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Pesticide residue patterns along edaphic and climatic gradients in Peruvian coastal and Andean agroecosystems

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A B S T R A C T

The intensive use of pesticides in commercial agriculture in developing countries poses risks to human and environmental health. In Peru, information on pesticide residue distributions and their relationships with environmental factors remains limited. This study quantified pesticide residues in crop leaves, soil, and water across contrasting agroecosystems in the coastal valleys of Chancay-Huaral and Pativilca and the high-Andean valleys of Mantaro and Tarma. A total of 86 samples were analyzed for 92 pesticide compounds using validated LC-MS/MS and GC–MS/MS methods. Associations with edaphoclimatic variables were assessed using multivariate and predictive approaches. Pesticide residues were detected predominantly in crop foliage, whereas soil and water showed lower detection frequencies (16% of sampling points). Coastal valleys exhibited higher detection frequency (528 vs. 72 detections) and a greater percentage of contaminated samples (100% vs 68%) than high-Andean systems. Among samples with detectable hazardous pesticides, 70% exceeded Codex Alimentarius maximum residue limits (MRLs). Banned compounds, including methamidophos and chlorpyrifos, were also detected, indicating gaps in regulatory compliance. Pesticide variables were filtered based on detection frequency ($\geq$ 5%) and WHO toxicological classification and grouped by chemical class to identify representative compounds. Occurrence patterns were significantly associated with clay, total organic carbon, available potassium, and precipitation according to ordination and predictive models. These results show that pesticide occurrence and magnitude are structured by environmental conditions and agricultural intensity, highlighting the need for geographically targeted monitoring and risk management strategies in Peru.

1. Introduction

The global population is projected to reach 9.7 billion by 2050, with most of the growth occurring in developing countries (United Nations, 2019). As a result, enhancing crop yields and/or cropping frequency on existing land (80%) will be essential (FAO, 2024). Meanwhile, climate change scenarios project the occurrence of extreme events, increases in global surface temperatures, and precipitation variability (Calvin et al., 2023), which raise the vulnerability of agricultural systems to potential pest and disease outbreaks (Nega, 2025). Formerly, the intensive use of agrochemicals has not only combated these threats, but also significantly contributed to increased crop productivity worldwide (Singh et al., 2020). However, there are potential toxicity to non-target organisms, human health risk, persistence in environmental matrices, and mobility into surface and groundwater systems (Ansari et al., 2024; Elumalai et al., 2025; Mohd Ghazi et al., 2023).

Pesticide use is rising in developing countries, particularly in South America (FAO, 2025; Olguín-Hernández et al., 2024). Despite evidence of synthetic pesticides' negative impacts on social and environmental sustainability (Hammond Wagner et al., 2016), farmers often prioritize immediate economic gains over long-term trade-offs, primarily due to a lack of knowledge (Olguín-Hernández et al., 2024; Robinson et al., 2007; Ponce-Caballero et al., 2022). Additionally, weak regulatory enforcement, fragile political structures, and uneven development among rural communities contribute to this issue (Coria and Elgueta, 2022; Hu, 2020). These countries face many problems related to the use, storage, and disposal of pesticides (Huepa Briñez et al., 2024). In 2020, Latin America and the Caribbean reported the highest global pesticide application rates, with Ecuador registering the maximum (13.74 kg ha^{-1}) (Staudacher et al., 2020). Basically, South America accounts for 90.9% of total pesticide use, mainly herbicides (51.5%) (Pizarro et al., 2024).

Peruvian agriculture features a wide variety of crops and farming practices; however, most studies focus on food products or specific high-

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input agricultural zones (Silva et al., 2023). The country is divided into three natural regions: coast, highlands, and forest. The coast is home to most industrial, commercial, local and export agriculture activities. The highlands, comprising the Andes, plateaus, and valleys, cover 27% of the territory; while the forest, mainly tropical rainforests, occupy 60% but are sparsely populated (Velazco and Pinilla, 2018). The coastal and central Andean valleys stand out for their contribution to national crop production and regional economic relevance; but, few comparative studies have assessed pesticide traces within multiple watersheds (Chávez-Dulanto et al., 2024; Galagarza et al., 2021; Honles et al., 2022). In addition, the governance is weakened by fragmented authority (Servicio Nacional de Sanidad Agraria (SENASA), Dirección General de Salud Ambiental e Inocuidad Alimentaria (DIGESA), Organismo Nacional de Sanidad Pesquera (SANIPES), Comisión Multisectorial Permanente de Inocuidad Alimentaria (COMPIAL), regional and local governments), contradictory norms, and poor implementation. Monitoring is mainly mandatory for exports, leaving domestic products less controlled. Instead, excessive regulation limits access to biological pesticides, while cheap, smuggled chemicals remain widely used (Atkinson et al., 2023).

Despite ongoing monitoring efforts, Peru does not currently maintain a publicly accessible, integrated database that systematically compiles pesticide residue and environmental contaminant data at the national scale. Instead, residue information is disseminated through annual SENASA reports, which summarize results by region based on a limited number of samples. The regional aggregation of these data restricts their utility for spatially explicit analyses and hinders the assessment of relationships between contamination patterns and environmental factors. Furthermore, existing monitoring programs are predominantly oriented toward evaluating pesticide residues in agricultural commodities, particularly fruits, with comparatively limited attention to the environmental context influencing contaminant occurrence and distribution (Galagarza et al., 2021; SENASA, 2024).

Pesticide fate in soils and agroecosystems is governed by three primary mechanisms: sorption, degradation, and leaching (Sadegh-Zadeh et al., 2017). Sorption is largely controlled by soil organic carbon (TOC) and cation exchange capacity (CEC), which can reduce pesticide mobility but also limit bioavailability for degradation. Temperature, precipitation, and soil moisture further shape these processes by affecting solubility, hydrolysis, leaching, and microbial activity (Kaur et al., 2023). These interacting processes define what edaphoclimatic factors are expected to regulate both the occurrence and magnitude of pesticide residues across environmental matrices.

Based on these mechanisms, we expect systematic differences between coastal and high-Andean agroecosystems. Coastal systems, characterized by higher temperatures, intensive horticulture, and irrigation, are likely to exhibit higher pesticide inputs and more frequent detections. In contrast, high-Andean systems, with cooler temperatures and different soil characteristics, may show reduced degradation rates but also lower application intensity. Furthermore, soils with higher TOC and CEC are expected to retain greater pesticide loads, resulting in higher concentrations in soils and plant tissues but reduced mobility into water (Wauchope et al., 2002).

This study addresses the following research question: How do edaphoclimatic factors interact with the occurrence, distribution, and magnitude of pesticide residues across contrasting Peruvian agroecosystems?. We tested the following hypotheses: (a) Pesticide detection frequency and concentrations are higher in coastal agroecosystems than in high-Andean systems due to greater application intensity and climatic conditions favoring persistence and transport, (b) TOC and CEC are positively associated with pesticide concentrations in soils and plant tissues, reflecting increased sorption and retention, (c) Precipitation and temperature significantly influence pesticide composition and distribution by modulating degradation and transport processes. To test these hypotheses, (i) we characterized the concentration and compositional profiles of pesticide residues in crop foliage, soils, and water across two contrasting agroecosystems in Peru; (ii) quantified the association of edaphoclimatic predictors on pesticide composition using multivariate ordination and permutational hypothesis testing; and (iii) identified key predictors of pesticide load using complementary predictive modeling approaches.

2. Materials and methods

2.1. Study area and sampling sites

The study areas included agricultural zones in the lower basins of the Chancay - Huaral (11°33′54.30″ S 77°12′20.50″ W) and Pativilca (10°42′29.78″ S 77°45′25.90″ W) rivers on the central Peruvian coast; and the inter-Andean agricultural valleys of the Mantaro (11°54′18.13″ S 75°21′2.52″ W) and Tarma (11°25′59.95″ S 75°31′55.15″ W) rivers in the central highlands (Fig. 1). The Chancay-Huaral Valley has a subtropical desert climate with scarce rainfall (< 55 mm year^{-1}), maximum temperatures from 18.5 to 27.0 °C, and minimum between 14.1 and 19.2 °C (SENAMHI, 2025). River flow varies from 6.5 m^3 s^{-1} (September - October) to 33.6 m^3 s^{-1} (March - April) (ANA, 2025). The Pativilca Valley has a temperate-arid climate (SENAMHI, 2021), with an average annual flow of 51.61 m^3 s^{-1}, over 94% is used for irrigation (ANA, 2015). The Mantaro River Basin, a national priority for water management due to environmental issues, including waste contamination, riparian degradation, and water quality concerns (ANA, 2023). The valley has temperate to cold and semi-dry to dry climates (SENAMHI, 2021), with agriculture using the second-largest volume of water rights (959.4 hm^3) after energy production (ANA, 2024), and rainfall ranges from 4.7 mm (June) to 122.9 mm (February) (ANA, 2025). The Ricrán River valley, part of the Tarma River Basin on the Atlantic slope, has an average monthly flow of 5.51 m^3 s^{-1} (ANA, 2015) and a temperate semi-arid climate influenced by persistently humid levels (SENAMHI, 2021).

