

# Supplementary Information (SI)

## Direct pesticide exposure of insects in nature conservation areas in Germany

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## Tables

Table A1 Description of the 21 study sites.

| Nr. | Location                      | State | FFH-ID *1 | FFH Area [ha] *1 | NSG-ID *2 | NSG Area [ha] *2 | Altitude [m a.s.l.] | X-Coord. [°] *3 | Y-Coord. [°] *3 | Protected habitat types (the transect is crossing) *4                                                 | Natura2000-code *4 |
|-----|-------------------------------|-------|-----------|------------------|-----------|------------------|---------------------|-----------------|-----------------|-------------------------------------------------------------------------------------------------------|--------------------|
| 1   | Lütjenholmer Heidedünen       | SH    | 1320-302  | 313              | 37570     | 18               | 5                   | 90.624          | 546.991         | Dry sand heaths with <i>Calluna</i> and <i>Genista</i>                                                | 2310               |
|     |                               |       |           |                  |           |                  |                     |                 |                 | Northern Atlantic wet heaths with <i>Erica tetralix</i>                                               | 4010               |
| 2   | Riedensee                     | MV    | 1836-301  | 113              | 33182     | 120              | 2                   | 116.835         | 541.527         | Xeric sand calcareous grasslands                                                                      | 6120               |
| 3   | Insel Koos                    | MV    | 1747-301  | 60406            | 33165     | 1574             | 2                   | 134.019         | 541.615         | Lowland hay meadows                                                                                   | 6510               |
| 4   | Geesower Hügel                | BB    | 2752-301  | 82               | 30009     | 39               | 20                  | 143.918         | 532.391         | Xeric sand calcareous grasslands                                                                      | 6120               |
|     |                               |       |           |                  |           |                  |                     |                 |                 | Sub-pannonic steppic grasslands                                                                       | 6240               |
| 5   | Oderhänge Mallnow             | BB    | 3552-306  | 305              | 30118     | 305              | 15                  | 144.675         | 524.740         | Xeric sand calcareous grasslands                                                                      | 6120               |
|     |                               |       |           |                  |           |                  |                     |                 |                 | Sub-pannonic steppic grasslands                                                                       | 6240               |
| 6   | Wisseler Dünen                | NW    | 4203-301  | 71               | 35714     | 79               | 15                  | 63.012          | 517.699         | Inland dunes with open <i>Corynephorus</i> and <i>Agrostis</i> grasslands                             | 2330               |
| 7   | Bislicher Insel               | NW    | 4305-301  | 1002             | 36965     | 1053             | 20                  | 65.114          | 516.483         | Rivers with muddy banks with Bidention-Vegetation                                                     | 3270               |
|     |                               |       |           |                  |           |                  |                     |                 |                 | Hydrophilous tall herb fringe communities of plains                                                   | 6430               |
| 8   | Gipskarstlandschaft Hainholz  | NI    | 4226-301  | 1327             | 33265     | 641              | 20                  | 102.659         | 516.870         | Lowland hay meadows                                                                                   | 6510               |
| 9   | Porphyrlandschaft bei Gimritz | ST    | 4437-302  | 819              | 38460     | 288              | 100                 | 118.478         | 515.668         | Sub-pannonic steppic grasslands                                                                       | 6240               |
|     |                               |       |           |                  |           |                  |                     |                 |                 | Siliceous rock with pioneer vegetation                                                                | 8230               |
| 10  | Ziegenbuschhänge bei Oberau   | SN    | 4847-301  | 112              | 37981     | 20               | 155                 | 135.577         | 511.947         | Lowland hay meadows                                                                                   | 6510               |
| 11  | Wipperdurchbruch              | TH    | 4631-302  | 6869             | 38140     | 672              | 285                 | 110.497         | 513.190         | Semi-natural (semi-)dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia) | 6210               |

Table A1 (cont.) Description of the 21 study sites.

| Nr. | Location                     | State | FFH-ID *1 | FFH Area [ha] *1 | NSG-ID *2 | NSG Area [ha] *2 | Altitude [m a.s.l.] | X-Coord. [°] *3 | Y-Coord. [°] *3 | Protected habitat types (the transect is crossing) *4                                                 | Natura2000-code *4 |
|-----|------------------------------|-------|-----------|------------------|-----------|------------------|---------------------|-----------------|-----------------|-------------------------------------------------------------------------------------------------------|--------------------|
| 12  | Bottendorfer Hügel           | TH    | 4634-303  | 133              | 38143     | 134              | 195                 | 114.070         | 513.143         | Calaminarian grasslands of the <i>Violetalia calaminariae</i>                                         | 6130               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Sub-pannonic steppic grasslands                                                                       | 6240               |
| 13  | Schwellenburg                | TH    | 4931-301  | 89               | 38111     | 23               | 210                 | 109.567         | 510.330         | Rupicolous calcareous or basiphilic grassland of the <i>Alyso-Sedion albi</i>                         | 6110               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Sub-pannonic steppic grasslands                                                                       | 6240               |
| 14  | Hofberg                      | TH    | 5327-305  | 260              | 38319     | 43               | 430                 | 102.285         | 506.975         | Rupicolous calcareous or basiphilic grassland of the <i>Alyso-Sedion albi</i>                         | 6110               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Semi-natural dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia)        | 6210               |
| 15  | Koppelstein - Helmestel      | RP    | 5711-301  | 4551             | 37188     | 87               | 160                 | 76.321          | 502.905         | Semi-natural (semi-)dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia) | 6210               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Lowland hay meadows                                                                                   | 6510               |
| 16  | Rueinhänge Dorscheider Heide | RP    | 5711-301  | 4551             | 37186     | 626              | 220                 | 77.488          | 501.158         | European dry heaths                                                                                   | 4030               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Siliceous rock with pioneer vegetation of the Sedo-Scleranthion                                       | 8230               |
| 17  | Brauselay                    | RP    | 5809-301  | 16273            | 37136     | 14               | 240                 | 71.848          | 501.437         | Subcontinental peri-pannonic scrub                                                                    | 40A0               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Stable xerothermophilous formations with <i>Buxus sempervirens</i> on rock slopes (Berberidion)       | 5110               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Silicate rocks with pioneer grassland                                                                 | 8230               |
|     |                              |       |           |                  |           |                  |                     |                 |                 | Tilio-Acerion forests of slopes, screes and ravines                                                   | 9180               |

Table A1 (cont.) Description of the 21 study sites.

| Nr. | Location         | State | FFH-ID *1 | FFH Area [ha] *1 | NSG-ID *2 | NSG Area [ha] *2 | Altitude [m a.s.l.] | X-Coord. [°] *3 | Y-Coord. [°] *3 | Protected habitat types (the transect is crossing) *4                                                 | Natura2000-code *4 |
|-----|------------------|-------|-----------|------------------|-----------|------------------|---------------------|-----------------|-----------------|-------------------------------------------------------------------------------------------------------|--------------------|
| 18  | Mittelberg       | BW    | 7319-341  | 853              | 30714     | 45               | 460                 | 88.853          | 487.456         | Semi-natural (semi-)dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia) | 6210               |
| 19  | Ipf              | BW    | 7327-341  | 3363             | 30585     | 60               | 650                 | 103.585         | 488.713         | <i>Juniperus communis</i> formations on calcareous grasslands                                         | 5130               |
|     |                  |       |           |                  |           |                  |                     |                 |                 | Semi-natural dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia)        | 6210               |
| 20  | Kürnberg         | BW    | 7427-341  | 990              | 30689     | 12               | 510                 | 102.485         | 486.440         | <i>Juniperus communis</i> formations on calcareous grasslands                                         | 5130               |
|     |                  |       |           |                  |           |                  |                     |                 |                 | Semi-natural (semi-)dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia) | 6210               |
| 21  | Mühlhauser Halde | BW    | 7916-311  | 3678             | 31149     | 52               | 720                 | 85.864          | 480.557         | <i>Juniperus communis</i> formations on calcareous grasslands                                         | 5130               |
|     |                  |       |           |                  |           |                  |                     |                 |                 | Semi-natural (semi-)dry grasslands and scrubland facies on calcareous substrates (Festuco-Brometalia) | 6210               |

\*1 <https://www.bfn.de/themen/natura-2000/natura-2000-gebiete/steckbriefe.html#c33722>

\*2 <https://geodienste.bfn.de/schutzgebiete?lang=de&layers=NSG>

\*3 Reference system DHDN, Gauß-Krüger Zone 3.

