Persistence of Aerially-Sprayed Naled in Coastal Sediments

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Abstract

Aerial sprays of the organophosphate pesticide, naled, were intensified over beach areas during the summer of 2016 to control the locally-acquired Zika outbreak in the continental U.S. Concerns were raised in beach frequented areas about contaminated sediments. The aim of this study was to evaluate the persistence and levels of naled and its byproduct, dichlorvos, in sediments obtained from the affected areas. Laboratory experiments were designed to simulate the effect of various natural conditions on the decomposition of naled in three sediment types (beach sand, marl, and calcinated beach sand). The three sediment samples were also exposed to field aerial sprays. After 30 min of exposure, more dichlorvos was detected in the sediments than naled, with 33 to 43% of the molar concentration initially applied as either naled or dichlorvos. Under dark conditions, trace levels of naled were observed after 24 hours on sediments. Higher temperature accelerated the natural decomposition of both naled and dichlorvos in sediments. The half-life of naled ranged from 3 to 5 h at 22.5°C and ranged from 1 to 3 h at 30°C. Expedited decomposition of naled was observed under sunlight conditions with a half-life of naled of 20 minutes. In the field, only dichlorvos was detected in the sediment samples at concentrations between 0.0011 to 0.0028 μmol/g one hour after aerial sprays. This data can be used towards a risk assessment that evaluates exposures to naled and dichlorvos through beach sands impacted by aerial spray activities.

Keywords: Mosquito control, Naled, Dichlorvos, Aerial spray, Sediments, Zika virus

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Introduction

The first local (mosquito-to-human) transmission of the Zika virus in the continental United States was documented in Miami, Florida, during the summer of 2016 (CDC 2019, Chen et al. 2018, Schmidt 2016). This outbreak resulted in increased mosquito eradication efforts (FDOH 2019), which included aerial pesticide sprays of the organophosphate, naled, in highly urban areas of Miami-Dade County. Local mosquito-borne transmission in Miami was first documented on August 1, 2016, in a 2.6 square kilometer area of Wynwood. It spread to other parts of Miami-Dade County, including an 11.7 square kilometer area of Miami Beach on August 19, 2016, and a 2.6 square kilometer area of the Little River area on October 13, 2016. Consequently, these areas were aerially sprayed with naled multiple times to eradicate mosquitoes (Stoddard 2018). These areas include major beach recreational sites and smaller parks that have soils with higher organic content. Concerns were raised among local community members about the presence of naled in sediments, in particular beach sand environments, considering typical recreational activities in the area that include beach volleyball, children playing with sand during beach visits, and contact of exposed skin (e.g., bare feet) with sand. Specifically, concerns were raised about dermal exposures to naled through direct skin contact with beach sands. To address community concerns about the safety of naled applications, more information was needed concerning the persistence of the pesticide, particularly in beach sands and sediments found in areas prone to mosquito proliferation and vector-borne disease transmission.

Naled (dimethyl 1,2-dibromo-2,2-dichloroethylphosphate, Tradename of Dibrom^{TM}) degrades in the environment primarily to dichlorvos (dimethyl 2,2-dichlorovinyl phosphate, Common name DDVP) through the removal of the two bromines (Gan et al. 2006a). Naled is the most widely used pesticide to eradicate mosquito populations by aerial application (Britch et al. 2018, Hemme et al. 2019). The efficacy of naled and dichlorvos against insects is through inhibition of cholinesterase, which is an enzyme required for the normal function of nervous systems (Čolović et al. 2013, Bilal et al. 2019). Humans can be exposed through inhalation, ingestion, or eye and skin contact. At excessive levels, exposure to naled and dichlorvos can cause neurotoxicity in humans (UF 2019). Several studies indicated that environmental factors, including photolysis, hydrolysis, and biomineralization dictate the degradation products of dichlorvos (Sleiman et al. 2008 Zhang et al. 2007). Although most of the breakdown products of dichlorvos are generally considered to be of low toxicity (ATSDR 1997), some reports suggest that the degradation pathway of dichlorvos in the air under sunlight conditions by hydroxyl radicals involves the formation of phosgene (CCl_2O), which is a stable highly toxic gas (Feigenbrugel et al. 2006). For this potential toxicity, studying the persistence of naled and its first degradation product, dichlorvos, within sediments is a formidable challenge.

The chemical partitioning can be inferred through the pesticide's solubility in water and its tendency to sorb toward the organic phase of the soil; the more soluble the compound and the more strongly it is partitioned towards the water phase (low K_{oc}). Dichlorvos is highly soluble in water with a solubility of about 16,000 mg/L (ATSDR 1997). The sorption of dichlorvos is considered low due to a very low organic carbon partition coefficient, $K_{oc} = 1.45$, Kenaga 1980). Thus, dichlorvos would be expected to leach from soil upon contact with water by partitioning toward the water phase making it more susceptible to hydrolysis. Naled has a lower water solubility (~2000 mg/L, AMVAC 2011). The K_{oc} of naled is 180, higher than that of dichlorvos, suggesting that naled would be less bioavailable in sediments and soils containing higher organic content and thus be more tightly bound.

Other general properties of naled include its sensitivity to UV light, which promotes its degradation (NPIC 1996). Enhanced degradation of naled has been observed in the presence of sulfur compounds under anaerobic conditions. Under these conditions, reduced forms of sulfur have been shown to degrade naled to dichlorvos immediately, with dichlorvos remaining in the environment for longer time periods (Gan et al. 2006a,b). The reactions with sulfur compounds are particularly relevant in terms of potential transformation pathways in coastal environments suggesting that dichlorvos could persist for more extended periods than originally thought.

To the best of our knowledge, the evaluation of the persistence of naled and dichlorvos in sediments after aerial spray application has not been reported. For naled, studies have been limited to evaluating the disappearance of naled deposited on cellulose paper. For instance, Hennessey et al. (1992) observed no natural decomposition of naled after 6 hours of application on cellulose pads under ambient conditions. However, (Tietze et al. 1996) found a correlation between the extent of humidity and sunlight with the decomposition of naled on filter paper. For dichlorvos, a few studies (Menzie 1972, Suzuki et al. 1998, Sattar 1990, Asemoloye et al. 2019) have evaluated the degradation in sediments. For example, Asemoloye et al. (2019) established the degradation pathway for dichlorvos in a soil rhizosphere under the action of fungi. Suzuki et al. (1998) developed a model for degradation using point measurements of dichlorvos levels on golf courses. However, none of these studies provide time-series field measurements of dichlorvos degradation in sediments under full-scale aerial spray operations, information that is needed to assess potential impacts to human populations in urban areas, such as those experienced during the 2016 Zika outbreak. Also, the characterization of the sediments in these prior studies was limited to bulk physical parameters.