Analysis zones in each basin were defined using a 1500 m buffer and a 20 km upstream distance from each stream outlet. Sampling sites were selected with Stratified Random Sampling using the AcATaMa plugin (Llano, 2024) in QGIS 3.38. Eighty six sampling sites were established, maintaining at least 200 m between points. Land cover strata were defined as agricultural and forest areas based on the ESA WorldCover 2021 dataset (Zanaga et al., 2022).

2.2. Sampling of leaves, water, and soil

Sampling was made in homogeneous crop plots following an “X” shape design to ensure representativeness. Leaves were collected from all plant parts (internal, external, upper, and lower), and soil samples were taken from a ~20 cm deep “V”-shaped hole, which corresponds to the biologically active topsoil most directly influenced by agricultural management and pesticide applications. Also, the 0–20 cm layer was the topsoil layer available in the majority of sampled soils. Soil and water samples for pesticide analysis were stored at ~4 °C. Leaf samples were placed in paper bags supplied by the analytical laboratory and transported according to the laboratory's sample handling recommendations (Table A1, Supplementary Material).

2.3. Pesticides analysis

The leaf pesticide analysis was performed using the PE-674 methodology, an in-house method according to the SANTE analytical quality control and method validation procedures in food and feed (EURL, 2025). For most selected analytes, the LOD and LOQ were 0.003 and 0.01 mg kg^{-1}, respectively, whereas metalaxyl showed higher limits (LOD = 0.033 mg kg^{-1}; LOQ = 0.10 mg kg^{-1}). For soil and water, the detection and quantification of semi-volatile organic compounds were performed using EPA Method 8270E Rev.6 (2018) by GC–MS/MS. Residual pesticides were detected using liquid chromatography

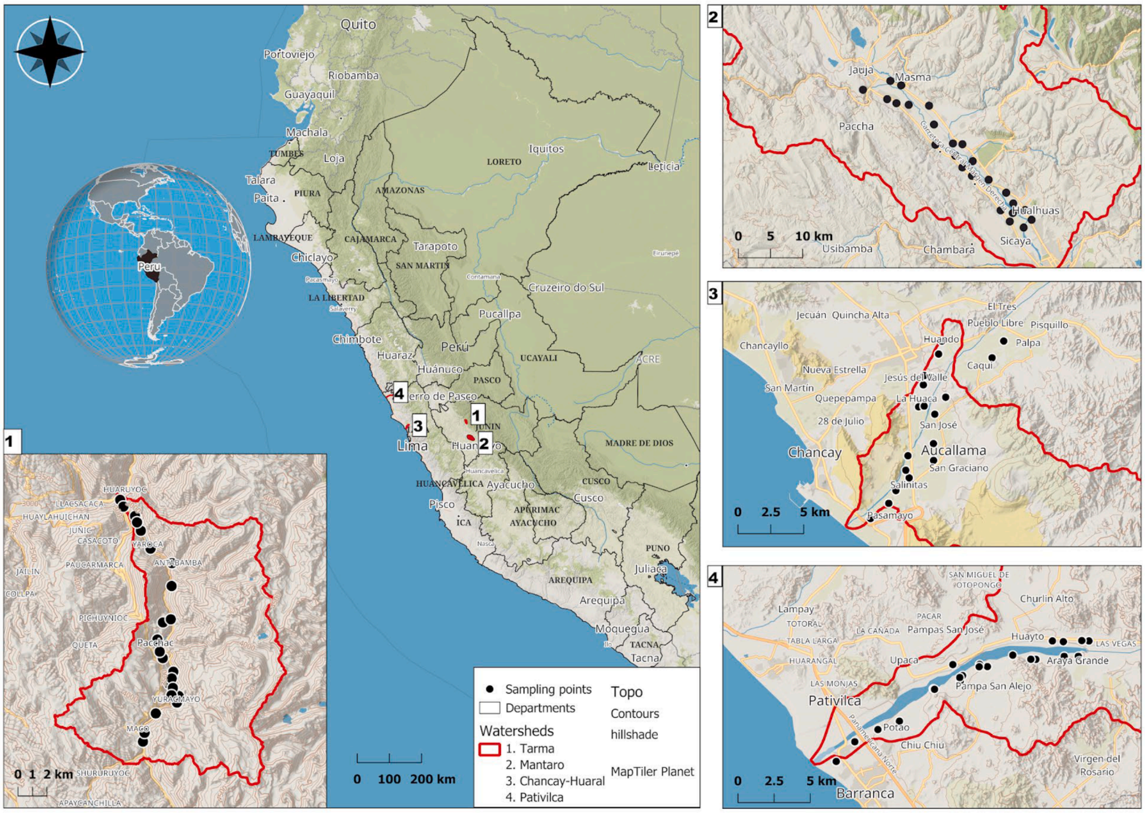

Fig. 1. Study areas corresponding to Tarma, Mantaro, Chancay-Huaral, and Pativilca Valleys.

(LC-MS/MS Triple quadrupole Agilent Technologies, Model: G6470B, Series: SG2210G212) and gas chromatography with a mass spectrometry detector (GC–MS/MS Bruker Scion Evoq, Model: SCION TQ, Series: GTQA1404F24). Calibration and quality control were performed with certified reference materials traceable to ISO 17,034 and ISO/IEC 17, 025 standards. Instrument precision was verified through repeated injections of calibration standards, with retention time and peak area RSDs below the criteria acceptance. Pesticide residues were analyzed by ISO/IEC 17,025-accredited commercial laboratories, AGQ Labs (AGQ PERU S.A.C.) and SLab (Sistema de Servicios y Análisis Químicos S.A.C.) in Lima, Peru.

2.4. Physicochemical soil analysis

Soil parameters included texture using the Bouyoucos procedure (Beretta et al., 2014), pH (inoLab® pH 7310), and electrical conductivity (EC) of the saturation extract (inoLab® Cond 7310). Total carbon (TC), total organic carbon (TOC), and total nitrogen (TN) were measured after dry combustion using an elemental analyzer (LECO CN828, LECO Ltd., Germany). Extractable phosphorus (P_a) according to the Olsen method for neutral and alkaline soils and the Bray-1 method for acidic soils (Dari et al., 2019). Finally, exchangeable cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) and extractable potassium (K_a) were determined by ammonium saturation, and inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer NexION 2000 Series P, Perkin Elmer Inc., USA). Analyses were done in “Laboratorio de Suelos, Aguas y Foliares” at “Instituto Nacional de Innovación Agraria” in Lima, Peru.

2.5. Climatic data

Satellite image–based data extraction enabled the estimation of key climatic variables. The resulting datasets provided consistent spatial and temporal coverage. Climatic data on temperature and precipitation were obtained from the WorldClim 2.1 database at a spatial resolution of 30 arc-seconds (~1 km), representing present-day conditions as the average for the period 1970–2000 (Fick and Hijmans, 2017). Wind speed at a height of 10 m was obtained from the Global Wind Atlas (GWA) 4.0, a free web-based application that provides wind resource mapping at a spatial resolution of 250 m (Davis et al., 2023). Figure A1 (Supplementary Material) shows a parallel coordinate plot with normalized values of precipitation, temperature, and wind speed variables. The median and media values are listed in Table A2 (Supplementary Material).

