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Widespread contamination of soils and vegetation with current use pesticide residues along altitudinal gradients in a European Alpine valley

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Pesticides are transferred outside of cropland and can affect animals and plants. Here we investigated the distribution of 97 current use pesticides in soil and vegetation as central exposure matrices of insects. Sampling was conducted on 53 sites along eleven altitudinal transects in the Vinschgau valley (South Tyrol, Italy), in Europe's largest apple growing area. A total of 27 pesticides (10 insecticides, 11 fungicides and 6 herbicides) were detected, originating mostly from apple orchards. Residue numbers and concentrations decreased with altitude and distance to orchards, but were even detected at the highest sites. Predictive, detection-based mapping indicates that pesticide mixtures can occur anywhere from the valley floor to mountain peaks. This study demonstrates widespread pesticide contamination of Alpine environments, creating contaminated landscapes. As residue mixtures have been detected in remote alpine ecosystems and conservation areas, we call for a reduction of pesticide use to prevent further contamination and loss of biodiversity.

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Current use pesticides (CUPs) are frequently detected in and outside of cropping areas, resulting in chemically fragmented landscapes[1,2]. While pesticide water monitoring has been established at the European scale in response to the EU Water Framework Directive[3], measurements of CUPs in terrestrial matrices are limited to a few studies that consider soil[4–7], vegetation[8–11], earthworms[5], and insects[12]. Intensive conventional crop production using synthetic pesticides is not only located in lowland areas, but also along valleys and river plains in mountainous regions such as the European Alps, where thermal conditions favour pesticide transport and exposure of mountain slopes[13,14]. Furthermore, alpine ecosystems inhabit a unique, ecologically sensitive, and protected biodiversity, making the understanding of pesticide exposure critical for conservation[15]. While CUPs are found in montane environments in glacial meltwater[14,16], mountain pine needles[11] and mountain soils[17], studies explicitly assessing CUP residues in terrestrial matrices along multiple, continuous altitudinal gradients are rare and, to our knowledge, limited to soils in the Himalayan region[18] and pine needles in the New Zealand Alps[19].

The Vinschgau valley (Val Venosta) is located in South Tyrol (Italy), Europe's most intensive apple cultivation area, where about 7000 apple farmers produce approximately 10% of the European apples. Recently, pesticide contamination in off-crop habitats, especially children's playgrounds, has been documented for the valley floor near the intensive apple plantations[8–10] and also in a side valley without apple production areas[20]. Pesticide transport to higher altitude and exposure of insects in soil and vegetation along mountain slopes was assumed[21], but not previously assessed. Hence, the aim of this study was to evaluate the extent of CUP distribution and exposure in two terrestrial key matrices for insects: soil, where for example most solitary bees (ca. 65% of species) excavate their nests[22] and vegetation, which is habitat and food resource for herbivorous insects such as grasshoppers (Orthoptera) or butterfly caterpillars (Lepidoptera). Our study was conducted in a mountainous landscape with multiple altitudinal gradients along the entire 80 km valley axis, which differs in apple cultivation intensity (Fig. 1). Sampling of soil and vegetation in open off-crop habitats along eleven transects ranging from the valley floor near apple plantations to meadows above the alpine tree line makes this study the most comprehensive landscape scale investigation of CUP contamination in terrestrial habitats of the European Alps. Moreover, using CUP residue detections we were able to predict exposure for the entire Vinschgau valley using regression analysis and subsequent mapping.

Results and discussion

CUP residues detected

CUP detections and concentrations in soil and vegetation. Of the 97 target CUPs analysed using an established HPLC-MS/MS method[23], a total of 27 different CUPs (10 insecticides, 11 fungicides, and 6 herbicides) were detected in soil and vegetation samples collected along the eleven altitudinal transects over a four-day period in May 2022 (Fig. 1). Of the total 27 CUPs, 23 CUPs were detected in soil (Supplementary Table 2) and 18 in vegetation (Supplementary Table 3). In soil, the insecticide methoxyfenozide was recorded most frequently in 21 (40%) of the 53 samples, followed by the fungicides fluazinam with 13 (25%) and trifloxystrobin with 8 (15%) detections. Five CUPs were recorded below limit of quantification (LOQ): the insecticide imidacloprid, and the fungicides azoxystrobin, cyflufenamid, fluopyram and myclobutanil. All five herbicides were recorded only once. In vegetation, fluazinam and trifloxystrobin were detected in all but one (T11_4: 1,550 m a.s.l.) of the 53 samples (98%). Penconazole was found in 35 (67%) and methoxyfenozide in 24 (45%) of all vegetation samples. Detections of flonicamid ($N = 1$; insecticide), azoxystrobin and fluopyram (each $N = 1$; fungicides), and pendimethalin ($N = 5$; herbicide) were all below LOQ.

The detected pesticide classes relate to the application pattern in apple cultivation in the study area with 20.12 kg ha^{-1} fungicide, followed by 11.08 kg ha^{-1} insecticide and 0.81 kg ha^{-1} herbicide active ingredients (AIs)[24]. An analysis of apple farmers application records in the Vinschgau Valley for the year 2017 showed that fungicides accounted for 50% of all applications, but insecticides were applied in highest amounts (43% of total applied pesticide AIs)[25]. Eighteen (66%) of the 27 detected CUPs were approved and recommended in integrated pome fruit production[26], (Supplementary Table 4). However, the fungicides azoxystrobin (3 detections in soil, 1 detection in vegetation, all <LOQ) and fluopyram (1 detection in soil, <LOQ) and the neonicotinoid insecticides thiacloprid (2 detections in soil, 1 detection in vegetation) were not approved for use in apple farming. In addition, the neonicotinoids imidacloprid and clothianidin, which were banned from field use in the EU since December 2020, were detected in soil (2 and 1 detection respectively), possibly due to previous applications and their longer dissipation times in soil ($DT_{50\ \mathrm{field\ soil}}$: imidacloprid 104–228 days, clothianidin: 13–305 days, Supplementary Tables 2 and 3). Four of the six herbicides (flazasulfuron, metazachlor, metolachlor-S and napropamide) were not approved for use in apple orchards. Because each was detected only once and mostly at lower altitudes, they could have originated from use in other agricultural crops, municipalities, or private gardens.

