Pesticides and transformation products in ambient air at source regions and their atmospheric transport to the Atlantic Ocean

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Popular science

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Eine Wissenschaftlerin im Kampf gegen die Pestizidbelastung. Article in the National Geographic magazine, January 2024

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List of abbreviations

AChE ..... Acetylcholinesterase
ADI ..... Acceptable Daily Intake
ASE ..... Accelerated solvent extraction
B ..... Bioaccumulation
BTs ..... Back trajectories
CCE ..... Cold-column extraction
CSS ..... Case study site
CUPs ..... Currently used pesticides
DCM ..... Dichloromethane
DDT ..... Dichlorodiphenyltrichloroethane
DIRs ..... Daily Inhalation Rates
DNA ..... Deoxyribonucleic acid
d-SPE ..... Dispersive solid phase extraction
EU ..... European Union
GC-MS ..... Gas chromatography coupled to mass spectrometry
GFF ..... Glass-fibre filter
GHS ..... Globally Harmonized System of Classification and Labelling of Chemicals
HCB ..... Hexachlorobenzene
HRMS ..... High-resolution mass spectrometry
HVAS ..... High-volume air samplers
K_{oa} ..... Octanol-air partition coefficient
LC-MS ..... Liquid chomatography coupled to mass spectrometry
LRAT ..... Long-range atmospheric transport
LRT ..... Long-range transport
LVAS ..... Low-volume air sampler
MDL ..... Method detection limit
$MgSO_4$ ..... Magnesium sulfate
MOE ..... Margin of exposure
MQL ..... Method quantification limit
NO_3 ..... Nitrate
O3 ..... Ozone
OCPs ..... Organochlorine pesticides
OECD ..... Organisation for Economic Co-operation and Development
OH ..... Hydroxyl
P ..... Persistence
PAS ..... Passive air sampler
PFAS ..... Per-and polyfluoroalkyl substances
PM 10 ..... Particulate matter with diameters of 10 µm or smaller
PM 2.5 ..... Particulate matter with diameters of 2.5 µm or smaller
POPs ..... Persistent organic pollutants
PSA ..... Primary secondary amine
PUF ..... Polyurethane foam
QFF ..... Quartz-fibre filter
QqQ ..... Triple quadrupole mass spectrometer
QuEChERS ..... Quick, Easy, Cheap, Effective, Rugged and Safe
RSD ..... Relative standard deviation
S/N ..... Signal-to-noise
SPE ..... Solid-phase extraction
SPRINT ..... Sustainable Plant Protection Transition: A Global Health Approach
T ..... Toxicity
TFA ..... Trifluoroacetate

TOF ..... Time-of-flight mass spectrometry
TP ..... Transformation product
vPvM ..... Very persistent and very mobile
WP ..... Work package

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1. Abstract

Pesticides are a group of chemicals used to prevent crops from pests, diseases, and weeds. They are widely applied in conventional agriculture. During or after application, they can be emitted into the atmosphere due to spray drift, volatilization or wind erosion. There, they can be transported by the wind over long distances and be deposited in regions far away from their sources. Organochlorine pesticides (OCPs) have been banned or restricted since the 1970s due to their persistence, bioaccumulation, toxicity, and long-range transport potential. Therefore, so-called currently used pesticides (CUPs) received more attention and replaced and complemented the restricted OCPs. However, the environmental occurrence and fate as well as potential adverse effects on human health or the environment are mostly unknown for these CUPs. In addition, studies on airborne pesticides had only covered a small number of CUPs and a high number of them is not monitored in the atmosphere. This raises the question, to what extent CUPs can be distributed and transported in the atmosphere.

This thesis aimed at identifying and quantifying currently used pesticides and transformation products (TPs) that are of relevance in the atmosphere across agricultural areas in Europe as well as their potential long-range transport to the marine atmosphere of the Atlantic Ocean. In addition, potential adverse human health effects were evaluated based on measured concentrations and calculated Daily Inhalation Rates (DIRs).

To achieve these aims, analytical methods for the determination of 329 OCPs, CUPs and TPs in the particulate and gaseous air phase were developed, optimized, and validated. The instrumental analysis was performed on a liquid chromatograph coupled to a time-of-flight mass spectrometer (LC-QTOF) and a gas chromatograph coupled to a triple quadrupole mass spectrometer (GC-QqQ). Different extraction methods were compared for the extraction of glass-fibre filters (GFFs, particle-bound pesticides) and PUF/XAD-2 columns (gaseous pesticides). GFFs were extracted using a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction with Milli-Q water/acetonitrile (1:2). PUF/XAD-2 columns were extracted using a cold-column extraction for air samples from agricultural areas. For the extraction of air samples from the Atlantic Ocean, the extraction method for the PUF/XAD-2 columns was further optimized to reduce matrix effects and method detection limits. A QuEChERS-like extraction was used for these samples. Method detection limits were in the pg/m³ range for both, particle-bound and gaseous pesticides. Therefore, the method was suitable for the determination of pesticides in higher concentrations across agricultural areas as well as background concentrations in the marine atmosphere. Samples were collected using high-volume air samplers (HVAS) equipped with GFFs and PUF/XAD-2 columns at two agricultural areas in Europe (Portugal and

the Netherlands) within the European Union (EU) funded project SPRINT and on board the research vessel *Polarstern* on a cruise between South America and Europe in 2023.

99 different pesticides and transformation products were detected in the air across agricultural areas in Europe in the pg/m³ to ng/m³ range. 11 of these were detected in the atmosphere for the first time. In 95 % of the air samples, multiple pesticides were detected with a maximum number of 34 pesticides per sample. To investigate potential human health effects, DIRs were calculated for individual pesticides and pesticide mixtures. DIRs were below the Acceptable Daily Intake (ADI) with a margin of exposure (MOE) of > 1000 for the highest calculated DIR. However, the ADI only includes the intake by food and drinking water and does not include the intake by inhalation. As 91 % of the detected pesticides were associated with potential adverse health effects, the intake via different routes could sum up for individual pesticides or pesticide mixtures and thereby potentially cause human health effects.

In addition, 22 pesticides were detected in the air across the Atlantic Ocean in the pg/m³ range. 15 CUPs and 4 TPs were found for the first time in the marine atmosphere across the Atlantic Ocean. Most of these compounds have calculated atmospheric half-lives below two days, which is why they have not been expected to be transported over longer distances. However, for 12 CUPs and 4 TPs, first evidence could be given for a potential long-range transport. For the determination of potential sources, air mass back trajectories were calculated. For most samples, an influence of marine air masses was found. Higher pesticide concentrations in the northern hemisphere compared to the southern hemisphere were found to occur from air masses originating from agricultural areas in Europe.

The results from the air samples from agricultural areas as well as from the Atlantic Ocean reveal that CUPs are present in the atmosphere and can potentially undergo long-range transport. This data is important to feed and validate environmental fate and exposure models to investigate potential adverse effects of CUPs and their TPs. In addition, the results highlight the need for further atmospheric pesticide studies that cover a high number of compounds in remote areas to gain more information on their atmospheric transport potential. For this, future studies should also include suspect or non-target screening using high-resolution mass spectrometers to identify pesticides of potential concern and to include the >2000 active substances currently registered for use worldwide.

2. Zusammenfassung

Pestizide sind Chemikalien, die zum Schutz von Pflanzen vor Schädlingen und Krankheiten eingesetzt werden. Sie sind in der konventionellen Landwirtschaft weit verbreitet und können während oder nach der Anwendung durch Sprühdrift, Verdampfung oder Winderosion in die Atmosphäre gelangen. In der Atmosphäre können sie mit dem Wind transportiert werden und sich in Regionen weit entfernt von ihrer Quelle ablagern. Organochlorpestizide (OCP) wurden seit den 1970er Jahren aufgrund ihrer Persistenz, Bioakkumulation, Toxizität und ihres Potenzials zum Langstreckentransport verboten oder eingeschränkt. Dadurch wurden die derzeit verwendeten Pestizide (*currently used pesticides*, CUPs) relevanter und ersetzten bzw. ergänzten die reglementierten OCPs. Das Vorkommen und der Verbleib in der Umwelt, sowie die potentiellen schädlichen Auswirkungen auf die menschliche Gesundheit oder die Umwelt, sind für die meisten CUPs jedoch weitestgehend unbekannt. Darüber hinaus haben bisherige Studien zu Pestiziden in der Luft nur eine kleine Anzahl von CUPs abgedeckt. Eine große Anzahl an CUPs wurde in der Atmosphäre bisher kaum oder gar nicht untersucht. Dies wirft die Frage auf, inwieweit CUPs in der Atmosphäre verbleiben und über längere Strecken transportiert werden können.

Ziel dieser Arbeit war es, derzeit verwendete Pestizide und Transformationsprodukte (TPs), die in landwirtschaftlichen Gebieten in Europa von Bedeutung sind, in der Atmosphäre zu identifizieren und zu quantifizieren. Zudem wurde untersucht, ob diese Substanzen in die Meeresatmosphäre des Atlantischen Ozeans transportiert werden. Darüber hinaus wurden basierend auf den gemessenen Konzentrationen und berechneten täglichen Inhalationsraten (DIRs) mögliche negative Auswirkungen auf die menschliche Gesundheit untersucht.

Um diese Ziele zu erreichen, wurden zunächst Analysemethoden für die Bestimmung von 329 OCPs, CUPs und TPs in der partikulären und gasförmigen Phase der Luft entwickelt, optimiert und validiert. Die instrumentelle Analyse wurde zum einen mit einem Flüssigkeitschromatographen, gekoppelt mit einem Flugzeit-Massenspektrometer (LC-QTOF) und zum anderen mit einem Gaschromatographen, gekoppelt an ein Triple-Quadrupol-Massenspektrometer (GC-QqQ), durchgeführt. Für die Extraktion von Glasfaserfiltern (GFFs, partikelgebundene Pestizide) und PUF/XAD-2-Säulen (gasförmige Pestizide) wurden unterschiedliche Extraktionsmethoden verglichen. Die GFFs wurden mittels einer Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS)-Extraktion mit Milli-Q Wasser/Acetonitril (1:2) extrahiert. Bei den PUF/XAD-2-Säulen wurde eine Kaltextraktion für die Luftproben, die in landwirtschaftlichen Gebieten in Europa genommen wurden, verwendet. Für die Extraktion von Luftproben über dem Atlantischen Ozean wurde die Extraktionsmethode für die PUF/XAD-2-Säulen weiter optimiert, um Matrixeffekte und die Nachweisgrenzen der Methode zu verringern. Diese Proben wurden mit einer auf QuEChERS basierenden Methode extrahiert. Die Nachweisgrenzen der Methode

lagen sowohl für partikelgebundene als auch für gasförmige Pestizide im pg/m³-Bereich. Daher ist die entwickelte Methode sowohl für die Bestimmung von Pestiziden in höheren Konzentrationen in landwirtschaftlichen Gebieten als auch für die Untersuchung von Hintergrundkonzentrationen in der Meeresatmosphäre geeignet. Die Proben wurden im Rahmen des von der Europäischen Union (EU) finanzierten Projekts SPRINT an zwei landwirtschaftlichen Standorten in Europa (Portugal und den Niederlanden), sowie an Bord des Forschungsschiffs *Polarstern* auf einer Seereise zwischen Südamerika und Europa mit Hilfe großvolumiger Luftsammler genommen.

99 unterschiedliche Pestizide und Transformationsprodukte wurden in der Luft in den untersuchten landwirtschaftlichen Gebieten in Europa im pg/m³ bis ng/m³-Bereich nachgewiesen. 11 dieser Substanzen konnten zum ersten Mal in der Luft nachgewiesen werden. In 95 % der Luftproben wurden mehrere Pestizide nachgewiesen, wobei die maximale Anzahl an Pestiziden pro Probe bei 34 Pestiziden lag. Um mögliche Auswirkungen auf die menschliche Gesundheit zu untersuchen, wurden die DIRs für einzelne Pestizide sowie Pestizidmischungen berechnet. Die DIRs lagen unter der zulässigen täglichen Aufnahmemenge (ADI), wobei die höchste berechnete DIR einen Margin of Exposure (MOE) von > 1000 aufwies. Der ADI-Wert umfasst jedoch nur die Aufnahme über Lebensmittel und Trinkwasser. Eine Aufnahme durch Inhalation ist hingegen in diesem Wert nicht berücksichtigt. Da 91 % der nachgewiesenen Pestizide mit potenziell gesundheitsschädlichen Effekten in Verbindung gebracht wurden, könnte sich die Aufnahme über verschiedene Wege für einzelne Pestizide oder Pestizidmischungen summieren und sich dadurch potenziell auf die menschliche Gesundheit auswirken.

Zudem wurden 22 Pestizide in der Luft über dem Atlantischen Ozean im pg/m³-Bereich nachgewiesen. 15 CUPs und 4 TPs wurden zum ersten Mal in der Meeresatmosphäre über dem Atlantischen Ozean gefunden. Die meisten dieser Verbindungen besitzen eine berechnete atmosphärische Halbwertszeit von weniger als 2 Tagen, weshalb ein Langstreckentransport für diese Substanzen nicht erwartet wurde. Für 12 CUPs und 4 TPs konnten jedoch erste Hinweise auf einen möglichen Langstreckentransport gefunden werden. Um mögliche Quellen der gefundenen Pestizide zu bestimmen, wurden Rückwärtstrajektorien berechnet. Diese ergaben für einen Großteil der Proben einen Einfluss durch marine Luftmassen. Zudem wurden höhere Pestizidkonzentrationen auf der Nordhalbkugel im Vergleich zur Südhalbkugel gefunden, welche durch einen Einfluss der Luftmassen aus landwirtschaftlichen Gebieten in Europa stammen können.

Die Ergebnisse der Luftproben aus landwirtschaftlichen Gebieten und dem Atlantischen Ozean zeigen, dass CUPs in der Atmosphäre präsent sind und potenziell über lange Strecken transportiert werden können. Diese Daten sind wichtig, um Schadstoffausbreitungsmodelle und Expositionsmodelle zu speisen und zu validieren. Damit können potenziell schädliche Auswirkungen von CUPs und ihren TPs

weiter untersucht werden. Zudem zeigen die Ergebnisse, dass weitere Studien zu Pestiziden in der Luft erforderlich sind, die eine große Anzahl an Pestiziden in abgelegenen Gebieten untersuchen. Dadurch können mehr Informationen über ihren potenziellen Langstreckentransport erhalten werden. Hierzu sollten künftige Studien auch Suspect oder Non-target Screening mittels hochauflösender Massenspektrometrie nutzen. Damit könnten potenziell bedenkliche Pestizide oder Transformationsprodukte aus den mehr als 2000 weltweit für die Verwendung registrierten Substanzen identifiziert werden.

3. Introduction

Pesticides are substances used to prevent crops from pests or diseases. They have been extensively used in agriculture with increasing quantities and number of compounds applied on fields over the last decades, reaching 3.70 million metric tons of global pesticide use in 2022 [1]. Rising temperatures due to climate change are expected to further increase the application of pesticides in the future due to increasing volatilization rates, degradation, and an increasing number of different pests [2, 3]. In the past, adverse effects of pesticides on the environment [4-7] and on human health [8-11] as well as decreasing biodiversity due to pesticide use [12, 13] have been reported.

Pesticides are classified according to their mode of action and the organisms on which the action is performed. The main pesticide groups are insecticides, herbicides, and fungicides. Organochlorine pesticides (OCPs), such as the insecticide dichlorodiphenyltrichloroethane (DDT, Figure 1a) or the fungicide hexachlorobenzene (HCB, Figure 1b) have been extensively investigated and regulated. They have been detected in the atmosphere for the first time in the 1960s [14]. Since then, they have been detected in areas where they never had been used, even in remote areas like the world oceans [15-21] and polar regions [22-35]. OCPs have been banned and restricted in industrialised countries since the 1970s but have still been used for vector control in developing countries [22]. Due to their persistence (P), bioaccumulation (B), toxicity (T), and their potential to undergo long-range transport (LRT), they have been included as part of the twelve initial persistent organic pollutants (POPs) in the Stockholm Convention on Persistent Organic Pollutants [36].

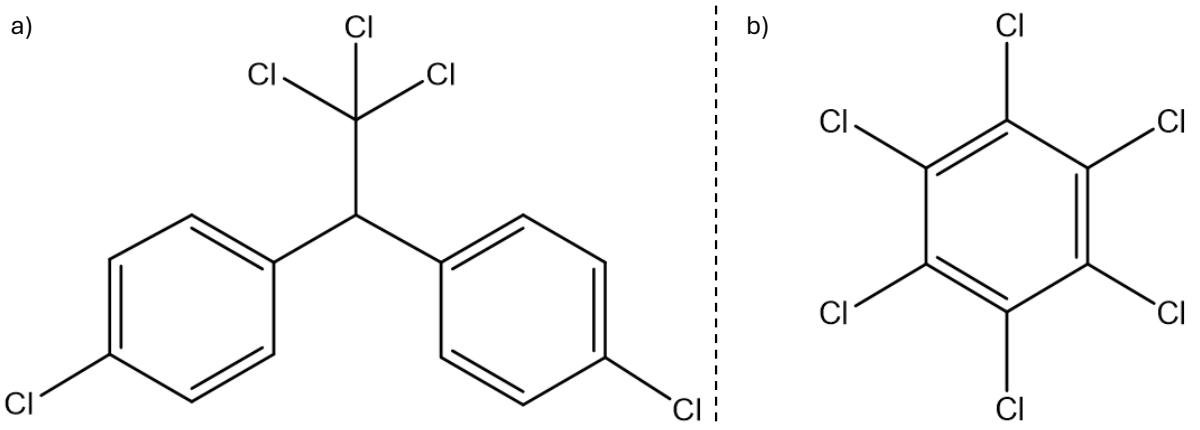

Figure 1: Structural formulas of two organochlorines, a) 4,4'-DDT and b) hexachlorobenzene

Subsequently, the production and use of CUPs received more attention. The group of CUPs includes compounds from a variety of chemical classes, such as carbamate insecticides, organophosphate insecticides, chloroacetanilide herbicides, phenoxyacid herbicides, neonicotinoid insecticides, pyrethroid herbicides, triazole fungicides, and other classes that are inspired by natural products. CUPs

are expected to be less persistent and toxic and to not be prone to long-range atmospheric transport (LRAT) due to their different physical-chemical properties compared to OCPs. However, some CUPs such as the organophosphate insecticide chlorpyrifos (Figure 2a) or the pyrethroid insecticide lambda-cyhalothrin (Figure 2b) have shown to be toxic. Chlorpyrifos affects the nervous system by inhibiting the acetylcholinesterase (AChE) activity and can persist in water or soil [37]. Lambda-cyhalothrin on the other hand could be related to neurotoxicity and reproductive toxicity in non-target organisms by oxidative stress. In addition, some CUPs have been detected in the air at remote areas far away from their application sites such as alpine regions [38-41], national parks [42, 43], the worlds' oceans [20, 21, 44-48], and polar regions [23-25, 49, 50].

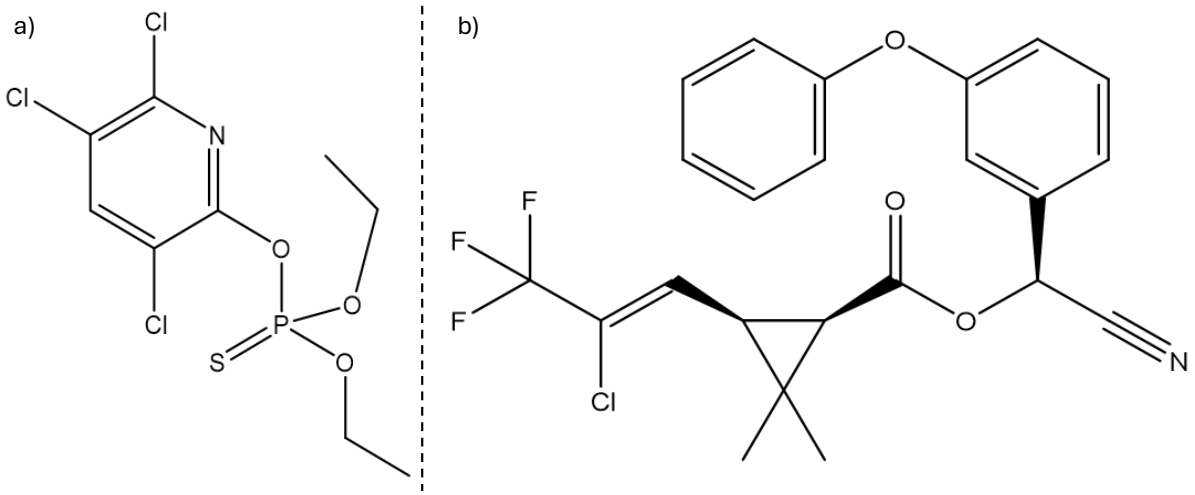

Figure 2: Structural formulas of two currently used pesticides, a) chlorpyrifos and b) lambda-cyhalothrin

3.1 Sources and emission pathways of pesticides

Pesticides in the atmosphere occur mainly from agricultural use as large quantities and high numbers of different compounds are used. Other sources include manufacturing and formulation processes, waste effluents, urban or industrial weed control, the use at parks, gardens, lawns, or golf courses, and large-scale arial spraying for vector control [51].

During and after application, pesticides can be emitted to the atmosphere due to spray drift, volatilization, or wind erosion (see Figure 3). The extent of individual emission pathways depends on the application technique and formulation type, the texture of the ground, the physicochemical properties of the pesticide, and the weather conditions during application. Up to 75 % of the applied pesticides can be emitted to the atmosphere due to spray drift during application [51]. A portion of this deposits within a short distance from the application site, while some pesticides can be carried by the wind over longer distances. This process depends on the aerosol size distribution and the pesticide properties [52]. Another pathway for pesticides to enter the atmosphere is volatilization from soil, water, or plant surfaces. Volatilization is a continuous process and can be the major route for pesticides

into the atmosphere. Losses due to volatilization can reach up to 90 % within three days and depend on the application technique of the pesticide [53, 54]. Pesticides applied on the soil surface are more likely to volatilize than pesticides that are incorporated into the soil. The volatilization from plant surfaces is usually larger than from soil as the plants have a lower adsorption capacity [55]. The third pathway of the emission of pesticides to the atmosphere is the transport of pesticides bound to soil particles by wind erosion [52]. The erosion of the soil is influenced by the horizontal wind speed, precipitation rate, temperature, soil weathering, the cultivation practice, and the particle size distribution of the topsoil [56]. Large particles with particle sizes between 500 to 1,000 µm in diameter tend to roll along the ground. They usually do not become airborne, but they can break down into smaller particles which can become airborne. Particles with particle sizes between 100 and 500 µm diameter are transported by saltation and are generally deposited near the source as they usually don't move vertically above one meter. Particles in the range of 0.002 and 10 µm are the most important particles for wind erosion as they can be suspended in the atmosphere and be transported over longer distances [51, 57]. Pesticides that became airborne can be carried by the wind and deposit in non-target areas due to dry and wet deposition. These compounds can be re-volatilized and re-enter the atmosphere and can be further transported and deposited downwind. This process can be repeated until pesticides are transformed or accumulated and can even continue for decades for very persistent compounds [58].

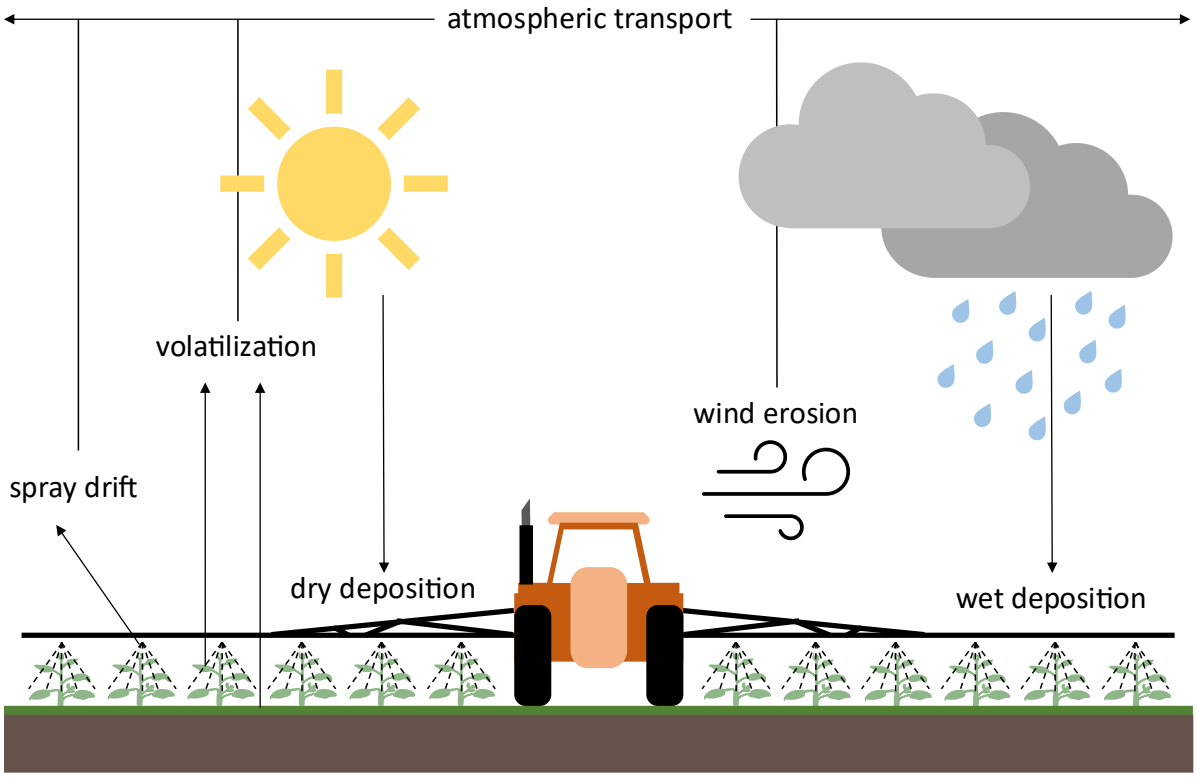

Figure 3: Sources, emission pathways and removal processes of pesticides in the atmosphere

3.2 Fate and distribution of pesticides in the atmosphere

Pesticides in the atmosphere can be distributed between the particulate and gaseous air phase. The factors that influence this distribution are further described in Section 3.2.1. Depending on the distribution and the properties of a compound, it can be removed from the atmosphere by different processes, as described in Section 3.2.2. Chemicals that are not removed from the atmosphere can be transported further away from their source even over long distances to remote areas. Factors that influence the atmospheric long-range transport of a chemical are described in Section 3.2.3.

3.2.1 Phase distribution

When pesticides are emitted into the atmosphere, they partition between the particulate and gaseous air phase. This depends on their physical-chemical properties, such as water solubility, vapor pressure, air-octanol and air-water partition coefficients, and the degradation or transformation reactions [59]. The distribution between the particulate and gaseous phase influences the residence time of a compound in the atmosphere as different removal processes are prevalent for the respective phase and influence the removal from the atmosphere by wet and dry deposition [51]. The partitioning between the particulate and gaseous air phase is described by the octanol-air partition coefficient K_{oa} [60]. Compounds with a higher K_{oa} are more likely to be bound to particles, whereas compounds with lower K_{oa} are more likely to be present in the gaseous phase. In temperate climates, most semi-volatile pesticides are expected to be transported in the gaseous phase and only a small fraction is adsorbed to atmospheric particles [59]. At lower temperatures, the equilibrium tends to shift from the gaseous phase to the particulate phase [60]. The distribution between the particulate and gaseous phase is also relevant for human risk assessment, as smaller particles (PM 2.5 and PM 10) can penetrate deeper into the respiratory system and pesticides that are bound to these particles or are present in the gaseous phase can cause human health issues such as asthma, neurobehavioral disorders, or cancer [9, 61, 62].

3.2.2 Photochemical reactions and deposition

Pesticides can be removed from the atmosphere by different processes. The main removal pathways are the photochemical degradation, wet deposition, and dry deposition. These processes influence the atmospheric residence time of a pesticide. Therefore, the atmospheric residence time of a pesticide is calculated by the following equation [63].

$$\tau_A = \frac{1}{k_{degr} + k_{wet} + k_{dry}}$$

with τ_A = atmospheric residence time / s

k_{degr} = photochemical degradation rate in air / 1/s

k_{wet} = wet deposition rate / 1/s

k_{dry} = dry deposition rate / 1/s

The atmospheric residence time determines the time that a compound can reside in the atmosphere dependent on the removal rates. However, pesticides that have been deposited on the earth's surface on soil, vegetation, or water can re-enter the atmosphere and be transported from place to place until they break down or reach a permanent sink [51]. For the degradation and deposition of a chemical, the distribution between the particulate and gaseous air phase is important, as the removal processes vary between the two phases [64]. Further details on the three main removal processes are given in the following paragraphs.

Photochemical reactions

The photochemical degradation of organic pollutants includes the photolysis and the reaction with hydroxyl (OH) radicals, nitrate (NO_3) radicals, and ozone (O_3) [63]. The dominant atmospheric removal process for pesticides present in the gaseous phase is the reaction with OH radicals [65]. The removal rates by OH radicals are influenced by the sunlight intensity, the OH radical concentration, and the air temperature. Highest OH radical concentrations can be detected during noon. They are 4 to 20 times higher in summer than in winter and are higher at lower latitudes [66]. To calculate the atmospheric residence time from the reaction with OH radicals, the mean global annual OH radical concentration in the atmospheric boundary layer of 5 x 10^5 molecules/cm³ is used [67]. The OH radical reactions with chemicals include (i) a H-atom abstraction from C-H and O-H bonds in saturated organic compounds, (ii) the OH radical addition to >C=C< and -C≡C- unsaturated bonds, (iii) the OH radical addition to aromatic rings, and (iiii) the OH radical interaction with -NH_2, >NH, >N-, -SH, and -S groups [65]. The removal of a chemical by the reaction with NO_3 radicals or ozone is only relevant for some specific compounds, such as unsaturated hydrocarbons and aromatics [68]. This reaction can be relevant in polluted urban atmosphere during night-time hours when high NO_3 concentrations are present [69]. Photolysis is an important removal process for pesticides that absorb light at wavelengths between 290 nm and 800 nm. Many pesticide classes, such as triazines, ureas, and some halogenated compounds carry no chromophore to absorb light above wavelengths of 290 nm [52]. For these compounds the reaction with OH radicals is assumed to be the main degradation process [70]. The degradation products of pesticides that result from these reactions in the atmosphere can themselves be of potential concern and can have very different characteristics than their parent compounds. They can be more toxic than their parent compound and can have different atmospheric half-lives which influences their potential atmospheric transport [52, 71]. The different properties of degradation or transformation products may also result in different removal processes compared to the parent compound. An example are the degradation products of triazines which have a similar toxicity than their parent compounds but can be more persistent [52, 72]. Studies also showed that pesticide

transformation products can have stronger endocrine disrupting effects than their parent compounds due to changes in gene expression and hormonal secretion [73]. Chemicals that act as endocrine disruptors can affect the epigenome by e.g. deoxyribonucleic acid (DNA) methylation and histone modifications which can cause chronic effects that can be passed on to future generations [74].

Wet and dry deposition

Deposition of pesticides from the atmosphere can be classified as wet deposition, including precipitation, and dry deposition. This depends on the partitioning between the gaseous and particulate phase of a compound. Wet deposition occurs from the uptake of a pesticides into a cloud or a rain droplet followed by the removal of the droplets by precipitation (rain, snow, or fog) [71]. Thereby, the main processes are (1) in-cloud scavenging or rain-out, and (2) below-cloud scavenging or wash-out [63, 68]. During heavy rain events, the pesticide concentration in the gaseous air phase decreases and can drop to zero for substances that are efficiently washed-out [68]. For the particulate phase, the scavenging depends on the physical properties of the particles where the particle size is the most important one. The process of particle removal is dominated by in-cloud processes. In these processes, pesticides attached to particles are washed out with the particle when precipitation occurs. Coarse particles can also be washed out by below-cloud scavenging [22]. Pesticides bound to particles have a higher removal rate compared to gaseous bound compounds as they are more likely be removed by rain and therefore, their atmospheric residence time is often shorter [68]. The wet deposition rate also depends on the season, as the intensity and duration of the precipitation usually varies during the year [71].

The process of dry deposition includes the uptake of a compound at the earth's surface by water, soil, and vegetation [63, 68]. It consists of three mechanisms: diffusion, impaction, and sedimentation [71]. For particles, the dry deposition depends on the size distribution and the shape of the particle. For pesticides present in the gaseous phase, the dry deposition is influenced by the physical-chemical properties of the compound, the characteristic of the earth's surface (soil or water) and the environmental conditions [68]. As described above, chemicals that are deposited to the earth's surface can be re-emitted to the atmosphere. This can occur in regions far from the chemical's emission areas, like polar regions or the world's oceans, or during periods when fewer pesticides are applied (e.g. during winter). During this time, the water surface can act as a source of a chemical to the air [75]. The knowledge on the deposition and re-emission processes that take place for a compound is crucial to determine the atmospheric residence time and the resulting transport distance, ambient air concentrations and potential impacts on humans or ecosystems [71].

3.2.3 Long-range Atmospheric Transport

Pesticides that are not removed from the atmosphere by photochemical reaction or deposition can undergo long-range atmospheric transport. The atmospheric transport is expected to be the major entrance pathway of chemicals into the environment [71]. According to the Stockholm Convention, a compound has the potential to undergo long-range atmospheric transport if one or more of the following three criteria are met: (i) the chemical was measured in levels that are of potential concern in locations distant from the source, (ii) monitoring data of a chemical show that long-range transport with the potential for transfer to a receiving environment may have occurred via air, water, or migratory species, or (iii) the atmospheric half-life of a chemical is greater than two days [76]. The atmospheric half-life of a compound is defined as the time in which the mass of a chemical is reduced by 50 %. For pesticides, it results mainly from the reaction with OH radicals. The atmospheric residence time is also influenced by the air temperature and the persistence of the substance [22, 68]. Compounds that are expected to have a low persistence in temperate climates can be more resistant to breakdown in polar regions [59]. In addition, chemicals which tend to adsorb more onto atmospheric particles can have higher removal rates due to wet and dry deposition [77]. CUPs are expected to be removed from the atmosphere due to lower vapour pressures, higher water solubilities, and lower chemical stability compared to OCPs. Therefore, shorter atmospheric half-lives are expected for these compounds. However, CUPs with atmospheric half-lives below two days have been found in remote areas since the 1990s, indicating that long range transport occurs even for these pesticides [20, 22, 42, 49, 78]. A reason for their long-range transport to polar regions is the grasshopper effect, as substances can travel longer distances due to repeated volatilization and deposition to and from the atmosphere [77, 79]. In addition, CUPs can also be transported by water currents and re-volatize into the atmosphere [21, 80].

3.3 Pesticides in the atmosphere

OCPs have been reported in the atmosphere for the first time in the 1960s [14]. Since then, they have been intensively investigated in the atmosphere around the globe, including remote areas such as the world's oceans [15-18, 81] and polar regions [19, 26, 27, 29-35]. Since their ban and restrictions in industrial countries in the 1970s [22] and their inclusion in the Stockholm Convention in 2004 [36], CUPs came more into the focus of atmospheric pollution as their number of different compounds, production and use highly increased since then.

Data on CUPs and OCPs in the atmosphere from 142 studies that have been conducted since the 1990s is summarized in Figure 4 and Table A4. Less than 50 % of the reviewed studies on pesticides in the atmosphere included CUPs in their research and often investigated only a small number of them (<100 CUPs, mostly around 30 to 50 CUPs, see Figure 4a). In addition to the small number of CUPs included, these studies also mostly cover small geographical areas in one country during a limited period of time. More than 50 % of the studies that were conducted since the 1990s focused on rural and urban areas,

where concentrations in the pg/m³ to ng/m³ range were detected (see Figure 4b). In addition, 20 % of atmospheric pesticide studies investigated their occurrence in agricultural areas. Here, concentrations were detected up to a few hundred ng/m³, with higher concentrations during the pesticide application periods in spring and summer. Some CUPs (up to 16) have also been investigated in remote areas such as mountain sites [40, 41], in marine areas such as the Bering and Chuckchi Sea [20], the Bohai Sea [47], and the North Pacific and Arctic Ocean [48], and in polar regions such as the Arctic [23, 25, 49] and Antarctica [21] and have been detected in concentrations in the low pg/m³ to low ng/m³ range. Only one study was found, that included all of the research areas, where pesticides have been found (rural, urban, agricultural, marine, and polar). This data is especially relevant for the knowledge on potential atmospheric transport of CUPs either by ocean currents or by atmospheric transport. However, most of the atmospheric pesticide studies only analysed pesticides by gas chromatography coupled to mass spectrometry (GC-MS) and did not include more polar or thermolabile compounds (see Figure 4c). Only in recent years, liquid chromatography coupled to mass spectrometry (LC-MS) was applied more often to gain data on these compounds and therefore, data on polar and thermolabile CUPs is only available for a small number of compounds yet.

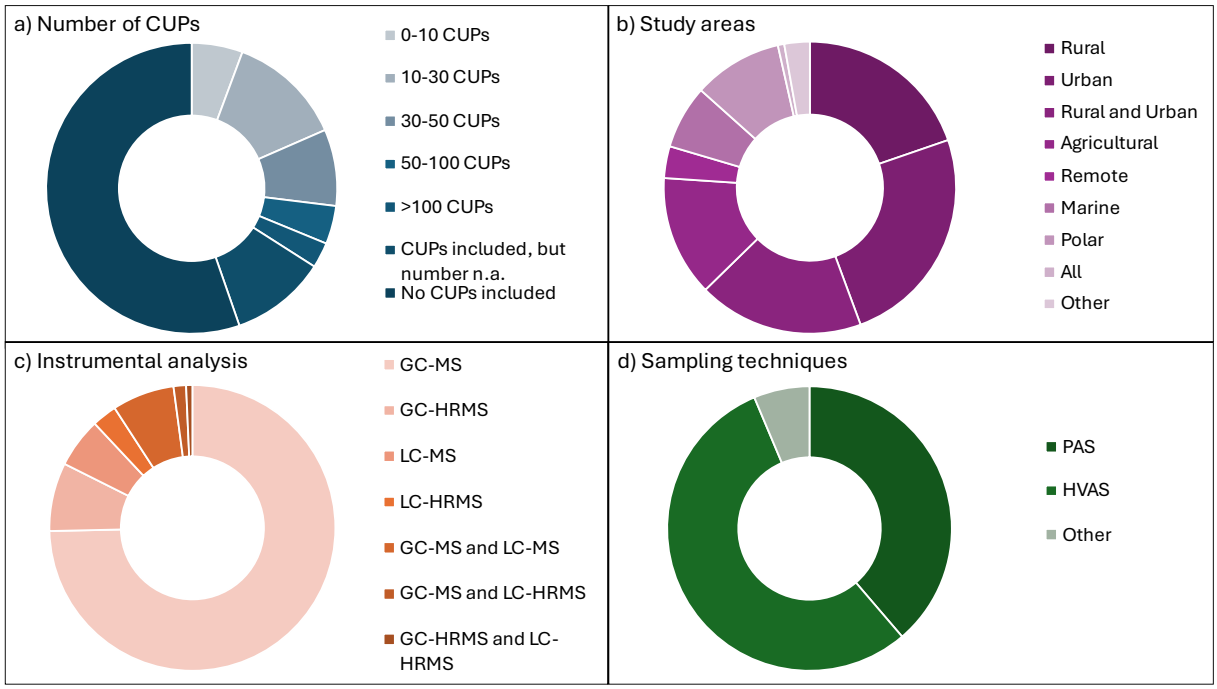

Figure 4: Literature review of 142 studies on pesticides in the atmosphere (for details see Table A4). a) Number of CUPs included in atmospheric pesticide studies. CUPs = currently used pesticides. b) Study areas covered in atmospheric pesticide studies. c) Instrumental analysis used in atmospheric pesticide studies. GC = gas chromatography, MS = mass spectrometry, HRMS = high-resolution mass spectrometry, LC = liquid chromatography. d) Air sampling techniques used in atmospheric pesticide studies. PAS = passive air sampler, HVAS = high-volume air sampler.

3.4 Sampling and analysis of pesticides

Pesticides in the air are commonly sampled with two different sampling techniques: passive air sampling (Section 3.4.1) and active air sampling (Section 3.4.2). For both sampling techniques, different

adsorbents are used to collect airborne pesticides. The different methods used for extraction and analysis of pesticides in air are described in Section 3.4.3.

3.4.1 Passive air sampling

Passive air sampling (PAS) is used to identify the presence of chemicals, including pesticides, in the atmosphere. In general, passive sampling is based on the diffusive uptake of a chemical present in the air in a sorbent over time (see Figure 5). Sorbents typically used in passive sampling are polyurethane foam (PUF) disks [29, 31, 40-42, 81-114] or XAD resins [32, 34, 39, 115-120]. The advantages of passive sampling are that it is inexpensive, easy to implement, noise-free, and it requires no electricity. Therefore, it can be used for large scale assessments of atmospheric contaminants even in remote areas where no power supply is available. However, a major challenge is the determination of the exact air volume interacting with the adsorbent material during the exposure period. The sampling rate is highly influenced by meteorological conditions such as the wind speed and the temperature as this affects the diffusion of the molecules as well as their gas-particle partitioning [121, 122]. Some studies therefore use active air samplers installed close to the passive samplers to calculate the sampling rate and to determine the pesticide concentrations. Another disadvantage of passive sampling is the uncertainty if a compound was present in the particulate or gaseous air phase. Different adsorbent materials are expected to sample only gaseous particles (e.g. XAD resin), while others can also adsorb particle-bound compounds (e.g. PUF). However, the literature on this is not consistent and differences in the literature may be associated with the sampling site characteristics, meteorological conditions, the type of adsorbent (the same material could have different densities, e.g. different PUFs) as well as different analytical processes [123]. Consequently, the quantitative determination of pesticides using passive samplers has high uncertainties that have to be considered when concentrations are calculated. However, passive sampling is an important technique to gain valuable information on the occurrence of pesticides in remote or inaccessible areas and on long-term trends [124].

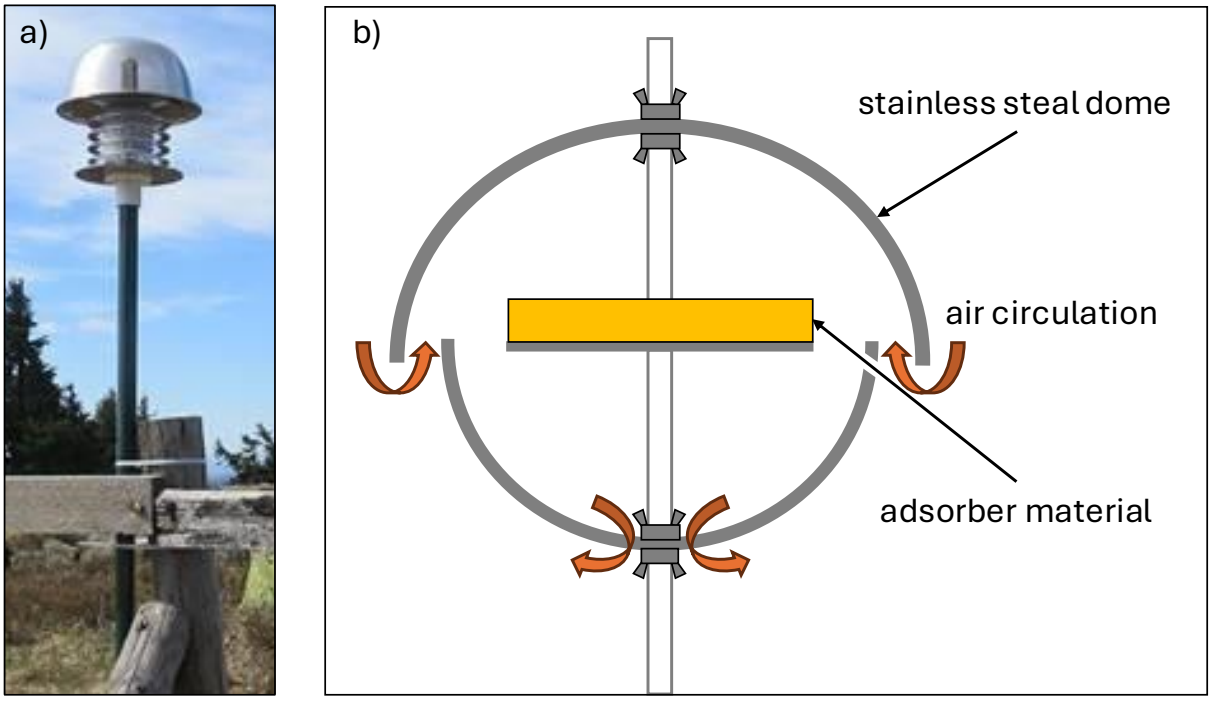

Figure 5: Example of a) a passive air sampler, picture by Vera Silva/Wageningen University & Research and b) a scheme of a passive air sampler

3.4.2 Active air sampling

Active air samplers are used to determine the concentration of pesticides in ambient air. Air is drawn through the adsorbent materials by means of a pump. It can be distinguished between high-volume air samplers (HVAS) and low-volume air samplers (LVAS) with the difference being in the amount of air that passes the adsorbents. Air volumes typically range between 18 and 90 m^3/h for HVAS and between 0.06 and 0.18 m^3/h for LVAS. To ensure the higher air volumes, a power supply is required at the sampling site for HVAS. This can make the method unfeasible for the use in remote areas and in large-scale sampling. However, active air sampling is highly important for the quantitative determination of pesticides in air as the exact sampling volume is known. In addition, active air samplers can provide information on the pesticide distribution between the particulate and gaseous air phase. This data is important for exposure modelling and risk assessments of pesticides as it can provide information on the inhalation quantity of pesticides and potential effects on human health.

In general, a filter is installed in front of a glass column filled with an adsorber material (see Figure 6). As filters, quartz-fibre filters (QFFs) or glass-fibre filters (GFFs) are commonly used to sample the particulate air phase. For the gaseous air phase, adsorbent materials commonly used are PUF or/and XAD resins [59]. The total air volume sampled (m^3) is measured and used for the calculation of pesticide concentrations. Typical sampling times range between 24 h and 1 week, depending on the detection limits of the analytical methods, expected air concentrations, and the purpose of the sampling. Important to consider for active sampling is the breakthrough volume, i.e. the moment when the adsorbent material is saturated by a compound and a loss of the compound occurs downstream.

Therefore, the breakthrough point has to be determined before the sampling and the sampling time should be selected depending on potential breakthrough of the investigated compounds [125].