2.6. Data analysis

We grouped the analytes into five classes following the Pesticide Action Network (PAN) International List of Highly Hazardous Pesticides and the classification of the World Health Organization (WHO) as references (PAN, 2024; WHO, 2020). The statistical analyses followed a structured workflow consisting of: (i) exploratory analysis (boxplots and Kruskal–Wallis tests); (ii) multivariate ordination to explore patterns in pesticide composition [Principal Component Analysis (PCA), Principal Coordinates Analysis (PCoA), and Detrended Correspondence Analysis (DCA)]; (iii) permutation-based hypothesis testing to assess differences between groups [Permutational Multivariate Analysis of Variance (PERMANOVA)]; (iv) constrained ordination to evaluate relationships with environmental variables [Redundancy Analysis (RDA)]; and (v) predictive modeling to identify key drivers of pesticide occurrence [Random Forest regression and classification, Multiple Linear Regression (MLR), and Generalized Additive Models (GAMs)]. The distribution of individual analytes across the principal categorical groupings (Zone and Valley) was examined using Kruskal-Wallis tests and stratified boxplots. Spearman correlation was applied to assess both the strength and the direction of the associations between the variables. PCA (linear reduction) and PCoA (metric distance-based ordination) were used to visualize patterns in pesticide composition and identify similarities among samples. PCoA was computed using wcmdscale (vegan) on the Bray-Curtis dissimilarity matrix of the raw pesticide concentrations. PERMANOVA (adonis2, vegan) was used to formally test whether pesticide composition differed significantly among categorical groupings and whether individual environmental variables were associated with compositional variation. Because PERMANOVA is sensitive to heterogeneous within-group dispersion (which can confound centroid-based testing), betadisper analysis was conducted to test for homogeneity of multivariate dispersion among Valley and Zone groups. DCA was applied to assess the gradient length of the primary compositional axis, which determines whether a linear or unimodal constrained ordination is more appropriate. The Axis 1 indicated predominantly linear responses (< 3 SD). Therefore, RDA was selected to explore the relationships between pesticide classes and environmental variables. RDA requires that the predictor matrix not contain severe multicollinearity, thus Variance Inflation Factors (VIFs) quantify how much the variance of a regression coefficient is inflated by collinearity with other predictors. A common threshold of VIF < 10 was applied. An iterative procedure was implemented: all 14 environmental predictors were included in a provisional RDA, the VIF of each predictor was computed (vif.cca, vegan) and VIF exceeding 10 was removed. Three variables were removed during iterative VIF selection: tmean, TC, and Sand. The 11 retained variables were precipitation, Ka, TOC, EC, Clay, Silt, Pa, CEC, $CaCO_3$, pH, wind_speed. RDA (anova.cca, 999 permutations) was used to examine pesticide species – environment relationships. Four predictive models were fitted to explain and predict Pest_total (total pesticide concentration) using the 11 VIF-selected environmental and soil predictors. The models span a range of complexity and interpretability: two ensemble tree-based models (RF Regression and RF Classification), a classical parametric linear model (MLR with stepwise selection), and a semi-parametric smooth additive model (GAM). Using multiple model types allows cross-validation of variable importance findings and reduces dependence on the assumptions of any single approach. Data were processed using R v4.3.0 (R Core Team, 2025).

To synthesize variable importance findings across all four predictive models (RF Regression, RF Classification, MLR, GAM), importance scores were normalized to the [0, 1] range within each model and assembled into a heatmap. This normalization allows direct visual comparison despite the different scales used by each model (%IncMSE, MDA, |t-value|, and F-statistic, respectively). Variables absent from a model (e.g., those excluded by stepwise selection or not significant in GAM) are indicated with a dash.

2.7. Model validation

Model performance was evaluated using complementary validation strategies to provide a robust assessment of generalization error: Out-of-Bag Error (OOB), Ten-Fold Cross-Validation with Five Repeats, and Hold-Out Validation (75/25 Split). For Random Forest (RF), performance was assessed using OOB estimation and a stratified 75/25 hold-out validation. The stepwise MLR model was evaluated using 10-fold cross-validation repeated five times (caret package), producing 50 independent estimates of prediction error and reducing the variance associated with a single data split. Additionally, a bootstrap procedure (100 resamples) was used to estimate a 95% percentile confidence interval for the RF regression RMSE and provide uncertainty bounds on this performance estimate.

3. Results

3.1. Pesticide analysis and distribution

Pesticide residues in water and soil were generally below detection limits. For water samples, the analytical laboratory established a common limit of detection (LOD)/quantification (LOQ) limit of 0.00008 mg L^{-1} for all target analytes. For soil samples, a table reporting the analyte-specific LOD/LOQ values has been added in Table A3 (Supplementary Material). Concentrations reported below this threshold were considered below the analytical detection limit.

In water samples, atrazine, metribuzin, metalaxyl, and pendimethalin were detected; in soil, atrazine, metribuzin, chlorothalonil, chlorpyrifos, and pyrimethanil. However, according to the Guidelines for drinking-water quality (WHO, 2022) and the Canadian Water Quality Guidelines for the Protection of Agricultural Water Uses (CCME, 2025), the concentrations did not exceed the limits, except for metribuzin detected in water in the Mantaro Valley. Likewise, it is noteworthy, chlorpyrifos in the soil in Tarma Valley (Table A4, Supplementary Material). Evidence of pesticide residues in water and soil was found at only 16% of the total sampling sites.

In contrast, for leaves samples, the following classes were established for grouping the analytes according to their hazardousness (WHO and PAN classification): Extremely hazardous, Highly hazardous, Moderately hazardous, Slightly hazardous, and Non-acute hazard. The classification of the compounds based on the chemical group and action mode is presented in Table A5 (Supplementary Material).

Given the large number of detected pesticide residues and the strong imbalance between regions, we reduced dimensionality while preserving ecological interpretability. Pesticide variables were filtered based on detection frequency (≥ 5%) and toxicological relevance (WHO classification). Compounds were then grouped by chemical class, and representative variables were selected to capture dominant pesticide signatures across agroecosystems (Table A6, Supplementary material). The final list of pesticide residues was the following: Omethoate (OMT), Methomyl (MTM), Chlorpyrifos (CPF), Imidacloprid (IMI), Thiamethoxam (THM), Cypermethrin (CYP), Fipronil (FIP_S), Difenoconazole (DFC), Tebuconazole (TEB), Atrazine (ATR), Metribuzin (MTB), Carbendazim & Benomyl (CBZ_BEN). FIP_S corresponded to the analytical residue definition expressed as the sum of fipronil and its sulfone metabolite, reported as fipronil, whereas CBZ_BEN represented the combined determination of carbendazim and benomyl according to the analytical method employed.

Ten of twelve analytes showed statistically significant differences across Zone, and ten across Valley. Notable exceptions were MTB (Zone: $p = 0.304$) and THM (Zone: $p = 0.404$; Valley: $p = 0.760$), suggesting these compounds are distributed uniformly across geographic strata. CYP, IMI, and DFC exhibited the strongest spatial stratification ($p < 0.001$ for both factors) (Table 1).

Concentrations varied markedly among compounds and locations. Several pesticides, including CPF, IMI, MTM, OMT, and THM, tended to occur at higher concentrations in coastal areas, whereas concentrations in highland areas were generally lower and less variable (Fig. 2A). Differences among valleys were also evident, indicating substantial spatial heterogeneity in pesticide occurrence across the study region (Fig. 2B).

As no specific Maximum Residue Limit (MRL) values were available

Table 1
Kruskal-Wallis test p-values by analyte for zone and valley groupings.

Analyte	KW p-value (Zone)	KW p-value (Valley)
MTM	0.0211	0.0460
OMT	0.0342	0.0187
CYP	< 0.001	< 0.001
CPF	0.0028	0.0110
DFC	0.0002	0.0003
FIP_S	0.0219	< 0.001
IMI	< 0.001	< 0.001
MTB	0.3042	0.0002
TEB	0.0001	0.0016
THM	0.4044	0.7604
ATR	0.0079	0.0222
CBZ_BEN	0.0209	0.0108

