Polluted paradise : occurrence of pesticide residues within the urban coastal zones of Santa Cruz and Isabela (Galapagos, Ecuador)

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Abstract

Although pesticides are frequently used for agriculture in the Galapagos Islands (Ecuador), there are, to date, no investigations of pesticide occurrences in its coastal waters. We examined the presence of pesticide residues in the coastal waters of urban areas in two islands of the Galapagos archipelago using a repeated sampling design. Quantification was performed by solid-phase extraction, followed by chemical analysis using liquid chromatography-tandem mass spectrometry (LC-MSMS) and gas chromatography-electron capture detector (GC-ECD). The diversity and concentration of pesticide residues in Santa Cruz island were higher compared to Isabela island. In total, sixteen pesticides were detected, including three persistent organic pollutants. Carbendazim (23.93 $\mu g \cdot L^{-1}$), cadusafos (4.74 $\mu g \cdot L^{-1}$), DDT (2.99 $\mu g \cdot L^{-1}$), diuron (1.61 $\mu g \cdot L^{-1}$) and aldrin (1.55 $\mu g \cdot L^{-1}$) were detected with the highest concentrations between samples. Repetitions in locations show that concentrations of pesticide residues varied considerably in space and time. Comparison with local products indicated agricultural activities on the islands as a possible source. Furthermore, ecological risk quotients showed a relatively high risk for the three biotic groups (i.e. algae, invertebrates, and fishes) evaluated for seven pesticides. Taken together, this study provides insights into the need to regulate, monitor and assess the presence of pesticides in the islands.

Keywords

Pesticides, Risk assessment, Seawater, Urban Areas, Island, Galapagos

Introduction

Pesticides are a useful tool to protect crops from pests, to control weeds and to regulate plant growth. Hence, they are responsible for significantly reducing harvest losses, thereby increasing the crop yield and enhancing overall food availability (Cooper & Dobson, 2007; Aktar et al., 2009). The benefits of using pesticides on an agricultural holding are often countered by unwanted and detrimental impacts on the environment (Van der Werf, 1996; Sankoh et al., 2016). Accidental spillages, aerial spraying, improper disposal, drainage, and runoff represent only a few processes that underlie the introduction of active pesticide compounds into the atmosphere, soil, groundwater and surface water. There, pesticide compounds can actively influence population dynamics and community structure through (i) direct

species-specific interaction and (ii) residue accumulation throughout successive trophic levels (Duke, 1977; Kole et al., 2001; Wilson & Tisdell, 2001; de Souza et al., 2020).

Worldwide, approximately 3 billion kg of pesticides are used annually (Sharma et al., 2020). Yet, according to Ali et al. (2019), approximately 1 % of the applied pesticides reach their target, while the remaining 99 % enters vegetables, fruits, soils and water. This dissipation depends on several local factors, including crop type, runoff, leaching and erosion (Wilson & Tisdell, 2001). Moreover, climatic conditions (rainfall, temperature, humidity, wind and sunlight), application strategy (frequency, intensity and type) and compound characteristics (toxicity, specificity and degradation rate) contribute to the fate of pesticide residues (Daam & Van Den Brink, 2010; Fantke et al., 2011; Barbash, 2013). In this context, rainfall is the main factor linked to runoff, washing, transport and leaching from arable land to aquatic ecosystems (McGrath et al., 2010; Barbash, 2013; Herrero-Hernández et al., 2017; Imfeld et al., 2020). Pesticides have the potential to exert adverse effects on a variety of biotic groups, including algae, invertebrates and fish (Alava & Ross, 2018; Rain-Franco et al., 2018; Russo et al., 2018; Tsygankov et al., 2019; Bighiu et al., 2020).

Pesticide application and the associated dispersal into the environment occurs globally, though the ecological consequences are highly dependent on the experienced exposure. For instance, agrochemical pollution studies in tropical regions indicated high levels of exposure to pesticides and, thus, a high risk to aquatic organisms (Castillo et al., 2000; De Gerónimo et al., 2014; Carazo-Rojas et al., 2018). This observation a highlights problems in developing countries associated with regulating the use of older, non-patented, toxic and environmentally persistent pesticides (Ecobichon, 2001). In Latin America, pesticides that are currently forbidden in the United States and European Union have been used legally for several decades (Solorzano, 1989; Shrader-Frechette, 1991; Vryzas et al., 2020; Ramírez-Morales et al., 2021). For instance, in Ecuador, DDT was applied inside houses between 1957 and 1999, distributed without any control, and used in agriculture for pest control (Grillo & Venora, 2011). A more recent example is the current legal use of carbendazim and chlorpyrifos in Ecuador, although both pesticides are banned by the European Union (EU).

These applications and impacts are not limited to the agricultural sites of continental Ecuador but extend to more remote systems. More specifically, recent studies have demonstrated that pesticide residues affect the endemic fauna in the unique ecosystems of the Galapagos Archipelago (Alava & Gobas, 2012; Alava & Ross, 2018), with pesticides such as heptachlor, parathion and methamidophos, being reported as commonly used in agricultural fields (Espin, 2018). Moreover, presence of persistent organic pollutants (organochlorine pesticides) has been observed in several animals within the archipelago, including sea lions, fish and sperm whales within (Alava et al., 2011, 2014; Godard-Codding et al., 2011). Yet, the degree of pollution within the coastal areas of these protected islands remains largely understudied, illustrating the need to monitor and evaluate pesticide occurrences. Such assessments are of paramount importance to determine the pesticide concentrations in the environment and to map risk areas for wildlife.

Within this study, we aim to assess the presence and ecotoxicological risk of pesticide residues within the urbanised coastal environment of the Galapagos Islands. To do so, we applied a repeated sampling design to (1) evaluate the current concentrations in two populated islands: Santa Cruz and Isabela, (2) determine the variability of pesticide residues in space and time, (3) compare the detected residues with available local agricultural data and (4) assess the ecotoxicological risk for three taxonomic groups (algae, invertebrates and fishes). The results of this study can provide a basis to identify and eliminate land-based contributions of harmful pesticides within this biodiverse archipelago.

1. Materials and methods

1.1 Study area

The Galapagos archipelago consists of 13 major volcanic islands and more than 40 islets. It is located approximately 972 km from the Ecuadorian continental coast and characterised by high levels of biodiversity and endemism. The climate varies slightly depending on the island (Elias, 2020), though is generally characterised by two distinct seasons due to the temporal variation in the multiple water currents and atmospheric conditions (Trueman & d'Ozouville, 2010). From May to December the hot

and wet season prevails with cool temperatures. The rest of the year is characterised by elevated temperatures and heavy rainfall.

Two of the major inhabited islands in Galapagos are Santa Cruz and Isabela. Santa Cruz is the main island for tourism with an area of 1,794 km^2 and about 15,701 inhabitants (INEC, 2015). This island has agricultural areas across an altitudinal (between 100 and 520 m a.s.l.) that facilitates crop diversification. Isabela is the largest island with an area of 5,376 km^2 and about 2,344 inhabitants (INEC, 2015). This island has agricultural fields on the southeast flank of the Sierra Negra volcano (Snell et al., 1996).

Fig.1 Location sites in Santa Cruz and Isabela islands in the Galapagos Archipelago.

