Pesticides and Pesticide-Related Products in Ambient Air in Germany

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Research

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Pesticides and pesticide-related products in ambient air in Germany

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Abstract

Background

Tree bark measurements conducted between 2014 and 2017 in a biosphere reserve have indicated the presence of pesticides from conventional agriculture in ambient air in

Germany. In the present study, we quantified pesticides and related substances in ambient air at 69 sites using passive air samplers and ventilation filter mats. It is, to our knowledge, so far the most comprehensive dataset on pesticides and their related products in ambient air in Germany.

Results

Samples were collected in 2019 and analysed for over 500 substances, of which 109 were detected, including 28 that are not approved for use in Germany. In each sampling site, we detected one to 36 substances, including at locations such as national parks and forests, where the presence of pesticides is not expected, e.g., on the highest mountain top in the national park “Harz” (13 substances) and in the "Bavarian Forest" (six substances). Glyphosate was detected in every sample. More than half of passive air samplers contained chlorothalonil, metolachlor, pendimethalin, terbuthylazine, prothioconazole-desthio, dimethenamid, prosulfocarb, flufenacet, tebuconazole, aclonifen, chlorflurenol, hexachlorobenzene (HCB), and γ-hexachlorocyclohexane (ɣ-HCH). Filter mats also contained boscalid. The statistical analysis showed that landscape classification and agricultural intensity were the primary factors influencing the number of substances detected in ambient air. Location, such as protected areas or regions of organic farming, had only a small effect on the number of substances recorded. Long-range transport likely accounts for the findings and active sampling of ambient air will probably detect more pesticides and higher concentrations than passive air sampler data presently suggest.

Conclusions

Airborne pesticide mixtures are ubiquitous in Germany, which is particularly concerning for glyphosate, pendimethalin, and prosulfocarb. Deposition of these pesticides on organic

products may disqualify them from the market, resulting in economic damage to farmers. Air concentrations of pesticides are a relevant issue and must be reduced.

Key words: pesticide, passive air sampler, glyphosate, chlorothalonil, metolachlor, pendimethalin, filter mat, ventilation system

Background

Data generated by the Global Atmospheric Passive Sampling (GAPS) network under the Stockholm Convention on persistent organic pollutants (POPs) illustrate a the worldwide transport of pesticides [1]. By contrast, the pollution of ambient air with currently used pesticides has received little attention. Only Sweden has set up an extensive monitoring program and made the data generally available [2] [3], but interest in these data is growing. A comprehensive measurement of pesticide air pollution was recently conducted in France [4]. In Germany, the Federal Office of Consumer Protection and Food Safety (Bundesamt für Verbraucherschutz und Lebensmittelsicherheit, BVL) launched a feasibility study for national pesticide monitoring [5].

The European Food Safety Authority (EFSA) authorises pesticide use in the European Union and recommends an exposure assessment that is based on standard values for active substances of low and medium volatility [6]. The assessment is based on the assumption that sprayed pesticides do not for drift far beyond their application site. EFSA classifies the volatility of a pesticide as low (less than 5×10^{-3} mm Hg at 25°C), medium (5×10^{-3} to 10^{-2} mm Hg), or high (more than 10^{-2} mm Hg). Highly volatile pesticides may require a separate estimate of air concentrations (Additional File 1).

In the Federal Republic of Germany, the BVL authorises the use of plant-protection products. Approximately 20 years ago, the approval process was modified to determine volatility by model calculations rather than through laboratory and field experiments [5]. Today, the BVL modelling software EVA 3.0 determines the potential of a substance for release into the air. Semi-open air-wind tunnel studies are also performed for substances with high vapour pressure to determine volatility in the vicinity of the application site. Despite these measures, airborne levels of pesticides are an ongoing issue. Organic farming in particular has been affected [7], as auxiliaries such as synthetic chemical pesticides or fertilisers are not permitted. European Union Regulation No. 2018/848 [8] governs the process of organic agriculture and its inspection, from seeds or animal feed to the final product on the market. Ambient air pollution poses problems beyond the control of the organic economy.

An example is an incident in the Schorfheide-Chorin region, the largest continuous organic farming area in Europe and a biosphere reserve. Here, organic grain fennel was not approved for marketing because it contained high levels of pendimethalin. At that time, the State Agency for the Environment Brandenburg (Landesamt für Umwelt, Brandenburg) commissioned the first scientific analysis to record all relevant substances within the affected areas by means of air quality tree bark monitoring [9]. This study was expanded to include 47 tree bark samples from all areas of Germany in 2018. Air quality tree bark monitoring uses standardised samplers to collect the first millimetre of the outer bark, which consists of dead tissue where a wide range of ambient air pollutants can accumulate over a timespan of 18–24 months. The outer bark is particularly suitable for biomonitoring because its collection does not interfere with processes such as cell growth. The samples were analysed for more than 500 pesticides and related substances, including glyphosate [9] [10] [11]. Pendimethalin and prosulfocarb were the most common pesticides found in the study, but POPs such as dichlorodiphenyltrichloroethane (DDT) and ɣ-HCH, the main compound in lindane, were also widespread. Glyphosate ranked fifth in detection frequency, demonstrating air transport of this pesticide.

Human exposure to glyphosate in Germany was previously measured in urine from 2000 test subjects [12], and levels did not differ significantly between individuals consuming only organically produced food and those consuming conventionally produced food, suggesting airborne transport of this pesticide.

Since no data on pesticide occurrence in ambient air were available from official sources, a consortium of organic producers, suppliers, and non-governmental organisations such as Bürgerinitiative Landwende, Schweisfurth Stiftung, and Umweltinstitut München e.V. was formed to enable an extension of the earlier tree bark work [10] [11] [9]. As the exact time of exposure cannot be determined through tree bark monitoring, the aim of the present study was to measure the extent to which airborne pesticides and related products are detectable in ambient air within a known timespan.

Owing to technical and financial constraints, a simple design was used. Passive samplers have been extensively validated in the GAPS network [13] [14] [15] but must be considered to yield only semi-quantitative results. The samplers enable the simultaneous collection of multiple substances, are relatively inexpensive, and their use is not technically demanding and can be accomplished by non-professional operators. To allow a wide range of sampling points to be analysed within the project's budget, the study focused on annual deposition.

In Germany, energy-saving regulation recommends a ventilation system for most new but also for existing buildings. Because of the airtight construction of buildings used today, controlling the entry of fresh air is essential. All available ventilation systems control the influx of fresh outside air into the building separately from the stale air leaving the building. Filter mats from ventilation systems, used to purify incoming outdoor air, were collected from 20 households and analysed. The filter mats were exposed over the same timespan as the passive air samplers, thus enabling a comparison of collected substances and concentrations. The filter mats can qualitatively exhibit the presence of pesticides.

In addition, 51 honeybee bread samples were analysed. These results could be compared to the German Bee Monitoring (Deutsches BienenMonitoring) database. Some additional tree bark samples were also added. A statistical analysis compared relevant location factors affecting the observed concentrations. Results and data are available in our previous report [16]. For brevity, this paper focuses on the findings for passive air samplers and filter mats.

Material and Methods

Definition of terms

A pesticide is the active substance of a plant-protection product, which can contain one or more pesticides plus formulation auxiliaries that ensure that pesticides are easy to handle and apply and have a long shelf life. We tested the samples for over 500 substances according to ASU L 00.00-115, guidelines for determining pesticide residues in agricultural and horticultural materials with a low content of fat [17]. The spectrum of pesticides and related substances tested (Additional File 2) was determined by a working group according to BVL § 64 LFGB (Lebensmittel und Futtermittelgesetzbuch, German Food and Feed Code) [17]. Some additional substances were added by the analysing laboratory because of consumer concerns.

The list of substances to be analysed includes those that are not pesticides in the strict sense: pesticide metabolites, safeners, synergists, auxiliary materials, and compounds unrelated to plant-protection products that are known to exert adverse health effects and may occur unintentionally in agricultural products, such as polychlorinated biphenyls (PCB´s)

[37]. We identified four additional substances that may be of relevance (HCB, anthraquinone, dichlorobenzophenone (DCBP-pp), and piperonyl butoxide (PBO); Additional File 3). All these substances are herein termed “pesticides and their related substances” unless a separate listing is required.

Our laboratory findings are concentrations of a substance in polyester filters (PEF) and polyurethane foam (PUF) disks, expressed as nanograms per sample (ng/sample) for passive air samplers or micrograms per square metre (µg/m²) for ventilation filters. These concentrations must not be confused with the concentrations of a substance in ambient air, which were not determined in this study.

Passive air samplers

For this project, specific passive air samplers were developed by *TIEM* technic. The collector (Figure 1) uses a PUF disk, similar to the standard TE-200-PAS collectors used by the GAPS network. The PUF disks (diameter: 14 cm; height: 1.35 cm) were obtained from Tisch Environmental (Cleves, OH, USA) and have been validated extensively for pesticide sampling [13] [14] [15] [18] and confirmed in the work of Zhang et al. [19] [20] [21].

However, no data were available on the efficacy of these passive air samplers in measuring glyphosate. In an experiment with controlled glyphosate application, Morshed et al. were unable to detect glyphosate in the otherwise effective PUF disk [22].

In addition to the openly exposed PUF in a TE-PAS-DD passive air sampler from Tisch Environmental, we also tested [23] the PEFs used for pollen mass [24] and AmberLite™ resin used by the GAPS network to measure glyphosate [23]. Unlike Morshed and colleagues [22], we were able to detect glyphosate in the openly exposed polyurethane of the TE-PAS-DD filter [23]. However, the PEF (diameter: 8 cm; height: 2 cm, with a round section 3 cm in diameter in the middle; obtained from Freudenberg Filtration Technologies, Weinheim, Germany) was far more effective. Therefore, the passive air sampler developed for this project combined the two sampling filters. An enclosed dome open to the outside air by a wide (1.5-cm) rim holds the PUF disk in a sheltered surrounding, while the PEF underneath is openly exposed (Figure 1).