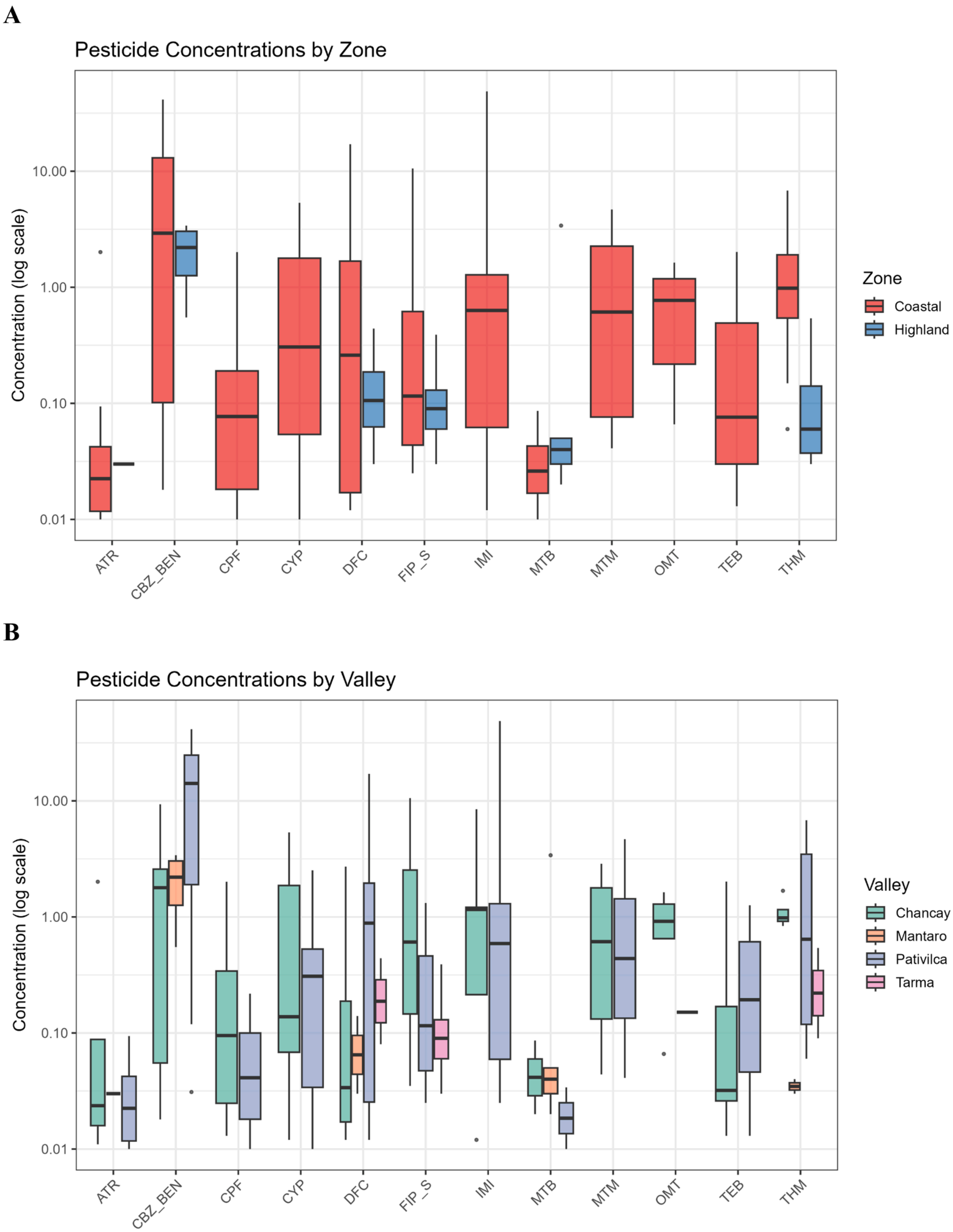

Fig. 2. Distribution of detected pesticide concentrations (log scale) by zone (A) and valley (B). Omethoate (OMT), Methomyl (MTM), Chlorpyrifos (CPF), Imidacloprid (IMI), Thiamethoxam (THM), Cypermethrin (CYP), Fipronil (FIP_S), Difenoconazole (DFC), Tebuconazole (TEB), Atrazine (ATR), Metribuzin (MTB), Carbendazim & Benomyl (CBZ_BEN).

for leaves, the MRL for fruit according to Codex Alimentarius was used as a reference (Table A7, Supplementary Material). For some crops, there were no available data, and we used other crops for comparison (FAO, 2025). Chlorpyrifos is currently banned nationwide; however, it was detected in purple maize (0.703 mg kg^{-1}), maize (0.01 - 2.01 mg kg^{-1}), avocado (0.095 mg kg^{-1}), cassava (0.015 mg kg^{-1}), mandarin (0.013 - 0.041 mg kg^{-1}), paprika (0.218 mg kg^{-1}), and panca chili (0.022 - 0.077 mg kg^{-1}) in Chancay-Huaral and Pativilca valleys.

In summary, most of the detected compounds belonged to the moderately and slightly hazardous classes. The Chancay-Huaral and Pativilca valleys had the highest occurrence. Moreover, among all samples containing pesticides classified as extremely, highly, or moderately hazardous, 70% exceeded the Codex Alimentarius MRLs, primarily in coastal horticultural crops (Table A7, Supplementary

Material).

3.2. Relationship between pesticide classes with edaphoclimatic and crop parameters

Spearman's correlation was used to evaluate the strength and direction of the relationship between the variable groups. In this sense, CYP, IMI, and DFC had moderate negative correlation with TOC, TC, Ka, CEC, and precipitation; and TEB with these last two. On the other hand, a moderate positive correlation between DFC and TEB with temperature ($|\rho| \geq 0.4$ and $p \leq 0.05$) (Figure A2, Supplementary Material).

3.3. Integrative multivariate analyses of pesticide distributions and environmental drivers

Principal component analysis (PCA) generated 24 components. The first two principal components explained 35.8% and 22.8% of the total variance, respectively, accounting for 58.6% cumulatively. Subsequent components individually explained <7% of the variance, indicating that the major structure of the dataset was captured by the first two axes (Table A8, Supplementary Material). Therefore, PC1 and PC2 were used for ordination and visualization. The PCA revealed that pesticide distribution is strongly structured along a temperature and soil property gradient. Compounds such as THM, CPF, and CYP were associated with higher temperatures, sandy soils, and alkaline conditions, whereas fungicides such as CBZ_BEN, TEB, and DFC were linked to finer-textured soils and higher electrical conductivity (Table A9, Supplementary Material) (Fig. 3).

Principal Coordinates Analysis (PCoA) based on a Bray-Curtis distance matrix was used to explore patterns of similarity or dissimilarity among samples in a reduced-dimensional space. The PCoA graphics group by valley (axis 1 = 22.4%, axis 2 = 12.6%) showed more clustering in Tarma valley (Fig. 4).

Multivariate analysis based on Bray–Curtis dissimilarities revealed that both crop type and geographic zone were significantly associated with differences in composition (PERMANOVA, $p = 0.001$ for both factors). Under a marginal model, crop explained a substantially larger proportion of the variance ($R^2 = 0.35$) compared to zone ($R^2 = 0.048$). When accounting for potential confounding effects with stratified permutations, both factors remained significant, with crop explaining 43.3% of the variance when controlling for zone, and zone explaining 13.2% when controlling for crop (PERMANOVA, $p = 0.001$ in both

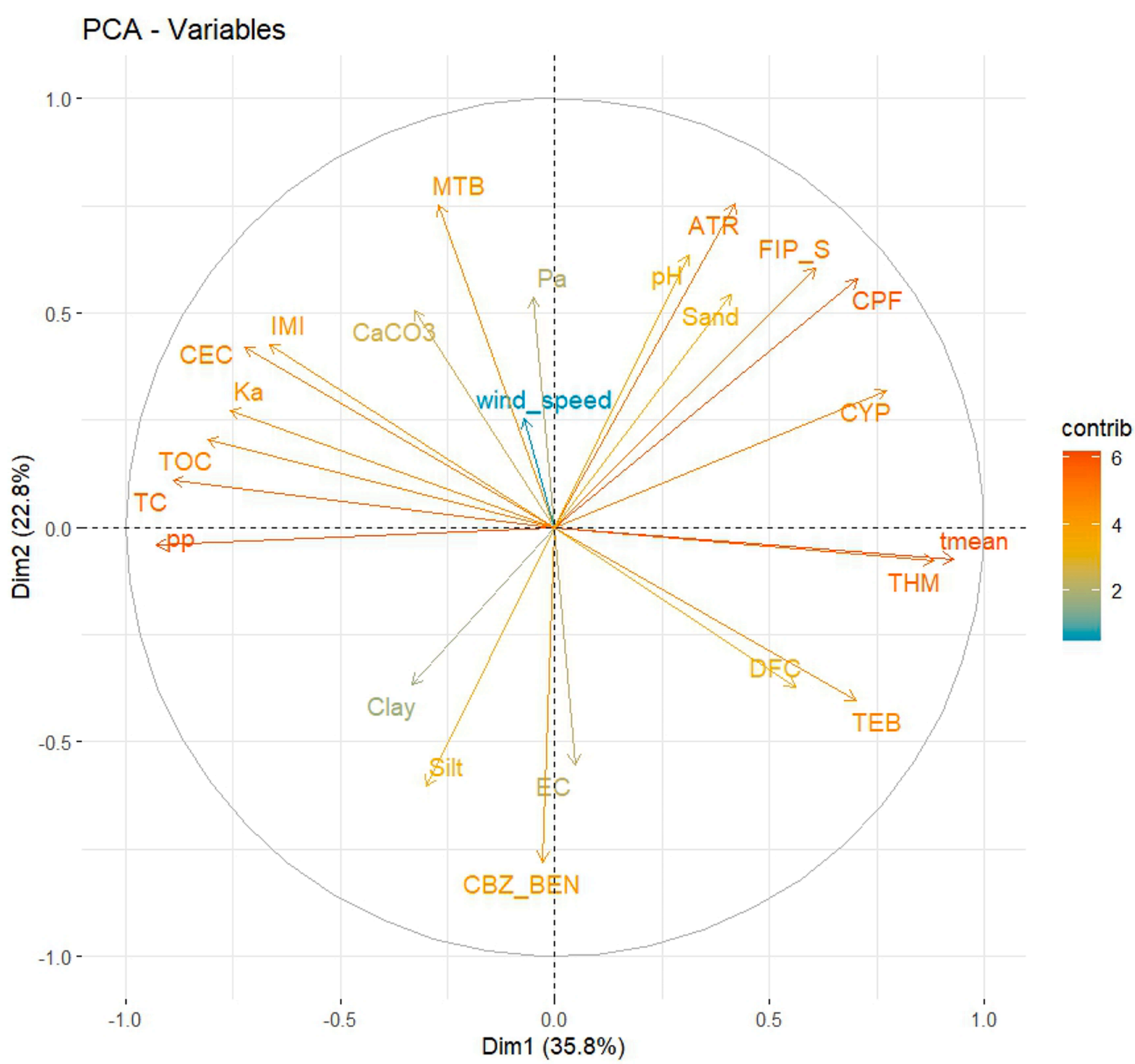

Fig. 3. Principal Component Analysis (PCA) of Pesticides and Edaphoclimatic data. Methomyl (MTM), Chlorpyrifos (CPF), Imidacloprid (IMI), Thiamethoxam (THM), Cypermethrin (CYP), Fipronil (FIP_S), Difenoconazole (DFC), Tebuconazole (TEB), Atrazine (ATR), Metribuzin (MTB), Carbendazim & Benomyl (CBZ_BEN). EC: Electrical conductivity, TC: Total carbon, TOC: Total organic carbon, Pa: Available phosphorus, Ka: Available potassium, CEC: Effective cation exchange capacity, tmean: Temperature mean, and pp: Precipitation.

