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Neonicotinoids and Their Degradates in San Francisco Bay Water

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Executive Summary

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) screened Bay waters for neonicotinoid pesticides, comparing levels to toxicity thresholds to inform placement of this class of emerging contaminants within the tiered risk-based framework. Neonicotinoids are one of the most widely used classes of insecticides in the world. Given their widespread use in agricultural and urban environments, and ubiquitous detections in surface waters, there is growing concern about consequences for non-target species such as aquatic invertebrates, insects, birds, and fish.

In the summer of 2017, open Bay water samples were collected during the RMP Status and Trends Water Cruise. Samples were analyzed for 19 neonicotinoids and metabolites. The only neonicotinoid detected was imidacloprid, an active ingredient used in both urban and agricultural applications. Imidacloprid was detected at a single site above the method detection limits (2.2-2.6 ng/L) in Lower South Bay at a level of 4.2 ng/L. This value is within the range of concentrations found in a separate RMP study in water samples collected from the South and Lower South Bay margins in 2017. Imidacloprid was detected at 3 of 12 of the margin sites at levels between 3.9 and 11 ng/L; no other neonicotinoids were detected. Of note, these RMP studies appear to represent the first evaluation of ambient neonicotinoid concentrations in an estuarine environment in the nation.

Two significant pathways of imidacloprid contamination to the Bay are treated wastewater and runoff from the surrounding, primarily urban landscape. Previous RMP monitoring of wastewater influent and effluent, consisting of 24-hour composite samples collected from eight wastewater treatment facilities in the Bay Area in September 2015, detected imidacloprid in 100% of samples at levels up to 310 ng/L. Independent surveys in both northern and southern California urban areas confirm that imidacloprid is a commonly detected insecticide in urban runoff. For example, a San Francisco Bay Area study in Fairfield and Suisun City detected imidacloprid at up to 1,462 ng/L in urban creek waters. However, these concentrations diminished to below detection limits in downstream samples as creek waters mixed with brackish waters from the Bay. While Bay Area agricultural runoff has not been well-characterized with respect to imidacloprid, this pathway may also be of potential interest.

A hydrodynamic dilution spreadsheet model was applied as an additional screening tool to explore predicted spatial patterns and temporal trends in imidacloprid concentrations in Bay subembayments. Model inputs were based on available data on concentrations in wastewater effluent and runoff. The model predicted that Lower South Bay levels of imidacloprid would be higher than in other subembayments. The Lower South Bay was also the only subembayment where imidacloprid concentrations were consistently predicted to be higher than method detection limits. The model indicated that wastewater was a dominant pathway for imidacloprid. However, stormwater discharges during the wet season could potentially lead to higher levels in the Bay, suggesting that dry season monitoring may not fully capture maximum concentrations.

The results of this simplified dilution model are based on limited input data and do not include all relevant processes and removal mechanisms; they should be interpreted with caution and best viewed as a first step toward quantifiable prediction of open Bay concentrations.

Open Bay and margins monitoring of imidacloprid revealed that detected concentrations in Lower South Bay were comparable to or greater than protective US and European Union thresholds that range from 4.8 to 10 ng/L. These observations, in combination with widespread and increasing use of this pesticide in urban settings, indicate that this contaminant should be classified as a Moderate Concern in the RMP tiered risk-based framework for contaminants of emerging concern. Other neonicotinoid pesticides and degradates should be classified as Possible Concern, given their more limited availability in urban use pesticide products, as well as additional uncertainties, particularly the lack of chronic toxicity data and potential for cumulative impacts to wildlife.

Additional monitoring is not recommended at this time, due to existing monitoring in urban streams conducted primarily by the California Department of Pesticide Regulation (CDPR). In the future, it may be appropriate for the RMP to explore opportunities for wet season monitoring in Bay water, or in urban runoff. Considering the low toxicity thresholds of these compounds (i.e., in the low ng/L range), analytical methods employed should be improved to provide method detection limits well below toxicity thresholds.

1. Introduction

Neonicotinoid insecticides, developed as alternatives to organophosphates and carbamates, are currently one of the most widely used classes of insecticides in the world, with uses registered in more than 120 countries (Bass et al., 2015). Reports received by the California Department of Pesticide Regulation (CDPR) show that the use of neonicotinoids increased by 70% between 2007 and 2016 in the state (Troiano et al., 2018). Neonicotinoids are widely used in urban and agricultural applications because of their efficacy; they are highly toxic to invertebrates and are systemic, which means they are translocated within plants, spreading to all plant tissues. New agricultural applications of neonicotinoids, such as seed treatments, as well as the replacement of pyrethroids in urban and agricultural applications, have contributed to the rapid increase in use (Simon-Delso et al., 2015; Wood and Goulson, 2017).

Neonicotinoids are persistent and, combined with their widespread use, are detected ubiquitously in the environment, including surface water and groundwater (Hladik and Kolpin, 2015; Morrissey et al., 2015; Schaafsma et al., 2015). This has led to growing concern about the consequences for non-target species such as insect pollinators, aquatic invertebrates, birds, and fish (Gibbons et al., 2015; Morrissey et al., 2015; Roessink et al., 2013; Troiano et al., 2018). Neonicotinoids have a similar structure to nicotine, with a mechanism that affects the central nervous system. The chemicals irreversibly bind to nicotinic acetylcholine receptors in insects, which suggests that besides causing mortality, low-level continual exposure may also result in sublethal, cumulative effects such as muscle tremors and cell energy exhaustion (Hook

et al., 2018; Maloney et al., 2017). Other sublethal effects include feeding inhibition (Alexander et al., 2007; Kreutzweiser et al., 2007; Nyman et al., 2013), reduced fecundity (Böttger et al., 2013), as well as reduced body size or mass in mayflies, fish, and birds (Alexander et al., 2008; Hayasaka et al., 2012). Additionally, as an avoidance response to toxic conditions, organism downstream drift (avoidance behavior) is also likely to occur in response to this class of insecticides (Beketov and Liess, 2008).

Of the many neonicotinoids produced today, imidacloprid was the first of the class to be registered in 1991, and is now one of the most widely used insecticides in the world (Culver and Finck-Haynes, 2017). In a nationwide study of U.S. streams, imidacloprid occurrence was significantly related to the amount of urban land use within the basin (Hladik and Kolpin, 2015). Urban uses of imidacloprid include indoor and outdoor pest control (e.g., ants and termites), residential landscape maintenance, as well as pet treatments for fleas and ticks (Ensminger et al., 2013; Sadaria et al., 2016). Manufacturers also incorporate imidacloprid into construction materials, like polystyrene insulation, vinyl siding, adhesives, sealants, and pressure-treated wood (Culver and Finck-Haynes, 2017; Sadaria et al., 2016). Imidacloprid can migrate from these building materials into water, soil, and even into the hives of insect pollinators via sawdust (Culver and Finck-Haynes, 2017).