In total, eight locations (four on each island) were selected for sample collection, all of which were located in the coastal zone near urbanisation (Fig. 1). Sites were selected along a gradient of apparent human disturbance. The locations in Santa Cruz were: SC1, located in Playa de los Alemanes next to a hotel, receiving a drainage pipe with water discharging into the sea; SC2, situated at a distance of approximately 0.3 km from the shore; SC3, located in the harbour next to the saltwater lagoon Laguna de las Ninfas, and SC4, situated at the Playa de la Estación beach. In Isabela, four locations were selected: ISA1 located next to the dock, ISA2 located at the in Playa del Amor beach, ISA3 situated in a pond a few meters from the sea, and ISA4 located on the beach next to ISA3. All methods were followed in accordance with the relevant guidelines and regulations of the Galapagos National Park Directorate under research permit PC-02-19.

2.2. Data collection and processing

2.2.1 Reference database

We developed a database of 2892 licensed products in Ecuador until 2019 based on publications of the government agency in charge of pesticide regulation and control in Ecuador (see Table B.1), and a historical review of the pesticides reported in the Galapagos Islands (see Table B.2). From this list, 75 pesticide compounds available in our stock were selected, for liquid chromatography-tandem mass spectrometry analysis (LC-MS/MS). Additionally, six organochlorine pesticides were selected for analysis using gas chromatography with an electron capture detector (GC-ECD).

128 2.2.2 Field study

129 During sampling (February 2019), locations in Santa Cruz were sampled four times, while locations in
130 Isabela were only sampled twice due to overall logistic constraints. Dates and times of monitoring were
131 selected according to the movement of the tides (see Fig. 2). For each location, samples were collected
132 in triplicate (i.e. 50 meters apart) resulting in (4 x 4 x 3) 48 samples in Santa Cruz and (2 x 4 x 3) 24
133 samples in Isabela. Metadata (i.e. dates, tides, rainfall, movement currents and the number of samples
134 of each sampling site) are provided in Table A.1.

135 Fig. 2. Sampling design for Santa Cruz and Isabela islands.

136 Water samples were collected 0 to 30 cm below the water surface in amber glass bottles (priorly cleaned
137 with acetone and distilled water), providing a volume of 1 L. Bottles were first rinsed three times with
138 the surrounding water before sampling. Subsequently, the samples were transported at low temperature
139 to the laboratory for further processing.

140 Within six hours after sampling, the samples were filtered through glass microfiber filters (GF/F
141 Whatman diameter 70 mm CAT No. 1825-047) to remove suspended solids. Solid-phase extraction
142 (SPE) was applied by pumping the filtrate through activated cartridges (Sep-Pak C18 Classic Cartridge,
143 360 mg sorbent per cartridge, 55 - 105 µm) following the procedure described by Deknock et al. (2019).
144 Cartridges were previously activated with 10 mL methanol to liberate adsorption sites and remove any
145 impurities. Acetone was used to rinse all glassware before use, and a blank sample of distilled water was
146 included as a control for every separate day samples were collected. Cartridges were individually
147 wrapped in aluminium foil, labelled, and stored at −20 °C before being transported to Ghent University,
148 Belgium, for further processing.

149 2.2.3 Pesticide analysis

150 Sample preparation depended on the analytical device that was used, i.e. gas chromatography coupled
151 with an electron capture detector (GC-ECD) for the heavily chlorinated compounds or liquid
152 chromatography-tandem mass spectrometry (LC-MS/MS) using a triple quadrupole system with
153 electrospray ionisation for all other pesticides. First, pesticides were desorbed from the Sep-Pak
154 cartridges using 10 mL of acetonitrile (C_2H_3CN). Then, two 4 mL aliquots of the eluent were evaporated

155 in a rotavapor. Pesticides were re-dissolved in (i) 2 mL of a 90:10 solution of Milli-Q ultrapure water
156 and acetonitrile for LC-MS/MS or (ii) 2 mL of hexane for GC-ECD.

157 Calibration curves were constructed for each active ingredient by analysing five (0.004, 0.01, 0.02, 0.04,
158 0.1 $\mu g \cdot L^{-1}$) or nine (0.001, 0.002, 0.005, 0.008, 0.01, 0.02, 0.05, 0.08 and 0.1 $\mu g \cdot L^{-1}$) concentration levels
159 for GC-ECD and LC-MS/MS, respectively. The operating conditions and parameters are presented in
160 Table A.2. To validate the analysis, the spike-placebo recovery method for each active ingredient was
161 conducted: a blank sample was spiked in six replicates and analysed at the same conditions and
162 extraction methodology as the other samples. Pesticides, recoveries, limits of detection (LOD), limits of
163 quantification (LOQ) and calculation of recovery are given in Table A.3; the qualification ions, dwell
164 time and retention time for each analysed pesticide is given in Table B.3. To present the most probable
165 environmental concentration, reported concentrations include the recovery percentage.

166 2.2.4 Risk quotients (RQ) and ecotoxicological risk assessment

167 Risk assessment is based on the calculation of a risk quotient (RQ), which comprises a useful tool for
168 fingerprinting the potential ecological risk of various pollutants in aquatic ecosystems (Kapsi et al.,
169 2019).

170 In this study, the RQ was calculated per individual biotic groups (algae, invertebrate and fish) as the
171 ratio between the measured environmental concentration (*MEC*) and the toxicant reference value (TRV),
172 following the procedure described by Kapsi et al., (2019) and Xie et al. (2019). For measured
173 environmental concentration, the highest of all measurements for each location was used. For toxicant
174 reference value, LC_{50} (concentration considered lethal for 50% of the population) or EC_{50} (concentration
175 considered to cause an effect for 50% of the population) were obtained from the USEPA ECOTOX
176 database (see Table A.4). To evaluate the RQ, a risk ranking criterion was used: four risk levels were
177 classified according to the individual RQs: very low risk or no risk ($RQ < 0.01$); low risk ($0.01 < RQ <$
178 0.1); medium risk ($0.1 < RQ < 1$) and high risk ($RQ > 1$).

179 2.2.5 Data processing and statistical analyses

180 We used MS® Excel® to analyse the derived pesticide residues concentrations from GC-ECD and LC-
181 MS/MS. R software (RStudio Team, 2019), PRIMER (Anderson et al., 2008) and ArcGIS version 10.5
182 were used to perform statistical and graphical analyses.

183 Data were log-transformed and normalised (i.e. subtraction of mean and division by standard deviation)
184 before the dissimilarity matrix based on Euclidean distances was calculated. This dissimilarity matrix
185 was used as input for PERMANOVA (Permutational Multivariate dissimilarity-based ANOVA)
186 analysis, using 10^4 permutations under a reduced model. This model allowed to determine the amount
187 of variation explained by the factors location and repetition, respectively. Furthermore, pesticide-
188 specific correlation analysis using Spearman's test was performed to assess a possible relation between
189 rainfall and concentration of contaminants.

190 **3. Results**

191 3.1 Occurrence of pesticide residues

192 Of the 81 compounds evaluated, 16 were detected (see Table 1) with observation frequencies within the
193 72 samples ranging between 1 % and 87 %. Five pesticides were observed in more than 50 % of the
194 samples. These included DDT (87 %; with a range between 0.16 – 2.99 $\mu g \cdot L^{-1}$), heptachlor (86 %; <
195 LOQ – 0.69 $\mu g \cdot L^{-1}$), cadusafos (77 %; < LOQ – 4.74 $\mu g \cdot L^{-1}$), aldrin (69 %; < LOQ – 1.55 $\mu g \cdot L^{-1}$) and
196 propiconazole (58 %; < LOQ – 0.17 $\mu g \cdot L^{-1}$). Highest concentrations found in Santa Cruz were 23.93
197 $\mu g \cdot L^{-1}$ (carbendazim) and 3.05 $\mu g \cdot L^{-1}$ (cadusafos), while in Isabela, the highest concentration found
198 were 4.74 $\mu g \cdot L^{-1}$ (cadusafos) and 2.99 $\mu g \cdot L^{-1}$ (DDT).