There is also little information about the distribution of naled in water, soil, and air. A study by (Schleier et al. 2009) reported some evidence of the deposition of naled at ground level after aerial spays to range from 0.57 ± 0.56 ng/cm^2 to 71 ± 5.8 ng/cm^2 within 1 h to 12 h. The main degradation pathway identified for naled in this study was photolysis. Schleier et al. (2009) also determined no detectable levels of naled in the air. Conversely, more studies have provided some information about the distribution of dichlorvos in various environmental phases. For instance, Howard (1991) determined the half-life of dichlorvos to be less than 3 days. This is believed to occur because dichlorvos reacts with the moisture present in air. In addition, studies have also shown that dichlorvos is degraded by hydrolysis in water and the rate of degradation can be affected by pH and increased temperature (Tietze et al., 1996; Latif et al., 1984). However, for all of these existing studies, time series measurements in sediments are lacking.

Overall, there are major gaps in the literature concerning the influence of soil and environmental conditions on naled and dichlorvos degradation. Data reported in the literature are based upon spot measurements with limited reporting on sediment properties. Herein, we assessed the persistence of naled and its degradation byproduct dichlorvos in various sediments after aerial spray events. Sediments were chosen to be representative of the range of organic content naturally found within the impacted areas. Furthermore, we investigated under laboratory-controlled conditions the effect of temperature and sunlight on the stability of naled and dichlorvos in beach sand, and marl soil, which is the typical soil that supports vegetation in the same area. These sediments were highly characterized through advanced microscopic and spectroscopic techniques. This current study thus provides unique information about naled persistence in sediments (studies previously on cellulose paper only) and new information about dichlorvos persistence in sediments after full-scale aerial spray activities using sediments that have undergone extensive characterization. This current study is a companion study to Jones et al. (2020), which documented the impacts of naled aerial sprays on fresh and marine waters.

2.0. Methods

2.1. Sediment Sample Collection and Characterization

Three types of sediment were used during this study. The first was beach sand collected from Miami Beach, Florida (GPS coordinates: latitude and longitude: 25˚46’50” N, 80˚07’48” W). The second sediment consisted of marl, a native soil of south Florida composed primarily of calcite (Li 2015) and suitable for growing crops due to high organic content. The marl sample was collected from a farm located in Homestead, Florida (25˚27’46” N, 80˚24’36” W). The third sediment used for experimentation was prepared from the beach sand by subjecting it to calcination (500 ˚C for 24 hours). The purpose of the calcination was to remove organic materials that may promote the degradation of organophosphates.

The sediment samples were then analyzed for the physical and chemical parameters (pH, turbidity, conductivity, and salinity) and gravimetrically for moisture content, % organic content, and grain size distribution. For the physical and chemical measurements, 400 g of sediments were placed into 800 mL of deionized water. Turbidity, pH and salinity measurements were acquired using Turner Designs TD-40 nephelometer, Orion Star A211 pH meter, and a YSI Water Quality Sonde Model 650, respectively. Standard gravimetric analyses were used to analyze for moisture content (100 ˚C for 24 hours) and % volatiles (550 ˚C for 24 hours). Gravimetric determination of grain size distribution was conducted with standard sieves (opening sizes: 2 mm, 1 mm, 0.25 mm, 0.11mm, and 0.07 mm). The inorganic carbon and total carbon content were analyzed using a Picarro G2131-i Isotopic CO_2 Cavity Ringdown Spectrometer, CRDS), with total organic carbon computed by difference. The physio-chemical properties including pH, turbidity, conductivity, salinity, and organic content are presented in Table 1.

The sediment samples were further analyzed by advanced microscopic and spectroscopic techniques. The samples were analyzed by a Zeiss Ultra Plus field emission scanning electron microscope (SEM) operating at 20kV accelerating voltage and equipped with an EDAX Apollo 10 detector, by a Philips 3710 X-ray powder diffractometer (XRD), and by a PerkinElmer Frontier FT-IR spectrometer. The surface elemental composition of beach sand and marl sediments were analyzed using a PHI VersaProbe II x-ray photoelectron spectrometer (XPS) running at X-ray power of 25 W at 15 kV with a beam size of 100 µm.

2.2. Laboratory Analysis

2.2.1. Materials

All chemicals were used as obtained. Naled, dichlorvos, and standards (surrogate consisting of 3,3',4,4'-tetrachlorobiphenyl (PCB 77) and internal consisting of tetrachloro-m-xylene (TCMX)) were purchased from Sigma-Aldrich (Milwaukee, WI 53209). Ethyl acetate was obtained from Fisher Scientific (Pittsburgh, PA, 15275).

2.2.3. Analytical Procedure

Naled and dichlorvos calibration standards ranging from 100 μM to 0.1 μM were prepared in ethyl acetate. All sets of experiments were conducted by spreading 30 g of air-dried sediments at the bottom of a 185 mm crystallization dish. A known amount of naled and 3,3'4,4'-tetrachlorobiphenyl (PCB 77), as a surrogate standard, dissolved in ethyl acetate was sprayed evenly on the sediment using an atomizer (DeVilbiss Healthcare Model 163 Atomizer) (Fig. S1). Simultaneously, the crystallization dish was rotated to facilitate uniform distribution of the naled solution on the sediment. An aliquot of 1 g of the sediment was then removed at predetermined time intervals from the crystallization dish and then placed into an amber vial containing 5 mL of ethyl acetate to stop the reaction. The vials were subsequently extracted on a multitube vortexer for 30 min and allowed to settle for an additional 20 min. One hundred microliters of the supernatant were then placed into a 200 μL glass insert in a 2 mL GC vial. Subsequently, 10 μL of TCMX solution was then added as an internal standard. Naled and dichlorvos were analyzed using an Agilent 7890A gas chromatograph coupled with 5975C mass spectrometer (GC-MS) (Agilent GC-MS, Santa Clara, CA) fitted with an Agilent J and W Standard Polysiloxane DB-5ms column using a 5 μL injection volume with inlet temperature set at 250°C and a flow rate of 1.2 ml/min. The column temperature program started at 50 °C for 4 min, then ramped to 100 °C at 25 °C/min and to 280 °C at 10 °C/min followed by 1 min hold at 280 °C and 3 min post run at 300 °C. The percent recovery of the extraction process was estimated from the concentration of the surrogate standard, PCB 77, to be 67%. This value was used to normalize the concentration values of naled and dichlorvos at different time intervals starting with 0 h and continuously as the degradation proceeded.

2.2.4. Degradation of naled in dark at 22.5°C and at 30°C

The atomizer was loaded with 30 mL of a 0.5 mM naled solution and was connected to a source of low pressure (<60 psi) nitrogen gas. Subsequently, 10 mL of the solution was sprayed evenly onto the 30 g of sediment in the crystallization dish. The 1 g sample at 0 h was collected into the 20 mL amber bottle immediately after spraying, with the addition of 5 ml ethyl acetate to stop the reaction and to produce a starting concentration of 20 μM based on surrogate percent yield. This process was repeated at 1, 2, 3, 4, 6, 10, 24, and 48 h. At the end of the experiment, samples were vortexed and allowed to settle. Subsequently, 100 μL of the supernatant were then extracted into a 200 μL insert in a 2 mL amber vial using the process described above. Samples were analyzed on the GC-MS as described above. The same method was carried out in the dark at 30°C. Temperatures for each experiment were controlled by incubating samples within a digital furnace (Bransted international model F47900) set at the required temperature.