The insecticides etofenprox and methoxyfenozide, the fungicides fluazinam, difenoconazole, penconazole and trifloxystrobin were the CUPs detected in highest concentrations in the vegetation at the lower transect sites (59.55–1370.85 µg kg^{-1}, Supplementary Tables 2 and 3). With the exception of difenoconazole, they were also the most frequently detected CUPs on high altitudinal sites between 1500 and 2300 m a.s.l. The only available pesticide use data for apple growing in the region from 2017[25] show that etofenprox was among the most frequently applied CUPs with 13,695 applications, used in 89% of all apple farms and 332 kg used. Methoxyfenozide was applied 6908 times in 48% of farms with 159 kg. The fungicides fluazinam (20,985 applications, used in 76% of farms, 1703 kg used) and penconazole (30,060 applications, 85% of farms and 269 kg) were also frequently applied. However, trifloxystrobin was only applied 412 times in 4% of all farms and only 8 kg AI were used. Comparing our recorded residues with the 2017 application data, it becomes apparent that residues of frequently applied CUPs are also often recorded and widely distributed. The exception is trifloxystrobin, although it might be possible that this fungicide was applied more often in 2022.

CUP residue mixtures in soil and vegetation. CUP residues were detected in 98% of all vegetation samples and 59% of all soil samples ($N = 53$). Multiple CUPs were frequently detected in a sample; in soil 26% of all samples contained more than one pesticide and 9% contained five or more CUPs. In vegetation, 98% of all samples contained at least two CUPs and 28% of samples five or more CUPs (Supplementary Table 5). The highest number of CUPs detected in a sample was 12 in soil and 13 in vegetation, both at the lowest sampling site in the Lower Vinschgau (site T7_1). Mean CUP sum concentrations were 25 times higher in vegetation (mean of 104.48 µg kg^{-1}) than in soil (mean of 4.15 µg kg^{-1}, $p < 0.001$). This pattern was driven by fungicides ($p < 0.001$) and insecticides ($p < 0.05$). Specifically, vegetation samples had significantly higher mean concentrations

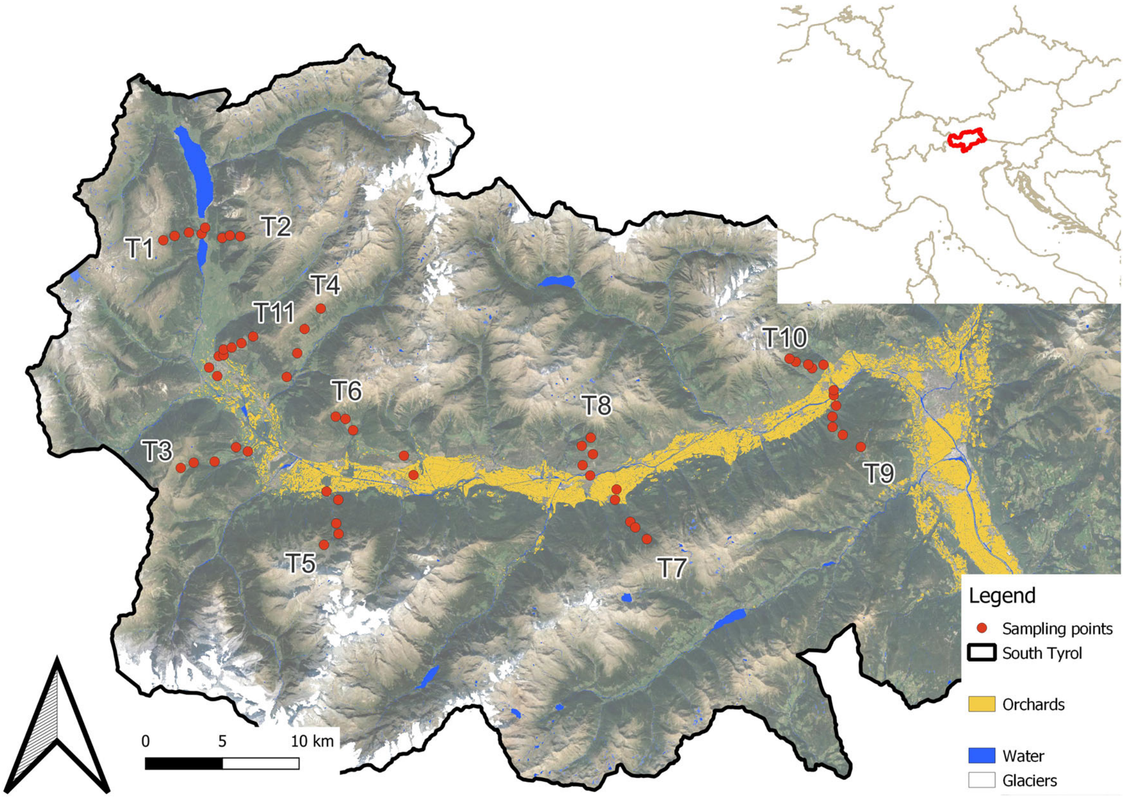

Fig. 1 Map of the study region, the Vinschgau valley in South Tyrol, Italy. Eleven altitudinal transects (T1-T11) with 53 sites (red dots) were established, where soil and vegetation was sampled between 8th and 11th May 2022, ranging from the valley floor to 2318 m above sea level (Base map: Google Satellite 2023[55]). Transects T1-T4 & T11 are situated in the Upper Vinschgau (UV), T5 & T6 in the Mid Vinschgau (MV) and T7-T10 in the Lower Vinschgau (LV) (further details in SI Tab. A1). Apple cultivation area is marked in yellow, surface water in blue and glaciers in white.

