AGED COMMERCIAL IMIDACLOPRID FORMULATION ALTERS THE THERMAL, OPTICAL, AND ELECTRICAL BEHAVIOR OF AQUEOUS MATRICES

JP Hernández[1], Fredy Mesa[2], JD Hernández[3], André Riveros[1]

[1]Universidad del Rosario, Escuela de Ciencias e Ingeniería, Bogotá, Colombia.

[2]Fundación Universitaria Los Libertadores, Faculty of Engineering and Basic Sciences, Bogotá, Colombia.

[3]Universidad de la Salle, Escuela de Ciencias Básicas y Aplicadas, Bogotá, Colombia.

Corresponding author: JP. Hernandez (juanp.hernandez@urosario.edu.co) [1]Universidad del Rosario, Escuela de Ciencias e Ingeniería, Bogotá, Colombia.

ABSTRACT

Environmental persistence of neonicotinoid insecticides is influenced by their long-term stability and interactions with aqueous matrices. In this study, the thermal, optical, and electrical properties of a commercial imidacloprid formulation (Confidor 350 SC) were characterized under environmentally representative conditions. Solutions were prepared using three types of water (Distilled, Rain, and Mud) and exposed to three temperatures (5 °C, 25 °C, and 50 °C), considering products with three expiration states (valid, near-expiry, and expired). Thermal analysis revealed that the formulation maintains macroscopic stability even after the expiration date; however, the aqueous matrix significantly modulates heat transfer dynamics. UV-Vis absorbance measurements showed spectral shifts dependent on water type and temperature, suggesting subtle chemical transformations. Electrical characterization, using impedance spectroscopy and current-voltage curves, revealed significant interactions among water type, storage time, and temperature that affect conductivity and dielectric behavior. Overall, the results indicate that although thermal properties remain relatively stable, optical and electrical tools allow more sensitive detection of aging effects and environmental conditions. This integrative approach provides a solid foundation for assessing the stability and transformation of pesticides in aquatic ecosystems, with implications for modeling their mobility and persistence in agricultural contexts.

INTRODUCTION

Imidacloprid is a neonicotinoid insecticide widely used in agriculture [1,2] due to its high efficacy against pest insects [3–5] and its ability to be systemically absorbed by plants [6]. These characteristics have positioned it as one of the most commercially distributed insecticides worldwide [1,7], available in several formulations. One formulation has the solid active ingredient dispersed as fine particles in an aqueous phase containing dispersants and wetting agents, yielding a stable suspension (concentrated suspension, SC). These suspensions offer practical advantages, as they are designed to be diluted in water and applied directly to crops affected by pest insects [8–10]. Although these formulations are designed to interact with water, little information is available on their thermal, optical, and electrical characteristics. Variables that vary with the expiration date and their interactions with different water matrices.

Imidacloprid´s extensive use has raised global concerns because its effects extend beyond target pests to pollinators and other beneficial species [11–16] that sustain ecosystem productivity [17–20]. Despite regulatory restrictions in several countries [21–23], the production and use of imidacloprid remain substantial, exceeding 23 Tons per year in China alone [24,25], thereby ensuring its continued presence in agricultural environments [26,27]. This persistence underscores the need for a critical evaluation of the released imidacloprid in water bodies [28], where multiple interactions may occur with dissolved substances such as organic matter and salts. Understanding this problem is therefore fundamental for predicting the environmental fate of imidacloprid and developing strategies to mitigate its long-term ecological impacts.

To address the interaction between imidacloprid and aquatic environments, it is necessary to understand how the formulation behaves across different liquid matrices and at varying temperatures. Commercial suspensions contain many components, such as active ingredients and adjuvants [28,29] that stabilize their colloidal structure. Over time, these components can undergo physical or chemical aging, leading to changes in particle-size distribution, ion release, or molecular rearrangement. Such formulations may change in stability when they interact with water of varying ionic strength or when temperature changes; their thermal and electrical behavior may then change [30–32]. Variation in these behaviors can reflect changes in solution solubility, aggregation dynamics, and the rate of degradation [33] or adsorption onto environmental surfaces [34,35]. Therefore, understanding how ecological matrices and product aging jointly affect the

physicochemical properties of imidacloprid formulations is crucial for predicting their persistence and environmental behavior [36,37].

In agricultural environments, imidacloprid formulations are routinely diluted in water prior to application [38,39], yet the physicochemical changes that occur during this process are seldom evaluated. The formulation changes its behavior immediately upon mixing with water due to the reduction in concentration. In addition, the properties of the water used can rapidly modify the stability and subsequent environmental behavior; this occurs with any water, whether distilled, rainwater, or soil-rich, muddy water [31,40–42]. Natural waters contain diverse ions, organic molecules, and suspended particles that can interact with both the active ingredient and its adjuvants. Understanding how different water matrices influence the formulation´s physicochemical behavior is essential for predicting its transformation under real conditions, where dilution, temperature, and matrix composition vary continuously.

Additionally, following field application, imidacloprid formulations may interact with the water from rainfalls, which can produce other variations in the soil [43,44]. Water retained in the soil, which produces temporary puddles or surface moisture, exhibits complex physicochemical conditions due to the presence of mineral particles, organic matter, and dissolved salts [40,41]. These conditions can influence the solubility, mobility, and stability of the insecticide, thereby affecting its persistence and toxicity potential. Experimentally evaluating formulations dissolved in rainwater or soil-representative solutions can provide insight into the compound's environmental fate and transformations under realistic exposure conditions.

The expiration of formulations represents an additional factor that may alter their physicochemical behavior [45,46]. Although manufacturers guarantee a shelf life of three to five years under controlled storage conditions [47]; both the active ingredient and the adjuvants can undergo transformations. These changes may affect system properties, including thermal, optical, and electrical responses, even when such alterations are not visually apparent. The lack of detailed information regarding the full composition of the formulation hinders the prediction of these changes, underscoring the importance of experimental evaluation under varying storage and exposure conditions.

In response to this panorama, the present study focuses on characterizing the thermal, optical, and electrical properties of a commercial imidacloprid formulation (Confidor SC). Three key

environmental variables were evaluated: storage duration, the type of water used as solvent (distilled, rain, and tap water), and exposure temperature. These factors may induce structural and functional transformations that can influence the product's colloidal stability, ionic mobility, and spectral response. The experimental approach aims to generate relevant evidence on the environmental potential risks of agrochemicals, as well as on the design of safer and more sustainable management strategies. The analysis addresses a critical gap in the environmental characterization of commercial formulations, which are often underestimated compared to the active ingredient, despite their environmental significance.

MATERIALS AND METHODS

Commercial formulation of imidacloprid and preparation of solvents

The experiments used the commercial formulation Confidor 350 SC (Bayer CropScience), a concentrated suspension of imidacloprid. Four different batches were tested: LB01001152, with an expiration period from February 2019 to February 2021(Expiration code: 19); LB00015283, with an expiration period from October 2020 to October 2022 (Expiration code: 20); LB00017641, with an expiration period from August 2022 to August 2024 (Expiration code: 22); and LB00019356, with an expiration period from January 2024 to January 2026 (Expiration code: 24).

Solutions were prepared using three types of water: distilled water, rainwater, and muddy water, the latter two were collected in Bogotá during April 2024. The muddy water was centrifuged at 3000 RCF for 5 minutes to remove suspended particles, then filtered through 2 µm paper. All water types were refrigerated at 4 °C before use.

Preparation of imidacloprid solutions

Each solution was prepared by adding 0.0566 ± 0.0012 g of Confidor 350 SC to 100 mL of the corresponding water type, measured with a graduated cylinder with a tolerance of ±1 mL. The mixtures were stirred on an orbital shaker at 150 rpm for 2 hours and stored at 4 °C in the dark; the containers were covered with aluminum foil. For measurements, 10 mL of each solution was extracted using a pipette with a tolerance of ±0.075 mL at 20 °C and transferred into 50 mL Falcon tubes.