2.2.5. Degradation Experiment under Simulated Sunlight Conditions

Simulated sunlight experiments were conducted in a similar fashion as the degradation experiment above. This time, after the spray, the crystallization dish was placed on a Kool plate (Model SK-24D-AW set at 25 ˚C) under a solar simulator (Oriel Sol3A Class AAA Solar Simulator with a 12 x 12 output beam utilizing the 1.0 SUN output, equivalent to 98,000 lumens/m^2). The sample at 0 min was taken immediately before the solar simulator was turned on. One-gram aliquots were taken at 10, 30, 60, 90, and 120 min of light exposure to the solar simulator and extracted into ethyl acetate for analysis as described above.

2.3. Field Experiment

The field samples were exposed to naled on August 28, 2018, near the center of the target aerial spray area located in East Naples in Collier County, Florida (26˚ 2' 47.9" N, 81˚ 40' 39.6" W; Air temperature 25 ˚C, 95% humidity, winds at 2.7 m/s ENE). The aircraft left the airport at 9:45 pm and landed at 11:10 pm local time. The targeted recovery of naled was calculated to be 0.00140 μmol/cm^2 (based on aerosol deposition of 0.46 fl. oz per acre of Dibrom® at a density of 1.81 g/mL and 87.4 % (w/w) naled). Details about the aerial spray missions, such as the airplane descriptions and spraying tracks relative to the sampling location, are provided in the supplemental text of Jones et al. (2020).

The set up for sediment samples consisted of utilizing six glass plates (surface area 20 cm by 26.5 cm). Two were used for beach sand, two for marl, and two for calcinated sand. The sediment on one of the two glass plates was earmarked for collection before the aerial spray as a control. The sediment on the second glass plate was earmarked for collection after the aerial spray. Thirty-five grams of corresponding sediment were then placed into each plate and spread carefully using a brush which resulted in a very thin layer that covered the plate surface area. The "before" and "after" samples were collected based upon the planned airplane timetable and visual observations of the airplane overhead. Once the sample times were determined, sample collection involved carefully pouring the sediment into a wide mouth amber bottle and adding 60 ml of ethyl acetate to stop the degradation reaction. The bottles were swirled to facilitate the mixing of the ethyl acetate with the sediment samples.

The "before" samples were collected at 9:30 pm prior to the aerial spray mission. The "after" samples were collected at 11:10 pm. The closest swath of the airplane observed overhead was at 10:15 pm. The "after" samples were thus exposed to the aerial spray for about an hour prior to collection. Since the samples were collected at night, they were not subject to solar radiation prior to collection (sunset at 7:45 pm and sunrise at 7:00 am). Subsequently, the samples were transported in a cooler to Florida Spectrum Environmental Services, Ft. Lauderdale, FL for analysis within 12 hours of the acquisition.

3.0. Results and Discussion

3.1. *Sediments characterization*

The physical and chemical properties of the sediments (Table 1) show that among the three sediments evaluated, calcinated sand had the lowest organic content and largest grain size. Scanning electron microscope images (Fig. 1a and 1b) further emphasize that the beach sands had a larger grain size and more uniform morphology than the marl sediment. The calcination of the beach sand improved the uniformity of the surface of the particles with a slight effect of increasing the average grain size (Fig. S1c). The elemental composition of both sediments by energy dispersive spectroscopy (Fig. S2b, d and f and Table S1), shows a high ratio of calcium carbonate and silicates with small amounts of magnesium and sulfur. Marl sediment was also identified to contain a high amount of calcium carbonate and low levels of magnesium, and sulfur. For marl, low levels of silicon and aluminum were also detected. These results are consistent with the XPS (Fig. 1 c and d). However, further investigation of the carbon peak (Fig. 1 c and d insets) indicates the presence of two components at 284.8 eV and 289.0 eV ascribed to organic carbon and calcium carbonate, respectively. This is further supported by the infrared spectrum (Fig. S3) for beach sand that reveals identifiable peaks at 1461, 1099, and 850, which represents C=C, SiO_2, and $CaCO_3$ respectively, and for marl sediments at 1779, 1413, 1081, and 874 cm^{-1} for C=O, C=C, Si-O , and $CaCO_3$, respectively. These IR results are consistent with previous works (Song et al., 2001; Patty et al., 2017). The XRD pattern (Fig. S4) for the beach sand showed characteristic peaks indicating the crystal structure of cristobalite SiO_2 at 21.48, 30.27° and aragonite $CaCO_3$ at 27.53, 33.78°. The calcination of the beach sand resulted in improving the aragonite $CaCO_3$ phase purity to dominate the XRD pattern with characteristic peaks at 26.82, 38.80, 42.64, 46.09, and 48.76 while the peaks at 37.04, and 50.71 are ascribed to lime CaO, suggesting the decomposition of some $CaCO_3$ to CaO after calcination (Fig. S4). The marl sediment pattern (Fig. S4) exhibited peaks representing characteristic crystal structure of coesite SiO_2 at 29.49, 39.52, 47.59, 56.71, and 57.75°, and calcite $CaCO_3$ at 36.07, 43.49, and 48.83°. Collectively, the characterization data indicate that the beach sand and marl sediment were composed mainly of $CaCO_3$, considerable amounts SiO_2 and organic matter, and trace levels of sodium, aluminum, magnesium, and sulfur.