\*4 EC European Commission (2013): EUR 28 Interpretation Manual of European Union habitats. [https://ec.europa.eu/environment/nature/legislation/habitatsdirective/docs/Int\\_Manual\\_EU28.pdf](https://ec.europa.eu/environment/nature/legislation/habitatsdirective/docs/Int_Manual_EU28.pdf)

*Table A2 Method limits of quantitation (MQL) and method limits of detection (MDL) for all 92 analytes.*

| <b>Substance</b>         | <b>CAS</b>  | <b>MQL (µg/l)</b> | <b>MDL (µg/l)</b> |
|--------------------------|-------------|-------------------|-------------------|
| <i><b>Herbicides</b></i> |             |                   |                   |
| 2,4-D                    | 94-75-7     | 0.0798            | 0.0264            |
| Aminopyralid             | 150114-71-9 | 0.0058            | 0.0018            |
| Bentazone                | 25057-89-0  | 0.0028            | 0.001             |
| Bromoxynil               | 1689-84-5   | 0.0042            | 0.0014            |
| Carfentrazone-ethyl      | 128621-72-7 | 0.1194            | 0.0394            |
| Chloridazon              | 1698-60-8   | 0.0012            | 0.0004            |
| Chlortoluron             | 15545-48-9  | 0.0006            | 0.0002            |
| Clomazone                | 81777-89-1  | 0.0018            | 0.0006            |
| Diflufenican             | 83164-33-4  | 0.0006            | 0.0002            |
| Dimethenamid-P           | 163515-14-8 | 0.0006            | 0.0002            |
| Ethofumesate             | 26225-79-6  | 0.0242            | 0.008             |
| Flazasulfuron            | 104040-78-0 | 0.005             | 0.0016            |
| Florasulam               | 145701-23-1 | 0.046             | 0.0152            |
| Flufenacet               | 142459-58-3 | 0.0032            | 0.001             |
| Fluroxypyr               | 69377-81-7  | 0.043             | 0.0142            |
| Flurtamone               | 96525-23-4  | 0.0006            | 0.0002            |
| Foramsulfuron            | 173159-57-4 | 0.0068            | 0.0022            |
| Isoproturon              | 34123-59-6  | 0.0008            | 0.0002            |
| Lenacil                  | 2164-08-1   | 0.03              | 0.01              |
| MCPA                     | 94-74-6     | 0.0796            | 0.0262            |
| Metamitron               | 41394-05-2  | 0.006             | 0.002             |
| Metazachlor              | 67129-08-2  | 0.0032            | 0.001             |
| Metobromuron             | 3060-89-7   | 0.003             | 0.001             |
| Metolachlor-S            | 87392-12-9  | 0.0014            | 0.0004            |
| Metsulfuron-methyl       | 317815-83-1 | 0.0154            | 0.0052            |
| Napropamide              | 15299-99-7  | 0.0004            | 0.0002            |
| Pendimethalin            | 40487-42-1  | 0.0058            | 0.002             |
| Picloram                 | 1918-02-1   | 0.1044            | 0.0344            |
| Propaquizafop            | 111479-05-1 | 0.0008            | 0.0002            |
| Propyzamide              | 23950-58-5  | 0.0046            | 0.0016            |
| Prosulfocarb             | 52888-80-9  | 0.001             | 0.0004            |
| Quinmerac                | 90717-03-6  | 0.0006            | 0.0002            |
| Quizalofop-P             | 94051-08-8  | 0.1862            | 0.0614            |
| Terbuthylazine           | 5915-41-3   | 0.0064            | 0.0022            |
| Tribenuron-methyl        | 101200-48-0 | 0.0124            | 0.004             |
| Tritosulfuron            | 142469-14-5 | 0.096             | 0.0316            |

Table A2. (cont.) Method limits of quantitation (MQL) and method limits of detection (MDL) for all 92 analytes.

| Substance         | CAS         | MQL (µg/l) | MDL (µg/l) |
|-------------------|-------------|------------|------------|
| <i>Fungicides</i> |             |            |            |
| Azoxystrobin      | 131860-33-8 | 0.0018     | 0.0006     |
| Benalaxyl         | 71626-11-4  | 0.001      | 0.0004     |
| Bixafen           | 581809-46-3 | 0.0008     | 0.0002     |
| Boscalid          | 188425-85-6 | 0.0052     | 0.0016     |
| Cyazofamid        | 120116-88-3 | 0.0542     | 0.0178     |
| Cyflufenamid      | 180409-60-3 | 0.0298     | 0.0098     |
| Cymoxanil         | 57966-95-7  | 0.008      | 0.0026     |
| Cyprodinil        | 121552-61-2 | 0.0092     | 0.003      |
| Difenconazole     | 119446-68-3 | 0.0042     | 0.0014     |
| Dimethomorph      | 110488-70-5 | 0.0044     | 0.0014     |
| Dimoxystrobin     | 149961-52-4 | 0.0006     | 0.0002     |
| Epoxiconazole     | 135319-73-2 | 0.0032     | 0.001      |
| Fenoxycarb        | 79127-80-3  | 0.0024     | 0.0008     |
| Fenpropimorph     | 67564-91-4  | 0.0062     | 0.002      |
| Fluazinam         | 79622-59-6  | 0.0048     | 0.0016     |
| Fludioxonil       | 131341-86-1 | 0.0224     | 0.0074     |
| Fluopicolid       | 239110-15-7 | 0.0034     | 0.0012     |
| Fluopyram         | 658066-35-4 | 0.0016     | 0.0006     |
| Iprovalicarb      | 140923-17-7 | 0.0016     | 0.0006     |
| Kresoxim methyl   | 143390-89-0 | 0.0058     | 0.002      |
| Mandipropamid     | 374726-62-2 | 0.007      | 0.0022     |
| Metalaxyl-M       | 70630-17-0  | 0.0016     | 0.0006     |
| Metconazole       | 125116-23-6 | 0.0008     | 0.0002     |
| Metrafenone       | 220899-03-6 | 0.0014     | 0.0004     |
| Myclobutanil      | 88671-89-0  | 0.0018     | 0.0006     |
| Paclobutrazol     | 76738-62-0  | 0.0032     | 0.001      |
| Penconazole       | 66246-88-6  | 0.0024     | 0.0008     |
| Pencycuron        | 66063-05-6  | 0.0008     | 0.0002     |
| Picoxystrobin     | 117428-22-5 | 0.0008     | 0.0002     |
| Prochloraz        | 67747-09-5  | 0.006      | 0.002      |
| Propamocarb       | 24579-73-5  | 0.001      | 0.0004     |
| Proquinazid       | 189278-12-4 | 0.0014     | 0.0004     |
| Prothioconazole   | 178928-70-6 | 0.1118     | 0.0368     |
| Pyraclostrobin    | 175013-18-0 | 0.001      | 0.0004     |
| Pyrimethanil      | 53112-28-0  | 0.0034     | 0.0012     |
| Spiroxamine       | 118134-30-8 | 0.0024     | 0.0008     |
| Tebuconazole      | 107534-96-3 | 0.0132     | 0.0044     |
| Trifloxystrobin   | 141517-21-7 | 0.0018     | 0.0006     |

Table A2. (cont.) Method limits of quantitation (MQL) and method limits of detection (MDL) for all 92 analytes.

| Substance                              | CAS         | MQL (µg/l) | MDL (µg/l) |
|----------------------------------------|-------------|------------|------------|
| <b><i>Insecticides, Acaricides</i></b> |             |            |            |
| Acetamiprid                            | 135410-20-7 | 0.001      | 0.0004     |
| Avermectin B1a                         | 65195-55-3  | 0.13       | 0.0428     |
| Chlorantraniliprole                    | 500008-45-7 | 0.0014     | 0.0004     |
| Clothianidin                           | 210880-92-5 | 0.007      | 0.0024     |
| Dimethoate                             | 60-51-5     | 0.0006     | 0.0002     |
| Etofenprox                             | 80844-07-1  | 0.001      | 0.0004     |
| Fenpyroximate                          | 111812-58-9 | 0.001      | 0.0004     |
| Flonicamid                             | 158062-67-0 | 0.0066     | 0.0022     |
| Hexythiazox                            | 78587-05-0  | 0.0016     | 0.0006     |
| Imidacloprid                           | 138261-41-3 | 0.0056     | 0.0018     |
| Indoxacarb                             | 173584-44-6 | 0.0034     | 0.0012     |
| Methiocarb                             | 2032-65-7   | 0.0024     | 0.0008     |
| Pirimicarb                             | 23103-98-2  | 0.0014     | 0.0004     |
| Pymetrozine                            | 123312-89-0 | 0.0012     | 0.0004     |
| Spinosad A                             | 131929-90-7 | 0.001      | 0.0004     |
| Spinosad D                             | 131929-63-0 | 0.0074     | 0.0024     |
| Tebufenozide                           | 112410-23-8 | 0.0018     | 0.0006     |
| Thiacloprid                            | 111988-49-9 | 0.0004     | 0.0002     |
| Thiamethoxam                           | 153719-23-4 | 0.0066     | 0.0022     |
| <b><i>Biocides (metabolites)</i></b>   |             |            |            |
| Fipronil desulfinyl                    | 205650-65-3 | 0.0034     | 0.0012     |
| Fipronil                               | 120068-37-3 | 0.0128     | 0.0042     |
| Fipronil sulfone                       | 120068-36-2 | 0.0044     | 0.0014     |