Experimental design

The study included a control group for each water type without formulation and twelve experimental treatments corresponding to the four Confidor SC formulations, classified by expiration date and dissolved in the three types of water: distilled, rain, and mud. Thermal evaluations and current-voltage measurements were conducted at 2°C and 55°C for 5 minutes using a water bath or chiller to achieve the desired conditions (Fig. 1B). Frequency response evaluations were performed at constant temperatures of 2°C, 22°C, and 40°C. In total, 39 conditions were assessed, including the controls.

Optical and thermal measurements

UV-Vis absorbance spectra were obtained using a NanoDrop 2000 spectrophotometer (Thermo Scientific) with a 5 µL sample volume. Measurements were taken every 5 nm between 200 and 400 nm, using the corresponding water type as the blank. Each sample was measured in triplicate.

Thermal heating and cooling curves were recorded using thermal probes connected to a Vernier interface. Before measurement, solutions were equilibrated at 22 ± 1 °C for one hour to standardize the initial temperature. Heating curves were obtained using a 55 °C water bath, and cooling curves were acquired with a chiller set to 2 °C. Probes were positioned at the center of Falcon tubes using clamps and double holders to ensure precision (Fig 1B). Each condition was evaluated in triplicate.

Electrical measurements

For all electrical characterizations, electrodes were constructed using stainless steel hypodermic needles connected to jumper wires and fixed onto glass microscope slides with a spacing equal to the slide's narrowest width. This setup was inserted into Falcon tubes containing the solutions (Fig 1 B, C).

Electric current was measured using a simple circuit with two 1 kΩ resistors, one placed before and one after the sample. The signal was generated with an InfiniiVision 1000 X-Series oscilloscope programmed with a 0.1 Hz triangular wave at 40 Vpp (Fig 1D). Data were recorded over a five-minute period while the tubes were maintained in either a water bath at 55 °C or a chiller at 2 °C. Voltage input and output were measured under the same configuration and thermal conditions. Peak values were recorded, and system gain was calculated using the equation 20Log(Vout/Vin).

Electrical impedance was evaluated at constant temperatures of 2 °C, 22 °C, and 40 °C. The frequency response of the samples was measured from 10 Hz to 10 MHz. Data were grouped into linear behavior segments (frequencies above 10^4 Hz for distilled water and above 10^6 Hz for rainwater and muddy water) and quasi-constant segments (frequencies below those thresholds).

Statistical analysis

Statistical analyses were conducted using multifactorial ANOVA, followed by Tukey post hoc tests, with a significance level of $p < 0.05$. Analyses were performed in RStudio (latest version) using the tidyverse, rstatix, npreg, and readxl packages [48]. Absorbance curves, heating/cooling constants, electrical currents, voltage values, and impedance variations were compared across water types and expiration dates using these procedures.

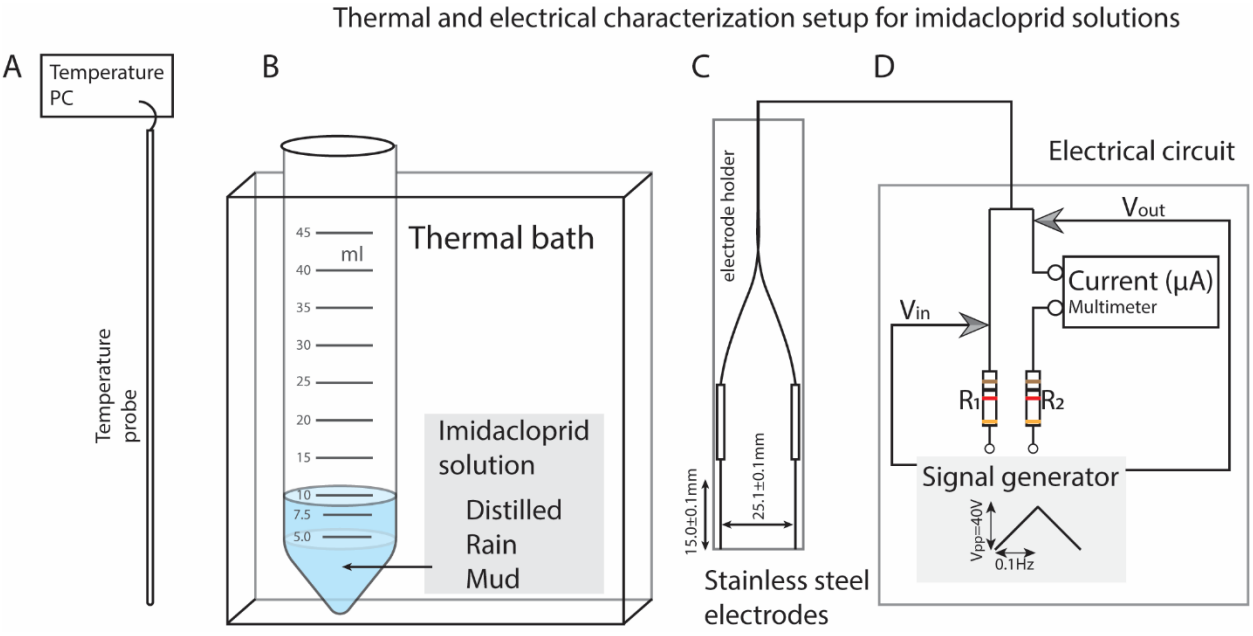

*Fig. 1 Diagram of the experimental setup used to characterize the electrical properties of imidacloprid solutions prepared with different water sources (distilled, rain, and mud). **A**) A temperature probe was inserted into the solutions to measure the solution temperature variation. **B**) The solutions (10 mL) were placed in 50 mL conical tubes and immersed in a temperature-controlled water bath. **C**) Stainless steel electrodes (25.1 ± 0.1 mm apart) were held in place by a fixed electrode holder. **D**) The electrodes were connected to a signal generator (triangular waveform, 0.1 Hz, Vpp = 40 V), forming a circuit with two 1 kΩ resistors (R_1 and R_2) and a multimeter to measure current (μA) and output voltage (Vout). This setup enabled the evaluation of how the water matrix and temperature modulate the electrical behavior of the formulations.*

RESULTS

Heating and cooling curves of imidacloprid in different aqueous matrices

Commercial imidacloprid formulations exhibit thermal stability at macroscopic scales. Heating and cooling processes were described by ascending and descending curves, respectively, according to the heat absorbed or released to the environment. In both cases, temperature variation was influenced by the type of water ($F_{2;6780}$=12.3, $p < 0.0001$ for cooling; $F_{2;6780}$=4.454, $p = 0.0120$ for heating); however, expiration date had not significant effect ($F_{4;6780}$=0.72, $p = 0.58$ for cooling; $F_{4;6780}$=0.19, $p = 0.95$ for heating). No interaction was observed between water type and expiration date in either process ($F_{8;6780}$=0.47, $p = 0.88$ for cooling; $F_{8;6780}$=0.15, $p = 0.99$ for heating).

Both heating and cooling followed exponential trends, reflecting how the solution gained or released heat over time. The curves depend on the initial (T_i) and final (T_f) temperatures, time (t), and a rate constant *k* that governs the speed of the process (Equation 1). During heating, the rate constants (mean ± s.e.m) were: k_{Mud}=0.239±0.001 s^{-1}, $k_{Distilled}$=0.255±0.004 s^{-1}, and k_{Rain}=0.254±0.004 s^{-1}. During cooling, the constants ranged from k_{Mud}=0.411±0.007 s^{-1}, k_{Rain}=0.424±0.011 s^{-1} to $k_{Distilled}$=0.461±0.015 s^{-1} (Figure 1). These results demonstrate that the formulation interacts with the water matrix, affecting its thermal behavior. Differences between aqueous media indicate that, upon interaction with the formulation, they heat or cool at different rates. In all cases, exponential models provided a good fit to the data, with coefficients of determination exceeding 0.98, indicating strong agreement with the observed thermal behavior of the solutions.

