# FINAL DATA REPORT FOR THE VIEQUES ISLAND BIOTA SAMPLING PROJECT

VIEQUES ISLAND, PUERTO RICO

# PREPARED BY

# NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION NATIONAL OCEAN SERVICE OFFICE OF RESPONSE AND RESTORATION

**AND** 

RIDOLFI Inc.





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# INFORME FINAL DE DATOS PARA EL PROYECTO DE MUESTREO BIOTA EN LA ISLA DE VIEQUES

# ISLA DE VIEQUES, PUERTO RICO

Preparado por

Administración Nacional Oceánica y Atmosférica Servicio Nacional de Océanos Oficina de la Respuesta y la Restauración

> y RIDOLFI Inc.

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# **RECONOCIMIENTOS**

Este estudio fue financiado en su totalidad por la Administración Nacional Oceánica y Atmosférica (NOAA, por sus siglas en inglés). Las muestras de cangrejos para este estudio se recolectaron con la colaboración de miembros del Servicio de Pesca y Vida Silvestre de EE.UU., la Agencia de Protección Ambiental de EE.UU. y la Junta de Calidad Ambiental de Puerto Rico (JCA). Un experto en materiales explosivos de la Marina de EE.UU. acompañó al equipo de recolección de muestras en las zonas donde está restringido el acceso al público.

# **CITATION**

National Oceanic and Atmospheric Administration and RIDOLFI Inc. (NOAA and Ridolfi).

2006. Final Data Report for the Vieques Island Biota Sampling Project, Vieques Island, Puerto Rico. NOAA, National Ocean Service, Office of Response and Restoration. Seattle, WA.

# **CONTACT INFORMATION**

For more information about this report or to obtain a copy, please visit <HTTP://mapping.orr.noaa.gov/website/portal/vieques/projectscrab.html> or contact Mike Buchman, NOAA/NOS/OR&R at (206) 526-6340.

### **EXECUTIVE SUMMARY**

In June 2005, the National Oceanic and Atmospheric Administration (NOAA) Office of Response and Restoration (ORR) conducted an investigation of land crab (*Cardisoma guanhumi*) and fiddler crab (*Uca spp.*) from Vieques Island, Puerto Rico. Assistance was provided by the U.S. Fish and Wildlife Service (USFWS), the U.S. Environmental Protection Agency (USEPA), the Puerto Rico Environmental Quality Board (EQB), and RIDOLFI Inc. under contract to NOAA. The primary purpose of the investigation was to characterize concentrations of explosive compounds, polychlorinated biphenyls (PCBs), organochlorine pesticides, and trace elements in land and fiddler crab. In addition, the Agency for Toxic Substances and Disease Registry (ATSDR) has used the land crab data presented in this report to write a Public Health Consultation (PHC), which is included in this report as Appendix H. Prior, limited investigations have been conducted by the ATSDR, the USFWS, and researchers from the University of Puerto Rico: this investigation was designed in part to build upon those previous efforts.

Results from the evaluations by ATSDR and NOAA will assist the USFWS in determining whether selected refuge areas can be opened to crab harvesting. In the future, the U.S. Navy, the USEPA, and the Puerto Rico EQB may also use portions of the land and fiddler crab data, as appropriate, in a full human health and ecological risk assessment for portions of Vieques Island.

From the 1940s until 2003, a portion of Vieques Island was used for military training exercises (gunfire and bombing). In 2001, the U.S. Navy transferred ownership of approximately 3,000 hectares (7,500 acres) of land on the west end of the island to the municipality of Vieques, the Puerto Rico Conservation Trust, and the USFWS. On May 1, 2003, the U.S. Navy ceased all military operations on and around the island and transferred its property on the east end of the island (approximately 5,800 hectares [14,575 acres]) to the USFWS. The land on the east end of the island and the land controlled by the USFWS on the west end of the island were then designated a national wildlife refuge. Approximately 9,300 Puerto Ricans live in the residential section of the island, which lies between the east and west ends. Land crab are an important subsistence resource to these islanders.

