shows, the majority of the pesticides found are fungicides. In EBK1 two insecticides and 3 herbicides, in EBK2 one insecticide and 2 herbicides were detected. In EBK1 the highest concentration of the fungicide in the wheat sample was fluoxastrobin (673 µg/kg DM) and in the wheat sample from EBK2 fludioxonil (791 µg/kg DM).

In the soil sample of the two locations many compounds (resp. 8 and 12) were detected, but with a concentration slightly above the average concentration of the soils from the protected nature reserves. In the rabbit droppings 8 compounds with a total concentration of 41.6 µg/kg DM were found. Except chlorpropham all compounds were also present in the wheat. Diphenyl, anthraquinone and prosulfocarb showed the highest concentrations. Antrhaquinone, diphenyl, diflufenican and fludioxonil were detected in all samples. In the rabbit droppings 39 beetles were counted (Aphodius sphacelatus(50%). Aphodius prodromus (33%) and Aphodius distinctus (17%).

Overall contamination

The wheat seed of the two locations showed a bright red colour, indicating that the seeds were coated with pesticides.

The fungicides with the found high concentrations, such as fluoxastrobin, fludioxonil, Prothioconazole, difenaconazole, metalaxyl, are also applied for seed coating. In order to avoid resistance development of plant parasitic fungi, the seeds are often coated with several fungicides. The two locations had been sown by two different farmers and therefore it might explain the fact that in the two vegetation samples of wheat two different fungicides were discovered. The herbicide methabenzthiazuron, found in the wheat and soil of EBK1, is in the EU not approved. Possibly the farmers of these locations don´t spray pesticides, however by using coated seed several pesticides enter the soil. The roots and plants take up the fungicides; hence also the wheat above the ground will be contaminated. It can be assumed that crops with these high amounts and number of different pesticides will not contribute to effective nature conservation. It can also be assumed that seeds coated with high concentrations of several fungicides will have very negative impact on the health of the soil and of the wild animals living there. Despite the exposure of many pesticides to rabbits and hares, moderate concentrations of fungicides and beetles were found in the droppings. The long-term effects of the found compounds on the health, the reproductive capacity and development of rabbits and insects are not known.

| Egelsberg, NRW | EBK1 | EBK1 | EBK2 | EBK2 | EBK2 |
|---|---|---|---|---|---|
| Compound | Winter wheat | Soil | Winter wheat | Soil | Rabbit droppings |
| | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| Anthraquinone | 13.0 | 10.0 | 10.0 | 8.0 | 6.5 |
| Chlorpropham | | 1.0 | | 1.0 | 2.8 |
| Chlortoluron | | | | 2.0 | |
| Cypermethrin | 3.8 | | | | |
| Dichlobenil | | | | 1.5 | |
| Difenoconazole | 57.8 | | 1.0 | | |
| Diphenyl | 6.7 | 4.0 | 8.9 | 4.0 | 17.5 |
| Diphenylamine | 1.0 | | 1.0 | | |
| Diflufenican | 2.0 | 2.0 | 4.0 | 3.0 | 1.6 |
| Epoxiconazole | | | 0.8 | 0.8 | |
| Fludioxonil | 288.0 | 1.0 | 791.0 | 1.0 | 3.4 |
| Fluoxastrobin | 673.0 | | | | 3.8 |
| Flusilazole | | | 1.0 | 1.0 | |
| Hexachlorobenzene | 2.0 | | 2.0 | 2.3 | |
| Metalaxyl | | | 9.0 | | |
| Methabenzthiazuron | 6.0 | 6.3 | | | |
| Pencycuron | | | | 1.0 | |
| Pendimethalin | 3.0 | 2.0 | 3.0 | 3.0 | |
| Phthalimide (Met. Folpet) | detected | 2.0 | detected | | 1.6 |
| Prochloraz | 3.1 | | | | |
| Prosulfocarb | 1.0 | | | | 4.3 |
| Prothioconazole-Desthio | 22.1 | | | | |
| Pyrimethanil | 2.9 | | | | |
| Tebuconazole | 1.0 | | 1.0 | | |
| | | | | | |
| Total pesticides µg/kg DM | 1086.22 | 28.21 | 832.7 | 28.58 | 41.6 |
| Insecticides µg/kg DM | 4.79 | 0 | 1 | 0 | 0 |
| Fungicides µg/kg DM | 1056.43 | 8.96 | 810.70 | 6.10 | 23.3 |
| Herbicides µg/kg DM | 12 | 11.25 | 7 | 10.48 | 10.6 |
| Repellent µg/kg DM | 13.0 | 10.0 | 10.0 | 8.0 | 6.5 |
| Number of different pesticides | t 18 | 8 | 14 | 12 | 8 |