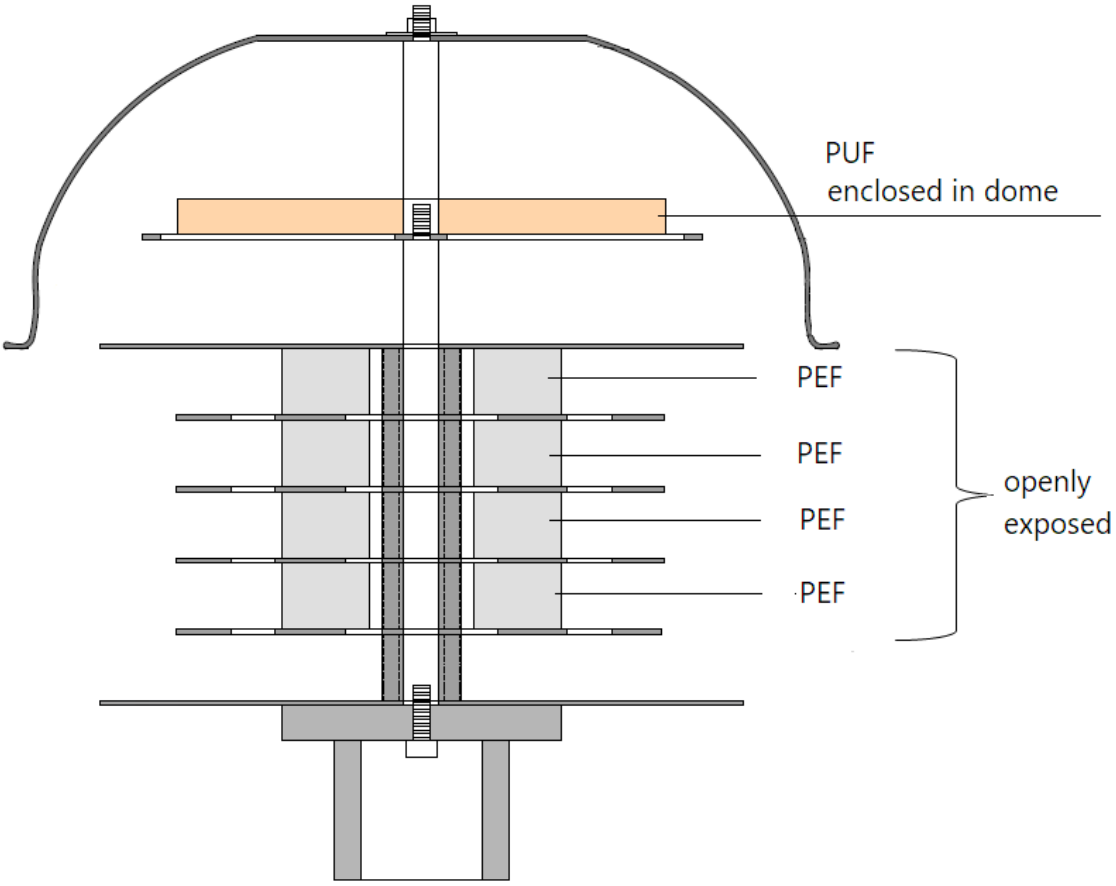

Figure 1: Passive air sampler developed by TIEM technic

The polyurethane foam (PUF) disk captures volatile and semi-voltatile pesticides and a polyester filter (PEF) captures glyphosate, aminomethylphosphonic acid (AMPA), and glufosinate.

The PUF disks were purified according to Shoeib et al. [25].

Sample collection

The installation of 49 samplers on site (Figure 2) was carried out by *TIEM* Integrated Environmental Monitoring. Volunteers were trained in installing and replacing the samplers and provided with tools such as nitrile gloves, aluminium foil, tweezers, and storage and transport containers. The measurement period extended from the first 2 weeks in April to mid-November of 2019. PUF disks were replaced in mid-June, mid-August, and early to mid-November. *TIEM* Integrated Environmental Monitoring provided new PUF disks and volunteers stored the used disks in temperature-controlled boxes at −18°C. At the end of the sampling period, all filters were shipped to *TIEM* Environmental Monitoring in temperature-controlled boxes with cooled thermal packs to avoid overheating, and were subsequently forwarded to the analysing laboratory under the same conditions.

Figure 2: Example of a passive air sampler in the field

Sample analysis

All three sets of PUF disks per sampling site were combined for testing for the >500 substances listed in the ASU L 00.00-115 guidelines (Additional File 2). Chemical analysis was conducted by KWALIS (Fulda, Germany), which is accredited by the German accreditation body (Deutsche Akkreditierungsstelle). The PUF disks were Soxhlet-extracted for 24 h using petroleum ether. Sample treatment was performed as reported previously [26]. The procedure used for the PUF samples differed from the ASU L 00.00-115 guidelines because of the extraction method.

The PEFs were extracted using aqueous hydrochloric acid. In a separate analysis, the concentrations of glyphosate, aminomethylphosphonic acid (AMPA), and glufosinate were determined using liquid chromatography-tandem mass spectrometry. The limits of quantification (LQ) for the PUF disks and PEFs are given in Additional File 4, which includes the values recorded from passive air samplers. Seven values were below the LQ but above the limit of detection (LD) (Additional File 4). Possible contamination from transport was assessed by analysing blank (unexposed) PEFs and PUF disks; the blanks did not contain any of the compounds.

Filter mats from ventilation systems

Passive air samplers are designed to minimise particulate contamination of the PUF disk [30] and therefore could not be used to assess pesticides on airborne particles. Instead, we collected filter mats from home ventilation systems, which are designed to remove dust and sometimes pollen from outside air entering buildings. Twenty volunteers submitted the filter mats in their homes for analysis.

Sample collection

All participants were asked to install a new filter mat on April 10, 2019 and ship it to *TIEM* Integrated Environmental Monitoring at the end of the measurement period (September 28 to October 8, 2019). The mats were forwarded to the analysing laboratory. All technical data and the characteristics of the sampling site were compiled in a protocol. Additional File 5 contains specifications of the ventilation systems sampled. Unexposed filter mats were tested as blank samples.

Sample analysis

The filter mats were analysed for the substances specified in ASU L 00.00-115 (Additional File 2) and for glyphosate, AMPA, and glufosinate. The compounds were extracted with acetonitrile. Additional File 6 gives the LQ and the concentrations measured. One value was below the LQ but above the LD. No pesticides were detected in the blank samples.

Selection of sampling sites

Volunteers willing to supervise a sampler or to donate a filter mat applied through a website. Sites of particular interest, such as national parks, were solicited as well. More than 250 sites were considered to obtain a reasonable nationwide coverage (Figure 3) and to represent a wide range of sampling characteristics. Six characteristics presumed to be related to pesticide exposure were defined before the study commenced (Table 1 and Additional File 7) and were also used in the statistical analysis of the data, which dealt with the relationship between site features and pesticide concentrations [16]. The number of sites per category is given for all passive air sampler sites (Additional File 8) and filter mat sites (Additional File 9). Two factors, agricultural intensity and risk of wind erosion, required some degree of estimation. Additional File 7 details the procedure used.

Table 1: Evaluation criteria for sampling sites

Factor	Description	Code in regression tree
Landscape classification	Alpenvorland (AVL)	a
in regression tree:	Nordostdeutsches Tiefland (NOTL)	b
“Naturraum“	Nordwestdeutsches Tiefland (NWTL)	c

	Östliches Mittelgebirge (OMG) Südwestdeutsches Mittelgebirge/Stufenland (SWMGS) Westliches Mittelgebirge (WMG)	d e f
Biogeographical region **“BioGeo“**	Atlantic Continental	a b
Risk of wind erosion **“Erosion3“**	0.0–1.0 1.5–2.0 2.5–3.0 3.5–5.0	a b c d
Protected area **“SchutzGebJN“**	no yes	a b
Agricultural intensity **“LwIntK“** Percentage of arable farming in a 4-m² area around the sampling site	low (ratio 0–20%) medium (ratio 20%–50%) high (ratio >50%)	a b c
Distance to the nearest possible source **“DistanzE“**	Close range: a few metres to 100 m Medium range: 100–1000 m Long range: over 1000 m	a b c
Organic production **“BioJN“**	no yes	a b

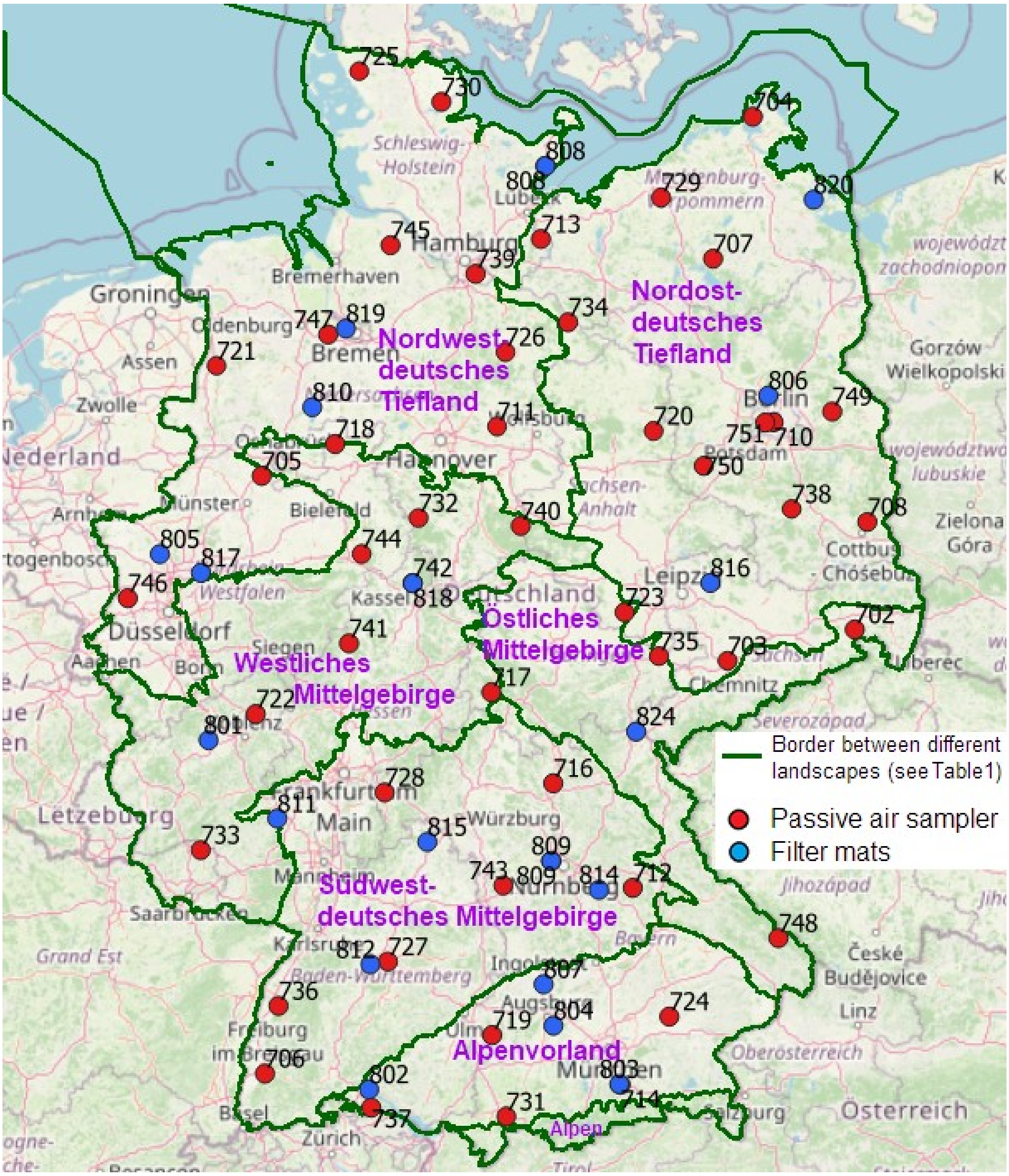

Figure 3: Location of sampling sites (passive air samplers and filter mats)

The location of the sampling sites is given with the adjacent site number 1. Site number 1 may be used to match location with the data in Additional Files 4 and 6.