Heating	Cooling	
$T = T_i - (T_i - T_f)e^{-kt}$	$T = T_f + (T_i - T_f)\, e^{-kt}$	Eq. 1

The heating and cooling rate constants (*k*) showed significant differences according to the type of water ($F_{2;12}$=37.062, $p < 0.0001$ for heating; $F_{2;12}$=25.139, $p < 0.0001$ for cooling). During heating, the *k* values of the distilled water solutions were significantly higher than those in muddy water, with no significant difference compared to rainwater (Tukey post hoc test: 95% CI: –0.0068, 0.0042, $p = 0.813$ for Distilled vs Rain; Tukey post hoc test: 95% CI: –0.0216, –0.0105, $p < 0.0001$

for Distilled vs Mud). The constants in rainwater solutions were also significantly higher than those in muddy water (Tukey post hoc test: 95% CI: 0.0092, 0.0203, $p < 0.0001$ for Mud vs Rain).

Regarding the cooling process, distilled water solutions again exhibited higher k values compared to both rainwater and muddy water (Tukey post hoc test: 95% CI: –0.0700, –0.0308, $p < 0.0001$ for Distilled vs Mud; Tukey post hoc test: 95% CI: –0.0565, –0.0172, $p < 0.0001$ for Distilled vs Rain). However, no significant difference was observed between rainwater and muddy water solutions (Tukey post hoc test: 95% CI: –0.0060, 0.0332, $p = 0.198$ for Mud vs Rain). The expiration date had no significant effect on the k values for either process ($F_{4;10} = 0.143$, $p = 0.962$ for heating; $F_{4;10} = 0.228$, $p = 0.916$ for cooling), indicating that the formulations remain thermally stable even after their expiration date.

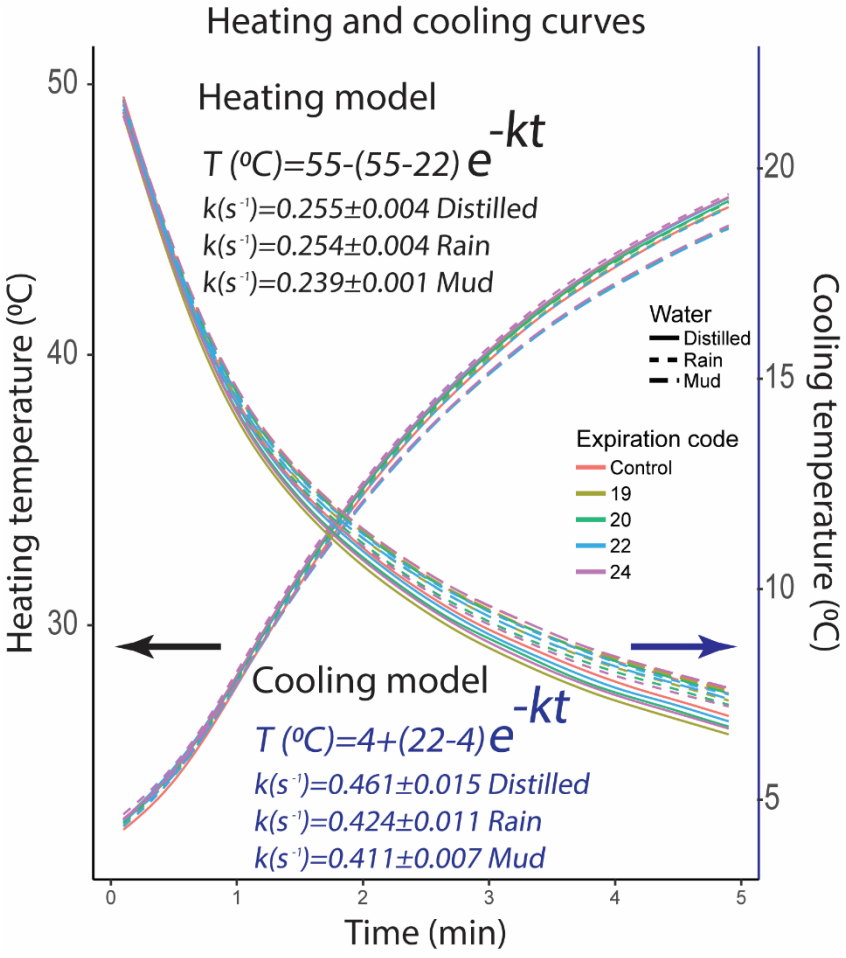

Fig. 2 Average heating and cooling curves of imidacloprid solutions prepared with distilled water (solid line), rainwater (dotted line), and muddy water (dashed line), across five expiration conditions (Expiration code: Control, 19, 20, 22, 24). Lines represent models fitted using an

exponential function. Significant differences in the rate constant k were observed between water types ($p < 0.001$), with no effect attributable to expiration date.

UV-Vis absorbance spectra of imidacloprid in different aqueous matrices

Imidacloprid solutions exhibited absorbance within the UV-Vis range (200–400 nm), with a marked decline between 350 and 400 nm. Overall, no significant differences were detected across the full spectrum in relation to water type ($F_{2;4422}$=2.41, p=0.090) or expiration date ($F_{3;4422}$=1.46, p=0.225). However, three intervals with well-defined absorbance peaks were identified: Interval 1 (208–217 nm), Interval 2 (257–263 nm), and Interval 3 (269–282 nm). The most intense peak occurred in Interval 2, followed by that of Interval 3, which corresponds to the characteristic spectral signature of imidacloprid.

In Interval 1, significant effects were observed for both water type ($F_{2;204}$=184.63, p<0.0001) and expiration date ($F_{3;204}$=8.64, p<0.0001), as well as their interaction ($F_{6;204}$=8.86, p<0.0001). The lowest absorbance values were recorded in solutions prepared with muddy water and from older batches (Figure 2B), suggesting a loss of UV-absorbing components in this region or their structural transformation over time.

In Interval 2, both water type ($F_{2;96}$=13.46, p<0.0001), expiration date ($F_{3;96}$=22.44, p<0.0001), and their interaction ($F_{6;96}$=6.932, p<0.0001) significantly influenced the results. Imidacloprid solutions from older batches showed significantly lower absorbance values (Figure 2C), suggesting a reduction in the effective concentration of the active ingredient.

In Interval 3, which corresponds to specific imidacloprid absorption, water type was the main factor affecting the response ($F_{2;312}$=18.39, p<0.0001). Although the expiration date had no significant main effect ($F_{3;312}$=1.61, p=0.186), a significant interaction with water type was detected ($F_{6;312}$=8.48, p<0.0001). This suggests that product aging may alter its spectral behavior in a water-type-dependent manner.