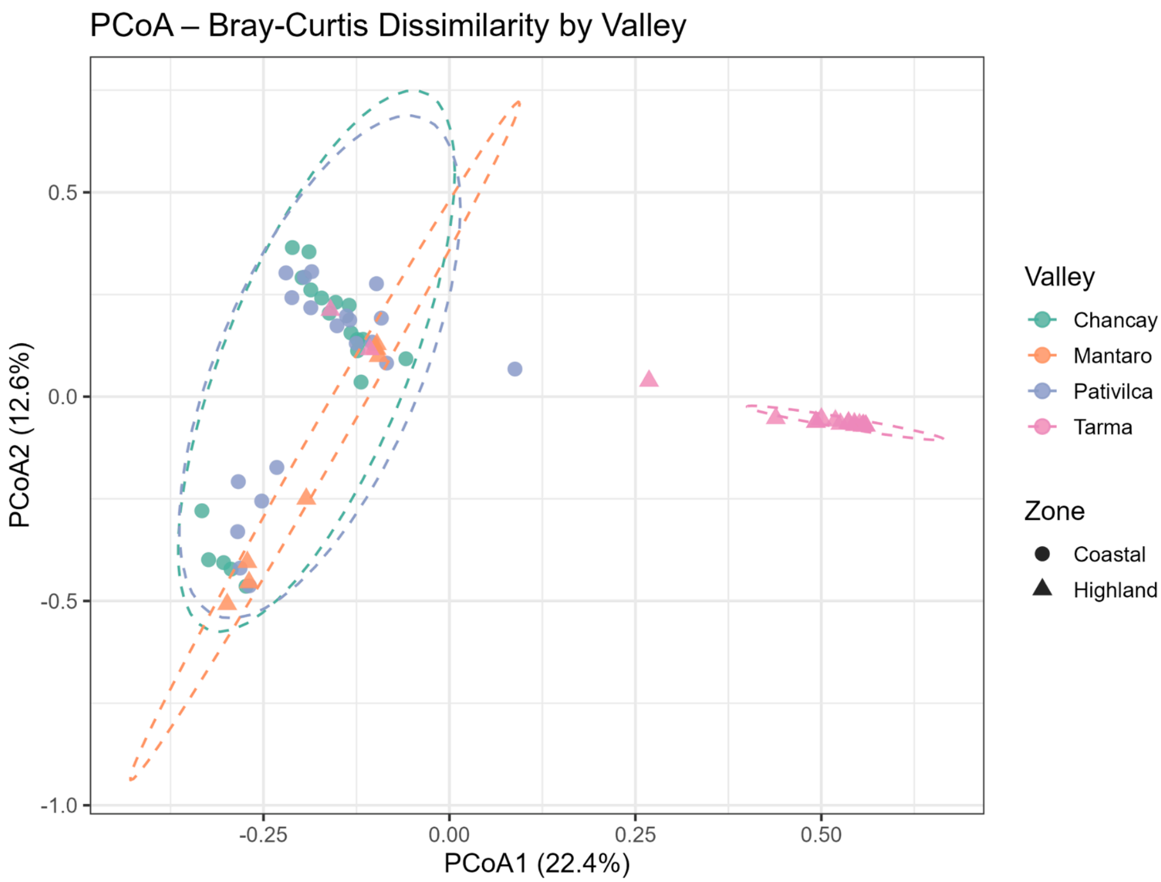

Fig. 4. Principal Coordinates Analysis (PCoA) of pesticide composition by valley. Axis labels show the percentage of total Bray-Curtis dissimilarity captured.

cases). Within-zone analyses further showed that crop type was significantly associated with compositional differences in both coastal ($R^2 = 0.44$, $p = 0.002$) and highland systems ($R^2 = 0.44$, $p = 0.001$), indicating consistent patterns across geographic contexts. However, tests for homogeneity of multivariate dispersion indicated significant differences among groups for both zone ($p = 0.013$) and crop (**$p < 0.001$), suggesting that the observed PERMANOVA results may reflect a combination of differences in group centroids and dispersion (Figure A3, A4, Supplementary Material). Also, individual environmental variables showed significant associations with compositional variation, particularly mean temperature ($R^2 = 0.14$), exchangeable potassium ($R^2 = 0.11$), and total organic carbon ($R^2 = 0.11$), while electrical conductivity was not significantly associated ($p = 0.253$) (Table A10, Supplementary Material).

DCA indicated a short gradient length for the first axis (< 3 SD units), suggesting a linear response pattern (Table A11, Supplementary Material). The gradient length of DCA Axis 1 indicated predominantly linear responses, confirming RDA as the appropriate constrained ordination method for this dataset.

Three variables were removed during iterative VIF selection: tmean, TC, and Sand (in order of removal). The 11 retained variables (pp, wind_speed, pH, EC, Pa, Ka, CaCO3, Silt, Clay, CEC, TOC) were used consistently across RDA and all predictive models, ensuring that variance inflation does not confound any downstream analysis, their final VIF values are shown in Table A12 (Supplementary material). RDA indicated that the set of environmental variables explained 42.3% of the total variation in composition. The first canonical axis (RDA1) accounted for 26.5% of the variance, representing the dominant environmental gradient, while the second axis (RDA2) explained an additional 7.3%, resulting in 33.8% cumulative variance explained by the first two axes. The overall RDA model was statistically significant (permutation test, $p < 0.05$), and the 11 environmental predictors together account for 43.6% of the total variance in pesticide composition.The RDA biplot revealed a dominant environmental gradient along the first axis (RDA1), separating soils characterized by higher organic carbon, exchangeable phosphorus and potassium, silt content, and precipitation from those with higher pH, electrical conductivity, and calcium carbonate. The second axis (RDA2) captured a weaker gradient associated mainly with wind speed. Many compounds were distributed near the origin, suggesting weaker or more complex relationships with the measured environmental variables. Sample distribution showed substantial overlap among valleys and zones, indicating that environmental gradients explain part, but not all, of the observed compositional variability (Fig. 5, Table A13, Supplementary Material).

3.4. Predictive modeling of pesticide–environment relationships

Four predictive models were fitted to explain and predict Pest_total (total pesticide concentration) using the 11 VIF-selected environmental and soil predictors. The models span a range of complexity and interpretability: two ensemble tree-based models (RF Regression and RF Classification), a classical parametric linear model (MLR with stepwise selection), and a semi-parametric smooth additive model (GAM). Using multiple model types allows cross-validation of variable importance findings and reduces dependence on the assumptions of any single approach.

Model validation results indicated moderate to low predictive capacity across approaches. For Random Forest (RF), out-of-bag (OOB) estimation yielded a R^2 of 0.102 and RMSE of 9.824. A stratified 75/25 hold-out split was then used to evaluate RF performance on a completely held-out test set; the RF model trained on 75% of detected plots achieved $R^2 = 0.258$ and RMSE = 12.613 on the 25% test set. For the stepwise