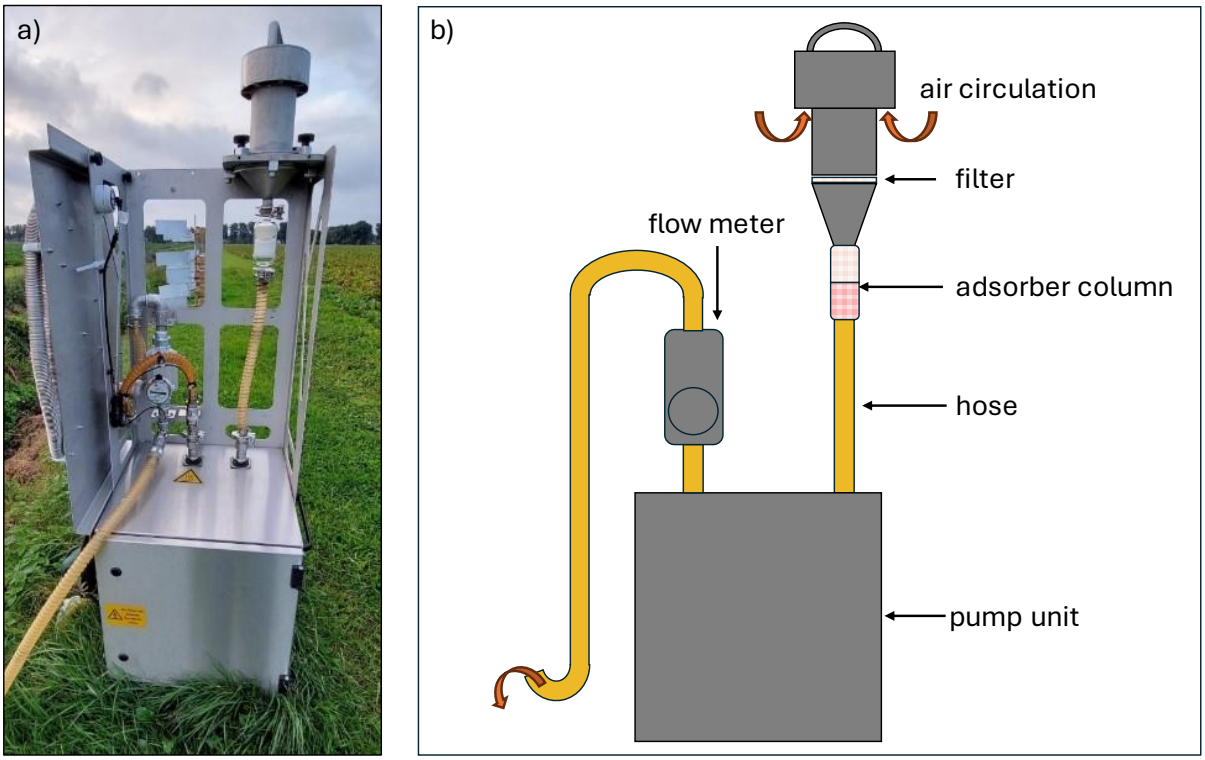

Figure 6: Example of a) a high-volume air sampler and b) a scheme of a high-volume air sampler

3.4.3 Analytical procedures

The analytical procedure for the quantification of pesticides usually consists of the extraction, a clean-up step, and the instrumental analysis. As depicted in Table A4, extraction methods commonly used for pesticides in air samples are Soxhlet extraction, accelerated solvent extraction (ASE), microwave-assisted extraction (MAE), and ultrasonic-assisted extraction (UAE). As extraction solvents, hexane, mixtures of hexane with other solvents (e.g. hexane-acetone or hexane-dichloromethane), acetone, dichloromethane, or ethyl-acetate are often used.

A clean-up step is often applied to reduce the interferences caused by co-extracted substances in the instrumental analysis, especially for GC-MS analyses. Commonly, a solid-phase extraction (SPE) with normal phase sorbents, such as alumina, silica gel, Florisil, or a combination of these, is used during this step [126]. This can lead to good cleaning effects for non-polar compounds such as organochlorines but is less effective for more polar pesticides.

As described in Section 3.3 and depicted in Figure 4c, GC-MS has mostly been used for the instrumental analysis of pesticides. In recent years, the application of LC-MS largely increased for the determination of more polar and thermolabile pesticides without prior derivatisation. In addition, high-resolution mass spectrometry (HRMS) coupled to LC or GC for the analysis of pesticides in the atmosphere became

more important in recent years, but until now there are still only a few studies available. HRMS is especially valuable for the investigation of a high number of target compounds as well as for suspect or non-target screening of emerging contaminants or transformation products. Due to the rising number of pesticides on the market (>2000 active substances) [127] and missing information on pesticide transformation products, HRMS is expected to become more relevant in the future.

3.5 Integration in the EU project SPRINT

This thesis was integrated into the European Union Horizon 2020 programme no. 862568 with the title "Sustainable Plant Protection Transition: A Global Health Approach" (SPRINT) (https://sprint-h2020.eu/). The aim of the project is to develop a Global Health Risk Assessment Toolbox to determine the health risks and impacts of pesticide mixtures on humans and the environment. The project consists of 28 institutions working on ten work packages (WPs) (see Figure 7). WP1, WP8, WP9, and WP10 included the Stakeholders platform, dissemination and communication activities, the project coordination, the data management, and the ethics requirements. In WP2, the pesticide distribution and current health state was investigated at ten case study sites (CSS) in Europe and one CSS in Argentina (see Figure 8) including the sampling and analysis of pesticides in different environmental compartments (e.g. soil, water, and air), in animals (e.g. blood and urine) and in humans (e.g. blood, urine, and wristbands). WP3 investigated the modelling and exposure assessment of pesticides for human health and the environment. WP4 and WP5 included an ecotoxicological assessment and health risk assessment of pesticide mixtures in terrestrial and marine organisms as well as on human health. WP6 and WP7 worked on a cost-benefit analysis and potential transition pathways and policy recommendations for a sustainable agriculture with the use of less pesticides.

The content of this thesis was involved in WP2 for the sampling and analysis of pesticides in ambient air at two CSS (Portugal and the Netherlands). In addition, the results from the ambient air samples are used in WP3 for the exposure modelling of pesticides in air on human health.

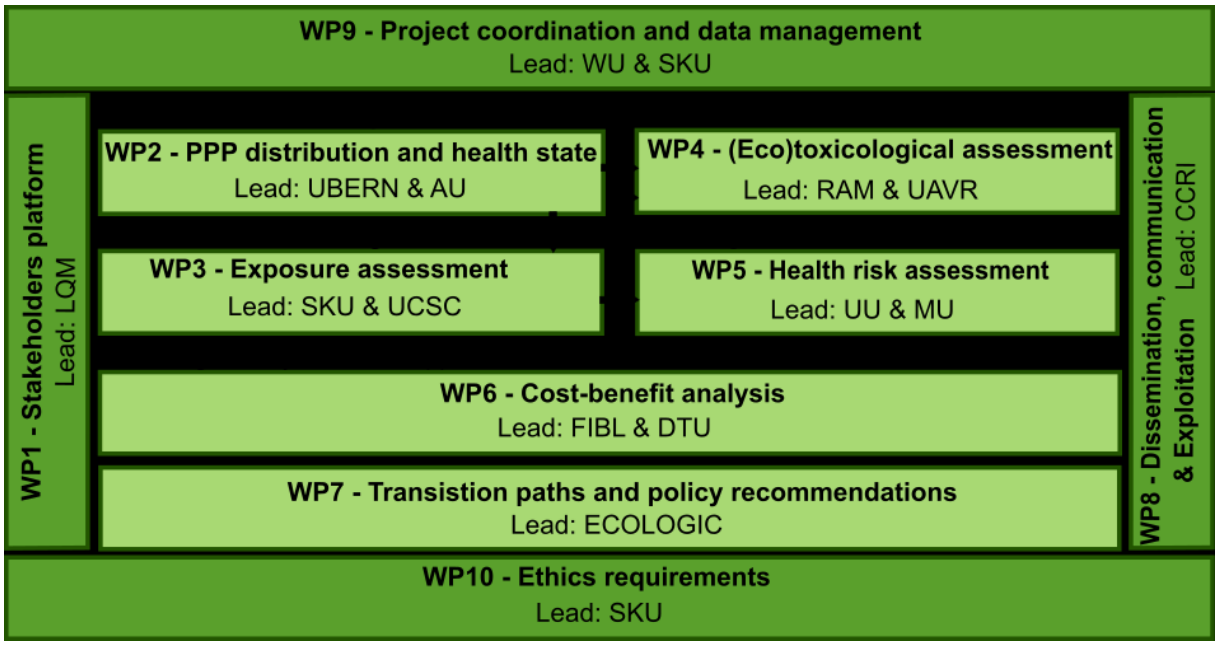

Figure 7: The ten work packages (WPs) included in the EU Horizon 2020 SPRINT project [128]

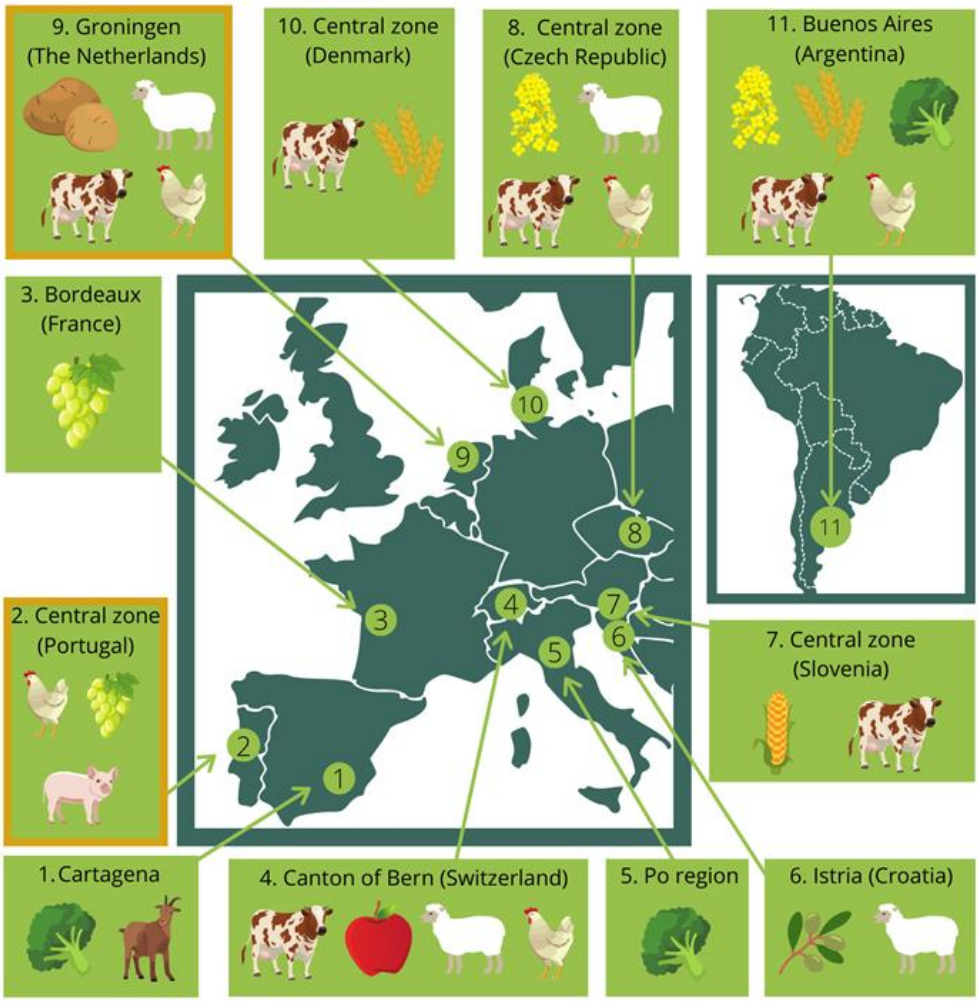

Figure 8: The eleven case study sites included in the EU Horizon 2020 SPRINT project for pesticide analysis [129]

4. Point of departure and objectives

At the beginning of this doctoral research, data on pesticides in the atmosphere, except for the well-studied organochlorine pesticides, have been rare, especially for remote areas. Currently used pesticides which replaced and complemented the banned OCPs had been expected not to be prone to long-range atmospheric transport due to their short calculated atmospheric half-lives. However, a small number of CUPs had been investigated and detected at remote areas, indicating that this assumption must be reconsidered. Studies on CUPs mostly focused on a small number of compounds using passive samplers. In addition, they had often used GC-MS for the instrumental analysis and had not included more polar or thermolabile CUPs that can only be determined by LC-MS. This raised the questions, which CUPs that have not yet been investigated can occur in the atmosphere close to application sites as well as in more remote areas, and in which concentrations they are present. This could give important information on the relevance of specific pesticides for human health or environmental exposure and on the potential long-range transport of CUPs to non-target areas.

Based on this point of departure and questions that have arisen, the aims of this PhD thesis were

(i) to develop an analytical method using liquid chromatography coupled to high-resolution mass spectrometry and gas chromatography coupled to triple quadrupole mass spectrometry for the simultaneous determination of organochlorine pesticides, currently used pesticides, and transformation products in the particulate and gaseous phase of the air,

(ii) to determine which pesticides are of relevance at European agricultural sites, how they are distributed in the air and if the concentrations are of concern for humans or the environment, and

(iii) to identify currently used pesticides that can undergo long-range atmospheric transport to the marine atmosphere of the Atlantic Ocean.

The aims were addressed by three studies included in the cumulative part of this thesis. The specific objectives of these studies were as follows:

Chapter 5.1: "Development of an analytical method for the determination of more than 300 pesticides and metabolites in the particulate and gaseous phase of ambient air"

Freya Debler, Juergen Gandrass. Analytical and Bioanalytical Chemistry, 416, 3059–3071, https://doi.org/10.1007/s00216-024-05254-4, 2024.

This study aimed at developing quantitative multi-methods for the analysis of 329 pesticides, including organochlorine pesticides, currently used pesticides, and transformation products in the particulate and gaseous phase of the air by using liquid chromatography coupled to HRMS (LC-QTOF) and gas

chromatography coupled to triple quadrupole mass spectrometry (GC-QqQ). The scope of target analytes was defined by a literature review and commercially available certified pesticide standards and was extended by target analytes from the EU SPRINT project. Instrumental methods were implemented on a LC-QTOF and a GC-QqQ and chromatographic and mass spectrometric parameters were optimized. The instrumental methods as well as the extraction methods for the particulate and gaseous air phase were optimized and validated for the quantification of pesticides in the pg/m³ to ng/m³ range.

Chapter 5.2: "Occurrence and distribution of pesticides and transformation products in ambient air in two European agricultural areas"

Freya Debler, Nelson Abrantes, Paula Harkes, Isabel Campos, Juergen Gandrass. Science of the Total Environment, 940, 173705, https://doi.org/10.1016/j.scitotenv.2024.173705, 2024.

The occurrence and distribution of organochlorine pesticides, currently used pesticides, and transformation products in the air was investigated at two agricultural areas in Europe (Portugal and the Netherlands). Particulate (GFFs) and gaseous (PUF/XAD-2 columns) air samples were taken for 14 months using high-volume air samplers next to agricultural fields in both countries. Particle phase fractions were calculated to determine the partitioning behaviour of CUPs between the particulate and gaseous air phase. In addition, hazard profiles were determined, and daily inhalation rates were calculated to evaluate potential risks to human health.

Chapter 5.3: "Currently used and legacy pesticides in the marine atmosphere from Patagonia to Europe"

Freya Debler, Juergen Gandrass, Martin Otto Paul Ramacher, Alkuin Maximilian Koenig, Simon Zimmermann, Hanna Joerss. Environmental Pollution, 373C, 126175, https://doi.org/10.1016/j.envpol.2025.126175, 2025.

This study investigated whether currently used pesticides are of relevance for long-range transport to the marine atmosphere of the Atlantic Ocean. Particulate and gaseous air samples were taken on a south-north transect across the Atlantic Ocean with high-volume air samplers to determine the occurrence and spatial distribution of CUPs. To examine potential sources of currently used pesticides resulting from atmospheric transport, air-mass back trajectories were computed.

5. Synopsis

5.1 Development of an analytical method for the determination of more than 300 pesticides and metabolites in the particulate and gaseous phase of ambient air

Pesticides have been detected in the environment even in remote areas such as the world's oceans and polar regions. This indicates that they are transported from their source regions to these areas through the atmosphere or the water phase. Legacy pesticides as well as some CUPs have been detected in the atmosphere in these remote areas in the past. However, most of these studies only included a small number of compounds with a focus on legacy pesticides and the use of GC-MS/MS for the instrumental analysis. Therefore, there is a high demand for a multimethod for the quantitative analysis of a high number of pesticides, including legacy pesticides, currently used pesticides, and transformation products, in ambient air.

The development of this multimethod is especially challenging as it should include pesticide concentrations in air at trace levels in the sub pg/m³-range that can be influenced by strong matrix effects due to the air matrix itself as well as matrix constituents from the sampling material. In addition, such a method should complement the scarce data and deliver missing information on currently used pesticides and their transformation products in ambient air. Consequently, the primary aim of this work was to develop a multimethod for the analysis of a broad range of pesticides and their transformation products in the particulate and gaseous phase of ambient air using an LC-QTOF and a GC-QqQ instrument.

The first step to develop a multimethod for the extraction of pesticides in ambient air was the development of the instrumental method on the LC-QTOF and the GC-QqQ. For the extraction of pesticides from GFFs (particulate air phase) and from PUF/XAD-2 columns (gaseous air phase), different extraction methods were compared in this work with regards to recovery rates and relative standard deviations for each of the 329 investigated pesticides. For the GFFs, four different extraction methods were compared: Soxhlet extraction, UAE, QuEChERS extraction and an extraction by diffusion. For all extraction methods, dichloromethane (DCM) was used as the extraction solvent. The QuEChERS extraction resulted in the highest number of compounds with recovery rates between 70 and 120 % and relative standard deviations (RSD) below 20 % and was therefore defined as the preferred method. For the PUF/XAD-2 columns, two different extraction methods using DCM as the extraction solvent were compared: Soxhlet extraction and cold-column extraction (CCE). The CCE showed better recovery rates (between 70 and 120 %) and better RSD (below 20 %) for the investigated compounds and was used as the preferred extraction method.

As a final step, the selected extraction methods for both, GFFs and PUF/XAD-2 columns, were validated according to the method performance acceptability criteria characterized in SANTE/12682/2019 [130]

using a matrix-matched calibration. Method quantification limits (MQLs) were determined as the lowest spike level meeting the performance acceptability criteria (recovery rates between 70 and 120 % and RSD < 20 %). The method detection limits (MDLs) were determined by a signal-to-noise ratio (*S/N*) of 3. Solvent and method blanks were analysed together with the validation extracts. For the PUF/XAD-2 columns, breakthrough experiments were performed to determine possible breakthrough during sampling with a high-volume air sampler. In addition, the precision and linearity of the instrumental method was determined. To determine the applicability of the method, air samples taken around agricultural fields in the Netherlands were analysed. The results showed that the method was able to determine pesticides in high concentrations during the application period as well as background concentrations when no pesticides were applied.

In conclusion, the two extraction methods developed in this study enable the determination of more than 300 pesticides in the low pg/m³ to ng/m³ range in the particulate and gaseous phase of ambient air, from which 263 pesticides on the GFFs and 75 pesticides on the PUF/XAD-2 columns fulfilled the strict SANTE criteria. The developed multimethod can be used to analyse a wide range of pesticides in the atmosphere to gather more information on their potential atmospheric transport and fate in the environment.

As a result of the work carried out as part of this doctoral thesis, the following paper has been published in *Analytical and Bioanalytical Chemistry.* The online version can be found at the following DOI: https://doi.org/10.1007/s00216-024-05254-4.

Development of an analytical method for the determination of more than 300 pesticides and metabolites in the particulate and gaseous phase of ambient air

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RESEARCH PAPER

Development of an analytical method for the determination of more than 300 pesticides and metabolites in the particulate and gaseous phase of ambient air

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Abstract
Pesticides can enter the atmosphere during spraying or after application, resulting in environmental or human exposure. The study describes the optimisation and validation of analytical methods for the determination of more than 300 pesticides in the particulate and gaseous phases of the air. Pesticides were sampled with high-volume air samplers on glass-fibre filters (GFFs) and glass columns filled with polyurethane foam (PUF) and XAD-2 resin. Comparing different extraction methods, a QuEChERS extraction with acetonitrile was selected for the GFFs. For the PUF/XAD-2 columns, a cold-column extraction with dichloromethane was used. Instrumental determination was performed using liquid chromatography/electrospray ionisation-time-of-flight mass spectrometry (LC/ESI-QTOF) and gas chromatography/electron impact ionisation-tandem mass spectrometry (GC/EI-MS/MS). Recovery experiments showed recovery rates between 70 and 120% for 263 compounds on the GFFs and 75 compounds on the PUF/XAD-2 columns. Semi-quantitative determination was performed for 39 compounds on the GFFs and 110 compounds on the PUF/XAD-2 columns. Finally, 27 compounds on the GFFs and 138 compounds on the PUF/XAD-2 columns could be determined only qualitatively. For the determination of the PUF/XAD-2 samples, signal suppression (LC) or signal enhancement (GC) due to matrix effects were determined. Method quantification limits of the optimised methods ranged from 30 to 240 pg/m^3 for the target compounds on the GFFs, and from 8 to 60 pg/m^3 on the PUF/XAD-2 columns. The applicability of the method was demonstrated by means of environmental air samples from an agricultural area in the Netherlands.

Keywords Pesticides · Ambient air · High-volume air sampling · QuEChERS · High-resolution mass spectrometry

Introduction

The global use of pesticides has experienced unprecedented growth over the last decades, driven by the demand for food production and pest management. As a result, in 2021, the global market for pesticides reached 43.3 billion US dollars, underscoring the magnitude of their prevalence in modern agricultural practices [1]. Despite their essential role in crop protection, the widespread application of pesticides has raised multiple environmental and health concerns [2–4].

During and after pesticide application, spray drift, volatilization, and wind erosion facilitate the transfer of these chemicals into the air. Depending on the physicochemical properties of the pesticide, product characteristics, texture of the ground, type of application, and weather conditions, pesticides can end up in the atmosphere. There they can partition between the particulate and gaseous phases and impact distant regions beyond their intended target areas [5–7]. This emphasizes the necessity for an in-depth understanding of the distribution of airborne pesticides and their potential exposure and effects on remote and non-target organisms, including humans and ecosystems.

To assess the presence and concentrations of airborne pesticides, appropriate sampling and analytical techniques are of importance. Adsorbent materials have been widely employed to capture these chemicals during air sampling. Most used adsorbents for the analysis of contaminants in air are polyurethane foams (PUF) and XAD resins for the

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sampling of the gaseous phase, while glass-fibre filters (GFFs) and quartz-fibre filters (QFFs) are preferred for trapping particle-bound pesticides [8, 9]. Sampling techniques include active and passive air sampling. Most air studies focus on passive sampling, with which a quantitative determination of pesticides cannot be determined. Therefore, this study uses active air sampling with high-volume air samplers [10, 11]. Furthermore, most studies analyse only a few selected pesticides, via the employment of GC-MS/MS methods [8, 9]. Consequently, more polar compounds and some currently used pesticides have often been overlooked in air, with emphasis placed on well-known legacy pesticides, such as organochlorines.

To address these limitations and enhance the capability to detect airborne pesticides, this study compares different extraction methods for the analysis of a broad spectrum of pesticides in air via GC-MS/MS and LC-QTOF analysis. Traditional Soxhlet extraction is an effective method for the extraction of pesticides but is time-consuming and requires substantial amounts of solvent. Typical solvent-based extraction methods of pesticides from air are ultrasonic-assisted extraction (UAE), accelerated solvent extraction (ASE), or microwave-assisted extraction (MAE) [8]. In this study, for the GFFs, also an extraction by diffusion was tested.

Drawing inspiration from the quick, easy, cheap, effective, rugged and safe "QuEChERS" approach utilized in food analysis, the adoption of a more cost-effective and efficient extraction method for the extraction of GFFs is proposed [12]. The QuEChERS method employs reduced solvent volumes, making it more economical and faster, and has demonstrated success in the analysis of PAHs in the particulate phase of air samples [13]. To our best knowledge, this is the first work applying the QuEChERS approach for the analysis of airborne particulate pesticides.

The objective of this study is to optimise and validate the extraction of a wide range of pesticides from GFFs and PUF/XAD-2 columns used in high-volume air samplers. The final extraction methods for both matrices are being applied to eight air samples taken within the scope of the EU project SPRINT at a case study site in the Netherlands.

Experimental

Consumables

All standards and reagents used were of the highest purity commercially available. Standards were obtained from Restek (Bellefonte, USA) as standard mixtures (LC Multiresidue Pesticide Kit and GC Multiresidue Pesticide Kit). Compounds not included in these mixtures were purchased from Sigma-Aldrich (Darmstadt, Germany) (2.4-D, clopyralid, dimethenamid-p, fluopicolide, fluroxypyr, imazapic, imazapyr, imazaquin, imazethapyr, MCPA, mecoprop-p, metamitron, napropamide, nicosulfuron, propaquizafop, quinmerac, quizalofop-p-ethyl, thifensulfuron-methyl) and from Dr. Ehrenstorfer (Augsburg, Germany) (allethrin, bentazone, bixafen, chlorimuron-ethyl, cycloxydim, dicamba, dichlorvos, diclosulam, halauxifen-methyl, S-metolachlor, metsulfuron-methyl). Isotope-labelled internal standards of >96% purity were purchased from Dr. Ehrenstorfer (Augsburg, Germany) (metalaxyl-D3, tebuconazole-D6, imidacloprid-D4, carbofuran-D4, metsulfuron-methyl-D3, thiabendazole-D6, trans-cypermethrin-D6, gamma-HCH-D6, chlorpyrifos-D10), Sigma-Aldrich (Darmstadt, Germany) (terbuthylazine-D5, bentazone-D7, dimethomorph-(dimethoxy-D6), MCPA-(methyl-D3)) and Cambridge Isotope Laboratories (Tewksbury, USA) (4.4′-DDE ring 13C12). Injection standard 13C3-caffeine (99%) was purchased from Sigma-Aldrich (Darmstadt, Germany), 13C8-PFOA (99%) was purchased from LGC Standards (Teddington, UK), d-TCEP (>98%) was purchased from Wellington Laboratories, and 13C12-PCB-141 (99%) was purchased from Cambridge Isotope Laboratories (Tewksbury, USA). All solvents were purchased in HPLC grade. Methanol was obtained from Merck (Darmstadt, Germany). Hexane, dichloromethane and acetone were purchased from Promochem (Wesel, Germany), and acetonitrile was purchased from VWR (Darmstadt, Germany). Acetic acid was purchased from Fluka Analytical. For the dispersive SPE, anhydrous magnesium sulphate (>99.5%, Sigma-Aldrich), sodium acetate (>99%, Merck), primary secondary amine (PSA, Agilent Technologies) and Bondesil C18 (Agilent Technologies) were used. Syringe filter with regenerated cellulose and a pore size of 0.2 µm (Whatman, Buckinghamshire, UK) were used for the filtration of sample extracts.

Selection of pesticides

The analytes considered in the present study were selected from the following criteria: (i) data from farmers on the pesticide application on the case study sites covered within the ongoing H2020 project SPRINT, (ii) known occurrence of pesticides from a study on pesticides in air in Germany [14] and (iii) known occurrence of pesticides in European agricultural soils [15, 16]. The reasons for the criteria above were (i) inclusion of pesticides currently applied on agricultural fields in Europe, (ii) inclusion of pesticides recently detected in the air in Europe and (iii) inclusion of pesticides that could be transported via air (volatilization or wind erosion) or evaporate from soil due to previous pesticide applications. From this information, a preliminary list of pesticides was designed, and standard mixtures of pesticides available on the market including these pesticides were bought. The pesticides included in this list were used for the method optimisation ("Optimised

instrumental methods" section). For the method validation and sample analysis, 65 further pesticides were included from the final scope within the EU project SPRINT [17] ("Validation of the final method" and "Summary of optimisation and validation of the final method" sections). Pesticides only included for method validation are tagged in the SI (Table S7 and S8). In total, the initial scope included 468 pesticides, including organochlorines, currently used pesticides, as well as pesticide metabolites, from which 335 substances relevant for the project were included in the method validation.

Sampling and sample media

Samples for the method validation and breakthrough experiments were taken at the research centre campus in Geesthacht, Germany. The campus is located in a forest area 5 km away from the city centre of Geesthacht and 1 km away from the next agricultural field. Two high-volume air samplers (self-constructed) were deployed in parallel. Samples were taken for seven days with sampled air volumes between 1400 and 2300 m^3. For the enrichment of pesticides in the gaseous phase of the air, glass columns with a glass frit, a slice of polyurethane foam (PUF, Tisch Environmental, Ohio, USA) and 55 g of Amberlite XAD-2 resin (Supelco, Munich, Germany) were used. The PUF/XAD-2 columns were prepared in a clean lab (class 10.000) and cleaned by Soxhlet extraction with solvents of different polarities for 24 h each. The columns were dried using high-purity nitrogen at a pressure of ~ 1.5 bar and sealed in alumina-coated polypropylene (PP) bags. Glass-fibre filters (GFFs) with a diameter of 15 cm for the analysis of airborne particles were purchased from Macherey-Nagel (Düren, Germany). They were baked out at 450 °C for 6 h, wrapped in aluminium foil and sealed in alumina-coated PP bags.

A subset of air samples collected at an experimental farm in the Dutch case study site, included in the EU project SPRINT campaign [17], was used to determine the applicability of the method. Eight samples were taken between May 2021 and January 2022. Four samples reflected pesticide concentrations during the pesticide application period (May to August 2021), and four samples reflected background concentrations during autumn and winter (October 2021 to January 2022). Exact sampling times and sample volumes are in the SI (Table S6).

Extraction of pesticides from glass-fibre filters

For the extraction of GFFs, four different extraction methods were compared. These were Soxhlet extraction, ultrasound-assisted extraction (UAE), extraction by diffusion and QuEChERS extraction. For all extraction techniques, three GFFs were spiked with the native and isotope-labelled internal standard mix before extraction.

Soxhlet extraction

Soxhlet extraction was performed with 250 mL dichloromethane for 16 h. The resulting extract was divided equally into two aliquots, and each aliquot was evaporated to a volume of 300 µL. To prepare for LC-QTOF analysis, 1 mL of methanol was added to one aliquot, and the extract was evaporated under a gentle stream of nitrogen to 150 µL using a Barkey device (Barkey GmbH & Co. KG, Leopoldshöhe, Germany). During the evaporation step, the walls of the vials were rinsed twice with methanol to minimize potential losses of analytes. The extract was then transferred to an LC vial, and 25 µL of the LC injection standard mix ($^{13}C_8$-PFOA and $^{13}C_3$-caffeine) was added. The volume was adjusted with Milli-Q water to achieve a ratio of Milli-Q/methanol of 30:70%, resulting in a total volume of 583 µL.

For GC analysis, 1 mL of hexane was added to the other aliquot, and the same evaporation steps were performed as for the LC analysis. The resulting extract was transferred to a GC vial, and 20 µL of the GC injection standard ($^{13}C_{12}$-PCB-141) was added. Before analysis, both extracts were filtered using a syringe filter.

QuEChERS extraction

For the QuEChERS extraction, 7 mL Milli-Q water and 15 mL acetonitrile (ACN) were added to the spiked GFFs. The mixture was shaken head-to-head for 30 min. Afterwards, 5 g of anhydrous magnesium sulphate (MgSO4) and 1.5 g of sodium acetate were added. The tube was then vortexed for 1 min and centrifuged at 3500 rpm for 5 min. For LC-QTOF analysis, an aliquot of 125 µL was transferred to a LC vial, and 25 µL of the LC injection standard mix and 350 µL of Milli-Q water were added. The extract was filtered by a syringe filter (0.2 µm, Whatman) prior to analysis. For the GC-MS/MS analysis, an aliquot of 4.5 mL was transferred into a 15 mL Eppendorf tube, and different steps for the clean-up with a dispersive SPE were tested as described in the "Clean-up of sample extracts" section. For the final d-SPE clean-up, MgSO4, primary secondary amine (PSA) and C18 were added. The tube was vortexed for 1 min and centrifuged at 3500 rpm for 15 min. An aliquot of 3.5 mL was transferred into a Barkey vial and evaporated under nitrogen to 150 µL. A solvent switch was performed by the addition of 150 µL of hexane, vortexing the mixture for 1 min, and transferring the upper hexane phase into a GC vial. 20 µL of the GC injection standard was added before analysis.

Ultrasound-assisted extraction

For the ultrasound-assisted extraction, the GFF was transferred into a 50-mL Eppendorf tube, and 30 mL dichloromethane were added. The tube was placed in an ultrasonic bath for 15 min. This step was repeated twice. The three aliquots were combined and divided equally into two aliquots. Each aliquot was evaporated to 300 µL.

For LC-QTOF analysis, 1 mL of methanol was added to one aliquot, and the extract was evaporated to 150 µL. The LC injection standard mix and Milli-Q water were added similar to the Soxhlet extraction, and the extract was filtered with a syringe filter (0.2 µm).

For the GC analysis, 1 mL of hexane was added to the second aliquot and evaporated under nitrogen to 150 µL. 20 µL of the GC injection standard was added, and the extract was filtered with a syringe filter (0.2 µm).

Extraction by diffusion

The fourth extraction method, which was tested for the GFFs, was the extraction by diffusion. The GFF was transferred into a round-bottom flask, and 50 mL of dichloromethane were added. The mixture was shaken on a horizontal shaker for 1 min and afterwards soaked for 1 h. This step was repeated twice with soaking times of 30 min. The extracts were combined and then separated equally into two aliquots. Each aliquot was evaporated to 300 µL. The subsequent steps were performed as described for the UAE.

Extraction of pesticides from PUF/XAD-2 columns

For the extraction of pesticides from PUF/XAD-2 columns, two different methods were compared: Soxhlet extraction and cold-column extraction, both using dichloromethane as extraction solvent. For each extraction technique, three PUF/XAD-2 columns were spiked with the native and isotope-labelled internal standard mix prior to the extraction.

Cold-column extraction

For the cold-column extraction, the PUF/XAD-2 columns were filled completely with dichloromethane and soaked for 1 h. This soaking step was repeated twice, with each subsequent soaking duration set at 30 min. Finally, the columns were purged with nitrogen for 1 min at a pressure of 1.5 bar. The resulting extract was divided equally into two aliquots, and the subsequent steps were performed as described in the "Soxhlet extraction" section under the "Extraction of pesticides from glass-fibre filters" section.

Soxhlet extraction

Soxhlet extraction of PUF/XAD-2 columns was conducted using 350 mL of dichloromethane for a total extraction time of 16 h. The obtained extracts were divided into two equal aliquots, and each aliquot was evaporated to a volume of 300 µL. The subsequent steps were identical to those described for the Soxhlet extraction of the GFFs ("Soxhlet extraction" section under the "Extraction of pesticides from glass-fibre filters" section).

Clean-up of sample extracts

For the final QuEChERS extraction method of the GFFs, different options of a d-SPE were tested for the GC analysis. These included a d-SPE using 750 mg MgSO4, 114 mg PSA and 114 mg C18, one with only MgSO4 and PSA, one using MgSO4 and C18 and a clean-up with only using a syringe filter (0.2 µm). For LC analysis, a d-SPE step was not added, which is general practice [12]. Due to high matrix effects, for the final CCE extraction method of the PUF/XAD-2 columns, a clean-up step using a d-SPE with 250 mg MgSO4, 38 mg PSA and 38 mg C18 was compared to a clean-up with a syringe filter for both, GC and LC analysis.

Instrumental analysis

The instrumental analysis was performed using liquid chromatography (Agilent LC 1290 Infinity II) coupled to a quadrupole time-of-flight mass spectrometer (Agilent QTOF mass spectrometer 6546). As ionisation source, an ESI source (AJS Spray Chamber G1958-65138) was used. The QTOF was operated in All-Ions (AI) mode. For separation, an Acquity HSS T3 C18 column (150 × 2.1 mm, 1.8 µm, Waters) was applied with the following optimised gradient: 5 % B (methanol) for 1 min, rise to 30 % B within 1 min, rise to 100 % B within 25 min, 100 % B for 5 min, 5 % B for 1 min. The flow was set to 0.3 mL/min.

For the GC analysis, two different systems were compared concerning method quantification limits. First, a gas chromatograph (Agilent 7890 B) coupled to a quadrupole time-of-flight mass spectrometer (Agilent 7250) was used. Due to high method quantification limits, this system was compared to a gas chromatograph coupled to a triple quadrupole mass spectrometer (Agilent 7010 GC) for compounds that were included in the pesticide list of the SPRINT project. Both instruments were fitted with a multimode injector (MMI) in pulsed splitless mode. The sample injection volume was 1 µL. The GC was equipped with two HP-5MS columns (15 m × 0.25 mm, 0.25 µm, Agilent Technologies) with mid-point backflush. The MS transfer line and the ion source (electron impact ionisation, EI) were set to 300 °C and 250 °C, respectively. The final oven program was initial

60 °C for 1 min, 10 °C/min to 160 °C and 5 °C/min to 300 °C and held for 5 min.

For the development of the instrumental analysis methods, different parameters were optimised. For the GC-QTOF, the temperature gradient for the GC oven was optimised. For the GC-triple quadrupole instrument, mass transition and the collision energy were determined and optimised. For the LC-QTOF, the gradient of methanol/Milli-Q water was optimised, and the source and mass-spectrometer parameters, namely nebulizer pressure, sheath gas temperature and pressure, drying gas temperature and pressure, fragmentor voltage, nozzle voltage, capillary voltage, and octopole voltage, were optimised.

Analytical method validation

Calibration

For the determination of instrumental detection limits (LODs), instrumental quantification limits (LOQs), and linearity, matrix-matched calibrations (extract of clean PUF/XAD-2 columns or clean GFFs) were used in concentration ranges from 0.05 to 500 pg/µL. Depending on the instrument, 8–10 calibration points were included. The LODs and LOQs were determined by the threefold (LOD) or tenfold (LOQ) signal-to-noise ratio of the calibration samples. Matrix-matched calibration levels of 100 pg/µL were injected ten times to evaluate the instrumental precision.

Matrix effects

During the ionisation process of the compounds, matrix effects were observed, resulting in either signal enhancement or signal suppression of the analytes. Interfering matrix constituents originated from sampled air as well as from pre-cleaned GFFs and PUF/XAD-2 columns. Samples with sufficient low pesticide concentrations could not be obtained. Thus, it was decided to use extracts from pre-cleaned GFFs and PUF/XAD-2 columns to compensate at least for these matrix interferences. Therefore, a comparative analysis was conducted between a solvent calibration and a partially matrix-matched calibration for both, LC-MS and GC-MS.

Blank experiments

Laboratory blanks were evaluated during the extraction process. Solvent blanks (n=3) were determined using 350 mL DCM for the PUF/XAD-2 columns and a mixture of 7.5 mL Milli-Q and 15 mL ACN for the GFFs. The solvents were spiked with the IS mixture and evaporated similarly to the validation samples. Column blanks and GFF blanks (n=3) were evaluated by spiking clean columns and GFFs with the IS mixture. Extraction, concentration and determination were done as described above for the respective matrix. During instrumental analysis, solvent blanks (methanol/Milli-Q water 30%/70% on the LC-QTOF and hexane on the GC-QQQ) were measured in between samples.

Recovery experiments

Recovery experiments for the target analytes were carried out using spiked GFF and PUF/XAD-2 samples at two different spiking levels, with triplicates for each level and matrix. The GFFs and PUF/XAD-2 columns were sampled for 7 days and spiked with the target analytes and IS mixture prior to the extraction. To identify pesticide concentrations present in the air, for each sampling period of seven days, two GFFs and PUF/XAD-2 columns were sampled. Recovery rates were determined by the internal standard method, allocating an isotope-labelled internal standard to each compound. In total, 14 different isotope-labelled internal standards were used. For compounds, where no direct internal standard was available, the allocation of isotope-labelled internal standards was tested according to the best fit of the following criteria: (i) retention time, (ii) mass and (iii) chemical structure. As method performance acceptability criteria, those described in the guideline SANTE/12682/2019 were used [18]. These included recovery rates between 70 and 120% with a repeatability (RSD) < 20%. As described in the guideline, the method LOQ was calculated as the lowest spike level of the validation meeting these criteria [18].

Breakthrough experiments

Breakthrough experiments were conducted for the PUF/XAD-2 columns to check the quantitative collection of the analytes in the gaseous phase. Two sampling columns were operated in series (n = 2). The upper column was spiked with the analyte mixture. The same setup was run in parallel without the spike of the analyte mixture. Subsequently, approximately 2000 m^3 of ambient air on our campus in Geesthacht were drawn through the columns within a sampling period of 7 days. Concentrations of pesticides detected on the second cartridge were determined as breakthrough after the correction with the non-spiked samples taken in parallel. The samples were extracted with the final extraction method for the PUF/XAD-2 columns.

Results and discussion

Optimised instrumental methods

Methods for the LC and GC analysis were optimised as described in the "Instrumental analysis" section.

Optimisation of chromatographic separation on the LC-QTOF

To optimise the chromatographic separation on the LC-QTOF, several gradient designs (different flow rates and slopes) were tested in both ionisation modes (positive ionisation (PI) and negative ionisation (NI)) in order to obtain a compromise between a good separation of the analytes and matrix constituents and a practical run time. The tested gradients as well as the final parameters are depicted in the SI (Section S1.1–S1.4). The final gradient run time was 35 min with a flow rate of 0.3 mL/min. Compared to other studies that are performing multi-residue analysis for pesticides on the LC, the run time of this gradient was slightly longer. This can be explained with a higher number of compounds that needed to be separated within the run time [16, 19].

Optimisation of the ESI ion source settings and MS parameters on the LC-QTOF

The parameters of the electrospray ionisation (ESI) source (nebulizer pressure, sheath gas flow and temperature and drying gas flow and temperature) and the TOF mass spectrometer (capillary voltage, nozzle voltage, fragmentor voltage and octopole voltage), which affect the ionisation of the substances, were optimised for both ionisation modes. Parameters and results for each optimisation step are depicted in the SI (Section S1.2–S1.4).

The fragmentor voltage had the most significant impact on analyte responses as depicted in Fig. 1. The higher the voltage was set, the lower was the average peak area. Therefore, a low fragmentor voltage of 75 V was chosen for the instrumental method. Table S1.4 (SI) summarizes the final parameters of the instrumental method.

Optimisation of chromatographic separation on the GC-QTOF

To optimise the chromatographic separation on the GC-QTOF, different temperature gradients with different start and end temperatures for the oven temperature were tested. The tested temperature gradients as well as the final parameters are presented in the SI (Section S1.5). The final gradient starts at a temperature of 60 °C, runs for 44 min, and ends with a temperature of 300 °C. The final oven temperature

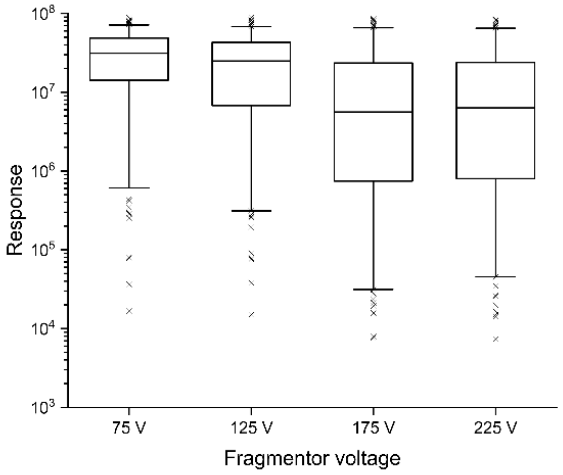

Fig. 1 Comparison of different values for the fragmentor voltage in ESI positive ionisation on the LC-QTOF. The box plots reflect the response of 249 analytes. The boxes contain 50% of the data, representing the interquartile range. The upper and the lower end of the box indicate the 75th and 25th percentile. The ends of the vertical lines designate the 5th and 95th percentile. The horizontal bar in the box indicates the median. A cross indicates outliers

settings are described in the "Instrumental analysis" section and the SI (Table S4).

This method was used for the optimisation of the extraction methods. Due to lower sensitivity and high MQLs, the results for the GC-QTOF were compared to a GC-QQQ system. The optimisation and method of the GC-QQQ is described in the following section.

Optimisation of MS parameters on the GC-QQQ

For the analysis on the GC-QQQ, the temperature gradient and the temperatures for the ion source and transfer line from the GC-QTOF were transferred to the instrument. Subsequently, mass transitions were determined for 33 compounds included in the pesticide list determined within the project SPRINT that are analysed by GC. Retention times were determined, and collision energies were optimised for these compounds. The final mass transitions and collision energies for each compound can be found in the SI (Table S9). As the GC-QQQ showed better sensitivity and lower MQLs for the analytes, it was used for the analysis of the validation samples and further sample analysis.

Extraction experiments

For the extraction of the GFFs and PUF/XAD-2 columns, different extraction methods were tested.

Comparison of different extraction methods for the extraction of GFFs

For the extraction of the GFFs, four different extraction methods were compared. The extraction using the QuEChERS approach together with a d-SPE using $MgSO_4$, C18 and PSA as described in the "QuEChERS extraction" section led to the best results in recovery rates and standard deviations. A comparison of all four extraction methods is depicted in Fig. 2. It can be seen that for the QuEChERS extraction, more than 200 pesticides had recovery rates between 70 and 120%, and for more than 300 compounds, recovery rates between 30 and 140% were determined. In comparison, for the other three extraction methods, only about 80 pesticides (diffusion), 90 pesticides (Soxhlet) and 60 pesticides (UAE) had recovery rates between 70 and 120%. Therefore, the QuEChERS method was the preferred extraction method for the GFFs and was used for the method validation and further sample analysis. This is a new approach for the analysis of pesticides in the particulate air phase. Previous studies mostly used Soxhlet extraction with different solvents, depending on the target analytes and instrumental analysis [8, 11]. However, these studies focused on a smaller number of compounds and the QuEChERS approach used in this study showed better recoveries for a high number of analytes compared to Soxhlet extraction.

Comparison of different extraction methods for the extraction of PUF/XAD-2 columns

For the extraction of PUF/XAD-2 columns, two different extraction methods were compared. Fig. 3 depicts the results of the recovery rates for all compounds. For the cold-column

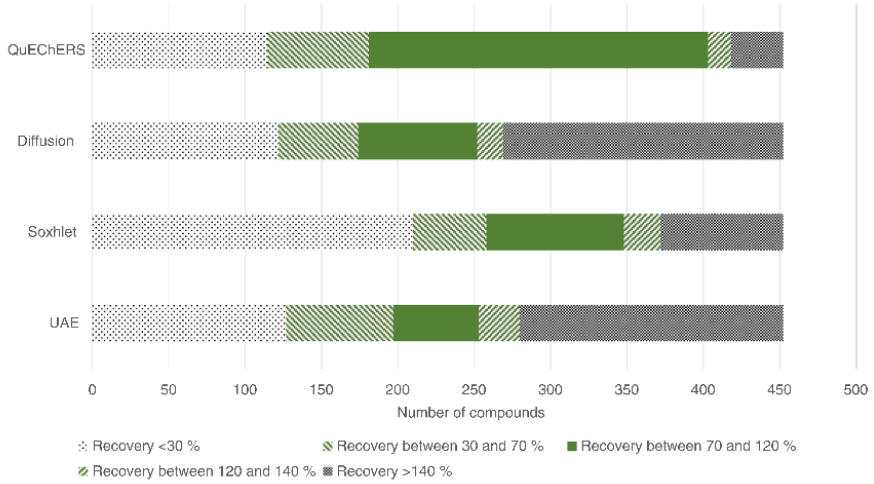

Fig. 2 Comparison of relative recovery rates from different extraction methods for the extraction of GFFs. The different bars show the number of compounds detected with recovery rates below 30%, between 30 and 70%, between 70 and 120%, between 120 and 140% and above 140%. UAE = ultrasound-assisted extraction

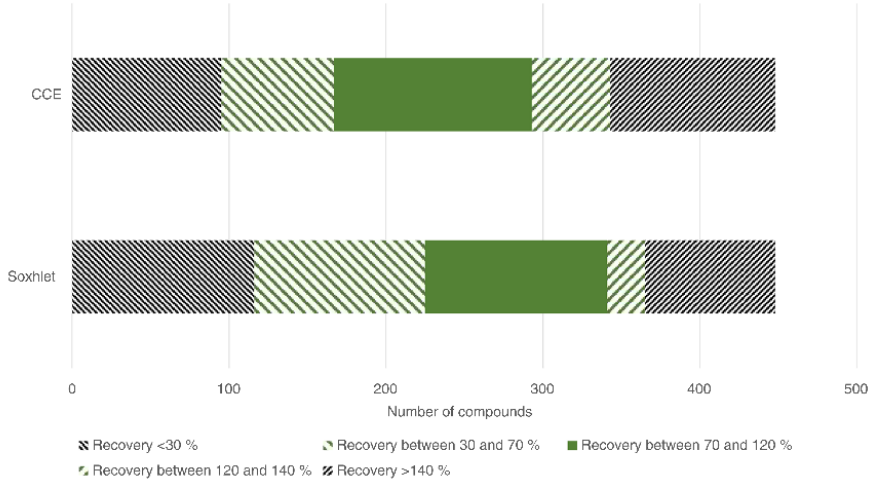

Fig. 3 Comparison of different extraction methods for the extraction of PUF/XAD-2 columns. The different bars show the number of compounds detected with recovery rates below 30%, between 30 and 70%, between 70 and 120%, between 120 and 140% and above 140%. CCE = cold-column extraction

extraction with dichloromethane, more compounds (126) were detected with recovery rates between 70 and 120% compared to the Soxhlet extraction (116). Furthermore, the median recovery rate is closer to 100% (92%) for the cold-column extraction, compared to the Soxhlet extraction (69%). In conclusion, more compounds could be quantified within a range of recovery rates between 70 and 120% with the CCE extraction, and therefore, this method was used for the validation of the method and further sample analysis. Other studies also used dichloromethane as the extraction solvent to determine pesticides in the gaseous air phase [8, 11, 20]. Although these studies focused on Soxhlet extraction or ASE, the cold-column extraction used in this study showed better recoveries and lower matrix effects for the analysis of a high number of target analytes.