Sampling sites were selected to reflect a wide range of conditions: intensively farmed land, areas far from agricultural activity, forests, and cities. We included sites where high exposure to pesticides could be expected (e.g., from intensive conventional farming) and sites where no relevant exposure was anticipated (e.g., organic farming, protected areas, city centres).

Statistical analysis

The presence of currently used pesticides in ambient air is the consequence of spraying and airborne transport, sometimes by binding to particulates. The concentrations are likely to depend on the extent of pesticide use at the sites of origin, the distance from the application sites, meteorological conditions in the transport range, and geographical properties such as soil erosion. Land use may also be involved. This study therefore recorded site characteristics for inclusion in the analysis in combinations, as it is likely that these are not stand-alone factors. For example, northern Germany has large flat areas where soil is prone to erosion and areas with intensive farming and wind conditions that favour long-range airborne transport. This means that statistical analyses of the relationship between site characteristics and pesticide concentrations must account for high-level interactions between factors. In view of the exploratory character of the analysis and the need to investigate high-level interactions, we used regression trees [27], i.e., a sequence of questions concerning the values of the explaining factors, ending in a prediction of the target quantity (pesticide concentration) that holds for all observations with the same answers in the question sequence. Such a sequence can easily be presented as a decision tree and is therefore simple to understand. The procedure selects the decision questions such that the final prediction of pesticide concentrations is as good as possible, where goodness is calculated as the variance of the difference between predicted and observed concentrations (the error variance). Observed concentrations enter the calculations as logarithms to make the variance a reasonable criterion. The importance of a factor is expressed as the coefficient of determination, the proportion of the maximal error variance (using only a constant as explanation) that is explained by the factor. The importance of the factor is in direct relation to the size of the proportion of the maximal error variance.

Results

Table 2 lists the concentrations of pesticides and related products measured in 49 passive air samplers and 20 filter mats, along with the number of pesticides detected over the study period per collection method. Eighty substances were detected in passive air samplers and 65 substances in filter mats. Glyphosate and AMPA were found with both methods. The number of substances per site ranged from six to 33 in passive air samplers and one to 36 in filter mats. Additional File 10 lists all 109 substances detected, 28 of which are no longer approved for use in Germany.

Thirty six substances were measured in both passive air samplers and filter mats, while 44 substances were detected exclusively in passive air samplers and 29 were detected only in filter mats.

Table 3 lists the substances that were detected in passive air samplers at more than one third of sites. Table 4 lists the substances that were detected in filter mats in at least one third of the sampling sites. As the quality of the filter materials were variable, the data are used only qualitatively.

Table 2: Pesticides and related substances detected in passive air samplers and filter mats

Parameter	Passive air samplers	Filter mats
Number of sampling locations	49	20
Number of substances detected	78	63
Glyphosate and AMPA	Both detected	Both detected

Number of substances detected per sampling site	6–33	1–36
Median	19	9
Number of substances detected by only one collection method	44	29
Number of substances detected that are not approved for use in Germany	21[a]	11
Polychlorinated biphenyls (unintentionally introduced into commercial products)	5	
Metabolites	4	6
Number of substances detected in both collection methods	36	
Number of substances detected in passive air samplers and filter mats (listed in Additional File 10)	109	
Number of substances detected that are not approved for use in Germany	28[a]	
Substances detected that are banned under the Stockholm Convention	14 (including five PCBs and five DDTs compounds)	
Details	Additional File 4	Additional File 6

[a]Including endosulfan sulfate and derivatives of DDT, which are metabolites of POPs listed under the Stockholm Convention.

Table 3: Substances detected in passive air samplers at more than one third of sampling sites

Substance	Active compound type	Detection frequency (N=49)	Maximum (ng/sample)	Minimum (ng/sample)	Total quantity in all 49 samples (ng)	Median (ng/sample)	Approved for use in Germany
Glyphosate	Herbicide	49/49	3176.8	20.3	13122.3	98.4	yes
Chlorothalonil	Fungicide	47/49	1866.2	0	23247.3	272.5	yes
Metolachlor	Herbicide	45/49	1273.3	0	8075.8	58.1	yes
Pendimethalin	Herbicide	44/49	3916.8	0	21942.0	145.5	yes
Terbuthylazine	Herbicide	44/49	905.9	0	6061.2	77.3	yes
Prothioconazole-desthio	Metabolite	42/49	329.0	0	2797.2	35.0	not regulated

Dimethenamid	Herbicide	40/49	1556.6	0	4960.8	37.6	yes
Prosulfocarb	Herbicide	40/49	2505.3	0	11872.9	90.7	yes
AMPA	Metabolite	40/49	402.6	0	2548.4	25.1	not regulated
Flufenacet	Herbicide	35/49	204.6	0	1872.9	20.0	yes
Tebuconazole	Fungicide	32/49	114.7	0	984.3	13.9	yes
Aclonifen	Herbicide	27/49	479.7	0	1816.3	12.2	yes
Chlorflurenol	Growth regulator	27/49	229.1	0	2687.7	53.9	no
HCB	Fungicide	27/49	46.3	0	805.5	10.8	no
Ɣ-HCH	Insecticide, Repellent	26/49	267.4	0	1431.0	16.5	no
2-Methyl-4-chlorophenoxyacetic acid (MCPA)	Herbicide	22/49	90.8	0	519.6	0.0	yes
Epoxiconazole	Fungicide	18/49	81.3	0	433.0	0.0	yes
Folpet	Fungicide	17/49	7613.8	0	8958.6	0.0	yes

Table 4: Substances detected in filter mats in at least one third of the sampling sites

Substance	**Active compound type**	**Detection frequency (N=20)**	**Approved for use in Germany**
Glyphosate	Herbicide	20/20	yes
AMPA	Metabolite	17/20	not regulated
Boscalid	Fungicide	13/20	yes
Anthraquinone	Repellent	9/20	no
Fenpropidin	Fungicide	9/20	yes
Azoxystrobin	Fungicide	8/20	yes
Tebuconazole	Fungicide	8/20	yes
Ametoctradin	Fungicide	7/20	yes
Dichlorane	Fungicide	7/20	no
Epoxiconazole	Fungicide	7/20	yes
Folpet	Fungicide	7/20	yes
Mandipropamid	Fungicide	7/20	yes

In addition to glyphosate and AMPA, we found tebuconazole, epoxiconazole, and folpet in both passive air samplers and filter mats. In passive air samplers, we commonly found high concentrations of prothioconazol-desthio, dimethenamid, and prosulfocarb. The most frequently detected substances were herbicides (nine out of 18), while fungicides dominated in filter mats (nine out of 12).

Figure 4 shows the 18 most abundant substances in the PUF samples. The maximum value for a single substance was measured for folpet (7613.8 ng/sample) at one location, and this high value may indicate proximity to a site of application.

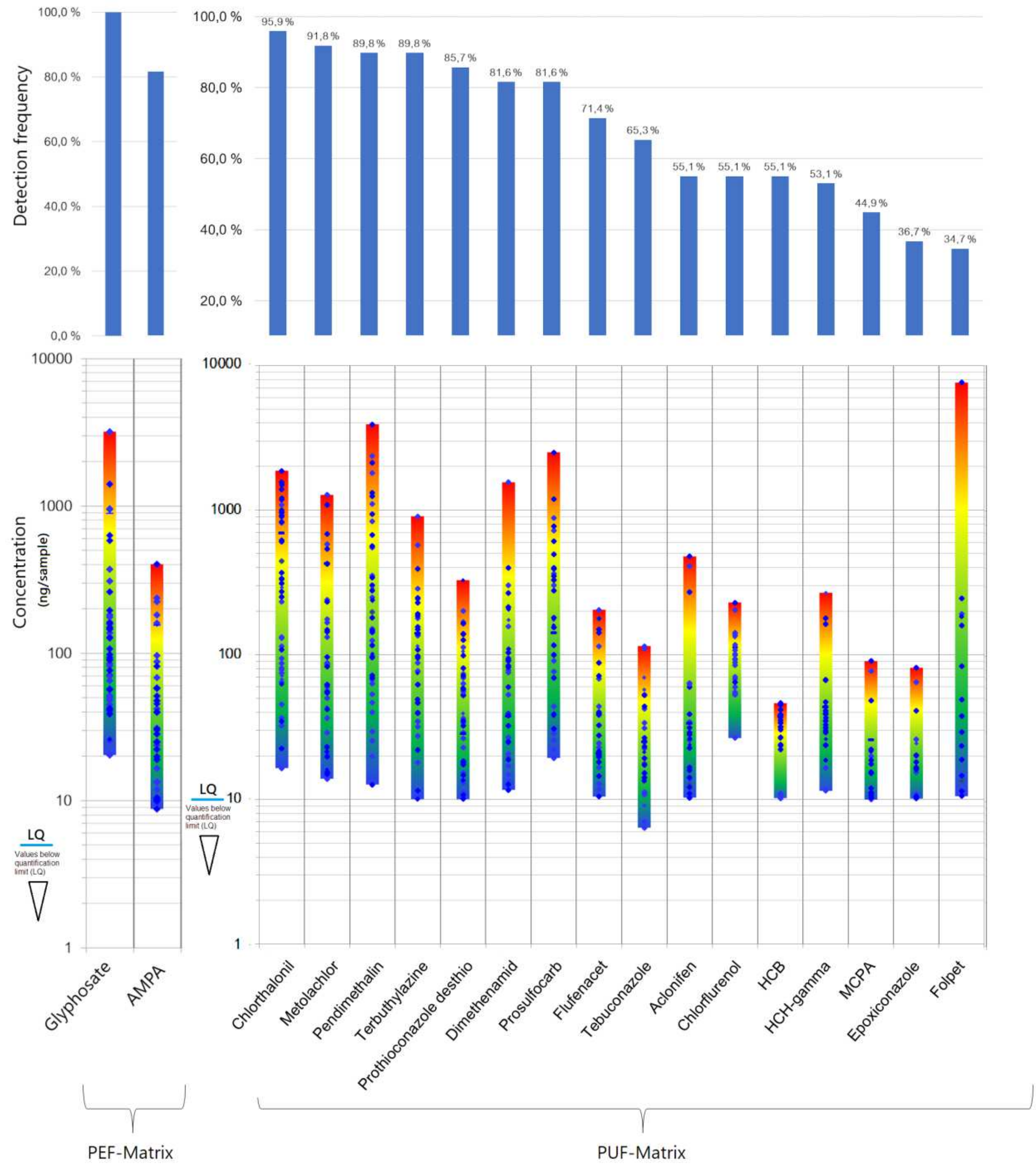

Figure 4: Most commonly detected pesticides and related products in passive air samplers

Values for pesticides and related products detected in more than one third of sampling sites on a logarithmic scale. Blue bars represent the detection frequency relative to all sites sampled. The coloured bars indicate the spread of the values. Blue diamonds represent individual values. See also Additional File 4.

Spatial distribution of pesticides and related products

Figure 5A shows the pesticide burden in the sampling sites as the number of substances detected in the samples and Figure 5B shows only the sites with the highest number of pesticides and related products.