At present, imidacloprid is considered the most toxic of the class. Toxicity thresholds for imidacloprid include the U.S. Environmental Protection Agency (USEPA) aquatic life benchmark of 10 ng/L for chronic invertebrate exposure in freshwater (USEPA, 2017); a predicted no effect concentration (PNEC) of 4.8 ng/L derived from chronic toxicity (EC_{10}) for *Cloeon dipterum* in freshwater (European Commission, 2015); and an annual average freshwater environmental quality standard (AA-EQS) of 8.3 ng/L, based on chronic toxicity data, which should protect freshwater ecosystems against adverse effects resulting from long-term exposure (Smit et al., 2015).

The toxicity concerns, paired with the environmental fate characteristics of neonicotinoids—mobile due to high water solubility and low affinity for soil, non-volatile, and persistent (Fossen, 2006)—are strong motivation to monitor these chemicals in the Bay. This report provides data from RMP efforts to screen Bay waters for neonicotinoid pesticides; it details data from open Bay monitoring, and synthesizes findings from previously reported South Bay margins monitoring (Heberger et al., 2020). Levels were compared to toxicity thresholds to inform placement of this class of emerging contaminants within the RMP tiered, risk-based framework.

2. Methods

2.1 Sample Collection

Bay water samples were collected in summer of 2017 as part of the biannual RMP Status and Trends water monitoring cruise. Grab samples of open Bay water (1 L, amber glass) were

collected at 22 Bay sites. Two field replicates and one field blank were also collected (Figure 1). After collection, samples were kept on ice (4ºC) in the dark, then shipped overnight on ice to the analytical laboratory, SGS AXYS (Sidney, British Columbia, Canada), within a nine day hold time.

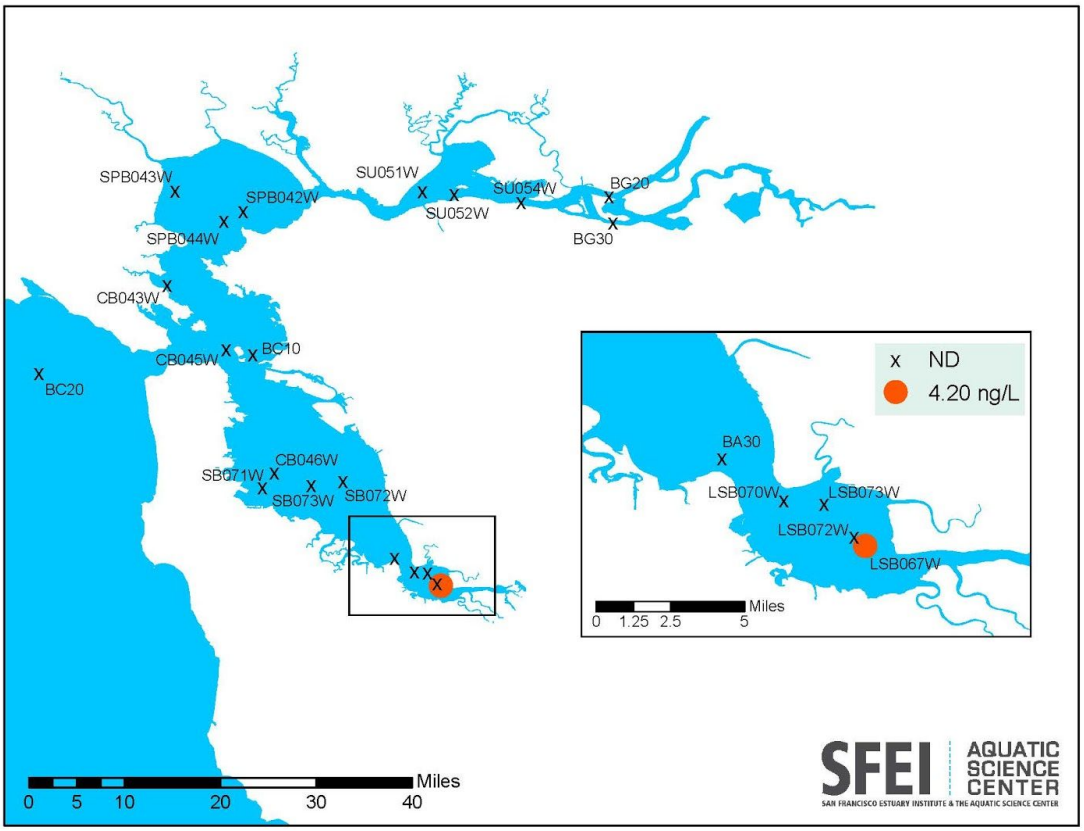

Figure 1. Map of open Bay sampling stations and results for imidacloprid. Samples were taken in the summer of 2017 during the RMP Status and Trends Water Cruise. Method detection limits for imidacloprid ranged between 2.2-2.6 ng/L.

2.2 Analysis

Samples were analyzed by SGS AXYS, using their new method MLA-114: Analysis of Neonicotinoids. This method was under development at the time of sample collection, necessitating preservation. Upon receipt by the laboratory, samples were pre-treated and preserved by adding 100 mL dichloromethane (DCM), transferred to 4 L amber glass bottles, and stored at -20°C prior to further extraction and analysis. The purpose of adding DCM was to reduce the proportion of analytes in the aqueous phase that is potentially available for biodegradation because imidacloprid is 100-200 times more soluble in DCM than water (M. Woudneh, personal communication). Freezing was considered the primary means of sample preservation. All samples were pre-treated between 9-14 days of sample collection and analyzed between 207-219 days after collection. No holding time requirements were established, although the goal was to meet a nine day hold time. The 9-day planned hold time

was exceeded due to confusion about the start date and a shortage of containers by the receiving laboratory.

Immediately prior to analysis, the contents of the sample container were transferred to a 2 L separatory funnel. The original container was rinsed three times with ~50 mL of DCM per rinse and added to the separatory funnel with the preserved sample (water and DCM). The DCM layer was then separated from the aqueous layer and transferred to a round bottom flask. The aqueous layer was returned to the original sample bottle. One mL of methanol was added to the DCM in the round bottom flask as a keeper, and the DCM was carefully removed by rotary evaporation to near dryness. The round bottom was rinsed three times with about 1 mL of methanol. The methanol rinse was added to the original sample container containing the aqueous sample. Once all the rinses had been collected, and mixed by gentle inversion, the sample was allowed to equilibrate for 30 minutes.

The sample was then sub-sampled (200 mL) and analyzed as described in SGS AXYS method MLA-114. Briefly, aqueous samples were filtered and the aqueous portion was cleaned up by solid phase extraction (SPE; Strata X cartridge). Residual methanol (~0.005%) in the sample was well below the SPE tolerance. Instrumental analysis of the sample extracts was performed on an ultra high-performance liquid chromatograph coupled to a triple quadrupole mass spectrometer running the manufacturer's MassLynx v.4.1 software. The mass spectrometer was run at unit mass resolution in the Multiple Reaction Monitoring (MRM) mode with positive or negative ionization.