Clean-up of sample extracts

Clean-up of GFF extracts for the GC analysis

The comparison of different clean-up steps for the GFF extracts for the GC analysis is depicted in Fig. 4. Best recovery rates were determined for the clean-up with a d-SPE using $MgSO_4$, PSA and C18 with a median value of the recovery rates at 77%. When the d-SPE was performed without PSA or C18, the median recovery rates were lower and were 31% for the d-SPE without C18 and 46% for a d-SPE without PSA. When only a syringe filter without prior d-SPE was used for the clean-up, the lowest median recovery rates of 23% were detected. Therefore, the clean-up was performed with a d-SPE using $MgSO_4$, PSA and C18 for the GC analysis of the validation and real GFF samples. This clean-up step is also in line with other studies using the QuEChERS extraction for other matrices like soil or fish [16, 21].

Clean-up of PUF/XAD-2 extracts for GC and LC analyses

The comparison of a clean-up step using a d-SPE with $MgSO_4$, PSA and C18 and a clean-up with a syringe filter without prior d-SPE for the extracts of the PUF/XAD-2 columns is depicted in Fig. 5. When using only a syringe filter, the median of the recovery rates is higher (86%) than for the clean-up with a d-SPE (66%). However, values vary less for a clean-up using the d-SPE compared to the syringe filter. When a d-SPE was used, some compounds could not be detected on the LC in PI and NI. For example, the IS MCPA-D_3 could not be detected anymore in LC/NI. These acidic compounds can be adsorbed to PSA during the d-SPE [22]. Therefore, the syringe filter without prior d-SPE was used for the clean-up during validation and sample analysis. This step is also comparable to other studies using syringe filters for the clean-up of pesticide extracts from the gaseous phase of the air [11]. Especially for the analysis of a broad number of compounds, losses of some compounds during a clean-up step could also be determined by other studies [23].

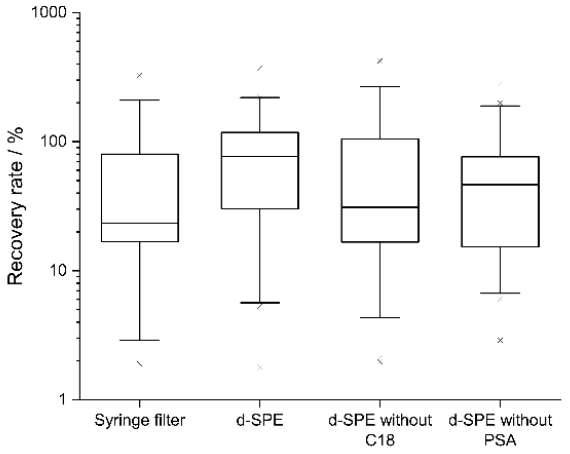

Fig. 4 Comparison of different clean-up steps for the extraction of GFFs for the GC analysis. The boxes contain 50% of the data, representing the interquartile range. The upper and the lower end of the box indicate the 75th and 25th percentile. The ends of the vertical lines designate the 5th and 95th percentile. The horizontal bar in the box indicates the median. A cross indicates outliers. d-SPE = dispersive solid-phase extraction; PSA = primary secondary amine

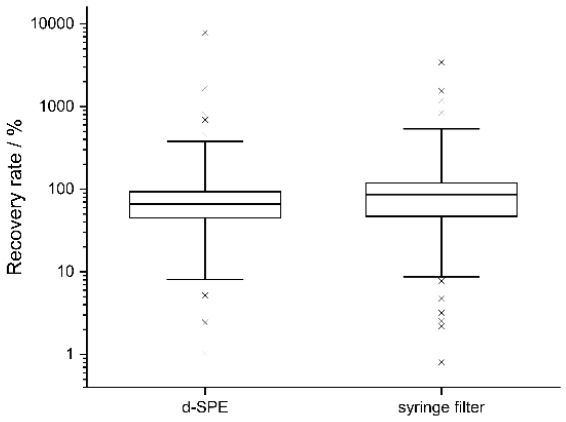

Fig. 5 Comparison of different clean-ups for the PUF/XAD-2 columns. The boxes contain 50% of the data, representing the interquartile range. The upper and the lower end of the box indicate the 75th and 25th percentile. The ends of the vertical lines designate the 5th and 95th percentile. The horizontal bar in the box indicates the median. A cross indicates outliers. d-SPE = dispersive solid-phase extraction

Validation of the final method

Precision

To evaluate the instrumental precision, the same calibration standard at 100 pg/µL was injected tenfold. The relative standard deviations for most compounds ranged from 0.7 to 18% on the LC-QTOF and from 6 to 16% on the GC-QQQ. For the three target analytes Captan (26%), Folpet (28%), and Triallate (30%), the relative standard deviations were above 20%.

Instrumental detection and quantification limits

Instrumental limits of detection (LOD) on the LC-QTOF ranged from 0.05 to 50 pg/µL in positive ionisation and from 0.05 to 50 pg/µL in negative ionisation mode. The instrumental limits of quantification (LOQ) were between 0.05 and 250 pg/µL in LC/PI and 0.1 and 250 pg/µL in LC/NI. For the GC, LODs and LOQs were determined on the GC-QTOF and the GC-QQQ. For the GC-QTOF, LODs were between 0.05 and 250 pg/µL with median values of 5 pg/µL, and LOQs were between 0.05 and 250 pg/µL with median values of 10 pg/µL. For the GC-QQQ, LODs between 0.05 and 5 pg/µL with median values of 0.1 pg/µL and LOQs between 0.05 and 10 pg/µL with median values of 1 pg/µL were determined. Due to tenfold lower LODs and LOQs on the GC-QQQ compared to the GC-QTOF, the validation of the samples was performed with the GC-QQQ instrument.

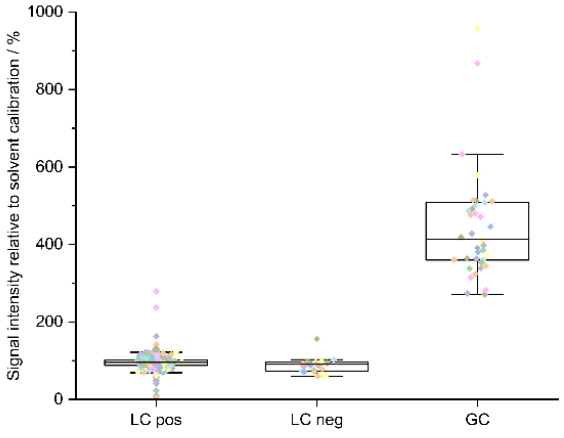

Fig. 6 Ratio of signal intensity of a matrix-matched calibration compared to a solvent calibration for the determination of pesticides from GFFs. The boxes contain 50% of the data, representing the interquartile range. The upper and the lower end of the box indicate the 75th and 25th percentile. The ends of the vertical lines designate the 5th and 95th percentile. The horizontal bar in the box indicates the median. The coloured squares represent the recovery rate for each compound

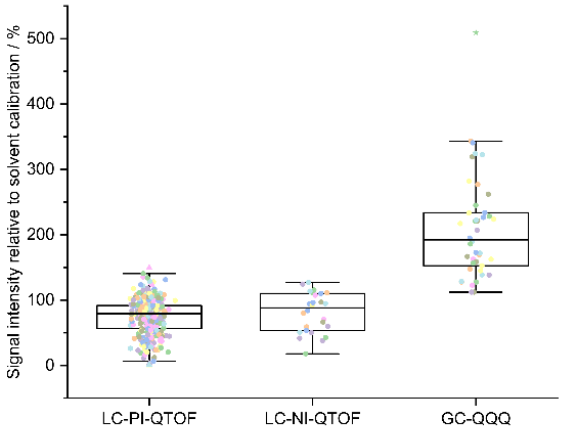

Fig. 7 Ratio of signal intensity of a matrix-matched calibration compared to a solvent calibration for the determination of pesticides from PUF/XAD-2 columns. The boxes contain 50% of the data, representing the interquartile range. The upper and the lower end of the box indicate the 75th and 25th percentile. The ends of the vertical lines designate the 5th and 95th percentile. The horizontal bar in the box indicates the median. The coloured squares represent the recovery rate for each compound

Matrix effects

The results for the ratios between the partially matrix-matched calibration and the solvent calibration (see the "Matrix effects" section) are depicted in Fig. 6 for the GFFs and in Fig. 7 for the PUF/XAD-2 columns. For GC-MS, the matrix-matched calibration for the PUF/XAD-2 columns exhibited a noteworthy signal enhancement compared to the solvent calibration, with signals showing an increase of signal ratios ranging from 112 to 509% with median values of 192%. For the matrix-matched calibration for the GFFs, signal ratios were between 200 and 1177%, and the median value was 398%. Conversely, in the case of LC-MS, a signal suppression was observed for most analytes for the matrix-matched calibration in both, positive ionisation and negative ionisation mode. For positive ionisation, signal ratios ranged between 0.2 and 149% with median values of 79% for the PUF/XAD-2 columns and between 5 and 279% with median values of 96% for the GFFs. For negative ionisation, the signal ratios for the PUF/XAD-2 columns were between 18 and 127% with median values of 88%. For the GFFs, the ratio between matrix-matched and solvent calibration in the negative ionisation mode ranged from 59 to 156% with median ratios of 91%.

These finding highlight the importance of considering matrix effects and employing matrix-matched calibrations to accurately quantify the analytes of interest in both LC-MS and GC-MS analyses. Such corrections are crucial to obtain reliable and precise results in the presence of matrix

interferences [24]. As addressed earlier, the matrix effect occurring from matrix constituents present in sampled air could only be partially included in this study, as a matrix-matched calibration from cleaned GFFs and PUF/XAD-2 columns was used to compensate at least for matrix effects from the sampling material.

Recovery experiments

For the recovery experiments, GFFs and PUF/XAD-2 columns were used, which were sampled for 7 days. The recovery experiments were conducted in triplicate at two different concentration levels to assess the accuracy of the analysis. PUF/XAD-2 columns and GFFs were spiked with native and internal standard mixtures. To account for losses during extraction and extract concentration, the analyte areas were normalized to the corresponding internal standard (IS).

For the GFFs, 263 compounds had recovery rates between 70 and 120%. In the case of the PUF/XAD-2 columns, 75 compounds were validated with recovery rates between 70 and 120%. For compounds that did not meet the SANTE criteria (as described in the "Recovery experiments" section), their determination was limited to qualitative assessment. Compounds for which recovery rates between 30 and 140% and relative standard deviations below 40% were detected were classified as "semi-quantitative". For the GFFs, 39 compounds were determined as semi-quantitative with recovery rates between 32 and 139% and standard deviations between 1.4 and 25%. In case of the PUF/XAD-2 columns, 110 compounds were validated as semi-quantitative, with recovery rates between 32 and 140% and corresponding standard deviations ranging from 1 to 40%.

The applied extraction methods proved to be highly effective for the analysis of pesticides present in the particulate and gaseous phases of the air. Nevertheless, the accurate quantification of compounds, particularly on the PUF/XAD-2 columns, presented notable challenges due to pronounced matrix effects. Despite the adoption of a matrix-matched calibration approach, these effects could not be satisfactorily corrected for certain compounds. Consequently, qualitative analysis emerged as a necessary alternative in these specific cases. When looking at compounds for which an isotope analogue was available as internal standard, most of the compounds for the extraction of GFFs showed recovery rates within the SANTE criteria (10 out of 14 compounds). For metalaxyl, gamma-HCH, imidacloprid and 4.4-DDE, recovery rates for the extraction from GFFs were not satisfactory, even with the use of their isotope analogues. For the PUF/XAD-2 columns, 7 out of 14 compounds met the SANTE criteria. For carbofuran, imidacloprid, gamma-HCH, MCPA, metsulfuron-methyl, tebuconazole and thiabendazole, SANTE criteria were not met. Relative standard deviations between the different validation samples ranged between 30 and 90%, obviously, due to different matrix constituents and effects of PUF/XAD-2 columns cleaned in identical manner. These deviations in precision are also described by other authors for the ESI source, when different batches of the same matrix were used, e.g. for plasma. Niessen et al. referred to this as a "relative matrix effect", whereas the difference in response between a spiked solvent sample and a spiked matrix-matched sample was referred to as an "absolute matrix effect". Jemal et al. [25] determined differences in matrix effects for mevalonic acid and its deuterated internal standard in plasma and urine for different batches and also observed differences between the analyte and the appropriate internal standard. To mitigate the impact of matrix effects arising from the PUF/XAD-2 columns, additional clean-up procedures can be explored, or the implementation of a 2D-LC approach may offer a potential solution. Muehlwald et al. [23] compared a d-SPE with the fractionation by 2D-LC for the clean-up of different vegetable matrices and explored better results for the 2D-LC. This knowledge holds promise for improving the accuracy and reliability of quantitative analyses in the presence of challenging matrix effects.

Method detection and quantification limits

The method quantification limits (MQLs) are determined by the lowest spiked concentrations for which the compound could be detected. For the GFFs, this resulted in MQLs between 30 and 240 pg/m^3. For the PUF/XAD-2 columns, MQLs between 8 and 60 pg/m^3 were determined. MQLs for each compound are depicted in the SI (Table S11 and S12). Compared to other studies, these values are in the same order of magnitude. Coscollà et al. [26] determined 35 pesticides in air samples with MQLs ranging from 2.6 to 75 pg/m^3.

Breakthrough experiments

In the breakthrough experiments with a sampling volume of 2000 m^3, 12 compounds (carbofuran, pyriproxyfen, chloridazon, cyprodinil metabolite CGA304075, 2.4-DDD, 2.4-DDT, 4.4-DDD, 4.4-DDT, alpha-HCH, delta-HCH, gamma-HCH and chlorpyrifos-methyl) were detected on the second PUF/XAD-2 column. The recovery rates for these compounds on the second column were below 1%, except for gamma-HCH (2%), chlorpyrifos-methyl (4%), 4.4-DDT (35%), 4.4-DDD (11%) and 2.4-DDT (21%), due to their volatile character. For these compounds, possible breakthrough should be considered when analysing real samples.

Analysis of environmental samples

Eight environmental samples were taken with a high-volume air sampler close to agricultural fields on a case study

site in the Netherlands within the EU project SPRINT. For the samples taken during the pesticide application period between May and August 2021, 35 different pesticides with concentrations ranging from 5 (<MQL) to 670 pg/m^3 were detected on the GFFs, and 20 different pesticides with concentrations between 6 (<MQL) and 1390 pg/m^3 were detected on the PUF/XAD-2 columns. In the samples from the sampling period between October 2021 to January 2022, when no pesticides were applied in the adjacent fields, 8 pesticides in concentrations between 12 and 69 pg/m^3 were detected on the GFFs, and 13 pesticides with concentrations of 2 (<MQL) to 61 pg/m^3 were detected on the PUF/XAD-2 columns. A figure showing the total concentration of pesticides in each sample is in the SI (Figure S17). The developed method therefore proved applicable for the trace analysis of pesticides in the air in concentrations in the low pg/m^3 to ng/m^3 range. Therefore, the method can be applied to determine pesticide background concentrations in air as well as higher pesticide concentrations that occur during pesticide application.

Summary of optimisation and validation of the final method

An optimised method for the quantification of airborne pesticides in the particulate and gaseous phase of ambient air was developed. For the optimisation of the method, the instrumental parameters on the LC-QTOF and GC-QQQ were optimised. These included the gradient, ion source and MS parameters. A matrix-matched calibration was used for the determination of pesticide concentrations. For the extraction of GFFs, four different extraction methods were compared: Soxhlet extraction, ultrasonic-assisted extraction, QuEChERS extraction and extraction by diffusion. For the PUF/XAD-2 columns, a Soxhlet extraction was compared with a cold-column extraction using dichloromethane. The best results were determined for a QuEChERS extraction of the GFFs and a cold-column extraction with dichloromethane for the PUF/XAD-2 columns. To further improve the recovery rates of the target analytes, different compositions of d-SPE constituents were compared for the GC analysis of the GFFs, and a clean-up with a d-SPE using $MgSO_4$, C18 and PSA was tested for the LC and GC analysis of the PUF/XAD-2 columns. For the GFFs, best results were determined when using a d-SPE according to [16] with $MgSO_4$, C18 and PSA. However, for the PUF/XAD-2 columns, a clean-up with a d-SPE did not improve the determination of the target analytes for the GC or LC analysis. This shows that the clean-up step according to QuEChERS is not sufficient for the clean-up of DCM extracts of the PUF/XAD-2 columns.

Recovery rates and variability of recovery rates were within the SANTE criteria for 263 compounds on the GFFs and 75 compounds on the PUF/XAD-2 columns. For the remaining compounds, matrix effects leading to signal suppression or signal enhancement influenced recoveries and variability of recoveries. Thus, these compounds could only be determined semi-quantitatively or qualitatively. The applicability of the method was successfully proven by the analysis of ambient air samples from an agricultural site in the Netherlands.

Conclusions

In this study, a comprehensive method was developed and validated for the determination of more than 300 pesticides in ambient air down to background concentrations in the pg/m^3 range. High-volume air samplers with GFFs and PUF/XAD-2 columns were applied with sampling volumes of approximately 2000 m^3. GFFs were extracted with a QuEChERS-based extraction method using acetonitrile, while a cold-column extraction with dichloromethane was used for the PUF/XAD-2 columns.

To the best of our knowledge, this is the first time that the QuEChERS approach was applied for the analysis of airborne particle-bound pesticides. For the instrumental determination, LC-QTOF and GC-QQQ instruments were used. Field samples taken at an agricultural area in the Netherlands demonstrated the applicability of the developed method for background pesticide concentrations down to 2 pg/m^3 as well as concentrations up to 1390 pg/m^3 during periods of pesticide application.

Quantitative determination of selected gaseous pesticides analysed with LC-QTOF was impaired due to signal suppression (matrix effects) and caused lower and variable recoveries. Thus, further optimisation of the method should aim at reducing signal suppression by exploration of alternative adsorbent materials and/or extraction solvents. Alternatively, the interference of matrix constituents could be reduced by a clean-up step prior to analysis or by comprehensive (LCxLC) mass spectrometry.

In conclusion, this study serves as a step forward in the analysis of airborne pesticides. The optimised method shows the potential for simultaneous detection and quantification of multiple pesticides in both the particulate and gaseous phase of the air.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00216-024-05254-4.

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Author contribution Freya Debler: Conceptualization, methodology, investigation, validation, writing—original draft. Juergen Gandrass: Conceptualization, supervision, writing—review and editing

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Declarations

Conflict of interest The authors declare no competing interests.

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5.2 Occurrence and distribution of pesticides and transformation products in ambient air in two European agricultural areas

The production and use of pesticides is still increasing, and more than 2000 pesticides are currently registered globally [127]. During and after application, pesticides can be emitted to the atmosphere and carried to areas far away from their application sites. There, they can deposit and can affect non-target organisms and environments. Data on the distribution and atmospheric transport of currently used pesticides is still scarce. However, some CUPs have been detected in remote areas indicating a potential atmospheric transport of these compounds. To gather more data on the atmospheric concentrations of currently used pesticides, the aim of this study was to investigate the distribution of pesticides in the atmosphere close to application sites as well as potential background concentrations during periods when no pesticides were applied.

To determine the pesticide concentrations in the atmosphere close to application sites, high-volume air samples were taken at two agricultural areas in Europe between April 2021 and June 2022. The developed and optimized method of the publication *Development of an analytical method for the determination of more than 300 pesticides and metabolites in the particulate and gaseous phase of ambient air* was applied to these samples. A total of 99 out of 329 investigated pesticides were detected in the air. To determine the distribution between the particulate and gaseous air phase, both air phases were analysed separately, and particle phase fractions were calculated. 97 % of the samples contained at least one pesticide and in 95 % of the samples, multiple pesticides were detected. Concentrations of the individual pesticides ranged between 0.003 ng/m³ for background concentrations and 10 ng/m³ during pesticide application periods.

For the evaluation of potential hazardous effects of the detected pesticides, hazard profiles were determined. 91 % of the observed pesticides could be linked to at least one out of eleven investigated human health effects, with 74 % being linked to multiple adverse human health effects. In addition, DIRs for adults, children, and infants were calculated for individual compounds as well as pesticide mixtures. The DIRs that were calculated for the highest mixture concentration present in one sample was around 173 times higher than the median DIR for single compounds. When compared to the ADI, DIRs were at least 1700 times below the ADI of the respective compound. As the ADI only accounts for uptake via food and drinking water and does not include the intake by inhalation or skin exposure, the total pesticide intake from all compartments could sum up to a higher value leading to a higher risk. In addition, data on pesticide mixture toxicity is not available and can therefore also sum up to a higher human health risk.

The results of this study provide valuable insights into the occurrence and distribution of legacy and currently used pesticides in the atmosphere across European agricultural areas. The data can be used

as an input for exposure modelling to better understand the behaviour of these compounds in the atmosphere and potential impacts on human health or the environment.

As a result of the work carried out as part of this doctoral thesis, the following paper has been published in *Science of the Total Environment.* The online version can be found at the following DOI: https://doi.org/10.1016/j.scitotenv.2024.173705.

Occurrence and distribution of pesticides and transformation products in ambient air in two European agricultural areas

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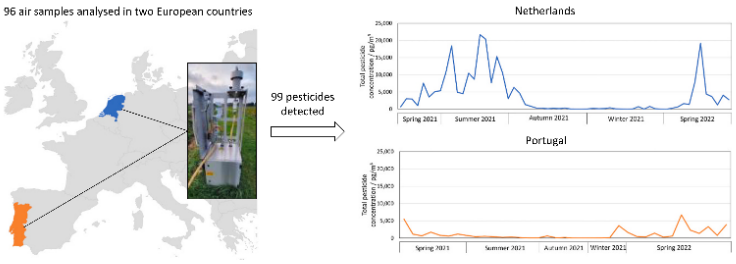
HIGHLIGHTS

- 99 pesticides and metabolites detected (3 to 10,000 pg/m^3) in ambient air.
- Gas-/particle-bound fractions of frequently detected pesticides.
- Multiple pesticides in most air samples.
- 11 pesticides reported for the first time in ambient air.
- Intake by inhalation relevant for human health risk assessment.

GRAPHICAL ABSTRACT



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ABSTRACT

Pesticides present a significant risk for both humans and the environment. However, quantitative data for a broad range of airborne pesticides in agricultural areas are missing. During or after the application, pesticides can reach the atmosphere and partition between the particulate and gaseous phase. As part of the EU project SPRINT, weekly ambient air samples were collected from two agricultural areas in Portugal (vineyard) and the Netherlands (potatoes, onions, and sugarbeet) between April 2021 and June 2022 using high-volume air samplers. The samples were analysed for 329 pesticides, of which 99 were detected. The most frequently detected compounds included the fungicides folpet, fenpropidin and mandipropamid, the insecticide chlorpyrifos-methyl, the herbicide terbuthylazine, and the metabolite prothioconazole-desthio, which were found with detection frequencies between 40 and 57 %. Pesticide concentrations ranged between 0.003 ng/m^3 and 10 ng/m^3. Remarkably, 97 % of the samples contained at least one pesticide and in 95 % of the samples, pesticide mixtures were present. The calculated particle phase fractions correlated with the octanol-air partitioning coefficient for most of the investigated compounds. Furthermore, calculated daily inhalation rates for individual pesticides and pesticide mixtures were far below the Acceptable Daily Intake (ADI) with a margin of exposure (MOE) of >1000 for the highest calculated daily inhalation rate for a child. However, as this value only includes pesticide intake from food and drinking water and considering that 91 % of the detected pesticides are associated with potential adverse human health effects. These findings highlight the broad range of airborne pesticides in agricultural

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areas and the need for quantitative data to include the intake of mixtures of highly hazardous pesticides by inhalation in human risk assessment.

1. Introduction

The production and use of synthetic chemicals is increasing more than any other drivers of global change, such as biodiversity loss or rising atmospheric CO_2 concentrations (Bernhardt et al., 2017). The growing world population demands a high and efficient food production and a high number of pesticides with large application volumes are used in the global agriculture with further growth being expected over the next decade (OEC, 2023; OECD, n.d.). In addition, climate change may lead to higher volatilization rates and degradation of pesticides due to rising temperatures and an increased number of pests is expected. Consequently, there could be a heightened necessity for increased spraying in the future to protect crops against these pests and diseases (Bernhardt et al., 2017; Delcour et al., 2015).

When pesticides are applied on agricultural fields, they can enter different environmental compartments, like soil or water, where they are widely studied. Even the influence of pesticides on biodiversity loss is discussed (Groh et al., 2022; Sigmund et al., 2023) and studies show a connection between the widespread application of pesticides and multiple environmental and human health concerns (Köhler and Triebskorn, 2013; Hertz-Picciotto et al., 2018; Jepson et al., 2020). During and after the application, pesticides can become airborne due to spray drift, volatilization, or wind erosion. This depends on different parameters, such as the physicochemical properties of the pesticide, the application method, field characteristics, and weather conditions (Majewski and Capel, 1995; Gil and Sinfort, 2005). Studies have shown that the emissions from spray drift can range from a few percent to 30 % and in some cases can even reach 50 % or more (van den Berg et al., 1999). Pesticides that reach the atmosphere are distributed between the particulate and gaseous phase contributing to atmospheric transport, which depends on the physicochemical properties of the compound, such as the vapour pressure or the octanol-air partitioning coefficient Koa (Pankow, 1987; Cousins and Mackay, 2001). The environmental fate of these compounds is a major concern, as they have been detected in the atmosphere in multiple European countries (Kruse-Plass et al., 2021; Carratalá et al., 2017; Schummer et al., 2010; Coscollà et al., 2010; Degrendele et al., 2016; Figueiredo et al., 2021) and even in remote areas such as the Arctic or Antarctica (Gao et al., 2019; Balmer et al., 2019; Bigot et al., 2016; Dickhut et al., 2005). However, most of these studies only focus on a small number of pesticides (up to 80 compounds) or use passive air samplers which makes a quantification of the compounds difficult as the determination of the exact volume is influenced by meteorological conditions (Galon et al., 2021; Melymuk et al., 2014). Therefore, high-volume air samplers are needed to determine pesticide concentrations in the atmosphere, but studies using these only investigated a small number of compounds, often focusing on organochlorine pesticides. Furthermore, studies on seasonal variations of the pesticide concentrations and distribution are only available for organochlorine pesticides and some currently-used pesticides (CUPs) (Degrendele et al., 2016; Li et al., 2014). In addition, these studies often overlook metabolites and transformation products (Galon et al., 2021; Yusá et al., 2009), despite the fact that these compounds can be toxic or persistent (Kotthoff et al., 2019; Ji et al., 2020). This is especially important when assessing potential risks, as metabolites or transformation products may result in higher risks by having e.g. different vapour pressures and can therefore more likely be emitted into the atmosphere (van den Berg et al., 1999). Furthermore, pesticides in the air pose a risk to humans by inhalation (Sanchez-Bayo, 2016; Pathak et al., 2022; Kalyabina et al., 2021), which depends on the distribution of the pesticide between the gaseous and particulate phase as smaller particles penetrate deeper into the respiratory system and can cause human health issues (WHO, 2003).

To address these gaps, a comprehensive study was conducted to analyse 329 pesticides, including 32 transformation products, in ambient air at two agricultural sites in Europe (Portugal and the Netherlands) using high-volume air samplers. The aim of this study is to determine the distribution between the particulate and gaseous phase as well as particle phase fractions. Additionaly, hazard profiles and daily inhalation rates were determined for the detected compounds to estimate potential risks to human health.

2. Materials and methods

2.1. Field campaign

96 air samples were collected between April 2021 and June 2022 in two agricultural areas in Aveiro District, Portugal and Borger-Odoorn, Drenthe, The Netherlands. The sampling was conducted by Wageningen University & Research and the University of Aveiro. The samples were taken at 1.5 m above ground with high-volume air samplers at an interval of one to two weeks, resulting in sample volumes of about 2000 m^3 of air. The air was sucked through glass-fibre filters and subsequently through adsorption cartridges. Particles were collected on glass-fibre filters (GFFs, 15 cm diameter, pore size of 0.6 µm, Macherey-Nagel, Düren, Germany), while glass columns filled with polyurethane foam (PUF, Tisch Environmental, Ohio, USA) and XAD-2 resin (Supelco, Munich, Germany) were used for the sampling of the gaseous phase. The GFFs and PUF/XAD-2 columns were wrapped with aluminium foil and sealed in polyethylene bags after sampling. They were stored at −20 °C after sampling and shipped frozen to Helmholtz-Zentrum Hereon for chemical analysis.

The two sampling sites cover different crop types (vineyards in Portugal, potatoes, sugar beets, onions, and cereals in the Netherlands) and different pesticide regulatory zones within the EU (Central and South EU) (European Commission, 2009). Meteorological data such as air temperature (T), wind direction (WD), wind speed (WS), and rainfall were collected from weather stations next to the sampling device (<100 m). Site characteristics are further described in the supplementary material (Figure SI28 and SI29).

2.2. Chemical analysis

In total, 329 pesticides (including 297 active substances and 32 transformation products: 108 insecticides, 91 fungicides, 88 herbicides, 5 acaricides, 3 antiparasitic, 1 synergist, and 1 plant growth regulator) were analysed in the air samples. The selection of pesticides and the multi-residue analysis was carried out as described by Debler and Gandrass (Debler, 2024). Briefly, GFFs were spiked with 500 ng of a standard mixture containing 15 mass-labelled internal standards (IS, see Table SI2) and extracted with a QuEChERS extraction method using a mixture of Milli-Q water/acetonitrile (1:2). The mixture was shaken head-to-head for 30 min. Anhydrous magnesium sulfate and sodium acetate were added and the mixture was vortexed and centrifuged (5 min, 3500 rpm). For the LC analysis, an aliquot of 125 µL was transferred to a LC vial, 25 µL of the injection standard (13C3-caffeine, 13C8-PFOA, and dTCEP, see table SI3) and 350 µL Milli-Q water were added and the extract was filtered by a syringe filter (0.2 µm, Whatman). For GC analysis, an aliquot of 4.5 mL was transferred, and a dispersive solid-phase extraction (d-SPE) was performed using anhydrous magnesium sulfate, primary secondary amine (PSA) and C18. 3.5 mL of the extract was transferred into a Barkey vial and evaporated under nitrogen to 150 µL. The solvent was exchanged to hexane and 20 µL of the injection standard (13C12-PCB-141) was added.

For the PUF/XAD-2 columns, a cold-column extraction was conducted. The columns were spiked with the IS mix and filled with dichloromethane. The columns were soaked for 1 h. This step was repeated twice, with soaking times of 30 min. The columns were purged with nitrogen at a pressure of 1.5 bar for 1 min. All three extracts were combined and divided equally into two aliquots. Each aliquot was evaporated under a gentle stream of nitrogen to a final volume of 150 µL. During this step, the solvent was exchanged to methanol for the LC analysis and to hexane for the GC analysis. Both extracts were filtered with a syringe filter (0.2 µm, Whatman) before analysis.

2.3. Instrumental analysis

Instrumental analysis was performed using liquid chromatography (Agilent LC 1290 Infinity II) coupled to a time-of-flight mass spectrometer (Agilent QTOF mass spectrometer 6546), operating in positive and negative electrospray ionisation. For chromatographic separation, an Acquity HSS T3 C18 column (150 × 2.1 mm, 1.8 µm, Waters) was used. The QTOF was operated in All-Ions (AI) mode.

For the gas chromatography, an Agilent 7010 GC was coupled to a tandem mass spectrometer (Agilent 7010 GC), operating in electron impact ionisation. Two 15 m HP-5ms columns (0.25 mm diameter, 0.25 µm film) with mid-point backflush were applied for chromatographic separation. The injector (300 °C) was operated in splitless mode with an injection volume of 1 µL. Further information on all analytical parameters were reported before by Debler and Gandrass (Debler, 2024).

2.4. Quality assurance

Three field blanks were collected at each sampling site during the sampling period and extracted in a similar manner as the samples. Procedural and instrumental blanks were analysed throughout the analysis to check for cross-contamination and interferences. Most compounds were not detected in the blanks. For compounds that were detected in the field blanks, minor corrections were performed by subtracting the average concentration of the field blanks.

Recovery rates were determined by spike-recovery tests as described by Debler and Gandrass (Debler, 2024). As method performance acceptability criteria, the parameters described in SANTE/12682/2019 were used (European Commission, 2020). For validated compounds (263 in the particulate phase and 75 in the gaseous phase), recovery rates (RR) ranged between 70 % and 120 % and relative standard deviations (RSD) below 20 %. With less stringent acceptability criteria (32 % < RR < 140 %, 1 % < RSD < 40 %), compounds were determined semi-quantitative (39 compounds in the particulate and 110 compounds in the gaseous phase). The remaining compounds (calibration curves R^2 > 0.97) were determined qualitatively (27 compounds in the particulate phase and 138 compounds in the gaseous phase).

Method quantification limits (MQLs) were determined as the lowest spike level of the validation meeting the performance acceptability criteria described above. For the method detection limits (MDLs), the signal-to-noise ratio (S/N) of 3 was used.

2.5. Statistical evaluation

Daily inhalation rates (DIRs) were calculated using the following formula:

$$DIR = \frac{c^{*}IR^{*}ED}{BW}$$

where DIR is the daily inhalation rate (ng/kg*day), c is the concentration of the compound (ng/m^3), IR is the inhalation rate (m^3/day), ED is the exposure duration and BW the bodyweight (kg). The exposure duration was set to one day. Applied inhalation rates were 20 m^3/day for adults, 10 m^3/day for children and 8 m^3/day for infants. For the bodyweight, values were set to 70 kg for adults, 15 kg for children, and 10 kg for infants (U.S. Environmental Protection Agency, 2011; U.S. Environmental Protection Agency and Office of Emergency and Remedial Response Toxics Integration Branch, 1991).

Pearson correlations were applied to establish the influence of weather conditions (temperature, precipitation, and wind direction) on pesticide concentrations and distribution in the air. Statistical analysis was performed using the software OriginPro 2023 (10.0.0.154). Statistics were conducted with calculated concentration values >MDL. For values <MDL, different substitution techniques (0, MDL, and MDL/2) were compared (see table SI7-SI9 in the supplemental information). Statistical analysis was performed for compounds with high detection frequencies above the MDL, and for which at least ten values were available.

3. Results and discussion

3.1. Pesticide occurrence and distribution

99 pesticides and transformation products were detected in the air samples in Portugal and the Netherlands (see Figs. 1 and 2 and table SI5 and SI6). Among the detected compounds were 31 herbicides, 35 fungicides, 19 insecticides, and 14 transformation products. In Portugal, 29 pesticides were detected in the particulate phase, while 24 pesticides were detected in the gaseous phase. In comparison, 67 pesticides were detected in the particulate phase in the Netherlands, whereas 54 pesticides were detected in the gaseous phase. Notably, 93 out of 96 samples (97 %) contained at least one pesticide. Furthermore, in 95 % of the samples, more than one pesticide was detected with average and maximum numbers of pesticides per sample of 12 and 34 compounds, respectively. To the best of the authors' knowledge, 11 pesticides were reported for the first time in ambient air: butocarboxim, THPI, chlorimuron-ethyl, clopyralid, isoprocarb, isoxaflutole, metolachlor oxanilic acid, nuarimol, oxamyl, rimsulfuron, and sedaxane.

Quantitative determination was performed for 27 pesticides (particulate phase) and 18 pesticides (gaseous phase) in Portugal, and 62 pesticides (particulate phase) and 39 pesticides (gaseous phase) in the Netherlands, with concentrations ranging from 0.003 to 10 ng/m^3 (median: 33 pg/m^3). All other compounds could only be determined qualitatively as described in 2.5. Concentrations were highest in spring and summer for both years. This was also the period where the highest application activity was observed. Pesticide concentrations outside the application period were lower and episodic (median: 21 pg/m^3, maximum: 744 pg/m^3) and probably resulted from emissions from soil or plants or the erosion of contaminated soils.

In the Netherlands, the most frequently detected pesticides were prothioconazole desthio (68 %), fenpropidin (56 %), fluopyram benzamide (53 %), fluopyram (30 %) and folpet (27 %). In Portugal, the most frequently detected pesticides are chlorpyrifos-methyl (86 %), chlorpyrifos (76 %), folpet (76 %), trans-permethrin (70 %), and terbuthylazine (68 %). All compounds most frequently detected in the Netherlands were approved by the EU by the time the sampling occurred. Chlorpyrifos-methyl, chlorpyrifos, and trans-permethrin frequently detected in Portugal were no longer approved for use in the EU during the sampling. However, chlorpyrifos and chlorpyrifos-methyl were approved in the EU until January 16th, 2020, and therefore their frequent detection could be due to volatilization from contaminated soil (Watts, 2012; Mulrooney et al., 2006). Considering all compounds, 11 non-approved pesticides including transformation products were detected in Portugal and 24 in the Netherlands. The maximum concentrations were found in Portugal for chlorpyrifos (3.5 ng/m^3) and for cyproconazole in the Netherlands (0.7 ng/m^3).

3.2. Phase distribution

The fraction of the particle phase was determined for all pesticides

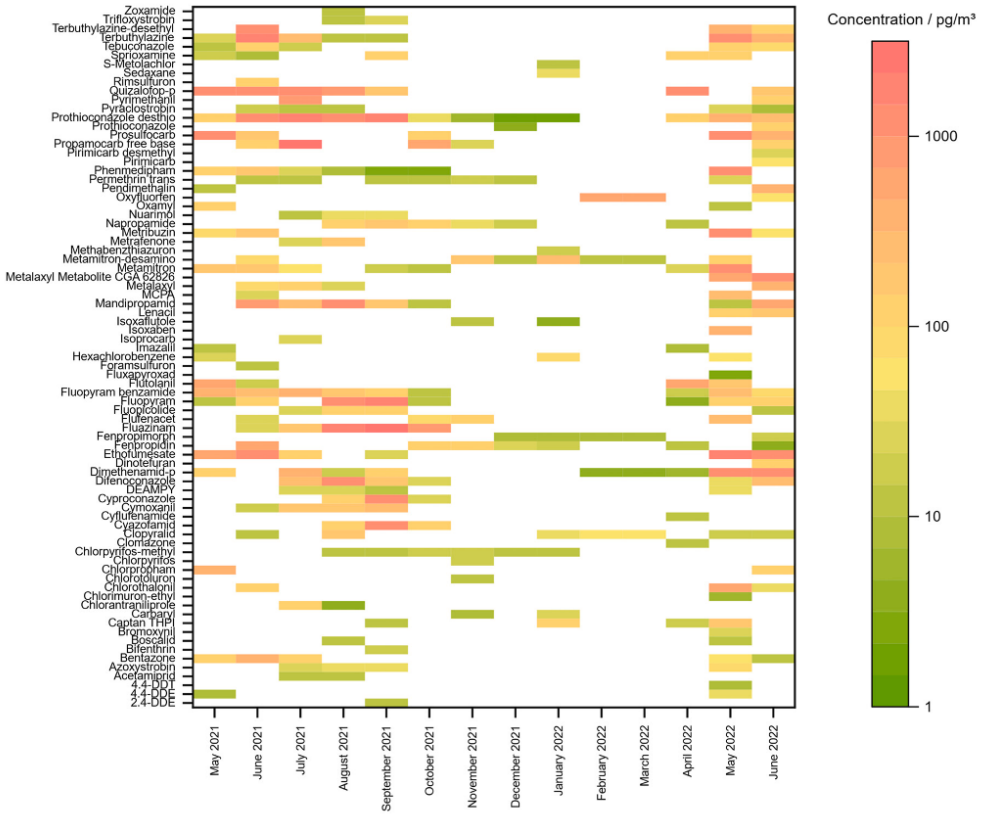

Fig. 1. Total concentrations of quantified pesticides in the Netherlands.

detected in both matrices with high detection frequencies and at least ten available values. This resulted in average particle phase fractions between 0.3 and 95 % for 3 compounds in Portugal and 9 compounds in the Netherlands (see table SI7 and SI8). In the Netherlands, fenpropidin and fluopyram were predominantly found in the particulate phase (average particle fraction >80 %). On the other hand, cymoxanil and ethofumesate were predominantly present in the gaseous phase (average particle fraction <21 %). Metamitron and prothioconazole-desthio were distributed between the particulate and gaseous phase with average particle fraction between 51 % and 65 %.

In Portugal, metalaxyl and terbuthylazine were predominant in the gaseous phase (average particle fraction <24 %), while trans-Permethrin was distributed between the particulate and gaseous phase with an average particle fraction of 48 %.

The observed partitioning behaviour of the analytes was correlated to the octanol-air coefficient Koa for all pesticides detected in both matrices. The Koa was significantly ($p < 0.05$) correlated with the average particle phase fraction for all investigated pesticides (r^2 = 0.81–0.89), showing that with higher Koa, the compound is more likely to be detected in the particulate phase (see Fig. 3).

Further factors, that could have influenced the phase distribution are environmental and sampling conditions, such as temperature, precipitation and the predominant wind direction. No or only low significant correlations between particle phase fractions and the environmental conditions were observed at both sampling sites. This suggests that other factors influence the phase distribution of these compounds, such as the amount, composition or origin of the particle phase.

3.3. Comparison of pesticide application and pesticide detection

For most pesticides, their detection correlated with their application on adjacent fields. In the Netherlands, 36 different pesticides were applied on the adjacent fields, including 19 herbicides, 12 fungicides, 3 insecticides and 1 adjuvant. In Portugal, 17 pesticides (16 fungicides and one insecticide) were applied on the adjacent fields during the sampling campaign. From all applied pesticides, 12 compounds were not covered by the applied analytical methods (alcohol ethoxylate, benthiavalicarb, copper oxychloride, copper sulphur, fosetyl-aluminium, glyphosate, maleic hydrazide, mancozeb, oxathiapiprolin, pyridat, sulphur, and trichoderma atroviride I-1237).

In Figs. 4 and 5, the seasonal variation of concentrations of fluopyram and its transformation product fluopyram benzamide, as well as fenpropidin, are exemplarily depicted in combination with their application on the adjacent fields. The diagrams illustrate that for fluopyram and fenpropidin, concentrations increase directly during and after applications and then gradually decrease afterwards. Information about the seasonal variations and times of application for all other compounds can be found in the supplementary information (table SI10 and SI11 and figures SI1 to SI27).

In total, 8 of the applied pesticides (clethodim, fipronil, florasulam, fluroxypyr, haloxyfop-p and pyraflufen-ethyl, cymoxanil, and kresoxim-methyl) were not detected in any sample, despite being applied on the field. A possible reason for this can be that some of these compounds (clethodim, fluroxypyr, haloxyfop-p, and pyraflufen-ethyl) could not be validated for the PUF/XAD-2 columns and had high MQLs for the GFFs (30–480 pg/m^3). In addition, some of the applied compounds were detected independently of their application on the adjacent fields,

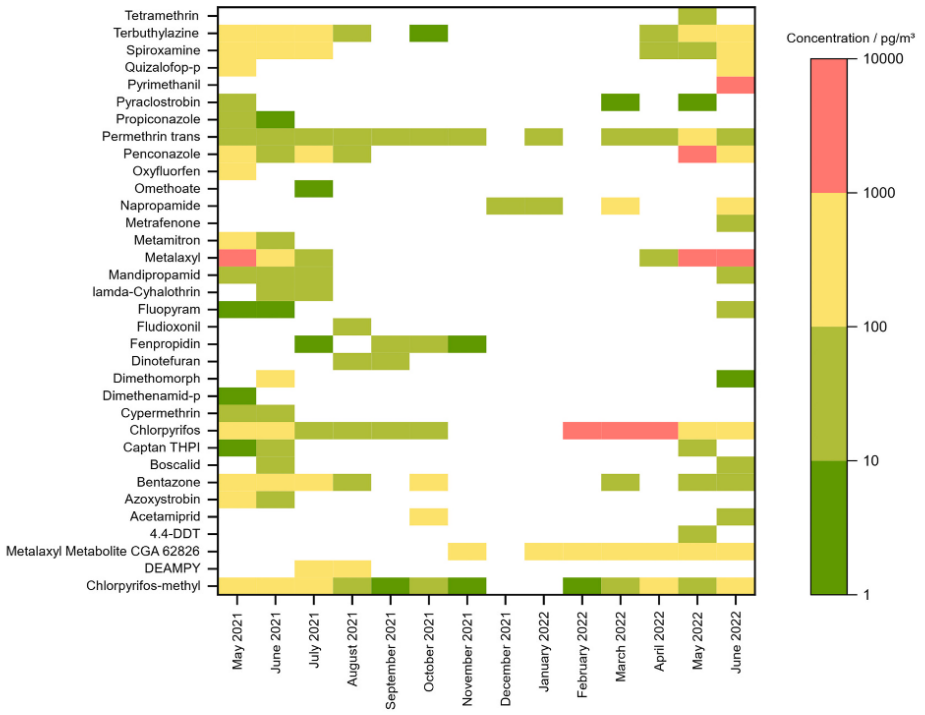

Fig. 2. Total concentration of quantified pesticides in Portugal.