of the most abundant fungicides than soil samples (fluazinam: mean vegetation = 43.52 $\mu g\,kg^{-1}$, mean soil = 2.13 $\mu g\,kg^{-1}$; trifloxystrobin: mean vegetation = 20.88 $\mu g\,kg^{-1}$, mean soil = 0.88 $\mu g\,kg^{-1}$, and penconazole: mean vegetation = 12.79 $\mu g\,kg^{-1}$; mean soil = 2.34 $\mu g\,kg^{-1}$, all $p < 0.001$). Thirteen of the 18 CUPs detected in vegetation had systemic properties (Supplementary Table 2 and 3), and their uptake from soil is possible, however when detected at the same sampling site concentrations in vegetation were in most cases orders of magnitude higher than in soil (e.g., acteamiprid 0.31 $\mu g\,kg^{-1}$ soil, 5.30 $\mu g\,kg^{-1}$ vegetation at T6_0, methoxyfenozide 7.01 $\mu g\,kg^{-1}$ soil 1370.85 $\mu g\,kg^{-1}$ vegetation, penconazole 3.32 $\mu g\,kg^{-1}$ soil 59.55 $\mu g\,kg^{-1}$ vegetation at T7_1), making dry and/or wet deposition on vegetation more likely. Complex multi-residue contamination is also observed in apple samples from South Tyrol with 4.4 pesticides detected on average in 2021[27]. An analysis of 681 pesticide spraying records from Vinschgau apple farmers from 2017 showed that pesticides were applied daily from March to September, with apple orchards being treated with pesticides on average 38 times during the growing season and more than one pesticide applied in 58% of all spraying events, in some cases up to nine[25]. Another study confirms this high pesticide intensity also for apple production in a mountainous landscape in Austria[28]. Although exceedances of legally permissible maximum application levels[25] or Maximum Residue Levels (MRLs) of single CUPs in food[27,29] were not recorded in apples in the study region, detections of multiple CUP residues are worrying because human and environmental risk assessment procedures in Europe do not consider possible mixture effects of pesticide cocktails[30–32]. However, exceedances were recorded in grass samples from the valley bottom in the Vinschgau valley[10], that could also represent e.g., lettuce grown in private gardens. Coupled with a lack of information on sublethal effects from chronic exposure and non-reporting of co-formulants and their ecotoxicity in commercial pesticides, it is currently not possible to predict the ecological or human impact of the detected CUP residue mixtures.

CUP residue distribution: valley location, distance to apple orchards, altitude, slope orientation, surrounding vegetation, remoteness and physical-chemical properties. CUP residues formed specific clusters for Upper and Lower Vinschgau, but not for Mid Vinschgau (Supplementary Fig. 3). This can be explained by the phenology of apple trees at the time of sampling: in the Lower Vinschgau the apple trees started to fruit while in the Upper Vinschgau they started to flower, whereas phenology of trees in Mid Vinschgau was in-between. Tree phenology influences the application of CUPs, as for example insecticides against the apple codling moth *(Cydia pomonella)* are applied during the flowering period, so that the majority of orchards were already treated in the Lower Vinschgau but not in the Upper Vinschgau.

The number of CUPs detected in soil and vegetation, as well as their respective sum concentrations per sampling site, were significantly positively correlated with the proportion of apple orchard area within a 1 km radius around the sampling sites (Supplementary Tables 1 and 6). This corresponds with findings on pesticide contamination of grass samples from playgrounds at the valley bottom[9]. Our samples taken from playgrounds in the valley floor (sites T3_0, T7_0 and T9_0, Supplementary Table 1) also revealed high number of CUPs (7–8 CUPs detected in vegetation and 2–9 CUPs in soil, see Fig. 2) and higher sum concentrations (Fig. 2) and were all located within the valley