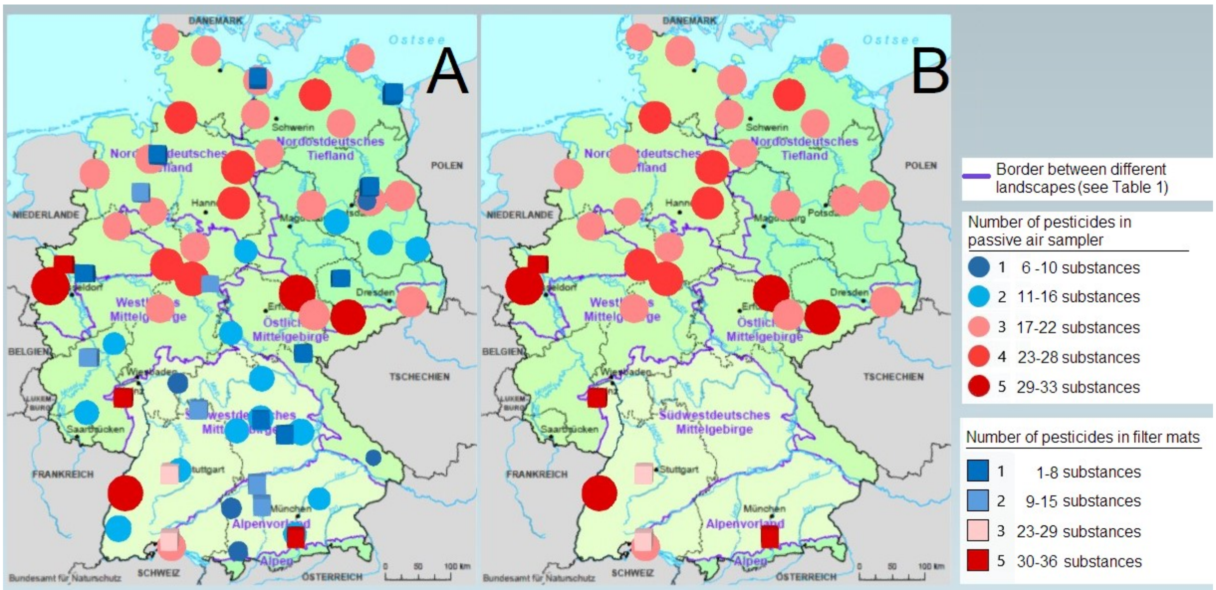

Figure 5: Number of substances detected at sampling sites

(A) All sampling sites. (B) Sampling sites where more than 16 substances were detected in passive air samplers and more than 22 substances were detected in filter mats.

Many of the sites with a high pesticide burden were in the northern regions of Germany, where intensive agriculture is possible. In the mountainous southern regions, high values may indicate vineyards and fruit crops. A considerable number of substances per site was also detected in unexpected places such as national parks in the Harz and Bavarian Forest, where we detected 13 substances in passive air samplers and six substances in filter mats (Additional File 11).

Results of the statistical analysis

For passive samplers, the statistical analysis of the number of pesticides and related substances identified landscape classification as the most influential factor in the overall observed variance (Table 5). However, agricultural activity in the immediate surroundings was the primary influence in the regression tree (Additional File 12; Table 5). Medium or high agricultural activity, noted for 39 sites, increased the overall median number of pesticides per site from 16.8 to 18.1.[1] The effect, which adds 6.3% to the total explained variance, is relatively small. Depending further on the landscape, the median number of pesticides increased to 23.8, with landscape contributing a total of 30.1% to the total explained variation. Landscape classification in general was the most important factor in the number of pesticides and related products we detected (Table 5), but its effects formed a complex pattern (Additional File 12). Both factors, agricultural activity and landscape classification, were not completely independent. Sites in protected areas (contribution to overall variance: 5.9%) reduced the number of substances detected to 15.8 in two of the landscape classes, Nordostdeutsches Tiefland and Westliches Mittelgebirge. However, in the other four landscape classes, the median increased to 23.8. Consequently, protected areas appear to offer little to no shelter against a large number of airborne pesticides and their related substances. Biogeographical regions, areas with risks of wind erosion and areas with biological production did not differ from other areas in the number of substances detected.

Table 5: Statistical analysis for the total number of substances detected per site in passive air samplers

Statistical Parameter	Coefficient of determination	Contribution of statistical parameter to total coefficient of determination (%)
Landscape classification	30.1	53.9
Biogeographical region		

[1]The sample median in the regression analysis is not identical to the descriptive statistical median.

Risk of wind erosion		
Protected areas	5.9	10.6
Agricultural intensity	13.5	24.2
Distance to the nearest possible source	6.3	11.3
Organic production		
Total explained variance	**55.8**	**100**

Additional File 12 shows the results as a regression tree.

Glyphosate, pendimethalin, and prosulfocarb

Glyphosate was detected at all sampling sites in both passive air samplers and filter mats (Figure 6), and concentrations peaked at 3176.8 ng/sample (median: 98.4 ng/sample; Table 3). AMPA was found at most but not all sites.

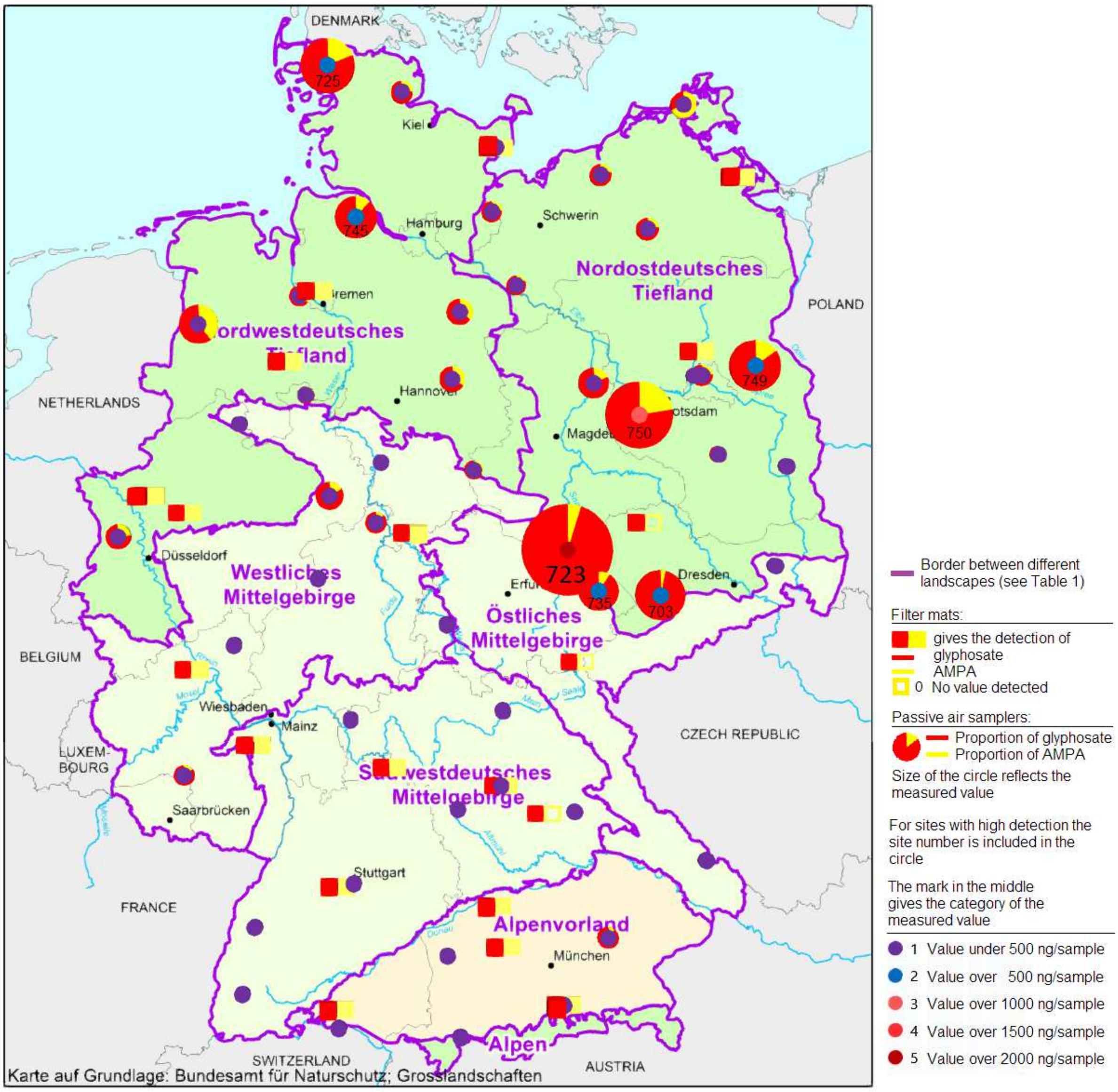

Figure 6: Levels of glyphosate and aminomethylphosphonic acid (AMPA)

Empty squares represent no detection. For filter mats, only detection (yes/no) is given, without the actual concentration levels.

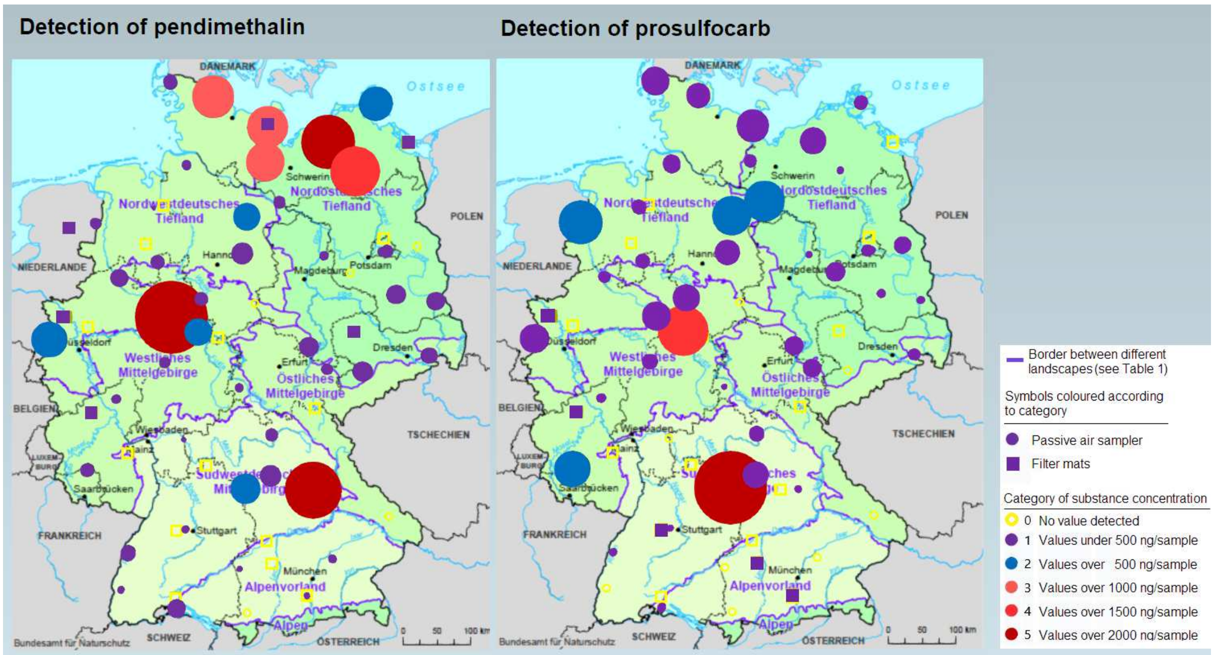

Figure 7: Levels of pendimethalin and prosulfocarb

The size of the circle is proportional to the maximum concentration detected (3916.8 ng/sample for pendimethalin and 2505.3 ng/sample for prosulfocarb).