Nineteen analytes were targeted for analysis, including neonicotinoids, neonicotinoid degradates, and pesticide synergists, with method detection limits (MDLs) ranging from 1 to 42 ng/L (Table 1). Because this was a new method under development, the laboratory explained that some of the target analyte results should be considered estimates (semi-quantitative).

2.3 Quality Assurance Review of Laboratory Results

Laboratory results were reviewed utilizing RMP QAPP methods (Yee et al., 2018). Of the 19 analytes analyzed, only two imidacloprid measurements were above detection limits, and no other analytes were detected. Six of the analytes were flagged by the lab to be of estimate value only because there is insufficient field data to completely understand the behavior of these compounds, and there is no commercially available isotope to track these analytes. Two additional analytes (desnitro-imidacloprid and 5-hydroxy-imidacloprid) were flagged by the RMP QA officer for poor recovery of the matrix spike. All of the flagged analytes were below the method detection limits.

Table 1. Analyte list and method detection limits (MDLs) in ng/L for pesticide suite assessed in Bay water samples using SGS AXYS method MLA-114.

Target Analyte List	**MDL (Min - Max)**

Acetamiprid	1.1 - 1.3
Acetamiprid-N-Desmethyl	2.2 - 2.6
Clothianidin	2.2 - 2.6
Desnitro-imidacloprid	2.2 - 2.6
Dinotefuran	2.2 - 11.7
Hydroxy-Imidacloprid, 5-	8.8 - 10.4
Imidacloprid	2.2 - 2.6
Imidacloprid olefin[1]	35 - 42
Imidacloprid urea[1]	2.2 - 2.6
Imidaclothiz	2.2 - 2.6
MGK 264-A[1]	9 - 10
MGK 264-B[1]	9 - 10
Nitenpyram	1.2 - 1.3
Piperonyl butoxide	1.1 - 1.3
Sulfoxaflor-A[1]	9 - 10
Sulfoxaflor-B[1]	9 - 10
Thiacloprid	1.1 - 1.3
Thiacloprid-amide	18 - 21
Thiamethoxam	2.2 - 2.6

[1]Analytes flagged by the lab where results are estimated concentrations.

3. Monitoring Data for San Francisco Bay

3.1 Neonicotinoids in Open Bay Waters

This extensive monitoring exercise resulted in a single neonicotinoid detection. Imidacloprid was detected above the method detection limits (2.2-2.6 ng/L) at a site in Lower South Bay, LSB067W (Figure 1). The field sample and field duplicate collected at this site contained concentrations of 4.57 ng/L and 3.83 ng/L respectively. The resulting average imidacloprid concentration of 4.2 ng/L is comparable to protective thresholds (4.8-10 ng/L).

3.2 Imidacloprid in South Bay Margins

The single imidacloprid detection in open Bay waters of Lower South Bay is comparable to detections observed in water samples collected from the South Bay margins sampling effort conducted by the RMP, also in the summer of 2017 (Heberger et al., 2020). These margin areas

are defined as mudflats and adjacent shallow areas of the Bay, and act as important habitat for fish, waterfowl, and other wildlife. Because the margins are more proximate to some types of urban pollution, there is a high potential for aquatic life to be exposed to contaminants in this habitat.

Margin water samples were analyzed for an extensive list of pesticides by the USGS Organic Chemistry Research Laboratory (OCRL; Sacramento, California). Similar to the open Bay, the only neonicotinoid detected in the margin water samples was imidacloprid; detections were reported in Lower South Bay and southern sloughs (the latter also described as the Extreme Lower South Bay in (Yee et al., 2019). Imidacloprid was detected with 33% frequency at concentrations ranging between 3.9-11.4 ng/L (MDL = 3.8 ng/L), values that are near or exceed the PNEC of 4.8 ng/L (Figure 2; Heberger et al., 2020).

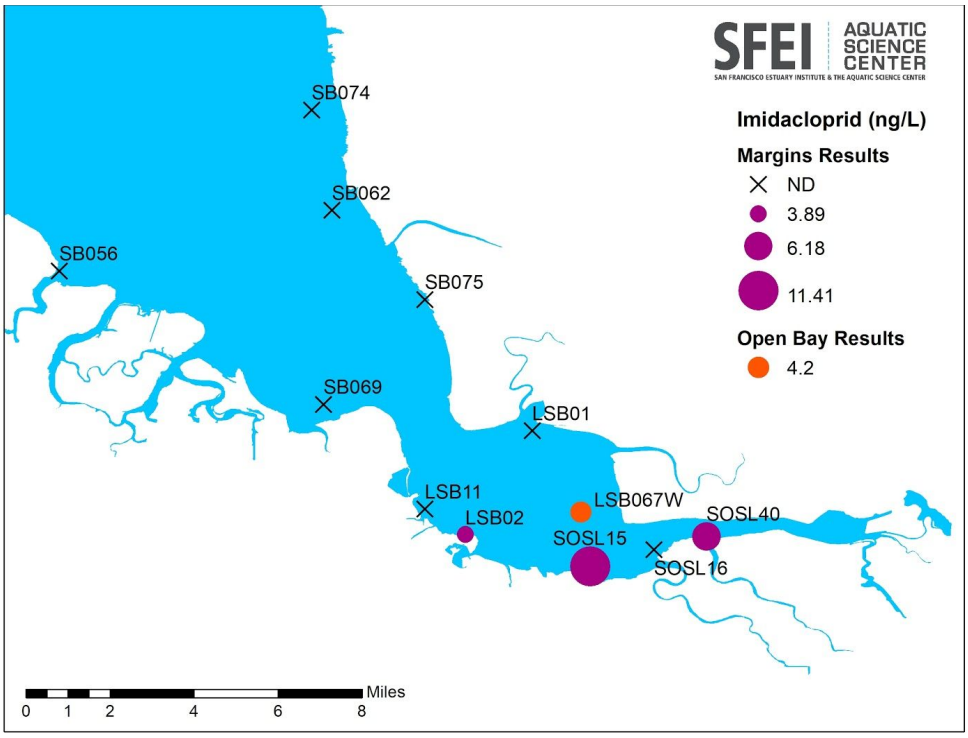

Figure 2. Map of margin sampling stations and water concentrations of imidacloprid (open Bay and margins). Margin water samples were taken in the summer of 2017 as an add-on study to the RMP Status and Trends South Bay Margins Sediment Cruise.