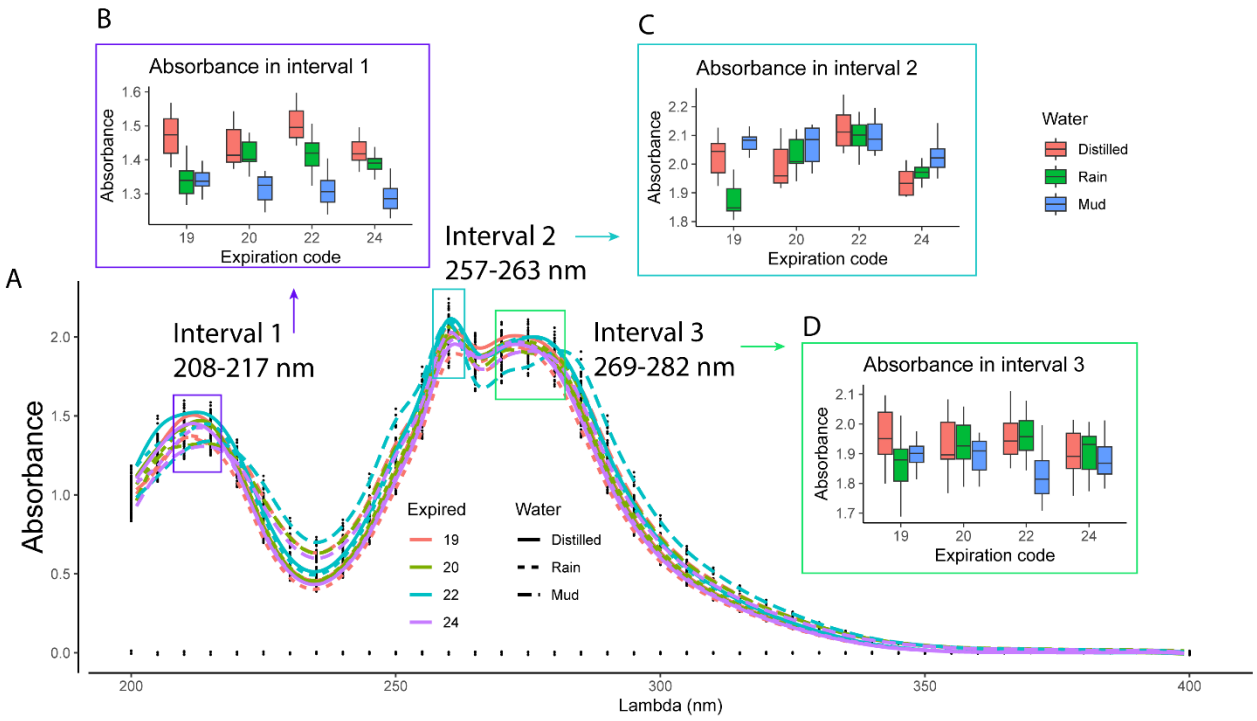

*Fig. 3 **A)** Average UV-Vis absorbance spectra (200–400 nm) for commercial imidacloprid solutions prepared with three types of water (Distilled, Rain, Mud) and varying expiration dates (19, 20, 22, 24). Three main peaks were identified: Interval 1 (208–217 nm), Interval 2 (257–263 nm), and Interval 3 (269–282 nm, associated with imidacloprid). **B)** Boxplots of absorbance in Interval 1: marked differences observed based on water type and product age. **C)** Boxplots of absorbance in Interval 2: predominant effect of expiration date, with reduced absorbance in older batches. **D)** Boxplots in Interval 3: variations mainly associated with water type and its interaction with expiration date.*

Variation in the electrical current of imidacloprid in aqueous solutions and temperature changes

Throughout the evaluation period, the electrical current measured in imidacloprid solutions showed significant dependence on water type ($F_{2;445543}$=14,421, p<0.0001), expiration date ($F_{1,445543}$=4,177, p<0.0001), and temperature ($F_{4;445543}$=29,285, p<0.0001). An increase in temperature was associated with higher current intensities, while lower temperatures led to decreased current, indicating that ionic mobility in the system is directly modulated by thermal context (Figure 3A).

The presence of imidacloprid increased current intensity in all evaluated matrices, so that the formulation contributes to the charged species capable of responding to an electric field. Solutions from older batches (Expiration code: 19 and 20) exhibited higher current values, possibly due to

an increased concentration of ionic species arising from degradation or dissociation processes (Figure 3B).

Analysis of the maximum current values (top 80th percentile) showed significant dependence on water type ($F_{2;89086}$=165,526, $p<0.0001$), expiration date ($F_{4;89086}$=52,869, $p<0.0001$), and temperature ($F_{1;89086}$=438,091, $p<0.0001$). A significant interaction was also found between water type and temperature ($F_{2;89086}$=6,135, $p<0.0001$), indicating that solution conductivity increases with temperature and varies by matrix. The lowest conductivity was recorded in distilled water during cooling, while rainwater and muddy water solutions reached the highest current intensities.

A significant interaction between water type and expiration date was also observed ($F_{8;89086}$=1,502, $p<0.0001$). Older formulations showed greater conductivity, particularly in muddy water, suggesting destabilization of components over time. This increase could be related to the release of charged species from degraded adjuvants or transformed the active ingredient. The muddy matrix may amplify this effect due to its high background conductivity and presence of colloids.

Additionally, the interaction between temperature and expiration date also had significant effects ($F_{4;89086}$=1,924, $p<0.0001$). Higher temperatures enhanced conductivity, whereas lower temperatures reduced it, confirming that thermal state amplifies or mitigates the effects of product aging. These findings indicate that the electrical stability of imidacloprid depends both on expiration time and thermal environment, with these variables acting synergistically depending on the aqueous matrix used.

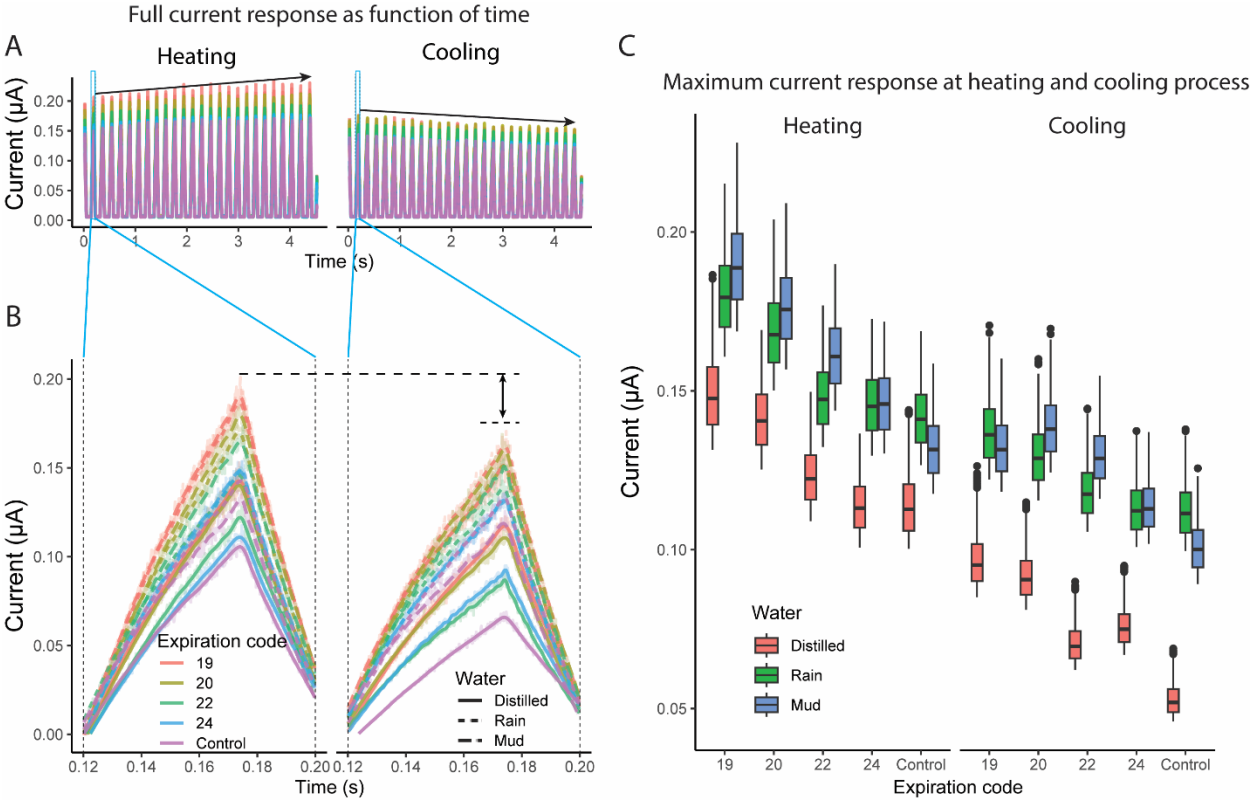

*Fig. 4 Electrical current behavior during heating and cooling processes. **A)** Segment of the current signal induced by a triangular voltage wave in imidacloprid solutions prepared with three types of water (Distilled, Rain, Mud). **B)** Distribution of maximum current recorded by water type and batch. Control solutions (without imidacloprid) exhibited the lowest values in all cases. **C)** Comparison of mean current during heating and cooling phases as a function of water type and product expiration date (Expiration code: 19, 20, 22, 24).*

Electrical gain of imidacloprid samples in aqueous solutions and temperature changes

The electrical gain of the system, defined as $20 \cdot \log_{10}[\text{Vout/Vin}]$, showed significant dependence on water type ($F_{2;4770}=5159.51$, $p<0.0001$), temperature ($F_{1;4770}=13560$, $p<0.0001$), and expiration date ($F_{4;4770}=111.31$, $p<0.0001$). Significant interactions were also found between water type and temperature ($F_{2;4770}=666.09$, $p<0.0001$), water type and expiration date ($F_{8;4770}=56.55$, $p<0.0001$), temperature and expiration date ($F_{4;4770}=35.64$, $p<0.0001$).