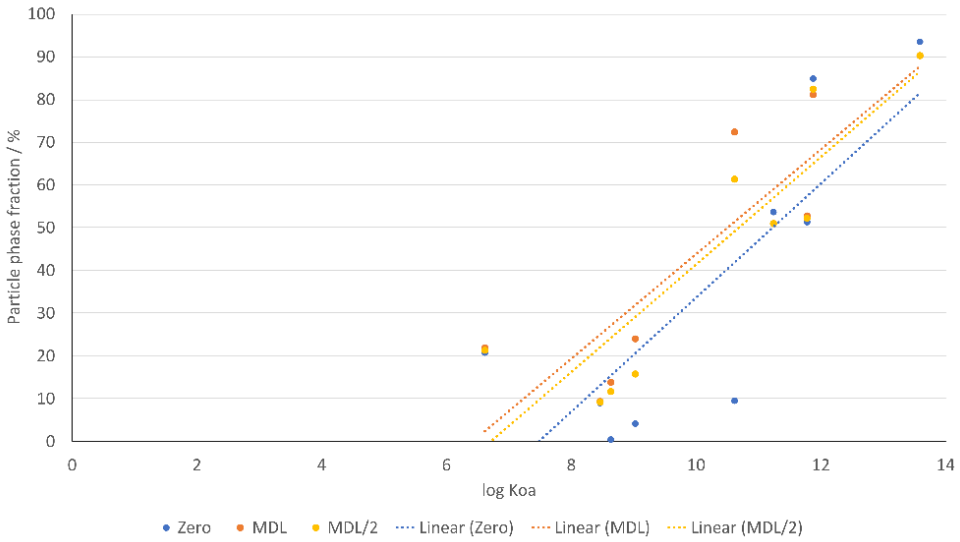

Fig. 3. Correlation between the log Koa and the particle phase fractions for frequently detected pesticides. Three different substitution techniques were compared for values below MDL (0, MDL and MDL/2). See details in table SI7 and SI8 (SI).

indicating that these pesticides could have been used on surrounding farms or been transported through the air from sources further away. When looking at the five most frequently detected pesticides in the Netherlands, four of them (prothioconazole desthio, fenpropidin, fluopyram benzamide, and fluopyram) were applied on the adjacent fields during the sampling time. Folpet was not applied on the fields but is commonly used for ornaments or vegetables and can therefore result from surrounding farms. In Portugal, three of the most frequently detected pesticides were not approved in the EU when the sampling occurred (as described earlier in 3.1). Folpet was applied on the adjacent fields in Portugal during the sampling time. Terbuthylazine was frequently detected in Portugal but not applied on the adjacent fields.

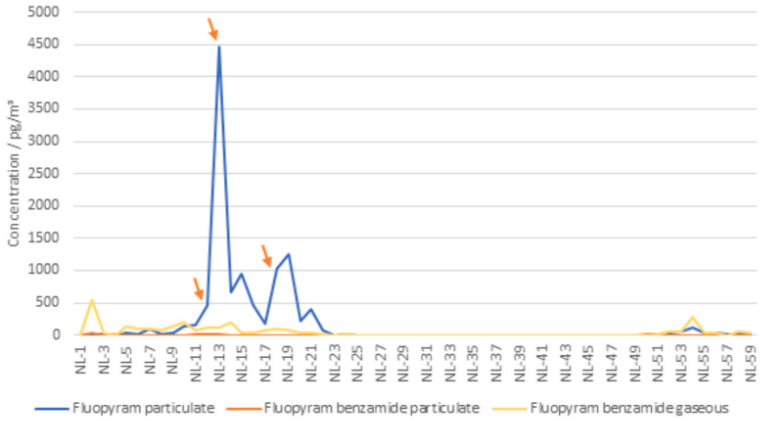

Fig. 4. Seasonal variation of fluopyram and its metabolite fluopyram benzamide concentrations in the particulate and gaseous phase in the Netherlands. Arrows indicate the time of application.

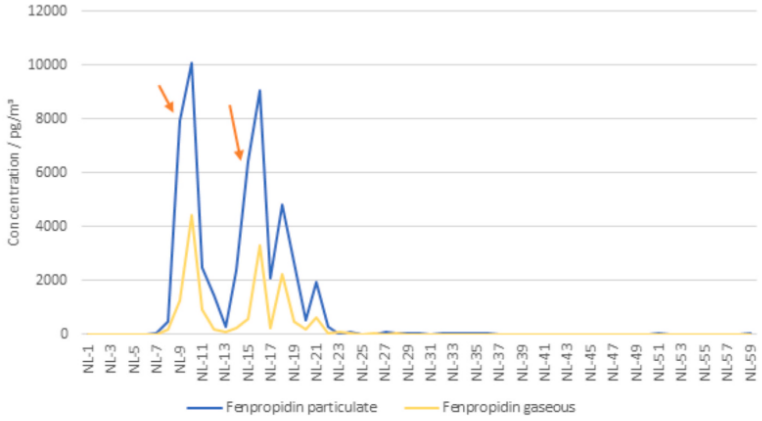

Fig. 5. Seasonal variation of fenpropidin concentrations in the particulate and gaseous phase in the Netherlands. Arrows indicate the time of application.

However, as it is commonly used in viticulture, it could result from the application on surrounding vineyards.

3.4. Hazard profile of the detected pesticides

Of all pesticides observed, 91 % (90 out of 99) can be linked to at least one out of the eleven considered adverse human health effects listed by the PPDB database (see Figs. 6 and 7 and Table SI12) and 42 % of the detected compounds are listed in the PAN International List of Highly Hazardous Pesticides with 83 % linked to acute or chronic toxicity and 62 % linked to environmental toxicity. Data for the human health effects were taken from the EFSA documents on pesticide risk assessment (EFSA, 2023). For several compounds, no data was available from these documents for one or more human health effects. For two of the nine pesticides not linked to any of the human health effects, no toxicity data was available at all. 74 % of pesticides could be linked to multiple adverse health effects with maximum number of effects per compound being 8 (chlorpyrifos). Fenpropidin, the most frequently detected pesticide in highest concentrations up to 10 ng/m^3, can be linked to 6 adverse health effects (neurotoxicity, reproductive and developmental toxicity, respiratory tract irritation, skin and eye irritation, and skin sensitising). Generally, the environmental or human risk assessment of pesticides or their transformation products is currently hampered by the lack of information regarding their modes of action and effect concentrations.

To determine potential exposure by inhalation, daily inhalation rates (DIRs) were calculated for median and maximum concentrations for both, individual compounds and mixtures (see table SI13 and SI14). The calculated DIRs were found to be higher for infants compared to adults, indicating that infants are more vulnerable to pesticide exposure. The DIRs reported here were in the same range as those found in South Africa (Degrendele et al., 2022) and Vietnam (Doan et al., 2021), but were higher compared to those found in China (Li et al., 2014; Zhou et al., 2020) and Brazil (Nascimento et al., 2017) and lower compared to DIRs from Spain (López et al., 2017) and the USA (Morgan et al., 2014) (see table SI15). In comparison to the Acceptable Daily Intake (ADI), all reported DIRs are more than three orders of magnitude below the respective values for single compounds. For fenpropidin, the highest DIR calculated for an infant was still 1700 times below the ADI for this substance. However, the ADI accounts only for uptake via food and drinking water and inhalation exposure (similar as skin exposure) could theoretically and in the worst-case lead to a higher risk. In addition,

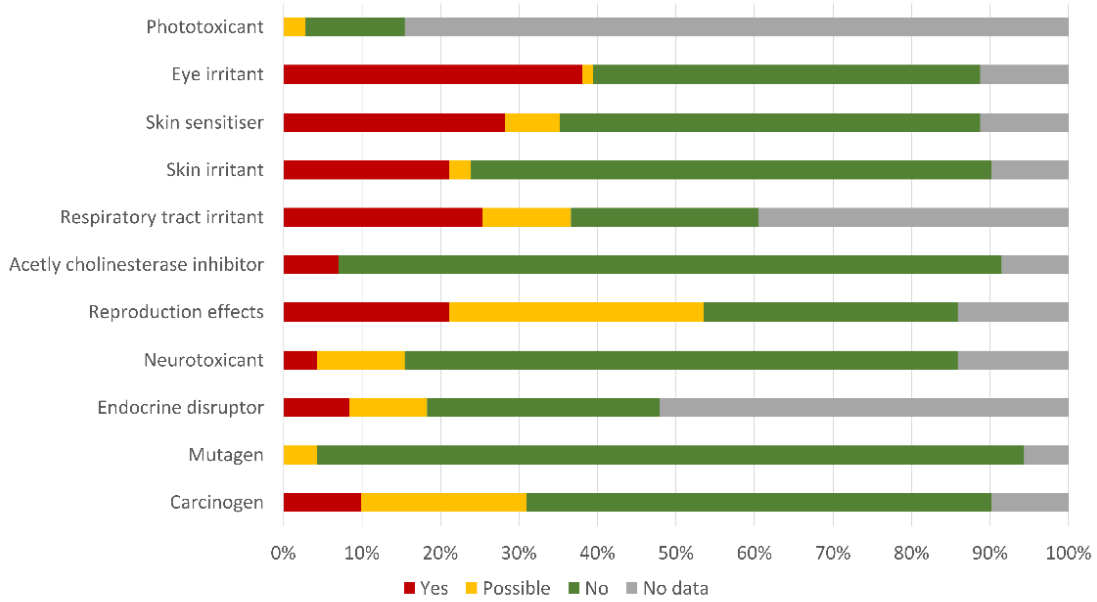

Fig. 6. Hazard profile of the detected compounds that are approved in the EU (source: EFSA).

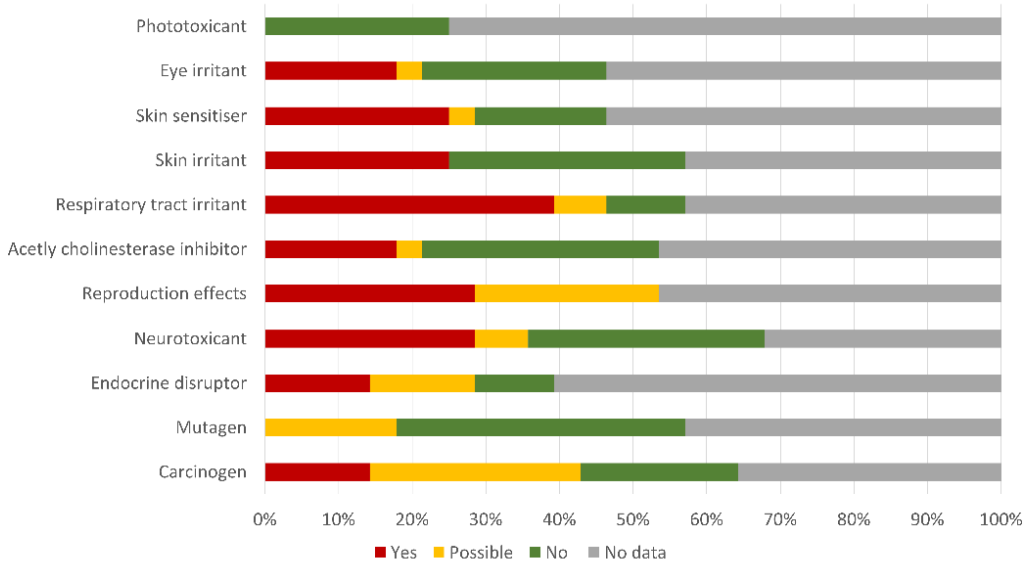

Fig. 7. Hazard profile of the detected compounds that are not approved in the EU (source: EFSA).

ADIs are only available for single compounds and data on mixture toxicities generally is not available.

4. Conclusions

The study conducted high-volume air sampling at two agricultural areas in Europe to determine the concentrations and particle phase fractions of pesticides in ambient air. The analysis revealed the widespread presence of a diverse range of pesticides and transformation products in the air, with concentrations between 0.003 and 10 ng/m^3. This indicates the atmosphere as an important pathway for transportation of pesticides, which is often overlooked and not yet included in monitoring programs across the EU.

Notably, 97 % of samples contained at least one pesticide and 95 % contained pesticide mixtures, with a maximum of 34 pesticides detected in a single sample. Moreover, pesticide transformation products were detected in 90 % of samples. The study found that pesticide concentrations were mainly driven by agricultural practices with the highest concentrations during spring and summer. However, pesticides were also detected in background concentrations of up to >700 pg/m^3,

indicating other sources or atmospheric transport of these compounds. Furthermore, differences were observed in phase distribution of pesticides with a significant correlation between the octanol-air partition coefficients of pesticides and their phase distribution.

The hazard profiles of the detected compounds revealed that 91 % of pesticides can be linked to at least one adverse human health effect and 42 % are included in the PAN International List of Highly Hazardous Pesticides, underlining the urgent need for risk assessment and regulations of these compounds. Daily inhalation rates for individual pesticides and pesticide mixtures were far below the Acceptable Daily Intake. However, these values only include pesticide intake from food and drinking water and no values are available for the effects of pesticide mixtures from inhalation. Therefore, further understanding of the potential effects of the reported concentrations is needed and the intake by inhalation should be included in risk assessment.

A comprehensive human health risk assessment for pesticides should consider intake by respiration for a wide spectrum of potentially hazardous pesticides, in addition to the uptake through food and drinking water. Furthermore, there is a vital need for improved knowledge on the modes of action and effect concentrations of pesticides, including their mixture toxicities.

CRediT authorship contribution statement

Freya Debler: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Nelson Abrantes:** Writing – review & editing, Resources, Investigation. **Paula Harkes:** Writing – review & editing, Resources, Investigation. **Isabel Campos:** Writing – review & editing, Resources, Investigation. **Juergen Gandrass:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.173705.

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5.3 Currently used and legacy pesticides in the marine atmosphere from Patagonia to Europe

The previous publication *Occurrence and distribution of pesticides and transformation products in ambient air in two European agricultural areas* focused on atmospheric pesticide concentrations across their source regions. The detection of 99 pesticides in these regions raised the question on how these compounds are further distributed across the atmosphere and if they can potentially undergo long-range atmospheric transport to remote areas such as the worlds' oceans or polar regions and thereby influence these pristine regions. Legacy pesticides such as organochlorines have been widely studied and detected in these remote areas, but data on CUPs is scarce and only a small number of them have been analysed in a few places. This raises concern on how CUPs are distributed across the atmosphere and if they can be transported over long distances. The aim of this study was to determine the occurrence and concentrations of pesticides in the atmosphere across the Atlantic Ocean and thereby identify CUPs that could potentially undergo long-range transport.

For the analysis of air samples from the Atlantic Ocean, the extraction method for the GFFs was applied as described in the publication *Development of an analytical method for the determination of more than 300 pesticides and metabolites in the particulate and gaseous phase of ambient air*. For the PUF/XAD-2 columns, the extraction method was further optimised to reduce matrix effects and to increase the number of compounds that can be quantified. Therefore, a QuEChERS-like approach was applied to the PUF/XAD-2 columns including the extraction with a mixture of Milli-Q water/acetonitrile + 1% acetic acid (1:2). For the GC-MS/MS analysis, a clean-up of the extracts was performed using a dispersive solid-phase extraction (d-SPE). The optimized extraction method was re-validated and applied to the air samples from the Atlantic Ocean. This approach reduced the matrix effects that were previously determined for the LC-QTOF analysis and increased the number of pesticides which matched the validation criteria of SANTE/12682/2019 [130].

Twelve particulate and gaseous air samples were taken with a high-volume air sampler between March and April 2023 on a transect along the Atlantic Ocean between Patagonia and Europe. Twenty-two pesticides were detected in the air samples, including fifteen CUPs, four transformation products, and three OCPs. Concentrations ranged between 1.6 and 420 pg/m³. All CUPs and TPs were detected for the first time in the atmosphere across the Atlantic Ocean. For twelve CUPs and four TPs, first empirical evidence was found that they may undergo long-range transport and should therefore be considered for future risk assessments.

To determine potential sources of the pesticides detected in this study, air mass back trajectories (BTs) and the mean rainfall rate at the trajectories passage were calculated. Potential sources of the pesticides included European agricultural areas in Spain and France, as well as the Canary Islands for

some samples taken along the European and African coastline. As the sampling took place during European spring, when pesticides are applied in agriculture, this can explain the occurrence of some of the detected CUPs along the European coastline. Samples taken along the South American coastline and between South America and Africa were mostly influenced by marine air masses, indicating that the compounds detected in these samples have been transported over a longer time or volatilized from seawater.

Consequently, this study identifies potential candidates for long-range transport from the group of CUPs and their TPs. This adds valuable information on the fate of these compounds in the environment and input data for future exposure modelling or risk assessments. In addition, the data shows, that even CUPs that are not expected to be transported over longer distances due to their calculated atmospheric residence time (< two days) and their physical-chemical properties can be detected in remote areas far away from their site of application.

As a result of the work carried out as part of this doctoral thesis, the following paper has been published in *Environmental Pollution.* The online version can be found at the following DOI: https://doi.org/10.1016/j.envpol.2025.126175.

Currently used and legacy pesticides in the marine atmosphere from Patagonia to Europe

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ABSTRACT

Pesticides can enter the atmosphere upon application due to spray drift, volatilization, or wind erosion. Subsequently, certain pesticides undergo atmospheric transport to non-target areas, where they deposit. To investigate their potential long-range transport, 329 pesticides were analyzed in air samples collected on a south-north Atlantic Ocean transect between South America and Europe in 2023. In total, twelve currently used pesticides (CUPs) and one transformation product (TP) were quantified in concentrations ranging from 1.6 to 420 pg/m^3. Additionally, nine pesticides (three CUPs, three TPs and three legacy pesticides) were detected in the air samples but could not be quantified as the method performance acceptability criteria were not met for these compounds. All CUPs and TPs were found in the marine atmosphere across the Atlantic Ocean for the first time. Higher pesticide concentrations were observed in the atmosphere of the northern hemisphere, while the number of pesticides per sample was comparable between the northern and southern hemisphere. Air mass back trajectories showed a high marine influence for the majority of samples, indicating a potential long-range transport of the found pesticides. This research provides the first empirical evidence for the long-range transport potential of 12 CUPs and 4 TPs to the remote atmospheric environment of the Atlantic Ocean. The calculated atmospheric half-lives of less than two days for these compounds indicate the importance to complement the model predictions with measurements of airborne pesticides in remote areas to assess their long-range atmospheric transport potential.

1. Introduction

The atmospheric transport of pesticides is a global issue leading to environmental and health impacts (Rani et al., 2021). During or after application, pesticides can end up in the atmosphere due to spray drift, volatilization, or wind erosion (Gil and Sinfort, 2005; Majewski and Capel, 1995). Consequently, they can be carried away from their application sites and deposit in regions far away from their intended source regions and therefore act as transboundary pollutants. Recent studies in the air in marine areas focus mostly on legacy pesticides amenable to gas chromatography-mass spectrometry (Lohmann et al., 2012; Pegoraro et al., 2016; Zhang et al., 2022; Li et al., 2020; Cincinelli et al., 2009; Xie et al., 2022). Due to their persistence, bioaccumulation, toxicity and the potential to undergo long-range atmospheric transport (LRAT), 18 legacy pesticides have been included in the Stockholm Convention on Persistent Organic Pollutants (POPs) since 2004 and have been banned or restricted globally (Stockholm Convention, 2024). This has led to a replacement by so-called currently used pesticides (CUPs). In addition, further CUPs have been developed, produced, and applied and more than 2000 pesticides are currently registered globally (British Crop Production Council, 2022). CUPs were expected to not be prone to LRAT due to their short atmospheric half-lives (< two days) (European

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Comission, 2009). However, some of them have been detected in the atmosphere in remote areas such as alpine regions (Feltracco et al., 2022; Ding et al., 2023a), national parks (Kruse-Plass et al., 2021), or polar regions (Mayer et al., 2024; Zhang et al., 2022; Zhong et al., 2012; Jantunen et al., 2015; Muir et al., 2019) indicating that their properties and environmental fate could make these compounds a concern.

An often overlooked aspect of pesticide contamination is the occurrence of transformation products (TPs). Some TPs can be toxic or persistent and may pose a greater risk than their parent compound (Kotthoff et al., 2019), such as some TPs of atrazine, which can be more persistent in soil compared to atrazine (Belfroid et al., 1998). Ji et al. (2020) also showed that the TPs of pyriproxyfen and malathion can have stronger endocrine disrupting effects than their parent compounds. Due to their different properties, some TPs are also more likely emitted into the atmosphere compared to their parent compounds (Atkinson et al., 1999; Woodrow et al., 2018). Furthermore, the absence of data on physical-chemical properties and persistency for numerous TPs impedes the accurate prediction of potential environmental or human health effects.

Previous studies on CUPs in the atmosphere mainly focused on terrestrial environments or coastal regions (Galon et al., 2021), while open oceans are only explored partly. Studies on airborne pesticides were conducted for example in the Mediterranean Area (Borras et al., 2011), the Western Pacific and Southern Ocean (Zhang et al., 2022), the Bohai Sea (Liu et al., 2018), and the Arctic Ocean (Zhong et al., 2012; Gao et al., 2019). Unlike legacy pesticides, CUPs are not included in regulatory Air Monitoring Programs in Europe, except partly in France (ATMO FRANCE, 2024) and Sweden (IVL Swedish Environmental Research Institute, 2021). A small number of CUPs is also included in a regulatory Air Monitoring Program in California, United States of America (California Department Of Pesticide Regulation, 2024). Especially data on the concentrations and distribution of airborne CUPs in the southern hemisphere are rare. In addition, there is a lack of data on the spatial distribution and transport pathways of CUPs in the marine atmosphere, as well as factors driving these patterns.

In this study, 329 pesticides, including 282 CUPs and 36 transformation products, were examined in the atmosphere across a south-north transect on the Atlantic Ocean. To cover the broad spectrum of analytes, both, gas chromatography and liquid chromatography coupled to mass spectrometry, were applied. The overall aim of this research was to investigate the potential of currently used pesticides to undergo long-range atmospheric transport. To achieve this, the major objectives of this research included (1) the determination of pesticide concentrations in the atmosphere of the Atlantic Ocean, (2) the investigation of the spatial distribution of pesticides across the Atlantic Ocean, and (3) the elucidation of potential sources and factors influencing pesticide transport in the investigated area.

2. Materials and methods

2.1. Sample collection

Air samples were collected during expedition PS135/1 and PS135/2 of the research vessel *Polarstern* between 12 March and April 07, 2023 (Schulze Tenberge and Fiedler, 2023; Alfred-Wegener-Institut Helmholtz-Zentrum für Polar-und Meeresforschung, 2017). A high-volume air sampler was installed on the observation deck. Air samples were taken using glass-fibre filters (GFFs, 15 cm diameter, Macherey-Nagel, Germany) for the particulate phase. For the gaseous phase, a slice of polyurethane foam (PUF, 1 inch, Tisch Environmental, USA) and 55 g of Amberlite XAD-2 resin (Supelco, Germany) were prepared in a glass column (PUF/XAD-2 column). The samples were collected along a latitudinal transect from Punta Arenas, Chile to Bremerhaven, Germany. In total, twelve air samples were taken with sampling durations between two and five days, depending on the distance to land and movement of air masses. This ensured detectable pesticide concentrations in each sample. The samples were stored at −20 °C on board, during transport, and until extraction at Helmholtz-Zentrum Hereon. An overview of the sampling dates and volumes is given in Table S1 of the Supporting Information (SI).

2.2. Target analytes and chemicals

329 pesticides were analyzed, including 282 CUPs, 11 legacy pesticides, and 36 transformation products (Table S7). 30 mass-labelled pesticides were used as internal standards (ISTD, Table S8). 13C8-perfluorooctanoic acid (13C8-PFOA), 13C3-caffeine, deuterated-tris(2-carboxyethyl)phosphine (dTCEP), and 13C12-polychlorinated biphenyl-141 (13C12-PCB-141) served as injection standards (InjS, Table S9). Detailed information on used chemicals for sample extraction and analysis is presented in Table S2.

2.3. Sample extraction and instrumental analysis

Multi-residue analysis of 329 pesticides was carried out as described in Debler and Gandrass (2024) for the glass-fibre filters (GFFs). Briefly, GFFs were spiked with 50 µL of a 10 ng/µL mass-labelled internal standard (ISTD) mix containing 30 mass-labelled internal standards (see Table S8). For the extraction, a Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) extraction with Milli-Q water/acetonitrile + 1 % acetic acid (1:2) was performed. The mixture was shaken head-to-head for 30 min and anhydrous magnesium sulfate and sodium acetate were added. The mixture was vortexed and centrifuged (5 min, 3500 rpm). For the analysis of the liquid chromatography coupled to a time-of-flight mass spectrometer (LC-QTOF), 125 µL of the extract were transferred to a LC vial. 25 µL of the LC injection standard mix (LC-InjS, see Table S9) and 350 µL Milli-Q water were added. The extract was filtered by a syringe filter (0.2 µm, Whatman) prior to analysis. For the gas chromatography coupled to a triple-quadrupole mass spectrometer (GC-MS/MS) analysis, an aliquot of 4.5 mL was transferred to an Eppendorf tube and a dispersive solid-phase extraction (d-SPE) was performed using anhydrous magnesium sulfate, primary secondary amine (PSA) and C18. An aliquot of 3.5 mL was transferred to a Barkey vial and evaporated under nitrogen to 150 µL. A solvent exchange to hexane was performed and 20 µL of the GC injection standard (GC-InjS, see Table S9) were added.

For the PUF/XAD-2 columns, the method was further optimized to reduce matrix effects and to improve the reproducibility of the method. After addition of the ISTD mix (500 ng of each compound), PUF/XAD-2 columns were extracted with the QuEChERS approach using a mixture of Milli-Q water/acetonitrile + 1 % acetic acid (1:2). 30 mL of the extract were transferred to two Eppendorf tubes containing anhydrous magnesium sulfate and sodium acetate. The mixture was vortexed and centrifuged. For the LC-QTOF analysis, 10 mL were transferred to a Barkey vial from one of the Eppendorf tubes and evaporated under nitrogen to 150 µL. After transfer of the extract to an LC vial, Milli-Q water and 25 ng of the LC injection standard mix (LC-InjS, see Table S9) were added. The extracts were filtered by a syringe filter (0.2 µm, Whatman) prior to analysis. For the GC-MS/MS analysis, 15 mL were transferred from the other extract into an Eppendorf tube and a dispersive SPE was performed. 10 mL of the extract were transferred to a Barkey vial and evaporated to 150 µL under nitrogen. A solvent exchange to hexane was performed and 20 ng of the GC injection standard (GC-InjS, see Table S9) were added.

Instrumental analysis of 313 target analytes was performed using liquid chromatography (Agilent LC 1290 Infinity II) coupled to a time-of-flight mass spectrometer (Agilent QTOF mass spectrometer 6546). Both, negative and positive electrospray ionisation (ESI) were employed. The QTOF was operated in All-Ions (AI) mode. For the analysis of 33 pesticides, an Agilent 7890 gas chromatograph was coupled to a tandem mass spectrometer (Agilent 7010), operating in electron impact ionisation (EI). An overview of parameter settings and

hardware components for the LC-QTOF analysis is given in Table S3 and Table S4. Detailed information on the GC-MS/MS analysis is provided in Tables S5 and Table S6.

2.4. Quality assurance and quality control

Procedural and instrumental blanks using clean GFFs and PUF/XAD-2 columns and solvents were processed together with the samples. Field blanks ($n = 3$) were taken during the cruise for both, GFFs and PUF/XAD-2 columns, and analyzed together with the samples. Pesticide concentrations in air samples were calculated by using the internal standard method and were field blank corrected.

Prior to sampling, GFFs were baked out at 450 °C for 6 h, wrapped in aluminium foil and sealed in alumina-coated polypropylene (PP) bags. PUF/XAD-2 columns were prepared in a clean lab (class 10.000) and cleaned by Soxhlet extraction for 24 h each, using methanol and dichloromethane. The columns were dried under nitrogen (1.5 bar) and sealed in alumina-coated PP bags until sampling.

Recovery rates were determined by spike-recovery tests as described by Debler and Gandrass (2024). Triplicates of matrix loaded GFFs and PUF/XAD-2 columns were spiked at two different spiking levels. As method performance acceptability criteria, the parameters characterized in SANTE/12682/2019 were applied (European Comission). Recovery rates ranged from 70 to 120 % for 263 compounds (GFFs) and 119 compounds (PUF/XAD-2 columns) with relative standard deviations (RSD) below 20 %. For additional 39 compounds (GFFs) and 108 compounds (PUF/XAD-2 columns), recovery rates ranged between 30 to 70 % and 120–140 %, resulting in semi-quantification. The remaining compounds with correlation coefficients (R^2) of the calibration curves >0.97 were qualitatively identified (27 compounds on the GFFs and 47 compounds on the PUF/XAD-2 columns). The recovery rates as well as the validation status for each compound are depicted in Table S10 (GFFs) and S11 (PUF/XAD-2 columns).

Breakthrough experiments were conducted for the PUF/XAD-2 columns by operating two columns in series. The upper columns were spiked with the analyte mixture. Pesticide concentrations detected on the second column were determined as breakthrough ($n = 3$).

Method quantification limits (MQLs) were determined as the lowest spike level of the validation meeting the performance acceptability criteria described above. For the method detection limits (MDLs), the signal-to-noise ratio (S/N) of 3 was used. The individual MDLs and MQLs can be found in Table S10 (GFFs) and S11 (PUF/XAD-2 columns).

2.5. Calculation of air mass back trajectories

To examine the influence of air mass origin, 96-h air mass back trajectories were computed for each sampling location using NOAA's HYSPLIT model (Stein et al., 2015) and the GDAS1 meteorological input (NOAA Air Resources Laboratory, 2019). To account for uncertainties related to the current atmospheric state and back trajectory computation, an ensemble of 27 back trajectories was launched every 6 h from a 3 × 3 horizontal grid centered on the current position of the ship (current latitude and longitude ± 0.5°) and three different starting altitudes (50, 150, and 250 m above sea level). The air mass origin corresponding to each sample was then evaluated based on 7 to 20 of such ensembles, i.e. 180 to 540 individual back trajectories, depending on the sampling time. To assess the possible wet deposition of pesticides during the atmospheric transport, the mean rainfall rate at the trajectories passage was calculated using the 6-h average rainfall field from the GDAS1 dataset.

3. Results and discussion

3.1. Occurrence of pesticides in the air above the Atlantic Ocean

In total, twenty-two pesticides were found in the air above the Atlantic Ocean including fifteen CUPs, four transformation products, and three legacy pesticides. All main pesticide groups were present and equally represented, namely six insecticides, five herbicides, seven fungicides, and four transformation products. Seventeen pesticides were present in the gaseous phase only, two pesticides were found in the particulate phase only, and three pesticides were found in both phases.

The six most abundant compounds with detection rates >50 % were flumioxazine (75 %), metalaxyl metabolite CGA 62826 (75 %), hexachlorobenzene (67 %), metamitron (67 %), bifenthrin (50 %), and fenpropidin (50 %). Concentrations for individual compounds ranged between 1.6 (flupyradifurone) and 420 pg/m^3 (clopyralid). Nine of the detected pesticides could only be qualitatively identified as the method performance acceptability criteria were not met for these compounds (see Section 2.4). Chemical properties, the range of concentrations, and their approval status in Europe, South America and Africa are depicted in Table 1. For further information on pesticides properties see Table S12.

In this study, fifteen CUPs and four transformation products were found for the first time in the atmosphere above the Atlantic Ocean to the best of the authors' knowledge. Mayer et al. (2024) detected tebuconazole, S-metolachlor, and fenpropidin at the Pallas Atmosphere-Ecosystem Supersite (PAL) in Finland in concentrations (0.062–170 pg/m^3) similar to the concentrations detected for these compounds or their transformation products in this study. Similar concentrations for tebuconazole were also detected by Zhang et al. (2022) in the Western Pacific and Southern Ocean.

Except for fenuron, all found CUPs and TPs were approved in at least one of the continents bordering the Atlantic Ocean during the sampling period (Table 1). Bifenthrin, cyflufenamid, flonicamid, fluopyram, and isoxaflutole are all compounds that have at least one carbon-bonded trifluoromethyl (CF_3) group and can therefore be precursors of the very persistent and very mobile (vPvM) substance trifluoroacetate (TFA; CF_3COO^-). Both the C-CF3-containing pesticides and TFA belong to the group of per- and polyfluoroalkyl substances (PFAS) according to the OECD definition (Freeling and Björnsdotter, 2023). While a restriction proposal for the entire class of PFAS is discussed under the European chemicals regulation REACH (European Chemicals Agency, 2024), active ingredients in plant protection products have been excluded from the proposed restriction (European Chemicals Agency, 2023). Under the European pesticide regulation, the approval periods for cyflufenamid, flonicamid, and fluopyram have been recently extended (European Commission, 2024).

3.2. Spatial distribution and potential sources of pesticides between South America and Europe

Total pesticide concentrations and total number of pesticides per sample along the transect are depicted in Fig. 1. Sum and individual pesticide concentrations were generally higher in the northern hemisphere with highest concentrations along the European coastline. In contrast, the number of pesticides per sample did not vary between the northern and southern hemisphere (min = 3, max = 10, median = 7). Five pesticides or TPs (2.4′-DDE, cyflufenamide, dicloran, fluopyram, and metolachlor oxanilic acid) were only found in the southern hemisphere along the coastline of South America. Dicloran, fluopyram, and the parent compound of metolachlor oxanilic acid are registered for use in Argentina and Brazil, which could explain their occurrence due to possible influence from agricultural activities. Five pesticides or TPs (4.4′-DDD, carbofuran, flonicamid, flupyradifurone, and tebuconazole) were only present in the northern hemisphere along the north African and European coastline, of which flonicamid, flupyradifurone, and tebuconazole were registered for use in Africa and the EU during the sampling campaign.

Air mass back trajectories were modelled for each sample to determine the origin of the air masses and discuss possible sources of the found pesticides (see Fig. 2 and Figs. S1–S8 in the SI). High residence

Table 1
Chemical properties, detection frequencies, concentrations and approval status of the found pesticides (NAFDAC Greenbook, 2022, US EPA, 2024; Argentina.gob.ar; Comité Permanent Inter-États De Lutte Contre La Sécheresse Dans Le Sahel, 2021; Ministério Da Agricultura E Pecuária, 2003; Office National De Sécurité Sanitaire Des Produits Alimentaires, 2013).

Compound	Type of pesticide[1]	Atmospheric half-life / days, 25 °C (US EPA, 2024)	Air phase in which the compound was found[2]	Instrumental analysis	Range of concentrations/ pg/m³	Detection frequency / %	Approval status EU[3]	Registration status north-western Africa[4]	Registration status eastern South America[5]
CUPs									
Bifenthrin	I	0.36	G	GC-QQQ	qualitative	50	not registered	registered for use	registered for use
Carbofuran	I	0.41	G	LC-QTOF	10*	8	not registered	not registered	registered for use
Clopyralid	H	19	G	LC-QTOF	184*-417*	33	registered for use	registered for use	registered for use
Cyflufenamide	F	1.7	G	LC-QTOF	qualitative	8	registered for use	registered for use	not registered
Dicloran	F	77	G	LC-QTOF	50*-60*	17	not registered	not registered	registered for use
Dimethomorph	F	0.1	P and G	LC-QTOF	22*-41	25	registered for use	registered for use	registered for use
Fenpropidin	F	0.1	P and G	LC-QTOF	8.3*-24	50	registered for use	registered for use	not registered for use
Fenuron	H	0.2	G	LC-QTOF	4.6*-16*	42	not registered	not registered	not registered
Flonicamid	I	13	G	LC-QTOF	132*	8	registered for use	registered for use	registered for use
Flumioxazine	H	0.2	G	LC-QTOF	qualitative	75	registered for use	not registered	registered for use
Fluopyram	F	1.7	P	LC-QTOF	14*-19*	17	registered for use	registered for use	registered for use
Flupyradifurone	I	0.4	G	LC-QTOF	1.6*	8	registered for use	registered for use	not registered
Isoxaflutole	H	1.8	G	LC-QTOF	62-335	42	registered for use	registered for use	registered for use
Metamitron	H	0.6	G	LC-QTOF	32-70	67	registered for use	registered for use	registered for use
Tebuconazole	F	0.9	G	LC-QTOF	114	8	registered for use	registered for use	registered for use
TPs									
Metalaxyl Metabolite CGA 62826	TP	0.4	G	LC-QTOF	qualitative	75	registered for use	registered for use	registered for use
Metolachlor ethane sulfonic acid	TP	0.2	G	LC-QTOF	qualitative	33	registered for use	registered for use	registered for use
Metolachlor oxanilic acid	TP	0.2	P	LC-QTOF	qualitative	8	registered for use	registered for use	registered for use
Prothioconazole desthio	TP	1.2	P and G	LC-QTOF	22-97	33	registered for use	registered for use	registered for use
legacy pesticides									
2.4′-DDE	I	1.4	G	GC-QQQ	qualitative	8	not registered	registered for vector control	not registered
4.4′-DDD	I	2.5	G	GC-QQQ	qualitative	8	not registered	registered for vector control	not registered
Hexachloro-benzene	I	633	G	GC-QQQ	qualitative	67	not registered	not registered	not registered

[1]I = insecticides, H = herbicides, F = fungicides, TP = transformation product
[2]G = gaseous phase, P = particulate phase
[3]Approval status of the compound or parent compound during sampling campaign according to the EU Pesticide Database (European Commission 2024)
[4]Included countries are CILSS countries (Benin, Burkina Faso, Cabo Verde, Chad, Ivory Coast, Gambia, Guinea, Guinea-Bissau, Mali, Mauritania, Niger, Senegal, Togo) (Comité permanent inter-États de lutte contre la sécheresse dans le Sahel (CILSS) 2021), Morocco (Office National de Sécurité Sanitaire des Produits Alimentaires 2013), and Nigeria (NAFDAC Greenbook 2022)
[5]Included countries are Argentina (Argentina.gob.ar) and Brazil (Ministério da Agricultura e Pecuária, 2003)
*Concentration below MQL

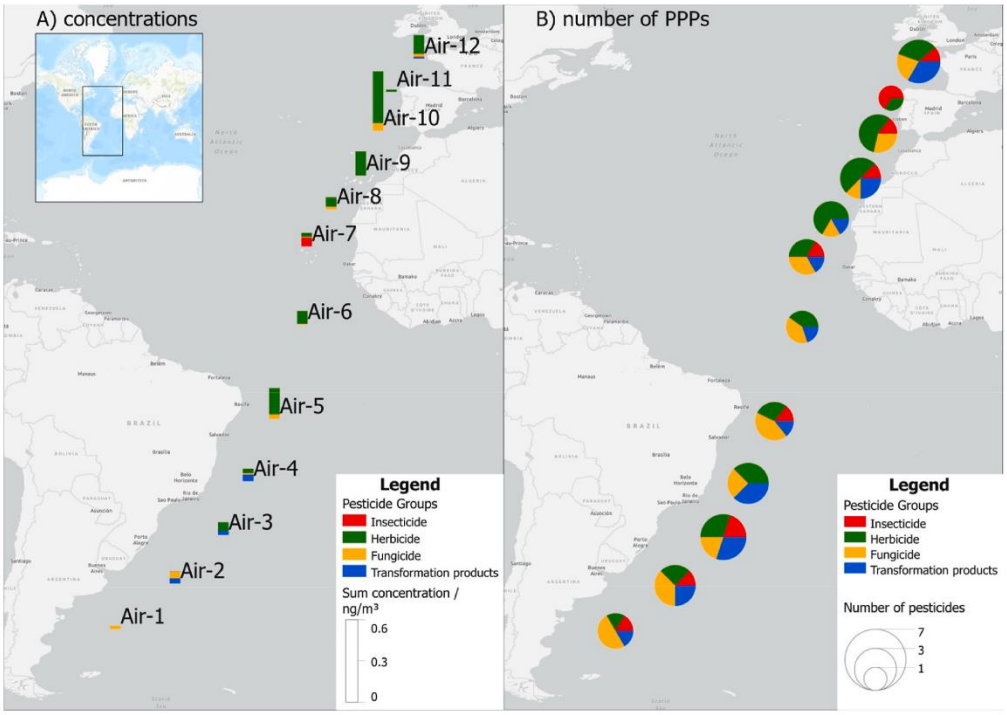

Fig. 1. Total A) pesticide concentrations and total B) number of pesticides found in the air above the Atlantic Ocean.

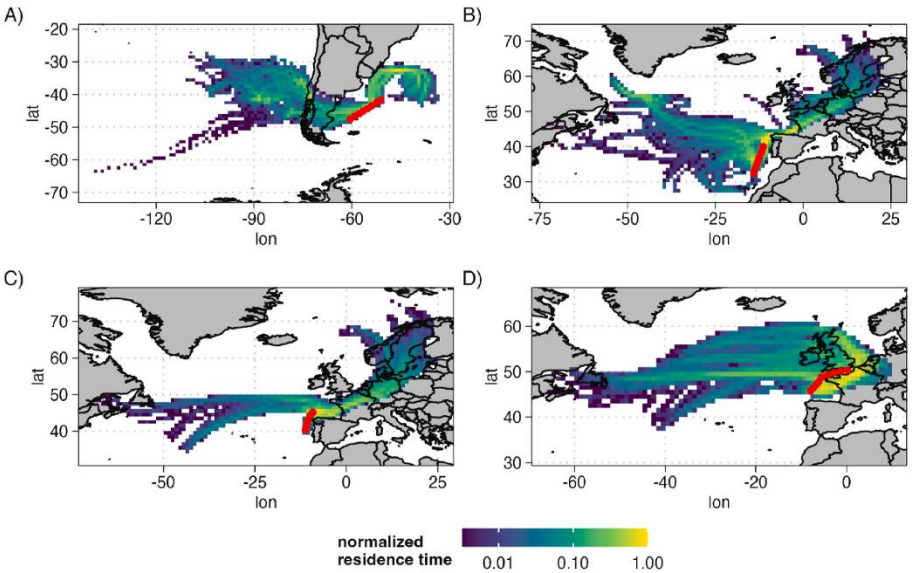

Fig. 2. Normalized residence times of air masses for samples A) PS135–1, B) PS135–10, C) PS135-11, and D) PS135-12. The air mass back trajectories were calculated for three different starting altitudes (50, 150, and 250 m above sea level).

times of air masses in the marine atmosphere can explain the low pesticide concentrations in samples PS135-Air-2 to PS135-Air-4 and PS135-Air-6 to PS135-Air-8. For sample PS135-Air-1, air masses were transported from southern Patagonia for the first half of the sampling period, and from the marine atmosphere for the second half of the sampling period (see Fig. 2). This could explain the low pesticide concentrations in this sample as southern Patagonia is an area with low agricultural influence and is covered largely by ice shields and glaciers.

Highest pesticide concentrations in the southern hemisphere were found in sample PS135-Air-5. Although air masses originated from marine areas, the comparatively high concentration in sample PS135-Air-5 can be explained by the presence of clopyralid (350 pg/m^3), a herbicide with a high atmospheric half-life (19 days). Highest pesticide concentrations in the northern hemisphere were quantified in samples PS135-Air-9 (360 pg/m^3), PS135-Air-10 (880 ng/m^3), and PS135-Air-12 (350 pg/m^3). Back trajectories show that air masses sampled in PS135-Air-10 have passed over the northwest of Spain and air masses sampled in PS135-Air-12 have passed over the northwest of France (see Fig. 2). In these areas, agricultural activities include the growing of crops, which could explain the detection of clopyralid, dimethomorph, flumioxazine, isoxaflutole, metalaxyl metabolite CGA 62826, metamitron, metolachlor ethane sulfonic acid, prothioconazole desthio, and tebuconazole as these compounds are typically used in maize, potato and cereal cultivation. Sample PS135-Air-9 was mainly influenced by marine air masses from the Atlantic Ocean. However, the back trajectories show an influence of the Canary Islands as the ship passed through Tenerife and Gran Canaria (see Fig. S8). Gran Canaria (405,381 t) and Tenerife (264,481 t) had the highest agricultural production of all Canary Islands in 2023 (Instituto Canario de Estadìstica, 2023). Therefore, higher pesticide concentrations can result from agricultural activities on the islands and the short distance to the islands during the sampling period. In comparison, PS135-Air-11 had only low pesticide concentrations. These can be explained by a high marine influence, as air masses resulted mainly from the atmosphere across the Bay of Biscay (see Fig. 2). Higher concentrations and a higher number of herbicides found along the European coastline can also be explained by the fact that the sampling took place during European spring, when herbicides are typically applied in agriculture. In addition, runoff from land during the pesticide application period could result in higher concentrations in the seawater, leading to a potential volatilization into the atmosphere. The modelling of the mean rainfall indicated that wet deposition was not likely to significantly influence pesticide concentrations in most of the samples (see Figs. S1–S12). Nevertheless, it needs to be considered that brief, but intense precipitation events might not be represented well in the 6 hourly rainfall data of the GDAS1 meteorological input to calculate back trajectories. For sample PS135-Air-12, mean rainfall rates between 0.1 and 0.8 mm/h were observed for air masses with high normalized residence times, which could explain lower pesticide concentrations compared to sample PS135-Air-10.

Possible sources of legacy pesticides include impurities or by-products in manufacturing processes. Dicofol formulations can be a source of DDT (Qiu et al., 2005) and Dicofol has been reported in agricultural use in Argentina (Gonzalez et al., 2010). In addition, DDT is still used for public health control in Africa and Asia (Liu et al., 2009; Chakraborty et al., 2010; van den Berg et al., 2021). Possible sources of HCB include emissions during the production of aluminum (Westberg et al., 2011) and magnesium (Deutscher and Cathro, 2001). Atmospheric measurements also indicate that combustion processes and industry in China (Liu et al., 2009) and India (Chakraborty et al., 2010) are possible HCB sources. These emissions of legacy pesticides in addition to their persistence can explain that they are still detected in the atmosphere across the Atlantic Ocean.

3.3. Long-range transport potential

Of the twenty-two pesticides found in this study, three compounds (fenpropidin, S-metolachlor, and tebuconazole) have been identified before to be prone to LRAT (Mayer et al., 2024). This study provides the first empirical evidence for the occurrence of additional twelve CUPs and four TPs in the atmosphere across the Atlantic Ocean, implying that these pesticides may undergo long-range transport (LRT). Within the international Stockholm Convention on Persistent Organic Pollutants the potential of a compound to undergo LRT is defined by, i) measured levels in locations distant from source regions that are of potential concern, ii) monitoring data showing the potential transport of a compound to a receiving environment via air, water, or migratory species, or iii) environmental fate properties and/or model results that demonstrate that the chemical has a potential for long-range environmental transport through air, water or migratory species (Stockholm Convention, 2020). The detection of the twelve CUPs and four TPs across the Atlantic Ocean distant from their source regions therefore indicates a potential transport of these compounds via air or water as defined in the Stockholm Convention.

National or supranational pesticide risk assessments, such as from the European Commission, include modelled atmospheric half-lives as a proxy for the assessment of the long-range atmospheric transport potential of a chemical (European Comission, 2009). Pesticides with atmospheric half-lives above two days resulting from the reaction with OH radicals are considered as prone to LRAT (European Comission, 2009). For the calculation of these values, annual mean OH concentrations (5×10^5 OH/cm^3) are applied (Atkinson, 1986). For three of the found pesticides, atmospheric half-lives based on EPI suite calculations (version 4.11) exceed this value (clopyralid 19 days, dicloran 77 days, and flonicamid 13 days), which can explain their occurrence. For all other compounds, the calculated atmospheric half-lives based on the reaction with OH radicals are below two days, indicating that different OH concentrations, temperatures or other factors may influence their transport. Pesticides can also be transported through water bodies and volatilize into the atmosphere which depends on their Henry's law constants. Most of the found CUPs and TPs have a moderate water solubility and low Henry's law constant, indicating that a long transport through water bodies cannot be excluded (see Table S12). Findings of carbofuran, cyflufenamide, dicloran, metalaxyl, and metolachlor in surface seawater samples from the Arctic Ocean (Ding et al., 2023b) and of tebuconazole in surface seawater samples in the Western Pacific and Southern Ocean (Zhang et al., 2022) underline this assumption.