The presence of pendimethalin and prosulfocarb adversely affects organic farming. Figure 7 shows the spatial distribution of these pesticides in our sampling. In passive air samplers, pendimethalin was not detected at only five sites. The values measured were high and the geographic distribution was widespread. The median of the values we measured (145.5 ng/sample) was below that of chlorothalonil (272.5 ng/sample). Chlorothalonil use became unauthorised in 2019, but application was permitted until May 5, 2020, after our sampling period. For prosulfocarb, we measured a maximum of 2505.3 ng/sample (median: 90.7 ng/sample) in passive air samplers, and the pesticide was not detected at nine sites. Filter mats barely captured pendimethalin (maximum 18.3 ng/m³, five values detected) or prosulfocarb (maximum 5.5 ng/m³, five values detected). The spatial distribution of multiple other pesticides and related products is given in the main report [16], as well as the analysis of honeybee bread and tree bark and a comparison of the major pesticides across sampling methods.

In the passive air samplers, our findings identified landscape classification and agricultural intensity as important factors influencing most of the values measured. The distance to the nearest potential source or an association with organic farming had little influence on the values, with the exception of metolachlor levels, which were significantly lower in sites of organic farming (Additional File 13). The data are linked in a complex manner and must be considered separately for each substance examined. Additional File 13 lists the results of the statistical analysis for passive air samplers. Since only 20 filter mats from ventilation systems were available, the statistical data are not included here.

Discussion

So far, the only available data on pesticides and their related products in ambient air in Germany was the tree bark study of 2018 [10]. The present study expands this database and is still the first of its kind. Despite the simple setup, a large number of pesticides and related substances were detected. Glyphosate, chlorothalonil, metolachlor, pendimethalin, and terbuthylazine were abundant, and high concentrations of prosulfocarb were also found. The concentrations collected in the PUF disks and PEFs varied greatly and were not restricted to values close to the quantification limits. The number of substances detected and their levels in the samples enabled the distinction between polluted and less polluted locations [16] and the assessment of factors influencing contamination. Although the pollution was generally higher in agriculturally intense regions, pesticides were also found in remote locations. This can likely be explained by long-range transport, which has not yet been assumed for currently used pesticides. Generally, the concentrations we found could be explained by several factors, such as landscape classification and agricultural activity. However, variables favouring long-range transport, such as soil erosion, wind conditions, and topography, must also be considered and on a substance-specific basis [14].

Temporal variations in pesticide levels

Our data represent sums over the entire measurement period and do not reflect temporal patterns, so whether the airborne concentrations were relatively constant over the collection period or differed by season or event is unknown. The temporal pattern of exposure was not an aim of this study, but it is highly relevant for a toxicological assessment. Sweden is the first European country to conduct long-term active sampling of airborne pesticides at rural sites surrounded by forests and located more than 1 km away from treated fields [2]; the data are available from the University of Uppsala [3]. Here, a defined air volume is led through a cartridge comprising a glass fibre filter, a PUF disk, an AmberLite resin core, and a second PUF [2]. The glass fibre filter is expected to capture aerosols, and volatile and semi-volatile substances can then be retained by the PUF. Kreuger and Lindström [2] showed that most of the pesticides and their related substances were captured in the glass fibre filter and the first PUF, while only 4% of the total pesticide content was found in the AmberLite resin and second PUF. Additional File 14 lists the number of substances detected in 2017 at the Hallahus site, the southernmost measuring station of the Swedish network. The weekly data for the glass fibre filter and the PUF are listed separately. Figure 8 is a graphic summary of the data. Ten to 35 substances of the 101 in the testing protocol were detected in the PUF. The glass fibre filter were analysed for 115 substances, adding six to 42 substances to the findings. Figure 8 shows the number of substances detected in the PUF and glass fibre filter.

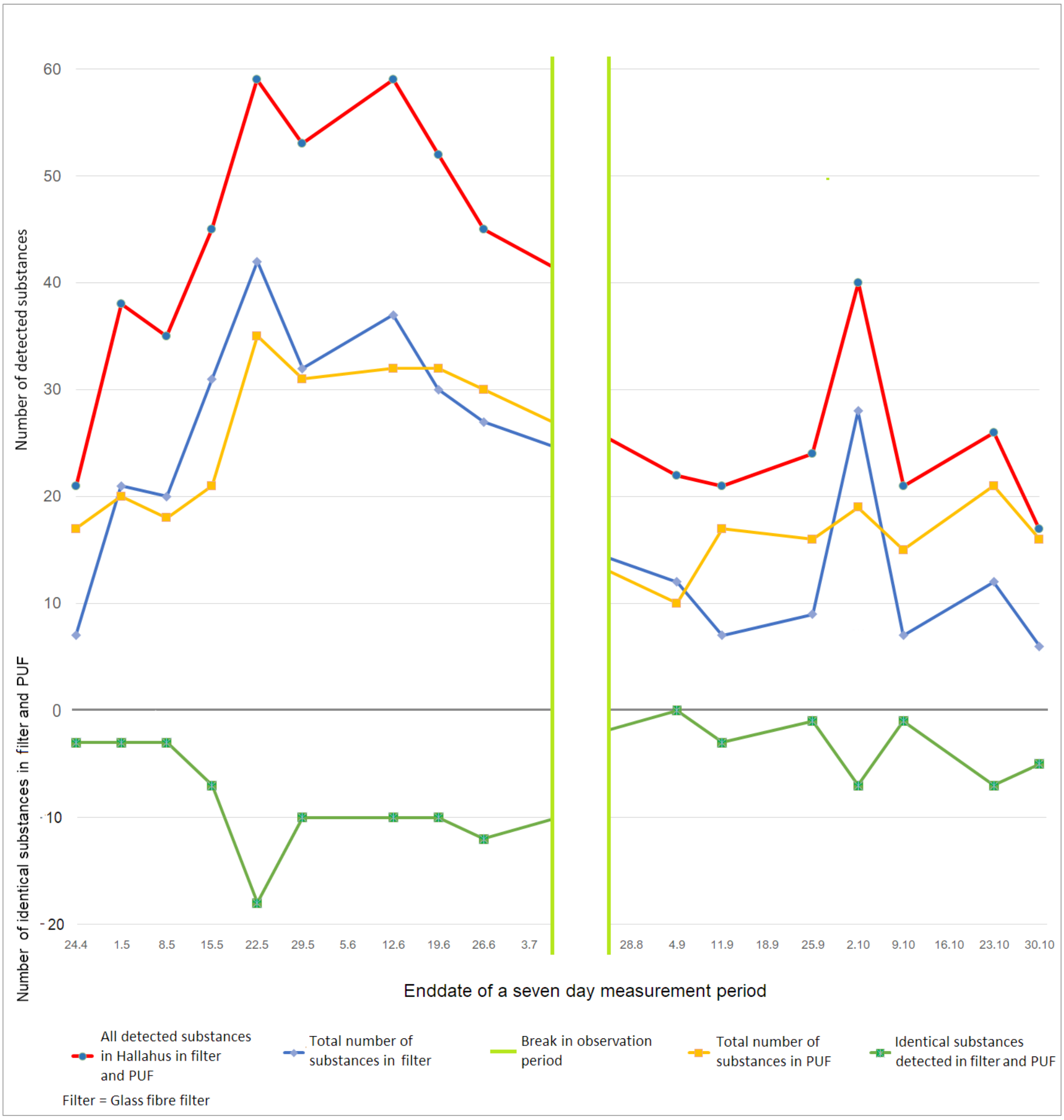

Figure 8: Number of substances detected by active air sampling in Hallahus, Sweden, in 2017 [3]

F, testing cartridge; P, pesticides; PUF, polyurethane foam (first section of the testing cartridge).The red line represents all substances detected in Hallahus, Sweden. The number was calculated by adding the total number of substances detected in the glass fibre filter (blue line) and the total number of substances detected in the PUF (yellow line). The number of identical substances detected in both glass fibre filter and PUF (green line) was then substracted from in the total to remove duplicates.

The Swedish data display a clear seasonal variation, with the number of substances detected decreasing in autumn (Additional File 14). A weekly maximum of 59 substances was detected twice in the first half of the year. In autumn (October 30, 2017), only 17 substances remained. The median over the measurement period was 36.5 for all substances in the glass fibre filter and PUF. Prosulfocarb and ɣ-HCH were detected consistently throughout the year [2]. Chlorpyrifos, propyzamide, and triallate were also detected during much of the year. In areas of intensive agriculture in Germany, a continuous presence of pesticide mixtures in ambient air is therefore highly likely and should be the subject of further investigation.

Comparing Swedish data with results from passive air samplers and filter mats

The two sampling methods in our study are likely to reflect airborne pesticides and their related products from differing origins. The PUF disk in the passive air sampler is designed to sample volatile and semi-volatile substances and exclude particles [28], while filter mats capture dust and sometimes pollen. Therefore, filter mats capture a different spectrum of substances. Twenty-nine substances in filter mats were not detected in the passive air samplers, while 44 substances were detected only in the passive air samplers and not in filter mats. However, while we assess these methods separately, the Swedish study [2] [3] measured substances in glass fibre and PUF simultaneously. The number of substances detected in the Swedish study [2] [3] peaked at 59. In one example, 37 substances were detected in the glass fibre filter and 32 in the PUF. The number of substances detected by both methods, in this case 10, is subtracted from the total to remove duplicates. We detected 36 substances in filter mats and 33 in PUF, much lower than the 59 detected in Sweden in glass fibre filters and PUF at a peak period. The pesticide load at any one point in Germany might therefore be significantly higher than our findings indicate.

Long-range transport

According to Kreuger and Lindström [2], many of the substances they detected did not originate in Sweden, as they are not authorised for use there, suggesting long-range transport. In Germany, which is centrally located in Europe, similar mechanisms are likely.

For instance, we detected chlorpyrifos at several eastern and western sites [16], although the use of chlorpyrifos is not permitted in Germany.