199 Table 1. Pesticide residues in coastal water samples with corresponding recovery values, the number of
200 locations, detected concentration ranges, and mean concentration per island obtained during the four
201 repetitions of monitoring in Santa Cruz and two repetitions in Isabela.

202 Table 2. Pesticide residues in coastal water samples in Santa Cruz island, with corresponding mean and
203 standard deviation obtained between subsamples during the sampling.

Table 3. Pesticide residues in coastal water samples in Isabela island, with corresponding mean and standard deviation between subsamples obtained during the sampling.

A difference in the number of pesticide residues were found between both islands: fifteen for Santa Cruz and ten for Isabela (see Fig. 3). Tables 2-3 show that the number and concentration of pesticides also differed among repetitions. For instance, the number of pesticides ranged between 9 and 13 in Santa Cruz and between 8 and 9 in Isabela. No significant difference was found for pesticide concentrations between tides. It should be pointed out that, from the 81 evaluated compounds, 44 presented recovery values between 70 % and 120 %, while 37 showed values lower than 70%. In the last case, desorption efficiency was rather low due to a lower affinity with the silica phase of the Sep-Pak® cartridges or strong adsorption on the silica phase. This low recovery is not exceptional when a multi-residue method is used (Deknock et al., 2019; Elfikrie et al., 2020; Xie et al., 2019).

Fig.3. Venn diagram representing the pesticides dectected on both islands (n=9). Pesticides detected only in Santa Cruz and Isabela respectively.

3.2 Differences in pesticide concentrations between locations and repetitions

In Santa Cruz, between 11 and 13 pesticides were found next to the coastal area (SC1-SC3-SC4), while nine pesticides were found at 0.3 km from the shore (SC2). In Isabela, an average of eight pesticides were found in locations next to a lake (ISA2-ISA3-ISA4), while only six pesticides were found closest to settlements (ISA1). PERMANOVA analysis indicated that both factors – locations and repetition – were significant ($p < 0.05$) and explained 13.64 % and 16.13 % of the total variation, respectively.

Variability of concentration in locations and repetitions for four pesticides in Santa Cruz are illustrated in Fig. 4. During repetitions 3 and 4, higher concentrations of aldrin, cadusafos, carbendazim, and fenpropimorph were observed. These pesticides also show a positive correlation with the amount of rainfall reported during the days of monitoring (from 0 mm to 20 mm). This relation was statistically verified through pesticide-specific correlation analysis with rainfall using Spearman's test (see Fig. A.1) and coefficients showing value ≥ 0.5 for cadusafos (0.8), carbendazim (0.5), aldrin (0.5) and fenpropimorph (0.6).

In Santa Cruz, concerning the residues detected with LC-MS/MS, only cadusafos was found in all the locations and repetitions. Higher concentration of this pesticide (1.12, 1.3 and 2.27 $\mu g \cdot L^{-1}$) were found in SC4 at the Playa de la Estación beach. For carbendazim (22.71 $\mu g \cdot L^{-1}$) and fenpropimorph (0.19 $\mu g \cdot L^{-1}$), higher concentrations were detected in SC3 next to Laguna de las Ninfas. Moreover, values of carbendazim increase significantly in SC3 during the third and fourth repetition (R3-R4): from a maximum concentration of 0.58 $\mu g \cdot L^{-1}$ during R3 to 22.71 $\mu g \cdot L^{-1}$ in R4. With regards to the pesticide residues detected with GC-ECD, highest concentrations of aldrin (0.64-0.77 $\mu g \cdot L^{-1}$) were found at SC1 in a tourist beach located next to a hotel. For the rest of pesticides in both methods lowest concentrations were detected in SC2.

In Isabela, variation in the concentration of pesticides was also detected. For example, in location ISA1, aldrin, cadusafos and DDT had a maximum concentration of 0.36, 1.48 and 0.22 $\mu g \cdot L^{-1}$ in the fifth repetition while it became 1.05, 0.87 and 1.14 $\mu g \cdot L^{-1}$ in the sixth repetition.

Figure 4. Distribution of pesticides concentrations and standard deviation during the monitoring in Santa Cruz island. A-D) aldrin concentrations, E-H) cadusafos concentrations, I-J), carbendazim concentrations, and K-L) fenpropimorph concentrations. L.T.= low tide, H.T.= high tide, R=repetition

3.3. Risk assessment for pesticides

The results identify six high-risk pesticides for algae, invertebrates and fish in Santa Cruz and four in Isabela (see Fig. 5). Percentage of cases considered a high-risk were heptachlor (100 %), cadusafos (66 %), aldrin (50 %), carbendazim (46 %), DDT (12.5 %), diuron (12.5 %) and malathion (4.2 %). More specifically, in Santa Cruz, a high risk was obtained for aldrin, cadusafos, carbendazim, diuron, heptachlor and malathion while in Isabela, a high risk was found for aldrin, cadusafos, DDT and heptachlor. Unfortunately, no data was found to analyse the risk of aldrin and cadusafos towards algae. Overall, a higher risk was observed at the locations in Santa Cruz, with algae potentially experiencing higher effects than invertebrates or fish. More specifically, for algae an RQ > 0.01 was found for 86 % of the pesticides analysed, while this was only 69 % for invertebrates and fish. In contrast, invertebrates seemed to experience the highest risk in Isabela, except for metalaxyl and propazine.

Although the risk assessment was primarily calculated with toxicity data of saline water (see attached Table S5) as described by Xie et al. (2019), some data were for freshwater biota due to limited accessibility of seawater data.

Figure 5. Risk quotients of the detected pesticides for algae, invertebrate and fishes in coastal seawaters in urban areas in Santa Cruz and Isabela islands in the Galápagos Archipelago.

4. Discussion

4.1 Detected pesticide residues

Concentrations of pesticide residues detected in the coastal seawater of Santa Cruz and Isabela were in the same range as observed in Central and Latin America water bodies (Mortensen et al., 1998; Castillo et al., 2000; Hernández-Romero et al., 2004; De Gerónimo et al., 2014; Carazo-Rojas et al., 2018; Starling et al., 2019), including Ecuadorian rivers (Deknock et al. (2019) and Montaño & Resabala (2005)) and coastal seas in Colombia (INVEMAR, 2010). In contrast, a study from Castro (1997) on coastal seawater in Colombia reported higher values of DDT (between 2.47 and 53.47 $\mu g \cdot L^{-1}$) and heptachlor (1.27 $\mu g \cdot L^{-1}$). This discrepancy could be related to various parameters such as the degradation of these pesticides, differences between locations, and different applications parameters as described in other aquatic studies (Kole et al., 2001; Bajaj & Singh, 2015; Srivastava et al., 2019; Zacharia, 2019; de Souza et al., 2020).

The observed DDT residues indicate that the origin of the pesticides found in tissues in sea lions and its prey (*Mugil curema* and *Ophistonema berlangai*, respectively) by Alava & Gobas (2012) is caused by its presence in the environment. Moreover, our results support the observation of increased levels of the biomarker CYP1A1 (i.e. an enzyme to analyse exposure to organic pollutants) found in sperm whales from Galapagos (Godard-Codding et al., 2011).