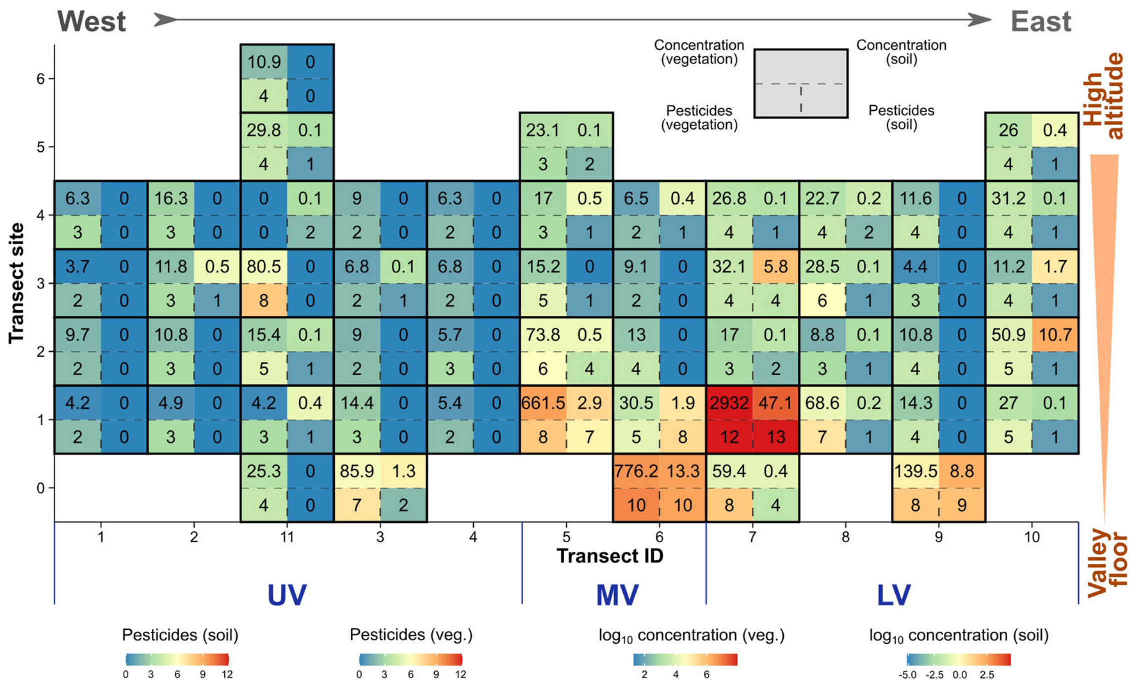

Fig. 2 Detected Current Use Pesticide sum concentrations and number of residues. Sum concentrations in µg kg^{-1} (above) and number of detected CUPs (below) in vegetation (left) and soil (right) for each of the 53 sampling sites, from valley floor (Tx_0) to highest sampling sites (Tx_6). See Fig. 1 for details on the location of the transects. Upper Vinschgau (UV), Mid Vinschgau (MV) and Lower Vinschgau (LV).

apple growing area with short distances to nearest orchards (20–90 m). We detected this CUP contamination of the landscape in May around the flowering time of apple trees in the Upper Vinschgau, and a higher contamination could be expected later in the season, as shown by others who have recorded CUP residues in this area year-round, even in winter when no pesticides are applied[10].

The number of detected CUPs in soil and vegetation samples and their sum concentrations decreased statistically significantly with altitude (Supplementary Table 6). A transect-by-transect analysis of the number of detected pesticides by individual altitude levels revealed a higher complexity of CUP mixtures at low altitudes near the valley floor than at sampling sites at higher altitudes for transects T3, T5, T6, T7, T9 in soil and T3, T5, T6, T7, T9, T10 in vegetation (Fig. 2).

The altitudinal transects in the Vinschgau revealed transport of CUP residues on a landscape scale. Air samples taken in 2019 in a Swiss valley neighbouring the study region contained three CUPs: the insecticide phosmet, the fungicides captan and fluazinam[20]. An air sampling study on the Vinschgau valley floor also found several CUPs, among them fluazinam, that were transported several kilometres away from their source of application[33]. Also in the present study, fluazinam was most frequently detected (98% of all samples) even at the highest altitudes (2318 m a.s.l.) and in the remote Matschertal (transect T4 from 1470 to 2300 m a.s.l.). Ambient air contaminated with pesticides and other agrochemicals has also been reported from other regions of Central Europe[28,34,35].

The distribution of CUPs along the transects did not always follow a linear decline in numbers and sum concentrations with increasing altitude (Fig. 2). Previous research in the valley bottom showed complex interactions between meteorological parameters and application patterns, with CUPs decreasing with increasing irradiance and distance from fields, but also influences of rainfall, wind and the proportion of apple orchards in the surrounding landscape[9]. Climatic and seasonal factors, the exchange of air masses carrying the CUPs, and the mountain slope surface have been identified as important factors for CUP distribution[15]. Foremost, low temperatures and high precipitation rates increase deposition of pesticides in mountains[14,36]. In soil, organic matter content can influence pesticide retention along mountain slopes[37]. In this study, the entire valley landscape was sampled over a four-day period, and meteorological parameters or soil characteristics at the various sites were not assessed. Hence, possible local differences among these factors along the altitudinal gradients that contribute to the observed differences in pesticide residues therefore require further investigation. In the sector of the study region with lowest apple cultivation intensity in the valley (Upper Vinschgau), the fungicides fluazinam, penconazole and trifloxystrobin were detected in similar concentrations along transects T1, T2 and T4, up to 7.5 km away from the nearest orchard and 2318 m altitude. This suggests that these CUPs were homogeneously distributed in the atmosphere on a regional scale during their transport from emission sources in the Lower Vinschgau valley, resulting in uniform contamination patterns at distant mountain sites.

To compare CUP distribution by wind onto north and south facing slopes, transects T3–T10 were located on opposite valley slopes (Fig. 1, Supplementary Table 1). There were no statistically significant differences between north- and south-facing transects, neither for CUP number nor sum concentrations in soil or vegetation (see Supplementary Information for details). The absence of such an exposure effect could be due to the reversal of wind direction in the Vinschgau between easterly (valley outwards) and westerly (valley inwards) winds, as it is also known for the Rhone Valley, Switzerland[38]. Additionally, thermal updrafts play a role in aerial pesticide transport from low altitude orchards to mountaintops[13]. However, the expected pronounced thermal updrafts on south-facing slopes were not reflected in differences in altitudinal CUP distribution between north- and south-facing slopes at the time of our sampling in May, but this might change with higher temperatures in summer.