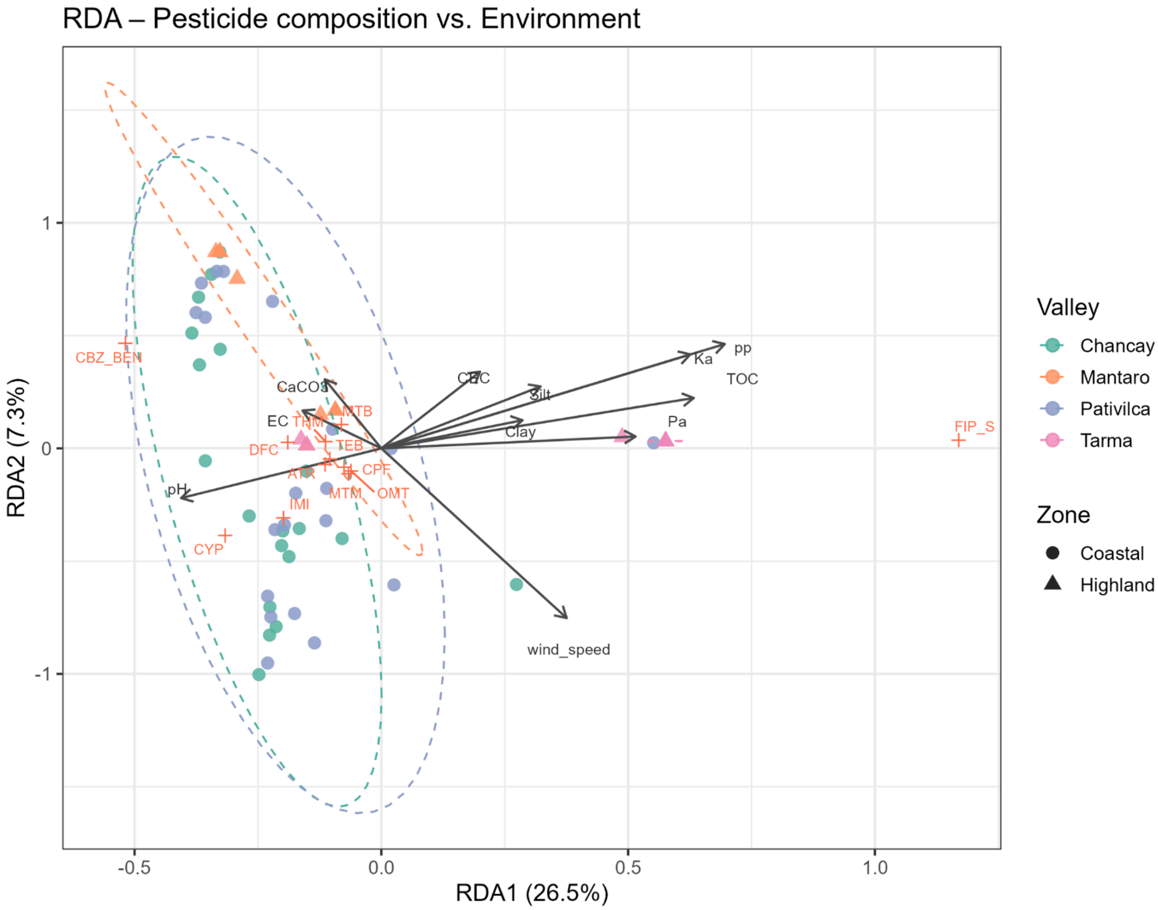

Fig. 5. Redundancy Analysis (RDA) between pesticide residues and edaphoclimatic variables. EC: Electrical conductivity, TOC: Total organic carbon, Pa: Available phosphorus, Ka: Available potassium, CEC: Effective cation exchange capacity, pp: Precipitation.

MLR model, the repeated 10-fold cross-validation yielded $R^2 = 0.379$ and RMSE = 9.061. Overall, MLR showed higher explained variance than RF under cross-validation ($R^2 = 0.379$ vs. 0.258), while RF performance differed between OOB and hold-out validation, indicating variability in predictive estimates across resampling strategies. Across all approaches, R^2 values remained moderate to low, suggesting limited predictive capacity.

Random Forest (RF), in regression mode, was applied to model the continuous response variable and to assess the relative importance of predictors in explaining their variability. The classification mode was used to distinguish between predefined groups based on pesticide composition and danger, enabling the identification of the most influential variables driving group separation. In the Regression analysis, precipitation (pp), potassium (Ka), and TOC emerged as the three most

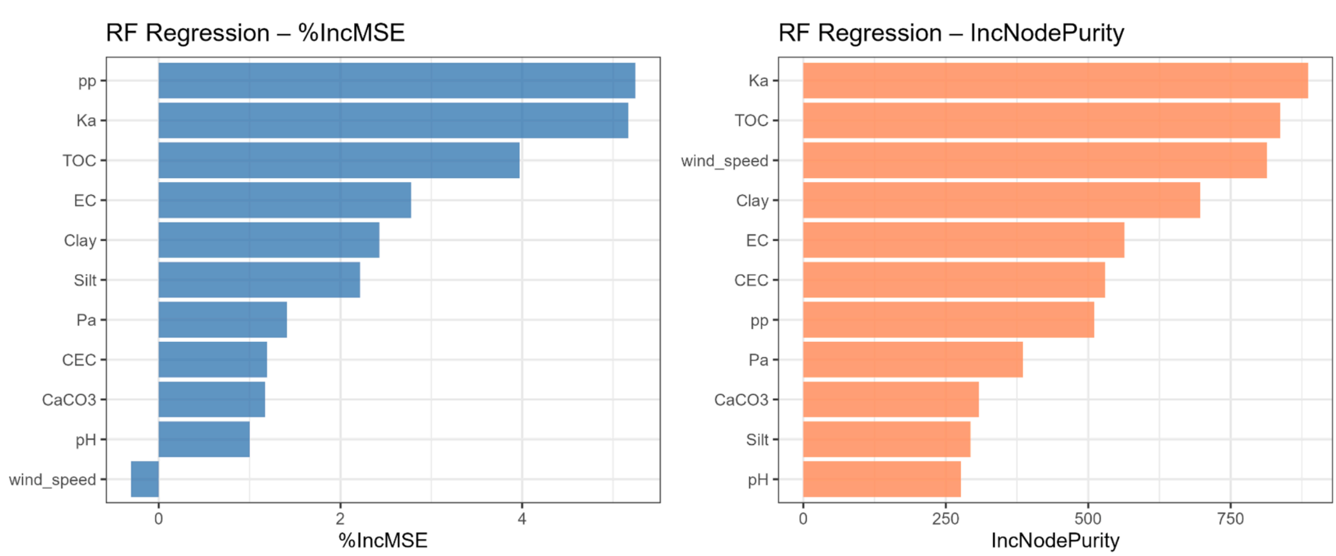

Fig. 6. Random Forest Regression variable importance: %IncMSE (left) and IncNodePurity (right).

important predictors by %IncMSE. Wind speed showed a negative %IncMSE value, indicating it contributed no predictive power beyond chance and can be considered uninformative for the regression task. Ka and TOC also ranked highly on IncNodePurity, confirming their relevance across both importance metrics (Fig. 6, Table A14, Supplementary Material).

On the other hand, the classification model established categories of Low, Medium, and High. TOC, Ka, and pp were the three strongest classifiers by Mean Decrease Accuracy (MDA), consistent with the regression importance rankings. Notably, the Medium class showed consistently lower or negative MDA values across most predictors, suggesting that intermediate pesticide loads are harder to classify, likely because this class represents a transitional zone with mixed contamination drivers (Fig. 7, Table A15, Supplementary Material).

Multiple Linear Regression (MLR) was included as a parametric baseline model because its coefficients are directly interpretable as marginal effects of each predictor on Pest_total. Stepwise selection retained 5 predictors (EC, Silt, Clay, CEC, TOC) from the original 11. Clay ($p = 0.003$) and TOC ($p = 0.035$) were the most statistically significant. The negative coefficient for Silt suggests that higher silt content is associated with lower total pesticide load, possibly reflecting greater adsorption or reduced runoff accumulation in silty soils. The negative TOC coefficient is counter-intuitive under simple sorption theory and may reflect complex interactions between soil organic matter, decomposition dynamics, and agrochemical application rates in these valleys. (Table A16, Figure A5, Supplementary Material). GAM extends MLR by allowing each predictor to have a smooth, nonlinear effect estimated from the data using penalized regression splines. GAM was selected to test whether nonlinear relationships between soil/climate predictors and Pest_total exist that cannot be captured by the linear MLR. Clay was the only statistically significant smooth term ($F = 7.67$, $p = 0.008$), with effective degrees of freedom (edf) $= 1.0$ indicating a linear effect — consistent with the MLR finding. Ka showed marginal significance ($p = 0.070$) with edf $= 2.75$, suggesting a weakly nonlinear relationship. All other predictors showed non-significant smooth terms and edf ≈ 1, indicating that the linear approximation of MLR is adequate for these variables (Table A17, Figure A6, Supplementary Material).

The synthesis of normalized variable importance scores revealed that clay, TOC, Ka, and pp show consistently high importance across all models, among the variables considered. Clay appears as moderately important in RF models and is the only significant predictor in GAM, while EC and CEC show secondary importance primarily in the linear models. Wind speed and Pa show low or negative importance across most models (Fig. 8).

Nevertheless, the limited predictive performance suggests that pesticide occurrence is influenced by additional factors not included in the models, such as pesticide application practices, irrigation management, crop-specific characteristics, hydrological connectivity, or temporal variability.

4. Discussion

The pesticide residues detected were predominantly classified within the moderate and low toxicity classes according to PAN and WHO. However, highly toxic pesticides may have minimal environmental impact if applied without affecting on-target organisms, whereas even low-toxicity, persistent compounds can become harmful when they are used excessively or at high doses (Nieder et al., 2018).