4.2 Pesticide application in insular and mainland Ecuador

Among the 16 pesticide residues found, three are banned by the Stockholm Convention of Persistent Organic Pollutants (Lallas, 2001), being aldrin, DDT and heptachlor. These substances are organic compounds that are resistant to environmental degradation, known to accumulate in the tissues of

organisms through the food chain and toxic for humans and wildlife (Wei et al., 2007). Although Ecuadorian laws prohibited the use of POPs, Espin (2018) reported that heptachlor was still being applied in crops cultivated in Santa Cruz. Moreover, external factors such as long-range atmospheric transport could transfer pesticides from the mainland to the coastal waters, as demonstrated by Iwata et al. (1993) and Wilkening et al. (2000).

In continental Ecuador, farmers conducted both extensive and intensive application of DDT, heptachlor, aldrin, chlordane, dieldrin, mirex and lindane between the 1950s and 1980s (Solorzano, 1989). Mainly DDT was used throughout history in Latin America against plagues carried by rats and to control pests (e.g. malaria), as illustrated by the application of at least 3500 tons in 1994 (López-Carrillo L et al., 1996; Echeverria, 2013). DDT was also used to eliminate plagues during the US base occupation in 1943 in Santa Cruz-Baltra (Alava & Ross, 2018) and was allowed (under permission) in Ecuador until 2008. Recent studies show the presence of residues of hexachlorocyclohexane, alachlor, lindane, heptachlor, aldrin, dieldrin, chlordane, endosulfan, DDT, DDD and endrin in soils, potatoes and fruits in the Ecuadorian mainland and suggest that remaining stocks of these POPs are still being used in farming practices (Vera, 2014; García, 2015; Coba, 2017).

4.3 Differences in pesticide concentrations

4.3.1 Spatial Variation

Spatiotemporal variation of pesticide residues in seawater has been described well (Khuman et al., 2020; Liu et al., 2018). However, traditional pesticide monitoring typically does not include repeated sampling over several days and/or tides. Our results show that changes between pesticides residues concentration may vary considerably within a short period. Although this variation could be inherent to the used methodology, Duke (1977) acknowledges that “pesticides are not necessarily homogeneously concentrated throughout an aquatic system”, and it is recommended to assess “key accumulation” areas, such as key organisms or other components of the ecosystem (i.e. sediments).

4.3.2 Environmental conditions

307 The variation of pesticide residues between locations and repetitions can be explained by the influence
308 of environmental conditions. Previous studies demonstrated that rainfall in tropical areas was the
309 primary cause of pesticide pollution in the aquatic environment by washing pesticides from their target
310 sites and transporting them via erosion and runoff events (Daam & Van Den Brink, 2010; Magallona,
311 1989). The variation of pesticide residue can also be due to the persistence of a compound in the function
312 of its physicochemical characteristics such as their organic carbon partition coefficient (K_{OC}),
313 bioconcentration factor (BCF), bioaccumulation factor (BAF), solubility (S) and half-life time in a
314 water-sediment system (DT_{50}) (Edwards, 1977).

315 It is important to emphasise that the sampled water column is only a fraction of the hydrosphere and that
316 pesticides can also occur within sediments, suspended particulate matter and living organisms (Duke,
317 1977; Edwards, 1977; Hurlbert, 1975). This illustrates clear opportunities for future studies aiming to
318 monitor and assess compound-specific distributions within the aquatic environment.

319 4.4 Pesticide residues common targets and agriculture production in Santa Cruz and Isabela islands
320 The origin of agricultural activities in the Galapagos Archipelago date back from the mid-1800s, when
321 the first farmers from mainland Ecuador arrived on the islands. They planted the same crops that they
322 cultivated on the mainland and slowly adapted to the local climate (MIT, 2008; Robinson et al., 2017).
323 Nowadays, agricultural production in the islands is based on traditional methods, opting for short-cycle
324 crops (corn, tomato, potato, pineapple, cucumber, pepper, bean, carrot, watermelon, and pumpkin) to
325 supply the demands of the local markets (Alava et al., 2014). Since pesticide residues found in water
326 bodies in mainland Ecuador were traced back to agricultural practices, the detection of these pesticide
327 residues in the Galapagos suggests similar practices in pesticides being applied. In comparison with
328 previous studies in agricultural basins in mainland Ecuador (Castro, 1997; UAE, 2012; Deknock et al.,
329 2019; Montaño & Resabala, 2005), similar pesticide residues were found for chlorpyrifos, malathion,
330 cadusafos, linuron, fenpropimorph and metalaxyl. Moreover, heptachlor, chlorpyrifos and malathion are
331 reported as commonly applied in Santa Cruz by Espin (2018) and MIT (2008).

332 The presence of pesticide residues within the considered sampling sites is strongly related to the farming
333 of coffee, banana and vegetables. To investigate the link between the detected pesticides and the crops

produced on the islands, we compared the registered pesticides in Ecuador and their target, with data for the annual crop production on the islands reported in 2014 (Table A.5). Detection of carbendazim is likely the result of its use in the high annual production of tomato (77.8 tons), corn (73.02 tons), cucumber (22.82 tons), pepper (17.68 tons) and potato (0.41 tons). Cadusafos is often used in banana crops with an annual production of 918 tons. Ethoprophos and fenpropimorph could be associated with the annual production of sugar cane (40 tons) and pineapple (30 tons) in Santa Cruz island, while malathion, metalaxyl, propiconazole, linuron, carbendazim and diuron could be linked to the annual production of corn (96.21 tons).

4.5 Risk assessment

Results from ecological risk assessments are essential for understanding the risks posed by pollutants to the marine environment (Ojemaye et al., 2020). The concentrations of residues in the coastal waters of urban areas in Santa Cruz and Isabela islands suggested a high risk for the entire sampling area. Clearly, residues of organic compounds (POPs), carbendazim, diuron and cadusafos were more likely to cause adverse ecological risk. In comparison with a previous study on risk assessment in tropical countries, Carazo-Rojas et al. (2018) found that RQ using highest values for 8/9 pesticides detected (included carbendazim, dimethoate and diuron) posed a non-acceptable risk to the aquatic environment. During the present study, although the status of high risk found for cadusafos, carbendazim, DDT, diuron and malathion could change if lowest values (i.e. values found during repetitions 1-2 in Santa Cruz) are used to calculate RQ; aldrin and heptachlor would preserve their status. The authors decided to apply this approach to highlight the evidence of POP bioaccumulation and biomagnification, demonstrated in sea lions and its prey by Alava et al. (2011)and Alava & Gobas (2012). To date, the lack of studies related to pesticides contamination in the islands makes it necessary to recommend future monitoring and include freshwater bodies, biological indicators and more locations around the evaluated islands to delineate high-risk zones for biota.

5. Conclusion

The monitoring of pesticide residues in the coastal waters of urban areas in the Galapagos archipelago revealed the presence of 16 pesticides around Santa Cruz and Isabela island. Analysis between factors

(locations and repetition) showed a significant effect in pesticide abundance and concentrations. Furthermore, evaluation of risk quotients (RQ) based on the highest concentrations of pesticides observed during repetitions, indicated that seven pesticides pose a high ecological risk for biota.