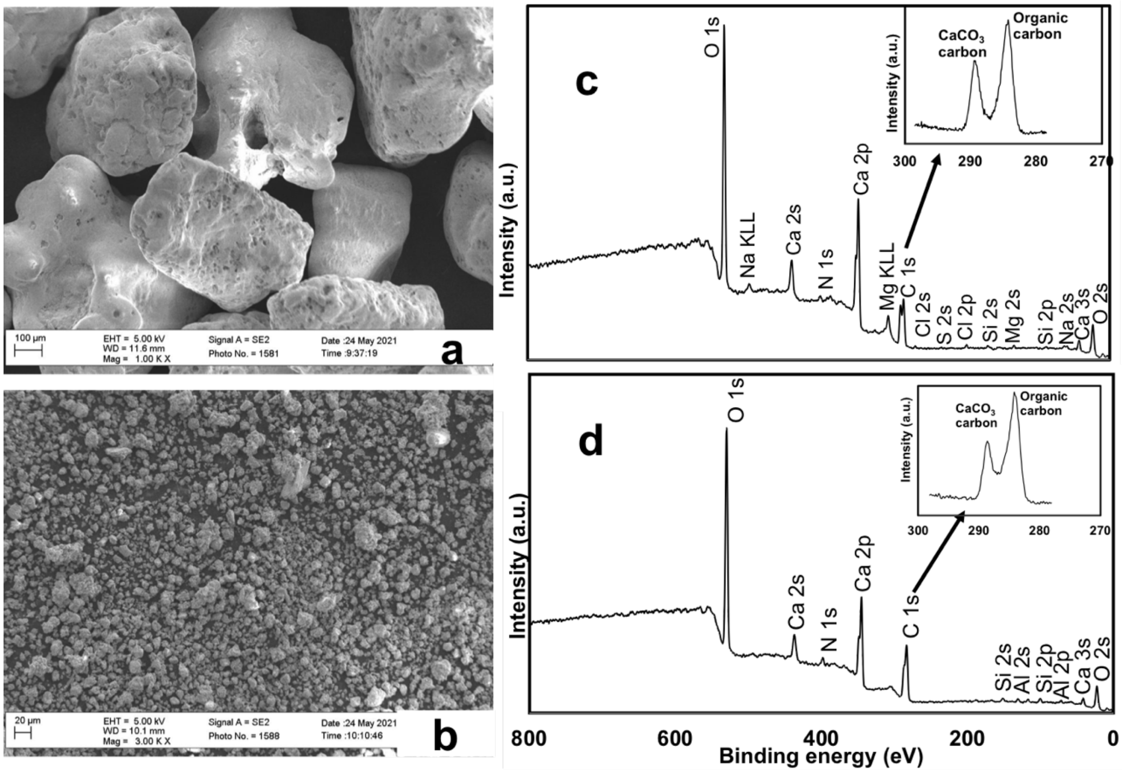

Fig. 1. Scanning electron micrographs of beach sand (a) and marl sediment (b), and x-ray photoelectron spectra of beach sand (c) and marl sediment (d). Insets: represent high resolution XPS analysis of the carbon peak.

3.2. Degradation of naled on beach sand and marl sediment in the dark at 22.5°C and 30°C

In this study, we investigated the half-life and kinetics of the natural decomposition of naled and its byproduct dichlorvos in the dark at 22.5°C and 30°C deposited on beach sand and marl sediments. The aim was to elucidate the persistence of the organophosphate insecticides in areas where they are frequently sprayed.

For experiments conducted in the dark at 22.5°C for beach sand and marl sediment, dichlorvos was detectable from the onset, and it represented about 30% of the naled concentration. This is consistent with our analysis of naled standard solutions. Fig. 2a shows the degradation of 20 µM naled sprayed on beach sand and subsequently the produced dichlorvos under dark conditions at room temperature. As the degradation progressed in the beach sand (Fig. 2a), both naled and dichlorvos degraded at a constant rate following pseudo-first-order kinetics. It is noteworthy that naled and dichlorvos are semivolatile pesticides with Henry's law constants at 25 °C of $6.5X10^{-5}$ and $5.7X10^{-7}$ atm-cu m/mol, respectively. This indicates the loss of these compounds due to volatilization is relatively insignificant, which is consistent with results reported by Bustos et al., 2018.

Table 1

Physical-chemical characteristics of sediment samples used for experimentation

	Physical-Chemical Measures						**Sieve Analysis (mm)**				**Geotechnical Characteristics of Grain Size**	
Sample	**pH**	**Turbidity (ntu)**	**Salinity (ppt)**	**Moisture content (%)**	**Volatiles**	**Total organic carbon**	**d_{10}**	**d_{30}**	**d_{50}**	**d_{60}**	**Uniformity Coefficient**	**Coefficient of Gradation**
Beach Sand	8.32	15000	0.31	0.24%	2.7%	3.64%	221	411	593	684	3.10	1.12
Marl	9.82	200	0.45	2.0%	4.9%	6.07%	22.6	52.9	209	339	15.0	0.36
Calcinated Beach Sand	10.39	30.5	0.56	0.046%	0.86%	_	296	465	634	718	2.43	1.02

Results further show that 75% of the naled and 50% of the dichlorvos were dissipated after 6 h of the reaction on the beach sand. This rate is relatively fast compared to the degradation of naled on cellulose pad reported by Hennessey et al. (1992), where they observed an insignificant decrease of naled after 6 h. The concentrations continued to decrease significantly to reach 98% natural decomposition of both naled

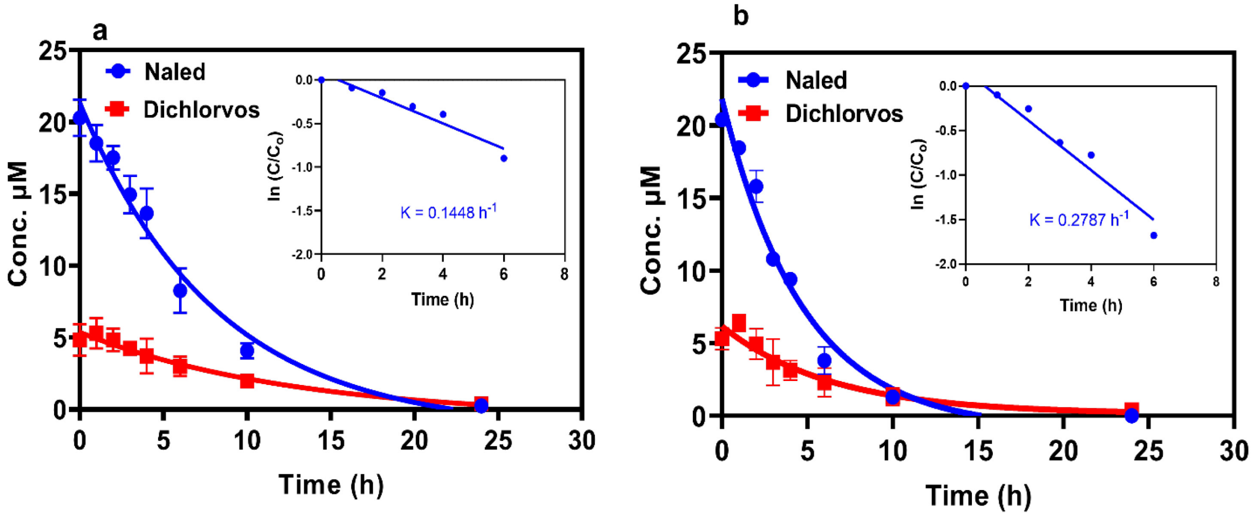

Fig. 2. Concentrations of naled in beach sand starting at approximately 20 µM and concentrations of dichlorvos produced during the degradation experiments at approximately 5 µM. (a) corresponds to experiments conducted in the dark at 22.5°C, and (b) in the dark at 30°C. Inserted graphs corresponds to the first order rate of naled for each.

and dichlorvos by 24 hr. At 48 h, both naled and dichlorvos were no longer detectable. No further degradation products were detected in the GC-MS chromatograms (Fig. S5), presumably due to the fast mineralization of naled and dichlorvos to inorganic products. Investigating the mechanistic pathways of this mineralization process to identify the intermediates constitutes the scope of our future studies.