3.4. Hazard profiles

All of the observed pesticides can be linked to at least one out of eleven considered adverse human health effects listed by the PPDB database (University of Hertfordshire, 2025), except for Fenuron for which no data on adverse human health effects is available. Further eight pesticides are included in the PAN International List of Highly Hazardous Pesticides, indicating potential risks for the environment and human health (Pesticides Action Network International, 2021). Data for the human health effects were taken from the pesticide risk assessments conducted by the EFSA (EFSA, 2023). Nine of the found compounds are carcinogenic (1) or possibly carcinogenic (8), three are genotoxic (1) or possible genotoxic (2), six compounds are neurotoxic (3) or possibly neurotoxic (3), six compounds are endocrine disruptors (5) or possible endocrine disruptors (1), and twelve are reprotoxic (5) or possible reprotoxic (7) (see Fig. 3 and Table S13). 68 % of the found pesticides could be linked to multiple human health effects with a maximum number of effects per compound being 6 (bifenthrin and fenpropidin). However, for some of the found compounds and observed human health effects, no data was available at all which impedes the human risk assessment of pesticides and their transformation products.

Additionally, pesticides in the marine atmosphere may potentially impact marine organisms, including seabirds and marine mammals. Upon deposition on the surface of seawater, these substances can also affect other marine organisms. POPs, such as the found DDT and HCB, are known to cause adverse effects on marine organisms (Sonne et al., 2020). DDT has been associated with the thinning of eggshells and subsequent reproductive effects in seabirds (Helander et al., 2008). Furthermore, DDT and HCB have been linked to endocrine disrupting effects in ringed seals (Routti et al., 2010) and harbour porpoises (Das et al., 2006). CUPs, although generally considered less persistent and bioaccumulative than legacy pesticides, have demonstrated potential risks to marine wildlife. Pyrethroids, such as the found bifenthrin, have

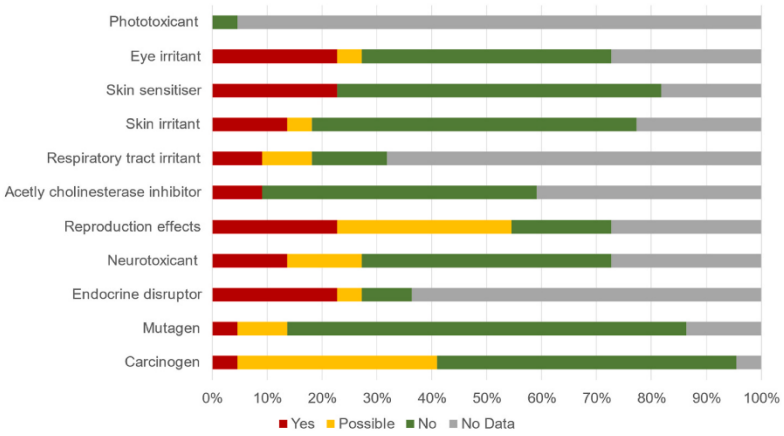

Fig. 3. Pesticides found in this study and their hazard profiles (source of the hazard properties for each found compound: EFSA, 2023. Chemical Hazards Database (OpenFoodTox)).

been observed to accumulate in marine mammals and can be transferred from mother to calf (Alonso et al., 2012). Additionally, pyrethroids have been associated with developmental neurotoxicity in zebrafish embryos (DeMicco et al., 2010). The carbamate carbofuran, quantified in this study, has been shown to influence the swimming behavior of the sea bass (*Dicentrarchus labrax*) (Hernández-Moreno et al., 2011). However, data on the adverse effects of CUPs on marine organisms, particularly on seabirds and marine mammals, remain limited, and for many CUPs, little to no data are available.

4. Conclusion

Pesticide concentrations were determined in air samples taken on board the RV *Polarstern* along a south-north transect on the Atlantic Ocean. In total, 22 pesticides (15 CUPs, 4 TPs, and 3 legacy pesticides) were quantified at concentrations between 1.6 and 420 pg/m^3, with up to 10 individual compounds present in one sample. The first evidence of the presence of 15 CUPs and 4 TPs in the marine atmosphere across the Atlantic Ocean was found in this study. For most of the found CUPs and TPs, the estimated atmospheric half-lives are below two days. Their detection in the atmosphere of the Atlantic Ocean therefore indicates that the LRT of these compounds could be underestimated in environmental risk assessments based on model predictions used for regulatory decisions in Europe. For future studies, we suggest to also include seawater samples to distinguish between the different long-range transport routes and to determine the influence of air-sea exchange on pesticide concentrations in the different compartments. This is also important to evaluate potential risks on marine organisms from measured pesticide concentrations in the marine environment.

The results indicate that further criteria apart from the atmospheric half-life as well as revised methods for the modelling of the atmospheric half-life (for example the inclusion of different temperatures or OH concentrations to include more accurate environmental data) should be considered in models currently used for environmental risk assessment. In addition, monitoring data on the occurrence and distribution of pesticides especially in areas far from the application sites is needed to further identify potential candidates for LRT. This is especially important to ensure that only pesticides are authorized globally that do not influence the environment or pose health risks far away from their intended application.

CRediT authorship contribution statement

Freya Debler: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Juergen Gandrass:** Writing – review & editing, Supervision, Conceptualization. **Martin Otto Paul Ramacher:** Writing – review & editing, Data curation. **Alkuin Maximilian Koenig:** Writing – review & editing, Data curation. **Simon Zimmermann:** Writing – review & editing, Validation. **Hanna Joerss:** Writing – review & editing, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.126175.

Data availability

Data will be made available on request.

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6. Conclusions and future perspectives

The main conclusions from the findings in this PhD thesis can be summarized as follows:

(i) The developed and validated methods are suitable for the ultra-trace analysis of 329 pesticides, including legacy pesticides, currently used pesticides, and transformation products in the particulate and gaseous phase of ambient air in the low pg/m³ to ng/m³ range.

(ii) Pesticide mixtures are omnipresent in the air across agricultural areas with up to 34 compounds per sample as well as in the marine atmosphere of the Atlantic Ocean with up to 10 compounds per sample.

(iii) First empirical evidence was found for the potential long-range transport of twelve currently used pesticides and four transformation products with calculated atmospheric half-lives below 2 days. This underlines the importance to investigate airborne pesticides as well in remote areas and to survey pesticides with low calculated atmospheric half-lives for which long-range atmospheric transport has not been expected.

(iv) Nine currently used pesticides and two transformation products were reported for the first time in ambient air and fifteen currently used pesticides and four transformation products were detected for the first time in the atmosphere across the Atlantic Ocean.

In more detail, the instrumental analysis was developed on an LC-QTOF and a GC-QqQ and included the optimization of the solvent and temperature gradients, the ion sources' and the MS parameters. For the extraction of GFFs and PUF/XAD-2 columns, different extraction techniques were compared. Highest improvement of recovery rates and relative standard deviations were achieved by a QuEChERS extraction using Milli-Q water/ACN + 1 % acetic acid for the GFFs and a cold-column extraction with dichloromethane for the PUF/XAD-2 columns. In addition, a clean-up step was performed for the GC-MS/MS analysis of GFFs using a dispersive solid-phase extraction with primary secondary amine (PSA), C_{18}, and magnesium sulphate ($MgSO_4$). To compensate for matrix constituents from the sampling material, a matrix-matched calibration of cleaned GFFs and PUF/XAD-2 was used for the instrumental analysis. Matrix effects from the matrix-matched calibration were found to increase the signal with median values of 398 % compared to a solvent calibration on the GC-QqQ and to reduce the signal with a median value of 79 % compared to a solvent calibration on the LC-QTOF. This highlights the importance of considering matrix effects and employing matrix-matched calibrations for the quantification of pesticides in ambient air in both GC-MS/MS and LC-HRMS analyses. Validation of the developed methods showed that they are selective, precise, accurate and robust according to the method performance acceptability criteria described in the guideline for pesticide analysis SANTE/12682/2019 for 263 compounds on the GFFs and 75 compounds on the PUF/XAD-2 columns.

In addition, 39 pesticides (GFFs) and 110 pesticides (PUF/XAD-2 columns) could be determined semi-quantitatively, and 27 pesticides (GFFs) and 138 pesticides (PUF/XAD-2 columns) could be determined qualitatively. The challenges for the quantitative determination of pesticides in air were the determination in the ultra-trace range as well as the compensation for matrix effects from the air and the sampling material. MDLs for most target analytes ranged from 0.02 to 0.2 ng/m³ for the GFFs, and from 0.0003 to 0.3 ng/m³ for the PUF/XAD-2 columns. Therefore, the methods are capable of detecting pesticides in ambient air in the low pg/m³ to ng/m³ range. For single pesticides, MDLs were higher due to stronger influences of matrix constituents on these compounds or lower extraction efficiency for these compounds.

The results from 96 air samples (GFFs and PUF/XAD-2 columns) taken at two agricultural areas in Portugal and the Netherlands showed that 99 different pesticides were present in the atmosphere, including 82 CUPs, 12 TPs and 5 OCPs. Concentrations ranged between 0.003 and 10 ng/m³. Prior studies only investigated legacy pesticides or a small number of CUPs and data on a high number of pesticides in ambient air was limited at the start of this PhD thesis. The high number of pesticides detected in this study indicates the importance of including a higher number of target pesticides to create a full picture of the actual pollution status of pesticides in the air and to not underestimate potential environmental or human health effects of chemical mixtures. As currently more than 2000 pesticides are registered globally, future studies should also consider performing suspect or non-target screening using high-resolution mass spectrometry to include compounds that are not currently in the focus of atmospheric transport or gain information on TPs relevant for atmospheric transport as they can have different properties than their parent compounds and therefore can for example be more persistent and more likely to stay airborne.

28 of the detected pesticides were not approved in the EU during the sampling period. Possible reasons for the detection of these compounds are a high persistence in the environment (e.g. for the OCPs), volatilization from the soil from applications in previous years when they have been approved in the EU or a potential long-range transport from other application areas where they are still registered for use. This data shows that information on pesticide occurrence in the air can not only be concluded from the approval status and application of a compound, but pesticide analysis should also consider compounds that are not currently registered for use or could be transported from other countries that still apply these compounds.

In addition, 95 % of the samples contained pesticide mixtures. This is especially important when potential human health effects are evaluated, as the presence of different compounds can enhance potential effects or sum up to a potential hazard to humans or other organisms. Therefore, DIRs were calculated for single compounds as well as pesticide mixtures for adults, children, and infants and were

compared to the ADI. Highest DIRs for single compounds were 1700 times below the ADI for this substance. However, DIRs calculated for the highest mixture concentration detected in one sample was around 173 times higher than the median DIR for single compounds. The ADI also only includes the intake by food and drinking water and does not consider the intake by inhalation or skin exposure. Therefore, when all intake sources are summed up, the total daily intake could be above the ADI. This highlights the importance to include all potential intake pathways in human health risk assessments and that threshold values are needed for the exposure by inhalation. Only if such values are available, a reliable statement can be given on the actual influence of pesticide intake by inhalation on human health and the question how much it contributes to the total human intake of pesticides. Another factor, when investigating the potential impact from airborne pesticides on human health is the distribution of a compound between the gaseous and particulate air phase as pesticides attached to small particles (PM 2.5) or present in the gaseous phase can penetrate deeper into the respiratory system. Therefore, particle phase fractions were calculated for pesticides with high detection frequencies. The calculated particle phase fractions were significantly correlated with the K_{OA} of the respective compound showing that pesticides with a higher K_{OA} were more likely to be attached to particles. In total, more pesticides were detected in the particulate phase compared to the gaseous phase. As no information on the particle size distribution could be given in this study, this information would be important to be evaluated in future studies to determine the influence of pesticides attached to small particles (PM 2.5) on human health.

To further investigate the potential long-range transport of pesticides, 12 air samples (GFFs and PUF/XAD-2 columns) were sampled in the atmosphere across the Atlantic Ocean between South America and Europe. For the analysis of pesticides in these samples, the extraction method of the PUF/XAD-2 columns was further optimized to be able to quantify more compounds in lower concentrations as expected in the marine atmosphere. The optimized method included a QuEChERS extraction with Milli-Q water/ACN + 1% acetic acid (1:2). For the GC-MS/MS analysis the extracts were cleaned by a d-SPE similar to the clean-up performed for the GFFs. MDLs of the optimized method ranged from 0.000005 to 0.29 ng/m³ for most target analytes. With the optimized method for the PUF/XAD-2 columns and the previously developed method for the GFFs, 22 different pesticides were detected in the marine atmosphere of the Atlantic Ocean in concentrations between 0.002 and 0.42 ng/m³. Prior studies only investigated OCPs and a small number of CUPs in the marine atmosphere and polar regions. The results from this study revealed, that fifteen CUPs and four transformation products were detected for the first time across the Atlantic Ocean. Most of these compounds had calculated atmospheric half-lives below two days. Therefore, they would not be expected to undergo long-range transport based on their atmospheric half-live and would not be expected to occur in a remote environment such as the Atlantic Ocean. This shows the limitations of previous studies and the

importance to include a higher number of compounds even with properties that would not expect them to undergo atmospheric transport. In future studies, the potential transport by water currents should also be considered to distinguish between the different transport routes. Also, the air-water exchange is an important factor to determine the potential transport routes and the source of a compound in the atmosphere as it can also occur from volatilization from the water surface. This is especially relevant for warmer areas such as the mid-Atlantic region, as higher air and water temperatures occur that can lead to higher re-emission rates from the surface seawater. Future research in other marine or polar regions of a high number of CUPs and TPs can therefore help to elucidate if and in which concentrations these compounds occur and if further pesticides have the potential to undergo long-range transport.

13 of the CUPs and TPs across agricultural areas as well as in the marine atmosphere detected in this PhD work have at least one carbon-bonded trifluoromethyl (CF_3) group. Therefore, they can be precursors of the very persistent and very mobile (vPvM) substance trifluoroacetate (TFA; CF_3COO^-). According to the Organisation for Economic Co-operation and Development (OECD) definition, TFA as well as C-CF_3-containing pesticides belong to the group of per- and polyfluoroalkyl substances (PFAS) [131]. Currently, a restriction proposal is discussed under REACH, the European Union chemicals regulation [132]. However, active ingredients used in plant protection products have been excluded from the proposed restriction [133]. Except for one of the detected pesticides, all of them are currently approved in the EU and for 10 of them the approval periods have been recently extended [134]. The findings of 13 of these PFAS-like pesticides in this PhD work show that C-CF_3-containing pesticides could contribute to the formation and emission of TFA and therefore contribute to PFAS concentrations in the environment. This highlights the importance to discuss the degradation of C-CF_3-containing pesticides to TFA on a regulatory level and to include C-CF_3-containing pesticides in PFAS-related studies in the environment.

In conclusion, the results from this thesis show, that the atmospheric transport of CUPs has been neglected in past studies. Therefore, the results from both studies on pesticides in the atmosphere, in agricultural areas as well as the marine atmosphere of the Atlantic Ocean, are expanding the scarce data on CUPs in the atmosphere and their potential atmospheric transport. To further fill the gap on CUPs occurrence and fate in the atmosphere, future studies should include a high number of pesticides and/or use suspect or non-target screening to further identify potential candidates for atmospheric transport. In addition, studies on pesticides in the atmosphere across marine areas should also include the air-sea exchange of CUPs to investigate the influence of pesticides concentrations in the surface water on atmospheric pesticide concentrations. In addition, the data generated in this thesis can be used to feed and validate environmental fate or exposure models. This can give further insights into

the distribution and fate of these compounds in the environment and potential effects on environmental or human health.

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A. Appendix

A.1 Physical-chemical properties and instrumental parameters of the investigated pesticides

Table A1: Phyiscal-chemical properties and instrumental parameters for the pesticides analysed by LC(ESI/PI)-QTOF. I = insecticide, H = herbicide, F = fungicide, TP = transformation product, A = acaricide, AP = antiparasitic, PGR = plant growth regulator, S = synergist

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
3-Hydroxycarbo-furan	237.1001	TP	Transformation product	238.1074	107.0491	163.0754	7.868	12.373	6.56E-04	5.96E-14
Abamectin	872.4922	I	Avermectin	895.4814	896.4747	305.2083	26.528	29.642	7.20E-25	1.37E-27
Acephate	183.0119	I	Organophos-phate	184.0192	142.9926	94.9893	3.883	9.839	9.52E-04	2.81E-12
Acetamiprid	222.0672	I	Neonicotionid	223.0745	225.0717	224.076	8.024	8.098	1.00E-09	6.92E-08
Acetamiprid-N-desmethyl	208.65	I	Transformation product	209.0576	211.0539	210.0606	8.502	8.23	3.25E-02	3.15E-08
Acibenzolar-S-methyl	209.9922	F	Benzothia-diazole	210.9994	136.0077	139.9735	17.413	8.413	5.13E-03	3.90E-09
Aclonifen	264.66	H	Diphenyl ether	265.0346	267.0314		20.869	10.206	5.79E-05	2.66E-09
Alanycarb	399.1286	I	Carbamate	252.0676	421.1151	422.1143	23.568	10.855	7.71E-06	1.72E-13
Aldicarb	190.0776	I	Carbamate	116.0525	89.0413	213.0649	10.225	8.36	2.49E-05	3.57E-09
Aldicarb sulfone	222.0674	I	Carbamate	240.1013	148.042	86.0595	4.695	6.291	0.164	2.83E-11
Aldicarb sulfoxide	206.0725	TP	Transformation product	207.0798	89.042	132.0478	4.337	6.622	4.4E-02	2.25E-13
Allethrin	302.1882	I	Pyrethroid	303.1955	135.0797	123.1158	23.841	10.151	4.40E+07	6.12E-07
Ametryn	227.1205	H	Triazine	228.1277	229.13	186.0791	15.611	9.99	1.53E-03	6.85E-09
Aminocarb	208.1212	I	Carbamate	209.1285	137.0835	152.1071	4.11	9.537	0.291	5.64E-10
Atrazine	215.68	H	Triazine	216.1	218.0964	217.102	15.488	9.626	1.12E-03	4.47E-09
Azadirachtin	720.7	I	Transformation product	743.2439	744.2471	745.2496	15.332	12.485	7.19E-08	2.75E-25
Azoxystrobin	403.1168	F	Strobilurin	404.1241	372.0979	344.1032	17.448	14.03	8.73E-10	8.01E-14
Azoxystrobin-O-demethyl	389.4	F	Transformation product	390.1056	391.1078	392.1101	16.114	15.281	7.39E-08	2.50E-16
Baycor (Bitertanol)	337.179	F	Triazole	338.1863	339.1894	269.1513	21.636	15.115	2.92E-09	1.63E-12

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Benalaxyl	325.1678	F	Acylamino acid	148.1117	91.0541	326.1753	21.302	8.724	4.56E-03	7.84E-10
Bendiocarb	223.0845	I	Carbamate	224.0915	167.0551	225.0935	12.402	7.497	5.03E-02	6.58E-11
Benzoximate	363.0874	A	Bridged diphenyl	199.0149	201.0116	200.017	21.698	9.387	1.35E-03	1.86E-10
Bifenazate	300.1474	I	Carbazate	301.1547	198.0913	170.094	18.833	14.665	9.11E-05	7.30E-13
Bixafen	413.031	F	Pyrazolium	412.0408	414.0379	413.043	20.726	14.164	7.97E-07	3.84E-12
Boscalid	342.0327	F	Carboxamide	343.0399	345.0373	344.0433	18.022	12.72	1.17E-06	4.25E-12
Bromucona-zole	376.9517	F	Triazole	377.959	375.9614	158.9746	18.916 / 20.348	11.153	1.53E-05	2.53E-10
Bupirimate	316.1569	F	Pyrimidinol	317.1642	318.1656	166.0962	19.524	8.936	1.77E-04	1.37E-08
Buprofezin	305.1562	I	Unclassified	306.1635	201.106	307.1633	23.509	8.066	7.75E-03	8.95E-09
Butafenacil	474.0805	H	Uracil	331.0072	179.9838	492.1114	19.338	13.086	4.80E-07	2.25E-12
Butocarboxim	190.0776	I	Carbamate	116.0526	117.0549	118.0475	10.22	8.733	1.06E-02	3.57E-09
Butoxycar-boxim	222.0674	I	Carbamate	223.0747	106.0321	166.0524	4.564	9.131	1.09E-03	2.83E-11
Carbaryl	201.079	I	Carbamate	202.0863	127.0542	145.0648	13.392	9.234	2.79E-03	3.14E-09
Carbendazim	191.0695	F	Benzimidazole	192.0768	160.05	132.0549	5.923	10.582	5.24E-05	1.49E-12
Carbetamide	236.1161	H	Carbamate	237.1234	238.1264	192.0642	11.46	9.86	1.61E-03	1.44E-10
Carbofuran	221.1052	I	Carbamate	222.1125	123.0441	165.091	12.545	9.218	0.141	1.63E-09
Carboxin	235.0667	F	Oxathiin	236.074	237.077	143.0157	13.512	10.081	9.09E-05	7.46E-12
Carfentrazone	384.13	H	Triazolone	384.0081	385.0115	-	16.12	14.722	2.93E-05	1.40E-13
Carfentrazone-ethyl	412.2	H	Triazolone	412.0408	414.0379	345.9927	20.725	10.277	1.60E-05	5.96E-11
Chlorantranili-prole	480.9708	I	Anthranilic diamide	483.9758	481.9781	285.9177	16.804	23.232	1.37E-10	1.37E-21
Chloridazon	221.64	H	Pyridazinone	222.0417	224.0382	223.0439	8.761	9.006	3.61E-03	6.54E-12
Chlorimuron-ethyl	414.0401	H	Sulfonylurea	415.0447	416.0465	417.041	18.463	16.428	1.87E-08	1.02E-11

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Chlorotoluron	212.0716	H	Urea	213.0789	140.0257	215.0739	14.669	10.64	7.92E-05	7.94E-10
Chloroxuron	290.0822	H	Dimethylurea	291.0895	72.0434	293.085	18.94	11.483	9.16E-06	1.57E-11
Clethodim	359.1322	H	Cyclohexane-dione	360.1395	362.1369	268.1346	18.749 / 23.021	13.534	3.55E-07	1.16E-11
Clofentezine	302.0126	A	Tetrazine	303.0199	138.0092	305.0138	21.74	10.897	4.64E-06	1.56E-09
Clomazone	239.7	H	Isoxazolidinone	240.0773	125.0136	127.0109	16.995	8.273	1.92E-02	7.32E-10
Clopyralid	190.9541	H	Pyridine compound	191.9614	193.9585	195.9558	4.408	7.967	2.83E-02	4.92E-09
Clothianidin	249.0087	I	Neonicotionid	250.016	131.9669	169.0533	7.192	14.064	8.24E-03	9.21E-16
Cyantranili-prole	473.7	I	Diamide	473.0071	475.005		14.711	24.566	2.44E-11	1.79E-23
Cyazofamid	324.0448	F	Cyanoimidazole	325.0521	108.01	261.0877	19.88	12.535	1.49E-06	5.29E-12
Cycluron	198.1732	H	Urea	199.1805	89.0699	69.0693	15.814	9.135	0.0472	1.24E-08
Cyflufenamide	412.4	F	Amide	413.1256	414.1275	415.1299	21.88	14.593	1.09E-04	3.76E-11
Cymoxanil	198.0753	F	Cyanoacet-amide oxime	199.0826	128.0455	53.0134	8.847	8.459	3.29E-03	3.31E-10
Cyproconazole	291.1138	F	Triazole	292.1211	293.1241	70.0394	18.487 / 19.048	10.437	2.27E-04	1.72E-10
Cyprodinil	225.1266	F	Anilinopyrimi-dine	226.1339	227.1368	228.1382	19.799	9.465	1.56E-03	1.91E-06
Cyprodinil metabolite CGA304075	241.29	F	Transformation product	242.1276	93.0553	108.0725	10.84	11.24	5.31E-04	1.99E-10
Cyromazine	166.0967	I	Triazine	167.104	85.0509	60.0556	3.544	12.596	3.72E-05	3.23E-13
DEAMPY	181.23	I	Transformation product	182.1281	183.1304	184.1326	6.141	12.159	3.84E-04	8.11E-13
Desmedipham	300.111	H	Carbamate	182.082	318.1455	154.0486	16.485	11.551	3.48E-06	6.88E-11
Dichlorvos	219.9459	I	Organophos-phate	220.9532	109.0036	222.9486	11.923	6.1	2.11	8.58E-07

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Diclobutrazol	327.0905	F	Conazole	328.0978	330.0951	70.0398	20.635	11.728	1.76E-05	2.89E-10
Diclosulam	404.9865	H	Sulfonanilide	405.9938	377.9584	407.9868	14.395	15.021	1.49E-06	7.55E-14
Dicrotophos	237.0766	I	Organophos-phate	238.0839	112.0746	193.0242	6.306	8.687	0.0213	1.20E-12
Diethofencarb	267.1471	F	Carbamate	124.0389	268.153	226.1063	17.377	7.378	0.0467	2.37E-10
Difenocona-zole	405.0647	F	Triazole	406.072	408.0694	251.0012	22.162	13.739	1.07E-07	1.69E-11
Diflubenzuron	310.0321	I	Benzoylurea	311.0371	141.0138	158.0402	20.124	10.606	1.57E-05	1.19E-11
Diflufenican	394.3	H	Carboxamide	395.0776	396.0802	397.0831	22.699	9.777	9.17E-05	3.77E-12
Diflufenican AE-B107137	283.2	H	Carboxamide	284.0499	285.053	286.0553	15.791	10.518	4.71E-03	2.46E-10
Dimethen-amid-p	275.0747	H	Chloroacet-amide	267.082	244.0557	168.0808	17.78	7.625	0.0367	6.08E-10
Dimethoate	228.9996	I	Organophos-phate	230.0069	124.9821	198.9647	7.964	9.147	2.04E-03	2.11E-11
Dimetho-morph	387.1237	F	Morpholine	388.131	390.1248	165.054	17.688 / 18.303	16.064	1.61E-05	1.01E-15
Dimoxystrobin	326.163	F	Strobilurin	116.0494	327.1705	205.0977	20.443	15.102	8.33E-06	4.43E-12
Diniconazole	325.0749	F	Triazole	326.0821	328.0765	327.0823	22.018	9.09	0.0808	8.45E-11
Dinotefuran	202.1066	I	Neonicotionid	203.1139	129.0897	114.1026	4.492	11.681	0.137	3.29E-14
Diuron	232.017	H	Phenylamide	233.0243	159.9698	132.9591	15.838	10.366	1.91E-04	5.33E-10
Doramectin	898.5079	AP	Glycoside	921.4871	922.4901	923.4921	27.196	30.619	3.64E-26	1.07E-27
Emamectin-benzoate	1007.5606	I	Avermectin	872.5061	886.5217	158.118	23.149 / 23.796	-	-	-
Epoxiconazole	329.0731	F	Triazole	330.0804	121.0444	101.0378	19.763	11.229	4.93E-04	3.98E-10
Eprinomectin	899.5031	AP	Avermectin	186.1104	154.0847	900.5002	26.142	-	-	-
Etaconazole	327.0541	F	Conazole	328.0614	158.9748	204.9797	19.433	10.41	9.2E-04	1.02E-09
Ethiofencarb	225.0823	I	Carbamate	226.0896	107.0491	164.0692	14.008	9.364	1.14E-04	5.02E-10

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Ethiprole	395.9826	I	Phenylpyrazole	396.9899	398.987	254.9673	17.867	21.891	3.41E-06	5.34E-19
Ethirimol	209.1528	F	Pyrimidinol	210.1601	98.0595	140.1059	10.111	12.09	1.99E-04	1.02E-12
Ethofumesate	286.0875	H	Benzofuran	304.1185	287.0915	241.0499	17.381	8.52	4.03E-03	1.88E-07
Famoxadone	374.1267	F	Oxazole	392.1605	393.1636	331.1416	21.231	10.38	8.99E-06	2.58E-12
Fenamidone	311.1092	F	Imidazole	312.1165	92.0495	236.1182	17.652	15.388	1.79E-05	2.82E-14
Fenarimol	330.0327	F	Pyrimidine	331.0399	268.0497	81.0438	19.346	9.798	2.49E-04	4.21E-13
Fenazaquin	306.1732	I	Quinazoline	307.1805	57.0691	308.181	25.884	11.229	1.15E-05	4.25E-08
Fenbucona-zole	336.1142	F	Triazole	337.1215	339.1158	125.0143	19.931	8.699	4.88E-05	1.53E-10
Fenhexamid	301.0636	F	Hydroxyanilide	302.0709	97.1001	143.0116	19.31	14.179	1.32E-05	8.51E-13
Fenobucarb	207.1259	I	Carbamate	208.1332	95.0491	152.0699	16.972	8.397	0.0221	8.29E-08
Fenoxycarb	301.1314	I	Carbamate	302.1387	116.0702	88.039	20.181	12.09	1.52E-06	1.45E-11
Fenpropidin	273.5	F	Unclassified	274.2516	275.2542	276.2567	16.672	11.87	0.0171	1.84E-05
Fenpropi-morph	303.2562	F	Morpholine	304.2635	147.1165	57.0697	16.959	8.931	3.51E-03	2.15E-07
Fenpyroximate	421.2002	I	Pyrazolium	422.2074	135.0427	366.1448	25.244	9.068	4.33E-05	4.91E-11
Fenuron	164.095	H	Urea	165.1022	72.0433	166.1045	7.606	8.065	0.0592	9.71E-10
Fipronil	435.9387	I	Phenylpyrazole	436.9421	367.9471	289.9731	20.29	11.463	2.01E-05	3.17E-18
Flazasulfuron	407.33	H	Sulfonylurea	408.0555	409.0571	410.0515	17.12	10.683	7.23E-07	6.10E-12
Flonicamid	229.0463	I	Pyridine compound	230.0536	231.0563	203.0407	5.482	12.529	4.99E-03	2.29E-14
Florasulam	359.29	H	Triazolopyrimi-dine	360.0339	361.0367	129.0298	10.453	13.369	3.48E-05	1.41E-13
Flubendiamide	682.0233	I	Benzene-dicarboxamide	407.9731	408.975	273.9335	20.658	16.74	6.16E-11	2.13E-14
Flufenacet	363.0665	H	Oxyacetamide	364.0737	124.0544	194.0965	19.405	9.828	2.88E-04	2.00E-11
Flufenoxuron	488.0362	I	Benzoylurea	489.0435	158.0397	491.0355	24.679	15.937	1.81E-10	2.64E-12

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Flumioxazine	354.3	H	N-phenylphtal-amides	355.1051	356.1083	327.1087	17.126	11.14	0.0183	5.17E-14
Fluometuron	232.0823	H	Phenylurea	233.0896	72.0444	160.0369	14.275	9.553	2.96E-03	8.44E-09
Fluopicolide	381.9654	F	Benzamide	382.9727	384.9699	386.9672	18.289	14.748	4.92E-05	1.82E-12
Fluopyram	396.71	F	Benzamide, pyramide	397.0512	399.0476	398.0531	19.404	13.59	1.76E-04	3.82E-11
Fluopyram benzamide	189.13	F	Benzamide, pyramide	190.0465	191.0488	170.0395	7.288	6.79	0.34	1.92E-08
Fluoxastrobin	458.0793	F	Strobilurin	459.0842	460.0863	461.0812	19.262	12.94	2.31E-07	2.81E-13
Flupyradi-furone	288.68	I	Butenolide	126.0092	128.0066	-	8.415	7.128	4.37E-03	1.29E-09
Fluquin-conazole	375.009	F	Triazole	376.0163	378.0136	306.981	19.239	12.315	2.87E-07	5.34E-13
Furalaxyl	301.34	F	Acylamino acid	302.1387	95.0128	242.1176	17.389	10.042	1.95E-04	1.92E-09
Flusilazole	315.1003	F	Triazole	316.1076	317.1099	165.0691	20.114	8.384	7.56E-05	5.06E-07
Flutolanil	323.1133	F	Oxathiin	324.1206	262.0648	65.0382	18.344	10.586	3.97E-05	1.11E-09
Flutriafol	301.1027	F	Triazole	302.1099	70.04	123.0227	15.124	13.466	7.76E-08	1.40E-11
Fluxapyroxad	381.3	F	Pyrazolium	382.0949	383.0969	342.0805	18.699	12.88	9.64E-06	9.52E-12
Foramsulfuron	452.4	H	Pyrimidinyl-sulfonylurea	182.0538	453.1138	454.0413	14.723	19.937	7.17E-12	4.28E-23
Forchlor-fenuron	247.0512	PGR	Phenylurea	248.0585	93.0437	129.0202	16.1	13.129	1.17E-06	6.80E-12
Formetanate HCl	257.0931	I	Formamidine	222.1217	165.1009	223.1259	3.919	11.415	1.61E-02	1.27E-12
Fuberidazole	184.0637	F	Benzimidazole	185.0709	156.0667	157.0748	7.725	11.697	3.93E-04	2.81E-08
Furathiocarb	382.1562	I	Carbamate	383.1619	252.0676	195.0463	23.57	9.075	2.99E-04	2.53E-07
Halauxifen-methyl	344.0131	H	Picolinic acid	345.0204	347.0176	346.0235	17.572	14.859	1.13E-04	4.67E-14

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Halofenozide	330.1135	I	Unclassified	105.0332	275.0569	331.1177	17.797	12.055	3.80E-06	3.58E-11
Haloxyfop-p	361.7	H	Aryloxyphenoxy -propionate	362.0362	364.0333	-	20.797	12.196	3.41E-04	3.74E-11
Hexaconazole	313.0749	F	Triazole	314.08	158.9752	70.0396	21.363	10.773	1.28E-04	2.18E-10
Hexythiazox	352.1012	A	Carboxamide	353.1085	228.0233	168.0565	24.314	11.584	2.25E-05	2.29E-09
Hydramethyl-non	494.1905	I	Unclassified	495.1978	323.1417	496.1978	22.09	16.019	8.20E-08	8.12E-11
Imazalil	296.0483	F	Imidazole	297.0556	299.0528	298.0587	14.502	10.795	2.99E-04	7.25E-08
Imazapic	275.127	H	Imidazolinone	276.1343	163.049	86.0958	9.264	16.966	1.95E-07	7.81E-17
Imazapyr	261.1113	H	Imidazolinone	262.1186	131.024	263.1198	7.009	14.758	3.87E-07	7.08E-17
Imazaquin	311.127	H	Imidazolinone	312.1343	86.0957	69.0693	13.022	17.409	5.64E-09	6.91E-18
Imazethapyr	289.1426	H	Imidazolinone	290.1499	69.0693	86.0958	11.531	16.971	9.79E-08	1.04E-16
Imidacloprid	255.0523	I	Neonicotionid	256.0596	209.0589	84.0556	6.89	10.961	4.45E-03	1.04E-13
Imidacloprid 5-hydroxy	271.66	I	Transformation product	272.0517	225.0511	274.0486	6.099	14.465	1.28E-04	1.08E-17
Imidacloprid-desnitro	210.66	I	Transformation product	211.0734	213.0699	212.0756	4.395	10.337	6.00E-02	5.39E-13
Indoxacarb-(S)	527.8	I	Oxadiazine	528.0749	550.0551	203.0173	22.302	15.604	2.28E-07	2.72E-13
Ipconazole	333.1608	F	Triazole	70.0399	334.1666	336.1634	22.78 / 23.474	11.199	2.27E-05	4.03E-10
Iprovalicarb	320.21	F	Carbamate	321.2173	203.1371	119.0843	19.286 / 19.369	11.068	1.04E-04	4.47E-10
Isoprocarb	193.1103	I	Carbamate	95.0489	194.1178	137.0955	14.849	8.571	0.0135	6.25E-08
Isoproturon	206.1419	H	Urea	207.1492	208.1523	72.0443	15.361	11.209	6.81E-05	1.89E-09
Isoxaben	332.4	H	Benzamide	165.0528	333.1789	334.1813	18.549	11.225	1.77E-05	2.05E-13
Isoxaflutole	359.3	H	Oxyacetamide	250.9958	360.0476	361.0504	16.044	10.441	1.37E-05	3.53E-11
Ivermectin	874.5079	AP	Avermectin	897.4971	898.5005	899.5035	27.804	-	-	-

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Kresoxim-methyl	313.3	F	Strobilurin	314.1387	222.0894	315.1388	20.539	10.238	1.24E-05	2.86E-08
Lenacil	234.29	H	Uracil	153.0642	235.1428	110.0594	15.966	11.591	1.51E-04	4.97E-10
Linuron	248.0119	H	Urea	249.0192	182.0213	251.0138	17.294	9.793	8.97E-04	1.15E-08
Lufenuron	509.9784	I	Benzoylurea	510.9803	512.9775	511.9839	24.058	13.753	3.15E-07	5.70E-11
Mandiprop-amid	411.1237	F	Mandelamide	412.131	328.1084	356.1028	18.103	16.62	1.88E-07	2.17E-15
Mefenacet	298.0776	H	Oxyacetamide	299.0849	120.0808	148.0757	18.905	10.945	7.80E-06	2.69E-13
Mepanipyrim	223.1109	F	Anilinopyrimi-dine	224.1182	225.1205	77.0383	19.143	9.451	2.71E-04	3.27E-07
Mepronil	269.1416	F	Benzanilide	270.1489	91.054	119.0489	18.594	9.98	2.6E-04	1.41E-10
Mesotrione	339.0413	H	Triketone	340.0461	227.9938	104.0121	9.494	17.504	1.99E-06	2.37E-18
Metaflumi-zone	506.1177	I	Carbazone	507.125	508.1281	287.077	23.473	18.848	7.91E-08	1.82E-13
Metalaxyl	279.1471	F	Phenylamide	280.1543	220.1332	192.1367	15.683	8.629	3.31E-03	8.05E-10
Metalaxyl Metabolite CGA 62826	265.3	F	Transformation product	266.1367	267.1392	268.1415	14.559	11.819	6.0E-04	2.51E-12
Metamitron	202.0855	H	Triazinone	203.0918	204.0942	77.0378	7.845	11.24	2.17E-05	5.85E-12
Metamitron-desamino	187.2	H	Transformation product	188.0809	189.0832	190.0858	8.448	9.702	2.81E-05	1.40E-09
Metazachlor	277.75	H	Chloroacet-amide	134.095	278.1039	210.066	15.733	9.765	3.64E-04	5.80E-11
Metconazole	319.1451	F	Triazole	320.1524	322.1469	321.1527	21.589	10.905	8.83E-05	3.03E-10
Methabenz-thiazuron	221.0623	H	Urea	222.0696	150.0242	165.0475	15.039	10.282	1.31E-04	6.29E-13
Methamido-phos	141.0013	I	Organophos-phate	142.0086	94.0038	124.981	3.532	6.65	7.59E-03	8.68E-10
Methiocarb	225.0823	I	Carbamate	226.0896	169.0682	227.0905	17.529	10.237	3.13E-04	1.14E-09

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Methiocarb sulfon	257.31	I	Transformation product	275.1042	258.0777	122.0713	9.022	10.271	4.56E-03	9.06E-12
Methiocarb sulfoxide	241.31	I	Transformation product	185.0612	242.0833	170.038	7.803	12.231	7.16E-03	7.20E-14
Methomyl	162.0463	I	Carbamate	163.0536	88.0216	106.0321	5.403	9.694	2.41E-03	2.02E-09
Methoprotryne	271.1467	H	Triazine	272.154	274.1479	170.0487	16.065	10.706	7.39E-04	1.06E-10
Methoxyfenozide	368.21	I	Diacylhydrazine	369.2173	149.0581	313.1534	18.816	13.504	3.71E-07	3.84E-12
Metobromuron	258.0004	H	Urea	259.0077	148.0631	169.96	14.746	9.277	1.97E-03	8.37E-09
Metolachlor	283.79	H	Chloroacetamide	284.1412	176.1425	252.1149	19.978	9.334	4.19E-03	1.49E-09
Metolachlor ethane sulfonic acid	329.4	H	Transformation product	330.1334	298.1065	160.1059	13.686	15.221	6.69E-08	7.21E-16
Metolachlor oxanilic acid	279.33	H	Transformation product	280.1513	248.1259	281.1543	15.76	12.539	3.12E-04	1.86E-13
Metrafenone	409.3	F	Benzophenone	409.0611	411.0592	209.0786	22.442	14.048	5.39E-05	1.15E-11
Metribuzin	214.0888	H	Triazinone	215.0961	216.0973	217.0899	12.343	10.02	5.79E-04	1.81E-12
Metsulfuron-methyl	381.0743	H	Sulfonylurea	382.0816	167.0548	199.0484	13.058	13.712	6.89E-09	7.52E-14
Mevinphos	224.045	I	Organophosphate	127.0146	193.0245	225.0509	7.785 / 9.406	8.713	0.0171	3.89E-09
Mexacarbate	222.1368	I	Carbamate	223.1441	151.0986	166.1221	7.904	10.155	0.136	6.22E-10
Monceren (Pencycuron)	328.1342	F	Phenylurea	329.1415	125.0134	218.0726	22.018	14.516	5.47E-09	7.95E-11
Monocrotophos	223.061	I	Organophosphate	224.0682	98.06	127.0149	5.876	10.452	5.76E-04	5.45E-13

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Monolinuron	214.0509	H	Urea	215.0582	126.01	148.0631	13.87	8.026	0.0724	1.56E-08
Moxidectin	639.3771	I	Avermectin	639.3653	640.3685	498.3464	27.169	20.596	1.11E-16	3.11E-16
Myclobutanil	288.1142	F	Triazole	289.1215	291.1189	70.0396	18.642	9.697	5.36E-04	3.34E-09
Napropamide	271.1572	H	Alkanamide	272.1645	129.114	199.0742	19.573	10.824	7.16E-05	3.77E-10
Neburon	274.064	H	Urea	275.0713	277.0684	57.0696	20.587	11.392	0.00208	1.25E-09
Nicosulfuron	410.1009	H	Sulfonylurea	411.1081	412.1107	413.1069	25.431	16.255	4.03E-09	1.39E-18
Nitenpyram	270.0884	I	Neonicotionid	271.0956	126.0087	225.1015	4.874	8.892	4.00E-09	7.88E-11
Novaluron	492.0123	I	Benzoylurea	158.0396	493.0148	141.0132	22.888	15.827	4.65E-07	6.78E-13
Nuarimol	314.0622	F	Pyrimidine	315.0695	317.0646	81.0439	17.437	13.746	8.35E-06	6.64E-13
Omethoate	213.0225	I	Organophos-phate	214.0297	182.9875	124.9811	4.158	10.989	3.31E-03	4.56E-14
Oryzalin	346.36	H	Dinitroaniline	347.1095	288.0518	348.1008	20.068	10.837	1.83E-05	1.91E-09
Oxadixyl	278.1267	F	Phenylamide	279.1339	219.1118	132.08	11.126	10.762	2.00E-05	4.27E-10
Oxamyl	219.0678	I	Carbamate	237.1016	72.0444	90.055	4.779	7.544	0.173	3.53E-11
Oxyfluorfen	361.7	H	Diphenyl ether	362.0361	363.0387	364.0332	23.656	9.205	1.27E-04	2.35E-07
Paclobutrazol	293.1295	F	Triazole	294.1368	70.04	296.1318	18.189	11.67	2.45E-05	3.90E-10
Penconazole	283.0643	F	Triazole	70.0397	284.0699	286.0669	20.684	10.906	7.95E-04	4.49E-06
Pendimethalin	281.31	H	Dinitroaniline	212.0644	282.1421	283.1451	24.822	18.835	5.81E-10	1.49E-18
Penoxsulam	483.4	H	Sulfonamide	484.067	485.0686	195.0637	14.609	15.186	7.69E-07	1.42E-14
Phenmedi-pham	300.111	H	Carbamate	136.0392	168.0662	301.1166	16.804	14.054	1.96E-08	5.72E-11
Phosmet	317.3	I	Organophos-phate	160.0379	317.9998	319.0014	17.419	9.245	1.91E-04	9.02E-09
Phosmet oxon	301.26	I	Organophos-phate	160.0377	302.0228	133.0271	11.528	9.818	1.17E-05	1.95E-11
Phoxim	298.3	I	Organophos-phate	299.0595	129.0435	300.0615	21.922	8.168	2.11E-03	7.39E-05

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Picoxystrobin	367.1031	F	Strobilurin type - methoxyacrylate	368.1104	145.0652	205.0835	20.236	11.777	1.12E-03	1.91E-10
Piperonyl-butoxide	338.4	S	Cyclic aromatic substance	356.2432	177.091	119.0855	23.987	13.19	6.96E-04	8.89E-11
Pirimicarb	238.143	I	Carbamate	239.1503	72.0431	182.127	10.211	9.162	4.32E-03	2.62E-09
Pirimicarb-desmethyl	224.26	I	Transformation product	72.0434	225.1335	226.1358	7.169	9.131	0.0688	1.28E-10
Pirimiphos-methyl	305.34	I	Transformation product	306.1018	164.1282	307.1036	22.065	8.743	2E-03	2.53E-06
Pirimiphos-methyl-N-desethyl	277.28	I	Transformation product	278.0708	279.0727	280.0653	15.023	7.82	0.0101	9.31E-08
Prochloraz	375.0308	F	Imidazole	376.0381	307.9987	70.0283	21.308	10.274	2.55E-04	7.58E-12
Prochloraz BTS 44595	325.6	F	Transformation product	325.0247	327.0217	329.018	21.77	13.298	3.04E-04	7.25E-12
Prochloraz BTS 44596	353.6	F	Transformation product	353.0187	355.0157	357.0123	21.638	13.792	6.97E-07	2.93E-12
Promecarb	207.1259	I	Carbamate	208.1332	109.0648	151.1117	17.862	8.54	0.0164	6.89E-08
Prometryn	241.1361	H	Triazine	242.1434	200.0943	158.0488	17.938	9.778	2.27E-03	9.09E-09
Propamocarb	188.27	F	Carbamate	189.1598	102.0545	144.1014	4.218	8.338	9.69	1.34E-10
Propaquizafop	443.1248	H	Aryloxyphenoxy propionate	444.1321	446.1301	70.0646	23.712	14.503	1.13E-09	2.51E-12
Propargite	350.1552	A	Sulphite ester	368.189	175.1117	231.1733	24.715	10.77	6.00E-06	9.17E-08
Propham	179.0946	H	Carbamate	138.0538	120.0433	180.1003	14.812	8.403	2.51	3.85E-08
Propiconazole	341.0698	F	Triazole	342.0771	344.0723	69.0693	21.126	10.494	1.33E-04	1.36E-09
Propoxur	209.1052	I	Carbamate	210.1125	65.0386	111.0441	12.259	8.753	5.29E-03	3.35E-09
Propyzamide	256.12	H	Benzamide	256.0272	258.0238	189.98	18.878	9.829	1.12E-03	1.03E-09