*Table A3. Soil half-lives and volume sold for use in 2019 for most commonly detected CUPs (H = Herbicide, F = Fungicide, I = Insecticide). Use volume for 2019 was extracted from BVL 2021, rank was calculated without carbon dioxide. T a.i. = metric tons of active ingredient.*

| group | substance       | presence |       | soil half life |       |       | persistence     | use 2019 |      | remarks            |
|-------|-----------------|----------|-------|----------------|-------|-------|-----------------|----------|------|--------------------|
|       |                 | in       | sites | DT50           | DT50  | DT50  |                 | in t a.i | rank |                    |
|       |                 | (of 21)  |       | typical        | lab   | field | interpretation  |          |      |                    |
| H     | Metolachlor-S   | 21       |       | 90             | 15    | 21    | moderate        | 573.6    | 14   |                    |
| H     | Prosulfocarb    | 21       |       | 11.9           | 11.9  | 9.8   | no              | 966.5    | 7    |                    |
| H     | Terbuthylazine  | 21       |       | 72             | 72    | 21.8  | moderate        | 972.9    | 6    |                    |
| H     | Dimethenamid-P  | 17       |       | 11             | 12.1  | 15.8  | no              | 594.0    | 13   |                    |
| H     | Flufenacet      | 14       |       | 19.7           | 19.7  | 39    | no              | 650.4    | 11   |                    |
| H     | Diflufenican    | 13       |       | 94.5           | 94.5  | 64.6  | moderate        | 303.7    | 21   |                    |
| F     | Azoxystrobin    | 21       |       | 78             | 84.5  | 180.7 | persistent      | 330.7    | 19   |                    |
| F     | Fluopyram       | 21       |       | 309            | 309   | 118.8 | persistent      | 82,8     | 65   |                    |
| F     | Pyraclostrobin  | 17       |       | 41.9           | 41.9  | 33.3  | moderate        | 74,5     | 67   |                    |
| F     | Bixafen         | 15       |       | 500            | 500   | 254   | very persistent | 84.4     | 62   |                    |
| F     | Boscalid)       | 14       |       | 484.4          | 484.4 | 254   | very persistent | 103.6    | 48   |                    |
| F     | Fluazinam       | 14       |       | 124            | 124   | 25.9  | persistent      | 102.3    | 50   |                    |
| F     | Dimoxystrobin   | 13       |       | 210            | 210   | 22.9  | persistent      | 15.4     | 123  |                    |
| F     | Kresoxim-Methyl | 10       |       | 16             | 0.87  | 1     | no              | 12.2     | 133  | mixture product    |
| I     | Thiacloprid     | 16       |       | 0.88           | 0.88  | 8.1   | no              | 93.8     | 56   | final year for use |

H = herbicide, F = fungicide, I = insecticide

*Table A4. Most common pesticide substances recorded at the 21 sites. Only substances that were recorded in  $\geq 10$  sites are shown.*

May

| <b>Herbicide</b> | <b>presence</b> | <b>Fungicide</b> | <b>presence</b> | <b>Insecticide</b> | <b>presence</b> |
|------------------|-----------------|------------------|-----------------|--------------------|-----------------|
| Prosulfocarb     | 21              | Azoxystrobin     | 21              | Thiacloprid        | 14              |
| Terbuthylazine   | 21              | Fluopyram        | 21              |                    |                 |
| Metolachlor-S    | 17              | Pyraclostrobin   | 17              |                    |                 |
| Dimethenamid-P   | 11              | Bixafen          | 15              |                    |                 |
| Diflufenican     | 10              | Dimoxystrobin    | 13              |                    |                 |
|                  |                 | Boscalid         | 12              |                    |                 |

August

| <b>Herbicide</b> | <b>presence</b> | <b>Fungicide</b> | <b>presence</b> | <b>Insecticide</b> | <b>presence</b> |
|------------------|-----------------|------------------|-----------------|--------------------|-----------------|
| Prosulfocarb     | 20              | Fluopyram        | 21              | Thiacloprid        | 11              |
| Metolachlor-S    | 16              | Azoxystrobin     | 17              |                    |                 |
| Dimethenamid-P   | 13              | Fluazinam        | 14              |                    |                 |
| Flufenacet       | 12              | Boscalid         | 12              |                    |                 |
|                  |                 | Kresoxim-Methyl  | 10              |                    |                 |

*Table A5 Examples of daily flight activity ranges of different insect groups. Potentially insects of these species and / or groups are collected with Malaise traps.*

| <b>Species</b>                  | <b>Insect group</b> | <b>Daily flight range</b> | <b>Source</b>                |
|---------------------------------|---------------------|---------------------------|------------------------------|
| <i>Lasioglossum. calceatum</i>  | Solitary bee        | > 1000 m                  | Beil <i>et al.</i> 2008      |
| <i>Hylaeus punctulatissimus</i> | Solitary bee        | 1100 m (Maximum)          | Zurbuchen <i>et al.</i> 2010 |
| <i>Chelostoma rapunculi</i>     | Solitary bee        | 1275 m (Maximum)          | Zurbuchen <i>et al.</i> 2010 |
| <i>Hoplitis adunca</i>          | Solitary bee        | 1400 m (Maximum)          | Zurbuchen <i>et al.</i> 2010 |
| <i>Aglaia urticae</i>           | Butterfly           | 150-1210 m                | Cant <i>et al.</i> 2005      |
| <i>Hesperia comma</i>           | Butterfly           | 50-1070 m                 | Hill <i>et al.</i> 1996      |
| <i>Musca domestica</i>          | Fly                 | Up to 7000 m              | Nazni <i>et al.</i> 2005     |

Sources:

Beil, M., Horn, H. & Schwabe, A. Analysis of pollen loads in a wild bee community (Hymenoptera: Apidae) – a method for elucidating habitat use and foraging distances. *Apidologie* **39** 456–467 (2008).

Cant, E. T., Smith, A. D., Reynolds, D. R., & Osborne, J. L. Tracking butterfly flight paths across the landscape with harmonic radar. *Proc. Roy. Soc. B: Biol. Sci.* **272** 785-790 (2005).

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*Table A6. Results of Pearson's correlation analysis for comparisons between the number of found pesticide residues and the amount of agricultural production area (arable crops, wine and fruit growing, in km<sup>2</sup>) in the respective radii (500-3500 m, see also Figure A3). Significant values in bold. A. All sites. B. The study site Brauselay was excluded from the analysis. Brauselay is the only site where vineyards are bordering the nature conservation area and not arable crops. Wine growing in Germany is using multiple fungicide application per season and differs from arable crops.*

A: All 21 sites.

| <b>Radius</b> | <b>t</b> | <b>df</b> | <b>p</b>     | <b>cor</b> |
|---------------|----------|-----------|--------------|------------|
| 500 m         | 1.015    | 19        | 0.323        | 0.227      |
| 1000 m        | 1.336    | 19        | 0.197        | 0.293      |
| 1500 m        | 1.394    | 19        | 0.179        | 0.305      |
| 2000 m        | 2.362    | 19        | <b>0.029</b> | 0.476      |
| 2500 m        | 1.269    | 19        | 0.220        | 0.279      |
| 3000 m        | 1.159    | 19        | 0.261        | 0.257      |
| 3500 m        | 1.919    | 19        | 0.070        | 0.403      |

B: 20 sites – Wine growing site Brauselay excluded.

| <b>Radius</b> | <b>t</b> | <b>df</b> | <b>p</b>     | <b>cor</b> |
|---------------|----------|-----------|--------------|------------|
| 500 m         | 1.291    | 18        | 0.213        | 0.291      |
| 1000 m        | 1.719    | 18        | 0.103        | 0.376      |
| 1500 m        | 1.883    | 18        | 0.076        | 0.406      |
| 2000 m        | 3.211    | 18        | <b>0.005</b> | 0.604      |
| 2500 m        | 1.766    | 18        | 0.094        | 0.384      |
| 3000 m        | 1.583    | 18        | 0.131        | 0.350      |
| 3500 m        | 2.499    | 18        | <b>0.022</b> | 0.508      |

*Table A7 Results of GLMM when excluding the wine growing site Brauselay. The number of detected CUPs was analysed in regard to amount of agricultural production area and the size of nature conservation area and FFH area in a radius of 2000 m of the transect center as well as biomass of insects collected by the malaise traps (fixed effects), while the study sites (area) function as random effects. Significant values in bold.*

*Formula:*

*pesticides ~ agricultural production area + nature\_protected\_area + FFH\_area + biomass + (1 | area)*

| <b>Combined data</b>                        | <b>Estimate</b> | <b>Std. Error</b> | <b>z value</b> | <b>Pr(&gt; z )</b> |
|---------------------------------------------|-----------------|-------------------|----------------|--------------------|
| (Intercept)                                 | 2.199           | 0.311             | 7.079          | <b>&lt;0.001</b>   |
| Agricultural production area                | 0.079           | 0.030             | 2.674          | <b>0.008</b>       |
| Nature conservation area (km <sup>2</sup> ) | 0.025           | 0.099             | 0.257          | 0.797              |
| FFH area                                    | 0.018           | 0.082             | 0.216          | 0.829              |
| Biomass                                     | 0.001           | 0.001             | 0.560          | 0.576              |
| <b>May</b>                                  | <b>Estimate</b> | <b>Std. Error</b> | <b>z value</b> | <b>Pr(&gt; z )</b> |
| (Intercept)                                 | 1.611           | 0.308             | 5.224          | <b>&lt; 0.001</b>  |
| Agricultural production area                | 0.111           | 0.030             | 3.664          | <b>&lt; 0.001</b>  |
| Nature conservation area (km <sup>2</sup> ) | -0.042          | 0.105             | -0.400         | 0.689              |
| FFH area                                    | 0.052           | 0.088             | 0.588          | 0.557              |
| Biomass                                     | 0.003           | 0.002             | 1.417          | 0.156              |
| <b>August</b>                               | <b>Estimate</b> | <b>Std. Error</b> | <b>z value</b> | <b>Pr(&gt; z )</b> |
| (Intercept)                                 | 1.916           | 0.390             | 4.906          | <b>&lt; 0.001</b>  |
| Arable land                                 | 0.063           | 0.041             | 1.547          | 0.122              |
| Nature conservation area (km <sup>2</sup> ) | 0.083           | 0.135             | 0.612          | 0.541              |
| FFH area                                    | -0.007          | 0.111             | -0.061         | 0.951              |
| Biomass                                     | <-0.001         | 0.002             | -0.058         | 0.954              |