These interactions reflect a complex dielectric response, in which gain progressively decreases with product aging, particularly under extreme thermal conditions. Solutions prepared with distilled water exhibited a more pronounced reduction in gain during the cooling phase, that is a reduced capacity of this medium to stabilize the structure of the active ingredient or its adjuvants.

In contrast, samples prepared with rainwater or muddy water showed a more stable response, with smaller variations in gain across expiration dates. This may be attributed to the presence of salts or organic compounds that buffer the dielectric effects of chemical aging. Thermal differences also played a key role: at elevated temperatures, gain tended to decrease across all media, but the decline was more pronounced in distilled water.

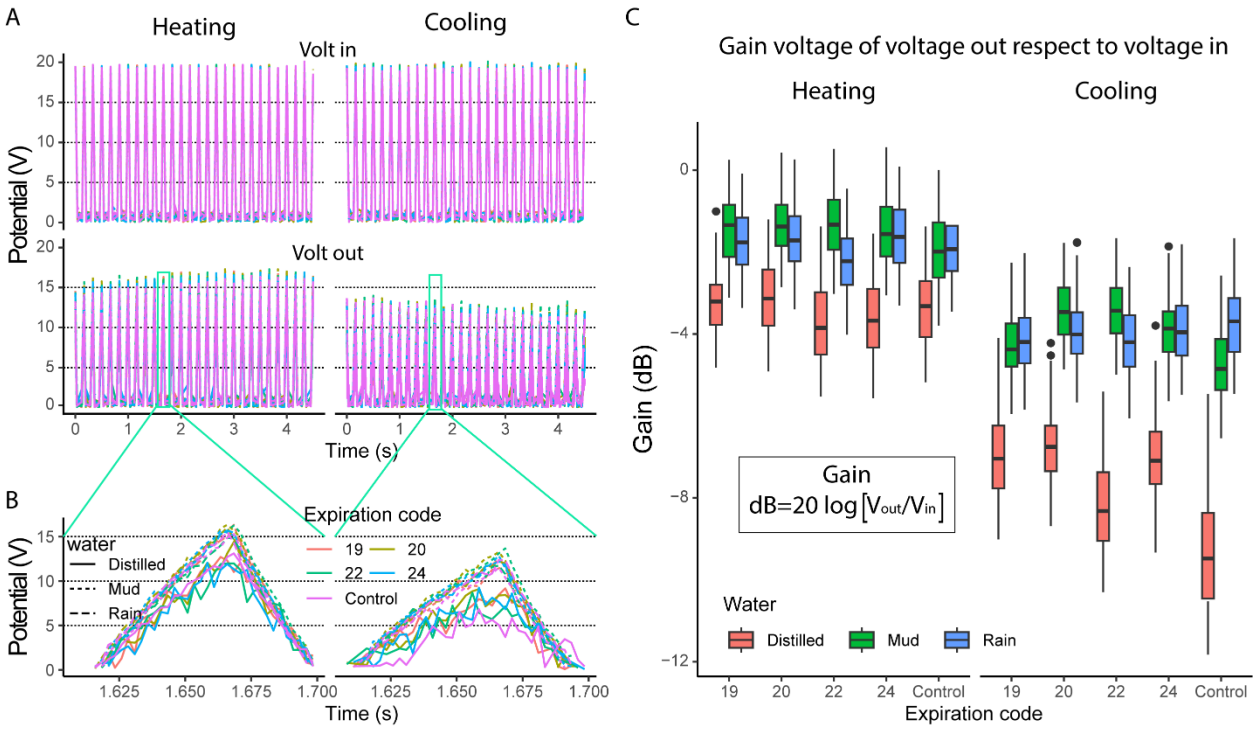

*Fig. 5 **A)** Electrical gain recorded during the heating and cooling phases for imidacloprid solutions in three types of water (distilled, rain, and muddy). **B)** Distribution of maximum gain recorded by water type and batch. **C)** Comparison of mean gain during heating and cooling phases as a function of water type and product expiration date (Expiration code: 19, 20, 22, 24); Control solutions (without imidacloprid) exhibited the lowest values in all cases.*

Electrical response to changes in excitation frequency

The system's electrical gain in response to frequency changes exhibited two behavioral patterns: a low-variability region (plateau) and a linear-response region (slope). These patterns depended on the type of water (Distilled, Rain, Mud) and the threshold frequency at which the transition between regions occurred. In distilled water solutions, the linear behavior emerged at frequencies $>10^4$ Hz, whereas in rainwater and muddy water, the transition occurred at frequencies $>10^5$ Hz (Figure 5A).

In the low-variability region, solutions prepared with distilled water exhibited the lowest gain values, while those prepared with rainwater and muddy water exceeded 60% gain: 70.5 ± 0.14% in rainwater and 67.7±0.14% in muddy water. This behavior was influenced by water type ($F_{2;4941}$=71,941, p<0.0001), expiration date ($F_{4;4941}$=13.16, p<0.0001), and temperature ($F_{2;4941}$=53.72, p<0.0001). A significant interaction was found between water type and expiration date ($F_{8;4935}$=69.7, p<0.0001), where gain decreased with product aging in distilled water, whereas the opposite trend was observed in rainwater and muddy water. No significant interaction was detected between temperature and water type in this region ($F_{4;4941}$=0.883, p=0.47) (Figure 5B).

In the linear region (high frequencies), water type was the main variable affecting the gain slope ($F_{2,36} = 125.6$, $p < 0.0001$), while expiration date ($F_{4;36}$=1.21, p=0.33) and temperature ($F_{2;36}$=0.002, p=0.98) had no significant effect. Shallower slopes were observed in distilled water, whereas steeper slopes were observed in rainwater and muddy water, indicating greater dielectric sensitivity to frequency changes. The interaction between water type and expiration date was significant ($F_{8;30}$=2745.2, p<0.0001), while the interaction between expiration date and temperature showed no effect ($F_{4;30}$=0.007, p=1.00).