3.3 Comparison to Neonicotinoid Concentrations in Other Estuaries

No comparable studies of neonicotinoids in estuarine environments in the U.S. have been reported. However, a recent study from Hook et al. (2018) investigated the impact of several pesticides, including imidacloprid, on shellfish aquaculture along the east coast of Australia. Sampling of shrimp aquaculture intake waters from estuarine, mixed-use (agricultural and urban) catchment sites was conducted after rain events, when pesticide concentrations were

expected to be highest. Imidacloprid was detected at five of seven sites at concentrations ranging from 2.6-415 ng/L (site mean concentrations: 2.8, 2.9, 13.6, 14.6, 345, ng/L).

A study of estuarine samples collected from the Seto Inland Sea in Japan between 2015 and 2018 reported an imidacloprid detection frequency of 26% (method quantification limit = 4 ng/L) and a maximum concentration of 213 ng/L (Hano et al., 2019). Imidacloprid was observed at higher levels during periods of agricultural application (June through September), which also coincides with the time of year with higher than average rainfall in the region. Four other neonicotinoids were also observed in some Seto Inland Sea samples, as was the imidacloprid metabolite, desnitro-imidacloprid.

San Francisco Bay imidacloprid detections fall within the lower end of the ranges reported in these monitoring studies. Of note, the San Francisco Bay samples were collected during the dry season, while these studies included sampling during periods of higher rainfall, when concentrations could be elevated from increased stormwater inputs. In addition, both Australian and Japanese studies evaluated locations influenced by higher levels of local agricultural land use relative to the Bay.

3.4 Imidacloprid in Urban Runoff and Municipal Wastewater

Urban runoff and wastewater effluent are thought to be significant pathways for imidacloprid to enter the Bay (Lin et al., 2018). In a study of neonicotinoid pesticides in streams across the U.S., imidacloprid was the most frequently detected (Hladik and Kolpin, 2015). The California Department of Pesticide Regulation's Surface Water Protection Program (SWPP) reported that imidacloprid detections from their northern California urban monitoring efforts have almost doubled since late 2013 (Ensminger, 2017). Most of the reported monitoring data from urban waters summarized in Table 2 indicate frequent detections at concentrations greater than the established toxicity thresholds ranging from 4.8 to 10 ng/L.

Of note, a 2014 study in Fairfield and Suisun City detected imidacloprid in urban creeks, and found that concentrations in downstream slough samples in Suisun Marsh declined below measurable levels as creek waters mixed with brackish Bay water (Weston et al., 2015a).

Two additional local studies are providing important monitoring data of imidacloprid concentrations in stormwater entering the Bay: MS4 stormwater permittees are collecting samples as part of their permit monitoring (BASMAA Regional Monitoring Coalition, Table 2); and the RMP is analyzing stormwater samples for imidacloprid for water years 2019, 2020, and 2021.

Table 2. Reported results of urban stream imidacloprid concentrations in California. Values were collected from a variety of literature sources (state and municipal agencies, academic efforts, etc.). Concentration ranges are minimum - maximum values, with medians in brackets.

Reference	Region	Sampling Time	Concentration (ng/L) [median]
BASMAA Regional Monitoring Coalition (via CEDEN)	Alameda, Contra Costa, Santa Clara, and San Mateo Counties	January, March 2018	<4 — 237 [18]
CDPR Surface Water Database (SURF)[1]	Alameda, Contra Costa, and Santa Clara Counties	Dry season 2015 to 2019	<10-50 — 13
		Wet season 2015 to 2019	<10-50 — 44
	Placer and Sacramento Counties	Dry Season 2015 to 2019	<10-50 — 43
		Wet season 2015 to 2019	<10-50 — 97
Ensminger et al., 2013[2]	Sacramento and Orange Counties	Wet season 2008 to 2011	<50 — 670 [<50]
		Dry season 2008 to 2011	<50 — 160 [50]
Murray, 2015	City of Santa Barbara	Dry season 2014	<5 (non-detect)
		Wet season 2014	8 — 76 [23.5]
Weston et al., 2015b[3]	City of Fairfield and Suisun City	February 2014	26.5 — 1,462 [461]

[1] Only urban creek water values reported.

[2] Samples included urban storm drains and small urban creeks.

[3] Includes mixed use and agricultural creeks.

Wastewater effluent is also a known pathway by which imidacloprid enters the Bay, likely from use in flea and tick control products washed off from pets (Sadaria et al., 2017a). In the San Francisco Bay Area, imidacloprid was detected in all influent and effluent 24-hr composites samples from eight wastewater treatment facilities collected in September 2015; levels in influent ranged from 58-306 ng/L, and levels in effluent ranged from 84-305 ng/L (Sadaria et al., 2017a). Wastewater treatment processes did not significantly remove imidacloprid from influent. These concentrations are in the high end of the range of values reported in effluents from elsewhere in the U.S., ranging between 19-387 ng/L (Hope et al., 2012; Sadaria et al., 2016).

4. Conceptual and Hydrodynamic Models of Imidacloprid in San Francisco Bay

4.1 Conceptual Model

A conceptual model of sources and pathways anticipated to be significant for imidacloprid was developed (Figure 3). Because of its high solubility and low affinity for soils, imidacloprid is highly mobile in the environment. Urban and agricultural runoff are expected to transport imidacloprid to the Bay from surrounding urban and agricultural land. Likewise, wastewater has been shown to transport significant levels of imidacloprid from pet flea treatment.

In the Bay Area, levels of imidacloprid in agricultural runoff are not well characterized relative to urban runoff. Weston et al. (2015) did not detect imidacloprid in a single Bay Area agricultural stream during two storm events (MDL = 10 ng/L), but did detect the pesticide in two mixed-use streams (13.5-62.9 ng/L) and in two urban streams (26.5-1,462 ng/L; Table 2). According to CDPR's Pesticide Use Reports, agricultural uses of imidacloprid are significantly lower in hubs of Bay Area agriculture, such as Napa and Solano counties (1,214 and 1,017 lbs applied; 2017 PUR data), relative to other agriculture-rich regions of the state, such as Sacramento and San Joaquin counties (3,787 and 26,691 lbs applied; 2017 PUR data). While monitoring data are limited, reduced agricultural use suggests that agricultural runoff may not be as significant as urban runoff for the highly urbanized San Francisco Bay.

In contrast, recent urban stormwater monitoring indicates urban runoff to be a significant pathway for imidacloprid, as has been observed elsewhere in California (Table 2). In addition to runoff, effluent discharged by municipal wastewater treatment plants can also transport residential uses of imidacloprid, particularly applications on pets that can be washed off and discharged to municipal wastewater facilities (Sadaria et al., 2017a).

Air is not expected to be a major pathway for this contaminant because it is non-volatile and has a low soil adsorption coefficient, indicating a low potential to be dispersed via air-borne soil particles (Fossen, 2006). However, a recent study from China found imidacloprid was transported via fine particulate matter in air, particularly in rural areas (Zhou et al., 2020). While this pathway is not included in the present conceptual model (Figure 3), should future studies suggest air or any other pathway is significant for the Bay, a revision may be warranted.