The remoteness and surrounding vegetation cover (i.e., forest as opposed to open shrub-/heathland) of sampling sites was considered another factor influencing the degree of deposition of aerial transported CUPs. Transect 4 in the upper valley, with three CUPs detected in the vegetation in similar concentrations between 1470 and 2300 m a.s.l., extended into the Matschertal (*Val di Mazia*), a side valley of the Vinschgau without intensive apple cultivation. Distances of respective sampling sites to the nearest apple orchards were high (1543–6445 m) and the side valley is not affected by the main Vinschgau valley winds. Likewise, the only site without any CUP detections in vegetation (T11_4 at 1550 m a.s.l.) was located in a secluded alpine meadow (*Malettes*) facing northwards. Contrary to our expectations, tree cover near sampling sites did not affect CUP detection in vegetation or soil. For example, at a smaller sampling site surrounded by spruce forest (T5_2, 1236 m a.s.l.), a rather high concentration of fluazinam (60.84 $\mu g\,kg^{-1}$) was recorded compared to large, open meadow sites at higher altitudes along the same transect with lower contamination (T5_4: 15.99 $\mu g\,kg^{-1}$, 1885 m a.s.l., and T5_5: 22.01 $\mu g\,kg^{-1}$ 2064 m a.s.l.). It is possible that trees could lead to higher pesticide concentrations on the ground by trapping fog, that is known to contain high concentrations of pesticides[36,39]. We did not compare forested conditions with closed canopy with open habitats, and the function of trees in CUP residue distribution needs further investigation.

It was expected that the upslope transport of the recorded CUPs would depend on their physical-chemical properties that determine their volatility: vapour pressure (vp [mPa]) and Henry's Law Constant (K_H [Pa m^3 mol^{-1}]). However, no influence of vapour pressure on CUP detections was found; neither for the maximum altitude at which the respective substance was found, nor for the respective sum detected CUP concentration (Supplementary Table 6). Of the 21 CUPs detected at higher altitudes, only the herbicide pendimethalin (highest detection below LOQ at site T1_4: 2318 m a.s.l.) was classified as moderately volatile (Supplementary Tables 2 and 3). However, pendimethalin is rapidly degraded by photochemical processes in the atmosphere, so no risk for long-range transport via air is expected according to the EFSA's conclusion (Supplementary Table 7). Nonetheless, 21 of the detected CUPs were recorded at altitudes of 300 m or more above the valley floor and seven CUPs were recorded even on the highest sampling sites at altitudes ranging from 2064 to 2318 m a.s.l. Six of these CUPs are not expected to enter atmosphere or be subject to atmospheric transport according to EFSA's conclusions in the respective peer reviews (see Supplementary Table 7 for KH, vp and categorisation). The only exception is the fungicide fluazinam, which is considered to be relatively persistent in air and has a medium to high volatilisation potential, possibly resulting in long-range transport. Atmospheric transport has also been demonstrated in air monitoring of CUPs in Germany, where supposedly non-volatile CUPs were detected across Germany, including national parks[34]. Air monitoring in Austria showed that the number and concentrations of the detected 67 pesticides are independent of their volatility[35]. Hence, K_H or vp cannot be considered as reliable descriptors of the distribution potential of CUPs in the environment. However, CUPs can be adsorbed to fine particles and then be distributed by air currents and winds over large distances[40,41]. Although this transport pathway with subsequent deposition along mountain slopes could provide a possible explanation for the occurrence of non-volatile CUPs at high altitude sites in the Vinschgau, the corresponding Kfoc values (Supplementary Tables 2 and 3) did not show any relationship with altitude. The application of the currently used parameters to describe the dispersal potential of CUPS must therefore be questioned and assessed more thoroughly.

Half-lives are also used for the interpretation of CUP detections (Supplementary Tables 2 and 3). For the most frequently recorded CUPs in this study, longer half-lives are known from soil field studies for the insecticide methoxyfenozide (39–133 days) and the fungicide penconazole (67–115 days). With most concentrations quantified, including the highest measurement (1370.85 $\mu g\,kg^{-1}$ in vegetation), the methoxyfenozide detections are likely to result from this year's application, whereas penconazole detections were mostly below LOQ (in 23 of 35 samples in vegetation and 5 of 7 samples in soil), so residues are assumed to result from applications in the previous year. The fungicide fluazinam, with a $DT_{50\ \mathrm{field\ soil}}$ range of 21–34 days, was always detected in quantifiable concentrations and also the insecticide Etofenprox with a shorter half-live range (7–25 days) was recorded in higher concentrations in the vegetation making spring applications in the sampling year likely. Transport from very recent applications is especially evident in the case of the fungicide trifloxystrobin, that has a reported half-live in soil of only 1–3 days, but was detected in all but one vegetation and 13 soil samples.

CUPs in protected areas. Several CUP residues were detected in soil and vegetation in protected areas, in the Stelvio National Park (sampling sites T3_3-4 and T5) around the Ortler-Cevedale mountain massif, and the Texel-Group Nature Park, a Natura 2000 area (sampling sites T10_3-5). Among the CUPs detected were the two omnipresent fungicides fluazinam and trifloxystrobin at all sites in conservation areas, additionally the insecticide methoxyfenozide, the fungicides azoxystrobin and penconazole were recorded at the sites on T5 and the insecticides acetamiprid and methoxyfenozide, and the fungicide penconazole along T10, exhibiting multiple CUP residue mixes. CUP detections in nature conservation areas were recently reported in Germany[12,34,42] and Austria[35]. Long-term butterfly monitoring in the Vinschgau valley speculated about CUP exposure at higher altitudes being related to observed population declines[21]. Interestingly, the area with the highest butterfly richness described is also the site where no CUP residues were detected in vegetation and only two CUPs were detected in soil T11_4 (Malettes: 1550 m a.s.l.; for a detailed discussion on potential butterfly exposure see SI). Methoxyfenozide, that was frequently detected in conservation areas is an ecdysone antagonist affecting moulting of insects in their larval stages and is known to cause various effects at sublethal concentrations[43,44]. Although the substance is approved in the EU until 2026 it is banned and not applied anymore in Germany and Switzerland since 2018.