*Table A8 Results of GLMM including all sites with separate analysis of May and August samples. The number of detected CUPs was analysed in regard to amount of agricultural production area and the size of nature conservation area and FFH area in a radius of 2000 m of the transect center as well as biomass of insects collected by the malaise traps (fixed effects), while the study sites (area) function as random effects. Significant values in bold.*

*Formula:*

*pesticides ~ agricultural production area + nature conservation area + FFH area + biomass + (1 | area)*

| <b>May</b>                                  | <b>Estimate</b> | <b>Std. Error</b> | <b>z value</b> | <b>Pr(&gt;  z )</b> |
|---------------------------------------------|-----------------|-------------------|----------------|---------------------|
| (Intercept)                                 | 1.624           | 0.036             | 5.309          | <b>&lt; 0.001</b>   |
| Agricultural production area                | 0.106           | 0.029             | 3.607          | <b>&lt; 0.001</b>   |
| Nature conservation area (km <sup>2</sup> ) | -0.046          | 0.105             | -0.438         | 0.661               |
| FFH area                                    | 0.048           | 0.087             | 0.552          | 0.581               |
| Biomass                                     | 0.004           | 0.029             | 1.747          | 0.081               |
| <b>August</b>                               | <b>Estimate</b> | <b>Std. Error</b> | <b>z value</b> | <b>Pr(&gt;  z )</b> |
| (Intercept)                                 | 2.054           | 0.377             | 5.455          | <b>&lt; 0.001</b>   |
| Agricultural production area                | 0.041           | 0.038             | 1.095          | 0.274               |
| Nature conservation area (km <sup>2</sup> ) | 0.067           | 0.135             | 0.499          | 0.618               |
| FFH area                                    | -0.015          | 0.112             | -0.135         | 0.892               |
| Biomass                                     | <0.001          | 0.002             | 0.141          | 0.888               |

## **Pesticide analysis.**

### *LC-MS/MS analysis.*

Table A8-1 and A8-2 show details on analytical method conditions. For a selective detection of the selected substances, the mass spectrometer was set to multiple reaction monitoring (MRM). For quantitation and confirmation of the selected substances, at least two MRM transitions, the retention time (RT) (cf. Table A8-3), and the signal-to-noise ratio of >10 were used, except for proquinazid with one MRM transition only. The LC-MS/MS data was processed using Agilent MassHunter Workstation (Quantitative analysis for QQQ version 10, Agilent Technologies, Inc., Santa Clara CA, USA).

### *Calibration standards.*

The substances in ethanol samples were quantified using matrix-matched external calibration (calibration standards,  $n=7$ ). Matrix-matched standards were prepared using blank ethanol, which was processed in the same manner as the ethanol field samples. Briefly, an aliquot of 50 ml of ethanol was completely evaporated under a gentle nitrogen stream. After evaporation, the sample was dissolved with 1 ml of methanol (LC-MS grade, >99.9%, Honeywell, Seelze, Germany), vortexed (60 s), filtered (13 mm HPLC syringe filter, 0.2  $\mu$ m, PTFE, hydrophobic). Several tens of millilitres of the blank ethanol solution were prepared to be used for preparation of matrix-matched calibration standards. The majority of substances for calibration standards were mixtures of neat analytical-quality standards, which were purchased from Restek, USA. The substances avermectin B1a, Dimethoate, fenpyroximate, hexythiazox, napropamid, proquinazid, and tebufenozide as individual standards were from Sigma-Aldrich, Seelze, Germany and LGC, Standards, UK.

### *QA/QC.*

To compensate for response drift bracketing calibrations were used, i.e. one set of calibration standards run before and one after a batch of samples ( $n=20$ ). Samples were evaluated on average of both calibrations after both calibrations were measured. The quality control program consisted of solvent blanks, method (ethanol) blanks and quality control samples (fortified blank ethanol) at three concentration levels (representing the lower, middle and upper levels of the calibration range) and were measured with each batch of samples ( $n=20$ ). Additionally, calibration standards were checked for linearity and the retention time of the substances for deviation after each batch of samples ( $n=20$ ).

### *Method detection limits (MDLs) and Method quantitation limits (MQLs)*

For determination of MDLs and MQLs a spiking level 2 times the estimated MDL of each of the selected substances was selected. Thereafter, blank ethanol sample (50 ml;  $n=7$  each substance) was spiked with the selected level, evaporated to dryness under a gentle nitrogen stream, dissolved in 1 ml of methanol, filtered and analysed. The results of the analysis were used for the calculation of the MDLs and MQLs.

The MQLs and MDLs were calculated using the linear regression parameters from the substance calibration curves with

$$MDL_S = 3.3 \times S / a \text{ and } MQL_S = 10 \times S / a$$

where  $S$  is the sample standard deviation of the replicate ( $n=7$ ) spiked ethanol sample analyses and  $a$  is the slope of the regression of calibration curve. The values 3.3 and 10 represent the signal-to-noise ratio. The individual MQLs and MDLs are shown in Table A2, whereby the values represent substance concentrations in  $\mu$ g/l divided by 50 (concentration factor of the 50 ml of the evaporated ethanol).

*Table A9/1. Procedures of analytical analysis: Agilent 1260 Infinity II UHPLC conditions.*

| Parameter          | Value                                                                                                                                                    |
|--------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|
| Column             | Agilent ZORBAX Eclipse Plus C18, 3x150 mm, 2.7 $\mu$                                                                                                     |
| Column temperature | 45 °C                                                                                                                                                    |
| Injection volume   | 1 $\mu$ L                                                                                                                                                |
| Speed              | Draw, 200 $\mu$ L/min Eject: 400 $\mu$ L/min                                                                                                             |
| Needle wash        | 12 seconds                                                                                                                                               |
| Mobile phase       | A) 98 % Water with 4 mM ammonium formate + 0.1 % acetic acid + 2% methanol<br>B) 98 % methanol with 4 mM ammonium formate + 0.1 % acetic acid + 2% water |
| Flow rate          | 0.45 mL/min                                                                                                                                              |
| Gradient programme | Time B%<br>0 2<br>1.0 50<br>4.0 65<br>14.0 100<br>20.0 100<br>20.1 2                                                                                     |
| Stop time          | 20.1 minutes                                                                                                                                             |
| Post time          | 3 minutes                                                                                                                                                |

*Table A9/2. Procedures of analytical analysis: Agilent 6495C MS parameters for positive and negative ion method.*

| Parameter               | Value                                                                                          |
|-------------------------|------------------------------------------------------------------------------------------------|
| Mass Spectrometer       | Agilent 6495C with electrospray ionization (ESI) operated in multiple reaction monitoring mode |
| Ionization mode         | Positive / Negative                                                                            |
| Gas temperature         | 250 °C; 11 L/min                                                                               |
| Nebulizer               | 38 psi                                                                                         |
| Sheath gas              | 350 °C; 12 L/min                                                                               |
| Capillary voltage       | 3,000 V / 3000 V                                                                               |
| Delta EMV               | 200                                                                                            |
| High pressure           | 150 V / 150 V                                                                                  |
| iFunnel RF              |                                                                                                |
| Low pressure iFunnel RF | 60 V / 60 V                                                                                    |
| MS1 and MS2 resolution  | Unit                                                                                           |

Table A9/3. MRM transitions of analytes in positive and negative ion mode method.