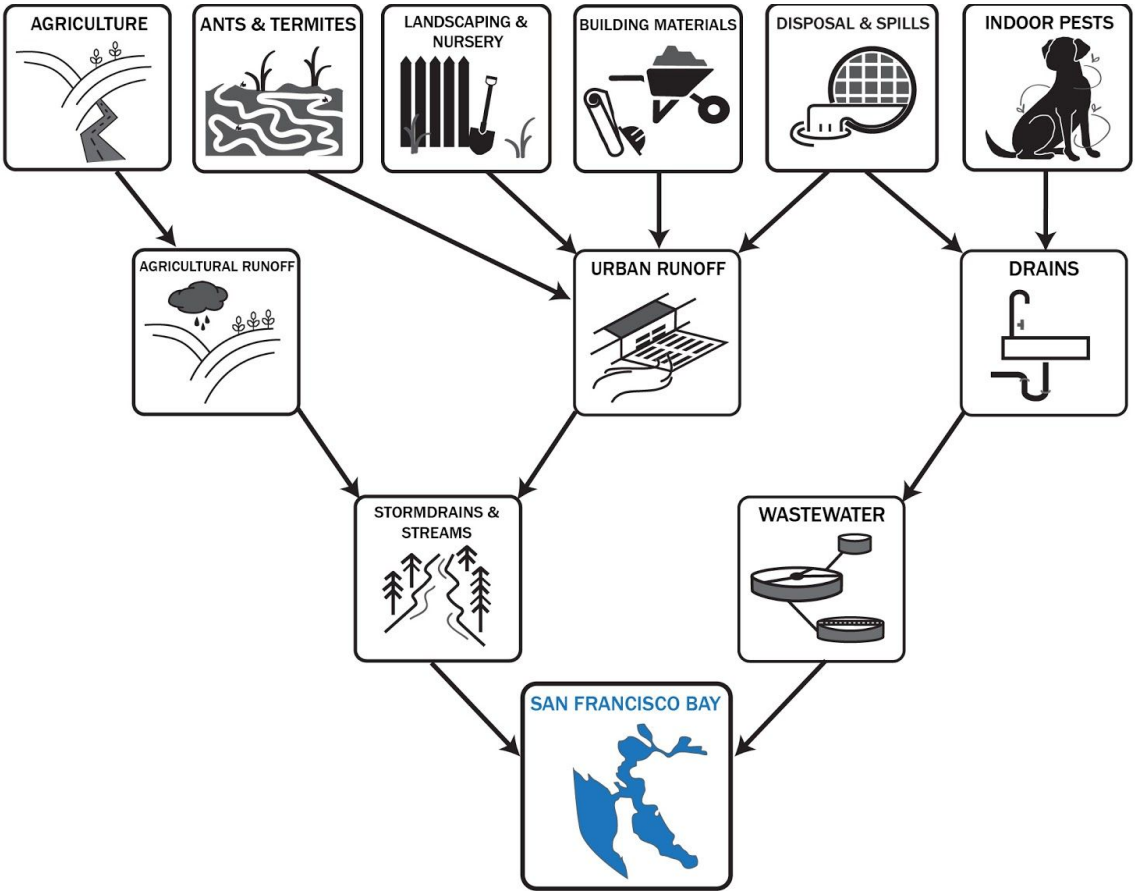

Figure 3. Conceptual model of major imidacloprid sources and pathways thought to influence contaminant loading in the San Francisco Bay watershed.

4.2 Hydrodynamic Model

Since wastewater effluent and local runoff (urban and agricultural) are anticipated to be the main pathways for imidacloprid to enter the Bay, a Bay hydrodynamic dilution model calculation was conducted to evaluate the contributions from these two pathways to open Bay concentrations. This modeling exercise was intended as a simple, screening level effort to evaluate our conceptual model and organize the limited monitoring data available to prioritize data gaps. This was done by assembling the Bay hydrodynamic dilution model, inputting available monitoring data on wastewater and runoff concentrations, and comparing predicted concentrations in Bay waters with monitoring data.

The hydrodynamic model was previously developed to approximate the dilution of persistent and water soluble contaminants discharged into the Bay. The spreadsheet version of the hydrodynamic model was developed for emerging contaminant applications, and condenses the Bay hydrodynamic model into a series of spreadsheets that summarize the relationship between concentrations in load streams (i.e., concentrations in local runoff, and in individual wastewater

or refinery discharges) and ambient concentrations in each subembayment of the Bay (Holleman et al., 2017; Lin et al., 2018). The spreadsheet hydrodynamic model used for the present study simulates the period from October 2012 to September 2013, and concentrations in the Bay are predicted for each two-month period (e.g., Oct.-Nov, Dec.-Jan.).

Runoff flows are derived from the Bay Area Hydrological Model (BAHM), a continuous simulation model developed to estimate flow and pollutant loads from Bay Area watersheds (Lin et al., 2018). The BAHM uses continuous rainfall and other meteorological records to compute streamflow hydrographs and pollutographs across multiple pollutant sources, spatial scales, and time steps. The BAHM therefore provides spatially and temporally resolved flow and load estimates suitable for the Bay hydrodynamic model. The runoff-related input to the hydrodynamic spreadsheet model is currently limited to a single contaminant concentration, which is applied to all runoff discharges from the BAHM.

Model inputs included concentrations for 34 individual wastewater treatment plants, five refineries, as well as single representative concentrations for all local runoff and Delta outflow, respectively (concentrations below). Concentrations from all sources were kept constant through all months based on the more limited understanding of the impact of season on imidacloprid concentrations in Bay Area pathways. The local runoff concentration selected for the model reflects a recently reported minimum concentration in urban stormwater runoff (Weston et al., 2015), as agricultural stormwater runoff and dry season stream concentrations are poorly characterized in the Bay Area. Delta outflow concentrations represent another data gap and were assumed to be zero in the model, in part due to lack of detection in northern embayments. The model was evaluated twice using the minimum and average concentrations from wastewater effluent to create a range of conditions for each subembayment. Imidacloprid concentrations used to model these discharges were:

- Wastewater effluent: 83.8 and 179 ng/L (minimum and average concentrations reported in Sadaria et al. 2016);
- Refineries: 0 ng/L
- Local runoff: 26.5 ng/L (the minimum reported urban stormwater concentration in Weston et al., 2015);
- Delta: 0 ng/L (no detections in northern embayments);

Modeled concentrations in the Bay are generally considered conservative (i.e., worst case scenario) because this simple, screening level model only simulates the dilution of discharges in Bay waters, and does not include degradation processes, sorption to sediment, and exchange with the atmosphere, which can significantly reduce concentrations of many contaminants in Bay waters. However, for substances like imidacloprid that are relatively persistent and water-soluble, the model may provide a reasonable upper bound approximation of open Bay water concentrations.