Additional File 15 contains the EFSA conclusions on the potential for volatilisation and long-range transport of the most widely detected pesticides in this study (glyphosate, metolachlor, pendimethalin, terbuthylazine, and prosulfocarb). Their vapour pressure classifies all of them as having low volatility [16], with the exception of metolachlor, which is of medium volatility. EFSA maintains that a substantial loss of active substance to the air is not to be expected; a loss to the air over the short range is only considered for pendimethalin. The potential for long-range transport is disregarded entirely. In view of our findings, the assumptions incorporated into the approval processes concerning the release of pesticides to the air are not adequate. There is a need to revise current EFSA estimates of pesticide releases and long-range air transport. This is particularly relevant for the renewal of the approval for glyphosate.

The findings indicate that a certain degree of intercontinental transport is also likely. Therefore, current-use pesticides can be expected to travel far from their application sites and be present in any air mass passing over land. However, at this point we are not aware of any scientific data on this matter.

Glyphosate, pendimethalin, and prosulfocarb

We detected glyphosate in all passive air samplers and filter mats, not surprisingly as it is the most widely used plant-protection product in Germany [29]. In France, a comprehensive study [4] collected airborne pesticides using Partisol™ Sequential Air Samplers for particulate matter. Glyphosate was detected in over 80% of samples, which were collected at a flow rate of 30 m³/h over 48 h. The findings of that study suggest that pesticides are generally present in ambient air.

Pendimethalin and prosulfocarb were of special interest in the present study because of their effects on organic farming. Organic products contaminated with these two pesticides to the extent that they could not be marketed as organic have been reported [11]. In consequence, organic farmers in Bavaria, where our study did not record exceptionally high values of these substances, refrain from growing sensitive crops such as herbs [30]. Overall, we detected pendimethalin and prosulfocarb in over four fifths of the samples and at high levels. The long-distance transport of these pesticides is clearly illustrated by Kreuger and Lindström [2], who found pendimethalin in nearly 40% of all samples even though this pesticide is not approved for use in Sweden and probably originated in neighbouring countries such as Denmark, Germany, and Poland. Prosulfocarb was detected frequently and at high concentrations, ranging from below 0.01 ng/m³ to 10 µg/m³ (maximum recorded: 30 µg/m³).

In France [4], pendimethalin is approved for use and was detected in more than 70% of samples. Prosulfocarb was detected at around 40% of sampling sites and exhibited the highest air concentrations (≥2 ng/m³), followed by pendimethalin and folpet (both ≥0.5 ng/m³). It should be noted here that the sampling rate used in the French study was lower (1 m³/h over 7 days for pesticides other than glyphosate) than in Sweden (400 m³/d over 7 days), perhaps accounting for the relatively low levels recorded.

Conclusion

Our findings indicate that pesticides and their related substances are ubiquitously present in ambient air in the Federal Republic of Germany. This has long been known for substances listed under the Stockholm Convention, such as DDT, PCBs, and γ-HCH. For pesticides and their related substances in current use, this is demonstrated to this extent in Germany for the first time. The findings show clearly that more than one substance is present in sometimes considerable loads at any location. Active monitoring of the airborne concentrations of these substances is therefore required, especially for glyphosate. This has, so far, not been considered significant in the pesticide approval procedure used by EFSA [31] [32], which underestimates the loss of pesticides to the atmosphere and their potential for long-range transport. Accordingly, the EFSA pesticide approval procedure should be revised. The lack of data does not permit conclusions about the health effects of inhalational exposure to pesticide mixtures, which is likely ongoing and must be investigated. Similarly, effects on sensitive ecosystems require further study. In addition to potential health and ecological effects, the concentrations of pesticides in ambient air also exert significant economic consequences. European Commission regulation 834/2007 governs the control of organic agriculture and its products to ensure that synthetic chemical additives such as pesticides and fertilisers do not interfere with the production process. However, organic farmers cannot protect their crops against air pollution by pesticides such as pendimethalin and prosulfocarb, which results in produce that cannot be marketed as organic. Initiatives to reduce pesticide use in conventional agriculture [33] would be an important first step in mitigating the economic losses to organic farmers and the potential health or ecosystem effects. For pendimethalin and prosulfocarb, which have already affected organic farmers in Germany, a search for alternatives is necessary if the European Union’s goal of coexistence anchored in EC Basic Organic Regulation No. 834/2007 between conventional and organic forms of production is to apply.

Abbreviations

AMPA, aminomethylphosphonic acid; BVL, Bundesamt für Verbraucherschutz und Lebensmittelsicherheit (Federal Office of Consumer Protection and Food Safety); DCBP-pp, dichlorobenzophenone; DDT, dichlorodiphenyltrichloroethane; EFSA, European Food Safety Authority; GAPS, Global Atmospheric Passive Sampling; HCB, hexachlorobenzene; ɣ-HCH, gamma-hexachlorocyclohexane; MCPA, 2-Methyl-4-chlorophenoxyacetic acid; PBO, piperonyl butoxide; PEF, polyester filter; POP, Persistent Organic Pollutants; PUF, polyurethane foam.

Supplementary information

Additional File 1. Vapour pressure categories for pesticides and estimated effects on air concentrations used by the EFSA.

Additional File 2. Active substance, active substance classes, and quantification limits (mg/kg) in routine examination to determine pesticide residues according to ASU L 00.00-115 for materials from agriculture and horticulture with a low content of fat.

Additional File 3. List of pesticides and related substances registered in ASU L 00.00-115 with no or not entirely agricultural origin. See also Additional Files 4 and 6.

Additional File 4. Pesticides and related substances detected in passive air samplers, including DCBP-pp, HCB, PBO, and five PCBs.

Additional File 5. Ventilation systems using filter mats in this study.

Additional File 6. Pesticides and related substances detected in filter mats, including anthraquinone and PBO.

Additional File 7. Sampling site characteristics.

Additional File 8. Distribution of site characteristics in 49 passive air sampler sites.

Additional file 9. Distribution of site characteristics in 20 filter mat sites.

Additional File 10. Substances detected in passive air samplers (PAS) and filter mats (FM).

Additional File 11. Figure S1: Aerial view of sampling site 1007-748 (Bayerischer Wald national park). Figure S2: Aerial view of sampling site 1000-740 (Brockengarten in the Harz national park).

Additional File 12. Results of the statistical analysis for the number of substances detected in passive air samplers given as a regression tree.

Additional File 13. Regression trees of pesticides and related substances frequently detected in passive air samplers without reference in the main text.

Additional File 14. Data sheets on substances detected in Hallahus, Sweden, in 2017.

Additional File 15. Vapour pressure and EFSA conclusions on the potential volatilisation and capacity for long-range transport of active substances frequently detected in the present study.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

This publication draws on the results of measurements taken in Sweden that are available to the public via the website of Swedish University of Agricultural Sciences at https://www.slu.se/en/departments/aquatic-sciences-assessment/environment/pesticide_monitoring/pesticide_data/.

Availability of data and material

The datasets generated and/or analysed during the current study are available at https://www.enkeltauglich.bio/supplementing-data-enscieu.

Competing interests

The authors declare that they have no competing interests.

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Author contributions

All authors made substantial and equal contributions to the manuscript. All authors read and approved the final manuscript, with the exception of Frieder Hofmann, the founder of TIEM Environmental Monitoring and head of this project, who passed away from cancer before the manuscript was finalised.