For the current investigation, land and fiddler crab were sampled from mudflats, mangrove wetlands, coastal forested areas, and sandy areas on the east and west ends of Vieques Island. Land crab were collected because of their importance in the diet of the island's residents. Fiddler crab were collected because they live in similar habitats, yet represent a slightly different pathway in the food web and serve as an additional indicator species for potential contaminant uptake. Because of their small size, a composite sample of fiddler crab also represents a far greater number of individuals per sampling station than is possible with the land crab.

Five to six individual land crab were collected from each of 12 sampling locations, which mainly represented potential or known harvest areas. Two reference locations of similar habitat were also sampled. Three composite samples of fiddler crab were collected at each of 12 sampling locations and one reference location: no fiddler crab were present at the on-island, Blue Horizon reference site. Following sample collection, the land crab and fiddler crab were processed and shipped according to the methods described in the *Final Sampling and Analysis Plan for the Vieques Island Biota Sampling Project*. Individual whole body land crab samples and composite, whole-body fiddler crab samples were analyzed for explosive compounds, PCBs, organochlorine pesticides, and trace elements. A limited number of land crab samples were subdivided into exoskeleton (i.e., the carapace and other parts of the shell) and soft tissue-only samples and these fractions were analyzed separately for trace elements. All analytical data were independently reviewed and validated to ensure their usability.

The fiddler crab data were compared to conservative ecological screening benchmarks; these conservative values provide a high degree of confidence that contaminant concentrations that do not exceed the benchmarks will not pose substantial adverse risk. Conversely, contaminant concentrations in excess of the conservative benchmarks do not necessarily indicate a definitive problem, but indicate the need for more detailed evaluations. Some of the benchmarks are specific to the protection of crab; when crustacean-specific benchmarks were not available, benchmarks protective of wildlife that eat contaminated prey (birds or small mammals) were used. Land crab data were also compared to just the crustacean-specific benchmarks, which include all organic benchmarks, cadmium, mercury, and vanadium.

Results generally indicate minimal occurrence of organic chemicals. Concentrations of many organic chemicals were below the sample-specific method detection limits (MDLs), and many of the detected values were just slightly above the MDLs. Explosive compounds were not detected in any land or fiddler crab. PCB compounds were detected in samples from only one area: Aroclor 1260 was found in a single land crab sample from Laguna Kiani, while Aroclor 1254 was found in all three fiddler crab composites from that sampling location. PCB concentrations in the crab samples, however, were well below the conservative ecological screening benchmark. PCBs have been reported by the U.S. Navy in the groundwater at Laguna Kiani in the past.

Unlike other organics, organochlorine pesticides, predominantly DDT and its metabolites, were detected in multiple land and fiddler crab samples. Levels of total DDT were generally higher in fiddler crab than in land crab, but there was concordance between the two species in the general pattern of sites having the highest average concentrations. Laguna Kiani, Red Beach, Blue Beach, and Bahia Tapon displayed higher concentrations of total DDT in both land and fiddler crab. The composition of DDT compounds does not suggest ongoing releases. These results are similar to those found in previous investigations.

The second most commonly detected pesticide was chlordane and its related compounds. Chlordane compounds were detected near the MDL in land crab from half of the sampling areas, including the on-island Blue Horizon reference location. Total chlordane (the sum of eight compounds) was detected at concentrations usually near the MDL in fiddler crab from all sampling locations except Mosquito Bay, including samples from the Humacao Wildlife Reserve reference location on mainland Puerto Rico. Again, there was concordance between the two species, with Laguna Kiani and Bahia Tapon having the highest total chlordane levels.

The occurrence of other pesticides was generally limited and sporadic. Aldrin, endrin, and dieldrin were detected at one to two sites each. Mirex was observed in most land crab and all fiddler crab samples only from the Live Impact Area (LIA). No pesticide concentrations in land or fiddler crab exceeded any ecological screening benchmarks.