## Buffer area Brauselay, Rheinland-Pfalz

Brauselay is a nature reserve in a slope area, on the right side of the river Mosel, district Cond in Cochum. In 2019 three insect traps (MF) at different heights of the slope in a wine growing area were installed by EVK. Out of the three MF locations the lowest and the highest locations were sampled, because the middle one with MF was not accessible.

Due to the conventional wine cultivation, in this study the two sampled locations were considered as buffer areas. The soil of the locations was very rocky and only a depth up to 12 cm was permeable.

## Brauselay1 (downhill, altitude 97 m)

Code of location: BL1-20/11/19

Coordinates: W 50.14185 L 7.18753

The sampled location Brauselay1 was at the border of the wine yard, at 65 m distance of the river Mosel. The following herbs and bushes were growing: old mans beard (Clematis vitalba), blackberry (Rubus fruticosus), raspberry (Rubus idaeus), dog rose (Rosa canina), wild strawberry (*Fragaria vesca), oregano* (*Origanum vulgare).* A walking route crossed the area. Samples were taken from blackberry (stalk with leaves), fallen grape leaves (that were blown in by the wind) and soil.

## Brauselay3 (uphill, altitude 131 m)

Code of location: BL3-20/11/19

Coordinates: W 50.14217 L 7.18808

The distance between Brauselay1 and 3 is in bird´s eye view 50 m. The vegetation and soil of both locations is similar. Samples were taken from blackberry (stalk with leaves) and soil

Results

As shown in the table, there were some remarkable results: in BL1 the two vegetation samples were heavily contaminated with many different fungicides and the soil in BL1 and BL3 was heavily contaminated with DDT and its metabolites. In the grape leaves and in the blackberry from BL1 respectively 29 and 24 different compounds with a total concentration of 160264 µg/kg DM and 1082 µg/kg DM was found. In the soil of BL1 36 different compounds with a total concentration of 2440 µg/kg DM were detected. Among the 22 different fungicides found in the grape leaves the highest concentration had ametoctradin (140 mg/kg DM) and dimethomorph (12.2 mg/kg DM). These two active compounds can be found combined in formulations (products for the market). In the grape leaves several other fungicides were found in concentrations around 1 mg/kg DM. Most of the pesticides in the grape leaves were also detected in the soil and in the blackberry, however with some exceptions. In general, the concentrations in blackberry were much lower. There was one compound dithianon, that was only found (in the high concentration of 504.3 µg/kg) in blackberries and not in the grape leaves or in the soil.

In all samples from BL1 and BL3 the compounds ametoctradin, anthraquinone, chlorpropham, diphenyl and procymidon were found. In the location BL3 less compounds and lower concentrations were found in the vegetation and in soil than in BL1. In the blackberry in 8 different compounds with in total 41.0 µg/kg DM were found and in the soil sample 19 compounds with in total 1415.5 µg/kg DM. In the soil sample from both locations more than one milligram of the extremely persistent insecticides DDT and its metabolites, aldrin and dieldrin were found. Partly these insecticides were found in the vegetation. Since 47 years these insecticides are banned. These compounds are residues from application long ago.