The analysis suggests that pesticide residues may originate from agricultural practices in the islands, as similar practices in pesticide use are applied throughout the Ecuadorian mainland and the Galapagos islands, including products banned by the Stockholm Convention of Persistent Organic Pollutants (POPs)

Although some pesticides may not be detected due to the limitations of the extraction method and detection limits of the equipment used, the pesticide data obtained from this study, in combination with literature values, can be used as a baseline for the development and implementation of pollution control measures. Consequently, this study highlights the need for (i) monitoring of freshwater areas to locate the source of pesticides, (ii) monitoring at different areas and species in the islands, to map risk areas for wildlife, (iii) including the analysis of pesticides in living organisms, suspended particulate matter and bottom sediments and (iv) analysing pesticide residues within and around other islands with agriculture production (e.g. San Cristobal and Floreana).

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.

Credit authorship contribution statement

Lenin Riascos-Flores: Conceptualisation, Methodology, Formal analysis, Investigation, Data Curation, Writing-Original Draft. **Stijn Bruneel:** Sample collection, Conceptualisation, Methodology, Investigation, Data Curation, Writing - Review & Editing. **Christine Van der Heyden:** Investigation, Writing - Review & Editing. **Arne Deknock:** Methodology, Writing - Review & Editing. **Wout Van Echelpoel**: Sample collection, Conceptualisation, Data Curation, Writing - Review & Editing. **Marie Anne Eurie Forio:** Conceptualisation, Writing - Review & Editing. **Nancy De Saeyer:** Methodology, Resources. **Wim Vanden Berghe:** Writing - Review & Editing **Pieter Spanoghe:** Resources, Writing

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Table 1. Pesticide residues in coastal water samples with corresponding recovery values, the number of locations, detected concentration ranges, and mean concentration per island obtained during the four repetitions of monitoring in Santa Cruz and two repetitions in Isabela.

Pesticide	Recovery (%)	#Locations detected	Concentration range (µg·L^{-1})	Mean and SD	#Locations detected	Concentration range (µg·L^{-1})	Mean and SD	Percentage of detection in 72 samples
		SANTA CRUZ			ISABELA			
Aldrin[b]	32 ± 12	4	< LOQ - 1.02	0.37 ± 0.28	4	0.08 - 1.55	0.79 ± 0.5	69%
Cadusafos[a]	81 ± 20	4	< LOQ - 3.05	0.80 ± 0.8	4	< LOQ - 4.74	1.07 ± 1.38	77%
Carbendazim[a]	18 ± 9	4	0.34 - 23.93	4.12 ± 5.51				27%
Chlorpyrifos[a]	37 ± 38	1	0.09	0.09 ± 0.00				1%
DDT(O,P')[b]	115 ± 8	4	0.16 – 0.26	0.21 ± 0.08	4	0.18 - 2.99	0.33 ± 0.57	87%
Dimethoate[a]	17 ± 9	1	0.28	0.28 ± 0.00				1%
Diuron[a]	108 ± 16	3	0.04 - 1.61	0.55 ± 0.4				23%
Ethoprophos[a]	92 ± 24	2	0.03 - 0.04	0.04 ± 0.01	4	< LOQ - 0.06	0.03 ± 0.02	14%
Fenpropimoph[a]	38 ± 18	4	< LOQ - 0.32	0.11 ± 0.06	3	< LOQ - 0.05	0.03 ± 0.01	18%
Flazasulfuron[a]	20 ± 10	2	0.11 - 0.38	0.24 ± 0.06				3%
Heptachlor[b]	104 ± 16	4	< LOQ - 0.69	0.21 ± 0.15	4	< LOQ - 0.27	0.17 ± 0.09	86%
Linuron[a]	87 ± 13	3	< LOQ - 0.03	0.02 ± 0.01				8%
Malathion[a]	91 ± 18	2	< LOQ - 0.4	0.15 ± 0.07	1	0.02 - 0.03	0.03 ± 0.01	10%
Metalaxyl[a]	117 ± 13	3	0.04 - 0.45	0.17 ± 0.09	1	0.25	0.25 ± 0.05	11%
Propazine[a]	85 ± 12				1	< LOQ	< LOQ	1%
Propiconazole[a]	75 ± 8	4	< LOQ - 0.17	0.03 ± 0.03	4	< LOQ - 0.07	0.02 ± 0.01	58%

[a]LOQ = 0.022 µg·L^{-1}; [b]LOQ = 0.05 µg·L^{-1}

Table 2. Pesticide residues in coastal water samples in Santa Cruz island, with corresponding mean and standard deviation obtained between subsamples during the sampling.

DATE/TIDE	R1 HIGH 14-02-2019				R2 LOW 15-02-2019				R3 LOW 24-02-2019				R4 HIGH 24-02-2019			
Location	SC1	SC2	SC3	SC4	SC1	SC2	SC3	SC4	SC1	SC2	SC3	SC4	SC1	SC2	SC3	SC4
	Mean and SD µg·L−1															
Aldrin[b]	0.77 ± 0.2	0.34 ± 0	< LOQ		0.28 ± 0.1	0.27 ± 0.28	< LOQ	0.06 ± 0	0.64 ± 0.46	0.34 ± 0.16	0.32 ± 0.17	0.28 ± 0.28	0.59 ± 0.02	0.05 ± 0.01	0.42 ± 0.52	0.35 ± 0.06
Cadusafos[a]	0.46 ± 0.56	0.36 ± 0	0.36 ± 0.32	1.12 ± 0	0.98 ± 1.4	0.15 ± 0.22	0.71 ± 1.02	0.56 ± 0	1.05 ± 1.27	0.41 ± 0.22	0.69 ± 1.2	2.27 ± 0	1.44 ± 1.4	0.75 ± 0	0.9 ± 0.74	1.3 ± 0
Carbendazim[a]									0.36 ± 0	0.45 ± 0.06	0.58 ± 0.15		0.9 ± 0.6	0.97 ± 0.19	22.71 ± 1.17	0.39 ± 0.04
Chlorpyrifos[a]									0.09 ± 0							
DDT(O,P')[b]	0.2 ± 0.01	0.19 ± 0	0.21 ± 0	0.22 ± 0.01	0.21 ± 0	0.18 ± 0.02	0.2 ± 0.01	0.22 ± 0.02	0.19 ± 0.02		0.22 ± 0.04	0.2 ± 0.01	0.21 ± 0.03		0.21 ± 0	0.21 ± 0.03
Dimethoate[a]				0.28 ± 0												
Diuron[a]		0.21 ± 0.05	0.22 ± 0.06				0.77 ± 0.21				0.16 ± 0.09		0.04 ± 0		1.5 ± 0.06	
Ethoprophos[a]				0.04 ± 0							0.03 ± 0					
Fenpropimoph[a]	0.04 ± 0							< LOQ			0.2 ± 0	< LOQ	0.09 ± 0	0.17 ± 0.21	0.19 ± 0	0.13 ± 0
Flazasulfuron[a]			0.38 ± 0	0.11 ± 0												
Heptachlor[b]	0.48 ± 0.26	0.15 ± 0.04	0.34 ± 0.09	0.22 ± 0.08	0.23 ± 0.06	0.23 ± 0.09	0.18 ± 0.1	0.24 ± 0.07	0.17 ± 0.08		0.1 ± 0.05	< LOQ	0.18 ± 0.01	0.17 ± 0.22	0.2 ± 0.25	0.14 ± 0.06
Linuron[a]			0.03 ± 0											< LOQ	0.03 ± 0	0.03 ± 0.01
Malathion[a]	0.36 ± 0.05			< LOQ				< LOQ								
Metalaxyl[a]			0.31 ± 0.2	0.35 ± 0			0.05 ± 0	0.09 ± 0	0.05 ± 0							
Propiconazole[a]	< LOQ	0.05 ± 0.06	0.08 ± 0.08	0.04 ± 0.04	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ			< LOQ	< LOQ	

[a]LOQ = 0.022 µg·L^{-1}; [b]LOQ = 0.05 µg·L^{-1}, R=repetition

Table 3. Pesticide residues in coastal water samples in Isabela island, with corresponding mean and standard deviation between subsamples obtained during the sampling.