CUP prediction. The sampling conducted in this study documented the CUP contamination at eleven transects at altitudes ranging from the valley floor at 517 m a.s.l. to 2318 m a.s.l. Although the sampling represents only a site-wise degree of contamination, it indicates large-scale CUP transport throughout the entire valley. The spatial prediction and interpolation approach derived from principal component analysis (PCA) with subsequent principal component regression (PCR) (Supplementary Fig. 4 and Tables 8 and 9 and further information on methods) based on the detected CUP residues in the Vinschgau's soil and vegetation, provides a mapped overview of the extent of CUP residue distribution for the entire valley (Fig. 3 and Supplementary Fig. 5). The PCA explained 53.2% of the variance on the first two components and subsequent PCR-model performance achieved good explanatory power for both the total number pesticides (adj. $R^2 = 69.6\%$, Fig. 3) and the sum concentrations of CUP in soil and vegetation (adj. $R^2 = 67.4\%$,

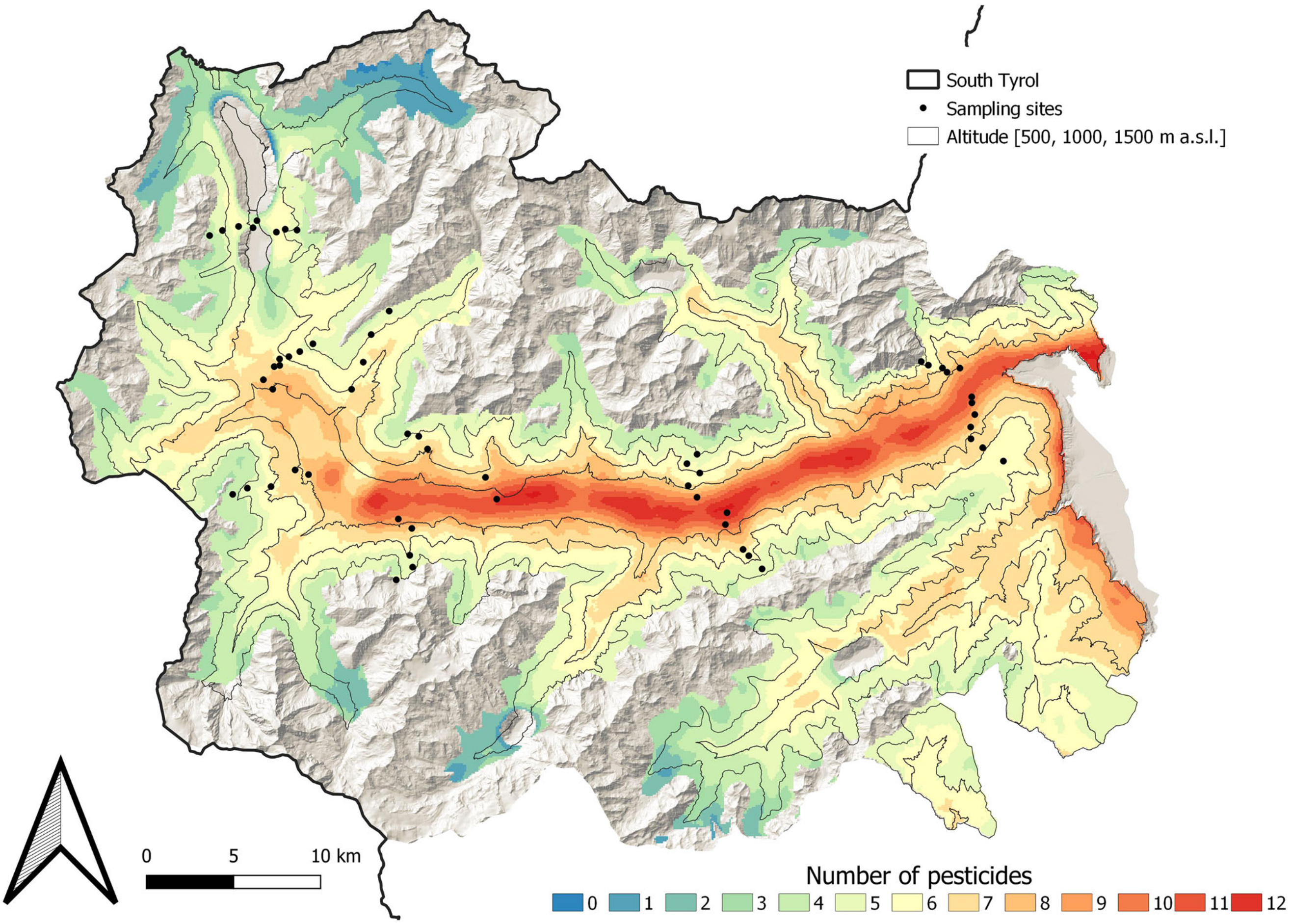

Fig. 3 Predicted number of CUP residues in soil and vegetation in the Vinschgau valley. The prediction is based on detected CUPs on the eleven transects using principal component regression (PCR). Transect sites are shown as black dots. Contour lines of 500, 1000 and 1500 m a.s.l. are shown.