### Overall contamination

The mass of fungicides, the high concentration of persistent insecticides mainly results from pesticides application in the wine yards. Out of the 22 different found fungicides in the soil of BL1 20 fungicides stem with a high probability from application in wine yards. The buffer zone is so polluted that there is a risk that it will affect insect conservation in the nearby nature reserve. The wine leaves contain five fungicides in quantities above 1 mg/kg dry matter. Probably the reason for this is that the owner tries to avoid build-up of resistant fungal strains on the grapes.

| Brauselay, Rheinland-Pfalz Compound | BL1 | BL1 | BL1 | BL3 | BL3 |
|---|---|---|---|---|---|
| | Blackberry | Grape leaves | Soil | Blackberry | Soil |
| | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *Aldrin* | | | 4.0 | | 2.0 |
| *Ametoctradin* | 414.4 | 140000.0 | 4.5 | 10.4 | 4.8 |
| *AMPA* | | | 7.2 | | |
| *Anthraquinone* | 2.1 | 7.9 | 22.0 | 2.1 | 12.0 |
| *Azoxystrobin* | | | 3.0 | | |
| *Boscalid* | | 132.8 | 722.0 | | 1.3 |
| *Carbendazim* | | | | | 1.6 |
| *Chlorpropham* | 4.5 | 2.0 | 1.0 | 3 | 1.0 |
| *Cyazofamid* | 5.4 | 369.6 | | | |
| *Cyflufenamid* | 4.1 | 70.1 | 1.7 | | |
| *Cyprodinil* | | 7.0 | 5.0 | | |
| *Dichlobenil* | | | 8.2 | | 6.1 |
| *Dicofol* | | | 7.0 | | 6.0 |
| *Dieldrin* | 2.2 | 10.4 | 133.0 | | 68.0 |
| *Difenoconazole* | 5.5 | 167 | 5.0 | | |
| *Dimethomorph* | 55 | 12200.0 | 131.0 | | |
| *Diphenyl* | 14.3 | 12.2 | 3.6 | 11.4 | 1.8 |

| Brauselay, Rheinland-Pfalz Compound | BL1 | BL1 | BL1 | BL3 | BL3 |
|---|---|---|---|---|---|
| | Blackberry | Grape leaves | Soil | Blackberry | Soil |
| | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM | µg/kg DM |
| *Dithianon* | 504.3 | | | | |
| *Fenarimol* | | | 5.0 | | |
| *Fenpyrazamine* | | | 1.8 | | |
| *Fludioxonil* | | 6.0 | 24.0 | | |
| *Fluopicolide* | 3.6 | 969.0 | 80.8 | | |
| *Fluopyram* | 3 | 1330.0 | 85.4 | | |
| *Fluquinconazole* | | | 1.5 | | |
| *Fluxapyroxad* | 7.3 | 2720.0 | 49.8 | | |
| *Glyphosate* | | | 0.428 | | |
| *Iprodion* | | | | | 1.6 |
| *Metrafenon* | 10.9 | 832.9 | 72.1 | | |
| *Myclobutanil* | | 1.7 | 21.0 | | |
| *o.p'-DDD* | | | 34.0 | | 15.0 |
| *o.p'-DDE* | 10.4 | | 6.0 | | 3.0 |
| *p.p'-DDD + o.p'-DDT* | 1.9 | 6.5 | 198.4 | | 112.0 |
| *p.p'-DDE* | | 55.2 | 654.0 | 2.1 | 388.0 |
| *p.p'-DDT* | | 63 | 50.4 | | 786.5 |
| *Penconazole* | 1.9 | 39 | 12.9 | | |
| *Pendimethalin* | 1.9 | 2.9 | | | |
| *Phthalimide (Met. Folpet)* | 17.0 | 757 | | 6 | 0.5 |
| *Procymidon* | 3.2 | 7.6 | 3.3 | 4.8 | 3.3 |
| *Proquinazid* | 4.9 | 18.6 | | | |
| *Prosulfocarb* | 1.2 | 1.7 | | 1.2 | |
| *Quinoxyfen* | | 3.6 | 34.0 | | |
| *Tebuconazool* | 1.4 | 145.6 | 31.0 | | |
| *Tetraconazole* | 2.0 | 354.5 | 23.3 | | |
| *Tetradifon* | | | 2.0 | | 1.0 |
| | | | | | |
| *Total pesticides µg/kg DM* | 1082.3 | 160293.8 | 2449.3 | 41.0 | 1415.5 |
| *Insecticides µg/kg DM* | 14.44 | 124.67 | 1088.8 | 2.08 | 1381.96 |
| *Fungicides µg/kg DM* | 1058.13 | 160116.0 | 1307.7 | 26.79 | 7.92 |
| *Herbicides µg/kg DM* | 7.57 | 6.56 | 16.77 | 4.19 | 7.12 |
| *Repellent µg/kg DM* | 2.1 | 7.9 | 22.0 | 2.1 | 12.0 |
| *Number of different pesticides* | 24 | 29 | 36 | 8 | 19 |