Statistical analyses revealed clear gradients in composition across sites, suggesting differences in contamination profiles associated with valley location. Presumably, the higher occurrence of pesticide residues observed in Coastal valleys compared with high-Andean valleys reflects the combined influence of management practices and environmental conditions. A previous study indicated that quinoa experienced stronger pest pressure at lower elevations than in the highlands. Similarly, this difference was observed between contrasting mean monthly temperature and total precipitation (Cruces et al., 2020). Coastal valleys near Lima city, with arid climatic conditions such as Chancay-Huaral and Chillón, supplying nearly one-third-of Peru's population (Chávez-Dulanto et al., 2024; INEI, 2025). In the Pativilca and Chancay-Huaral valleys, systemic insecticides, protective fungicides, and herbicides were more frequently detected, consistent with intensive horticultural production systems with frequent pesticide applications in high-value crops. Whereas, in the Mantaro and Tarma valleys, where

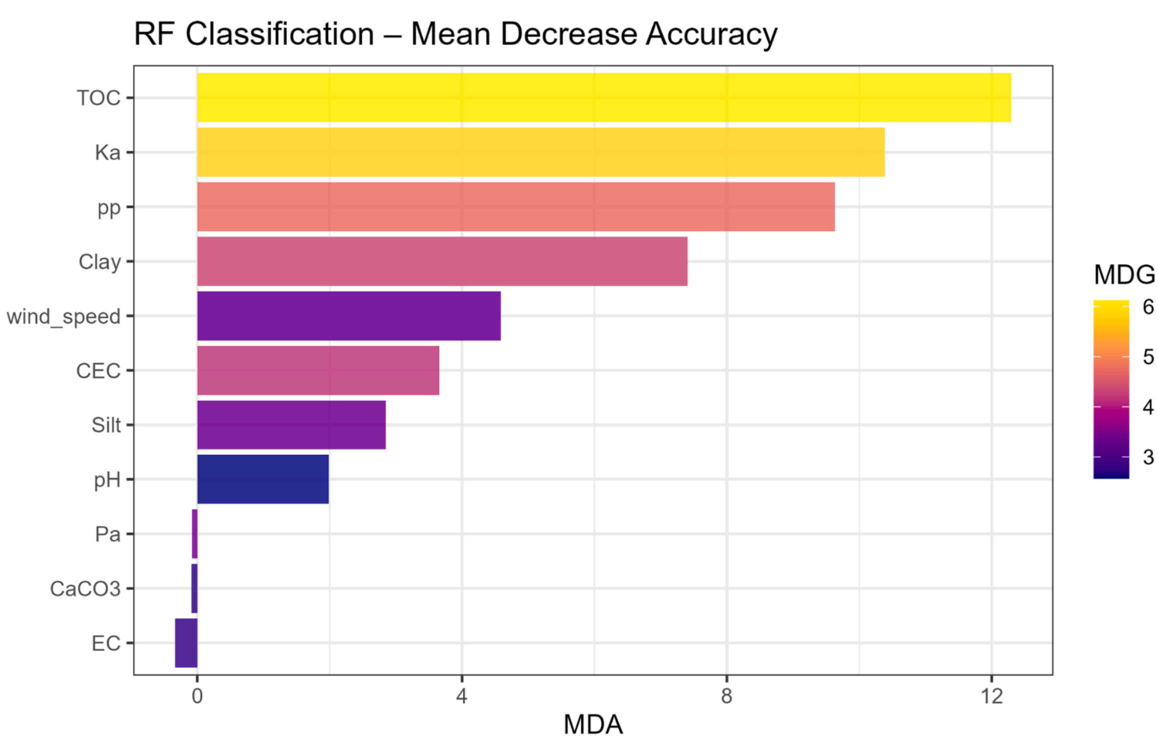

Fig. 7. Random Forest Classification variable importance. Mean Decrease Accuracy (MDA) colored by Mean Decrease Gini (MDG).

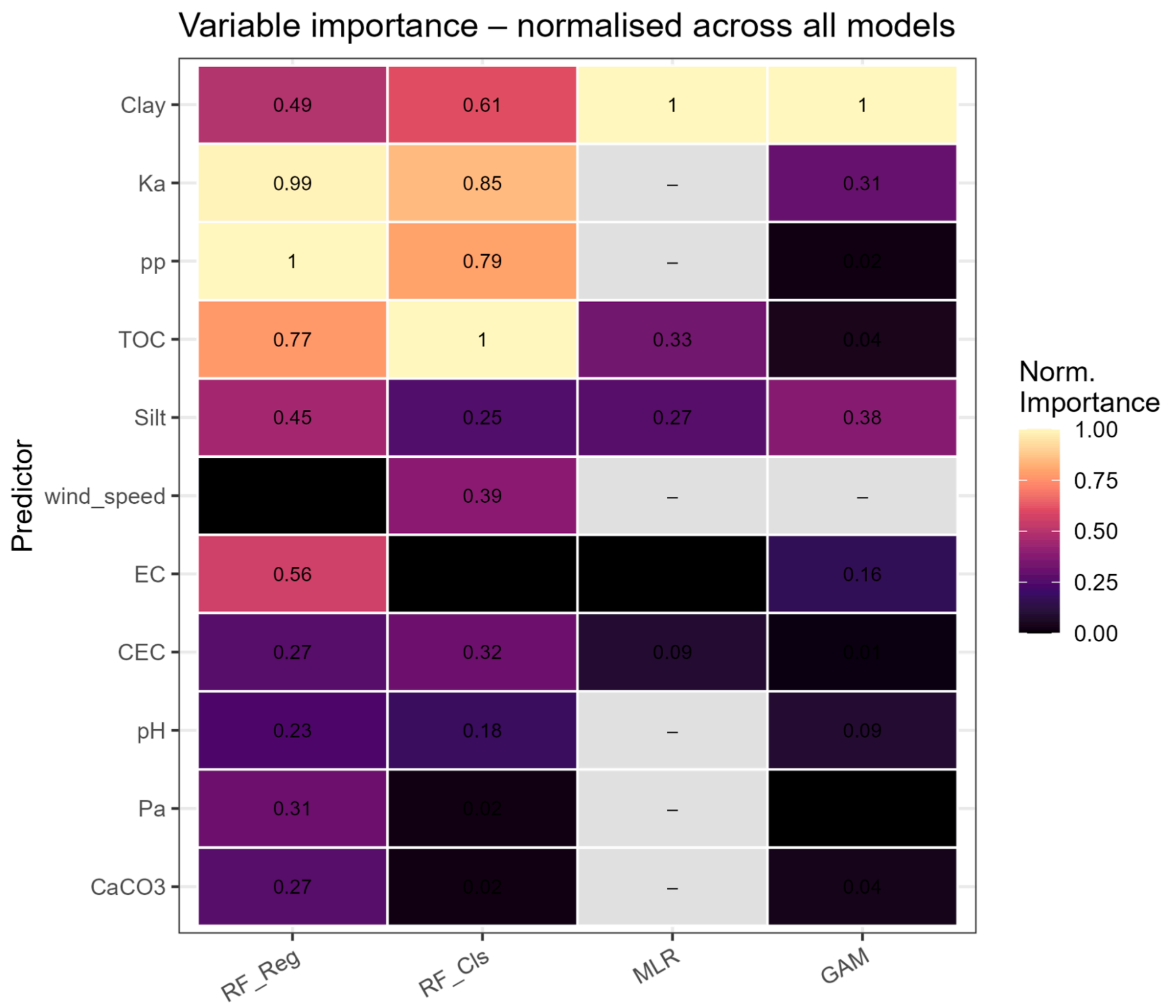

Fig. 8. Normalized variable importance heatmap across RF Regression, RF Classification, MLR, and GAM. Values are scaled 0–1 within each model. Grey cells (–) indicate variables not retained by that model.

crops such as potato, pea, and maize predominate, the residues were less diverse and not so much detected. This difference may be attributed to less pesticide-intensive use (Beltrán-Tolosa et al., 2022) and distinct edaphoclimatic conditions, such as higher altitude, lower temperatures, soils with higher total carbon content, and lower electrical conductivity, all of which do not favor translocation processes (Ouyang et al., 2020; Xi et al., 2021). Low-input agriculture prevails in the highlands, even so, 88% of Peruvian farmers regularly apply pesticides (Honles et al., 2022). It is noteworthy that higher temperatures and more continuous cropping cycles in coastal valleys can increase pest pressure and pesticide use. In addition, pesticide residues and intensive applications were consistently higher in short-cycle horticultural crops than perennial crops. Therefore, contamination patterns differed between coastal and Andean systems due to differences in crop types, pesticide application frequency, climate, soil properties, and hydrology, all of which influence pesticide behavior and persistence (Hammond Wagner et al., 2016; Tudi et al., 2021).

Foliar dominance of pesticide residues likely reflects recent application events, but this pattern is also consistent with compound-specific physicochemical properties and degradation dynamics. Several of the detected compounds, including chlorpyrifos, cypermethrin, and tebuconazole, are characterized by relatively high hydrophobicity (log K_ow > 3), which promotes strong sorption to leaf cuticles and reduces rapid wash-off. In contrast, more polar compounds such as imidacloprid and thiamethoxam exhibit systemic behavior and can persist within plant tissues following uptake (Papadopoulou et al., 2016; Chen et al., 2015). Degradation rates further support this interpretation: many of these compounds exhibit relatively short half-lives on plant surfaces due to photolysis and volatilization, implying that detectable foliar residues are indicative of recent or repeated applications. Conversely, lower detection frequencies in soil and water are consistent with dilution, transport, and matrix-specific degradation processes, including microbial breakdown and leaching. Together, these compound-specific properties provide mechanistic support for the observed dominance of pesticide residues in crop foliage (Meng et al., 2022).