As in previous investigations, trace elements were ubiquitously detected in both land and fiddler crab samples across all sampling locations. The widespread detection of numerous trace

elements in crab samples likely reflects exposure to elements naturally occurring in soil, sediment, groundwater, and surface water. Elevated levels, especially those significantly greater than the reference site, tend to suggest the potential for exposure to anthropogenic sources. In general, the results are variable. Differences were observed both within and among sampling areas, from element to element, and between the two crab species. However, there were observations of concordance between the two species that tend to suggest consistent exposures.

In land crab, average concentrations of beryllium, iron, mercury, selenium, thallium, uranium, vanadium, and zinc were either not different among locations or were not significantly greater than concentrations at the reference locations. For all other trace elements, at least one area had significantly greater concentrations than were observed at a reference location. However, in some cases this was because of elevated concentrations measured in a single crab.

In its PHC, the ATSDR concluded that levels of PCBs, organochlorine pesticides, and trace elements found in land crab were much lower than levels reported in the scientific literature as causing harmful health effects. Therefore, the ATSDR does not expect harmful health effects to occur in adults and children as a result of eating land crabs from Vieques Island. DDE concentrations were also below the Food and Drug Administration's regulatory limit for shellfish consumption.

The land crab data were also screened against ecological screening benchmarks for cadmium, mercury, and vanadium meant to be protective of other crustacean species. All concentrations of mercury were below the ecological screening benchmark. Vanadium concentrations were either below the MDL or above the screening benchmark. Average vanadium among areas did not differ from means observed from either reference though, suggesting that vanadium levels may represent baseline conditions. The cadmium benchmark was exceeded in four samples from three sampling locations (Boca Quebrada, Laguna Kiani, and the LIA). Levels in crab from the LIA were significantly greater than those from either reference. This ecological screening indicates that the possibility of adverse impacts to land crab due to the body burden of cadmium, and perhaps vanadium, cannot be eliminated for some specific areas.

One land crab from each sampling area was dissected into exoskeleton and soft tissue fractions, which were analyzed separately for trace elements. The purpose was to evaluate the two fractions for indications of preferential bioconcentration. In general, more compounds were detected in the soft crab tissue than in the exoskeleton. The exoskeletons did not contain beryllium, mercury, or selenium. Concentrations of half of all detected trace elements were greater in the exoskeleton than in the soft tissue; concentrations of barium, calcium, chromium, and magnesium were at least an order of magnitude greater. Average cadmium, copper, silver, and zinc concentrations were three to ten times higher in the soft tissue.

Concentrations of beryllium, manganese, mercury, nickel, thallium, and uranium in fiddler crab did not exceed ecological screening benchmarks in any samples. No benchmarks were available for cobalt, iron, and silver. Concentrations of ten trace elements measured in fiddler crab exceeded ecological screening benchmarks in one or more samples. Of these, aluminum, arsenic, vanadium, and zinc exceeded wildlife screening benchmarks in all samples from all sampling areas, including the reference location. Concentrations of barium, cadmium, chromium, copper, and selenium exceeded screening benchmarks to varying degrees and at various locations. Lead concentrations exceeded the benchmark at only one location (Laguna Kiani). Three of the compounds that exceeded benchmarks (cadmium, lead, and selenium) were not detected in the Humacao Wildlife Reserve reference samples at concentrations above the benchmarks.

The occurrence of PCBs in both land crab and fiddler crab from Laguna Kiani, which is coincident with past reports by the US Navy of PCBs in groundwater at this same site, demonstrate that PCBs at this location are bioavailable and capable of entering the food web. The co-occurrence of maximum concentrations of other contaminants in these same samples for both species suggests that other contaminant releases may be occurring within this area as well. Although the concentrations of organics reported here are below screening benchmarks, the limited extent of sampling in this preliminary study makes it difficult to draw firm conclusions regarding the degree of risk that releases at this site may pose. Further characterization of the nature and extent of releases at this site is recommended as part of the ongoing remedial investigation or as monitoring to verify the effectiveness of removal actions.