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Figures

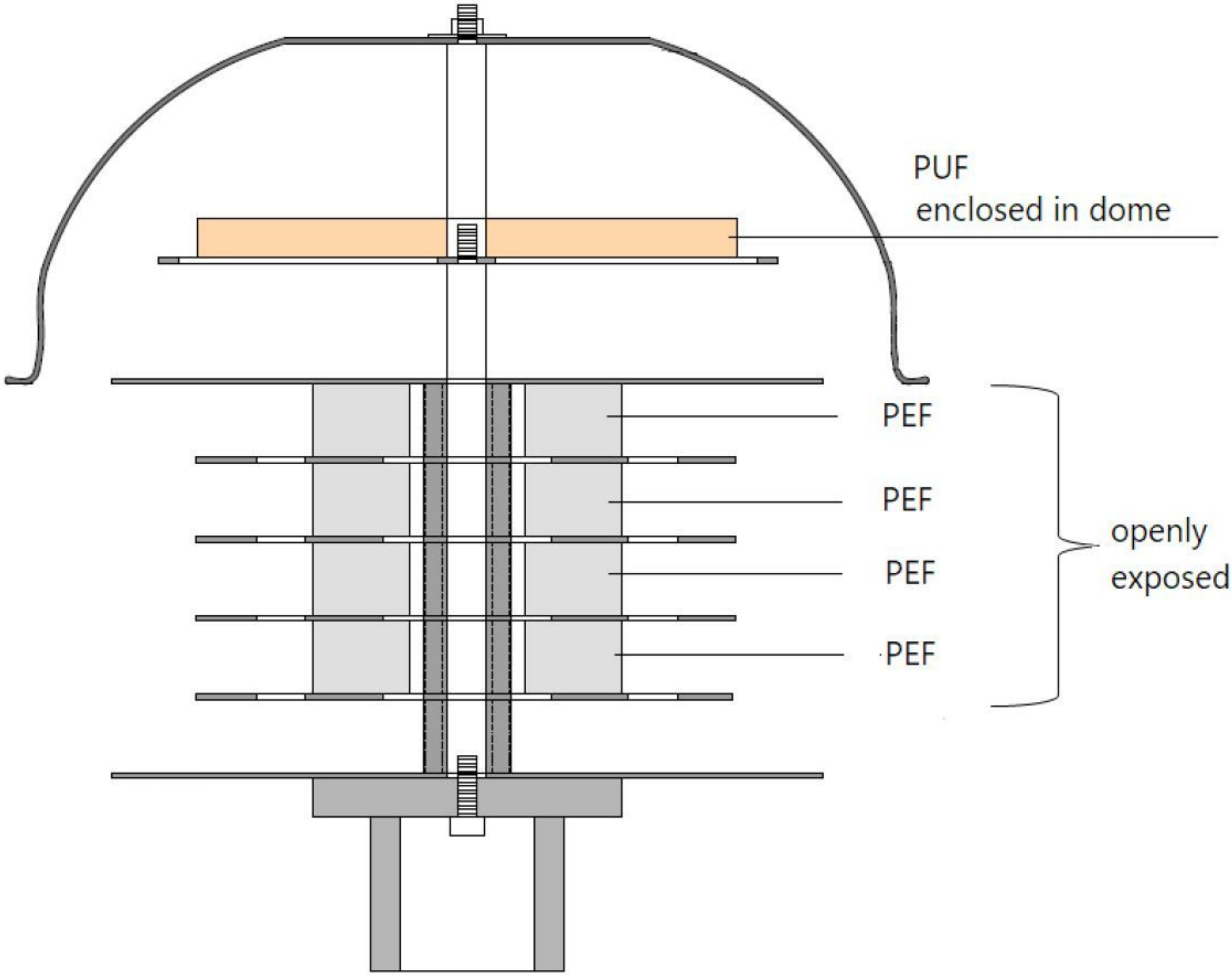

Figure 1

Passive air sampler developed by TIEM technic

Figure 2

Example of a passive air sampler in the field

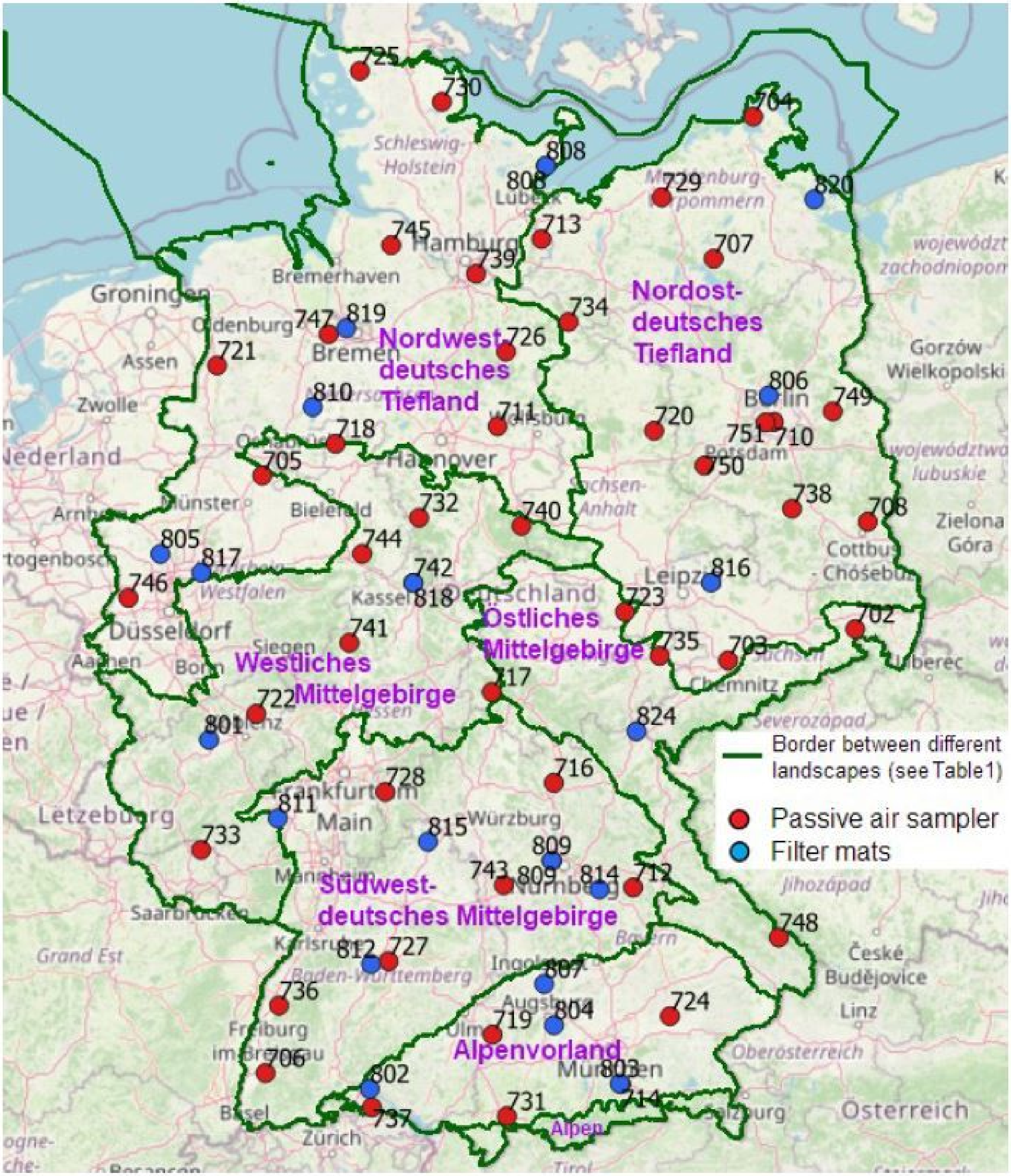

Figure 3

Location of sampling sites (passive air samplers and filter mats) Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

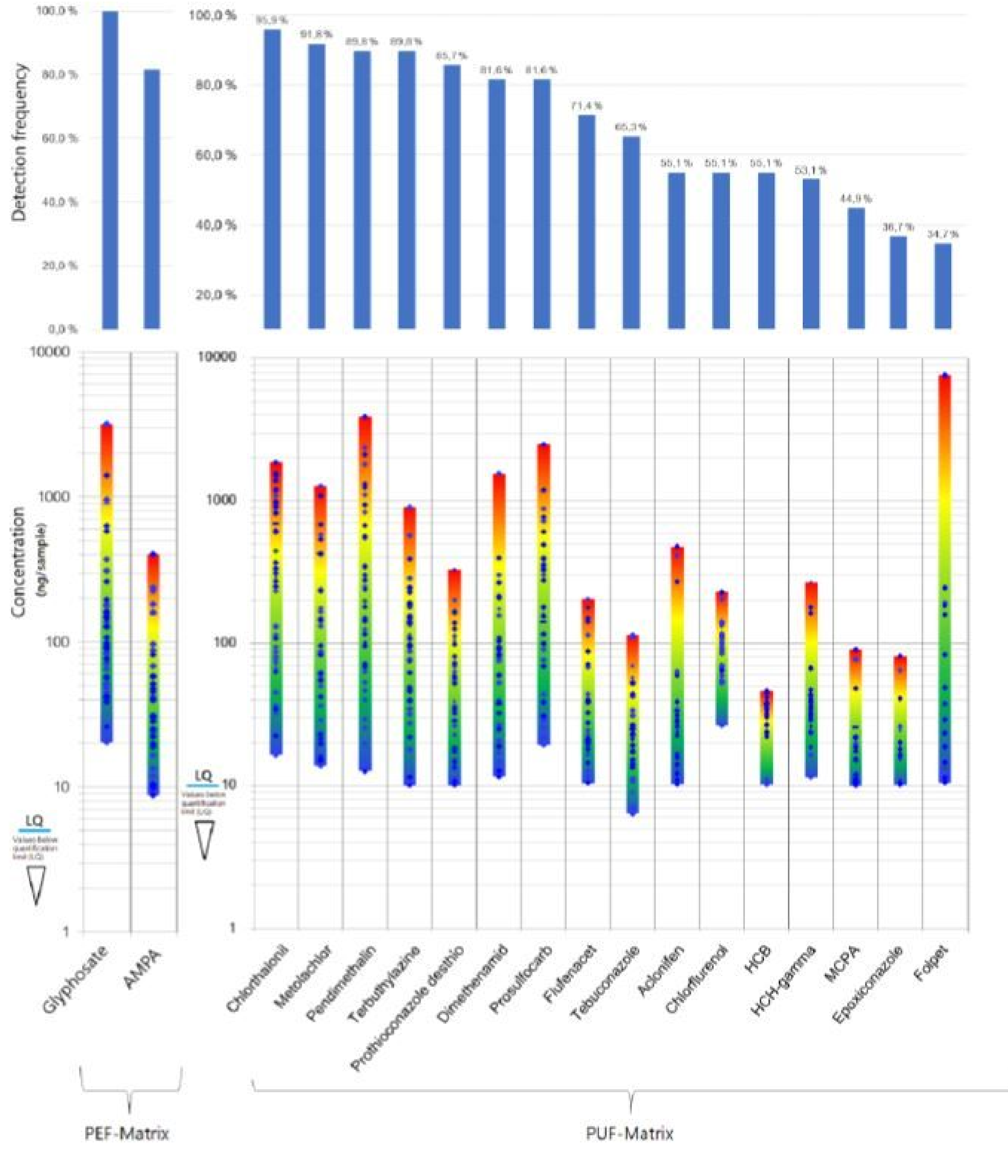

Figure 4

Most commonly detected pesticides and related products in passive air samplers

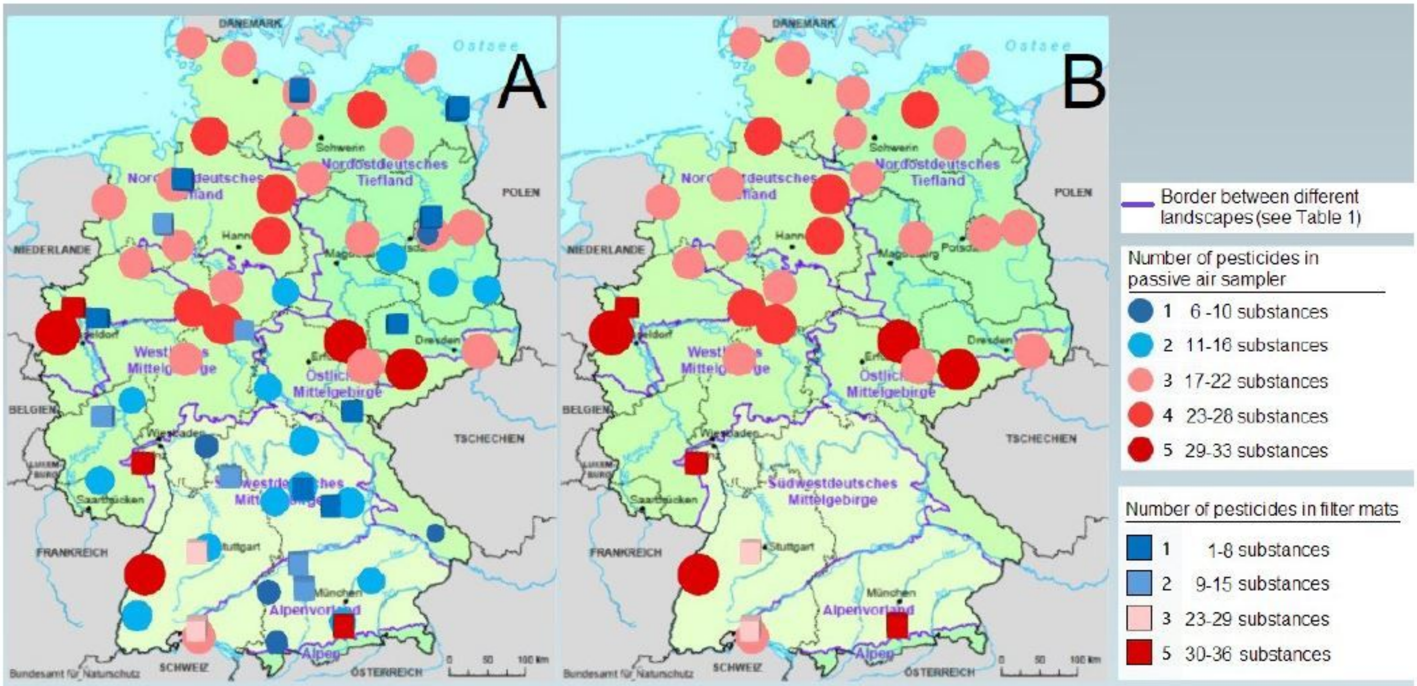

Figure 5

Number of substances detected at sampling sites. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