The soil of Brauselay was among the samples of this study by far the most contaminated, except for Pommern2 (also located in the Mosel valley). However, it needs to be said that the total pesticide content of 2449.3 µg/kg is quite normal for arable soils (unpublished data). It is remarkable that the blackberries growing on this location are, compared with the soil, very clean. They seem to be able to take up nutrients from the soil and keep the largest part of the pesticides out of their tissues. Another positive observation of this location is that the AMPA content of the soil is very low (7.2 µg/kg) and of glyphosate even lower. It is clear that this herbicide has seldom been used in the wine yards. Of this location insect MF catches will become only available of the year 2020 in the framework of the DINA project.

## Buffer area Pommern2, Rheinland-Pfalz

The sampled location in the nature reserve Pommern is located 150 m from the river Mosel, 10 km west of the city Pommern, and belongs to the district Cond in Cochem. There used to be many wine yards.

In this area the EVK installed 2 MF. For this study only one location was sampled, the other was not accessible.

The vegetation is divers – amongst others, the European spindle (*Euonymus europaeus*) was growing. The soil of the location was very rocky and only a depth up to 10 cm was permeable.

Code of location: PM2-20/11/19

Coordinates: W 50.16995 L 7.24068

Samples were taken from blackberry (whole stem) and soil.

Results

In particular the soil of this sampled location is very contaminated with many pesticides. In the soil 42 different pesticides were found with a total concentration of 6742 µg/kg DM and in the black berry 10 different pesticides with a total concentration of 42.50 µg/kg DM. The pesticide concentration of the black berry is approximately the average of in this study other investigated vegetation samples. Diphenyl showed in the black berry sample the highest concentration.

Despite the total concentration is moderate, the very toxic metabolite of DDT and the very toxic insecticide etofenprox were present in this sample.

In the soil were found a total concentration of 6365 µg/kg DM the very persistent and toxic insecticides: aldrin, dieldrin, beta-endosulfan, dieldrin, DDT and several metabolites (DDE, DDD), lambda cyhalothrin, and the persistent acricides tetradicfon and dicofol (moderately persistent). Since decennia are most of these insecticides (e.g. DDT, aldrin, dieldrin) banned and therefore these compounds are remains from historical application. The majority of the other found compounds were fungicides; it is likely that they came by drift (e.g. diphenyl), partly from historical application (e.g. the persistent compounds boscalid, quinoxifen).

From all investigated soil sampled of this study, the soil from Pommern2 was the most contaminated.

Overall contamination

Although the sampled location is assigned as protected area, the soil is very polluted by the use of pesticide in earlier times. Probably it will take more than hundreds of years before the contamination is not measurable anymore. This location is so polluted that the expectation of an effective insect conservation is very low. Nothing is known about the effects of the mixtures and the metabolites of the more than 40 different found compounds on the survival, neither on the reproduction and the development of the insect fauna.