| Substance           | Quantifier                  |                  |                |                 | Qualifiers               |                  |                |                 |                          |
|---------------------|-----------------------------|------------------|----------------|-----------------|--------------------------|------------------|----------------|-----------------|--------------------------|
|                     | Retention time<br>(minutes) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) |
| <i>Herbicides</i>   |                             |                  |                |                 |                          |                  |                |                 |                          |
| 2,4-D               | 9.83                        | 221.0            | 161.0          | Negative        | 12                       | 219.0            | 161.0          | Positive        | 12                       |
| Aminopyralid        | 9.84                        | 207.0            | 134.0          | Positive        | 32                       | 207.0            | 107.0          | Positive        | 52                       |
| Bentazone           | 8.42                        | 239.0            | 132.0          | Positive        | 29                       | 239.0            | 197.0          | Positive        | 21                       |
|                     |                             |                  |                |                 |                          | 241.0            | 199.0          | Positive        | 4                        |
| Bromoxynil          | 9.13                        | 274.0            | 79.0           | Negative        | 37                       | 275.7            | 79.0           | Negative        | 8                        |
|                     |                             |                  |                |                 |                          | 275.7            | 81.0           | Negative        | 8                        |
| Carfentrazone-ethyl | 13.35                       | 412.0            | 346.1          | Positive        | 22                       | 412.0            | 277.1          | Positive        | 30                       |
|                     |                             |                  |                |                 |                          | 412.0            | 366.1          | Positive        | 15                       |
| Chloridazon         | 7.15                        | 222.0            | 77.0           | Positive        | 36                       | 222.0            | 92.0           | Positive        | 24                       |
|                     |                             |                  |                |                 |                          | 222.0            | 65.1           | Positive        | 44                       |
| Chlortoluron        | 9.02                        | 213.1            | 72.0           | Positive        | 8                        | 213.1            | 46.1           | Positive        | 8                        |
| Clomazone           | 10.61                       | 240.1            | 125.0          | Positive        | 20                       | 240.1            | 89.1           | Positive        | 56                       |
| Diflufenican        | 14.72                       | 395.1            | 266.0          | Positive        | 24                       | 395.1            | 238.0          | Positive        | 40                       |
|                     |                             |                  |                |                 |                          | 395.1            | 246.0          | Positive        | 36                       |
| Dimethenamid-P      | 11.34                       | 276.1            | 244.0          | Positive        | 13                       | 276.1            | 168.1          | Positive        | 25                       |
| Ethofumesate        | 10.96                       | 304.1            | 121.1          | Positive        | 30                       | 287.0            | 121.0          | Positive        | 10                       |
|                     |                             |                  |                |                 |                          | 304.1            | 241.0          | Positive        | 4                        |
| Flazasulfuron       | 10.18                       | 408.1            | 182.1          | Positive        | 28                       | 408.1            | 139.1          | Positive        | 40                       |
|                     |                             |                  |                |                 |                          | 408.1            | 83.0           | Positive        | 40                       |
| Florasulam          | 7.40                        | 360.0            | 129.0          | Positive        | 28                       | 360.0            | 144.0          | Positive        | 20                       |
|                     |                             |                  |                |                 |                          | 360.0            | 192.0          | Positive        | 12                       |
| Flufenacet          | 12.43                       | 364.1            | 152.1          | Positive        | 16                       | 364.1            | 194.2          | Positive        | 4                        |
|                     |                             |                  |                |                 |                          | 364.1            | 124.1          | Positive        | 36                       |
| Fluroxypyr          | 8.31                        | 255.0            | 209.0          | Positive        | 19                       | 255.0            | 181.0          | Positive        | 29                       |
| Flurtamone          | 10.77                       | 334.1            | 227.0          | Positive        | 44                       | 334.1            | 275.2          | Positive        | 20                       |
|                     |                             |                  |                |                 |                          | 334.1            | 303.2          | Positive        | 20                       |
| Foramsulfuron       | 8.97                        | 453.0            | 181.9          | Positive        | 46                       | 453.0            | 255.1          | Positive        | 21                       |
| Isoproturon         | 10.11                       | 207.2            | 46.1           | Positive        | 8                        | 207.2            | 72.1           | Positive        | 5                        |
| Lenacil             | 10.09                       | 235.1            | 82.1           | Positive        | 36                       | 235.1            | 55.1           | Positive        | 44                       |
| MCPA                | 9.88                        | 201.0            | 141.0          | Negative        | 12                       | 201.0            | 143.0          | Negative        | 12                       |
| Metamitron          | 6.78                        | 203.1            | 77.0           | Positive        | 32                       | 203.1            | 175.1          | Positive        | 12                       |
|                     |                             |                  |                |                 |                          | 203.1            | 104.1          | Positive        | 20                       |
| Metazachlor         | 10.14                       | 278.1            | 134.2          | Positive        | 15                       | 278.1            | 105.1          | Positive        | 44                       |
|                     |                             |                  |                |                 |                          | 278.1            | 79.1           | Positive        | 60                       |
| Metobromuron        | 9.81                        | 259.0            | 170.0          | Positive        | 20                       | 259.0            | 148.0          | Positive        | 15                       |
| Metolachlor-S       | 12.87                       | 284.1            | 176.2          | Positive        | 29                       | 284.1            | 134.1          | Positive        | 37                       |
| Metsulfuron-methyl  | 8.22                        | 382.1            | 199.0          | Positive        | 20                       | 382.1            | 167.0          | Positive        | 12                       |
| Napropamide         | 12.37                       | 272.2            | 129.0          | Positive        | 12                       | 272.2            | 171.1          | Positive        | 16                       |
|                     |                             |                  |                |                 |                          | 272.2            | 58.1           | Positive        | 28                       |

Table A9/3. (cont.). MRM transitions of analytes in positive and negative ion mode method.

| Substance         | Quantifier                  |                  |                |                 | Qualifiers               |                  |                |                 |                          |
|-------------------|-----------------------------|------------------|----------------|-----------------|--------------------------|------------------|----------------|-----------------|--------------------------|
|                   | Retention time<br>(minutes) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) |
| Pendimethalin     | 16.16                       | 282.1            | 212.1          | Positive        | 4                        | 282.1            | 194.1          | Positive        | 16                       |
|                   |                             |                  |                |                 |                          | 282.1            | 43.2           | Positive        | 32                       |
| Picloram          | 5.70                        | 240.9            | 194.8          | Positive        | 25                       | 240.9            | 167.9          | Positive        | 37                       |
|                   |                             |                  |                |                 |                          | 240.9            | 140.8          | Positive        | 53                       |
| Propaquizafop     | 15.45                       | 444.1            | 100.1          | Positive        | 15                       | 444.1            | 371.0          | Positive        | 10                       |
| Propyzamide       | 11.84                       | 256.0            | 190.0          | Positive        | 10                       | 256.0            | 173.0          | Positive        | 20                       |
|                   |                             |                  |                |                 |                          | 256.0            | 145.0          | Positive        | 36                       |
| Prosulfocarb      | 15.10                       | 252.1            | 91.2           | Positive        | 20                       | 252.1            | 128.2          | Positive        | 8                        |
|                   |                             |                  |                |                 |                          | 252.1            | 65.1           | Positive        | 60                       |
| Quinmerac         | 7.19                        | 222.0            | 204.0          | Positive        | 18                       | 222.0            | 141.0          | Positive        | 38                       |
|                   |                             |                  |                |                 |                          | 222.0            | 114.0          | Positive        | 56                       |
| Quizalofop-P      | 12.80                       | 345.1            | 162.9          | Positive        | 40                       | 345.1            | 91.1           | Positive        | 28                       |
|                   |                             |                  |                |                 |                          | 345.1            | 180.0          | Positive        | 60                       |
| Terbuthylazine    | 11.28                       | 230.1            | 174.1          | Positive        | 15                       | 230.1            | 96.1           | Positive        | 24                       |
|                   |                             |                  |                |                 |                          | 230.1            | 68.0           | Positive        | 40                       |
| Tribenuron-methyl | 9.20                        | 396.1            | 181.0          | Positive        | 20                       | 396.1            | 180.9          | Positive        | 16                       |
|                   |                             |                  |                |                 |                          | 396.1            | 155.0          | Positive        | 8                        |
| Tritosulfuron     | 9.98                        | 446.0            | 195.0          | Positive        | 23                       | 446.0            | 145.0          | Positive        | 54                       |
| <i>Fungicides</i> |                             |                  |                |                 |                          |                  |                |                 |                          |
| Azoxystrobin      | 10.18                       | 404.1            | 372.1          | Positive        | 8                        | 404.1            | 344.1          | Positive        | 24                       |
|                   |                             |                  |                |                 |                          | 404.1            | 329.1          | Positive        | 32                       |
| Benalaxyl         | 13.57                       | 326.2            | 148.1          | Positive        | 27                       | 326.2            | 91.1           | Positive        | 48                       |
|                   |                             |                  |                |                 |                          | 326.2            | 121.1          | Positive        | 32                       |
| Bixafen           | 12.96                       | 414.0            | 394.0          | Positive        | 20                       | 414.0            | 266.0          | Positive        | 20                       |
| Boscalid          | 11.19                       | 343.0            | 307.1          | Positive        | 16                       | 343.0            | 271.2          | Positive        | 32                       |
|                   |                             |                  |                |                 |                          | 343.0            | 272.1          | Positive        | 32                       |
| Cyazofamid        | 12.38                       | 325.0            | 108.0          | Positive        | 8                        | 325.0            | 44.1           | Positive        | 28                       |
|                   |                             |                  |                |                 |                          | 325.0            | 261.0          | Positive        | 4                        |
| Cyflufenamid      | 12.96                       | 413.1            | 295.1          | Positive        | 10                       | 413.1            | 359.1          | Positive        | 10                       |
|                   |                             |                  |                |                 |                          | 413.1            | 223.0          | Positive        | 20                       |
| Cymoxanil         | 6.93                        | 199.1            | 128.0          | Positive        | 4                        | 199.1            | 110.9          | Positive        | 12                       |
|                   |                             |                  |                |                 |                          | 199.1            | 83.0           | Positive        | 20                       |
| Cyprodinil        | 11.83                       | 226.1            | 76.9           | Positive        | 50                       | 226.1            | 92.9           | Positive        | 40                       |
|                   |                             |                  |                |                 |                          | 226.1            | 65.1           | Positive        | 56                       |
| Difenconazole     | 14.39                       | 406.1            | 251.0          | Positive        | 20                       | 406.1            | 188.0          | Positive        | 40                       |
|                   |                             |                  |                |                 |                          | 406.1            | 337.0          | Positive        | 10                       |
| Dimethomorph      | 11.17                       | 388.1            | 301.1          | Positive        | 20                       | 388.1            | 139.0          | Positive        | 36                       |
|                   |                             |                  |                |                 |                          | 388.1            | 165.1          | Positive        | 32                       |
| Dimoxystrobin     | 13.19                       | 327.2            | 205.1          | Positive        | 12                       | 327.2            | 116.0          | Positive        | 20                       |
|                   |                             |                  |                |                 |                          | 327.2            | 58.0           | Positive        | 40                       |
| Epoxiconazole     | 12.21                       | 330.1            | 121.0          | Positive        | 16                       | 330.1            | 101.2          | Positive        | 52                       |
|                   |                             |                  |                |                 |                          | 330.1            | 95.0           | Positive        | 60                       |