Supplementary Fig. 5) for all areas for which the model was applicable (i.e., parametrised, see SI). We combined soil and vegetation data in the approach because both terrestrial matrices are relevant for a multitude of organisms and, for example, insects live and feed in both habitats and are therefore exposed in both. As shown in Fig. 2 detected concentrations were generally lower in soil. The analysis was also performed using vegetation data only, and the result did not differ to a great extent (Supplementary Fig. 6).

According to the model, the non-target areas outside the orchards on the valley floor in Mid to Lower Vinschgau, where apple cultivation is most intensive (see also Supplementary Figs. 9–12), carry the highest predicted CUP burden, with up to 12 different CUPs. We analysed all predicted CUP sum concentrations and only 0.4% exceed the highest value of almost 3000 $\mu g\, kg^{-1}$, which appears reasonable, given that it is highly unlikely that we detected the absolute highest concentration in the whole Vinschgau valley during our sampling campaign. Furthermore, only 3.0% of the predicted sum concentrations are above the second highest measured value of 776 $\mu g\, kg^{-1}$. The regression analysis shows CUP detections in mountain areas on both valley sides, whereby the contamination in the Upper Vinschgau valley and altitudes > 1500 m a.s.l. was predicted to be lower (below 8.5 CUPs and 2.03 $\mu g\, kg^{-1}$), although there was no area without predicted CUP exposure. The interpolated distribution maps (Fig. 3 and Supplementary Fig. 5) summarise the positive correlation of CUP contamination and apple cultivation intensity and the negative correlation of CUP contamination with altitude and distance of sampling sites to CUP emission sources, among other factors (see Supplementary Information for further details). It has to be noted that the regression analysis is based on the residues detected in the landscape in May 2022. The only available evaluation of farmers spraying records in the Vinschgau is from 2017 and shows most applications in spring between mid-March and End of May, however, there is no day between beginning of March and end of September without pesticide applications[25]. In 2017, insecticide applications peaked in early April and fungicides at the beginning of May. Application patterns are weather dependent and vary from year to year, but our sampling period falls within the time of high pesticide applications. As applications continue until the end of September, accumulation of CUPs is possible, resulting in even higher concentrations and numbers than those found here. Thus, landscape contamination patterns are certain to change throughout the year, depending on how many CUPs are applied and what weather conditions affect their distribution. Nonetheless, the results from regression analysis should be interpreted with care due to the uncertainties associated with extrapolative approaches and serve only as an indicator for the general distribution patterns and potential concentrations of CUPs observed throughout the Vinschgau valley. In its current state, the extrapolative results primarily represent land-use and land-cover parameters. However, future work should further investigate the temporal distribution patterns of CUPs, which likely show strong seasonal differences, and leverage additional geospatial predictors (e.g., meteorological and geological when available at high spatial resolution) in concert with more novel modelling approaches (e.g., random forests) to improve spatiotemporal predictive accuracy.

Conclusion

This investigation provides to the best of our knowledge the first comprehensive picture of CUP contamination of soil and vegetation at the landscape-scale along altitudinal gradients in one of the most intensive apple growing regions in Europe. In particular, valley meadows near apple orchards were contaminated with up to 13 different CUPs, mainly insecticides and fungicides. In addition, CUP residues were detected at all sampling sites, even at remote alpine meadows at 2318 m altitude. In the Vinschgau valley, a superposition of seasonal and diurnal winds, mountain-valley circulations and large-scale weather conditions determines the aerial CUP transport throughout the valley, resulting in landscape-level deposition and contamination along the valley and from valley floor to mountaintops with no noticeable differences between north- or south-facing slopes of the valley. This contamination pattern is particularly worrying considering that we sampled in early May and pesticide applications continues through late September. Additionally, there may be more CUPs in use than the selected 97 we analysed, which could further increase the number of CUP residues and complexity of mixtures. Similar contamination patterns leading to chemical landscapes are expected in other regions where intensive agriculture is practiced in sensitive environments such as mountain valleys. To better understand the fate of and exposure to CUPs, long-term and large-scale, terrestrial monitoring programmes are required[4,9,10] and should be incorporated in the current suggestion for an EU Directive on Soil Monitoring[45].

Our results show that physicochemical indicators used in the regulation of CUPs to describe the distribution potential in the environment are no robust predictors. Particle-bound transport could play a role in CUP aerial transport and needs further investigation. It also seems likely that frequently applied CUPs, that are used in high quantities in many farms simply are recorded more often in the landscape, independent of the physical-chemical properties of the molecules.

According to the regulation for CUP placement in the EU, authorities should assess "*its fate and distribution in the environment, particularly contamination of … air and soil taking into account locations distant from its use following long-range environmental transportation*"[46]. However, our analysis demonstrates that CUP residues are not confined to fields and orchards where they were applied, but are distributed throughout the entire landscape and even contaminate protected and remote areas. We also showed that measures taken by local authorities to control pesticide drift are not sufficient to protect non-target areas and biodiversity from pesticide contamination[8]. Therefore, the assessment of CUPs needs to be adjusted and contamination of remote areas or protected regions needs to be considered in the regulation.

Another key finding of this study is the presence of multiple CUPs in the landscape, as only one of the 53 vegetation samples did not contain a CUP residue mixture. Mixture complexity might even be higher in reality as we only analysed our samples for a fraction of the more than 400 CUPs in use in the EU. As highlighted before, the fundamental flaw in the regulatory system of evaluating the effect of only a single CUP is a gross over-simplification and does not reflect realistic exposure of organisms[32]. Exposure of organisms to pesticide mixtures at low concentrations might result in synergistic effects at sublethal levels leading to population declines in the long run[47,48].