The half-lives of naled and dichlorvos were approximately 5 h and 6 h, and the rate constant for naled was 0.1448 h^{-1} (Fig. 4). The study of the degradation of naled in various types of sediments is very scarce in the literature. For instance, Sattar et al. (1990) observed half-lives of 16 days for dichlorvos in silty clay acid soil (pH=5.5, organic matter 0.9%, moisture 14.4%) and sandy clay neutral soil (pH=6.9, organic matter 1.1%, moisture 10.5%) for experiments conducted at room temperature. The differences in the degradation rates between our results and the ones reported by Sattar et al. may be attributed to differences in the organic matter and calcium carbonate content and the pH of the sediments. The sediments used in this study were found to be alkaline (Table 1) with high levels of calcium carbonate. For instance, studies in water have shown that the degradation rates of dichlorvos increased in basic pHs (Latif et al. 1984). Furthermore, Durik et al. 2009 found direct correlation between the pH and the hydrolysis of organophosphorus pesticides, such as chlorpyrifos. The hydrolysis of organophosphorus pesticides was attributed to SN_2 nucleophilic attacks by the hydroxide ion on the tetrahedral phosphorus atom resulting in the formation of alkyl phosphate compounds. Other nucleophiles like sulfur and chloride found in the beach sand and marl sediments (Fig. 1) could enhance the breakdown of naled and dichlorvos. However, more research is needed to elucidate these mechanistic pathways.

To evaluate the effect of biodegradation, we calcinated samples of the beach sand at 500 ˚C for 24 h to sterilize any organisms in the sediment. These samples were sprayed with naled according to the aforementioned procedure. Fig. S6 shows that the natural decomposition of naled was slightly slower with a rate of 0.1111 h^{-1} compared to the beach sand. This decrease in the rate of naled degradation might be attributed to the removal of microbes and organic matter after calcination. Thus, biodegradation appears to be advantageous to the natural disappearance of naled.

We conducted another set of experiments at 30°C in dark conditions, which corresponds to the average air temperature in Miami, Florida, during the summer evening hours, when aerial sprays typically occur. As displayed in Fig. 2b, the degradation of naled in beach sand at 30°C was faster than the one observed at 22.5°C with approximately 80% naled and 60% of dichlorvos degraded at 6 h. At 24 h both naled and dichlorvos were no longer detected in the beach sand at 30°C. Results also showed an increase in the rate constant (0.2787 h^{-1}) for naled compared to the result of the experiment carried out in dark at 22.5°C (Fig. 4). This indicates that an increase in temperature enhances the degradation of both naled and dichlorvos in beach sand. These results are consistent with the degradation trends reported by Gan et al. (2006b) and Jones et al. (2020). For instance, Jones et al. conducted experiments to determine the persistence of naled and dichlorvos in fresh and marine water in the dark at 23°C and 30°C. They reported the half-lives of naled and dichlorvos to range between 12 to 20 h at 23°C compared to a half-life of about 6 to 9 h at 30°C.

On the other hand, the degradation of naled and dichlorvos in marl sediment (Fig. 3) was faster than that in beach sand. No initial increase in the concentration of dichlorvos was detected, indicating simultaneous degradation of both organophosphates. About 85% of naled and dichlorvos initial concentrations were reduced after 6 h of interaction with the marl sediment. After 10 h, both organophosphates were no longer detectable (Fig. 3a) at room temperature. Overall, the half-life for naled and dichlorvos in marl sediment at room temperature was calculated to be at 3 h for both. Marl soil is known to support vegetation. As a result, we carried out a total organic carbon TOC analysis to determine the organic matter in the beach and marl sediments. Table 1 shows that the marl contains more organic content at 6.07% compared to the beach sand at 3.64%. The increased organic components in addition to the presence of biological components could be responsible for the accelerated degradation of naled and dichlorvos, in the same manner as reported by (Asemoloye et al. 2019). Altering the experimental condition from room temperature to 30°C greatly impacted the rate of naled and dichlorvos degradation in marl sediment. The starting concentration for naled was 20 μM, and from the onset 8 μM dichlorvos was detected. After 6 hours of degradation both naled and dichlorvos were no longer detectable (Fig. 3b). At 22.5°C, the rate constant of naled was 0.3228 h^{-1}, while at 30°C the rate constant was 0.8350 h^{-1} (Fig. 4). This is consistent with our previous studies in water

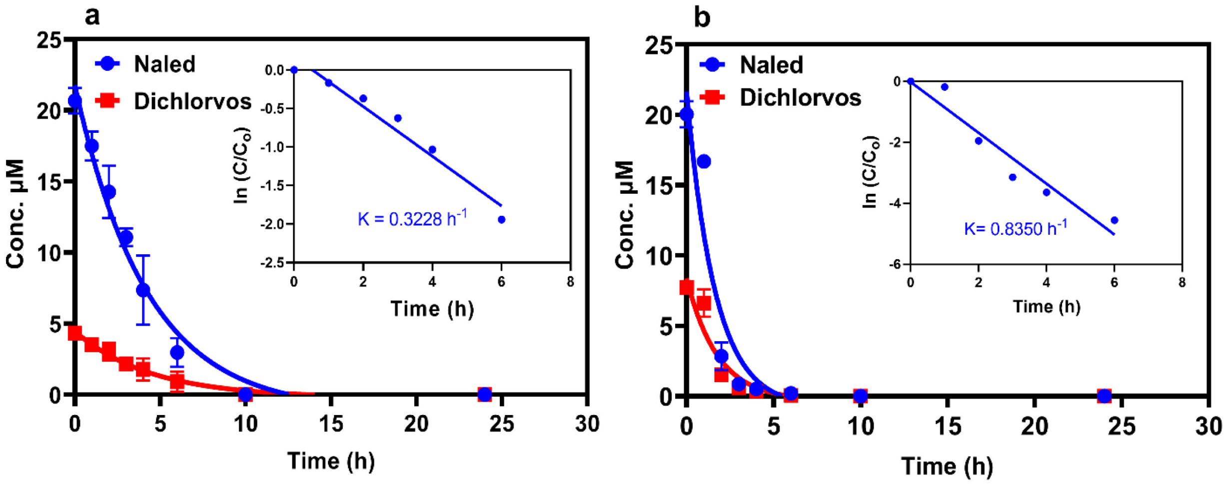

Fig. 3. Concentration of naled in marl: (a) corresponds to experiments conducted in the dark at 22.5°C, and (b) in the dark at 30°C. Inserted graphs corresponds to the first order rate of naled for each.

samples suggesting that increasing temperature accelerates the degradation of naled and dichlorvos. For naled, half-lives decreased by 40 to 50 % when temperatures increased from 23 to 30 ˚C (Jones et al., 2020). For dichlorvos, the half-lives in water decreased by a factor of 4.7 between temperatures of 23 to 39 ˚C (Faust and Suffet 1966). Similarly, Gan et al. 2006b measured a 7-fold decrease in half-lives between these same temperatures in aqueous samples. Therefore, given the trends observed in water samples, the shorter half-life that was observed is expected. Taken collectively, both naled and dichlorvos degrade to non-detectable levels in both beach and marl sand in less than 1 day under dark conditions.

3.3. Degradation experiment under simulated sunlight conditions

In Miami, Florida, aerial sprays take place in the night or towards the early morning hours. Given that naled can persist for several hours, naled should still be at detectable levels as daylight progresses. Therefore, we have also reported the effects of sunlight on the degradation of naled and dichlorvos in beach sand. Under simulated sunlight conditions, decomposition of naled and dichlorvos was observed with non-detectable levels of dichlorvos after 60 minutes (Fig. 5). Low levels of naled were observed in one of the three experimental replicates after 120 minutes. On average, the half-life for naled and dichlorvos was computed as 20 and 30 minutes (Fig. 5a), and the rate constant of naled was computed as 0.02149 min $^{-1}$ (Fig. 5b).