Table A9/3. (cont.). MRM transitions of analytes in positive and negative ion mode method.

| Substance       | Quantifier                  |                  |                |                 | Qualifiers               |                  |                |                 |                          |
|-----------------|-----------------------------|------------------|----------------|-----------------|--------------------------|------------------|----------------|-----------------|--------------------------|
|                 | Retention time<br>(minutes) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) |
| Fenoxycarb      | 12.96                       | 302.1            | 88.0           | Positive        | 29                       | 302.1            | 256.1          | Positive        | 8                        |
|                 |                             |                  |                |                 |                          | 302.1            | 116.0          | Positive        | 17                       |
| Fenpropimorph   | 10.95                       | 304.3            | 57.1           | Positive        | 32                       | 304.3            | 130.0          | Positive        | 25                       |
|                 |                             |                  |                |                 |                          | 304.3            | 98.1           | Positive        | 32                       |
| Fluazinam       | 15.28                       | 462.9            | 416.0          | Negative        | 10                       | 462.9            | 398.0          | Negative        | 9                        |
| Fludioxonil     | 11.08                       | 247.0            | 126.0          | Negative        | 32                       | 247.0            | 169.0          | Negative        | 32                       |
|                 |                             |                  |                |                 |                          | 247.0            | 152.0          | Negative        | 32                       |
| Fluopicolid     | 11.44                       | 382.9            | 172.9          | Positive        | 20                       | 382.9            | 144.9          | Positive        | 56                       |
|                 |                             |                  |                |                 |                          | 382.9            | 109.1          | Positive        | 60                       |
| Fluopyram       | 12.18                       | 397.0            | 145.0          | Positive        | 61                       | 397.0            | 172.9          | Positive        | 41                       |
|                 |                             |                  |                |                 |                          | 397.0            | 207.9          | Positive        | 37                       |
| Iprovalicarb    | 12.06                       | 321.2            | 119.0          | Positive        | 16                       | 321.2            | 116.1          | Positive        | 16                       |
|                 |                             |                  |                |                 |                          | 321.2            | 91.1           | Positive        | 56                       |
| Kresoxim methyl | 13.24                       | 314.1            | 222.1          | Positive        | 10                       | 314.1            | 267.0          | Positive        | 0                        |
|                 |                             |                  |                |                 |                          | 314.1            | 206.0          | Positive        | 0                        |
| Mandipropamid   | 10.99                       | 412.1            | 328.1          | Positive        | 8                        | 412.1            | 356.1          | Positive        | 4                        |
|                 |                             |                  |                |                 |                          | 412.1            | 125.0          | Positive        | 40                       |
| Metalaxyl-M     | 9.84                        | 280.2            | 220.1          | Positive        | 10                       | 280.2            | 160.1          | Positive        | 20                       |
|                 |                             |                  |                |                 |                          | 280.2            | 45.1           | Positive        | 36                       |
| Metconazole     | 13.85                       | 320.1            | 70.1           | Positive        | 24                       | 320.1            | 125.0          | Positive        | 48                       |
|                 |                             |                  |                |                 |                          | 320.1            | 43.0           | Positive        | 60                       |
| Metrafenone     | 13.96                       | 409.1            | 209.1          | Positive        | 8                        | 409.1            | 166.1          | Positive        | 40                       |
|                 |                             |                  |                |                 |                          | 409.1            | 226.9          | Positive        | 16                       |
| Myclobutanil    | 11.72                       | 289.1            | 70.1           | Positive        | 16                       | 289.1            | 89.1           | Positive        | 60                       |
|                 |                             |                  |                |                 |                          | 289.1            | 125.1          | Positive        | 32                       |
| Paclobutrazol   | 11.31                       | 294.1            | 70.1           | Positive        | 16                       | 294.1            | 125.2          | Positive        | 36                       |
|                 |                             |                  |                |                 |                          | 294.1            | 57.2           | Positive        | 20                       |
| Penconazole     | 13.18                       | 284.1            | 70.1           | Positive        | 15                       | 284.1            | 123.1          | Positive        | 56                       |
|                 |                             |                  |                |                 |                          | 284.1            | 159.0          | Positive        | 30                       |
| Pencycuron      | 14.17                       | 329.1            | 125.1          | Positive        | 24                       | 329.1            | 217.9          | Positive        | 12                       |
|                 |                             |                  |                |                 |                          | 329.1            | 89.1           | Positive        | 60                       |
| Picoxystrobin   | 12.79                       | 368.1            | 205.2          | Positive        | 4                        | 368.1            | 145.0          | Positive        | 20                       |
|                 |                             |                  |                |                 |                          | 368.1            | 115.0          | Positive        | 56                       |
| Prochloraz      | 13.74                       | 376.0            | 308.0          | Positive        | 4                        | 376.0            | 70.1           | Positive        | 24                       |
|                 |                             |                  |                |                 |                          | 376.0            | 265.9          | Positive        | 12                       |
| Propamocarb     | 5.64                        | 189.2            | 102.0          | Positive        | 12                       | 189.2            | 144.0          | Positive        | 8                        |
|                 |                             |                  |                |                 |                          | 189.2            | 74.0           | Positive        | 24                       |
| Proquinazid     | 17.10                       | 372.9            | 289.0          | Positive        | 20                       |                  |                |                 |                          |
| Prothioconazole | 14.04                       | 344.0            | 154.0          | Positive        | 40                       | 344.0            | 125.0          | Positive        | 40                       |
|                 |                             |                  |                |                 |                          | 344.0            | 102.0          | Positive        | 40                       |
| Pyraclostrobin  | 13.47                       | 388.1            | 193.8          | Positive        | 8                        | 388.1            | 164.1          | Positive        | 12                       |
|                 |                             |                  |                |                 |                          | 388.1            | 163.1          | Positive        | 20                       |

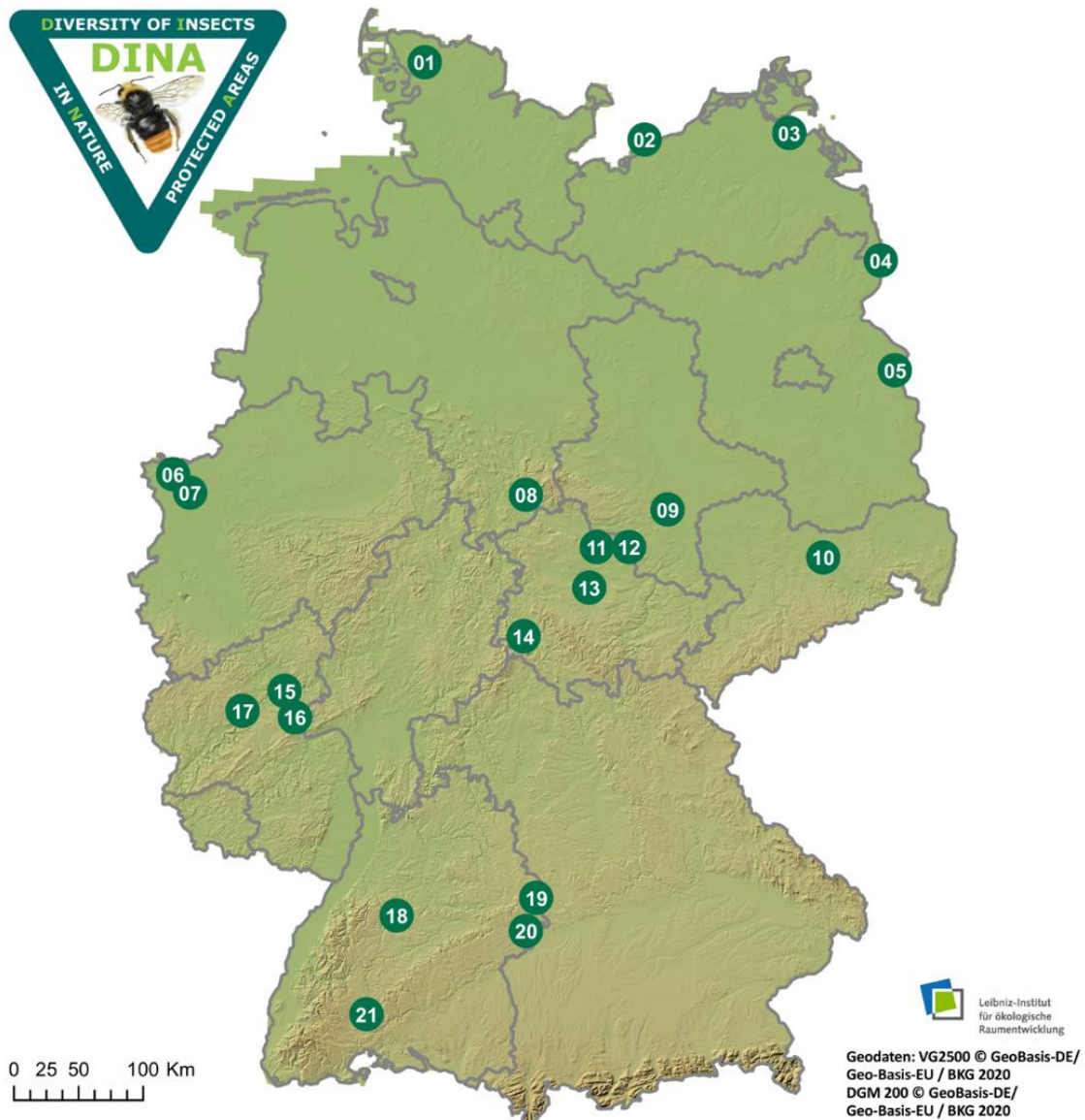
Table A9/3. (cont.). MRM transitions of analytes in positive and negative ion mode method.