DATE/TIDE	R5 LOW 22-02-2019				R6 HIGH 22-02-2019			
Location	ISA1	ISA2	ISA3	ISA4	ISA1	ISA2	ISA3	ISA4
	Mean and SD							
	µg·L−1							
Aldrin[b]	0.36 ± 0.4	0.17 ± 0	0.99 ± 0.37	0.77 ± 0.07	1.05 ± 0.68	0.34 ± 0	0.81 ± 0.21	1.04 ± 0.29
Cadusafos[a]	1.48 ± 2.56	1.19 ± 1.51	0.57 0.9	2.12 ± 2.4	0.87 ± 0.00	0.63 ± 0.51	0.77 ± 1.02	0.66 ± 1.07
DDT(O,P')[b]	0.22 ± 0.01	0.24 ± 0.01	0.23 ± 0.01	0.2 ± 0.03	1.14 ± 1.6	0.21 ± 0.02	0.19 ± 0.01	0.21 ± 0.02
Ethoprophos[a]	0.02 ± 0.01	0.06 ± 0.00	0.03 ± 0.00		< LOQ		0.05 ± 0.00	0.02 ± 0.01
Fenpropimoph[a]						0.03 ± 0.03	< LOQ	0.04 ± 0.00
Heptachlor[b]	0.21 ± 0.02	1.63 ± 0.08	0.18 ± 0.02	0.15 ± 0.08	0.07 ± 0.01	0.26 ± 0.02	0.09 ± 0.08	0.18 ± 0.01
Malathion[a]				0.02 ± 0.01				0.03 ± 0.01
Metalaxyl[a]		0.25 ± 0.05						
Propazine[a]			< LOQ					
Propiconazole[a]	< LOQ	< LOQ	0.04 ± 0.04	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

[a]LOQ = 0.022 µg·L^{-1}; [b]LOQ = 0.05 µg·L^{-1}, R=repetition

Graphical abstract

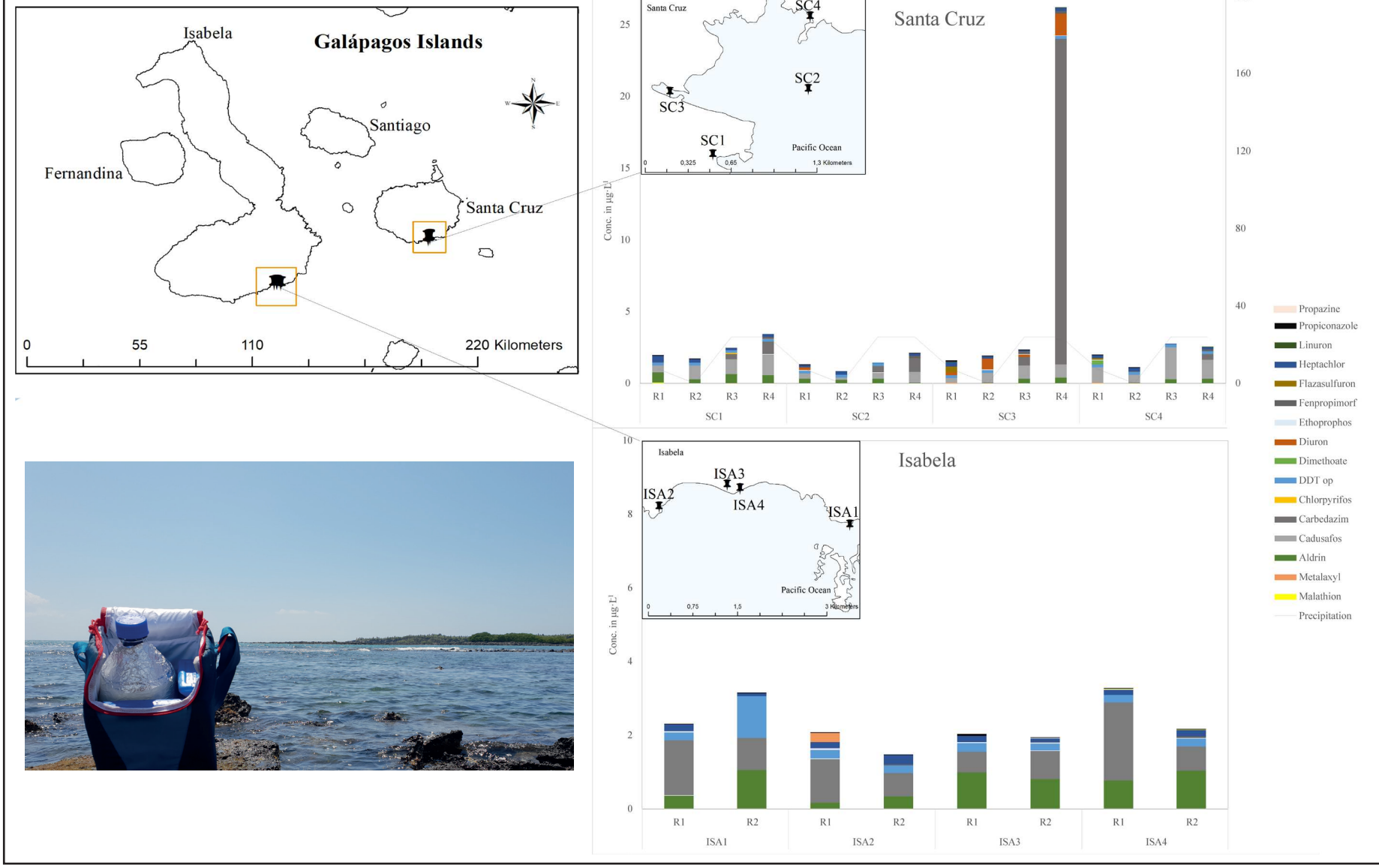

Fig. 1. Location sites in Santa Cruz and Isabela islands in the Galapagos Archipelago.