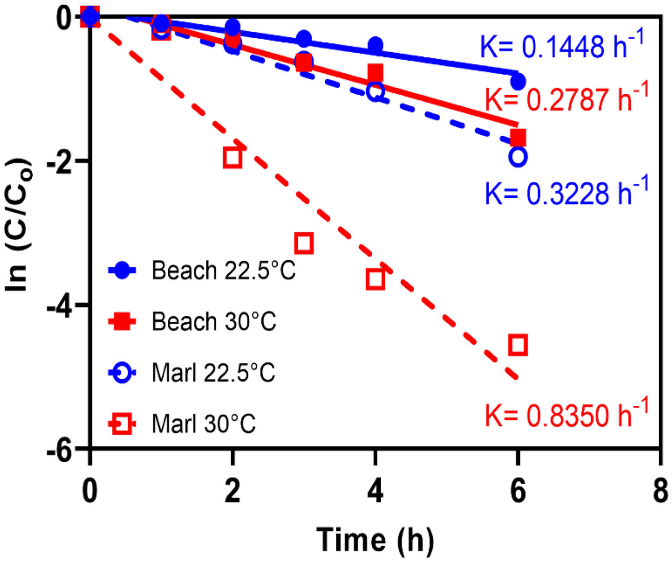

Fig. 4. Naled degradation rates (Ln C/Co) plotted against time (h) for beach and marl sediments, comparing the experiments run in the dark at temperatures of 22.5°C and 30°C. Displayed alongside is the rate constant for each experiment.

The half-life of naled at 20 min was relatively small compared to the 82 min measured by Tietze et al. (1996) on filter paper subjected to sunlight. The shorter half-life in the current study in comparison to the results from Tietze et al. could be due to the differences between natural soils and filter paper, differences in temperature (22.5 ˚C versus 39 ˚C), and differences in sunlight intensity. The primary mechanism for the degradation of naled is through the attack of nucleophiles (Gan et al. 2006a). Natural sediments likely contain more nucleophiles than filter paper. In terms of sunlight, the intensity of the simulated sunlight was higher (98,000 lumens/m^2) in the current study by about a factor of 10 compared to the sunlight intensity measured in the Tietze et al. study (9,600 lumens/m^2). Additional evidence exists from studies in aqueous samples that show that sunlight accelerates the degradation of naled and dichlorvos. For instance, Bustos et al., 2019 reported the photodegradation of dichlorvos in aqueous matrices under sunlight and UVC254 irradiation. They found that dichlorvos undergoes photodegradation by superoxide and hydroxyl radicals under simulated sunlight in water containing dissolved molecular oxygen. The main degradation products were identified to be 2,2-dichlorovinyl methyl phosphate, dimethyl phosphate, and dichloro-acetaldehyde. However, in absence of oxygen, the degradation of dichlorvos under UVC254 irradiation was presumed to follow a direct photolysis pathway (Bustos et al., 2019).

Furthermore, in natural water samples, shortened half-lives by a factor of 30 to 100 were observed for naled under simulated sunlight conditions in comparison to aqueous samples not subjected to sunlight (Jones et al. 2020). In deionized water, half-lives were shortened by a factor of almost 500 from 126 hours to 0.3 hours at room temperature. Also, under simulated sunlight conditions, dichlorvos was produced from naled in water samples, although both species were relatively short-lived (half-lives of an hour or less) in comparison to samples without sunlight conditions (half-lives of days) (Jones et al. 2020). Comparing the Jones et al. 2020 results with the half-life from the current sunlight degradation experiment (20 minutes) suggests that the degradation rates were within the same order of magnitude in aqueous solutions under sunlight conditions. Jones et al. also found that dichlorvos was always greater than naled levels. This is the opposite of what was observed in sediment samples, which showed that the molar concentrations of naled were greater than dichlorvos under sunlight conditions.

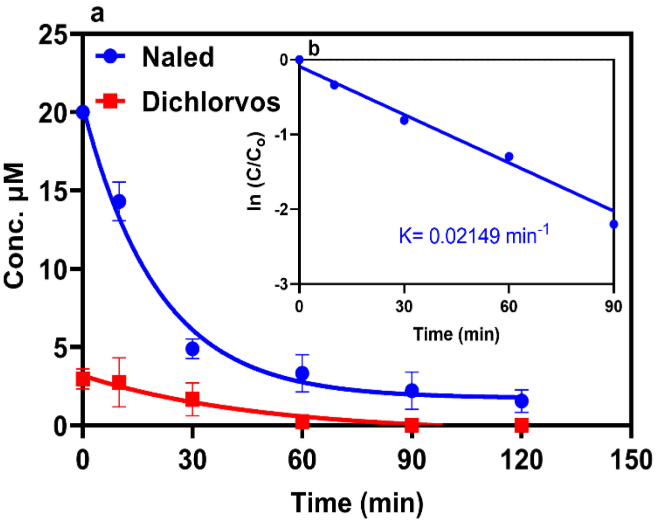

Fig. 5. Concentrations of naled in beach sand starting at 20µM and concentrations of dichlorvos produced during the degradation experiments at 3µM. (a) corresponds to experiments conducted under simulated light conditions at room temperature, and (b) Rate of degradation of naled.

Overall, the laboratory experiments focused on evaluating the impacts of temperature and sunlight on the natural decomposition of naled and dichlorvos from sediments as these factors can be used for management purposes to determine times that are adequate for human use of recreational areas. To further understand the mechanisms of degradation, future studies should also evaluate the impacts from microbes by conducting experiments with unsterile natural sediments in comparison with sterilized sediments.

3.4. Field experiments

For the sample set collected prior to aerial sprays, results from field experiments show that all three sediments were negative for both naled and dichlorvos. After the spray, only dichlorvos was positive in the sediment samples after the spray with concentrations ranging from 0.001 to 0.003 µmol/g (Table 2). Considering the target application rate of naled (5.3 kg/km^2), the amount of organophosphate observed at ground level in the sediments after about an hour after exposure to the aerial spray represented between 5 and 13% of the molar amount originally applied as naled. Interestingly the beach sand appears to have retained the highest amount in the form of dichlorvos (13% of the original naled applied). The organic content of the marl, originally believed to play a larger role in the degradation, did not have as large as an effect retaining 9% as dichlorvos. The calcinated sand retained the least amount (5% as dichlorvos) of the original naled applied. Overall, there appears to be a natural decomposition of over 87% between the target dose via the airplane aerial spray and observations in the sediments after one hour of exposure.