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Prosulfocarb	251.39	H	Thiocarbamate	252.1403	253.1426	128.1055	23.255	10.925	6.91E-05	9.36E-07
Prothiocona-zole	343.0313	F	Triazolinthione	326.1734	327.1759	188.9668	21.314	13.502	8.20E-10	9.47E-13
Prothiocona-zole-desthio	312.2	F	Transformation product	312.0639	314.0606	313.0664	20.347	11.779	2.92E-05	4.57E-11
Pymetrozine	217.0964	I	Pyridine	218.1036	105.0443	78.9937	4.169	11.729	3.17E-04	3.54E-13
Pyracarbolid	217.1103	F	Anilide	218.1176	125.0592	97.0278	13.142	9.83	2.32E-03	4.35E-10
Pyraclostrobin	387.0986	F	Strobilurin	388.1059	390.1037	389.1089	21.529	17.318	8.93E-06	1.15E-15
Pyraflufen-ethyl	413.2	H	Phenylpyrazole	413.0247	415.0214	414.0266	21.425	12.179	1.96E-04	1.20E-09
Pyrethrin I	328.4	I	Pyrethrin	161.0946	329.2082	133.0998	25.324	10.4	0.0391	7.73E-07
Pyrethrin II	372.5	I	Pyrethrin	373.197	374.2004	375.2028	23.022	10.348	6.08E-04	7.39E-10
Pyridaben	364.1376	I	Pyridazinone	365.1449	147.1168	367.1381	25.8	8.882	1.13E-03	2.26E-10
Pyrimethanil	199.1109	F	Anilinopyrimi-dine	200.1182	107.0604	82.0644	16.232	8.675	0.0112	2.46E-06
Pyrimethanil M605F002	215.25	F	Transformation product	216.1121	217.1144	107.0692	8.448	10.34	2.4E-03	2.56E-10
Pyriofenone	365.8	F	Benzoylpyridine	368.1035	184.014	366.1063	22.212	14.72	7.84E-05	2.56E-13
Pyriproxyfen	321.1365	I	Unclassified	322.1438	323.1471	96.0442	23.927	13.136	4.69E-04	6.34E-10
Pyroxsulam	434.35	H	Triazolopyrim-idine	435.0661	195.0617	436.0675	13.186	15.86	8.37E-07	2.94E-16
Quinmerac	221.0244	H	Quinoline	222.0306	204.02	141.0567	8.202	10.115	4.32E-03	1.13E-11
Quinoxyfen	306.9967	F	Quinoline	308.004	310.0012	196.9782	24.159	11.064	1.29E-04	9.65E-09
Quizalofop-p	344.7	H	Aryloxyphenoxy-propionate	345.0599	347.0569	346.0632	20.517	14.718	5.23E-06	1.74E-13
Quizalofop-p-ethyl	372.0877	H	Aryloxyphenoxy-propionate	373.095	375.0928	374.0981	23.259	10.643	2.80E-06	7.40E-11
Rotenone	394.1416	I	Isoflavone	395.1489	396.1523	213.0888	20.157	13.009	4.68E-06	8.31E-13

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Sedaxane	331.4	F	Pyrazole	332.1548	333.1569	159.0349	19.237 / 20.098	12.21	3.05E-05	6.90E-11
Siduron	232.1576	H	Phenylurea	233.1648	94.0648	137.0702	17.688 / 18.034	12.357	6.60E-06	1.07E-09
Simetryn	213.1048	H	Triazine	214.1121	96.0549	215.113	12.891	10.542	3.51E-04	5.16E-09
Spinetoram	747.4921	I	Spinosyn	748.4994	749.5028	142.1228	22.591	25.298	1.14E-13	1.26E-23
Spinosyn A	732	I	Spionsyn	732.465	733.4668	142.1227	21.631	24.767	2.15E-13	8.35E-24
Spinosyn D	746	I	Spionsyn	746.4788	747.482	142.1223	22.417	25.121	1.10E-13	1.31E-23
Spirotetramat	373.1889	I	Tetramic acid	374.1962	302.1751	330.204	19.465	14.217	8.20E-07	6.94E-13
Spirotetramat-enol	301.4	I	Transformation product	302.1732	303.1754	304.1777	15.211	15.862	3.40E-08	2.27E-15
Spirotetramat-enol-glucoside	463.5	I	Transformation product	302.1718	464.2233	303.1749	7.169	21.711	6.61E-16	1.31E-23
Spirotetramat-keto-hydroxy	317.4	I	Transformation product	300.1563	318.1669	214.0867	16.759	14.746	2.23E-08	3.57E-14
Spirotetramat-mono-hydroxy	303.4	I	Transformation product	304.1885	305.1907	306.1928	12.915	15.617	1.24E-07	1.10E-15
Spiroxamine	297.2668	F	Morpholine	298.2741	100.1119	144.1377	17.204 / 17.359	10.869	0.0171	1.94E-07
Spirodiclofen	411.3	I	Tetronic acid	411.1124	313.0368	71.0853	25.406	11.498	8.07E-06	1.26E-07
Spiromesifen	370.5	I	Tetronic acid	273.1476	255.1358	274.15	24.789	11.101	1.95E-05	2.33E-07
Sulfentrazone	385.9819	H	Aryl triazolinone	386.986	388.9828	306.9927	13.44	12.338	1.18E-06	5.02E-12
Tebuconazole	307.1451	F	Triazole	308.1524	70.04	310.1479	20.889	11.927	9.95E-06	5.18E-10
Tebufenozide	352.2151	I	Diacylhydrazine	133.0647	297.1586	353.2202	20.371	10.538	1.31E-04	8.62E-11
Tebufenpyrad	333.1608	A	Pyrazolium	334.1664	336.1632	117.0204	23.472	13.792	1.60E-05	1.61E-11
Tebuthiuron	228.1045	H	Urea	229.1118	172.0903	62.0059	13.237	10.099	6.17E-03	6.77E-12
Teflubenzuron	379.9742	I	Benzoylurea	158.1178	159.1198	380.978	23.838	12.75	7.19E-08	1.20E-11

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Temephos	465.9897	I	Organophos-phate	466.9939	124.9812	467.9954	23.75	13.056	1.17E-05	1.96E-09
Terbuthylazine	229.71	H	Triazine	230.1155	232.1119	231.1175	18.352	9.03	4.87E-03	5.94E-09
Terbuthylazine -desethyl	201.66	H	Transformation product	202.0842	204.0804	203.0864	13.818	9.019	0.0967	2.04E-09
Terbutryn	241.1361	H	Triazine	242.1434	186.0791	91.0319	18.248	10.068	1.69E-03	9.09E-09
Tetraconazole	371.0215	F	Triazole	372.0288	374.026	373.0317	19.406	10.321	1.8E-04	6.20E-07
Thiabendazole	201.0361	F	Benzimidazole	202.0433	131.0604	175.0325	7.057	11.532	2.8E-04	2.00E-11
Thiacloprid	252.0236	I	Neonicotionid	253.0309	126.0087	90.0338	9.309	10.329	2.85E-03	2.45E-10
Thiamethoxam	291.0193	I	Neonicotionid	292.0266	211.0619	181.0526	5.585	13.351	1.45E-03	6.87E-15
Thidiazuron	220.0419	H	Phenylurea	221.0492	102.0111	222.05	12.853	12.603	3.32E-04	3.59E-13
Thiencarba-zone-methyl	390.4	H	Triazolone	391.0337	392.0363	130.0595	11.763	17.197	1.10E-08	4.80E-18
Thifensulfuron -methyl	387.0307	H	Sulfonylurea	388.038	410.02	389.0403	12.462	13.338	5.32E-07	4.08E-14
Thiobencarb	257.0641	H	Thiocarbamate	258.0714	89.0386	100.0757	21.768	8.362	2.93E-03	3.93E-07
Thiofanox	218.1089	I	Carbamate	218.1177	219.1197	220.1215	13.158	9.166	0.0469	6.28E-09
Thiophanate-methyl	342.0456	F	Benzimidazole	343.0529	311.0242	151.0317	12.579	12.32	2.71E-04	2.94E-13
Tolyfluanid	347.3	F	Sulphamide	346.9821	348.9788	237.963	21.156	8.407	1.01E-03	7.44E-07
Tolylfluanid metabolite DMST	214.29	F	Transformation product	215.0829	216.0858	217.0784	13.423	7.116	0.0373	9.38E-08
Triadimefon	293.0931	F	Triazole	294.1004	69.0699	197.0709	18.57	11.249	7.32E-06	1.16E-09
Triadimenol	295.1088	F	Triazole	70.0397	296.1141	298.1102	18.984	12.017	7.91E-06	1.58E-11
Tri-allate	304.7	H	Thiocarbamate	304.0058	306.0027	86.0592	24.732	7.909	0.0175	5.66E-06
Trichlorfon	255.9226	I	Organophos-phate	256.9299	220.9532	109.0039	7.809	9.668	3.4E-03	2.65E-12

Parameter	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Tricyclazole	189.0361	F	Triazolobenzo-thiazole	190.04333	136.0216	163.0314	10.076	10.259	0.0691	1.62E-10
Trifloxystrobin	408.1297	F	Strobilurin	186.0519	145.0255	409.1354	22.424	9.859	1.75E-04	1.07E-07
Trifloxystrobin metabolite CGA 321113	394.3	F	Transformation product	186.0504	395.1176	396.1201	20.957	14.192	2.64E-05	3.36E-10
Triflumizole	345.0856	F	Imidazole	346.0929	278.0536	348.0881	22.46	10.078	4.48E-04	2.34E-07
Triflumuron	358.0332	I	Benzoylurea	359.0405	138.9931	156.0196	21.637	11.546	1.92E-06	4.07E-12
Triticonazole	317.1295	F	Triazole	318.1368	319.1575	70.0394	19.501	11.508	6.49E-06	1.48E-10
Vamidothion	287.0415	I	Organophos-phate	288.0488	118.0315	146.0634	7.797	13.515	2.67E-04	8.58E-16
Zoxamide	335.0247	F	Benzamide	336.0319	186.9694	338.0272	21.386	12.635	4.89E-05	3.26E-11

Table A2: Phyiscal-chemical properties and instrumental parameters for the pesticides analysed by LC(ESI/NI)-QTOF. I = insecticide, H = herbicide, F = fungicide, TP = transformation product, A = acaricide, AP = antiparasitic, PGR = plant growth regulator, S = synergist

Compound	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
2,4-D	219.9694	H	Phenoxy	160.9565	162.9535	218.9619	14.62	8.649	0.152	9.21E-09
Bentazone	240.0569	H	Benzo-thiazinone	239.0496	240.0524	175.0869	11.979	9.39	6.03E-03	1.99E-10
Bromoxynil	276.91	H	Hydroxybenzo-nitrile	275.8492	273.8507	277.8467	14.876	11.658	2.69E-04	8.60E-10
Chlorfluazuron	538.963	I	Benzoylurea	537.9557	539.953	517.9502	25.222	15.933	7.71E-10	1.48E-14
Chlorimuron-ethyl	414.0401	H	Sulfonylurea	412.0252	413.0269	414.0221	20.384	15.628	1.87E-08	1.02E-11
Chlorothalonil 4-hydroxy	247.5	F	Transformation product	244.9092	246.9062	248.9024	14.649	12.15	1.35E-03	2.13E+11
Chlorpyrifos-methyl-TCPy	198.43	I	Transformation product	195.9125	197.9096	199.9066	16.993	7.982	0.0721	4.23E-09
Chlorpyrifos-methyl-desmethyl	330.5	I	Transformation product	305.8715	307.8686	195.9127	13.549	10.808	7.99E-05	4.47E-09
Clopyralid	190.9541	H	Pyridine compound	189.9468	191.9439	145.9567	4.475	7.967	0.0283	4.92E-09
Cycloxydim	325.1712	H	Cyclohexane-dione	324.1639	325.167	326.1597	17.002	15.019	1.19E-04	4.78E-14
Dicamba	219.9694	H	Benzoic acid	218.9616	220.9587	222.9559	15.247	9.26	0.0349	3.52E-09
Fipronil	435.9387	I	Phenylpyrazole	434.9314	436.9285	329.9586	20.29	11.463	2.01E-05	3.17E-18
Fipronil sulfone	453.1	I	Transformation product	450.9279	452.925	451.9295	21.519	18.207	6.69E-06	3.99E-16
Fluazifop-p	327.25	H	Unclassified	326.064	327.0672	328.0698	18.093	11.865	9.77E-04	5.05E-11
Fluazinam	463.9514	F	Phenylpyridin-amine	462.9441	464.9414	463.9469	23.677	10.23	5.41E-05	5.23E-09
Fludioxonil	248.0397	F	Phenylpyrrole	247.0325	248.0355	249.0378	17.873	11.783	2.09E-05	3.10E-11

Compound	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m³/mol
Flufenoxuron	488.0362	I	Benzoylurea	487.029	489.0268	488.0321	24.662	15.937	1.81E-10	2.64E-12
Fluroxypyr	253.9661	H	Pyridine compound	194.9531	196.9502	252.9585	11.609	12.537	4.23E-07	4.54E-14
Hexaflumuron	459.9816	I	Benzoylurea	458.9743	460.9717	438.9679	22.693	3.073	3.44E-03	1.08E-11
Lufenuron	509.9784	I	Benzoylurea	508.9711	510.9685	509.9743	24.053	13.753	3.15E-07	5.70E-11
MCPA	200.024	H	Aryloxylalkanoic acid	199.0167	201.0141	141.0109	15.42	10.515	6.84E-03	1.37E-08
Mecoprop-p	214.0397	H	Aryloxylalkanoic acid	141.0108	213.0321	215.0291	17.558	10.595	1.97E-03	1.82E-08
Meptyldinocap phenol	296.32	F	Transformation product	295.131	296.1332	297.1354	25.956	10.684	7.56E-05	2.21E-07
Spiromesifen	370.5	I	Tetronic acid	367.2031	368.2056	369.2077	18.806	11.101	1.95E-05	2.33E-07
Teflubenzuron	379.9742	I	Benzoylurea	378.967	380.9642	338.9547	23.767	12.75	7.19E-08	1.20E-11
Triflumuron	358.0332	I	Benzoylurea	357.0259	84.9903	154.0067	21.631	11.546	1.92E-06	4.07E-12

Table A3: Phyiscal-chemical properties and instrumental parameters for the pesticides analysed by GC-QQQ. I = insecticide, H = herbicide, F = fungicide, TP = transformation product, A = acaricide, AP = antiparasitic, PGR = plant growth regulator, S = synergist

Compound	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m^3/mol
2,4'-DDD	319.9508	I	Organochlorine	235 -> 165	237 -> 165	-	25.085	9.346	8.45E-04	4.34E-05
2,4'-DDE	317.9351	I	Organochlorine	235 -> 165	237 -> 165	-	24.178	9.121	5.99E-03	3.52E-05
2,4'-DDT	353.9118	I	Organochlorine	235 -> 165	237 -> 165	-	26.264	10.309	1.68E-03	1.53E-05
4,4'-DDD	319.9508	I	Organochlorine	235 -> 165	237 -> 165	-	26.38	9.589	1.23E-03	4.34E-05
4,4'-DDE	317.9351	I	Organochlorine	246 -> 176.1	248 -> 176.1	-	24.781	9.279	3.44E-03	3.52E-05
4,4'-DDT	353.9118	I	Organochlorine	237 -> 165	235 -> 165	-	27.579	10.378	1.43E-04	1.53E-05
alpha-HCH	289.8571	I	Organochlorine	180.9 -> 145	183 -> 145	-	16.435	8.896	3.44E-02	2.56E-04
beta-HCH	289.8571	I	Organochlorine	181 -> 145	183 -> 145	-	17.527	8.896	3.44E-02	2.56E-04
Bifenthrin	422.126	I	Pyrethroid	181.1 -> 165.1	181.1 -> 166.1	-	29.552	12.538	6.53E-05	1.91E-05
Captan	300.9312	F	Phthalimide	118.9 -> 83.9	107 -> 79	-	23.124	9.343	3.91E-04	4.59E-09
Captan THPI	151.0633	F	Transformation product	151.1 -> 80.1	151.1 -> 106	-	12.825	6.204	5.27E-04	3.05E-08
Chlorothalonil	265.8786	F	Chloronitrile	265.9 -> 133	265.9 -> 231	-	18.505	7.137	1.28E-02	1.52E-07
Chlorpropham	213.0557	H	Carbamate	171 -> 127	154 -> 127	-	15.51	9.518	3.45E-02	2.85E-08

Compound	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m^3/mol
Chlorpyrifos	350.9234	I	Organophos-phate	196.9 -> 169	314 -> 258	-	21.479	8.882	3.99E-03	2.52E-06
Chlorpyrifos-methyl	322.8921	I	Transformation product	285.9 -> 93	285.9 -> 271	-	19.746	8.124	8.44E-03	1.43E-06
cis-Permethrin	390.0789	I	Pyrethroid	163 -> 127	183.1 -> 168	-	32.842	10.617	3.57E-06	2.88E-07
Cyfluthrin	433.0648	I	Pyrethroid	163 -> 127	165 -> 127	163 -> 91.1	34.012 / 34.185 / 34.415 / 34.6	14.162	4.44E-08	9.21E-07
Cypermethrin	415.0742	I	Pyrethroid	163 -> 127	163 -> 91.1	165 -> 127	34.79 / 34.838 / 34.912 / 35.01	10.825	6.64E-01	7.89E-07
delta-HCH	289.8571	I	Organochlorine	180.9 -> 145	183 -> 145	-	17.527	8.896	3.44E-02	2.56E-04
Deltamethrin	504.9713	I	Pyrethroid	181.1 -> 127	182.1 -> 152.1	-	37.761	9.89	1.10E-05	6.06E-08
Dicloran	205.965	F	Chlorophenyl	206 -> 176	176 -> 148	-	16.811	8.519	7.01E-03	4.12E-09
Dieldrin	379.8677	I	Chlorinated hydrocarbon	263 -> 193	263 -> 191	-	25.577	8.785	3.89E-02	5.41E-07
Fenvalerate	419.1288	I	Pyrethroid	125 -> 89	225 -> 119	-	36.358	10.971	4.39E-07	1.19E-07
Folpet	296.8999	F	Phthalimide	259.8 -> 130	261.8 -> 130	-	23.126	8.354	6.67E-04	1.54E-09
gamma-HCH	289.8571	I	Organochlorine	181 -> 145	219 -> 183	-	18.337	8.896	3.44E-02	2.56E-04

Compound	Molecular Mass	Pesticide group	Chemical class	Quantifier	Qualifier 1	Qualifier 2	Retention time	log K_{oa}	Vapor pressure	Henry's law constant
	g/mol						min		Pa	atm-m^3/mol
Hexachloro-benzene	283.8102	F	Organochlorine	283.8 -> 214	283.8 -> 248.9	-	16.687	6.888	2.67E-01	8.92E-04
lambda-Cyhalothrin	449.1006	I	Pyrethroid	197 -> 141	208 -> 181	-	31.495	11.218	3.47E-07	1.35E-05
Metalaxyl	279.1471	F	Phenylamide	132 -> 117	206.1 -> 132.1	-	20.176	9.553	3.31E-03	8.05E-10
tau-Fluvalinate	502.1271	I	Pyrethroid	181 -> 152	250.1 -> 200.1	-	36.759 / 36.879	13.037	2.69E-05	1.45E-08
Tebuconazole	307.1451	F	Triazole	252.1 -> 127	252.1 -> 165	-	28.048	11.933	9.95E-06	5.18E-10
Terbuthylazine	229.1094	H	Triazine	214.1 -> 132	214.1 -> 173	-	17.684	9.028	4.87E-03	5.94E-09
Tetramethrin	331.1784	I	Pyrethroid	164.1 -> 107.1	164.1 -> 135.1	-	29.276 / 29.532	11.197	2.57E-03	5.57E-09
trans-Permethrin	390.0789	I	Pyrethroid	163 -> 127	183.1 -> 168	-	33.091	10.617	3.57E-06	2.88E-07

Table A4: Literature review on pesticides in the atmosphere since the 1990s. n.a. = not available, PUF = polyurethane foam, ASE = accelerated solvent extraction, UAE = ultrasound assisted extraction, MAE = microwave assisted extraction, HVAS = high-volume air sampler, LVAS = low volume air sampler, MVAS = medium volume air sampler, PAS = passive air sampler

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
CUPs									
Baker, 1996	California	Medium and low volume samplers	Teflon filters, XAD-2	22	n.a.	up to 160 µg/m³	1986-1995	GC-NP, GC-EC, GC-ELC and HPLC-UV	[135]
Majewski, 1998	Mississippi River from New Orleans, LA to St. Paul, MN	HVAS	PUF	45	Soxhlet extraction	0.05-80 ng/m³	June, 1994	GC/MS	[78]
Waite, 2002	Canada	HVAS	Borosilicate microfibre filter and PUF/XAD-2 sandwich	CUPs	Soxhlet extraction	0.09-60 ng/m³	1989-1990	GC-MS	[136]
Baraud, 2003	France (rural and urban)	HVAS and LVAS	QFF and PUF	CUPs	Soxhlet extraction	1-5130 ng/m³	2001	HPLC-UV	[137]
Waite, 2004	Canada	HVAS	Borosilicate microfibre filter and PUF/XAD-2 sandwich	CUPs	Soxhlet extraction	0.01-4.2 ng/m³	1989-1990	GC-MS	[138]
Waite, 2005	Canadian Prairies	HVAS	Borosilicate microfibre filter and PUF/XAD-2 sandwich	10	Soxhlet extraction	0.01-5.46 ng/m³	2002	GC-MSD and GC-MS/MS	[139]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Bailey, 2007	British Columbia, Canada	HVAS	GFF and PUF/XAD-2	5	ASE	10-28580 pg/m³	2004-2005	GC-MS	[140]
Esteve-Turrillas, 2008	Indoor air in research laboratory	PAS	Semipermeable membrane device (SPMD)	CUPs	Solvent extraction	5-1325 ng/m³	n.a.	GC-MS/MS	[141]
Borrás, 2011	Mediterranean area	HVAS	GFF, XAD-2 and XAD-4	16	UAE	0.08-1428.28 ng/m³	n.a.	GC-MS	[46]
Coscollà, 2011	Spain	Large-volume sampler	PM10	40	MAE	1.32-625.8 pg/m³	2010	GC-MS	[142]
Hart, 2012	Valencia Region, Spain	HVS	PM10	42	MAE	6-149 pg/m³	2010	GC-MS/MS	[143]
Schummer, 2012	Luxembourg	PAS	XAD-2	50	ASE	100-42100 ng/sample	2008-2009	GC-MS/MS	[115]
Coscollà, 2013a	Valencia Region, Spain	HVAS	PM10	40	MAE	7-141 pg/m³	2010	LC-MS/MS	[144]
Coscollà, 2013b	Centre Region, France	Cascade impactor	Particles	49	ASE	0.163-1.779 ng/m³	2009	GC-MS and LC-MS/MS	[145]
Coscollà, 2014	Valencia, Spain	LVAS	QFF	35	MAE	16-174 pg/m³	n.a.	LC-HRMS	[146]
Li, 2014	South China	HVAS	GFF and PUF	17	Soxhlet extraction	47.8-1765 pg/m³	2011-2012	GC-MS	[147]
Yusà, 2014	Valencia, Spain	HVAS	QFF	82	MAE	1.63-117.01 pg/m³	2010	LC-MS/MS	[148]
Zivan, 2016	Hula Valley, Israel	HVAS	QFF and PUF	3	UAE and Soxhlet extraction	up to 328 ng/m³	2010-2012	GC-MS	[149]
López, 2017a	Spain	HVAS	QFF (PM10)	CUPs	MAE and UAE	8-30000 pg/m³	2008-2014	LC-MS/MS, LC-HRMS and GC-MS	[150]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
López, 2017b	Valencia Region, Spain	HVAS	QFF (PM10)	35	Hard cap espresso extraction	8.1-60 pg/m³	2014	LC-HRMS	[151]
Liu, 2018	Bohai Sea, China	HVAS	Glass microfiber filters and PUF/XAD-2	4	Soxhlet extraction	0.06-550 pg/m³	2016-2017	GC-MSD	[47]
Lopez, 2018	Valencia Region, Spain	LVAS	PUF/XAD-2	28	Microwave extraction	411 - 11011 pg/m³	2017	UHPLC-HRMS	[152]
Villiot, 2018	Reims, France	HVAS	QFF and PUF	CUPs	ASE	0.12-15 ng/m³	2012-2015	GC-MS and LC-MS/MS	[153]
Anh, 2019	Vietnam	PAS	PUF	CUPs	Soxhlet extraction	43-330 ng/m³	2015	GC-MS	[82]
Gao, 2019	North Pacific and Arctic Oceans	HVAS	GFF and XAD-2	5	UAE	0.68-17 ng/m³	2016-2017	GC-MS	[48]
Cortes, 2020	Chile	PAS	PUF	38	Soxhlet extraction	444-14624 pg/m³	2015-2016	HPLC-MS/MS	[83]
Fuhrimann, 2020	Africa	PAS	PUF	27	Soxhlet extraction	n.a.	2010-2018	LC-MS/MS	[84]
Figueiredo, 2021	Agricultural fields	HVAS	GFF and XAD-2	CUPs	ASE	up to 2754 ng/m³	2016-2017	LC-MS/MS	[154]
Guida, 2021	Southeastern Brazil	PAS	PUF	CUPs	Soxhlet extraction	3-15125 pg/m³	2015-2016	GC-MS	[85]
Lopez, 2021	Valencia Region, Spain	HVAS	GFF and PUF/XAD-2/PUF	CUPs	MAE	14.4-4373 pg/m³	2020	GC-MS/MS and LC-HRMS	[155]
Décuq, 2022	France	HVAS	Tenax TA	27	n.a.	0.04-22.44 ng/m³	2018	GC-MS	[156]
Degrendele, 2022	South Africa	MVAS	QFF and PUF/XAD/PUF	30	Soxhlet extraction	0.181-25 ng/m³	2018	LC-MS/MS	[157]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Lopez, 2022	Spain	HVAS	QFF	CUPs	MAE	n.a. (NTS)	2021	LC-HRMS	[158]
Martin, 2022	France	PAS	PUF	36	ASE	up to 23481 ng/sample	2013	GC-MS/MS and LC-MS/MS	[86]
Zhao, 2023	North China Plain	PAS	PUF	CUPs	UAE	0.59-26 pg/m³	2021-2022	LC-MS/MS	[87]
Mayer, 2024	Europe	HVAS	QFF and PUF/XAD-2/PUF	76	Soxhlet extraction	24 fg/m³ to 3.9 ng/m³	2020	GC-MS/MS and LC-MS/MS	[49]
Ni, 2024	Shanghai, China	LVAS	GFF and XAD-2	33	UAE	407-2980 pg/m³	2021-2023	GC-MS/MS	[159]
Wang, 2024	China	HVAS	GFF and PUF	76	Soxhlet extraction	0.007-158000 pg/m³	2019-2020	GC-MS	[160]
OCPs and CUPs									
Siebers, 1994	Northern Germany (Lower Saxony)	Bulk sampler	Rain	11	Soxhlet extraction	up to 710 ng/L	1990-1992	GC-MS	[161]
Chernyak, 1996	Bering and Chukchi sea	HVAS	Fog, GFF, PUF	16	Soxhlet extraction	0.7-1.1 pg/m³	Summer 1993	GC/MS	[20]
Halsall, 1998	Alert, Tagish (Canada) and Dunai (Russia) - Polar	HVAS	GFF, PUF	24	Soxhlet extraction	0.01-901 pg/m³	1993 and 1994	GC-HRMS	[162]
Sanusi, 1999	Remote, rural and urban area, Rhine region	HVAS	GFF and XAD-2	11	Soxhlet extraction	0.052 - 185 ng/m³	1993 and 1994	GC-ECD	[163]
Sanusi, 2000	Alsace region, France	HVAS	GFF and XAD-2	11	Soxhlet extraction	0.052-185 ng/m³	1993-1994	GC-ECD and HPLC-UV	[164]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Peck, 2005	Iowa	HVAS	GFF and XAD-2	51	Soxhlet extraction	0.0015-91.2 ng/m³	2000-2002	GC-MS	[165]
Scheyer, 2005b	Strasbourg, France	HVAS	GFF, XAD-2	27	Soxhlet extraction	0.013-163 ng/m³	2002	GC-MS/MS	[166]
White, 2006	Potatoe cultivation in Prince Edward Island, Canada	HVAS	Teflon-coated glass fiber filter and PUF/XAD-2 sandwich	9	Soxhlet extraction	0.74 - 458 ng/m³	1998 and 1999	GC-MS	[167]
Yao, 2006	Agricultural regions, Canada	HVAS	GFF and PUF/XAD-2 sandwich	11	Soxhlet extraction	0.01 - 9460 pg/m³	2003	GC-ECD, GC-MSD	[168]
Scheyer, 2007	Alsace region, France	HVAS	GFF and XAD-2	27	Soxhlet extraction	29-1643 pg/m³	2002-2003	GC-MS	[169]
Meire, 2012	Brazilian mountains	PAS	PUF	OCPs and CUPs	Soxhlet extraction	0.1-5600 pg/m³	2007-2008	GC-MS	[40]
Arinaitwe, 2016	Lake Victoria, East Africa	HVAS	GFF and PUF	6	ASE	1.17-255 pg/m³	1999-2004 and 2008-2010	GC-MS	[170]
Coscollà, 2017	France	LVAS	QFF and PUF	57	ASE	0.12-1128 ng/m³	2006-2013	GC-MS and LC-MS/MS	[171]
Pucko, 2017	Canadian Arctic	HVAS	GFF and PUF	CUPs and OCPs	Soxhlet extraction	0.01-16.58 pg/m³	2012	GC-MS	[23]
Guida, 2018	Brazilian mountains	PAS	PUF	OCPs and CUPs	Soxhlet extraction	3-3202 pg/m³	2013-2015	GC-MS	[41]
Nascimento, 2018	Salvador city, Brazil	HVAS	QFF (PM2.5)	34	UAE	0.88-255 pg/m³	n.a.	GC-MS	[172]
Climent, 2019	Chile	PAS	PUF	34	MAE	8.7-3470 pg/m³	2015-2016	GC-MS/MS	[88]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Levy, 2020	Strasbourg	PAS	XAD-2	103	PSE	0.4-0.8 ng/sample	2016	GC-MS/MS and LC-MS/MS	[116]
Röhler, 2020	Svalbard	HVAS	GFF and PUF	28	Soxhlet extraction	n.a. (NTS)	2015	GCxGC-LRMS	[24]
Kruse-Plass, 2021	Germany	PAS	PUF	>500	Soxhlet extraction	6-8000 ng/sample	2019	GC-MS/MS and LC-MS/MS	[42]
Miglioranza, 2021	Patagonia, Argentina	PAS	XAD	30	Soxhlet extraction	14-400 pg/m³	2010-2012	GC-MS	[117]
Yera, 2021	Sao Paulo, Brazil	HVAS	QFF (PM2.5)	10	UAE	17-336 pg/m³	2018	GC-MS	[173]
Veludo, 2022	South Africa	PAS	PUF	52	Soxhlet extraction	0.003-1.3 ng/m³	2017-2018	GC-MS/MS and LC-MS/MS	[89]
Zaller, 2022	Austria	PAS	PUF and PEF	566	Soxhlet extraction	10.4-4759 ng/sample	2020	GC-MS	[90]
Zhang, 2022	Western Pacific and Southern Ocean	HVAS	GFF and XAD-2	221	UAE	0.003-190 pg/m³	2018-2019	GC-MS/MS	[21]
Ding, 2023	Western Canadrian mountains	PAS	XAD-2	17	Soxhlet extraction	0.58-200 pg/m³	2007-2008	GC-MS	[39]
Zhu, 2024	Arctic	HVAS	QFF and PUF/XAD-2/PUF	OCPs and CUPs	Soxhlet extraction	n.a. (NTS)	2019	GC-HRMS and LC-HRMS	[25]
OCPs									
Alegria, 2000	Belize, Central America	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.2-2868 pg/m³	1995-1996	GC-MS	[174]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Buehler, 2001	Lake Superior	HVAS	QFF and XAD-2	OCPs	Soxhlet extraction	0.14-130 pg/m³	1996-1998	GC-MS	[175]
Sofuoglu, 2001	Chicago	HVAS	GFF and PUF/XAD-2 sandwich	7	Soxhlet extraction	0.07 - 0.15 ng/m³	June - October 1995	GC-ECD	[176]
Wennrich, 2002	Germany	PAS	PDMS-coated stir bars and silicone tubing	OCPs	Thermodesorption	18.5-7469 ng/m³	2001	GC-MS	[177]
Jaward, 2003	Europe	PAS	PUF	OCPs	Soxhlet extraction	0.05-65 ng/sample	2002	GC-MS	[91]
Wania, 2003	Great Lakes	PAS	XAD-2	OCPs	Solvent extraction	0.07-62 pg/m³	2000	GC-MS	[118]
Farrar, 2004	Toronto, Canada	PAS	Ethylene vinyl acetate (EVA)	OCPs	Dissolved by immersion	65-380 pg/sample	2001	GC-MS	[178]
Harner, 2004	Toronto, Canada	PAS	PUF	OCPs	Soxhlet extraction	8.1-817 pg/m³	2000	GC-MS	[92]
Harrad, 2004	Birmingham, UK	HVAS	GFF and PUF	4	Soxhlet extraction	1 - 6000 pg/m³	1999-2000	GC-MS	[179]
Pozo, 2004	Chile	PAS	PUF	OCPs	Soxhlet extraction	1.9-99 pg/m³	2002-2003	GC-MS	[93]
Shen, 2005	North America	PAS	XAD-2	OCPs	Solvent extraction	0.01-46 ng/sample	2000-2001	GC-MS	[119]
Gioia, 2005	US Mid-Atlantic region	HVAS	QFF and PUF	22	Soxhlet extraction	0.06-518 pg/m³	2000-2001	GC-MSD	[180]
Gouin, 2005	Great Lakes	PAS and HVAS	PUF	OCPs	Soxhlet extraction	13-430 pg/m³	2002-2003	GC-MS	[181]
Motelay-Massei, 2005	Toronto, Canada	PAS	PUF	OCPs	Soxhlet extraction	0.35-1283 pg/m³	2000-2001	GC-MS	[94]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Scheyer, 2005a	Strasbourg, eastern France	HVAS	GFF and PUF	OCPs	Soxhlet extraction	2 - 2168 pg/m³	2001-2003	GC-ECD	[166]
Alegria, 2006	Chiapas, Mexico	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.13-1566 pg/m³	2000-2001	GC-MS	[182]
Farrar, 2006	Europe	PAS	Polymer-coated glass	OCPs	Solvent extraction	170-1775 pg/m³	2002	GC-MS	[183]
Klanova, 2006	Czech Republic	PAS	PUF	OCPs	Soxhlet extraction	5-445 ng/sample	2004	GC-MS	[95]
Lammel, 2007	China and Yellow Sea	HVAS	QFF and PUF	16	Soxhlet extraction	0.9 - 409 pg/m³	2003	GC-ECD	[15]
Dvorska, 2008	Kosetice, Czech Republic	HVAS	QFF and PUF	OCPs	Soxhlet extraction	0.00025-0.84 ng/m³	1996-2005	GC-MS	[184]
Yang, 2008	Guangzhou, China	HVAS	QFF and PUF	17	ASE	1.6-20829 pg/m³	2005-2006	GC-MS	[185]
He, 2010	Singapore	PAS and HVAS	QFF and PUF	OCPs	ASE	1-621 pg/m³	2008	GC-MS	[186]
Cindoruk, 2011	Turkey	HVAS	GFF and PUF	OCPs	UAE and Soxhlet extraction	519.7-1030.7 pg/m³	2008-2009	GC-MS	[187]
Devi, 2011	India	PAS	PUF	OCPs	Soxhlet extraction	0.3-403 pg/m³	2009	GC-MS	[96]
Halse, 2011	Europe	PAS and HVAS	PUF	OCPs	Soxhlet extraction	0.15-45 pg/m³	2006	GC-MS	[188]
Park, 2011	Korea	HVAS	QFF and PUF/activated carbon filter (ACF)	17	Soxhlet extraction	4.32-344.3 pg/m³	2008	GC-HRMS	[189]
Pozo, 2011	Indian agricultural regions	PAS	PUF	20	Soxhlet extraction	1-9500 pg/m³	2006-2007	GC-MS	[97]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Li, 2012	China	HVAS	GFF and PUF	3	Soxhlet extraction	0.1-308.6 pg/m³	2008	GC-ECD	[190]
Lin, 2012	China seas	HVAS	GFF and PUF	OCPs	Soxhlet extraction	1-860 pg/m³	2006	GC-MS	[16]
Pribylova, 2012	Central and Eastern Europe	PAS	PUF	12	Soxhlet extraction	0.1-2320 ng/sample	2006-2008	GC-MS	[98]
Yu, 2012	Shanghai, China	HVAS	QFF and PUF	OCPs	Soxhlet extraction	71.1-142.2 pg/m³	2008-2009	GC-ECD	[191]
Bogdal, 2013	Africa, Latin America, Caribbean, and Pacific Region	PAS	PUF	OCPs	Soxhlet extraction	0.01-2255 pg/m³	n.a.	GC-MS	[81]
Galbán-Malagón, 2013	Southern Ocean and Antarctic Peninsula	HVAS	QFF and PUF	3	Soxhlet extraction	0.04-51.8 pg/m³	2008-2009	GC-ECD	[26]
Hapeman, 2013	National Parks, South Florida	HVAS	GFF and PUF	1	Soxhlet extraction	0.52-17 ng/m³	2001-2006	GC-MS	[192]
Khairy, 2013	Alexandria, Egypt	PAS and HVAS	Low density polyethylene sheets (LDPE), GFF and PUF	25	Cold extraction and ASE	2.5-240 pg/m³		GC-MSD	[193]
Sofuoglu, 2013	Acadia National Park, Maine, USA	HVAS	GFF and PUF	10	Soxhlet extraction	0.3-300 pg/m³	2007-2010	GC-ECD	[43]
Tombesi, 2014	Buenos Aires, Argentina	PAS	PUF	OCPs	Soxhlet extraction	1-16000 pg/m³	2006-2007	GC-MS	[99]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Wu, 2014	Arctic	HVAS	PUF	1	ASE	24-180 pg/m³	2008	GC-MSD	[27]
Peverly, 2015	Chicago	PAS	PUF	OCPs	Soxhlet extraction	2.7-85 pg/m³	2012-2013	GC-MS	[100]
Bossi, 2016	North Greenland	HVAS	QFF and PUF/XAD-2/PUF	OCPs	Soxhlet extraction	0.001-160 pg/m³	2008-2013	GC-HRMS	[28]
de la Torre, 2016	Spain	PAS	PUF	OCPs	Soxhlet extraction	0.03-561 pg/m³	2008-2013	GC-HRMS	[101]
Kirchner, 2016	Alpine Stations, Alps	LVAS	n.a.	OCPs	n.a.	0.007-837 pg/m,³	2005-2013	GC-MS	[194]
Li, 2016	Western China	PAS	PUF	OCPs	Soxhlet extraction	0-241 ng/sample	2013	GC-MS	[102]
Pegoraro, 2016	South Atlantic Ocean	HVAS	GFF and PUF	22	Soxhlet extraction	0.2-17.8 pg/m³	2014	GC-MS	[17]
Takazawa, 2016	Cape Hedo, Japan	HVAS	QFF, PUF and activated carbon fiber	OCPs	Soxhlet extraction	0.71-83 pg/m³	2009-2014	GC-HRMS	[195]
Tominaga, 2016	Sao Paulo City	PAS	PUF	12	Soxhlet extraction	1.26-126 pg/m³	2010-2015	GC-MS	[103]
Bengston Nash, 2017	East Antarctic	PAS	PUF	38	Soxhlet extraction	0.01-39 pg/m³	2010-2015	GC-HRMS	[29]
Luek, 2017	Atlantic Ocean, Southern Oceans and Antarctica	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.1-100 pg/m³	2007-2008	GC-MS	[30]
Pozo, 2017a	Ross Sea, Antarctica	PAS	PUF	OCPs	Soxhlet extraction	0.02-30.6 pg/m³	2010-2011	GC-MS	[31]
Pozo, 2017b	Urban area, Chile	PAS	PUF	OCPs	Soxhlet extraction	0.1-30 pg/m³	2008-2009	GC-MS	[105]

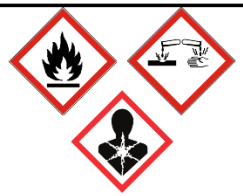
Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Pozo, 2017c	India	PAS	PUF	OCPs	Soxhlet extraction	70-216 pg/m³	2014	GC-MS	[104]
Zhang, 2017	Hawaii	PAS	XAD-2	OCPs	ASE	0.01-54 ng/sample	2011	GC-MS/MS	[120]
Gevao, 2018	Kuwait	HVAS	GFF and PUF	OCPs	Soxhlet extraction	4.5-1352 pg/m³	n.a.	GC-MS/MS	[196]
Gong, 2018	Lijiang, China	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.1-128 pg/m³	2009-2013	GC-MS	[197]
Kurt-Karakus, 2018	Turkey	PAS	PUF	22	Soxhlet extraction	2.14-64 pg/m³	2014-2015	GC-MSD	[106]
Nøst, 2018	Cape Verde	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.1-100 pg/m³	2012-2013	GC-MS	[198]
Can-Güven, 2019	Turkey	PAS	PUF	22	Soxhlet extraction	0.88-97 pg/m³	2013	GC-MS	[107]
Hao, 2019	Western Antarctica	PAS	XAD-2	OCPs	Soxhlet extraction	101-278 pg/m³	2010-2018	GC-HRMS	[32]
Navarro, 2019	Spain	PAS	PUF	OCPs	Soxhlet extraction	0.01-20 ng/m³	2016-2018	GC-MS	[108]
Pegoraro, 2019	Córdoba, Argentina	PAS	PUF	12	ASE	0.33-416 pg/m³	2014	GC-MS/MS	[109]
Yu, 2019	Northern China	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.03-6.3 ng/m³	2015-2016	GC-MSD	[199]
Li, 2020	Pacific ocean	HVAS	GFF and PUF	13	ASE	0.1-61 pg/m³	2006-2007	GC-MS/MS	[18]
Mao, 2020	China	HVAS	PUF	1	Soxhlet extraction	14-522 pg/m³	2012-2015	GC-MS/MS	[200]
Wu, 2020	Antarctic marginal seas	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.081-10 pg/m³	2013-2014	GC-MS	[33]
Zheng, 2020	East Asia to Arctic Ocean	HVAS	GFF and XAD-2	7	UAE	0.1-1.21 ng/m³	2016-2017	GC-MS	[19]

Publication	Sampling area	Sampling technique	Matrix	Number of analysed compounds	Extraction method	Range of concentrations	Year of sampling	Instrumental analysis	Reference
Dien, 2021	Japan	HVAS	QFF, PUF and activated carbon fiber	OCPs	Soxhlet extraction	8.8-550 pg/m³	2003-2018	GC-HRMS	[201]
Hao, 2021	Arctic	PAS	XAD-2	OCPs	Soxhlet extraction	0.005-32 pg/m³	2011-2018	GC-HRMS	[34]
Iakovides, 2021	Island of Crete	HVAS	GFF and PUF	OCPs	Soxhlet extraction	0.1-50 pg/m³	2013-2015	GC-MSD	[202]
Prats, 2021	Barcelona, Spain	PAS	PUF	OCPs	Soxhlet extraction	0.5-49 pg/m³	2019-2020	GC-MS	[110]
Schuster, 2021	Worldwide (GAPS study)	PAS	PUF	OCPs	Soxhlet extraction and ASE	0.36-15.3 pg/m³	2005-2014	GC-MS/MS	[111]
Avila, 2022	Colombia	PAS	PUF	OCPs	n.a.	0.27-28 ng/sample	2017-2018	n.a.	[112]
Lee, 2022	South Korea	HVAS	QFF and PUF	22	Soxhlet extraction	0.3-580 pg/m³	2020	GC-HRMS	[203]
Llanos, 2022	Chile	PAS	PUF	13	Soxhlet extraction	0.1-96 pg/m³	2016-2018	GC-MS/MS	[113]
Mamontova, 2022	Eastern Siberia	PAS	PUF	OCPs	Soxhlet extraction	0.03-253 pg/m³	2011-2017	GC-ECD	[114]
Galbán-Malagón, 2023	Antarctic Peninsula	HVAS	QFF and PUF	OCPs	Soxhlet extraction	0.25-4.26 pg/m³	2009	GC-ECD	[35]
Iakovides, 2023	Cyprus	HVAS	GF/A and PUF	OCPs	Soxhlet extraction	1.22-72.13 pg/m³	n.a.	GC-MS	[204]
Khuman, 2023	South Korea	HVAS	QFF and PUF	OCPs	Soxhlet extraction	1-642 pg/m³	2008-2017	GC-HRMS	[205]
Wang, 2023	China	HVAS	GFF and PUF	24	Soxhlet extraction	0.05-1000 pg/m³	2019-2020	GC-MS	[206]

Table A5: Safety data information on pesticides and transformation products according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
2,4'-DDD	1-chloro-2-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene CAS: 53-19-0	 Warning	H351	P203, P280, P318, P405, and P501
2,4'-DDE	1-chloro-2-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene CAS: 3424-82-6	 Warning	H302, H351, H400, and H410	P203, P264, P270, P273, P280, P301+P317, P318, P330, P391, P405, and P501
2,4'-DDT	1-chloro-2-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene CAS: 789-02-6	 Danger	H301, H311, H330, H351, H372, H373, H400, and H410	P203, P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P318, P319, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
2,4-D	2-(2,4-dichlorophenoxy)acetic acid CAS: 94-75-7	 Danger	H302+H312, H317, H318, H334, H335, H400, H410, and H412	P233, P260, P261, P264+P265, P270, P271, P272, P273, P280, P284, P301+P317, P302+P352, P304+P340, P305+P354+P338, P319, P321, P330, P333+P317, P342+P316, P362+P364, P391, P403, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
3-Hydroxycarbofuran	(3-hydroxy-2,2-dimethyl-3H-1-benzofuran-7-yl) N-methylcarbamate CAS: 16655-82-6	 Danger	H300	P264, P270, P301+P316, P321, P330, P405, and P501
4,4'-DDD	1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene CAS: 72-54-8	 Danger	H301, H312, H351, H400, and H410	P203, P264, P270, P273, P280, P301+P316, P302+P352, P317, P318, P321, P330, P362+P364, P391, P405, and P501
4,4'-DDE	1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethenyl]benzene CAS: 72-55-9	 Danger	H301, H302, H311, H315, H331, H332, H351, H372, H400, and H410	P203, P260, P261, P262, P264, P270, P271, P273, P280, P301+P316, P301+P317, P302+P352, P304+P340, P316, P317, P318, P319, P321, P330, P332+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501
4,4'-DDT	1-chloro-4-[2,2,2-trichloro-1-(4-chlorophenyl)ethyl]benzene CAS: 50-29-3	 Danger	H301+H311, H351, H372, H400, and H410	P203, P260, P262, P264, P270, P273, P280, P301+P316, P302+P352, P316, P318, P319, P321, P330, P361+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Abamectin	(1'R,2R,3S,4'S,6S,8'R,10'E,12'S,13'S,14'E,16'E,20'R,21'R,24'S)-2-butan-2-yl-21',24'-dihydroxy-12'-[(2R,4S,5S,6S)-5-[(2S,4S,5S,6S)-5-hydroxy-4-methoxy-6-methyloxan-2-yl]oxy-4-methoxy-6-methyloxan-2-yl]oxy-3,11',13',22'-tetramethylspiro[2,3-dihydropyran-6,6'-3,7,19-trioxatetracyclo[15.6.1.1^{4,8}.0^{20,24}]pentacosa-10,14,16,22-tetraene]-2'-one;(1'R,2R,3S,4'S,6S,8'R,10'E,12'S,13'S,14'E,16'E,20'R,21'R,24'S)-21',24'-dihydroxy-12'-[(2R,4S,5S,6S)-5-[(2S,4S,5S,6S)-5-hydroxy-4-methoxy-6-methyloxan-2-yl]oxy-4-methoxy-6-methyloxan-2-yl]oxy-3,11',13',22'-tetramethyl-2-propan-2-ylspiro[2,3-dihydropyran-6,6'-3,7,19-trioxatetracyclo[15.6.1.1^{4,8}.0^{20,24}]pentacosa-10,14,16,22-tetraene]-2'-one CAS: 71751-41-2	 Danger	H260, H314, H317, H334, and H373	P223, P231+P232, P233, P260, P261, P264, P271, P272, P280, P284, P301+P330+P331, P302+P335+P334, P302+P352, P302+P361+P354, P304+P340, P305+P354+P338, P316, P319, P321, P333+P317, P342+P316, P362+P364, P363, P370+P378, P402+P404, P403, P405, and P501
Acephate	N-[methoxy(methylsulfanyl)phosphoryl]acetamide CAS: 30560-19-1	 Warning	H302	P264, P270, P301+P317, P330, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Acetamiprid	N-[(6-chloropyridin-3-yl)methyl]-N'-cyano-N-methylethanimidamide CAS: 160430-64-8	 Danger	H301, H302, H330, H332, H361d, H400, H410, and H412	P203, P260, P261, P264, P270, P271, P273, P280, P284, P301+P316, P301+P317, P304+P340, P316, P317, P318, P320, P321, P330, P391, P403+P233, P405, and P501
Acetamiprid-N-desmethyl	N'-[(6-chloropyridin-3-yl)methyl]-N-cyanoethanimidamide CAS: 190604-92-3	 Danger	H301, H315, H319, and H335	P261, P264, P264+P265, P270, P271, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P319, P321, P330, P332+P317, P337+P317, P362+P364, P403+P233, P405, and P501
Acibenzolar-S-methyl	S-methyl 1,2,3-benzothiadiazole-7-carbothioate CAS: 135158-54-2	 Danger	H315, H317, H319, H335, H360d, H400, and H410	P203, P261, P264, P264+P265, P271, P272, P273, P280, P302+P352, P304+P340, P305+P351+P338, P318, P319, P321, P332+P317, P333+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Aclonifen	2-chloro-6-nitro-3-phenoxyaniline CAS: 74070-46-5	 Warning	H317, H351, H400, and H410	P203, P261, P272, P273, P280, P302+P352, P318, P321, P333+P317, P362+P364, P391, P405, and P501