| Substance                       | Quantifier                  |                  |                |                 |                          | Qualifiers       |                |                 |                          |
|---------------------------------|-----------------------------|------------------|----------------|-----------------|--------------------------|------------------|----------------|-----------------|--------------------------|
|                                 | Retention time<br>(minutes) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) |
| Pyrimethanil                    | 10.73                       | 200.1            | 82.0           | Positive        | 5                        | 200.1            | 106.9          | Positive        | 20                       |
|                                 |                             |                  |                |                 |                          | 200.1            | 77.1           | Positive        | 40                       |
| Spiroxamine                     | 11.09                       | 298.3            | 144.1          | Positive        | 16                       | 298.3            | 100.1          | Positive        | 32                       |
|                                 |                             |                  |                |                 |                          | 298.3            | 41.1           | Positive        | 60                       |
| Tebuconazole                    | 13.19                       | 308.1            | 70.0           | Positive        | 40                       | 308.1            | 124.9          | Positive        | 47                       |
|                                 |                             |                  |                |                 |                          | 308.1            | 57.1           | Positive        | 28                       |
| Trifloxystrobin                 | 14.30                       | 409.1            | 186.0          | Positive        | 12                       | 409.1            | 145.0          | Positive        | 52                       |
|                                 |                             |                  |                |                 |                          | 409.1            | 116.0          | Positive        | 24                       |
| <i>Insecticides, Acaricides</i> |                             |                  |                |                 |                          |                  |                |                 |                          |
| Acetamiprid                     | 6.69                        | 223.0            | 126.1          | Positive        | 18                       | 223.0            | 90.1           | Positive        | 35                       |
| Avermectin B1a                  | 17.70                       | 890.5            | 307.2          | Positive        | 12                       | 890.5            | 305.1          | Positive        | 8                        |
|                                 |                             |                  |                |                 |                          | 890.5            | 145.0          | Positive        | 24                       |
| Chlorantraniliprole             | 10.03                       | 483.9            | 452.9          | Positive        | 16                       | 483.9            | 285.9          | Positive        | 8                        |
| Clothianidin                    | 6.66                        | 250.0            | 169.0          | Positive        | 8                        | 250.0            | 131.9          | Positive        | 8                        |
| Dimethoate                      | 6.48                        | 230.0            | 125.0          | Positive        | 24                       | 230.0            | 47.0           | Positive        | 56                       |
|                                 |                             |                  |                |                 |                          | 230.0            | 199.0          | Positive        | 4                        |
| Etofenprox                      | 18.66                       | 394.2            | 177.2          | Positive        | 13                       | 394.2            | 359.2          | Positive        | 12                       |
|                                 |                             |                  |                |                 |                          | 394.2            | 107.1          | Positive        | 45                       |
| Fenpyroximate                   | 16.43                       | 422.2            | 366.2          | Positive        | 12                       | 422.2            | 135.0          | Positive        | 36                       |
|                                 |                             |                  |                |                 |                          | 422.2            | 107.0          | Positive        | 64                       |
| Flonicamid                      | 5.84                        | 230.0            | 174.0          | Positive        | 15                       | 230.0            | 148.1          | Positive        | 24                       |
|                                 |                             |                  |                |                 |                          | 230.0            | 98.1           | Positive        | 48                       |
| Hexythiazox                     | 16.45                       | 353.1            | 168.1          | Positive        | 24                       | 353.1            | 227.9          | Positive        | 8                        |
|                                 |                             |                  |                |                 |                          | 353.1            | 116.1          | Positive        | 56                       |
| Imidacloprid                    | 6.57                        | 256.0            | 175.1          | Positive        | 22                       | 256.0            | 209.1          | Positive        | 12                       |
|                                 |                             |                  |                |                 |                          | 256.0            | 84.0           | Positive        | 20                       |
| Indoxacarb                      | 14.30                       | 528.0            | 203.0          | Positive        | 40                       | 528.0            | 293.0          | Positive        | 9                        |
|                                 |                             |                  |                |                 |                          | 528.0            | 149.9          | Positive        | 25                       |
| Methiocarb                      | 11.03                       | 226.1            | 169.1          | Positive        | 4                        | 226.1            | 121.1          | Positive        | 15                       |
| Pirimicarb                      | 8.20                        | 239.1            | 72.1           | Positive        | 20                       | 239.1            | 182.2          | Positive        | 13                       |
|                                 |                             |                  |                |                 |                          | 239.1            | 109.1          | Positive        | 32                       |
| Pymetrozine                     | 5.66                        | 218.0            | 105.0          | Positive        | 20                       | 218.0            | 79.0           | Positive        | 49                       |
|                                 |                             |                  |                |                 |                          | 218.0            | 78.1           | Positive        | 45                       |
| Spinosad A                      | 13.64                       | 732.5            | 142.1          | Positive        | 30                       | 732.5            | 98.0           | Positive        | 45                       |
| Spinosad D                      | 14.58                       | 746.5            | 142.1          | Positive        | 15                       | 746.5            | 98.0           | Positive        | 55                       |
| Tebufozide                      | 12.94                       | 353.2            | 133.0          | Positive        | 16                       | 353.2            | 297.1          | Positive        | 0                        |
|                                 |                             |                  |                |                 |                          | 353.2            | 105.1          | Positive        | 44                       |
| Thiacloprid                     | 6.86                        | 253.0            | 126.0          | Positive        | 20                       | 253.0            | 99.1           | Positive        | 44                       |
|                                 |                             |                  |                |                 |                          | 253.0            | 90.1           | Positive        | 44                       |
| Thiamethoxam                    | 5.98                        | 292.0            | 211.1          | Positive        | 10                       | 292.0            | 181.1          | Positive        | 28                       |
|                                 |                             |                  |                |                 |                          | 292.0            | 131.9          | Positive        | 40                       |

Table A9/3. (cont.). MRM transitions of analytes in positive and negative ion mode method.

| Substance           | Quantifier                  |                  |                |                 | Qualifiers               |                  |                |                 |                          |
|---------------------|-----------------------------|------------------|----------------|-----------------|--------------------------|------------------|----------------|-----------------|--------------------------|
|                     | Retention time<br>(minutes) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) | Precursor<br>ion | Product<br>ion | Ion<br>polarity | Collision<br>energy (eV) |
| <i>Biocides</i>     |                             |                  |                |                 |                          |                  |                |                 |                          |
| Fipronil desulfinyl | 11.70                       | 386.8            | 350.8          | Negative        | 20                       | 386.8            | 350.8          | Negative        | 20                       |
| Fipronil            | 12.77                       | 435.0            | 333.0          | Negative        | 12                       | 435.0            | 250.0          | Negative        | 28                       |
| Fipronil sulfone    | 13.27                       | 450.8            | 218.8          | Negative        | 40                       | 450.8            | 243.8          | Negative        | 70                       |

## Figures:



### Sites

- |                                          |                                 |
|------------------------------------------|---------------------------------|
| 01 Lütjenholmer Heidedünen               | 11 Wipperdurchbruch             |
| 02 Riedensee                             | 12 Bottendorfer Hügel           |
| 03 Insel Koos, Kooser See, Wampener Riff | 13 Schwellenburg                |
| 04 Geesower Hügel                        | 14 Hofberg                      |
| 05 Oderhänge Mallnow                     | 15 Koppelstein – Helmestäl      |
| 06 NSG Wisseler Dünen                    | 16 Rheinhänge Dörscheider Heide |
| 07 NSG Bislicher Insel                   | 17 Brauselay                    |
| 08 Gipskarstlandschaft Hainholz          | 18 Mittelberg                   |
| 09 Porphyrlandschaft bei Gimritz         | 19 Ipf                          |
| 10 Ziegenbuschhänge bei Oberau           | 20 Kürnberg                     |
|                                          | 21 Mühlhauser Halde             |

Figure A1 Map with location of study sites in Germany (Created by Lisa Eichler/Hanna Poglitsch using Esri ArcMap 10.8.1 (<https://support.esri.com/de/products/desktop/arcgis-desktop/arcmap/10-8>)).