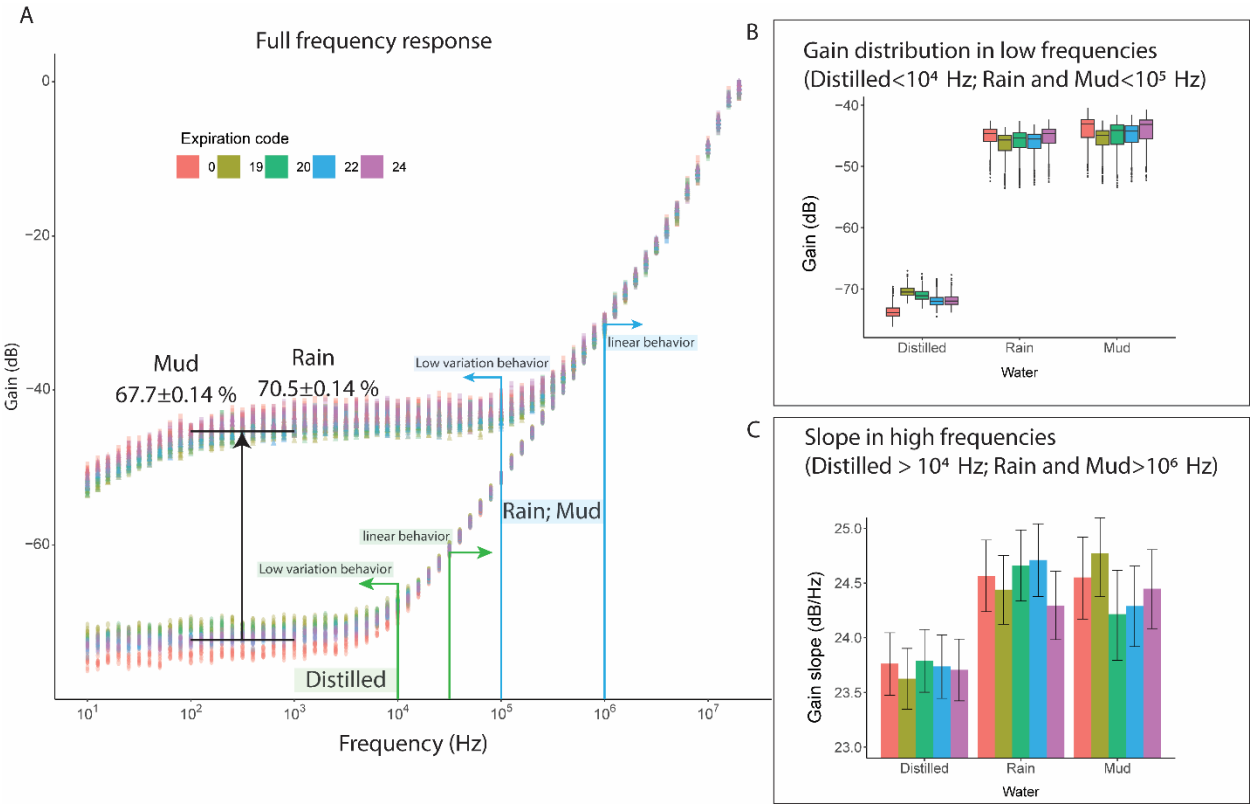

*Fig. 6 Frequency response of electrical gain for imidacloprid solutions dissolved in different types of water (Distilled, Rain, Mud). **A)** Logarithmic gain curves as a function of frequency, grouped by water type. A steeper increase is observed in distilled water. **B)** Mean gain values in the low-frequency region, where the response remains relatively constant. **C)** Mean gain values in the high-frequency region, showing differences in slope according to water type.*

Overall, the results demonstrate that the thermal, optical, and electrical properties of imidacloprid solutions vary significantly depending on water type, temperature, and product expiration date. The observed differences in heating/cooling constants, absorbance spectra, electrical current, and system gain reflect a complex interplay among these factors. In addition, specific frequency regions were identified where the system's dielectric response either stabilized or shifted in a matrix- and aging-dependent manner. These patterns will be further explored in the Discussion section, with a focus on their physicochemical and environmental implications.

DISCUSSION

1. Thermal stability and interaction with aqueous matrices

The results indicate that commercial imidacloprid formulations exhibit notable thermal stability, even beyond their expiration date [49]. The absence of significant effects related to product aging suggests that, at least at the macroscopic level, thermal properties are not compromised over time. However, differences in heating and cooling constants across water types reveal that the aqueous matrix plays a key modulatory role. The faster thermal transfer observed in distilled water may be attributed to its lower content of dissolved solids and the absence of colloidal components that could buffer thermal energy transfer [50]. In contrast, muddy water, rich in organic matter and salts, showed a lower thermal constant, likely due to a higher combined specific heat of the system [51].

2. Optical transformations and spectral effects

Although the overall UV-Vis spectrum did not show significant differences between water types or expiration dates, interval-based analyses revealed specific modifications. The reduction in absorbance observed in older batches suggests degradation or transformation processes affecting the active ingredient and its adjuvants [52,53]. This loss was particularly evident in the 257–263 nm range, which corresponds to the most intense peak, indicating a decrease in the effective concentration of imidacloprid. Variations detected in the 269–282 nm interval, considered the

spectral signature of the compound, suggest that the aqueous environment may alter the system's electronic interactions, possibly through changes in pH or reactions with compounds present in natural water matrices [54].

3. Conductivity and ionic mobility

The electrical current results showed a clear effect of water type, temperature, and expiration date. The increase in current with temperature is consistent with enhanced ionic mobility, as predicted by the Nernst–Einstein equation [51]. However, the fact that older formulations exhibited higher current values suggests the decomposition of components that release additional ionic species. This effect was most pronounced in muddy water, likely due to the chemical complexity of the medium, which may promote degradation of the active ingredient or dissociation of adjuvants [52]. It is possible that these solutions behave like conductive colloidal systems, where the presence of organic and inorganic materials increases the baseline conductivity.

4. Electrical gain and dielectric behavior

The progressive decrease in electrical gain with product aging, particularly in distilled water, reveals a loss in the system's dielectric efficiency. This effect may result from a reduction in medium polarization due to the degradation of components with high dielectric constants [54]. In contrast, in more complex matrices such as rainwater and muddy water, aging effects were less pronounced, possibly due to a buffering effect from dissolved salts or organic compounds that help preserve dielectric response. The marked differences observed during the cooling phase in distilled water suggest that under low thermal energy conditions, the system’s dielectric structure is more vulnerable to chemical degradation.

5. Frequency Response and Capacitive Properties

Analysis of gain in response to frequency changes revealed that the system’s dielectric stability depends on water type and product age. In distilled water, the gain was low in the plateau region, and the transition to linear behavior occurred at lower frequencies, suggesting a reduced capacity of the medium to store or release electrical charge as a function of frequency. The steeper slopes observed in more complex matrices indicate greater frequency sensitivity, possibly associated with multiple dielectric relaxation processes induced by the presence of ions and polar molecules. In

this context, imidacloprid aging appears to act as a modulator of these properties, with matrix- and temperature-dependent effects.

Limitations

One limitation of this study is the lack of detailed information on the composition of the formulation adjuvants, which constrains precise molecular-level interpretation of the observed transformations. Additionally, the controlled laboratory conditions do not capture the full complexity of agricultural environments, where factors such as UV radiation, mechanical agitation, and microbial activity may alter product behavior. Nonetheless, the results presented here establish clear relationships among expiration date, water type, and the physicochemical response of commercial imidacloprid, providing a solid framework for future environmental impact assessments and optimization of product use.

Although this study did not directly measure parameters such as pH or the intrinsic conductivity of the aqueous matrices, these properties likely contributed to the differences observed in thermal and electrical responses. Previous research has shown that the presence of ions, organic matter, and other impurities can significantly affect the colloidal stability and conductivity of pesticide formulations in solutions [55–57].

Overall, the results reveal that the physicochemical stability of commercial imidacloprid formulations is modulated by both the type of water used and the storage duration, with particularly notable effects on the system's electrical properties. While thermal responses indicated apparent stability, optical and electrical assessments revealed transformations associated with product aging and interaction with complex aqueous matrices. The modulatory role of water type has been previously documented, highlighting that dissolved organic matter and salts can influence both colloidal stability and the chemical activity of pesticides. These findings not only enhance our understanding of product behavior under controlled conditions but also provide an experimental framework for future investigations into its persistence and transformation in real-world environments. The integration of thermal, optical, and electrical tools offers a complementary and robust approach for evaluating commercial formulations, particularly in the context of agricultural use and potential environmental impact.

CONCLUSIONS

The results of this study demonstrate that the physicochemical stability of commercial imidacloprid depends on storage duration, the type of water used as solvent, and the exposure temperature. Although heating and cooling curves did not show marked differences with respect to expiration date, indicating macroscopic thermal stability, spectroscopic analyses revealed alterations in specific regions of the spectrum associated with the active ingredient. These modifications became more pronounced with product aging and through interaction with aqueous matrices containing organic and inorganic compounds, suggesting possible chemical degradation or specific interactions with the matrix.