Predicted concentrations in Lower South Bay (5.5-16.1 ng/L) were consistently in the range or above measured concentrations, and confirmed that the Lower South Bay was expected to have the highest concentrations compared to other subembayments. In contrast, the model suggested concentrations in other subembayments would typically be below MDLs in the dry season, consistent with the open Bay monitoring results (Table 3, Figure 1). Both the model and the monitoring data suggest that lower MDLs are needed to adequately characterize imidacloprid in Bay waters.

Table 3. Modeled subembayment concentration ranges (ng/L) of imidacloprid. Bold values exceed the imidacloprid maximum method detection limit of this study (2.6 ng/L). Predicted concentration ranges are based on modeling all 34 wastewater effluent discharges at minimum (83.8 ng/L) and average (179 ng/L) concentrations reported in Sadaria et al. (2016).

	Suisun Bay	San Pablo Bay	Central Bay	Upper South Bay	Lower South Bay
Oct-Nov	0.8 - 1.6	0.5 - 0.8	0.6 - 1.1	1.8 - **3.3**	**6.6 - 11.1**
Dec-Jan	1.2 - 1.8	1.6 - 2.1	1.3 - 1.9	**3.5 - 5.3**	**10.1 - 16.1**
Feb-Mar	1.2 - 2.0	0.8 - 1.4	0.9 - **2.7**	2.5 - **4.5**	**7.8 - 14.7**
Apr-May	1.2 - 2.1	0.7 - 1.2	0.7 - 2.5	2.1 - **4.1**	**6.6 - 13**
Jun-Jul	0.9 - 1.8	0.5 - 0.9	0.5 - 1.9	1.7 - **3.5**	**5.5 - 11.2**
Aug-Sept	0.8 - 1.6	0.4 - 0.8	0.5 - 1.5	1.6 - **3.3**	**5.4 - 11.1**
Yearly Average	1.0 - 1.8	0.7 - 1.2	0.8 - 1.9	2.2 - **4.0**	**7.0 - 12.9**

An examination of the relative contributions of runoff and wastewater in this screening level modeling exercise confirmed that wastewater is a dominant pathway for discharge of imidacloprid to the Bay. In the dry season, wastewater was predicted to contribute at least three-quarters of the contaminant load in each subembayment. In the wet season, when stormwater discharges are higher, wastewater was predicted to contribute at least half the load of imidacloprid in each subembayment.

The model evaluations indicate that local runoff, particularly from urban landscapes, is expected to be an additional source of imidacloprid in the Bay during the wet season. Using constant imidacloprid concentrations and temporally resolved flows, the dilution model indicated that imidacloprid concentrations in all subembayments were likely to be higher during the wet season due to stormwater discharges. Modeled loads from February and March were 11-29% greater than modeled yearly averages (Table 3). These results suggest that dry season monitoring may not capture the highest concentrations for water-soluble contaminants when stormwater is also an important pollution pathway.

The estimate of stormwater contributions is based on the lowest observed concentration of 26 ng/L in an urban stream from Weston et al. (2015). However, given the spatial and temporal

variability of imidacloprid on landscape, this value, measured in small urban streams, is likely not representative of concentrations in larger tributaries with greater potential for contaminant dilution, and in other urban areas with different land use distributions and landscape characteristics. A single value also cannot account for differences in stream concentrations during wet and dry weather, which has been observed in other parts of California (Batikian et al., 2019; Murray, 2015). As a result, the current model results should be interpreted with caution and best viewed as a first step toward quantifying stormwater contribution to open Bay concentrations.

While runoff is identified in the conceptual model as a major pathway of imidacloprid loading to the Bay, this modeling effort using a single concentration does not resolve spatial and temporal runoff variation. Therefore, the current lack of measured imidacloprid concentrations in runoff makes it difficult to reliably assess and quantify this pathway. Since a model is only as good as the data that support it, it is imperative that monitoring data be collected to support model applications and further refine this initial estimate to present a fuller and more accurate picture of stormwater and runoff contributions. The monitoring data should be collected at various representative locations across the region and under various hydrologic conditions (dry, wet, average) to capture the spatial and temporal variation of imidacloprid loading.

5. Neonicotinoid Toxicity and Risk

Neonicotinoids are commonly detected in streams globally, leading to concerns about impacts to aquatic ecosystems (Bonmatin et al., 2015a; Hladik et al., 2018). Besides mortality, exposure to neonicotinoids can cause a number of sublethal effects on aquatic organisms. Mayflies, caddisflies, and chironomid midges appear to be the most sensitive invertebrate species (Cavallaro et al., 2017; Sánchez-Bayo et al., 2016). Most toxicity studies on neonicotinoids have focused on insect pollinators and freshwater aquatic invertebrates, and there is much less known about impacts to marine organisms (Pisa et al., 2015a).

The European Union established a PNEC for imidacloprid of 4.8 ng/L, which was derived from the chronic toxicity EC_{10} (effective concentration, for 10% of individuals to have observed immobilization) value of 33 ng/L for the freshwater mayfly, *Cloeon dipterum* (EC 2015; Roessink et al., 2013). Later, a European Water Framework Directive annual average freshwater environmental quality standard (AA-EQS) of 8.3 ng/L was established based on chronic toxicity data, which should protect freshwater ecosystems against adverse effects resulting from long-term exposure (Smit et al., 2015). The USEPA established an aquatic life benchmark for chronic invertebrate exposure in freshwater of 10 ng/L (USEPA, 2017). These toxicity thresholds are based on freshwater species data; comparable thresholds designed to protect marine and estuarine species are not available.

A review of neonicotinoid aquatic invertebrate studies, mostly based on freshwater species, indicated toxicities can vary by multiple orders of magnitude between species (Morrissey et al., 2015), in part due to detoxification ability of species (Sánchez-Bayo et al., 2016). For example,

toxic impacts of imidacloprid were observed in one common test species, *Daphnia magna*, in the range of 100,000 ng/L, while toxic impacts in another test species, *Chironomus dilutus,* are observed closer to 100 ng/L (Morrissey et al., 2015).

A summary of available toxicity data for estuarine and marine species exposed to imidacloprid is provided in Table 4. All but one of these studies were based on acute toxicity tests; there is a significant lack of chronic toxicity studies. This is of concern because imidacloprid lethality and toxicity has been observed to be significantly greater when exposed for long periods of time for pollinators, which have been studied more extensively than other organisms (Pisa et al., 2015b). Imidacloprid is significantly less directly toxic to fish and mammals, but there are concerns about indirect effects through the food web, as well as difficult to measure effects on growth, development, and reproduction (EC, 2016, CDPR, 2016). A recent study in Lake Shinji, Japan, linked use of neonicotinoid pesticides since 2003 to dramatic declines in zooplankton biomass, which resulted in cascading effects to higher trophic levels, including the collapse of the smelt harvest (Yamamuro et al., 2019).

Table 4. Summary of imidacloprid toxicity levels for various brackish and marine species.