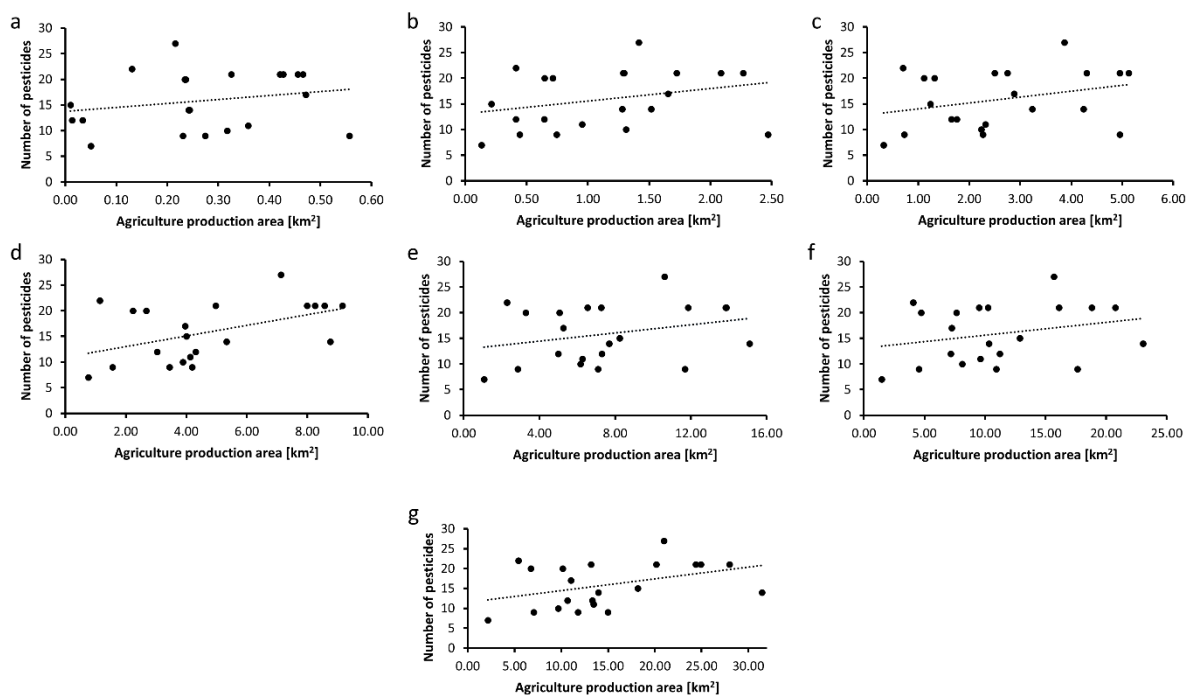


Figure A2. Correlation between the number of pesticide residues and the amount of arable land in the respective radii from 500-3500 m (a=500 m, b=1000m, c=1500 m, d=2000 m, e=2500 m, f=3000 m, and g=3500 m, for values see also Table A6). All 21 sites included.



Figure A3 **A:** Malaise trap for collecting flying insects. Collecting bottle can be seen in the top right corner (Martin Sorg). **B:** Collecting bottle with ethanol and insect sample after running for 14 days (Thomas Hörren) (© EVK, Creative Commons 4.0).

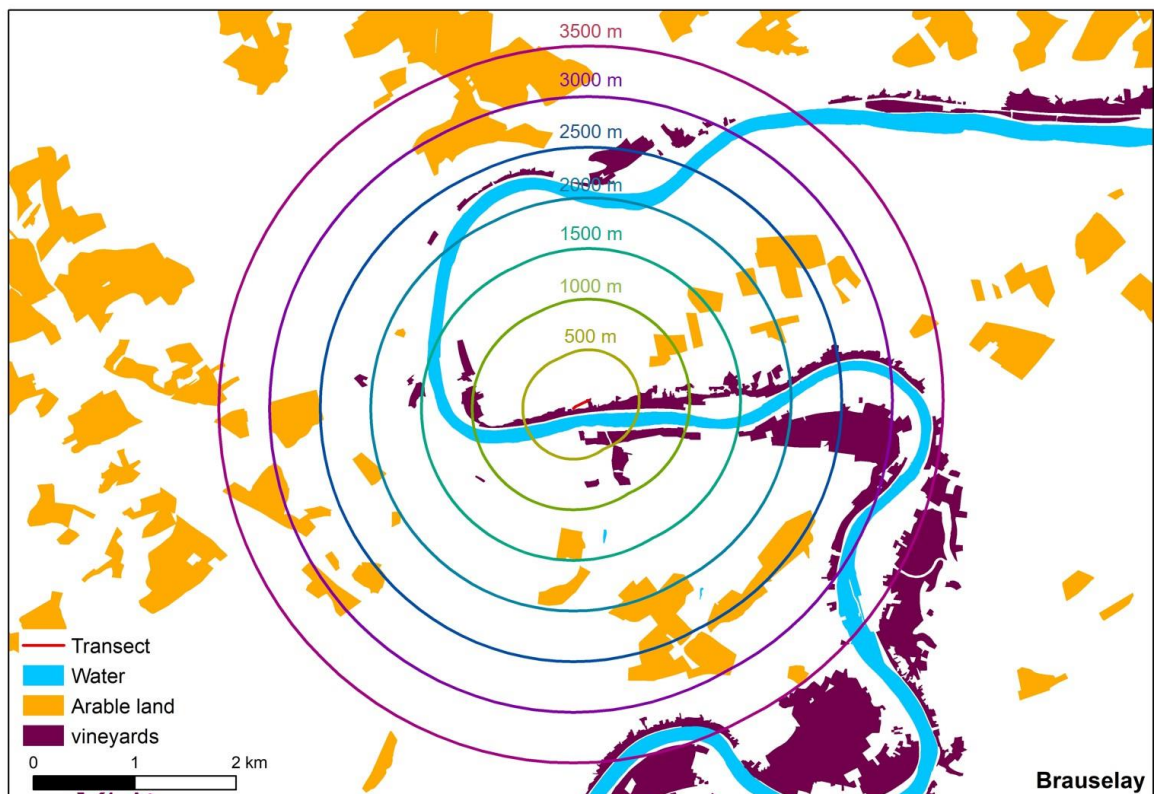
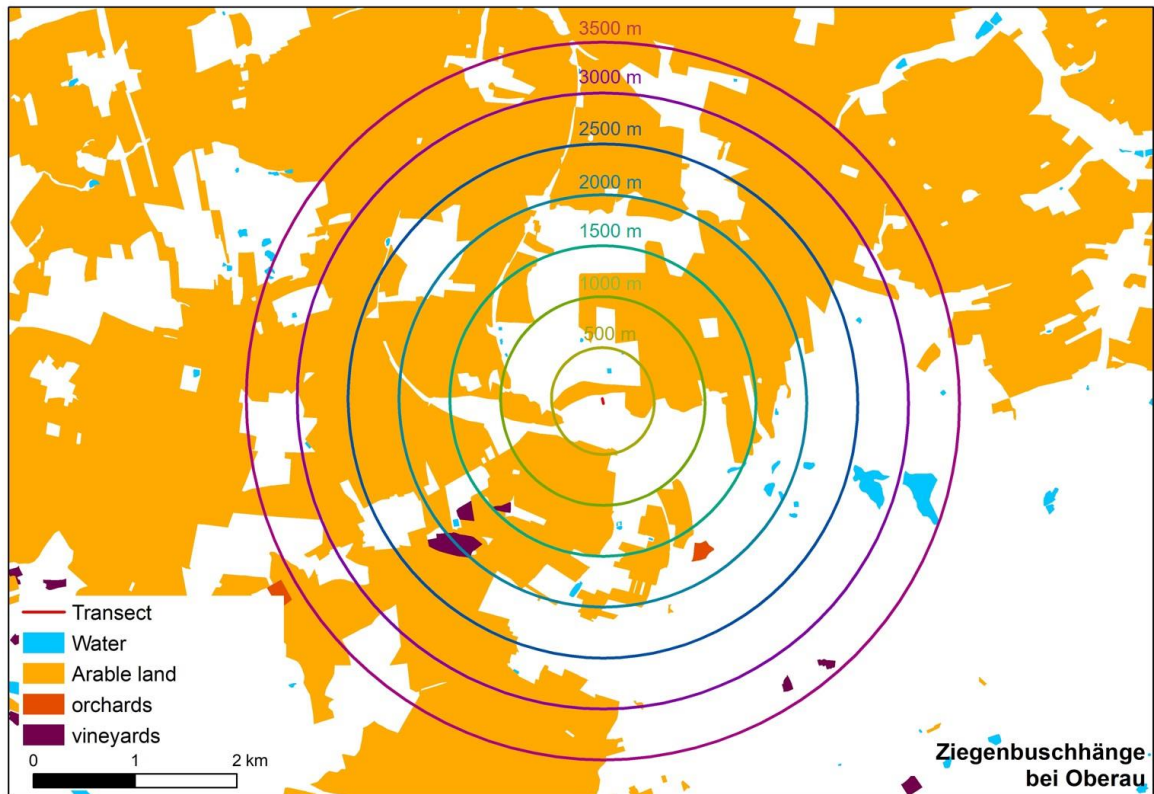


Figure A4 Calculation of buffer radii at sites. **A:** site 10 Ziegenbuschhänge bei Oberau **B:** site 17 Brauselay, situated in a wine growing area. (Created by Lisa Eichler using Esri ArcMap 10.8.1 (<https://support.esri.com/de/products/desktop/arcgis-desktop/arcmap/10-8>).