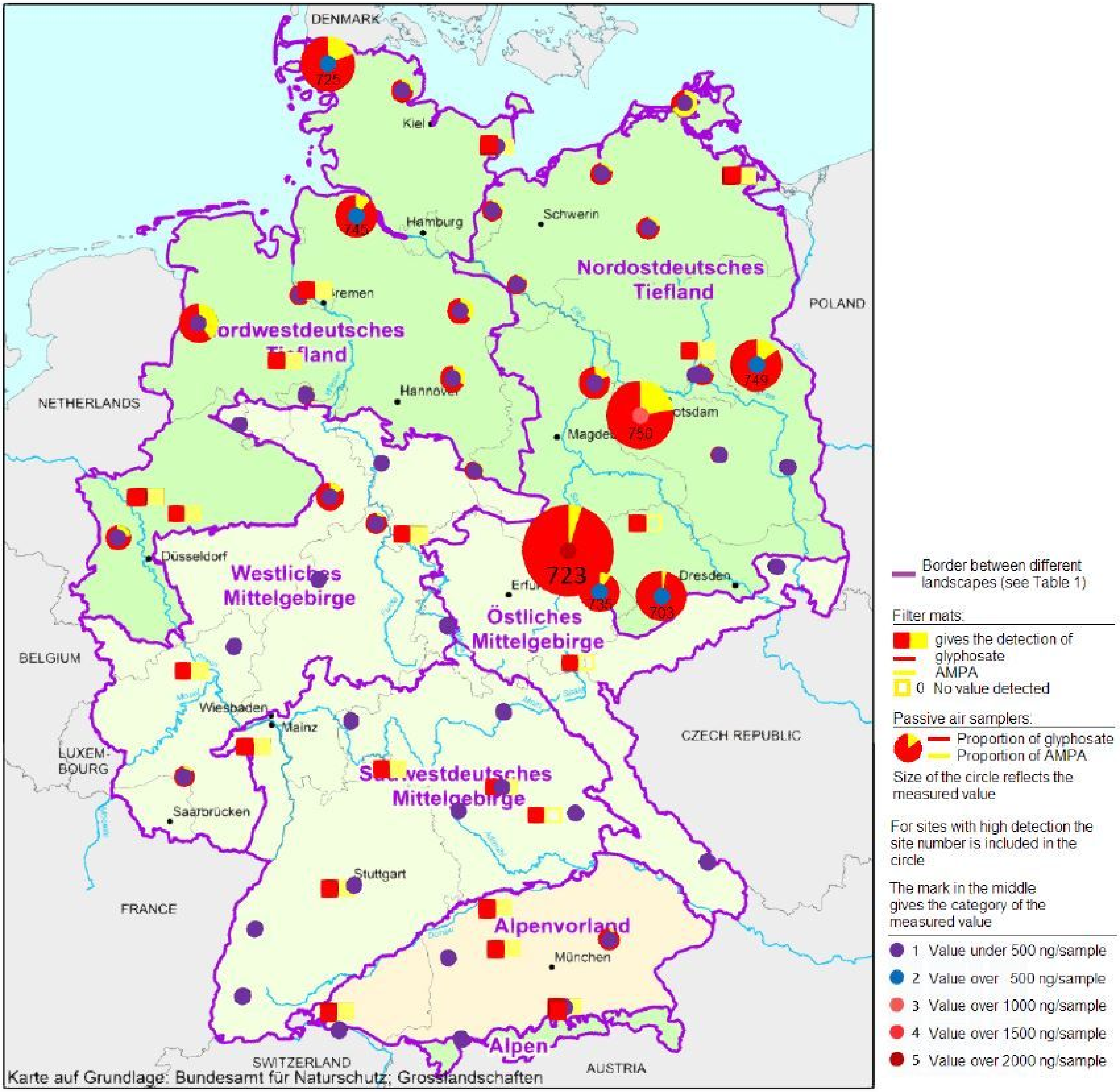

Figure 6

Levels of glyphosate and aminomethylphosphonic acid (AMPA) Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

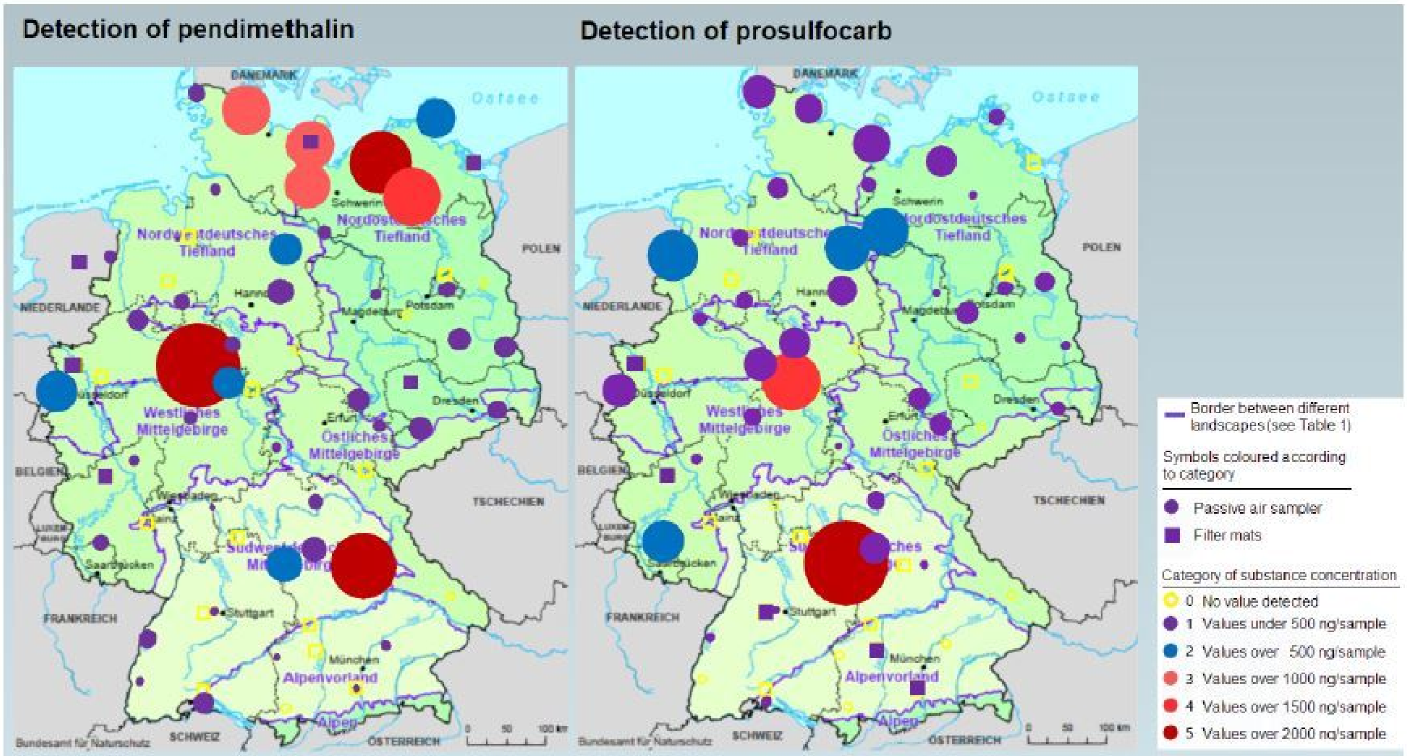

Figure 7

Levels of pendimethalin and prosulfocarb Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

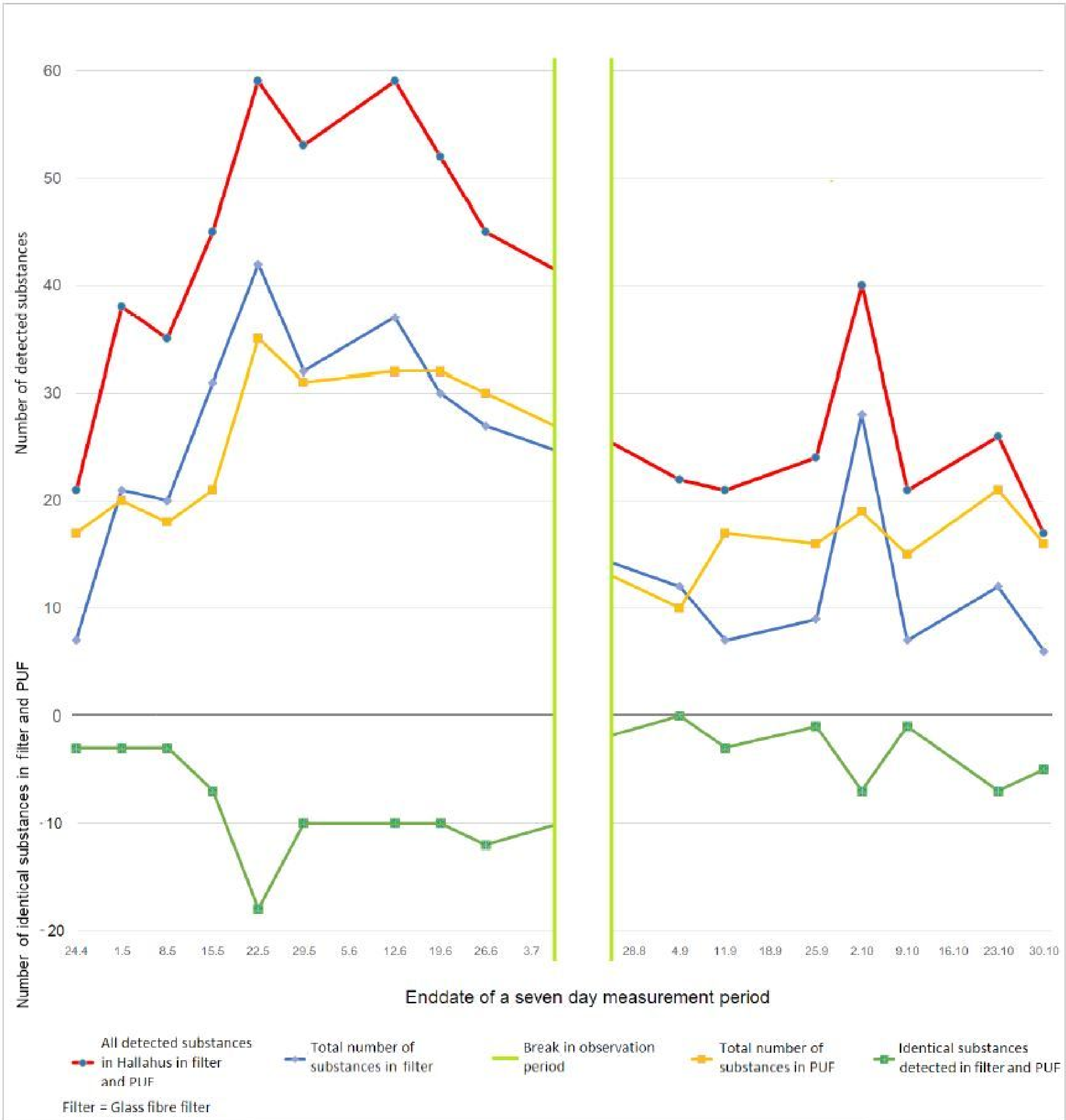

Figure 8

Number of substances detected by active air sampling in Hallahus, Sweden, in 2017 [3]

Supplementary Files

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