Species	Toxicity Threshold (ng/L)	Threshold Type	Reference
Mysidopsis bahia (Mysid shrimp)	21,000	96 hr mortality NOEC	Pisa et al., 2015b (original Ward, 1991)
	23	Growth effects NOEC	
	643	Reproductive effects NOEC	
Artemia (Brine shrimp)	3.61×10^8	LD_{50} 48 hr	Song et al., 1997
Callinectes sapidus (Blue crab)	10,000 (megalopae)	LC_{50} 24 hr	Osterberg et al., 2012
	1,112,000 (juveniles)	LC_{50} 24 hr	
Chironomus dilutus	2,410,000	LC_{50} 14 d	Cavallaro et al., 2017
	390,000	LC_{50} 40 d	
Oncorhynchus mykiss (Rainbow trout)	1.2×10^6 (fry)	LD_{50}	Gibbons et al., 2015
Cyprinodon variegatus (Sheepshead minnow)	161×10^8	LC_{50} 96 hr	Anatra-Cordone and Durkin, 2005 (original Ward,

			1990)
Penaeus monodon (Black Tiger shrimp)	175,000	LC_{50} 48 hr	Hook et al., 2018

The toxicity studies in Table 4 are based on exposure to a single compound, and do not account for more complex environmental exposures, which include degradates present in mixtures, as well as confounding factors such as biogeochemical characteristics and the presence of other contaminants (Bonmatin et al., 2015b). Research on imidacloprid degradation has shown that residual toxicity varies among degradates (Cavallaro et al., 2017; Diamond, 2017; Todey et al., 2018a). The urea derivative (imidacloprid-urea or IMD-UR) is a commonly detected product of photolysis but did not show residual toxicity to the mosquito, *Culex pipiens* (Todey et al., 2018b)**.** The other photolysis product, desnitro-imidacloprid (DN-IMD), has been reported to have a higher binding affinity for nicotinic acetylcholine receptor sites—the main component of the neonicotinoid toxicity mechanism—which is also implicated in mammalian toxicity (Diamond, 2017). While none of these degradates were detected in Bay water samples, this may be due to insufficiently low MDLs.

Very few studies have investigated the cumulative toxic effects of neonicotinoid mixtures. Because neonicotinoids have similar modes of actions, a concentration-additive mixture toxicity might be expected. However, a study assessing the toxicity of neonicotinoid mixtures to *Chironomus dilutus* found that different neonicotinoid mixtures had different synergisms or antagonisms that could not be easily predicted (Maloney et al., 2017). Maloney et al. (2017) did find that mixtures containing imidacloprid had a dose-level or dose-ratio dependent synergism, suggesting that higher concentrations could increase synergistic interactions.

Additionally, the varied usage and systemic nature of neonicotinoids suggests that organisms could be exposed to these contaminants through multiple pathways. While the most relevant pathway of exposure for aquatic life is through water, a 2017 study of amphipods investigated the impact of additional dietary exposure through consumption of contaminated plant material (Englert et al., 2017). This work found evidence of additive and synergistic effects triggered by combined exposure pathways (water and diet).

Imidacloprid is likely the most toxic neonicotinoid (Sánchez-Bayo et al., 2016). For example, the USEPA classified imidacloprid as “highly-toxic” to honey bees [LD_{50} = 0.018 µg/bee], while thiacloprid was categorized as “slightly toxic” [LD_{50} = 14.6 µg/bee] (de Lima e Silva et al., 2017; Fishel, 2016). The same degree of toxicity differential between imidacloprid and thiacloprid is also consistent with soil invertebrate species, as well as *Chironomus dilutus* in both acute and chronic conditions (de Lima e Silva et al., 2017; Maloney et al., 2017). A similar, second generation neonicotinoid pesticide, clothianidin, has been shown to exert chronic toxicity comparable to imidacloprid for the midge, *Chironomus dilutus* (Cavallaro et al., 2017). In a comparison of imidacloprid, acetamiprid, clothianidin, dinotefuran, and thiamethoxam,

imidacloprid was also the most toxic for both birds and fish (Fishel, 2016; Simon-Delso et al., 2015).

The reason for varying toxicity among neonicotinoids is not entirely understood. In honey bees (*Apis mellifera*), imidacloprid interacts with nicotinic acetylcholine receptors, which are involved in higher level neuronal processes in the brain (Simon-Delso et al., 2015). Dinotefuran and clothianidin, in comparison, bond with receptors that exhibit lower nerve-exciting activity than imidacloprid (Simon-Delso et al., 2015). The long half-life and high water solubility of imidacloprid relative to other neonicotinoids are other characteristics that likely contribute to the compound's greater toxicity (Bonmatin et al., 2015b; Todey et al., 2018b).

5.1 Risk Evaluation for San Francisco Bay

The RMP assigns emerging contaminants monitored in Bay water, sediment, and aquatic life to tiers in a tiered risk-based framework (Sutton et al., 2017). The degree of concern associated with a particular chemical or chemical class guides both RMP monitoring activities and water quality management actions. The criteria listed below are used for placement in each tier.

- High Concern – Bay occurrence data suggest a high probability of a moderate or high level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the EC_{10}, the effect concentration where 10% of the population exhibit a response).
- Moderate Concern – Bay occurrence data suggest a high probability of a low level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the PNEC or NOEC but less than the EC_{10} or another low level effects threshold).
- Low Concern – Bay occurrence data suggest a high probability of minimal effect on Bay wildlife (i.e., Bay concentrations are well below toxicity thresholds and potential toxicity to wildlife is sufficiently characterized).
- Possible Concern – Uncertainty in toxicity thresholds suggests uncertainty in the level of effect on Bay wildlife. Bay occurrence data exist; in some cases, they may be constrained by analytical methods with insufficient sensitivity.

Secondary factors that may impact tier assignments include trends in use of the chemical or trends in Bay concentrations, as well as the potential for cumulative impacts.

Imidacloprid: Moderate Concern

Aggregated open Bay and margins monitoring data indicated that imidacloprid concentrations in Lower South Bay were comparable to or greater than protective thresholds, including the European Union PNEC (4.8 ng/L), AA-EQS (8.3 ng/L), and the USEPA freshwater aquatic life benchmark (10 ng/L). These observations, in combination with widespread and increasing use of this pesticide in urban settings, suggest this contaminant be classified as a Moderate Concern for the Bay.

Both 2017 RMP monitoring studies of imidacloprid were conducted in the dry season; modeling suggests that additional imidacloprid loads from stormwater could result in higher levels in the wet season. It may be appropriate to explore opportunities for wet season monitoring of open Bay waters. New data on imidacloprid in stormwater generated by stormwater agencies and the RMP will be useful to evaluate stormwater loads. Both wet season Bay monitoring and more stormwater monitoring are important for evaluating and managing the risks from this contaminant. Analytical methods employed must be optimized to provide method detection limits well below toxicity thresholds in the low ng/L level.