Electrical analyses showed that both current and system gain decreased with extended storage time, particularly in solutions prepared with distilled water. This behavior may reflect a loss in ionic mobility and structural reorganization of the adjuvants. Additionally, the dielectric response to frequency variation exhibited a loss of linearity in aged samples, supporting the hypothesis of structural transformations at the colloidal or molecular level within the formulation. These findings are further supported by changes in the impedance phase, reinforcing the value of these measurements as sensitive tools for monitoring formulation stability.

Taken together, these findings underscore the importance of evaluating entire pesticide formulations, rather than just the active ingredient, under realistic environmental conditions. The interaction between factors such as water type, temperature, and storage time can significantly influence both product efficacy and environmental behavior. Therefore, studying the stability and transformation of these formulations should be prioritized to develop more responsible and sustainable management strategies.

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COMPETING INTERESTS

The authors do not have any competing interests to declare.

REFERENCES

1. Sharma A, Kumar V, Shahzad B, Tanveer M, Sidhu GPS, Handa N, et al. Worldwide pesticide usage and its impacts on ecosystem. SN Applied Sciences. Springer Nature; 2019. doi:10.1007/s42452-019-1485-1

2. Fouad MR, Abdel-Raheem SAA. An overview on the fate and behavior of imidacloprid in agricultural environments. Environmental Science and Pollution Research. Springer; 2024. doi:10.1007/s11356-024-35178-6

3. Jie M, Gao Y, Kuang D, Shi Y, Wang H, Jing W. Relationship between imidacloprid residues and control effect on cotton aphids in arid region. Environ Geochem Health. 2021;43: 1941–1952. doi:10.1007/s10653-020-00776-z

4. Al-Hawadi JS, Al-Sayaydeh RS, Al-Rawashdeh ZB, Ayad JY. Monitoring of imidacloprid residues in fresh fruits and vegetables from the central parts of Jordan. Heliyon. 2023;9. doi:10.1016/j.heliyon.2023.e22136

5. Asif MU, Muhammad R, Sohail M. Comparative efficacy of Neem derivatives and imidacloprid against some cotton pests. 2018. Available: https://www.researchgate.net/publication/327511814

6. Kurwadkar S, Evans A. Neonicotinoids: Systemic Insecticides and Systematic Failure. Bulletin of Environmental Contamination and Toxicology. Springer New York LLC; 2016. pp. 745–748. doi:10.1007/s00128-016-1968-3

7. CRESSEY D. Neonics vs bees. Nature. 2017; 156–158.

8. Food and Agriculture Organization of the United Nations. Manual on the development and use of FAO and WHO specifications for chemical pesticides. Manual on the development and use of FAO and WHO specifications for chemical pesticides. FAO; WHO; 2022. doi:10.4060/cb8401en

9. Kah M, Beulke S, Tiede K, Hofmann T. Nanopesticides: State of knowledge, environmental fate, and exposure modeling. Crit Rev Environ Sci Technol. 2013;43: 1823–1867. doi:10.1080/10643389.2012.671750

10. Knowles A. Recent developments of safer formulations of agrochemicals. Environmentalist. 2008. pp. 35–44. doi:10.1007/s10669-007-9045-4

11. Balieira KVB, Mazzo M, Bizerra PFV, Guimarães AR de JS, Nicodemo D, Mingatto FE. Imidacloprid-induced oxidative stress in honey bees and the antioxidant action of caffeine. Apidologie. 2018;49: 562–572. doi:10.1007/s13592-018-0583-1

12. Zafeiridou G, Theophilidis G. The action of the insecticide imidacloprid on the respiratory rhythm of an insect: The beetle Tenebrio molitor. Neurosci Lett. 2004;365: 205–209. doi:10.1016/j.neulet.2004.04.084

13. Aguiar JMRBV, Nocelli RCF, Giurfa M, Nascimento FS. Neonicotinoid effects on tropical bees: Imidacloprid impairs innate appetitive responsiveness, learning and memory in the stingless bee Melipona quadrifasciata. Science of the Total Environment. 2023;877. doi:10.1016/j.scitotenv.2023.162859

14. Brandt A, Gorenflo A, Siede R, Meixner M, Büchler R. The neonicotinoids thiacloprid, imidacloprid, and clothianidin affect the immunocompetence of honey bees (Apis mellifera L.). J Insect Physiol. 2016;86: 40–47. doi:10.1016/j.jinsphys.2016.01.001

15. Raymann K, Motta EVS, Girard C, Riddington IM, Dinser JA, Moran NA. Imidacloprid decreases honey bee survival rates but does not affect the gut microbiome. Appl Environ Microbiol. 2018;84. doi:10.1128/AEM.00545-18

16. Sánchez-Bayo F, Belzunces L, Bonmatin JM. Lethal and sublethal effects, and incomplete clearance of ingested imidacloprid in honey bees (Apis mellifera). Ecotoxicology. 2017;26: 1199–1206. doi:10.1007/s10646-017-1845-9

17. Potts SG, Biesmeijer JC, Kremen C, Neumann P, Schweiger O, Kunin WE. Global pollinator declines: Trends, impacts and drivers. Trends in Ecology and Evolution. 2010. pp. 345–353. doi:10.1016/j.tree.2010.01.007

18. Klein AM, Vaissière BE, Cane JH, Steffan-Dewenter I, Cunningham SA, Kremen C, et al. Importance of pollinators in changing landscapes for world crops. Proceedings of the Royal Society B: Biological Sciences. Royal Society; 2007. pp. 303–313. doi:10.1098/rspb.2006.3721

19. Grant KJ, DeVetter L, Melathopoulos A. Honey bee (Apis mellifera) colony strength and its effects on pollination and yield in highbush blueberries (Vaccinium corymbosum). PeerJ. 2021;9. doi:10.7717/peerj.11634

20. Decourtye A, Alaux C, Le Conte Y, Henry M. Toward the protection of bees and pollination under global change: present and future perspectives in a challenging applied science. Current Opinion in Insect Science. Elsevier Inc.; 2019. pp. 123–131. doi:10.1016/j.cois.2019.07.008

21. Günal AÇ, Erkmen B, Paçal E, Arslan P, Yildirim Z, Erkoç F. Sub-lethal Effects of Imidacloprid on Nile Tilapia (Oreochromis niloticus). Water Air Soil Pollut. 2020;231. doi:10.1007/s11270-019-4366-8

22. Stehle S, Ovcharova V, Wolfram J, Bub S, Herrmann LZ, Petschick LL, et al. Neonicotinoid insecticides in global agricultural surface waters – Exposure, risks and regulatory challenges. Science of the Total Environment. 2023;867. doi:10.1016/j.scitotenv.2022.161383

23. Fuentes E, Gaffard A, Rodrigues A, Millet M, Bretagnolle V, Moreau J, et al. Neonicotinoids: Still present in farmland birds despite their ban. 2023.

24. Wang JZ, Hou J, Wang LX, Zhu ZY, Han BJ, Chen LY, et al. Pollution characteristics, environmental issues, and green development of neonicotinoid insecticides in China: Insights from Imidacloprid. Environmental Pollution. Elsevier Ltd; 2025. doi:10.1016/j.envpol.2024.125394

25. Zhang S, Jiang JQ. Occurrence and Distribution of Neonicotinoid Pesticides in Chinese Waterways: A Review. Environments - MDPI. 2023;10. doi:10.3390/environments10120206

26. Bonmatin JM, Giorio C, Girolami V, Goulson D, Kreutzweiser DP, Krupke C, et al. Environmental fate and exposure; neonicotinoids and fipronil. Environmental Science and Pollution Research. 2015;22: 35–67. doi:10.1007/s11356-014-3332-7

27. Gupta S, Gajbhiye VT. Adsorption-desorption, persistence, and leaching behavior of dithiopyr in an alluvial soil of India. J Environ Sci Health B. 2002;37: 573–586. doi:10.1081/PFC-120015440

28. Tišler T, Jemec A, Mozetič B, Trebše P. Hazard identification of imidacloprid to aquatic environment. Chemosphere. 2009;76: 907–914. doi:10.1016/j.chemosphere.2009.05.002

29. Bori J, Ribalta C, Xavier D, Riva M, Ribó J. Environmental impacts of an imidaclopridcontaining formulation: from soils to waters. 2015.