Some pesticides deposited on plant surfaces can be partially transferred to soils through wash-off or leaf fall; however, environmental processes may reduce their persistence in soil and water. The fate of pesticides is determined by processes such as sorption, degradation (decomposition), and leaching (movement), where soil and climate operate synergistically. Sorption regulates both the degradation and leaching; soil organic matter and clay are the primary components that provide a strong capacity for pesticide sorption (Sadegh-Zadeh et al., 2017), especially humic acids show the greatest ability to retain pesticide molecules. In some cases, pesticides that are minimally toxic or non-toxic to soil microbial communities have shown degradation (Vischetti et al., 2020). However, elevated TOC and CEC enhance sorption, decreasing leaching but potentially hindering degradation due to reduced bioavailability. Additionally, temperature influences pesticide sorption by altering the compound's solubility and rate of hydrolysis (Kaur et al., 2023), but low temperatures slow degradation.

Strong sorption reduces leaching risk, but can also reduce bioavailability for degradation, so pesticides may persist longer in the soil matrix (Sandeep et al., 2024). This was observed in the Mantaro and Tarma valleys, which showed higher values of TOC and CEC, and reported pesticides in soils. Sandy soils with low TOC, such as the Chancay-Huaral and Pativilca valleys, retain fewer pesticides, with consequent higher leaching and potential groundwater contamination, but it is expected that these emissions to freshwater were minimal along the arid Peruvian coast because low moisture restricts pesticide mobility. As well, the limited mobility of pesticides in soil may partially constrain their transport to surrounding water bodies (Esteve-Llorens et al., 2022).

Nevertheless, the relationships between environmental variables and pesticide occurrence should be interpreted with caution, as compounds with contrasting physicochemical properties were analyzed collectively. Differences in polarity, sorption affinity, and persistence influence environmental fate: hydrophobic compounds (e.g., cypermethrin) tend to sorb to organic matter, while more polar compounds (e.g., imidacloprid, thiamethoxam) are more mobile. Likewise, persistent compounds (e.g., tebuconazole) may accumulate. Consequently, the observed associations with TOC likely reflect composite responses rather than uniform mechanisms.

A systematic review assessed aquifer pesticide contamination between 1998 and 2020, herbicides, particularly atrazine and glyphosate, were the most frequently detected CUPs and are increasingly subject to bans or restrictions due to their environmental risks (Grondona et al., 2023); atrazine has also been reported in Pativilca and Mantaro valleys. In the Guayas River Basin (Ecuador), the most commonly detected pesticides included cadusafos, butachlor, and pendimethalin (Deknock et al., 2019); the latter of which was also found in the Pativilca valley.

Total organic carbon (TOC), Ka, and precipitation showed the strongest associations with pesticide occurrence and concentrations in crops according to prediction models. Soil properties such as carbon content are key factors controlling pesticide fate. Soil surfaces retain agrochemicals through ion exchange, and organic matter enhances CEC due to its high cation-holding capacity and large surface area (Bajeer et al., 2012; Sarkar et al., 2020; Vagi and Petsas, 2022), particularly for hydrophobic pesticides. This could mean that more organic matter and higher CEC help to reduce pesticide translocation to crop leaves. The nutrients have a positive impact on plant tolerance or resistance to pathogens (Dordas, 2008), in consequence minor pesticide use.

Crop type is also an important factor, because perennial crops are generally less susceptible to weed competition than short-cycle crops (Dupré et al., 2020). Residues were consistently higher in short-cycle horticultural crops, which are typically managed under more intensive pest control regimes, including more applications than perennial crops. This highlights the need for the targeted regulation and monitoring of high-value vegetable production systems.

On the other hand, the Peruvian national framework, aligned with the Codex Alimentarius standards, harmonizes regulations with international trade while promoting consumer protection, awareness, and monitoring of foodborne risks (Ramirez-Hernandez et al., 2020). The presence of banned compounds such as methamidophos and chlorpyrifos could be linked to informal product rotations, residual use of older formulations, or limitations in agrochemical market monitoring systems (Chávez-Dulanto et al., 2024). Since 1 August 2024, the export, manufacture, formulation, commercialization, distribution, storage, and/or packaging of agricultural chemical pesticides containing the active ingredient chlorpyrifos have been prohibited, according to R.D. N° 0032–2023-MIDAGRI-SENASA-DIAIA (El Peruano, 2024). However, chlorpyrifos was detected in purple maize, maize, avocado, cassava, mandarin, paprika, and panca chili in the Chancay-Huaral and Pativilca valleys. According to the last report of SENASA (SENASA, 2024), the matrices of plant-based foods with the highest percentage of non-compliance due to pesticide residues (> 50%) were celery, spinach, paprika, quinoa, sweet granadilla, bell pepper, strawberry, lettuce, peach, pineapple, apple, and yellow chili. Comparing with the present study, the crops that stood out and were detected in Lima, influence area of the Chancay-Huaral and Pativilca valleys, were paprika (96.72%), spinach (85.71%), bell pepper (66.67%), yellow chili (59.46%), and passion fruit (55.17%); while in Junin, influence area of the Mantaro and Tarma valleys, spinach (81.08%) and potato (41.67%).

There are many risks with the pesticide application; vulnerable groups of farmers, aged 15–30, continue to apply pesticides without technical oversight (Chávez-Dulanto et al., 2024; MINSA, 2025), with high poisoning rates reported in coastal valleys (Hammond Wagner et al., 2016). Although Integrated Pest Management (IPM) offers safer alternatives and highlights the need for government-supported farmer training (Angon et al., 2023). However, pesticide use persists in industrial crops due to its quick results and lower labor needs (Chávez-Dulanto et al., 2024). More selective application and climate-adapted practices could improve long-term management while reducing health and environmental risks (Calvin et al., 2023; Nega, 2025; Silva et al., 2023). Advancing IPM will require stronger training, preventive actions, and stakeholder engagement, alongside better dissemination of successful cases and improved regulatory compliance across the region (Olguín-Hernández et al., 2024; Staudacher et al., 2020).

This study had limitations that should be acknowledged. The degradation products were not analyzed separately from parent compounds, improving consistency across sites but preventing a more detailed assessment of their individual persistence in the studied systems. Additionally, the results should be interpreted in light of the study design, which is based on a single sampling campaign. Given the high temporal variability associated with application schedules, climatic conditions, and degradation processes, the observed patterns should not be interpreted as persistent or seasonal trends. Instead, the results provide a context-specific characterization of pesticide distribution under the conditions prevailing at the time of sampling. Longitudinal or multi-season monitoring would be required to capture temporal dynamics and confirm the persistence of the observed patterns.

This study moves beyond descriptive monitoring by showing that pesticide occurrence and composition are systematically structured by edaphoclimatic gradients across contrasting agroecosystems. By integrating multivariate ordination and predictive modeling, we identify soil carbon, cation exchange capacity, and temperature as key factors shaping pesticide distribution, providing mechanistic insight into how sorption, degradation, and transport processes operate under different environmental conditions.

Nevertheless, this study provides key insights into pesticide residue distribution across contrasting agroecosystems and identifies environmental factors associated with their occurrence, revealing the risks to crop quality, sustainability, the environment, and human health. The findings highlight the need to strengthen monitoring, promote sustainable practices such as IPM, and develop evidence-based regulations adapted to diverse agroecosystems. Training and awareness programs should also be tailored to the local contexts. Integrating these insights into management and policy offers an opportunity to reduce contamination, protect food security, and foster resilient production systems.

5. Conclusions

Pesticide residues were detected predominantly in crop foliage, whereas soil and water showed limited occurrence (16% of sampling points), this pattern is explained by compound-specific physicochemical characteristics and degradation processes. 70% of samples containing hazardous pesticides exceeded Codex Alimentarius MRLs, mainly in coastal horticultural systems. Residue distribution was strongly associated with key edaphoclimatic variables, including clay, total organic carbon, available potassium, and precipitation, distinguishing coastal from high-Andean agroecosystems. The results reflect conditions at the time of sampling; multi-season monitoring is needed to capture temporal variability and confirm persistence. However, these findings have important implications for pesticide monitoring and risk assessment in Peru. The frequent exceedance of regulatory limits, together with the detection of banned compounds, highlights the need to strengthen regulatory enforcement, improve pesticide management practices, and promote safer alternatives such as integrated pest management.

CRediT authorship contribution statement

Wendy E. Pérez: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Ricardo Flores-Marquez:** Writing – review & editing, Writing – original draft, Methodology, Investigation. **Carlos Carbajal:** Writing – review & editing, Writing – original draft, Visualization, Software, Methodology, Investigation. **Richard Solórzano-Acosta:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

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

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.envc.2026.101559.

Data availability

Data will be made available on request.

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