Of this location MF biomass catches will become only available of the year 2020 in the framework of the DINA project. It is remarkable that though the soil of this location is even more polluted than that of Brauselay1, the pesticide content of the blackberries is almost the same (42.5 µg/kg DM ) as in Brauselay1 (41 µg/kg DM ). The astronomically high content of DDT (5478.2 µg) in the soil might be explained by the fact that this location had been abandoned earlier as wine yard. In the more recently abandoned wine yard (of Brauselay1), the DDT and other pesticide residues might have partially washed away with erosion into the river Mosel. In abandoned wine yards erosion is as a rule very low, so the residues are better conserved. In the soil of this location an exceptionally high content of anthraquinone was found (107.0 µg/kg dry matter). At this moment we have no explanation for this measurement.

| Pommern2, Rheinland-Pfalz | Blackberry | Soil |
|---|---|---|
| Compound | µg/kg DM | µg/kg DM |
| *Aldrin* | | 2.0 |
| *Ametoctradin* | | 2.1 |
| *AMPA* | | 43.7 |
| *Anthraquinone* | 2.00 | 107.0 |
| *Azoxystrobin* | | 1.3 |
| *Beta-Endosulfan* | | 1.0 |
| *Boscalid* | | 44.9 |
| *Carbendazim* | | 1.5 |
| *Chlorpropham* | 2.00 | 1.0 |
| *Cyprodinil* | 6.00 | 7.0 |
| *Dichlobenil* | | 4.1 |
| *Dicofol* | | 13.0 |

| Pommern2, Rheinland-Pfalz | Blackberry | Soil |
|---|---|---|
| Compound | µg/kg DM | µg/kg DM |
| *Dieldrin* | | 246.0 |
| *Diphenyl* | 12.50 | 9.1 |
| *Dimethomorph* | | 29.6 |
| *Endosulfan-Sulfaat* | | 5.0 |
| *Etofenprox* | 3.00 | |
| *Fenarimol* | | 3.0 |
| *Phenylfenol-2* | | 1.4 |
| *Fludioxonil* | 3.00 | |
| *Fludioxonil* | | 7.0 |
| *Fluopicolide* | | 1.1 |
| *Fluquinconazole* | | 2.4 |
| *Phthalimide (Met. Folpet)* | 6.00 | 1.6 |
| *Glyphosate* | | 3.07 |
| *Iprodion* | | 3.1 |
| *Lambda-Cyhalothrin* | | 0.7 |
| *Methabenzthiazuron* | | 1.0 |
| *Metrafenon* | | 14.7 |
| *Myclobutanil* | | 24.0 |
| *o,p'-DDD* | | 22.0 |
| *o,p'-DDE* | | 5.0 |
| *p,p'-DDD + o,p'-DDT* | | 176.7 |
| *p,p'-DDE* | 2.00 | 414.0 |
| *p,p'-DDT* | | 5478.2 |
| *Penconazole* | | 1.3 |
| *Pendimethalin* | 3.00 | |
| *Procymidon* | 5.00 | 12.4 |
| *Pyrifenox* | | 2.0 |
| *Quinoxyfen* | | 21.0 |
| *Tebuconazole* | | 26.0 |
| *Tetradifon* | | 1.0 |
| *Tolylfluanid* | | detected |
| *Vinchlozolin* | | 1.0 |
| | | |
| *Total pesticides µg/kg DM* | 42.50 | 6742.1 |
| *Insecticides µg/kg DM* | 5.04 | 6364.58 |
| *Fungicides µg/kg DM* | 32.5 | 207.62 |
| *Herbicides µg/kg DM* | 4.99 | 52.86 |
| *Repellent µg/kg DM* | 2.00 | 107.0 |
| *Number of different pesticides* | 10 | 42 |

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