30. Halkijevic I, Licht K, Kosar V, Bogdan L. Degradation of the neonicotinoid pesticide imidacloprid by electrocoagulation and ultrasound. Sci Rep. 2024;14. doi:10.1038/s41598-024-59568-5

31. AlNeyadi SS, Alhassani MT, Mukhtar MR, Alblooshi HK, Jama SA, Al Mujaini I, et al. Hydrophilic magnetic COFs: The Answer to photocatalytic degradation and removal of imidacloprid insecticide. Heliyon. 2024;10. doi:10.1016/j.heliyon.2024.e39042

32. Kaewket K, Ngamchuea K. Microporous carbon for fast and simple electrochemical detection of imidacloprid insecticide in fruit and water samples. RSC Adv. 2023;13: 4532–4541. doi:10.1039/d3ra00192j

33. Sharma T, Toor AP, Rajor A. Photocatalytic degradation of imidacloprid in soil: Application of response surface methodology for the optimization of parameters. RSC Adv. 2015;5: 25059–25065. doi:10.1039/c5ra02224j

34. Sumon KA, Ritika AK, Peeters ETHM, Rashid H, Bosma RH, Rahman MS, et al. Effects of imidacloprid on the ecology of sub-tropical freshwater microcosms. Environmental Pollution. 2018;236: 432–441. doi:10.1016/j.envpol.2018.01.102

35. Qurie M, Alkhatib M, Bufo SA, Scrano L, Khamis M, Ayyad I, et al. Removal of imidacloprid from polluted water using adsorption and membrane separation technologies. Desalination Water Treat. 2021;242: 178–186. doi:10.5004/dwt.2021.27852

36. Zou Z, Huang X, Guo X, Jia C, Li B, Zhao E, et al. Efficient degradation of imidacloprid in soil by thermally activated persulfate process: Performance, kinetics, and mechanisms. Ecotoxicol Environ Saf. 2022;241. doi:10.1016/j.ecoenv.2022.113815

539 37. Mahapatra B, Adak T, Patil NKB, Pandi GGP, Gowda GB, Yadav MK, et al. Effect of
540 Abiotic Factors on Degradation of Imidacloprid. Bull Environ Contam Toxicol. 2017;99:
541 475–480. doi:10.1007/s00128-017-2159-6

542 38. Liu W, Pan T, Liu H, Jiang M, Zhang T. Adsorption behavior of imidacloprid pesticide on
543 polar microplastics under environmental conditions: critical role of photo-aging. Front
544 Environ Sci Eng. 2023;17. doi:10.1007/s11783-023-1641-0

545 39. Warne MSJ, Turner RDR, Davis AM, Smith R, Huang A. Temporal variation of
546 imidacloprid concentration and risk in waterways discharging to the Great Barrier Reef and
547 potential causes. Science of the Total Environment. 2022;823.
548 doi:10.1016/j.scitotenv.2022.153556

549 40. Bauke SL, Amelung W, Bol R, Brandt L, Brüggemann N, Kandeler E, et al. Soil water
550 status shapes nutrient cycling in agroecosystems from micrometer to landscape scales.
551 Journal of Plant Nutrition and Soil Science. John Wiley and Sons Inc; 2022. pp. 773–792.
552 doi:10.1002/jpln.202200357

553 41. Alibabaei K, Gaspar PD, Lima TM. Modeling soil water content and reference
554 evapotranspiration from climate data using deep learning method. Applied Sciences
555 (Switzerland). 2021;11. doi:10.3390/app11115029

556 42. Zhou L, Yu D, Wang Z, Wang X. Soil water content estimation using high-frequency
557 ground penetrating radar. Water (Switzerland). 2019;11. doi:10.3390/w11051036

558 43. Thuyet DQ, Jorgenson BC, Wissel-Tyson C, Watanabe H, Young TM. Wash off of
559 imidacloprid and fipronil from turf and concrete surfaces using simulated rainfall. Science
560 of the Total Environment. 2012;414: 515–524. doi:10.1016/j.scitotenv.2011.10.051

561 44. Yadav IC, Watanabe H. Soil erosion and transport of Imidacloprid and Clothianidin in the
562 upland field under simulated rainfall condition. Science of the Total Environment.
563 2018;640–641: 1354–1364. doi:10.1016/j.scitotenv.2018.06.008

564 45. Perrot T, Bonmatin JM, Jactel H, Leboulanger C, Goffaux R, Gaba S. Temporal and spatial
565 trends of imidacloprid-related hazards in France. Science of the Total Environment.
566 2024;945. doi:10.1016/j.scitotenv.2024.173950

46. Rondeau G, Sánchez-Bayo F, Tennekes HA, Decourtye A, Ramírez-Romero R, Desneux N. Delayed and time-cumulative toxicity of imidacloprid in bees, ants and termites. Sci Rep. 2014;4. doi:10.1038/srep05566

47. Getter K. Using old pesticides may be perilous to your plants - MSU Extension. 2015 [cited 10 May 2025]. Available: https://www.canr.msu.edu/news/using_old_pesticides_may_be_perilous_to_your_plants

48. Posit team. RStudio: Integrated Development Environment for R. Boston, MA; 2023.

49. Mchenery Bsc JG. IMIDACLOPRID FOR SALMONIDS ENVIRONMENTAL ASSESSMENT IN SUPPORT OF AN IMPORT TOLERANCE REQUEST Final: Original signed and on file.

50. Minnesota Department of Health. Imidacloprid and Groundwater Imidacloprid. 2020. Available: https://www.regulations.gov/document?D=EPA-HQ-OPP-2008-0844-0140

51. Gao S, Li S, Sun S, Chen M. Recent Advances in Photocatalytic Degradation of Imidacloprid in Aqueous Solutions Using Solid Catalysts. Catalysts. Multidisciplinary Digital Publishing Institute (MDPI); 2024. doi:10.3390/catal14120878

52. Tariq SR, Niaz Z, Chotana GA, Ahmad D, Rafique N. Photocatalytic degradation of imidacloprid using Ag2O/CuO composites. RSC Adv. 2023;13: 19326–19334. doi:10.1039/d3ra02109b

53. Akbari Shorgoli A, Shokri M. Photocatalytic degradation of imidacloprid pesticide in aqueous solution by TiO2 nanoparticles immobilized on the glass plate. Chem Eng Commun. 2017;204: 1061–1069. doi:10.1080/00986445.2017.1337005

54. Malmberg CG, Maryott AA. Dielectric Constant of Water from 0 0 to 100 0 C. J Res Natl Bur Stand (1934). 1956.

55. Ayodhya D. Recent advancement in pesticide formulations for pest management and residue analysis by analytical techniques in agriculture using nanocomposites. Review of Materials Research. 2025;1: 100130. doi:10.1016/j.revmat.2025.100130

593 56. Carpio MJ, Sánchez-Martín MJ, Rodríguez-Cruz MS, Marín-Benito JM. Effect of Organic
594 Residues on Pesticide Behavior in Soils: A Review of Laboratory Research. Environments.
595 2021;8: 32. doi:10.3390/environments8040032

596 57. Eitzen L, Ruhl AS, Jekel M. Impact of natural organic matter and inorganic ions on the
597 stabilization of polystyrene micro-particles. Science of the Total Environment. 2024;927.
598 doi:10.1016/j.scitotenv.2024.172043

599