These results show faster degradation in field settings compared to the degradation experiments conducted under laboratory conditions. In the laboratory (under dark conditions at 30 ºC), both naled and dichlorvos can be observed at 1 h (Fig. 2b and 3b), and only about 10% and <1% of the naled and dichlorvos were lost after one hour in the sand, respectively, and 15% and 14% in the marl, respectively. Field samples were collected one hour after the observed aerial spray overhead with 87% to 95% natural decomposition of active ingredient. Of note, the field experiments differ from the laboratory experiments in that no naled was detected in the field. The only species detected in the field sediment samples was dichlorvos. A similar observation was observed in a concurrent study focused on evaluating naled and dichlorvos in water samples (Jones et al. 2020). In this concurrent study, although naled was sprayed only dichlorvos was detected in the marine water, freshwater, and deionized water samples subjected to the same spray conditions. The amount detected in the water, given the surface area of the water sample, represented only 10% of the applied naled amount on a molar basis. The amount observed in the sediment samples (5 to 13%) is consistent with the amount observed in the aqueous samples within the concurrent study (Jones et al. 2020).

The differences between the application rates and the amount observed in the sediment at ground level could be due to several reasons, which include that the active ingredients were lost during the fall from the airplane through contact with aerosols in the air, they never reached the ground, or they decomposed faster than anticipated. Dichlorvos is known to be volatile (Howard 1991) and remains aerosolized in the atmosphere, explaining the loss at ground level. When applied to air under dry conditions, the dichlorvos vaporizes (Eisenreich et al. 1981) and reacts with moisture in the air. Increased degradation in air is associated with higher temperatures, higher humidity, and higher pH conditions (ATSDR 1997). It is possible that as the naled was sprayed, it converted to dichlorvos, which in turn remained volatilized.

Table 2

Results from sediments exposed to field scale aerial sprays of naled

Sample ID	Moisture Content (%)	Before Spray (µmol/g)		After Spray (µmol/g)		Fraction of target dose observed (%)
		Naled	Dichlorvos	Naled	Dichlorvos	
Beach Sand	0.61	ND	ND	ND	0.00275	12.9
Marl	2.14	ND	ND	ND	0.00194	9.1
Calcinated Sand	1.45	ND	ND	ND	0.00110	5.2

ND = Not Detected
Detection limits: naled = 0.0001 µmol/g, dichlorvos = 0.0002 µmol/g
Practical limit of quantification: naled = 0.0003 µmol/g, dichlorvos = 0.0005 µmol/g

Two different studies conducted after an aerial spray in the Florida Keys also found that the amount detected at ground level on filter paper samplers (Barger et al. 2020) or cellulose pads (Hennessey et al. 1992) was less than the target spray amount. In the Barger et al. (2020) study, the amount found on filter paper collected one hour after the aerial spray varied from 27 to 41% of the original target dose (0.00186 µmol/cm^2). In Hennessey et al. (1992) study, the amount of recovered naled on cellulose pads was lower than 1% of the original target dose of 0.00207 µmol/cm^2 when sampled at times of 1.5 and 6 hours after the aerial spray (Hennessey et al. 1992). Hennessey et al. (1992) also found no statistical difference in the amount of naled detected between 1.5 hours and 6 hours. Dichlorvos was not measured in the Florida Keys study. The significant natural decomposition of naled observed in the current study (>99.5% for naled in the current study) is thus consistent with the Hennessey et al. study that measured 99% natural decomposition of naled at ground level. The fate of the lost naled and dichlorvos should be investigated further, especially in light of the finding that degradation products of dichlorvos in air under sunlight conditions can be toxic through the generation of phosgene (Feigenbrugel et al. 2006).

Overall, the results of this study provide preliminary information needed to assess persistence of naled and dichlorvos in coastal sediments in response to an urgent concern by the public after intensive mosquito control activities during the Zika outbreak in south Florida. Results show that in spite of the large losses of measured active ingredient at ground level, dichlorvos was measured at levels of 0.00275 µmol/g in beach sands one hour after aerial sprays. The no observable adverse effect level (NOAEL) for cholinesterase inhibition for repeat exposures is 0.45 µmol of dichlorvos per kg body weight per day (U.S. EPA 2006). The NOAEL assuming no safety factor and assuming that 100 percent of the dichlorvos is absorbed would correspond to 164 grams of sand per kg body weight per day. It is unknown if this level is reasonable given the potential exposure scenarios at beaches. A risk assessment is recommended to evaluate whether the levels observed in beach sand are acceptable, given the typical activities that take place at recreational beach sites. Further research is warranted to evaluate the time sequence of naled and dichlorvos degradation (including full characterization of degradation byproducts) in beach sands, which will help public health professionals identify periods during which the beaches should be closed after aerial spray activities. In summary, the results of the current study can be used in risk assessments that consider both naled and dichlorvos on beaches to better understand ecological impacts and to develop improved public health recommendations.

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References

AMVAC Chemical Corporation, 2011. Dibrom Emulsive, Material Safety Data Sheet. Available on-line at http://amvac-chemical.com/products/documents/DIBROM%208%20Emulsive%20254_14.pdf. Accessed October 20, 2016.

Agency for Toxic Substances and Disease Registry (ATSDR), 1997. Toxicological Profile for Dichlorvos. U.S. Dept of Health and Human Services, ATSDR, Division of Toxicology and Toxicology Information Branch. Atlanta, GA.

Asemoloye, M.D., Jonathan, S.G., Ahmad, R., 2019. Degradation of 2, 2-Dichlorovinyl Dimethyl Phosphate (Dichlorvos) through the Rhizosphere Interaction between Panicum Maximum Jacq and Some Selected Fungi. *Chemosphere*, 221: 403-411.

Bargar, T.A., Anderson, C.. Sowers, A., 2020. Mortality and Cholinesterase Inhibition in Butterflies Following Aerial Naled Applications for Mosquito Control on the National Key Deer Refuge. *Arch Environ Contam Toxicol*, 79**:** 233–245.

Bilal, M., Hafiz, M.N. Iqbal, H.M.N., Barceló, D., 2019. Persistence of Pesticides-Based Contaminants in the Environment and their Effective Degradation using Laccase-assisted Biocatalytic Systems. *Science of The Total Environment*, 695: 133896.

Britch, S.C., Linthicum, K.J., Aldridge, R.L., Breidenbaugh, M.S., Latham, M.D., Connelly, P.H., Rush, M.J.E., Remmers, J.L., Kerce, J.D., Silcox, C.A., 2018. Aerial ULV Control of *Aedes Aegypti* with Naled (Dibrom) inside Simulated Rural Village and Urban Cryptic Habitats. *PLoS ONE* 13(1): e0191555.

Bustos, N., Cruz-Alcalde, A., Iriel, A., Fernández Cirelli, A., Sans, C, 2019. Sunlight and UVC-254 irradiation induced photodegradation of organophosphorus pesticide dichlorvos in aqueous matrices. *Science of The Total Environment*, 649, 592–600.

Centers for Disease Control and Prevention (CDC), 2019. 2016 Case Counts in the U.S. https://www.cdc.gov/zika/reporting/2016-case-counts.html (accessed on July 1, 2019).