Other Neonicotinoid Pesticides: Possible Concern

Other current-use pesticides have been classified as Possible Concern for the Bay (Sutton et al., 2017). No other neonicotinoid pesticides were observed in either open Bay or South Bay margins monitoring, likely reflecting the more limited uses of these pesticides in the urban environment, as well as analytical limitations (MDLs). However, this does not provide sufficient evidence to indicate this class poses minimal risks to Bay wildlife (Low Concern). Current monitoring data for Bay water are limited to measurements during the dry season, which may not capture the full range of neonicotinoid concentrations in the Bay, as highlighted by the modeling exercise (Section 4). Stormwater discharges during the wet season can make a significant additional contribution to pesticide loads in the Bay.

Also, there is uncertainty in appropriate toxicity thresholds for other neonicotinoids and degradates because of limited information on toxicity. Several studies indicate that imidacloprid is more toxic than other neonicotinoids, but exposures to mixtures of neonicotinoid pesticides can produce complex, cumulative impacts in organisms (Maloney et al., 2017). Cumulative exposure to multiple neonicotinoids potentially present at levels below MDLs could be a cause for concern, particularly given the observed sensitivity of some aquatic invertebrates to this pesticide class. There are also insufficient chronic toxicity studies for all neonicotinoid pesticides. Sufficient uncertainty exists to suggest that Possible Concern is warranted for this class.

Periodic monitoring could be considered in the future, particularly if new urban uses for neonicotinoids (other than imidacloprid) are registered, or if market shares for existing uses are observed to increase. Monitoring of Bay water during the wet season, or monitoring of stormwater, would be appropriate. As stated previously, considering the toxicity thresholds of these compounds in the low ng/L range, analytical methods employed must be optimized to provide MDLs well below toxicity thresholds.

6. Conclusions

Water samples collected in the summer of 2017 during the RMP's Status and Trends Water Cruise were assessed for the presence of neonicotinoids and degradates in San Francisco Bay. Imidacloprid was the only neonicotinoid detected in open Bay water samples. Imidacloprid was

detected at one Lower South Bay site at concentrations comparable to the PNEC for imidacloprid (4.8 ng/L), and were below detection limits (2.6 ng/L) at other sampled sites throughout the Bay (n = 22 total). Nearby margin samples also collected during the summer of 2017 in Lower South Bay detected imidacloprid (3.9 - 11.4 ng/L) in the same range as toxicity thresholds (4.8-10 ng/L). Similar to the open Bay, the only neonicotinoid detected in the margin water samples was imidacloprid.

No other ambient monitoring has been done for neonicotinoids in estuaries or bays in the U.S. for comparison. An assessment of neonicotinoid levels in Australian and Japanese estuaries (Hano et al., 2019; Hook et al., 2018) showed comparable or higher imidacloprid concentrations than those measured in the Bay. Both studies sampled at sites influenced by agriculture during periods of wetter weather; therefore, influence of stormwater discharges and agriculture runoff may explain some of the higher levels observed.

The potential importance of sampling during the wet season was also illustrated through a modeling exercise, which showed that while wastewater remains a dominant pathway for the pesticide, urban runoff can also contribute a significant load of imidacloprid during the wet season. This suggests that dry season monitoring of Bay water may not capture maximum concentrations for these water-soluble contaminants, and wet season and stormwater monitoring may be considered.

Given that open Bay and margins imidacloprid concentrations in Lower South Bay were comparable to or greater than protective thresholds, as well as the widespread and increasing use of imidacloprid in households, it is recommended that imidacloprid be listed as a contaminant of Moderate Concern. Other neonicotinoids are considered to be of Possible Concern for the Bay. Wet season monitoring in Bay waters would provide valuable information to further evaluate risks from imidacloprid. Additionally, other neonicotinoids could contribute to risk for aquatic life through cumulative exposure.

Management of neonicotinoids may be underway. Recently, CDPR published a pollinator risk determination, which was mandated by legislation and requires the agency to take action within two years of publication (Troiano et al., 2018). As a result of the re-evaluation, CDPR determined that additional mitigation measures are needed to protect pollinators from the use of neonicotinoids in agriculture. CDPR is holding two webinars later this year to share information and gather feedback from the public on proposed pollinator protection mitigation measures.

In April 2020, USEPA proposed modifications to the allowable uses of imidacloprid to address risks to aquatic invertebrates and honey bees, such as ending spray applications to residential turf and bulb vegetables, reducing maximum application rates for some agricultural uses, and adding application instructions for minimizing spray drift and runoff (USEPA, 2020). The USEPA proposal does not address the sources of imidacloprid in wastewater effluent—pet spot-on flea treatments (Sadaria et al., 2017b)—nor does it address most outdoor urban uses (e.g., applications for structural pest control, wood treatments, treatments for pests in non-residential

turf, ornamentals, and trees). USEPA plans to finalize its risk mitigation decision in late 2020 (https://www.epa.gov/pesticide-reevaluation/registration-review-schedules).

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Appendix. Methods and Quality Assurance

Samples were analyzed by SGS AXYS, using a new method MLA-114: Analysis of neonicotinoids. This method describes the determination of a suite of pesticides, pesticide metabolites and pesticide synergists in aqueous and solid samples. A list of analytes covered by the method and typical reporting limits are provided in Table 1 of the report.

Dataset completeness

Total pesticide and degradate results were reported for 22 water samples, two blind field replicates and one field blank. Additionally, eight lab replicates, four matrix spike/matrix spike replicates, three method blanks, and six laboratory control samples (LCSs) were also analyzed. These field and laboratory control samples meet the minimum requirement in the 2017 RMP QAPP of one per 20 samples. Data were reported not blank corrected.

Blank Contamination

Pesticides and degradates were not found in the field or method blanks at concentrations above the method detection limits. All field and method blank results were NDs.

Detections

Target analyte list included 19 analytes, shown in Table 1. All results were reported as non-detect, except for 2 imidacloprid measurements.

Accuracy and Precision for Imidacloprid Detections

Accuracy was evaluated using matrix spikes. The average % error for imidacloprid was greater than the RMP MQO (Measurement Quality Objective) of 35% (Yee et al., 2017), but less than 70%; therefore results are reported as qualified, but not censored. Precision was evaluated using matrix spike replicates. The relative standard deviation for imidacloprid was 4% and met the RMP MQO of 35%.

Six of the analytes (imidacloprid olefin, imidacloprid urea, MGK 264-A, MGK 264-B, Sulfoxaflor-A, Sulfoxaflor-B) were flagged by the lab for results that are of estimate value only because there is not enough field data to completely understand the behavior of these compounds, and there is no commercially available isotope to track these analytes. Two additional analytes (desnitro-imidacloprid and 5-hydroxy-imidacloprid) were flagged by the RMP QA officer for poor recovery of the matrix spike, where % error was greater than 70%. All of the flagged analytes were non-detect.