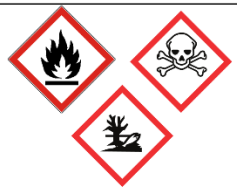
Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Alanycarb	ethyl 3-[benzyl-[methyl-[(Z)-1-methylsulfanylethylideneamino]oxycarbonylamino]sulfanylamino]propanoate CAS: 83130-01-2	 Danger	H302, H330, and H400	P260, P264, P270, P271, P273, P284, P301+P317, P304+P340, P316, P320, P330, P391, P403+P233, P405, and P501
Aldicarb	[(E)-(2-methyl-2-methylsulfanylpropylidene)amino] N-methylcarbamate CAS: 116-06-3	 Danger	H300+H310+H330, H300, H310, H311, H330, H400, and H410	P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Aldicarb sulfone	[(E)-(2-methyl-2-methylsulfonylpropylidene)amino] N-methylcarbamate CAS: 1646-88-4	 Danger	H300, H310, H330, and H400	P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Aldicarb sulfoxide	[(E)-(2-methyl-2-methylsulfinylpropylidene)amino] N-methylcarbamate CAS: 1646-87-3	 Danger	H300 and H400	P264, P270, P273, P301+P316, P321, P330, P391, P405, and P501
Allethrin	(2-methyl-4-oxo-3-prop-2-enylcyclopent-2-en-1-yl) 2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane-1-carboxylate CAS: 584-79-2	 Warning	H302+H332, H400, and H410	P261, P264, P270, P271, P273, P301+P317, P304+P340, P317, P330, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
alpha-HCH	(1R,2R,3S,4S,5S,6S)-1,2,3,4,5,6-hexachlorocyclohexane CAS: 319-84-6	 Danger	H301, H312, H351, H400, and H410	P203, P264, P270, P273, P280, P301+P316, P302+P352, P317, P318, P321, P330, P362+P364, P391, P405, and P501
Ametoctradin	5-ethyl-6-octyl-[1,2,4]triazolo[1,5-a]pyrimidin-7-amine CAS: 865318-97-4	 Warning	H302	P264, P270, P301+P317, P330, and P501
Ametryn	4-N-ethyl-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine CAS: 834-12-8	 Danger	H302, H331, H400, and H410	P261, P264, P270, P271, P273, P301+P317, P304+P340, P316, P321, P330, P391, P403+P233, P405, and P501
Aminocarb	[4-(dimethylamino)-3-methylphenyl] N-methylcarbamate CAS: 2032-59-9	 Danger	H301+H311, H400, and H410	P262, P264, P270, P273, P280, P301+P316, P302+P352, P316, P321, P330, P361+P364, P391, P405, and P501
Atrazine	6-chloro-4-N-ethyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine CAS: 1912-24-9	 Warning	H317, H319, H373, H400, and H410	P260, P261, P264+P265, P272, P273, P280, P302+P352, P305+P351+P338, P319, P321, P333+P317, P337+P317, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Azadirachtin	dimethyl (1S,4S,5R,6S,7S,8R,11S,12R,14S,15R)-12-acetyloxy-4,7-dihydroxy-6-[(1S,2S,6S,8S,9R,11S)-2-hydroxy-11-methyl-5,7,10-trioxatetracyclo[6.3.1.$0^{2,6}$.$0^{9,11}$]dodec-3-en-9-yl]-6-methyl-14-[(E)-2-methylbut-2-enoyl]oxy-3,9-dioxatetracyclo[6.6.1.$0^{1,5}$.$0^{11,15}$]pentadecane-4,11-dicarboxylate CAS: 11141-17-6	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501
Azoxystrobin	methyl (E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yl]oxyphenyl]-3-methoxyprop-2-enoate CAS: 131860-33-8	 Danger	H331, H400, and H410	P261, P271, P273, P304+P340, P316, P321, P391, P403+P233, P405, and P501
Azoxystrobin-O-demethyl	(E)-2-[2-[6-(2-cyanophenoxy)pyrimidin-4-yl]oxyphenyl]-3-methoxyprop-2-enoic acid CAS: 1185255-09-7	 Danger	H301, H311, H315, H319, H331, H335, and H410	P261, P262, P264, P264+P265, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P316, P319, P321, P330, P332+P317, P337+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501
Bitertanol	3,3-dimethyl-1-(4-phenylphenoxy)-1-(1,2,4-triazol-1-yl)butan-2-ol CAS: 55179-31-2	 Danger	H302 and H330	P260, P264, P270, P271, P284, P301+P317, P304+P340, P316, P320, P330, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Benalaxyl	methyl 2-(2,6-dimethyl-N-(2-phenylacetyl)anilino)propanoate CAS: 71626-11-4	 Warning	H400 and H410	P273, P391, and P501
Bendiocarb	(2,2-dimethyl-1,3-benzodioxol-4-yl) N-methylcarbamate CAS: 22781-23-3	 Danger	H300, H301, H311+H331, H312, H400, and H410	P261, P262, P264, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P316, P317, P321, P330, P361+P364, P362+P364, P391, P403+P233, P405, and P501
Bentazone	2,2-dioxo-3-propan-2-yl-1H-2λ^6,1,3-benzothiadiazin-4-one CAS: 25057-89-0	 Warning	H302, H317, H319, H361a, and H412	P203, P261, P264, P264+P265, P270, P272, P273, P280, P301+P317, P302+P352, P305+P351+P338, P318, P321, P330, P333+P317, P337+P317, P362+P364, P405, and P501
Benzoximate	[(E)-C-(3-chloro-2,6-dimethoxyphenyl)-N-ethoxycarbonimidoyl] benzoate CAS: 29104-30-1	-	H412	P273 and P501
beta-HCH	(1R,2R,3R,4R,RS,6R)-1,2,3,4,5,6-hexachlorocyclohexane CAS: 319-85-7	 Danger	H301, H312, H351, H400, and H410	P203, P264, P270, P273, P280, P301+P316, P302+P352, P317, P318, P321, P330, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Bifenthrin	(2-methyl-3-phenylphenyl)methyl (1R,3R)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate CAS: 82657-04-3	 Danger	H300, H317, H331, H351, H372, H400, and H410	P203, P260, P261, P264, P270, P271, P272, P273, P280, P301+P316, P302+P352, P304+P340, P316, P318, P319, P321, P330, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Bixafen	N-[2-(3,4-dichlorophenyl)-4-fluorophenyl]-3-(difluoromethyl)-1-methylpyrazole-4-carboxamide CAS: 581809-46-3	 Warning	H303+H313+H333, H400, and H410	P273, P301+P317, P302+P317, P304+P317, P391, and P501
Boscalid	2-chloro-N-[2-(4-chlorophenyl)phenyl]pyridine-3-carboxamide CAS: 188425-85-6		H411	P273, P391, and P501
Bromoxynil	3,5-dibromo-4-hydroxybenzonitrile CAS: 1689-84-5	 Danger	H301, H317, H330, H361, H361d, H400, and H410	P203, P260, P261, P264, P270, P271, P272, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P318, P320, P321, P330, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Bromuconazole	1-[[4-bromo-2-(2,4-dichlorophenyl)oxolan-2-yl]methyl]-1,2,4-triazole CAS: 116255-48-2	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Bupirimate	[5-butyl-2-(ethylamino)-6-methylpyrimidin-4-yl] N,N-dimethylsulfamate CAS: 41483-43-6	 Danger	H311, H317, H351, and H410	P203, P261, P262, P264, P270, P272, P273, P280, P302+P352, P316, P318, P321, P333+P317, P361+P364, P362+P364, P391, P405, and P501
Buprofezin	2-tert-butylimino-5-phenyl-3-propan-2-yl-1,3,5-thiadiazinan-4-one CAS: 69327-76-0	 Warning	H373, H400, and H410	P260, P273, P319, P391, and P501
Butafenacil	(2-methyl-1-oxo-1-prop-2-enoxypropan-2-yl) 2-chloro-5-[3-methyl-2,6-dioxo-4-(trifluoromethyl)pyrimidin-1-yl]benzoate CAS: 134605-64-4	 Warning	H373, H400, and H410	P260, P273, P319, P391, and P501
Butocarboxim	[(E)-3-methylsulfanylbutan-2-ylideneamino] N-methylcarbamate CAS: 34681-10-2	 Danger	H226, H301, H311, H319, H331, H400, and H410	P210, P233, P240, P241, P242, P243, P261, P262, P264, P264+P265, P270, P271, P273, P280, P301+P316, P302+P352, P303+P361+P353, P304+P340, P305+P351+P338, P316, P321, P330, P337+P317, P361+P364, P370+P378, P391, P403+P233, P403+P235, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Butoxycarboxim	[(E)-3-methylsulfonylbutan-2-ylideneamino] N-methylcarbamate CAS: 34681-23-7	 Warning	H302	P264, P270, P301+P317, P330, and P501
Captan	2-(trichloromethylsulfanyl)-3a,4,7,7a-tetrahydroisoindole-1,3-dione CAS: 133-06-2	 Danger	H317, H318, H331, H351, and H400	P203, P261, P264+P265, P271, P272, P273, P280, P302+P352, P304+P340, P305+P354+P338, P316, P317, P318, P321, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Captan THPI	3a,4,7,7a-tetrahydroisoindole-1,3-dione CAS: 85-40-5	-	-	-
Carbaryl	naphthalen-1-yl N-methylcarbamate CAS: 63-25-2	 Danger	H301, H302, H332, H351, H400, and H410	P203, P261, P264, P270, P271, P273, P280, P301+P316, P301+P317, P304+P340, P317, P318, P321, P330, P391, P405, and P501
Carbendazim	methyl N-(1H-benzimidazol-2-yl)carbamate CAS: 10605-21-7	 Danger	H317, H340, H360, H360fd, H400, and H410	P203, P261, P272, P273, P280, P302+P352, P318, P321, P333+P317, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Carbetamide	[(2R)-1-(ethylamino)-1-oxopropan-2-yl] N-phenylcarbamate CAS: 16118-49-3	 Danger	H302, H351, H360, H360d, and H411	P203, P264, P270, P273, P280, P301+P317, P318, P330, P391, P405, and P501
Carbofuran	(2,2-dimethyl-3H-1-benzofuran-7-yl) N-methylcarbamate CAS: 1563-66-2	 Danger	H300+H330, H400, and H410	P260, P264, P270, P271, P273, P284, P301+P316, P304+P340, P316, P320, P321, P330, P391, P403+P233, P405, and P501
Carboxin	6-methyl-N-phenyl-2,3-dihydro-1,4-oxathiine-5-carboxamide CAS: 5234-68-4	 Warning	H302, H317, H373, H400, and H410	P260, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P319, P321, P330, P333+P317, P362+P364, P391, and P501
Carfentrazone-ethyl	ethyl 2-chloro-3-[2-chloro-5-[4-(difluoromethyl)-3-methyl-5-oxo-1,2,4-triazol-1-yl]-4-fluorophenyl]propanoate CAS: 128639-02-1	 Warning	H400 and H410	P273, P391, and P501
Chlorantraniliprole	5-bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-2-(3-chloropyridin-2-yl)pyrazole-3-carboxamide CAS: 500008-45-7	 Warning	H319, H335, H400, and H410	P261, P264+P265, P271, P273, P280, P304+P340, P305+P351+P338, P319, P337+P317, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Chlorfluazuron	N-[[3,5-dichloro-4-[3-chloro-5-(trifluoromethyl)pyridin-2-yl]oxyphenyl]carbamoyl]-2,6-difluorobenzamide CAS: 71422-67-8	 Warning	H319, H400, and H410	P264+P265, P273, P280, P305+P351+P338, P337+P317, P391, and P501
Chloridazon	5-amino-4-chloro-2-phenylpyridazin-3-one CAS: 1698-60-8	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501
Chlorimuron-ethyl	ethyl 2-[(4-chloro-6-methoxypyrimidin-2-yl)carbamoylsulfamoyl]benzoate CAS: 90982-32-4	 Warning	H332, H373, H400, and H410	P260, P261, P271, P273, P304+P340, P317, P319, P391, and P501
Chlorothalonil	2,4,5,6-tetrachlorobenzene-1,3-dicarbonitrile CAS: 1897-45-6	 Danger	H317, H318, H330, H335, H351, H400, and H410	P203, P260, P261, P264+P265, P271, P272, P273, P280, P284, P302+P352, P304+P340, P305+P354+P338, P316, P317, P318, P319, P320, P321, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Chlorothalonil 4-hydroxy	2,4,5-trichloro-6-hydroxybenzene-1,3-dicarbonitrile CAS: 28343-61-5	 Danger	H301 and H373	P260, P264, P270, P301+P316, P319, P321, P330, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Chlorotoluron	3-(3-chloro-4-methylphenyl)-1,1-dimethylurea CAS: 15545-48-9	 Warning	H351, H361, H361d, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Chloroxuron	3-[4-(4-chlorophenoxy)phenyl]-1,1-dimethylurea CAS: 1982-47-4	 Warning	H332, H400, and H410	P261, P271, P273, P304+P340, P317, P391, and P501
Chlorpropham	propan-2-yl N-(3-chlorophenyl)carbamate CAS: 101-21-3	 Warning	H351, H373, and H411	P203, P260, P273, P280, P318, P319, P391, P405, and P501
Chlorpyrifos	diethoxy-sulfanylidene-(3,5,6-trichloropyridin-2-yl)oxy-λ^5-phosphane CAS: 2921-88-2	 Danger	H301, H312, H319, H330, H400, and H410	P260, P264, P264+P265, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P305+P351+P338, P316, P317, P320, P321, P330, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Chlorpyrifos-methyl	dimethoxy-sulfanylidene-(3,5,6-trichloropyridin-2-yl)oxy-λ^5-phosphane CAS: 5598-13-0	 Danger	H302, H317, H331, H334, H400, and H410	P233, P260, P261, P264, P270, P271, P272, P273, P280, P284, P301+P317, P302+P352, P304+P340, P316, P321, P330, P333+P317, P342+P316, P362+P364, P391, P403, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Chlorpyrifos-methyl-TCPy	3,5,6-trichloro-1H-pyridin-2-one CAS: 6515-38-4	 Danger	H302, H318, H400, H410, and H411	P264, P264+P265, P270, P273, P280, P301+P317, P305+P354+P338, P317, P330, P391, and P501
cis-Permethrin	(3-phenoxyphenyl)methyl (1R,3R)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate CAS: 61949-76-6	 Warning	H302, H317, H332, H400, and H410	P261, P264, P270, P271, P272, P273, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P333+P317, P362+P364, P391, and P501
Clethodim	2-[(E)-N-[(E)-3-chloroprop-2-enoxy]-C-ethylcarbonimidoyl]-5-(2-ethylsulfanylpropyl)-3-hydroxycyclohex-2-en-1-one CAS: 99129-21-2	 Warning	H302, H317, and H412	P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P321, P330, P333+P317, P362+P364, and P501
Clofentezine	3,6-bis(2-chlorophenyl)-1,2,4,5-tetrazine CAS: 74115-24-5	 Warning	H312, H400, and H410	P273, P280, P302+P352, P317, P321, P362+P364, P391, and P501
Clomazone	2-[(2-chlorophenyl)methyl]-4,4-dimethyl-1,2-oxazolidin-3-one CAS: 81777-89-1	 Warning	H302+H332, H312, H315, H319, H400, H410, H411, and H412	P261, P264, P264+P265, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P317, P321, P330, P332+P317, P337+P317, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Clopyralid	3,6-dichloropyridine-2-carboxylic acid CAS: 1702-17-6	 Danger	H318, H410, and H411	P264+P265, P273, P280, P305+P354+P338, P317, P391, and P501
Clothianidin	1-[(2-chloro-1,3-thiazol-5-yl)methyl]-3-methyl-2-nitroguanidine CAS: 210880-92-5	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501
Cyantraniliprole	5-bromo-2-(3-chloropyridin-2-yl)-N-[4-cyano-2-methyl-6-(methylcarbamoyl)phenyl]pyrazole-3-carboxamide CAS: 736994-63-1	 Warning	H400 and H410	P273, P391, and P501
Cyazofamid	4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)imidazole-1-sulfonamide CAS: 120116-88-3	 Warning	H400 and H410	P273, P391, and P501
Cycluron	3-cyclooctyl-1,1-dimethylurea CAS: 2163-69-1	 Warning	H302	P264, P270, P301+P317, P330, and P501
Cyflufenamide	N-[(E)-N-(cyclopropylmethoxy)-C-[2,3-difluoro-6-(trifluoromethyl)phenyl]carbonimidoyl]-2-phenylacetamide CAS: 180409-60-3	 Warning	H332, H400, H410, and H411	P261, P271, P273, P304+P340, P317, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Cyfluthrin	[cyano-(4-fluoro-3-phenoxyphenyl)methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate CAS: 68359-37-5	 Danger	H300+H330, H331, H362, H370, H400, and H410	P203, P260, P261, P263, P264, P270, P271, P273, P284, P301+P316, P304+P340, P308+P316, P316, P318, P320, P321, P330, P391, P403+P233, P405, and P501
Cymoxanil	(1E)-2-(ethylcarbamoylamino)-N-methoxy-2-oxoethanimidoyl cyanide CAS: 57966-95-7	 Warning	H302, H317, H361, H361fd, H373, H400, and H410	P203, P260, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P318, P319, P321, P330, P333+P317, P362+P364, P391, P405, and P501
Cypermethrin	[cyano-(3-phenoxyphenyl)methyl] 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate CAS: 52315-07-8	 Danger	H301, H332, H335, H373, H400, and H410	P260, P261, P264, P270, P271, P273, P301+P316, P304+P340, P317, P319, P321, P330, P391, P403+P233, P405, and P501
Cyproconazole	2-(4-chlorophenyl)-3-cyclopropyl-1-(1,2,4-triazol-1-yl)butan-2-ol CAS: 94361-06-5	 Danger	H301, H302, H360, H360d, H361, H373, H400, and H410	P203, P260, P264, P270, P273, P280, P301+P316, P301+P317, P318, P319, P321, P330, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Cyprodinil	4-cyclopropyl-6-methyl-N-phenylpyrimidin-2-amine CAS: 121552-61-2	 Warning	H315, H317, H319, H400, and H410	P261, P264, P264+P265, P272, P273, P280, P302+P352, P305+P351+P338, P321, P332+P317, P333+P317, P337+P317, P362+P364, P391, and P501
Cyprodinil metabolite CGA304075	4-[(4-cyclopropyl-6-methylpyrimidin-2-yl)amino]phenol CAS: 195157-66-5	 Warning	H317 and H410	P261, P273, P280, P333+P313, P362+P364, and P391
Cyromazine	2-N-cyclopropyl-1,3,5-triazine-2,4,6-triamine CAS: 66215-27-8	 Warning	H315, H319, H335, and H410	P261, P264, P264+P265, P271, P273, P280, P302+P352, P304+P340, P305+P351+P338, P319, P321, P332+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
DEAMPY	2-(diethylamino)-4-methyl-1H-pyrimidin-6-one CAS: 42487-72-9	 Warning	H302	P264, P270, P301+P317, P330, and P501
delta-HCH	(1R,2S,3R,4R,5S,6S)-1,2,3,4,5,6-hexachlorocyclohexane CAS: 319-86-8	 Danger	H301, H302, H312, H351, H400, and H410	P203, P264, P270, P273, P280, P301+P316, P301+P317, P302+P352, P317, P318, P321, P330, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Deltamethrin	[(S)-cyano-(3-phenoxyphenyl)methyl] (1R,3R)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropane-1-carboxylate CAS: 52918-63-5	 Danger	H300, H301, H317, H319, H331, H335, H361, H372, H400, and H410	P203, P260, P261, P264, P264+P265, P270, P271, P272, P273, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P316, P318, P319, P321, P330, P333+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Desmedipham	[3-(ethoxycarbonylamino)phenyl] N-phenylcarbamate CAS: 13684-56-5	 Warning	H361d, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Dicamba	3,6-dichloro-2-methoxybenzoic acid CAS: 1918-00-9	 Danger	H302+H332, H318, H335, H400, H410, and H412	P261, P264, P264+P265, P270, P271, P273, P280, P301+P317, P304+P340, P305+P354+P338, P317, P319, P330, P391, P403+P233, P405, and P501
Dichlorvos	2,2-dichloroethenyl dimethyl phosphate CAS: 62-73-7	 Danger	H300, H301, H311, H317, H330, H331, and H400	P260, P261, P262, P264, P270, P271, P272, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P333+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Diclobutrazol	1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)pentan-3-ol CAS: 66345-62-8	 Warning	H319 and H411	P264+P265, P273, P280, P305+P351+P338, P337+P317, P391, and P501
Dicloran	2,6-dichloro-4-nitroaniline CAS: 99-30-9	 Danger	H300+H310+H330, H373, and H411	P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P319, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Diclosulam	N-(2,6-dichlorophenyl)-5-ethoxy-7-fluoro-[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide CAS: 145701-21-9	 Warning	H400 and H410	P273, P391, and P501
Dicrotophos	[(E)-4-(dimethylamino)-4-oxobut-2-en-2-yl] dimethyl phosphate CAS: 141-66-2	 Danger	H300+H330, H310, H311, H400, and H410	P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Dieldrin	(1R,2S,3S,6R,7R,8S,9S,11R)-3,4,5,6,13,13-hexachloro-10-oxapentacyclo[6.3.1.1^{3,6}.0^{2,7}.0^{9,11}]tridec-4-ene CAS: 60-57-1	 Danger	H300, H301, H310, H330, H351, H372, H400, and H410	P203, P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P318, P319, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Diethofencarb	propan-2-yl N-(3,4-diethoxyphenyl)carbamate CAS: 87130-20-9	 Warning	H319	P264+P265, P280, P305+P351+P338, and P337+P317
Difenoconazole	1-[[2-[2-chloro-4-(4-chlorophenoxy)phenyl]-4-methyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole CAS: 119446-68-3	 Warning	H302+H332, H319, H400, and H410	P261, P264, P264+P265, P270, P271, P273, P280, P301+P317, P304+P340, P305+P351+P338, P317, P330, P337+P317, P391, and P501
Diflubenzuron	N-[(4-chlorophenyl)carbamoyl]-2,6-difluorobenzamide CAS: 35367-38-5	 Warning	H312, H373, H400, and H410	P260, P273, P280, P302+P352, P317, P319, P321, P362+P364, P391, and P501
Diflufenican	N-(2,4-difluorophenyl)-2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxamide CAS: 83164-33-4	 Warning	H302+H312, H400, H410, and H412	P264, P270, P273, P280, P301+P317, P302+P352, P317, P321, P330, P362+P364, P391, and P501
Diflufenican AE-B107137	2-[3-(trifluoromethyl)phenoxy]pyridine-3-carboxylic acid CAS: 36701-89-0	 Warning	H302+H312+H332, H315, H319, and H412	P261, P280, P301+P312, P305+P351+P338, P321, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Dimethenamid-p	2-chloro-N-(2,4-dimethylthiophen-3-yl)-N-[(2S)-1-methoxypropan-2-yl]acetamide CAS: 163515-14-8	 Danger	H302, H317, H331, H334, H400 and H410	P233, P260, P261, P264, P270, P271, P272, P273, P280, P284, P301+P317, P302+P352, P304+P340, P316, P321, P330, P333+P317, P342+P316, P362+P364, P391, P403, P403+P233, P405, and P501
Dimethoate	2-dimethoxyphosphinothioylsulfanyl-N-methylacetamide CAS: 60-51-5	 Warning	H302 and H312	P264, P270, P280, P301+P317, P302+P352, P317, P321, P330, P362+P364, and P501
Dimethomorph	(E)-3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl)-1-morpholin-4-ylprop-2-en-1-one CAS: 113210-97-2		H411	P273, P391, and P501
Dimoxystrobin	(2E)-2-[2-[(2,5-dimethylphenoxy)methyl]phenyl]-2-methoxyimino-N-methylacetamide CAS: 149961-52-4	 Warning	H332, H351, H361, H361d, H400, and H410	P203, P261, P271, P273, P280, P304+P340, P317, P318, P391, P405, and P501
Diniconazole	(E)-1-(2,4-dichlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)pent-1-en-3-ol CAS: 83657-24-3	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501
Dinotefuran	1-methyl-2-nitro-3-(oxolan-3-ylmethyl)guanidine CAS: 165252-70-0	 Warning	H302, H400, and H410	P264, P270, P273, P301+P312, P330, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Diuron	3-(3,4-dichlorophenyl)-1,1-dimethylurea CAS: 330-54-1	 Warning	H302, H351, H373, H400, and H410	P203, P260, P264, P270, P273, P280, P301+P317, P318, P319, P330, P391, P405, and P501
Doramectin	(1'R,2R,3S,4'S,6S,8'R,10'E,12'S,13'S,14'E,16'E,20'R,21'R,24'S)-2-cyclohexyl-21',24'-dihydroxy-12'-[(2R,4S,5S,6S)-5-[(2S,4S,5S,6S)-5-hydroxy-4-methoxy-6-methyloxan-2-yl]oxy-4-methoxy-6-methyloxan-2-yl]oxy-3,11',13',22'-tetramethylspiro[2,3-dihydropyran-6,6'-3,7,19-trioxatetracyclo[15.6.1.1^{4,8}.0^{20,24}]pentacosa-10,14,16,22-tetraene]-2'-one CAS: 117704-25-3	 Danger	H300, H301, H302, H360, H361, H362, H370, H372, H400, and H410	P203, P260, P263, P264, P270, P273, P280, P301+P316, P301+P317, P308+P316, P318, P319, P321, P330, P391, P405, and P501
Emamectin-benzoate	(1'R,2R,3S,4'S,6S,8'R,10'E,12'S,13'S,14'E,16'E,20'R,21'R,24'S)-2-[(2S)-butan-2-yl]-21',24'-dihydroxy-12'-[(2R,4S,5S,6S)-4-methoxy-5-[(2S,4S,5S,6S)-4-methoxy-6-methyl-5-(methylamino)oxan-2-yl]oxy-6-methyloxan-2-yl]oxy-3,11',13',22'-tetramethylspiro[2,3-dihydropyran-6,6'-3,7,19-trioxatetracyclo[15.6.1.1^{4,8}.0^{20,24}]pentacosa-10,14,16,22-tetraene]-2'-one CAS: 119791-41-2	 Danger	H301+H311+H331, H318, H319, H370, H372, H400, and H410	P260, P261, P262, P264, P264+P265, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P305+P354+P338, P308+P316, P316, P317, P319, P321, P330, P337+P317, P361+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Epoxiconazole	1-[[(2S,3R)-3-(2-chlorophenyl)-2-(4-fluorophenyl)oxiran-2-yl]methyl]-1,2,4-triazole CAS: 133855-98-8	 Danger	H351, H360, H360df, H361, H400, H410, and H411	P203, P273, P280, P318, P391, P405, and P501
Eprinomectin	N-[(2S,3R,4S,6S)-6-[(2S,3S,4S,6R)-6-[(1'R,2R,3S,4'S,6S,8'R,10'E,12'S,13'S,14'E,16'E,20'R,21'R,24'S)-2-[(2S)-butan-2-yl]-21',24'-dihydroxy-3,11',13',22'-tetramethyl-2'-oxospiro[2,3-dihydropyran-6,6'-3,7,19-trioxatetracyclo[15.6.1.1^{4,8}.0^{20,24}]pentacosa-10,14,16,22-tetraene]-12'-yl]oxy-4-methoxy-2-methyloxan-3-yl]oxy-4-methoxy-2-methyloxan-3-yl]acetamide CAS: 133305-88-1	 Warning	H315 and H319	P264, P264+P265, P280, P302+P352, P305+P351+P338, P321, P332+P317, P337+P317, and P362+P364
Etaconazole	1-[[2-(2,4-dichlorophenyl)-4-ethyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole CAS: 60207-93-4		H411	P273, P391, and P501
Ethiofencarb	[2-(ethylsulfanylmethyl)phenyl] N-methylcarbamate CAS: 29973-13-5	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Ethiprole	5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinylpyrazole-3-carbonitrile CAS: 181587-01-9	 Warning	H332, H373, H400, and H410	P260, P261, P271, P273, P304+P340, P317, P319, P391, and P501
Ethirimol	5-butyl-2-(ethylamino)-4-methyl-1H-pyrimidin-6-one CAS: 23947-60-6	 Warning	H312	P280, P302+P352, P317, P321, P362+P364, and P501
Ethofumesate	(2-ethoxy-3,3-dimethyl-2H-1-benzofuran-5-yl) methanesulfonate CAS: 26225-79-6	 Warning	H400, H410, and H411	P273, P391, and P501
Famoxadone	3-anilino-5-methyl-5-(4-phenoxyphenyl)-1,3-oxazolidine-2,4-dione CAS: 131807-57-3	 Warning	H373, H400, H401, and H410	P260, P273, P319, P391, and P501
Fenamidone	(5S)-3-anilino-5-methyl-2-methylsulfanyl-5-phenylimidazol-4-one CAS: 161326-34-7	 Warning	H400 and H410	P273, P391, and P501
Fenarimol	(2-chlorophenyl)-(4-chlorophenyl)-pyrimidin-5-ylmethanol CAS: 60168-88-9	 Warning	H361, H361fd, H362, and H411	P203, P260, P263, P264, P270, P273, P280, P318, P391, P405, and P501
Fenazaquin	4-[2-(4-tert-butylphenyl)ethoxy]quinazoline CAS: 120928-09-8	 Danger	H301, H332, H400, and H410	P261, P264, P270, P271, P273, P301+P316, P304+P340, P317, P321, P330, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Fenbuconazole	4-(4-chlorophenyl)-2-phenyl-2-(1,2,4-triazol-1-ylmethyl)butanenitrile CAS: 114369-43-6	 Warning	H400 and H410	P273, P391, and P501
Fenhexamid	N-(2,3-dichloro-4-hydroxyphenyl)-1-methylcyclohexane-1-carboxamide CAS: 126833-17-8		H411	P273, P391, and P501
Fenobucarb	(2-butan-2-ylphenyl) N-methylcarbamate CAS: 3766-81-2	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501
Fenoxycarb	ethyl N-[2-(4-phenoxyphenoxy)ethyl]carbamate CAS: 72490-01-8	 Warning	H351, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Fenpropidin	1-[3-(4-tert-butylphenyl)-2-methylpropyl]piperidine CAS: 67306-00-7	 Danger	H302+H332, H312, H317, H318, H319, H335, H373, H400, and H410	P260, P261, P264, P264+P265, P270, P271, P272, P273, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P305+P354+P338, P317, P319, P321, P330, P333+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Fenpropimorph	(2R,6S)-4-[3-(4-tert-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine CAS: 67564-91-4	 Warning	H302, H315, H361, H361d, and H411	P203, P264, P270, P273, P280, P301+P317, P302+P352, P318, P321, P330, P332+P317, P362+P364, P391, P405, and P501
Fenpyroximate	tert-butyl 4-[[(1,3-dimethyl-5-phenoxypyrazol-4-yl)methylideneamino]oxymethyl]benzoate CAS: 111812-58-9	 Danger	H301, H317, H330, H373, H400, and H410	P260, P261, P264, P270, P271, P272, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P319, P320, P321, P330, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Fenuron	1,1-dimethyl-3-phenylurea CAS: 101-42-8	 Warning	H319, H335, H361, H400, H410, and H411	P203, P261, P264+P265, P271, P273, P280, P304+P340, P305+P351+P338, P318, P319, P337+P317, P391, P403+P233, P405, and P501
Fenvalerate	[cyano-(3-phenoxyphenyl)methyl] 2-(4-chlorophenyl)-3-methylbutanoate CAS: 51630-58-1	 Danger	H301, H315, H319, H335, H400, and H410	P261, P264, P264+P265, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P319, P321, P330, P332+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Fipronil	5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfinyl)pyrazole-3-carbonitrile CAS: 120068-37-3	 Danger	H301, H311, H330, H331, H372, H400, and H410	P260, P261, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P319, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Fipronil sulfone	5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(trifluoromethylsulfonyl)pyrazole-3-carbonitrile CAS: 120068-36-2	 Danger	H301 and H400	P264, P270, P273, P301+P316, P321, P330, P391, P405, and P501
Flazasulfuron	1-(4,6-dimethoxypyrimidin-2-yl)-3-[3-(trifluoromethyl)pyridin-2-yl]sulfonylurea CAS: 104040-78-0	 Warning	H400 and H410	P273, P391, and P501
Flonicamid	N-(cyanomethyl)-4-(trifluoromethyl)pyridine-3-carboxamide CAS: 158062-67-0	 Warning	H302	P264, P270, P301+P317, P330, and P501
Florasulam	N-(2,6-difluorophenyl)-8-fluoro-5-methoxy-[1,2,4]triazolo[1,5-c]pyrimidine-2-sulfonamide CAS: 145701-23-1	 Warning	H400 and H410	P273, P391, and P501
Fluazifop-p	(2R)-2-[4-[5-(trifluoromethyl)pyridin-2-yl]oxyphenoxy]propanoic acid CAS: 83066-88-0	 Warning	H315, H319, H335, and H412	P261, P264, P264+P265, P271, P273, P280, P302+P352, P304+P340, P305+P351+P338, P319, P321, P332+P317,

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
				P337+P317, P362+P364, P403+P233, P405, and P501
Fluazinam	3-chloro-N-[3-chloro-2,6-dinitro-4-(trifluoromethyl)phenyl]-5-(trifluoromethyl)pyridin-2-amine CAS: 79622-59-6	 Danger	H315, H317, H318, H332, H361, H361d, H373, H400, and H410	P203, P260, P261, P264, P264+P265, P271, P272, P273, P280, P302+P352, P304+P340, P305+P354+P338, P317, P318, P319, P321, P332+P317, P333+P317, P362+P364, P391, P405, and P501
Flubendiamide	1-N-[4-(1,1,1,2,3,3,3-heptafluoropropan-2-yl)-2-methylphenyl]-3-iodo-2-N-(2-methyl-1-methylsulfonylpropan-2-yl)benzene-1,2-dicarboxamide CAS: 272451-65-7	 Warning	H400 and H410	P273, P391, and P501
Fludioxonil	4-(2,2-difluoro-1,3-benzodioxol-4-yl)-1H-pyrrole-3-carbonitrile CAS: 131341-86-1	 Warning	H400 and H410	P273, P391, and P501
Flufenacet	N-(4-fluorophenyl)-N-propan-2-yl-2-[[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl]oxy]acetamide CAS: 142459-58-3	 Warning	H302, H317, H373, H400, and H410	P260, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P319, P321, P330, P333+P317, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Flufenoxuron	N-[[4-[2-chloro-4-(trifluoromethyl)phenoxy]-2-fluorophenyl]carbamoyl]-2,6-difluorobenzamide CAS: 101463-69-8	 Warning	H332, H362, H400, and H410	P203, P260, P261, P263, P264, P270, P271, P273, P304+P340, P317, P318, P391, and P501
Flumioxazine	2-(7-fluoro-3-oxo-4-prop-2-ynyl-1,4-benzoxazin-6-yl)-4,5,6,7-tetrahydroisoindole-1,3-dione CAS: 103361-09-7	 Danger	H360, H361d, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Fluometuron	1,1-dimethyl-3-[3-(trifluoromethyl)phenyl]urea CAS: 2164-17-2	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501
Fluopicolide	2,6-dichloro-N-[[3-chloro-5-(trifluoromethyl)pyridin-2-yl]methyl]benzamide CAS: 239110-15-7	 Warning	H361d, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Fluopyram	N-[2-[3-chloro-5-(trifluoromethyl)pyridin-2-yl]ethyl]-2-(trifluoromethyl)benzamide CAS: 658066-35-4	 Warning	H400, H410, and H411	P273, P391, and P501
Fluopyram-benzamide	2-(trifluoromethyl)benzamide CAS: 360-64-5	 Warning	H315, H319, and H335	P261, P264, P264+P265, P271, P280, P302+P352, P304+P340, P305+P351+P338, P319, P321, P332+P317, P337+P317, P362+P364, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Fluoxastrobin	(E)-1-[2-[6-(2-chlorophenoxy)-5-fluoropyrimidin-4-yl]oxyphenyl]-1-(5,6-dihydro-1,4,2-dioxazin-3-yl)-N-methoxymethanimine CAS: 361377-29-9	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501
Flupyradifurone	3-[(6-chloropyridin-3-yl)methyl-(2,2-difluoroethyl)amino]-2H-furan-5-one CAS: 951659-40-8	 Warning	H302, H373, H400, H410, and H412	P260, P264, P270, P273, P301+P317, P319, P330, P391, and P501
Fluquinconazole	3-(2,4-dichlorophenyl)-6-fluoro-2-(1,2,4-triazol-1-yl)quinazolin-4-one CAS: 136426-54-5	 Danger	H301, H311, H312, H315, H331, H372, H400, and H410	P260, P261, P262, P264, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P316, P317, P319, P321, P330, P332+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501
Fluroxypyr	2-(4-amino-3,5-dichloro-6-fluoropyridin-2-yl)oxyacetic acid CAS: 69377-81-7	-	H412	P273 and P501
Flusilazole	bis(4-fluorophenyl)-methyl-(1,2,4-triazol-1-ylmethyl)silane CAS: 85509-19-9	 Danger	H302, H351, H360, H360d, and H411	P203, P264, P270, P273, P280, P301+P317, P318, P330, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Flutolanil	N-(3-propan-2-yloxyphenyl)-2-(trifluoromethyl)benzamide CAS: 66332-96-5	 Warning	H400, H410, and H411	P273, P391, and P501
Flutriafol	1-(2-fluorophenyl)-1-(4-fluorophenyl)-2-(1,2,4-triazol-1-yl)ethanol CAS: 76674-21-0	 Warning	H302, H312, H332, H411, and H412	P261, P264, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P362+P364, P391, and P501
Fluxapyroxad	3-(difluoromethyl)-1-methyl-N-[2-(3,4,5-trifluorophenyl)phenyl]pyrazole-4-carboxamide CAS: 907204-31-3	 Warning	H351, H362, H400, and H410	P203, P260, P263, P264, P270, P273, P280, P318, P391, P405, and P501
Folpet	2-(trichloromethylsulfanyl)isoindole-1,3-dione CAS: 133-07-3	 Warning	H317, H319, H332, H351, and H400	P203, P261, P264+P265, P271, P272, P273, P280, P302+P352, P304+P340, P305+P351+P338, P317, P318, P321, P333+P317, P337+P317, P362+P364, P391, P405, and P501
Foramsulfuron	2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoyl]-4-formamido-N,N-dimethylbenzamide CAS: 173159-57-4	 Warning	H400, H410, and H412	P273, P391, and P501
Forchlorfenuron	1-(2-chloropyridin-4-yl)-3-phenylurea CAS: 68157-60-8	 Warning	H351 and H411	P203, P273, P280, P318, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Formetanate HCl	[3-(dimethylaminomethylideneamino)phenyl] N-methylcarbamate;hydrochloride CAS: 23422-53-9	 Danger	H300, H317, H330, H400, and H410	P260, P261, P264, P270, P271, P272, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Fuberidazole	2-(furan-2-yl)-1H-benzimidazole CAS: 3878-19-1	 Danger	H302, H311, H317, H330, H351, H373, H400, and H410	P203, P260, P261, P262, P264, P270, P271, P272, P273, P280, P284, P301+P317, P302+P352, P304+P340, P316, P318, P319, P320, P321, P330, P333+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501
Furalaxyl	methyl 2-[N-(furan-2-carbonyl)-2,6-dimethylanilino]propanoate CAS: 57646-30-7	 Warning	H302 and H412	P264, P270, P273, P301+P317, P330, and P501
Furathiocarb	(2,2-dimethyl-3H-1-benzofuran-7-yl) N-[butoxycarbonyl(methyl)amino]sulfanyl-N-methylcarbamate CAS: 65907-30-4	 Danger	H301, H315, H317, H319, H330, H334, H373, H400, and H410	P233, P260, P261, P264, P264+P265, P270, P271, P272, P273, P280, P284, P301+P316, P302+P352, P304+P340, P305+P351+P338, P316, P319, P320, P321, P330, P332+P317, P333+P317, P337+P317, P342+P316,