Chen, J., Beier, J.C., Cantrell, R.S., Cosner, C., Fuller, D.O., Guan, Y., Zhang, G., Ruan, S., 2018. Modeling the Importation and Local Transmission of Vector-borne Diseases in Florida: The case of Zika outbreak in 2016. *Journal of Theoretical Biology*, 455: 342-356.

Čolović, M.B., Krstić, D.Z., Lazarević-Pašti, T.D., Bondžić, A.M., Vasić, V.M., 2013. Acetylcholinesterase Inhibitors: Pharmacology and Toxicology. *Current Neuropharmacology*, 11: 315-335.

Duirk, S. E., Desetto, L. M., Davis, G. M., 2009. Transformation of Organophosphorus Pesticides in the Presence of Aqueous Chlorine: Kinetics, Pathways, and Structure-Activity Relationships. *Environmental Science & Technology*, 43: 2335-2340.

Eisenreich, S.J., Looney, B.B., Thornton, J.D., 1981. Airborne Organic Contaminants in the Great Lakes Ecosystem. *Environmental Science & Technology*, 15(1): 30-38.

Faust, S.D., Suffet, I.H., 1966. Recovery, Separation, and Identification of Organic Pesticides from Natural and Potable waters. *Residue Reviews*, 15: 44-116.

Feigenbrugel, V., Le Person, A., Le Calvé, S., Mellouki, A., Muñoz, A., and Wirtz, K., 2006. Atmospheric Fate of Dichlorvos: Photolysis and OH-Initiated Oxidation Studies. *Environmental Science & Technology*, 40: 850-857.

Florida Department of Health (FDOH), 2019. About Zika. https://zikafreefl.org/about-zika/ (accessed July 1, 2019)

Gan, Q., Singh, R.M., Jans, U., 2006a. Degradation of Naled and Dichlorvos Promoted by Reduced Sulfur Species in Well-defined Anoxic Aqueous Solutions. *Environmental Science and Technology*, 40 (3): 778-783.

Gan, Q., Singh, R.M., Wu, T., Jans, U., 2006b. Kinetics and Mechanism of Degradation of Dichlorvos in Aqueous Solutions Containing Reduced Sulfur Species. *Environmental Science and Technology*, 40 (18): 5717-5723.

Hemme, R. R., Vizcaino, L., Harris, A. F., Felix, G., Kavanaugh, M., Kenney, J. L., Nazario, N.M., Godsey, M.S., Barrera, R., Miranda, J., Lenhart, A., 2019. Rapid Screening of Aedes Aegypti Mosquitoes for Susceptibility to Insecticides as Part of Zika Emergency Response, Puerto Rico. *Emerging Infectious Diseases*, *25*(10): 1959-1961.

Hennessey, M.K., Nigg, H.N., Habeck, D.H., 1992. Mosquito (Diptera: Culicidae) Adulticide Drift into Wildlife Refuges of the Florida Keys. *Environmental Entomology*, 21(4): 714-721.

Howard, P.H., 1991. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Lewis Publishers, Chelsea, MI.

Jones, A.S., Cohen, D., Alberdi, F., Sanabria, A., Clausell, N., Roca, M., Fionah, A.K., Kumar, N., Solo-Gabriele, H.M., Zahran, E., 2020. Persistence of Aerially Applied Mosquito-Pesticide, Naled, in Fresh and Marine Waters. *Science of the Total Environment*, 725, 138391.

Kenaga, E.E., 1980. Predicted Bioconcentration Factors and Soil Sorption Coefficients of Pesticides and Other Chemicals. *Ecotoxicology and Environmental Safety*, 9(4): 26-38.

Latif, S., Haken, J.K., Wainwright, M.S., 1984. Gas Chromatographic Analysis of Insecticidal Preparations Using Carbon Dioxide Propellants. *Journal of Chromatography*, 287: 77-84.

Li, Y., 2015. Calcarous soils in Miami-Dade County, Document SL 183. University of Florida, Soil and Water Science Department, UF/IFAS Extension. Original publication date July 2001. Reviewed October 2015. Visit the EDIS website at http://edis.ifas.ufl.edu.

Menzie, C.M., 1972. Fate of Pesticides in the Environment. *Annual Reviews of Entemology*, 17: 199-222.

National Pesticide Information Center (NPIC), 1996. Extoxnet Extension Toxicology Network, Pesticide Information Profiles, Naled. Available at: http://extoxnet.orst.edu/pips/naled.htm

Patty, D. J., Loupatty, G., Sopalauw, F., 2017. Interpretation FTIR spectrum of seawater and sediment in the Ambon Bay (TAD). *The 6th International Conference on Theoretical and Applied Physics*, 1801, 060005-1–060005-6.

Sattar, M.A., 1990. Fate of Organophosphorus Pesticides in Soils. Chemosphere, 20 (3/4): 387-396.

Schmidt, C.W., 2016. Zika in the United States, How are We Preparing? *Environmental Health Perspectives*, 124(9): A157-A165.

Schleier, J. J., Peterson, R. K., 2009. Deposition and Air Concentrations of Permethrin and Naled Used for Adult Mosquito Management. *Archives of Environmental Contamination and Toxicology*, 58(1), 105–111.

Sleiman, M., Ferronato, C., Chovelon, J.-M., 2008. Photocatalytic Removal of Pesticide Dichlorvos from Indoor Air: A Study of Reaction Parameters, Intermediates, and Mineralization. *Environmental Science & Technology*, 42: 3018-3024.

Song, Z., Chouparova, E., Jones, K. W., Feng, H., Marinkovic, N. S., 2001. FTIR Investigation of Sediments from NY/NJ Harbor,San Diego Bay, and the Venetian Lagoon. *NSLS Activity Report,* 2, 112–16.

Stoddard, P.K., 2018. Managing Aedes Aegypti Populations in the First Zika Transmission Zones in the Continental United States. *Acta Tropica*, 187: 108-118.

Suzuki, T., Kondo, H., Yaguchi, K., Maki, T., Suga, T., 1998. Estimation of Leachability and Persistence of Pesticides at Golf Courses from Point-source Monitoring and Model to Predict Pesticide Leaching to Groundwater. *Environmental Science & Technology*, 32: 920-929.

Tietze, N.S., Shaffer, K.R., Hester, P.G., 1996. Half-life of Naled under Three Test Scenarios. *Journal of the American Mosquito Control Association*, 12 (2 part 1): 251-254.

U.S. Environmental Protection Agency (EPA), 2006. Interim Reregistration Eligibility Decision for Dichlorvos (DDVP). EPA Office of Pesticide Programs. EPA 738-R-06-013 (June 2006).

U.S. Environmental Protection Agency (U.S. EPA), 2015. SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods; Office of Resource Conservation and Recovery: Washington, DC, USA. http://www3.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm (accessed on March 10, 2019).

University of Florida (UF), IFAS Extension (UF), 2019. Pesticides and Cholinesterase. https://edis.ifas.ufl.edu/pi221 (Accessed July 4, 2019).

Zhang, Q., Qu, X., Wang, W., 2007. Mechanism of OH-initiated Atmospheric photooxidation of Dichlorvos: A Quantum Mechanical Study. *Environmental Science & Technology*, 41: 6109-6116.