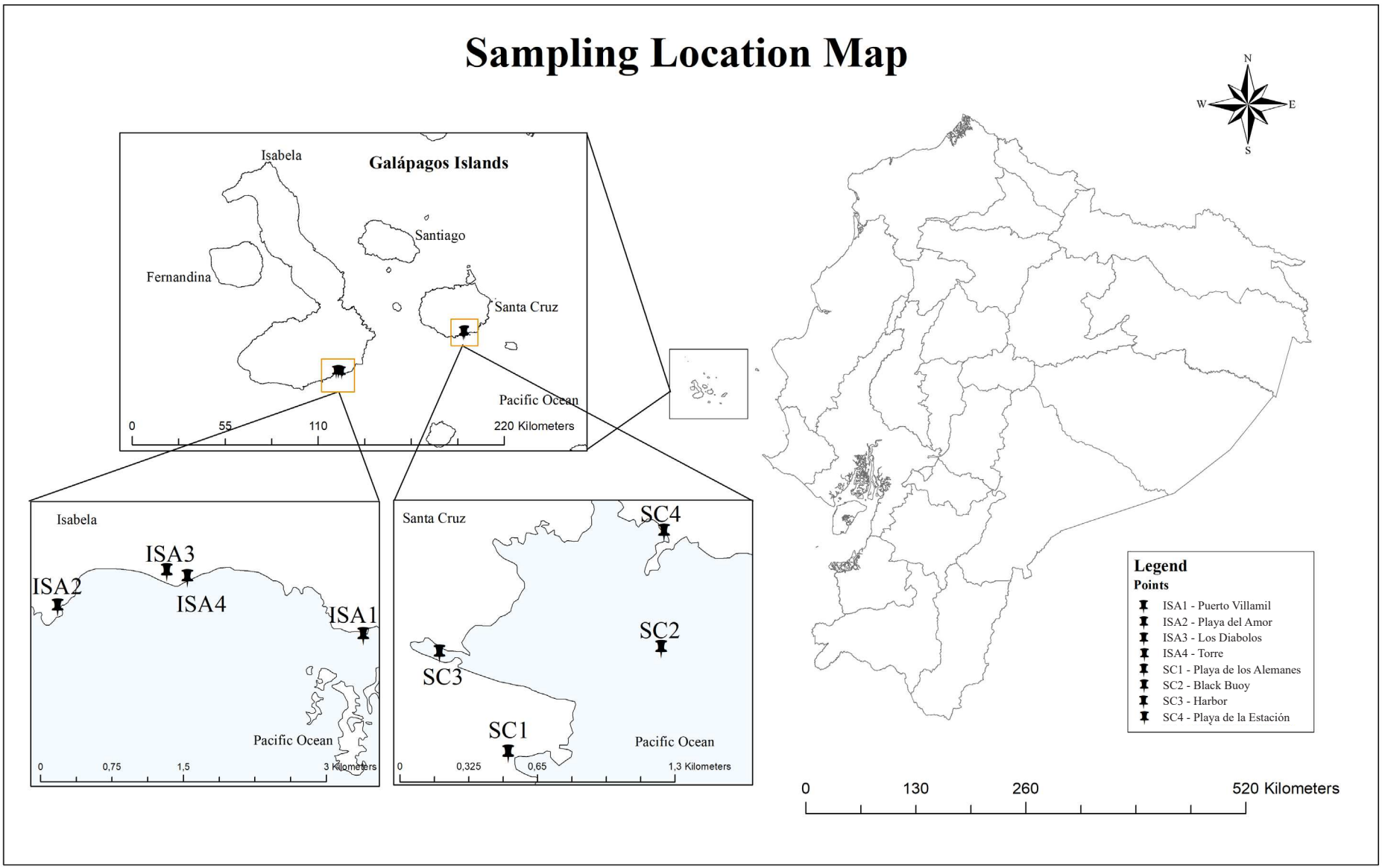

Fig. 2. Sampling design for Santa Cruz and Isabela islands.

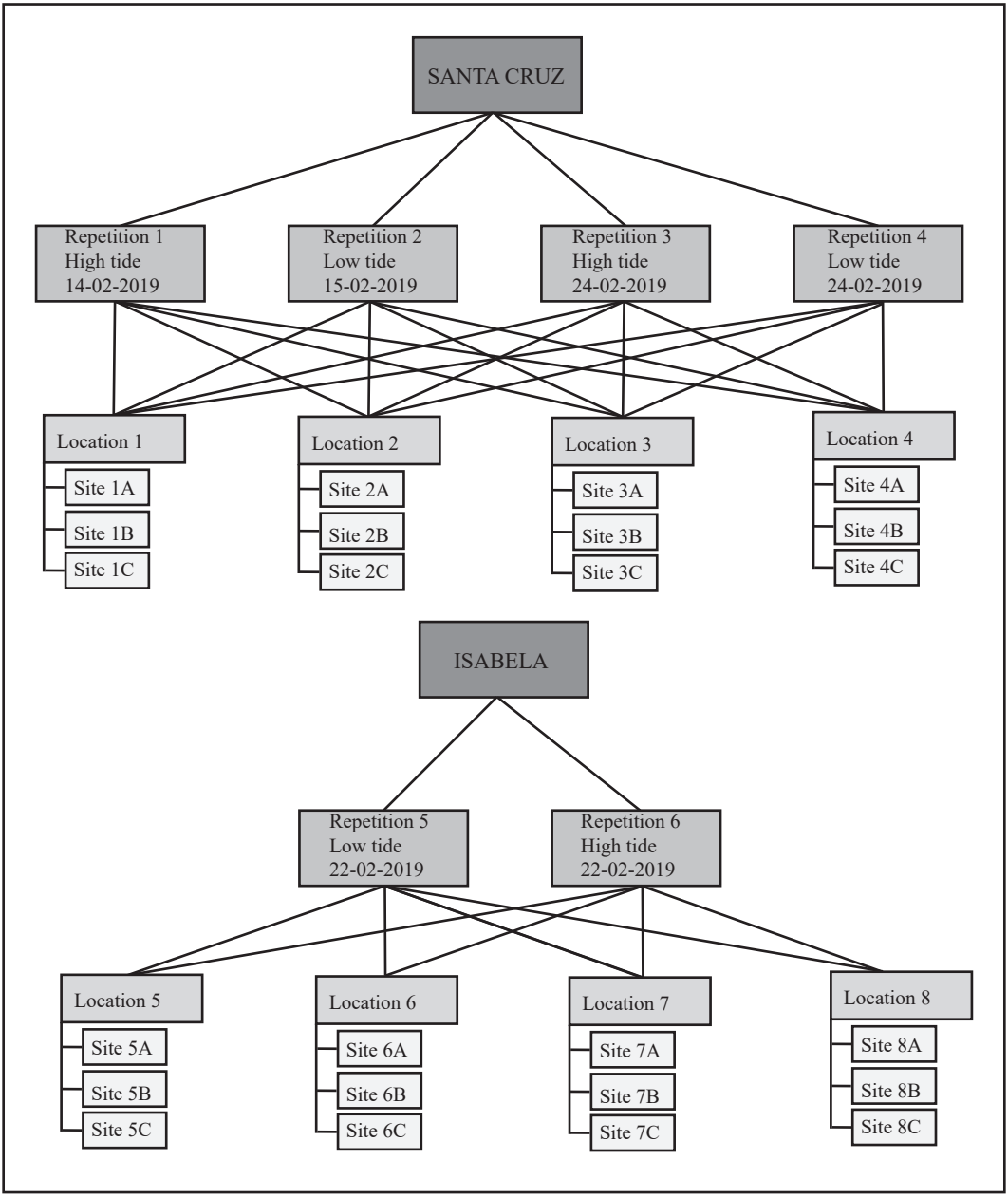

Figure 3. Venn diagram representing the pesticides detected on both islands (n=9). Pesticides detected only in Santa Cruz and Isabela respectively.