The results of this study highlight the need for changes in cultivation practices for the Vinschgau valley, but also for other regions with pesticide-intensive agricultural production. The observed landscape-scale distribution of CUPs and contamination of protected areas and the resulting exposure of biodiversity and humans could only be reduced by a wider use of conservation biological control measures[49] and a general, immediate and drastic reduction of pesticide use and risks as outlined in the European Green Deal and the Montreal Convention on Biodiversity meeting for 2030[50,51].

Methods

Study region. The Vinschgau valley (*Val Venosta*) is located in the province of South Tyrol in the north-east of Italy[52], neighbouring Austria and Switzerland. The upper Vinschgau valley is north-south oriented, while the mid and lower Vinschgau valley are west-east oriented (Fig. 1). Due to its location in the North-Italian Alps, directly south of the main Alpine ridge, several massive mountain groups surround the Vinschgau valley: the Ötztaler Alps in the north, the Sesvenna group adjoining the upper Vinschgau in the west, and the Ortler Alps in the south, with the Ortler reaching 3905 m a.s.l. With around 18,400 ha, South Tyrol has the largest continuous area for apple cultivation in Europe and produces 50% of all Italian and 10% of all European apples[51].

Sampling and pesticide analysis. Eleven altitudinal transects (T), extending from the valley floor from 517 m a.s.l. up to 2318 m a.s.l. with a total of 53 sampling sites were preselected and established on both mountain slopes of the Vinschgau valley and sampled for soil and vegetation between May 8th and May 11th, 2022. (Fig. 1, Supplementary Table 1). Composite soil samples consisting of 25 subsamples were taken on a grassland area of 5 × 5 m per transect point with a soil corer (diameter: 13 mm, 10 cm deep, Rasengrün, Ingelheim, Germany) in a depth of 0–10 cm after removing vegetation from the soil surface. Likewise, diverse, above-ground vegetation consisting of differing grasses and herbaceous plants was hand collected randomly in an area of approximately 30 m^2 around each transect point using laboratory gloves, filling half of a 1 L Ziploc freezer bag. Both soil and vegetation samples were stored at 4 °C until further processing in the laboratory (for details on sample processing and extraction see SI).

Soil and vegetation were analysed for 97 CUPs, using a high-performance liquid chromatography coupled with an electrospray ionisation tandem mass spectrometry system (HPLC-ESI-MS/MS; HPLC: Agilent Technologies LC 1260 Infinity II series, MS/MS: Agilent Technologies 6495 C, Santa Clara CA, USA). Details on the selection of the target CUPs and analytical HPLC-MS/MS method and instrument parameters are published[12,23] and can also be found in and the Supplementary Information (see text and Figs. 1 and 2).

As a measure of ecosystem contamination, CUP sum concentrations were calculated for each sampling site as sum of all single positive CUP detections in soil and vegetation separately. For pesticides detected at a level below LOQ but above LOD the respective LOD was used as concentration value for subsequent calculations as minimum residue that can be assumed with certainty to be present in the sample. The arithmetic mean of CUP sum concentrations on all sampling sites was used for comparison of magnitude of contamination between soil and vegetation (see Supplementary Information for details).

Mapping of principal component regression. PCA was used to test to what extent environmental factors and land cover attributes can explain total number of CUP and sum concentration in soil and vegetation at individual sampling sites. A total of 13 variables was considered: These were location characteristics found to correlate with degree of CUP contamination (altitude of sampling site, height difference and distance to nearest orchard) as well as land use and land cover attributes also significantly influencing CUP contamination (area share of apple orchards, sampling site characteristic in altitudinal or valley floor locations (alpine grassland, rock, other agriculture, green urban areas, vegetation, pastures, meadows and water)). All predictor data was z-score transformed (scaled and centered) to prevent bias towards variables with higher variance[53] (for further details see Supplementary Information).

Principal components derived from PCA were subsequently used for PCR with the aim of extrapolating and predicting CUP contamination throughout the entire Vinschgau valley. PCR combines dimension-reduction of a dataset (PCA) with least-squares regression[53]. PCR was applied for an area of ca. 1014 km^2 in which spatial attributes were in accordance with the real sampling points, i.e., in a range of ±5% (e.g., <2400 m a.s.l.), because model accuracy degraded substantially for areas outside the parametrised room (for further details see Supplementary Information). Model prediction applies primarily to open meadows, hence, prediction results for the total number of pesticides excluding forest land cover is available in the Supplementary Information (Fig. 7).

Data availability

All data that were calculated in this study are available in the Supplementary Information.

Code availability

Detailed calculations and a script for producing the maps can be obtained[54].

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Author contributions
C.A.B. planned and supervised the project and wrote the manuscript. C.A.B. and N.B. selected CUPs for analysis. C.A.B., N.E., K.H. and J.G.Z. coordinated the logistics and arranged the necessary permissions from relevant authorities. N.E and N.B. performed the analytical analysis and prepared the data. N.E. performed the statistical analysis. J.W. and N.E. performed the landscape regression analysis and prepared the figures. C.A.B., N.E., J.W., K.H. and J.G.Z. discussed the results. All authors commented and improved the manuscript and agreed on the final version. The Project was funded by University of Natural Resources and Life Sciences (BOKU), Vienna, Austria and RPTU- Landau. Open Access funding enabled and was organised by Projekt DEAL.

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