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
				P362+P364, P391, P403, P403+P233, P405, and P501
gamma-HCH	1,2,3,4,5,6-hexachlorocyclohexane CAS: 319-85-7	 Danger	H301, H312, H351, H400, and H410	P203, P264, P270, P273, P280, P301+P316, P302+P352, P317, P318, P321, P330, P362+P364, P391, P405, and P501
Halauxifen-methyl	methyl 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxyphenyl)pyridine-2-carboxylate CAS: 943831-98-9	 Warning	H400 and H410	P273, P391, and P501
Halofenozide	N'-benzoyl-N'-tert-butyl-4-chlorobenzohydrazide CAS: 112226-61-6	 Warning	H317 and H411	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501
Haloxyfop-p	(2R)-2-[4-[3-chloro-5-(trifluoromethyl)pyridin-2-yl]oxyphenoxy]propanoic acid CAS: 95977-29-0	 Warning	H302 and H412	P264, P270, P273, P301+P317, P330, and P501
Hexachlorobenzene	1,2,3,4,5,6-hexachlorobenzene CAS: 118-74-1	 Danger	H350, H372, H400, and H410	P203, P260, P264, P270, P273, P280, P318, P319, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Hexaconazole	2-(2,4-dichlorophenyl)-1-(1,2,4-triazol-1-yl)hexan-2-ol CAS: 79983-71-4	 Warning	H302, H317, and H411	P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P321, P330, P333+P317, P362+P364, P391, and P501
Hexaflumuron	N-[[3,5-dichloro-4-(1,1,2,2-tetrafluoroethoxy)phenyl]carbamoyl]-2,6-difluorobenzamide CAS: 86479-06-3	 Warning	H332, H400, and H410	P261, P271, P273, P304+P340, P317, P391, and P501
Hexythiazox	(4S,5S)-5-(4-chlorophenyl)-N-cyclohexyl-4-methyl-2-oxo-1,3-thiazolidine-3-carboxamide CAS: 78587-05-0	 Warning	H400 and H410	P273, P391, and P501
Hydramethylnon	N-[[(1E,4E)-1,5-bis[4-(trifluoromethyl)phenyl]penta-1,4-dien-3-ylidene]amino]-5,5-dimethyl-4,6-dihydro-1H-pyrimidin-2-amine CAS: 67485-29-4	 Danger	H302, H319, H332, H360, H372, H400, and H410	P203, P260, P261, P264, P264+P265, P270, P271, P273, P280, P301+P317, P304+P340, P305+P351+P338, P317, P318, P319, P330, P337+P317, P391, P405, and P501
Imazalil	1-[2-(2,4-dichlorophenyl)-2-prop-2-enoxyethyl]imidazole CAS: 35554-44-0	 Danger	H301, H302, H318, H332, H351, H373, H400, and H410	P203, P260, P261, P264, P264+P265, P270, P271, P273, P280, P301+P316, P301+P317, P304+P340, P305+P354+P338, P317, P318, P319, P321, P330, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Imazapic	5-methyl-2-(4-methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)pyridine-3-carboxylic acid CAS: 104098-48-8	 Warning	H400 and H410	P273, P391, and P501
Imazapyr	2-(4-methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)pyridine-3-carboxylic acid CAS: 81334-34-1	 Warning	H319, H400, and H412	P264+P265, P273, P280, P305+P351+P338, P337+P317, P391, and P501
Imazaquin	2-(4-methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)quinoline-3-carboxylic acid CAS: 81335-37-7	 Warning	H312, H400, and H410	P273, P280, P302+P352, P317, P321, P362+P364, P391, and P501
Imazethapyr	5-ethyl-2-(4-methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)pyridine-3-carboxylic acid CAS: 81335-77-5	 Warning	H312, H400, and H410	P273, P280, P302+P352, P317, P321, P362+P364, P391, and P501
Imidacloprid	(NE)-N-[1-[(6-chloropyridin-3-yl)methyl]imidazolidin-2-ylidene]nitramide CAS: 138261-41-3	 Danger	H301, H302, H400, and H410	P264, P270, P273, P301+P316, P301+P317, P321, P330, P391, P405, and P501
Imidacloprid 5-hydroxy	(NE)-N-[1-[(6-chloropyridin-3-yl)methyl]-5-hydroxyimidazolidin-2-ylidene]nitramide CAS: 380912-09-4	 Danger	H301 and H410	P264, P273, P301+P310, P391, and P501
Imidacloprid-desnitro	1-[(6-chloropyridin-3-yl)methyl]-4,5-dihydroimidazol-2-amine CAS: 115970-17-7	 Warning	H302 and H373	P260, P264, P270, P301+P312, P314, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Indoxacarb-(S)	methyl (4aS)-7-chloro-2-[methoxycarbonyl-[4-(trifluoromethoxy)phenyl]carbamoyl]-3,5-dihydroindeno[1,2-e][1,3,4]oxadiazine-4a-carboxylate CAS: 173584-44-6	 Danger	H301, H317, H332, H372, H400, and H410	P260, P261, P264, P270, P271, P272, P273, P280, P301+P316, P302+P352, P304+P340, P317, P319, P321, P330, P333+P317, P362+P364, P391, P405, and P501
Ipconazole	2-[(4-chlorophenyl)methyl]-5-propan-2-yl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol CAS: 125225-28-7	 Danger	H302, H332, H360d, H361, H373, H400, and H410	P203, P260, P261, P264, P270, P271, P273, P280, P301+P317, P304+P340, P317, P318, P319, P330, P391, P405, and P501
Iprovalicarb	propan-2-yl N-[(2S)-3-methyl-1-[1-(4-methylphenyl)ethylamino]-1-oxobutan-2-yl]carbamate CAS: 140923-17-7	 Warning	H351	P201, P202, P280, P308+P313, P405, and P501
Isoprocarb	(2-propan-2-ylphenyl) N-methylcarbamate CAS: 2631-40-5	 Warning	H302, H400, and H410	P264, P270, P273, P301+P317, P330, P391, and P501
Isoproturon	1,1-dimethyl-3-(4-propan-2-ylphenyl)urea CAS: 34123-59-6	 Warning	H332, H351, H373, H400, and H410	P203, P260, P261, P271, P273, P280, P304+P340, P317, P318, P319, P391, P405, and P501
Isoxaben	2,6-dimethoxy-N-[3-(3-methylpentan-3-yl)-1,2-oxazol-5-yl]benzamide CAS: 82558-50-7	-	H413	P273 and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Isoxaflutole	(5-cyclopropyl-1,2-oxazol-4-yl)-[2-methylsulfonyl-4-(trifluoromethyl)phenyl]methanone CAS: 141112-29-0	 Warning	H361, H361d, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Ivermectin	(1R,4S,5'S,6R,6'R,8R,10E,12S,13S,14E,16E,20R,21R,24S)-6'-[(2S)-butan-2-yl]-21,24-dihydroxy-12-[(2R,4S,5S,6S)-5-[(2S,4S,5S,6S)-5-hydroxy-4-methoxy-6-methyloxan-2-yl]oxy-4-methoxy-6-methyloxan-2-yl]oxy-5',11,13,22-tetramethylspiro[3,7,19-trioxatetracyclo[15.6.1.1^{4,8}.0^{20,24}]pentacosa-10,14,16,22-tetraene-6,2'-oxane]-2-one CAS: 71827-03-7	 Danger	H300, H312, H361, H373, and H400	P203, P260, P264, P270, P273, P280, P301+P316, P302+P352, P317, P318, P319, P321, P330, P362+P364, P391, P405, and P501
Kresoxim-methyl	methyl (2E)-2-methoxyimino-2-[2-[(2-methylphenoxy)methyl]phenyl]acetate CAS: 143390-89-0	 Warning	H351, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
lambda-Cyhalothrin	[(R)-cyano-(3-phenoxyphenyl)methyl](1S,3S)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate CAS: 91465-08-6	 Danger	H301+H311, H312, H319, H330, H370, H400, and H410	P260, P262, P264, P264+P265, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P305+P351+P338, P308+P316, P316, P317, P320, P321, P330, P337+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Lenacil	3-cyclohexyl-1,5,6,7-tetrahydrocyclopenta[d]pyrimidine-2,4-dione CAS: 2164-08-1	 Warning	H351, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Linuron	3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea CAS: 330-55-2	 Danger	H302, H351, H360, H360df, H373, H400, and H410	P203, P260, P264, P270, P273, P280, P301+P317, P318, P319, P330, P391, P405, and P501
Lufenuron	N-[[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy)phenyl]carbamoyl]-2,6-difluorobenzamide CAS: 103055-07-8	 Danger	H317, H360, H372, H400, and H410	P203, P260, P261, P264, P270, P272, P273, P280, P302+P352, P318, P319, P321, P333+P317, P362+P364, P391, P405, and P501
Mandipropamid	2-(4-chlorophenyl)-N-[2-(3-methoxy-4-prop-2-ynoxyphenyl)ethyl]-2-prop-2-ynoxyacetamide CAS: 374726-62-2	 Warning	H400 and H410	P273, P391, and P501
MCPA	2-(4-chloro-2-methylphenoxy)acetic acid CAS: 94-74-6	 Warning	H302+H312+H332, H400, and H410	P261, P264, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Mecoprop-p	(2R)-2-(4-chloro-2-methylphenoxy)propanoic acid CAS: 16484-77-8	 Danger	H302, H318, H400, H410, and H411	P264, P264+P265, P270, P273, P280, P301+P317, P305+P354+P338, P317, P330, P391, and P501
Mefenacet	2-(1,3-benzothiazol-2-yloxy)-N-methyl-N-phenylacetamide CAS: 73250-68-7		H411	P273, P391, and P501
Mepanipyrim	4-methyl-N-phenyl-6-prop-1-ynylpyrimidin-2-amine CAS: 110235-47-7	 Warning	H351, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Mepronil	2-methyl-N-(3-propan-2-yloxyphenyl)benzamide CAS: 55814-41-0		H401 and H411	P273, P391, and P501
Meptyldinocap phenol	2,4-dinitro-6-octan-2-ylphenol CAS: 3687-22-7	 Danger	H301, H315, H317, H318, and H410	P261, P264, P264+P265, P270, P272, P273, P280, P301+P316, P302+P352, P305+P354+P338, P317, P321, P330, P332+P317, P333+P317, P362+P364, P391, P405, and P501
Mesotrione	2-(4-methylsulfonyl-2-nitrobenzoyl)cyclohexane-1,3-dione CAS: 104206-82-8	 Warning	H361, H361d, H373, H400, and H410	P203, P260, P273, P280, P318, P319, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Metaflumizone	1-[(Z)-[2-(4-cyanophenyl)-1-[3-(trifluoromethyl)phenyl]ethylidene]amino]-3-[4-(trifluoromethoxy)phenyl]urea CAS: 139970-56-2	 Warning	H361fd, H362, H373, H400, and H410	P203, P260, P263, P264, P270, P273, P280, P318, P319, P391, P405, and P501
Metalaxyl	methyl 2-(N-(2-methoxyacetyl)-2,6-dimethylanilino)propanoate CAS: 57837-19-1	 Warning	H302, H317, and H412	P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P321, P330, P333+P317, P362+P364, and P501
Metalaxyl Metabolite CGA 62826	2-(N-(2-methoxyacetyl)-2,6-dimethylanilino)propanoic acid CAS: 87764-37-2	 Warning	H302, H317, and H412	P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P321, P330, P333+P317, P362+P364, and P501
Metamitron	4-amino-3-methyl-6-phenyl-1,2,4-triazin-5-one CAS: 41394-05-2	 Warning	H302+H332, and H400	P261, P264, P270, P271, P273, P301+P317, P304+P340, P317, P330, P391, and P501
Metamitron-desamino	3-methyl-6-phenyl-4H-1,2,4-triazin-5-one CAS: 36993-94-9	 Warning	H302+H332, and H400	P261, P264, P273, P312, P391, and P501
Metazachlor	2-chloro-N-(2,6-dimethylphenyl)-N-(pyrazol-1-ylmethyl)acetamide CAS: 67129-08-2	 Warning	H302, H317, H351, H400, and H410	P203, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P318, P321, P330, P333+P317, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Metconazole	5-[(4-chlorophenyl)methyl]-2,2-dimethyl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol CAS: 125116-23-6	 Danger	H302, H314, H318, H361, H361d, and H411	P203, P260, P264, P264+P265, P270, P273, P280, P301+P317, P301+P330+P331, P302+P361+P354, P304+P340, P305+P354+P338, P316, P317, P318, P321, P330, P363, P391, P405, and P501
Methabenzthiazuron	1-(1,3-benzothiazol-2-yl)-1,3-dimethylurea CAS: 18691-97-9	 Danger	H330, H400, and H410	P260, P271, P273, P284, P304+P340, P316, P320, P391, P403+P233, P405, and P501
Methamidophos	[amino(methylsulfanyl)phosphoryl]oxymethane CAS: 10265-92-6	 Danger	H300, H310, H311, H330, and H400	P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Methiocarb	(3,5-dimethyl-4-methylsulfanylphenyl) N-methylcarbamate CAS: 2032-65-7	 Danger	H300+H330, H301, H400, and H410	P260, P264, P270, P271, P273, P284, P301+P316, P304+P340, P316, P320, P321, P330, P391, P403+P233, P405, and P501
Methiocarb sulfon	(3,5-dimethyl-4-methylsulfonylphenyl) N-methylcarbamate CAS: 2179-25-1	 Warning	H302 and H410	P264, P270, P273, P301+P312, P330, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Methiocarb sulfoxide	(3,5-dimethyl-4-methylsulfinylphenyl) N-methylcarbamate CAS: 2635-10-1	 Danger	H300 and H400	P264, P270, P273, P301+P316, P321, P330, P391, P405, and P501
Methomyl	methyl N-(methylcarbamoyloxy)ethanimidothioate CAS: 16752-77-5	 Danger	H300+H330, H336, H400, and H410	P260, P261, P264, P270, P271, P273, P284, P301+P316, P304+P340, P316, P319, P320, P321, P330, P391, P403+P233, P405, and P501
Methoprotryne	4-N-(3-methoxypropyl)-6-methylsulfanyl-2-N-propan-2-yl-1,3,5-triazine-2,4-diamine CAS: 841-06-5	 Danger	H310	P262, P264, P270, P280, P302+P352, P316, P321, P361+P364, P405, and P501
Methoxyfenozide	N'-tert-butyl-N'-(3,5-dimethylbenzoyl)-3-methoxy-2-methylbenzohydrazide CAS: 161050-58-4	 Warning	H400, H410, and H411	P273, P391, and P501
Metobromuron	3-(4-bromophenyl)-1-methoxy-1-methylurea CAS: 3060-89-7	 Warning	H302, H332, H351, H373, H400, and H410	P203, P260, P261, P264, P270, P271, P273, P280, P301+P317, P304+P340, P317, P318, P319, P330, P391, P405, and P501
Metolachlor	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide CAS: 51218-45-2	 Danger	H317, H330, H400, and H410	P260, P261, P271, P272, P273, P280, P284, P302+P352, P304+P340, P316, P320, P321, P333+P317, P362+P364,

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
				P391, P403+P233, P405, and P501
Metolachlor oxanilic acid	2-[2-ethyl-N-(1-methoxypropan-2-yl)-6-methylanilino]-2-oxoacetic acid CAS: 152019-73-3	 Warning	H317, H319, and H412	P261, P264+P265, P272, P273, P280, P302+P352, P305+P351+P338, P321, P333+P317, P337+P317, P362+P364, and P501
Metrafenone	(3-bromo-6-methoxy-2-methylphenyl)-(2,3,4-trimethoxy-6-methylphenyl)methanone CAS: 220899-03-6	 Warning	H400 and H410	P273, P391, and P501
Metribuzin	4-amino-6-tert-butyl-3-methylsulfanyl-1,2,4-triazin-5-one CAS: 21087-64-9	 Danger	H302, H331, H400, and H410	P261, P264, P270, P271, P273, P301+P317, P304+P340, P316, P321, P330, P391, P403+P233, P405, and P501
Metsulfuron-methyl	methyl 2-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoylsulfamoyl]benzoate CAS: 74223-64-6	 Warning	H400 and H410	P273, P391, and P501
Mevinphos	methyl (E)-3-dimethoxyphosphoryloxybut-2-enoate CAS: 7786-34-7	 Danger	H300+H310, H330, H331, H400, and H410	P260, P261, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Mexacarbate	[4-(dimethylamino)-3,5-dimethylphenyl] N-methylcarbamate CAS: 315-18-4	 Danger	H300, H312, H400, and H410	P264, P270, P273, P280, P301+P316, P302+P352, P317, P321, P330, P362+P364, P391, P405, and P501
Monceren (Pencycuron)	1-[(4-chlorophenyl)methyl]-1-cyclopentyl-3-phenylurea CAS: 66063-05-6	 Warning	H400 and H410	P273, P391, and P501
Monocrotophos	dimethyl [(E)-4-(methylamino)-4-oxobut-2-en-2-yl] phosphate CAS: 6923-22-4	 Danger	H300+H330, H311, H341, H400, and H410	P203, P260, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P318, P320, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Monolinuron	3-(4-chlorophenyl)-1-methoxy-1-methylurea CAS: 1746-81-2	 Warning	H302, H373, H400, and H410	P260, P264, P270, P273, P301+P317, P319, P330, P391, and P501
Myclobutanil	2-(4-chlorophenyl)-2-(1,2,4-triazol-1-ylmethyl)hexanenitrile CAS: 88671-89-0	 Warning	H302, H319, H361, and H411	P203, P264, P264+P265, P270, P273, P280, P301+P317, P305+P351+P338, P318, P330, P337+P317, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Napropamide	N,N-diethyl-2-naphthalen-1-yloxypropanamide CAS: 15299-99-7	 Warning	H319 and H411	P264+P265, P273, P280, P305+P351+P338, P337+P317, P391, and P501
Neburon	1-butyl-3-(3,4-dichlorophenyl)-1-methylurea CAS: 555-37-3	 Warning	H302	P264, P270, P301+P317, P330, and P501
Nicosulfuron	2-[(4,6-dimethoxypyrimidin-2-yl)carbamoylsulfamoyl]-N,N-dimethylpyridine-3-carboxamide CAS: 111991-09-4	 Warning	H315, H319, H400, and H410	P264, P264+P265, P273, P280, P302+P352, P305+P351+P338, P321, P332+P317, P337+P317, P362+P364, P391, and P501
Nitenpyram	(E)-1-N'-[(6-chloropyridin-3-yl)methyl]-1-N'-ethyl-1-N-methyl-2-nitroethene-1,1-diamine CAS: 150824-47-8	 Warning	H302	P264, P270, P301+P317, P330, and P501
Novaluron	N-[[3-chloro-4-[1,1,2-trifluoro-2-(trifluoromethoxy)ethoxy]phenyl]carbamoyl]-2,6-difluorobenzamide CAS: 116714-46-6	 Warning	H400 and H410	P273, P391, and P501
Nuarimol	(2-chlorophenyl)-(4-fluorophenyl)-pyrimidin-5-ylmethanol CAS: 63284-71-9	 Warning	H302 and H319	P264, P264+P265, P270, P280, P301+P317, P305+P351+P338, P330, P337+P317, and P501
Omethoate	2-dimethoxyphosphorylsulfanyl-N-methylacetamide CAS: 1113-02-6	 Danger	H300, H311, and H400	P262, P264, P270, P273, P280, P301+P316, P302+P352, P316, P321, P330, P361+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Oryzalin	4-(dipropylamino)-3,5-dinitrobenzenesulfonamide CAS: 19044-88-3	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501
Oxadixyl	N-(2,6-dimethylphenyl)-2-methoxy-N-(2-oxo-1,3-oxazolidin-3-yl)acetamide CAS: 77732-09-3	 Warning	H302 and H412	P264, P270, P273, P301+P317, P330, and P501
Oxamyl	methyl (1Z)-2-(dimethylamino)-N-(methylcarbamoyloxy)-2-oxoethanimidothioate CAS: 23135-22-0	 Danger	H300+H330, H311, H312, H336, H400, H410, and H411	P260, P261, P262, P264, P270, P271, P273, P280, P284, P301+P316, P302+P352, P304+P340, P316, P317, P319, P320, P321, P330, P361+P364, P362+P364, P391, P403+P233, P405, and P501
Oxyfluorfen	2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene CAS: 42874-03-3	 Warning	H400 and H410	P273, P391, and P501
Paclobutrazol	(2R,3R)-1-(4-chlorophenyl)-4,4-dimethyl-2-(1,2,4-triazol-1-yl)pentan-3-ol CAS: 76738-62-0	 Danger	H228, H302+H332, H312, H315, H317, H319, H335, H361, H361d, H400, and H410	P203, P210, P240, P241, P261, P264, P264+P265, P270, P271, P272, P273, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P317, P318, P319, P321, P330, P332+P317, P333+P317, P337+P317, P362+P364,

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
				P370+P378, P391, P403+P233, P405, and P501
Penconazole	1-[2-(2,4-dichlorophenyl)pentyl]-1,2,4-triazole CAS: 66246-88-6	 Warning	H302, H361, H361d, H400, and H410	P203, P264, P270, P273, P280, P301+P317, P318, P330, P391, P405, and P501
Pendimethalin	3,4-dimethyl-2,6-dinitro-N-pentan-3-ylaniline CAS: 40487-42-1	 Warning	H302, H317, H361d, H400, and H410	P203, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P318, P321, P330, P333+P317, P362+P364, P391, P405, and P501
Penoxsulam	2-(2,2-difluoroethoxy)-N-(5,8-dimethoxy-[1,2,4]triazolo[1,5-c]pyrimidin-2-yl)-6-(trifluoromethyl)benzenesulfonamide CAS: 219714-96-2	 Warning	H400 and H410	P273, P391, and P501
Phenmedipham	[3-(methoxycarbonylamino)phenyl] N-(3-methylphenyl)carbamate CAS: 13684-63-4	 Warning	H400 and H410	P273, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Phosmet	2-(dimethoxyphosphinothioylsulfanylmethyl)isoindole-1,3-dione CAS: 732-11-6	 Danger	H301, H302+H312, H330, H332, H361f, H370, H400, and H410	P203, P260, P261, P264, P270, P271, P273, P280, P284, P301+P316, P301+P317, P302+P352, P304+P340, P308+P316, P316, P317, P318, P320, P321, P330, P362+P364, P391, P403+P233, P405, and P501
Phosmet oxon	2-(dimethoxyphosphorylsulfanylmethyl)isoindole-1,3-dione CAS: 3735-33-9	 Danger	H300, H312, H330, H361, H370, and H410	P260, P273, P280, P304+P340, P310, P391, and P403+P233
Phoxim	(Z)-N-diethoxyphosphinothioyloxybenzene carboximidoyl cyanide CAS: 14816-18-3	 Danger	H301, H302, H311, H317, H330, H361, H400, and H410	P203, P260, P261, P262, P264, P270, P271, P272, P273, P280, P284, P301+P316, P301+P317, P302+P352, P304+P340, P316, P318, P320, P321, P330, P333+P317, P361+P364, P362+P364, P391, P403+P233, P405, and P501
Picoxystrobin	methyl (E)-3-methoxy-2-[2-[[6-(trifluoromethyl)pyridin-2-yl]oxymethyl]phenyl]prop-2-enoate CAS: 117428-22-5	 Warning	H319, H332, H400, and H410	P261, P264+P265, P271, P273, P280, P304+P340, P305+P351+P338, P317, P337+P317, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Piperonyl-butoxide	5-[2-(2-butoxyethoxy)ethoxymethyl]-6-propyl-1,3-benzodioxole CAS: 51-03-6	 Warning	H319, H335, H400, and H410	P261, P264+P265, P271, P273, P280, P304+P340, P305+P351+P338, P319, P337+P317, P391, P403+P233, P405, and P501
Pirimicarb	[2-(dimethylamino)-5,6-dimethylpyrimidin-4-yl] N,N-dimethylcarbamate CAS: 23103-98-2	 Danger	H301+H331, H317, H351, H400, and H410	P203, P261, P264, P270, P271, P272, P273, P280, P301+P316, P302+P352, P304+P340, P316, P318, P321, P330, P333+P317, P362+P364, P391, P403+P233, P405, and P501
Pirimicarb-desmethyl	[5,6-dimethyl-2-(methylamino)pyrimidin-4-yl] N,N-dimethylcarbamate CAS: 30614-22-3	 Danger	H300, H315, H319, H335, and H400	P261, P264, P264+P265, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P319, P321, P330, P332+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Pirimiphos-methyl	4-dimethoxyphosphinothioyloxy-N,N-diethyl-6-methylpyrimidin-2-amine CAS: 29232-93-7	 Danger	H302, H312, H315, H319, H370, H372, H400, and H410	P260, P264, P264+P265, P270, P273, P280, P301+P317, P302+P352, P305+P351+P338, P308+P316, P317, P319, P321, P330, P332+P317, P337+P317, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Pirimiphos-methyl-N-desethyl	4-dimethoxyphosphinothioyloxy-N-ethyl-6-methylpyrimidin-2-amine CAS: 67018-59-1	 Danger	H302, H315, H318, and H335	P261, P264, P264+P265, P270, P271, P280, P301+P317, P302+P352, P304+P340, P305+P354+P338, P317, P319, P321, P330, P332+P317, P362+P364, P403+P233, P405, and P501
Prochloraz	N-propyl-N-[2-(2,4,6-trichlorophenoxy)ethyl]imidazole-1-carboxamide CAS: 67747-09-5	 Warning	H302, H332, H400, and H410	P261, P264, P270, P271, P273, P301+P317, P304+P340, P317, P330, P391, and P501
Prochloraz BTS 44595	1-propyl-1-[2-(2,4,6-trichlorophenoxy)ethyl]urea CAS: 139520-94-8	 Warning	H302	P301+P312+P330
Prochloraz BTS 44596	3-(hydroxymethylidene)-1-propyl-1-[2-(2,4,6-trichlorophenoxy)ethyl]urea CAS: 139542-32-8	 Warning	H302, H315, and H319	P264, P280, P301+P312, P302+P352, P305+P351+P338, and P332+P313
Promecarb	(3-methyl-5-propan-2-ylphenyl) N-methylcarbamate CAS: 2631-37-0	 Danger	H301, H400, and H410	P264, P270, P273, P301+P316, P321, P330, P391, P405, and P501
Prometryn	6-methylsulfanyl-2-N,4-N-di(propan-2-yl)-1,3,5-triazine-2,4-diamine CAS: 7287-19-6	 Warning	H332, H400, H410, and H411	P261, P271, P273, P304+P340, P317, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Propamocarb	propyl N-[3-(dimethylamino)propyl]carbamate CAS: 24579-73-5	 Warning	H302	P264, P270, P301+P317, P330, and P501
Propaquizafop	2-(propan-2-ylideneamino)oxyethyl (2R)-2-[4-(6-chloroquinoxalin-2-yl)oxyphenoxy]propanoate CAS: 111479-05-1	 Warning	H317, H332, H400, and H410	P261, P271, P272, P273, P280, P302+P352, P304+P340, P317, P321, P333+P317, P362+P364, P391, and P501
Propargite	[2-(4-tert-butylphenoxy)cyclohexyl] prop-2-ynyl sulfite CAS: 2312-35-8	 Danger	H315, H318, H331, H351, H400, and H410	P203, P261, P264, P264+P265, P271, P273, P280, P302+P352, P304+P340, P305+P354+P338, P316, P317, P318, P321, P332+P317, P362+P364, P391, P403+P233, P405, and P501
Propham	propan-2-yl N-phenylcarbamate CAS: 122-42-9	 Warning	H302	P264, P270, P301+P317, P330, and P501
Propiconazole	1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1,2,4-triazole CAS: 60207-90-1	 Danger	H302, H317, H360, H360d, H400, and H410	P203, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P318, P321, P330, P333+P317, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Propoxur	(2-propan-2-yloxyphenyl) N-methylcarbamate CAS: 114-26-1	 Danger	H300, H301, H311, H331, H400, and H410	P261, P262, P264, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P316, P321, P330, P361+P364, P391, P403+P233, P405, and P501
Propyzamide	3,5-dichloro-N-(2-methylbut-3-yn-2-yl)benzamide CAS: 23950-58-5	 Warning	H351, H400, and H410	P203, P273, P280, P318, P391, P405, and P501
Prosulfocarb	S-benzyl N,N-dipropylcarbamothioate CAS: 52888-80-9	 Warning	H302, H317, H400, H410, and H411	P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P321, P330, P333+P317, P362+P364, P391, and P501
Prothioconazole	2-[2-(1-chlorocyclopropyl)-3-(2-chlorophenyl)-2-hydroxypropyl]-1H-1,2,4-triazole-3-thione CAS: 178928-70-6	 Warning	H400 and H410	P273, P391, and P501
Prothioconazole-desthio	2-(1-chlorocyclopropyl)-1-(2-chlorophenyl)-3-(1,2,4-triazol-1-yl)propan-2-ol CAS: 120983-64-4	 Warning	H302, H315, H319, and H335	P261, P264, P264+P265, P270, P271, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P319, P321, P330, P332+P317, P337+P317, P362+P364, P403+P233, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Pymetrozine	6-methyl-4-[(E)-pyridin-3-ylmethylideneamino]-2,5-dihydro-1,2,4-triazin-3-one CAS: 123312-89-0	 Warning	H332, H351, H361fd, H410, and H412	P203, P261, P271, P273, P280, P304+P340, P317, P318, P391, P405, and P501
Pyracarbolid	6-methyl-N-phenyl-3,4-dihydro-2H-pyran-5-carboxamide CAS: 24691-76-7	-	H412	P273 and P501
Pyraclostrobin	methyl N-[2-[[1-(4-chlorophenyl)pyrazol-3-yl]oxymethyl]phenyl]-N-methoxycarbamate CAS: 175013-18-0	 Danger	H315, H331, H335, H400, and H410	P261, P264, P271, P273, P280, P302+P352, P304+P340, P316, P319, P321, P332+P317, P362+P364, P391, P403+P233, P405, and P501
Pyraflufen-ethyl	ethyl 2-[2-chloro-5-[4-chloro-5-(difluoromethoxy)-1-methylpyrazol-3-yl]-4-fluorophenoxy]acetate CAS: 129630-19-9	 Warning	H400 and H410	P273, P391, and P501
Pyrethrin I	[(1S)-2-methyl-4-oxo-3-[(2Z)-penta-2,4-dienyl]cyclopent-2-en-1-yl] (1R,3R)-2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane-1-carboxylate CAS: 121-21-1	 Warning	H302, H312, H332, H400, and H410	P261, P264, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P362+P364, P391, and P501
Pyrethrin II	[(1S)-2-methyl-4-oxo-3-[(2Z)-penta-2,4-dienyl]cyclopent-2-en-1-yl] (1R,3R)-3-[(E)-3-methoxy-2-methyl-3-oxoprop-1-enyl]-2,2-	 Warning	H302, H312, H332, and H410	P261, P264, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
	dimethylcyclopropane-1-carboxylate CAS: 121-29-9			
Pyridaben	2-tert-butyl-5-[(4-tert-butylphenyl)methylsulfanyl]-4-chloropyridazin-3-one CAS: 96489-71-3	 Danger	H301+H331, H400, and H410	P261, P264, P270, P271, P273, P301+P316, P304+P340, P316, P321, P330, P391, P403+P233, P405, and P501
Pyrimethanil	4,6-dimethyl-N-phenylpyrimidin-2-amine CAS: 53112-28-0		H411	P273, P391, and P501
Pyrimethanil M605F002	2-(4-hydroxyanilino)-4,6-dimethylpyrimidine CAS: 81261-84-9	 Warning	H315, H317, and H319	P280 and P305+P351+P338
Pyriofenone	(5-chloro-2-methoxy-4-methylpyridin-3-yl)-(2,3,4-trimethoxy-6-methylphenyl)methanone CAS: 688046-61-9	 Warning	H351 and H410	P203, P273, P280, P318, P391, P405, and P501
Pyriproxyfen	2-[1-(4-phenoxyphenoxy)propan-2-yloxy]pyridine CAS: 95737-68-1	 Warning	H400 and H410	P273, P391, and P501
Pyroxsulam	N-(5,7-dimethoxy-[1,2,4]triazolo[1,5-a]pyrimidin-2-yl)-2-methoxy-4-(trifluoromethyl)pyridine-3-sulfonamide CAS: 422556-08-9	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Quinmerac	7-chloro-3-methylquinoline-8-carboxylic acid CAS: 90717-03-6	-	H413	P273 and P501
Quinoxyfen	5,7-dichloro-4-(4-fluorophenoxy)quinoline CAS: 124495-18-7	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501
Quizalofop-p	(2R)-2-[4-(6-chloroquinoxalin-2-yl)oxyphenoxy]propanoic acid CAS: 94051-08-8	 Danger	H301	P264, P270, P301+P316, P321, P330, P405, and P501
Quizalofop-p-ethyl	ethyl (2R)-2-[4-(6-chloroquinoxalin-2-yl)oxyphenoxy]propanoate CAS: 100646-51-3	 Warning	H302, H400, H410, and H413	P264, P270, P273, P280, P301+P317, P302+P352, P317, P321, P330, P362+P364, P391, and P501
Rotenone	(1S,6R,13S)-16,17-dimethoxy-6-prop-1-en-2-yl-2,7,20-trioxapentacyclo[11.8.0.0^{3,11}.0^{4,8}.0^{14,19}]henicosa-3(11),4(8),9,14,16,18-hexaen-12-one CAS: 83-79-4	 Danger	H301, H315, H319, H335, H400, and H410	P261, P264, P264+P265, P270, P271, P273, P280, P301+P316, P302+P352, P304+P340, P305+P351+P338, P319, P321, P330, P332+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Sedaxane	N-[2-(2-cyclopropylcyclopropyl)phenyl]-3-(difluoromethyl)-1-methylpyrazole-4-carboxamide CAS: 874967-67-6	 Warning	H351, H400, H410, and H411	P203, P273, P280, P318, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Siduron	1-(2-methylcyclohexyl)-3-phenylurea CAS: 1982-49-6	-	-	-
Simetryn	2-N,4-N-diethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine CAS: 1014-70-6	 Warning	H302, H332, H400, and H410	P261, P264, P270, P271, P273, P301+P317, P304+P340, P317, P330, P391, and P501
Spinetoram	(2R,5R,9R,10S,14R,15S,19S)-15-[(2R,5S,6R)-5-(dimethylamino)-6-methyloxan-2-yl]oxy-7-[(2R,3R,4R,5S,6S)-4-ethoxy-3,5-dimethoxy-6-methyloxan-2-yl]oxy-19-ethyl-14-methyl-20-oxatetracyclo[10.10.0.0^{2,10}.0^{5,9}]docos-11-ene-13,21-dione CAS: 935545-74-7	 Warning	H317, H361, H361f, H400, and H410	P203, P261, P272, P273, P280, P302+P352, P318, P321, P333+P317, P362+P364, P391, P405, and P501
Spinosyn A	(1S,2R,5S,7R,9R,10S,14R,15S,19S)-15-[(2R,5S,6R)-5-(dimethylamino)-6-methyloxan-2-yl]oxy-19-ethyl-14-methyl-7-[(2R,3R,4R,5S,6S)-3,4,5-trimethoxy-6-methyloxan-2-yl]oxy-20-oxatetracyclo[10.10.0.0^{2,10}.0^{5,9}]docosa-3,11-diene-13,21-dione CAS: 131929-60-7	 Warning	H400 and H410	P273, P391, and P501
Spinosyn D	(1S,2S,5R,7S,9S,10S,14R,15S,19S)-15-[(2R,5S,6R)-5-(dimethylamino)-6-methyloxan-2-yl]oxy-19-ethyl-4,14-dimethyl-7-[(2R,3R,4R,5S,6S)-3,4,5-trimethoxy-6-methyloxan-2-yl]oxy-20-oxatetracyclo[10.10.0.0^{2,10}.0^{5,9}]docos	 Warning	H400 and H410	P273, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
	a-3,11-diene-13,21-dione CAS: 131929-63-0			
Spirodiclofen	[3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl] 2,2-dimethylbutanoate CAS: 148477-71-8	 Danger	H317, H350, H361f, H373, and H410	P203, P260, P261, P272, P273, P280, P302+P352, P318, P319, P321, P333+P317, P362+P364, P391, P405, and P501
Spiromesifen	[2-oxo-3-(2,4,6-trimethylphenyl)-1-oxaspiro[4.4]non-3-en-4-yl] 3,3-dimethylbutanoate CAS: 283594-90-1	 Warning	H317, H332, H400, and H410	P261, P271, P272, P273, P280, P302+P352, P304+P340, P317, P321, P333+P317, P362+P364, P391, and P501
Spirotetramat	[3-(2,5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl] ethyl carbonate CAS: 203313-25-1	 Warning	H317, H319, H335, H361, H361fd, H400, and H410	P203, P261, P264+P265, P271, P272, P273, P280, P302+P352, P304+P340, P305+P351+P338, P318, P319, P321, P333+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Spirotetramat-enol	3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]dec-3-en-2-one CAS: 382608-09-5		H411	P273, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Spirotetramat-enol-glucoside	3-(2,5-dimethylphenyl)-8-methoxy-4-[(2S,3R,4S,5S,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)oxan-2-yl]oxy-1-azaspiro[4.5]dec-3-en-2-one CAS: 1172614-86-6		H411	P273, P391, and P501
Spirotetramat-keto-hydroxy	3-(2,5-dimethylphenyl)-3-hydroxy-8-methoxy-1-azaspiro[4.5]decane-2,4-dione CAS: 1172134-11-0		H411	P273, P391, and P501
Spirotetramat-mono-hydroxy	3-(2,5-dimethylphenyl)-4-hydroxy-8-methoxy-1-azaspiro[4.5]decan-2-one CAS: 1172134-12-1		H411	P273, P391, and P501
Spiroxamine	N-[(8-tert-butyl-1,4-dioxaspiro[4.5]decan-3-yl)methyl]-N-ethylpropan-1-amine CAS: 118134-30-8	 Warning	H302+H312+H332, H315, H317, H361d, H373, H400, and H410	P203, P260, P261, P264, P270, P271, P272, P273, P280, P301+P317, P302+P352, P304+P340, P317, P318, P319, P321, P330, P332+P317, P333+P317, P362+P364, P391, P405, and P501
Sulfentrazone	N-[2,4-dichloro-5-[4-(difluoromethyl)-3-methyl-5-oxo-1,2,4-triazol-1-yl]phenyl]methanesulfonamide CAS: 122836-35-5	 Warning	H319, H332, H373, and H411	P260, P261, P264+P265, P271, P273, P280, P304+P340, P305+P351+P338, P317, P319, P337+P317, P391, and P501
tau-Fluvalinate	[cyano-(3-phenoxyphenyl)methyl] (2R)-2-[2-chloro-4-(trifluoromethyl)anilino]-3-methylbutanoate CAS: 102851-06-9	 Warning	H302, H315, H400, and H410	P264, P270, P273, P280, P301+P317, P302+P352, P321, P330, P332+P317, P362+P364, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Tebuconazole	1-(4-chlorophenyl)-4,4-dimethyl-3-(1,2,4-triazol-1-ylmethyl)pentan-3-ol CAS: 107534-96-3	 Warning	H302, H361, H361d, H400, H410, and H411	P203, P264, P270, P273, P280, P301+P317, P318, P330, P391, P405, and P501
Tebufenozide	N-tert-butyl-N'-(4-ethylbenzoyl)-3,5-dimethylbenzohydrazide CAS: 112410-23-8		H411	P273, P391, and P501
Tebufenpyrad	N-[(4-tert-butylphenyl)methyl]-4-chloro-5-ethyl-2-methylpyrazole-3-carboxamide CAS: 119168-77-3	 Danger	H301, H302, H317, H332, H373, H400, and H410	P260, P261, P264, P270, P271, P272, P273, P280, P301+P316, P301+P317, P302+P352, P304+P340, P317, P319, P321, P330, P333+P317, P362+P364, P391, P405, and P501
Tebuthiuron	1-(5-tert-butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea CAS: 34014-18-1	 Warning	H302, H319, H373, H400, and H410	P260, P264, P264+P265, P270, P273, P280, P301+P317, P305+P351+P338, P319, P330, P337+P317, P391, and P501
Teflubenzuron	N-[(3,5-dichloro-2,4-difluorophenyl)carbamoyl]-2,6-difluorobenzamide CAS: 83121-18-0	 Warning	H400 and H410	P273, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Temephos	[4-(4-dimethoxyphosphinothioyloxyphenyl) sulfanylphenoxy]-dimethoxy-sulfanylidene-λ^5-phosphane CAS: 3383-96-8	 Danger	H302, H311, H312, H332, H372, H400, and H410	P260, P261, P262, P264, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P316, P317, P319, P321, P330, P361+P364, P362+P364, P391, P405, and P501
Terbuthylazine	2-N-tert-butyl-6-chloro-4-N-ethyl-1,3,5-triazine-2,4-diamine CAS: 5915-41-3	 Warning	H302, H332, H373, H400, and H410	P260, P261, P264, P270, P271, P273, P301+P317, P304+P340, P317, P319, P330, P391, and P501
Terbuthylazine-desethyl	2-N-tert-butyl-6-chloro-1,3,5-triazine-2,4-diamine CAS: 30125-63-4	 Warning	H317	P261, P272, P280, P302+P352, P321, P333+P317, P362+P364, and P501
Terbutryn	2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine CAS: 886-50-0	 Warning	H302, H317, H319, H332, H400, and H410	P261, P264, P264+P265, P270, P271, P272, P273, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P317, P321, P330, P333+P317, P337+P317, P362+P364, P391, and P501
Tetraconazole	1-[2-(2,4-dichlorophenyl)-3-(1,1,2,2-tetrafluoroethoxy)propyl]-1,2,4-triazole CAS: 112281-77-3	 Warning	H302+H332, H400, H410, and H411	P261, P264, P270, P271, P273, P301+P317, P304+P340, P317, P330, P391, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Tetramethrin	(1,3-dioxo-4,5,6,7-tetrahydroisoindol-2-yl)methyl 2,2-dimethyl-3-(2-methylprop-1-enyl)cyclopropane-1-carboxylate CAS: 7696-12-0	 Warning	H302, H351, H371, H373, H400, and H410	P203, P260, P264, P270, P273, P280, P301+P317, P308+P316, P318, P319, P330, P391, P405, and P501
Thiabendazole	4-(1H-benzimidazol-2-yl)-1,3-thiazole CAS: 148-79-8	 Warning	H400 and H410	P273, P391, and P501
Thiacloprid	[3-[(6-chloropyridin-3-yl)methyl]-1,3-thiazolidin-2-ylidene]cyanamide CAS: 111988-49-9	 Danger	H301, H302, H332, H336, H351, H360, H360fd, H400, and H410	P203, P261, P264, P270, P271, P273, P280, P301+P316, P301+P317, P304+P340, P317, P318, P319, P321, P330, P391, P403+P233, P405, and P501
Thiamethoxam	(NE)-N-[3-[(2-chloro-1,3-thiazol-5-yl)methyl]-5-methyl-1,3,5-oxadiazinan-4-ylidene]nitramide CAS: 153719-23-4	 Danger	H228, H302+H332, H400, and H410	P210, P240, P241, P261, P264, P270, P271, P273, P280, P301+P317, P304+P340, P317, P330, P370+P378, P391, and P501
Thidiazuron	1-phenyl-3-(thiadiazol-5-yl)urea CAS: 51707-55-2	 Warning	H312+H332, H315, H319, H335, H400, and H410	P261, P264, P264+P265, P271, P273, P280, P302+P352, P304+P340, P305+P351+P338, P317, P319, P321, P332+P317, P337+P317, P362+P364,

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
				P391, P403+P233, P405, and P501
Thiencarbazone-methyl	methyl 4-[(3-methoxy-4-methyl-5-oxo-1,2,4-triazole-1-carbonyl)sulfamoyl]-5-methylthiophene-3-carboxylate CAS: 317815-83-1	 Warning	H400 and H410	P273, P391, and P501
Thifensulfuron-methyl	methyl 3-[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)carbamoylsulfamoyl]thiophene-2-carboxylate CAS: 79277-27-3	 Warning	H400 and H410	P273, P391, and P501
Thiobencarb	S-[(4-chlorophenyl)methyl] N,N-diethylcarbamothioate CAS: 28249-77-6	 Warning	H302, H315, H319, H332, H335, H400, and H410	P261, P264, P264+P265, P270, P271, P273, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P317, P319, P321, P330, P332+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Thiofanox	[(3,3-dimethyl-1-methylsulfanylbutan-2-ylidene)amino] N-methylcarbamate CAS: 39196-18-4	 Danger	H300, H310, H400, and H410	P262, P264, P270, P273, P280, P301+P316, P302+P352, P316, P321, P330, P361+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Thiophanate-methyl	methyl N-[[2-(methoxycarbonylcarbamothioylamino)phenyl]carbamothioyl]carbamate CAS: 23564-05-8	 Warning	H317, H332, H341, H351, H400, and H410	P203, P261, P271, P272, P273, P280, P302+P352, P304+P340, P317, P318, P321, P333+P317, P362+P364, P391, P405, and P501
Tolylfluanid	N-[dichloro(fluoro)methyl]sulfanyl-N-(dimethylsulfamoyl)-4-methylaniline CAS: 731-27-1	 Danger	H315, H317, H319, H330, H331, H335, H372, H373, H400, and H410	P260, P261, P264, P264+P265, P270, P271, P272, P273, P280, P284, P302+P352, P304+P340, P305+P351+P338, P316, P319, P320, P321, P332+P317, P333+P317, P337+P317, P362+P364, P391, P403+P233, P405, and P501
Tolylfluanid metabolite DMST	1-(dimethylsulfamoylamino)-4-methylbenzene CAS: 66840-71-9	 Warning	H302 and H412	P264, P270, P273, P301+P317, P330, and P501
trans-Permethrin	(3-phenoxyphenyl)methyl (1R,3S)-3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropane-1-carboxylate CAS: 51877-74-8	 Warning	H302, H317, H332, H400, and H410	P261, P264, P270, P271, P272, P273, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P333+P317, P362+P364, P391, and P501
Triadimefon	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-one CAS: 43121-43-3	 Warning	H302, H317, and H411	P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P321, P330,

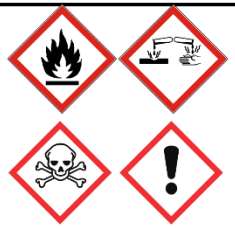
Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
				P333+P317, P362+P364, P391, and P501
Triadimenol	1-(4-chlorophenoxy)-3,3-dimethyl-1-(1,2,4-triazol-1-yl)butan-2-ol CAS: 55219-65-3	 Danger	H302, H332, H360, H362, H411, and H412	P203, P260, P261, P263, P264, P270, P271, P273, P280, P301+P317, P304+P340, P317, P318, P330, P391, P405, and P501
Tri-allate	S-(2,3,3-trichloroprop-2-enyl) N,N-di(propan-2-yl)carbamothioate CAS: 2303-17-5	 Warning	H302, H317, H373, H400, and H410	P260, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P319, P321, P330, P333+P317, P362+P364, P391, and P501
Trichlorfon	2,2,2-trichloro-1-dimethoxyphosphorylethanol CAS: 52-68-6	 Danger	H301, H302+H312, H317, H334, H400, and H410	P233, P260, P261, P264, P270, P271, P272, P273, P280, P284, P301+P316, P301+P317, P302+P352, P304+P340, P317, P321, P330, P333+P317, P342+P316, P362+P364, P391, P403, P405, and P501
Tricyclazole	8-methyl-[1,2,4]triazolo[3,4-b][1,3]benzothiazole CAS: 41814-78-2	 Danger	H301, H302, and H411	P264, P270, P273, P301+P316, P301+P317, P321, P330, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Trifloxystrobin	methyl (2E)-2-methoxyimino-2-[2-[[(E)-1-[3-(trifluoromethyl)phenyl]ethylideneamino]oxymethyl]phenyl]acetate CAS: 141517-21-7	 Warning	H317, H362, H400, and H410	P203, P260, P261, P263, P264, P270, P272, P273, P280, P302+P352, P318, P321, P333+P317, P362+P364, P391, and P501
Trifloxystrobin metabolite CGA 321113	(2E)-2-methoxyimino-2-[2-[[(E)-1-[3-(trifluoromethyl)phenyl]ethylideneamino]oxymethyl]phenyl]acetic acid CAS: 252913-85-2	 Warning	H317 and H410	P273, P280, P333+P313, P391, and P501
Triflumizole	N-[4-chloro-2-(trifluoromethyl)phenyl]-1-imidazol-1-yl-2-propoxyethanimine CAS: 68694-11-1	 Danger	H302, H317, H360, H373, H400, H410, and H411	P203, P260, P261, P264, P270, P272, P273, P280, P301+P317, P302+P352, P318, P319, P321, P330, P333+P317, P362+P364, P391, P405, and P501
Triflumuron	2-chloro-N-[[4-(trifluoromethoxy)phenyl]carbamoyl]benzamide CAS: 64628-44-0	 Danger	H330, H400, and H410	P260, P271, P273, P284, P304+P340, P316, P320, P391, P403+P233, P405, and P501
Triticonazole	(5E)-5-[(4-chlorophenyl)methylidene]-2,2-dimethyl-1-(1,2,4-triazol-1-ylmethyl)cyclopentan-1-ol CAS: 131983-72-7		H411	P273, P391, and P501
Vamidothion	2-(2-dimethoxyphosphorylsulfanylethylsulfanyl)-N-methylpropanamide CAS: 2275-23-2	 Danger	H301, H312, and H400	P264, P270, P273, P280, P301+P316, P302+P352, P317, P321, P330, P362+P364, P391, P405, and P501

Compound name	IUPAC name CAS number	Pictograms	H statements	P statements
Zoxamide	3,5-dichloro-N-(1-chloro-3-methyl-2-oxopentan-3-yl)-4-methylbenzamide CAS: 156052-68-5	 Warning	H317, H400, and H410	P261, P272, P273, P280, P302+P352, P321, P333+P317, P362+P364, P391, and P501

Table A6: Safety data information for other used chemicals according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Chemical	CAS number	Pictograms	H statements	P statements
2-propanol	67-63-0	 Danger	H225, H319, and H336	P210, P233, P240, P241, P242, P243, P261, P264+P265, P271, P280, P303+P361+P353, P304+P340, P305+P351+P338, P319, P337+P317, P370+P378, P403+P233, P403+P235, P405, and P501
Acetic acid	64-19-7	 Danger	H302+H332, H360, H360df, H373, H400, and H410	P203, P260, P261, P264, P270, P271, P273, P280, P301+P317, P304+P340, P317, P318, P319, P330, P391, P405, and P501
Acetone	67-64-1	 Danger	H225, H319, and H336	P210, P233, P240, P241, P242, P243, P261, P264+P265, P271, P280, P303+P361+P353, P304+P340, P305+P351+P338, P319, P337+P317, P370+P378, P403+P233, P403+P235, P405, and P501
Acetonitrile	75-05-8	 Danger	H225, H302, H312, H319, and H332	P210, P233, P240, P241, P242, P243, P261, P264, P264+P265, P270, P271, P280, P301+P317, P302+P352, P303+P361+P353, P304+P340, P305+P351+P338, P317, P321, P330, P337+P317, P362+P364, P370+P378, P403+P235, and P501
Ammonium formate	540-69-2	 Warning	H315, H319, and H335	P261, P264, P264+P265, P271, P280, P302+P352, P304+P340, P305+P351+P338, P319, P321, P332+P317, P337+P317, P362+P364, P403+P233, P405, and P501
Dichloromethane	75-09-2	 Warning	H302, H315, H319, H335, H336, H341, H351, and H373	P203, P260, P261, P264, P264+P265, P270, P271, P280, P301+P317, P302+P352, P304+P340, P305+P351+P338, P318, P319, P321, P330, P332+P317, P337+P317, P362+P364, P403+P233, P405, and P501

Chemical	CAS number	Pictograms	H statements	P statements
Formic acid	64-18-6	 Danger	H226, H302, H314, H318, and H331	P210, P233, P240, P241, P242, P243, P260, P261, P264, P264+P265, P270, P271, P280, P301+P317, P301+P330+P331, P302+P361+P354, P303+P361+P353, P304+P340, P305+P354+P338, P316, P317, P321, P330, P363, P370+P378, P403+P233, P403+P235, P405, and P501
Hexane	110-54-3	 Danger	H225, H304, H315, H317, H319, H336, H361, H373, H411, and H412	P203, P210, P233, P240, P241, P242, P243, P260, P261, P264, P264+P265, P271, P272, P273, P280, P301+P316, P302+P352, P303+P361+P353, P304+P340, P305+P351+P338, P318, P319, P321, P331, P332+P317, P333+P317, P337+P317, P362+P364, P370+P378, P391, P403+P233, P403+P235, P405, and P501
Magnesium sulfate, anhydrous	7487-88-9	 Warning	H302, H312, and H332	P261, P264, P270, P271, P280, P301+P317, P302+P352, P304+P340, P317, P321, P330, P362+P364, and P501
Methanol	67-56-1	 Danger	H225, H301, H311, H331, and H370	P210, P233, P240, P241, P242, P243, P260, P261, P262, P264, P270, P271, P280, P301+P316, P302+P352, P303+P361+P353, P304+P340, P308+P316, P316, P321, P330, P361+P364, P370+P378, P403+P233, P403+P235, P405, and P501
Sodium acetate, anhydrous	127-09-3	-	-	-
Nitrogen, liquid	7727-37-9	 Warning	H280 and H281	P282, P336+P317, and P410+P403
Ultrapure water	7732-18-5	-	-	-

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