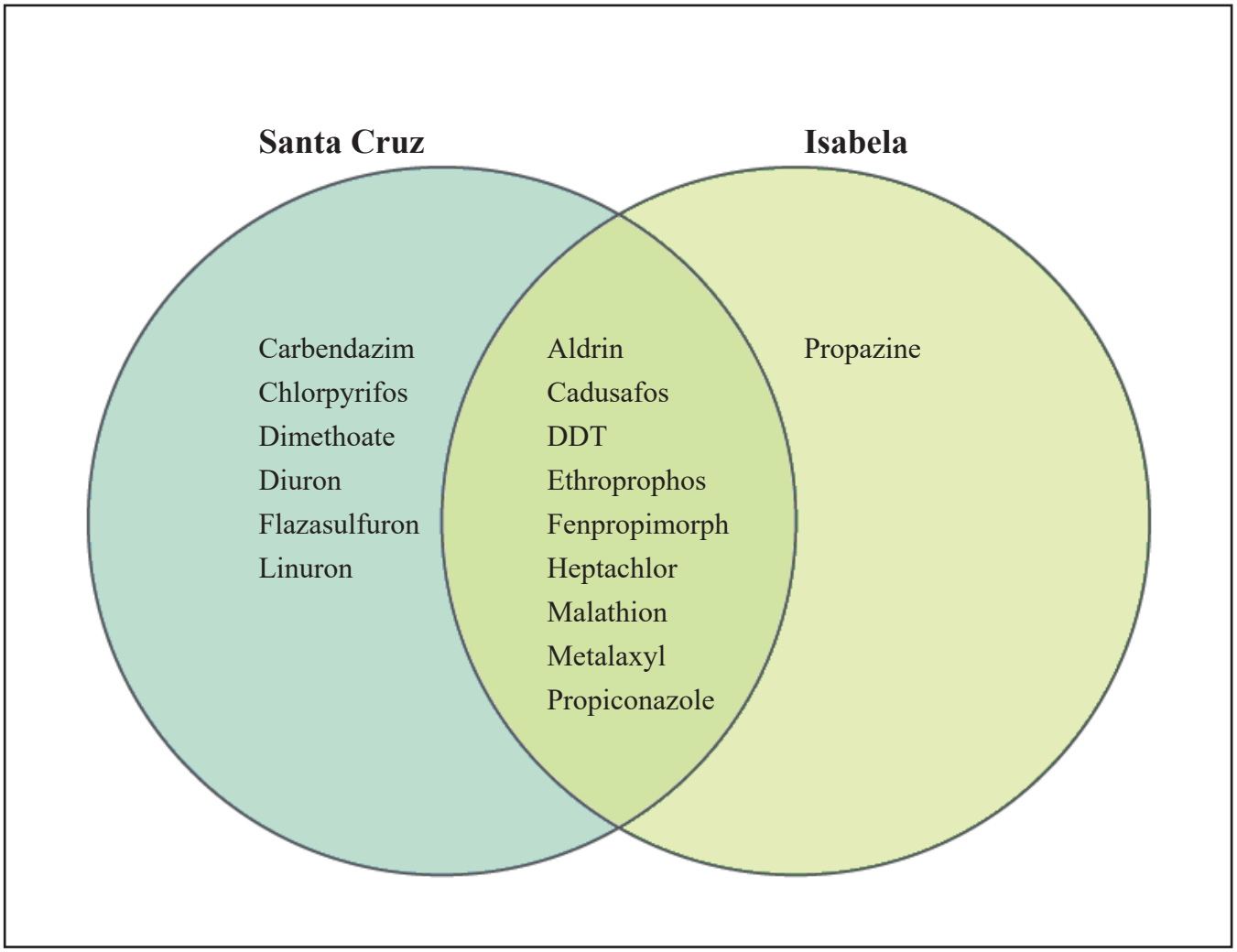

Figure 4. Distribution of pesticides concentrations and standard deviation during the monitoring in Santa Cruz island. L.T.= low tide, H.T.= high tide. A-D) aldrin concentrations, E-H) cadusafos concentrations, I-J), carbendazim concentrations, and K-L) fenpropimorph concentrations. R=repetition.

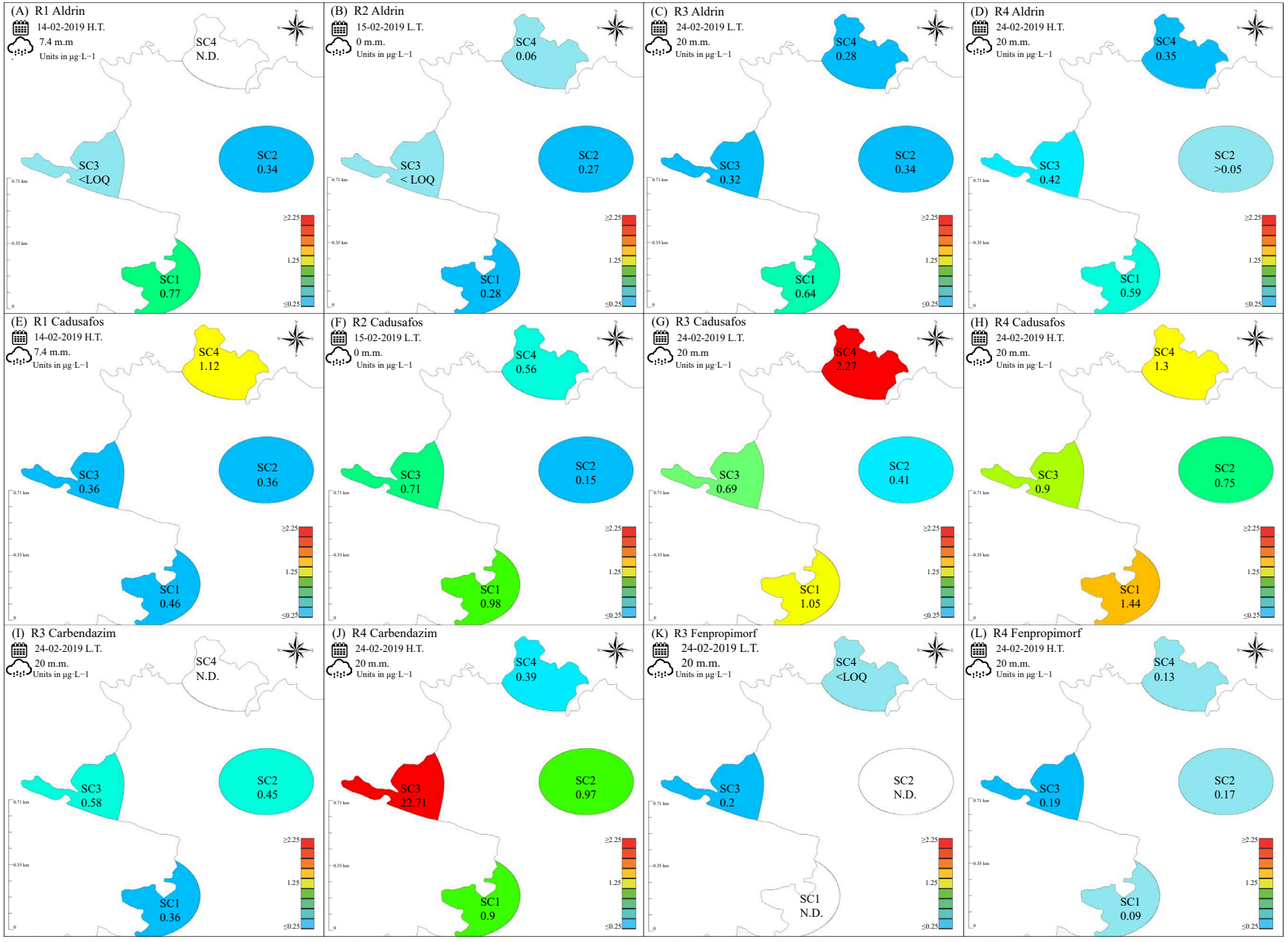

Figure 5. Risk quotients of the detected pesticides for algae, invertebrate and fishes in coastal seawaters in urban areas in Santa Cruz and Isabela islands in the Galápagos Archipelago.