The concordance observed between the two species in some contaminants detected may indicate exposure pathways at other sites as well. Examples include mirex, arsenic, and cadmium observed at the LIA and total DDT at Blue Beach, Red Beach, and Bahia Tapon. Although values were below screening benchmarks, these observations demonstrate an exposure mechanism for these areas.

The screening-level assessment presented in this report should not be viewed as a full ecological risk assessment. This screening assessment applied conservative assumptions about exposure that are not necessarily realistic or appropriate for characterizing actual risk. Instead, it offers a high level of confidence in determining situations where a low probability of adverse impacts are present, and facilitates determining the need for, and degree of, further investigation. The screening-level assessment acknowledges that any chemical concentrations exceeding the conservative benchmark values may be considered *potentially* hazardous, although they are not necessarily so until further, more realistic, site-specific assessments determine this. The preliminary screening of crab chemical body burdens presented here cannot eliminate the possibility that some analytes may be present at levels sufficiently high to cause adverse impacts to crab. To fully identify and characterize potential risk to the environment, further analysis of appropriate portions of these data, as well as evaluations for other ecological receptors, may be warranted, particularly with regard to PCBs, total DDT, and some trace elements. The need for additional evaluation, as applicable, should be determined in the human health and environmental risk assessment activities required for the ongoing remedial investigation of sites on Viegues Island.

# **RESUMEN EJECUTIVO**

En junio de 2005, la Oficina de la Respuesta y la Restauración de la Administración Nacional Oceánica y Atmosférica (ORR, NOAA, por sus siglas en inglés, respectivamente) llevó a cabo una investigación sobre el cangrejo terrestre (*Cardisoma guanhumi*) y el cangrejo violinista (*Uca spp.*) en la Isla de Vieques, Puerto Rico, en colaboración con el Servicio de Pesca y Vida Silvestre de EE.UU. (USFWS, por sus siglas en inglés), la Agencia de Protección Ambiental de EE.UU. (USEPA, por sus siglas en inglés), la Junta de Calidad Ambiental de Puerto Rico (JCA) y RIDOLFI Inc. bajo contrato con NOAA. El propósito principal de la investigación fue definir las concentraciones de compuestos de explosivos, policlorobifenilos (PCB), pesticidas organoclorados y oligoelementos en los jueyes y en los cangrejos violinistas. Además, la Agencia para Sustancias Tóxicas y Registro de Enfermedades (ATSDR, por sus siglas en inglés) ha utilizado los datos obtenidos del cangrejo terrestre presentados en este informe para redactar una Consulta de Salud Pública (CSP), que se incluye en este informe como Apéndice H. Anteriormente, ATSDR, USFWS e investigadores de la Universidad de Puerto Rico han realizado investigaciones limitadas: esta investigación fue diseñada en parte para ampliar estos esfuerzos previos.

Los resultados de las evaluaciones de ATSDR y NOAA ayudarán a USFWS a determinar si las áreas de refugio seleccionadas pueden abrirse para la cría de cangrejos. En el futuro, la Marina de EE.UU., USEPA y JCA de Puerto Rico también pueden utilizar porciones de los datos sobre el cangrejo terrestre y sobre el cangrejo violinista, según el caso, en una completa evaluación de los riesgos para la salud humana y la ecología en áreas de la Isla de Vieques.

Desde los años 1940 hasta 2003, una parte de la Isla de Vieques se utilizó para ejercicios de entrenamiento militar (fuego de artillería y bombardeos). En 2001, la Marina de Estados Unidos traspasó la propiedad de aproximadamente 3.000 hectáreas (7.500 acres) de tierra en el extremo occidental de la isla al municipio de Vieques, al Fideicomiso de Conservación de Puerto Rico y a USFWS. El 1º de mayo de 2003, la Marina de Estados Unidos suspendió todas las operaciones militares en y alrededor de la isla y traspasó su propiedad en el extremo oriental de la isla (aproximadamente 5.800 hectáreas [14.575 acres]) a USFWS. Las tierras del extremo oriental de la isla y las controladas por USFWS en el extremo occidental de la isla se declararon entonces

refugio natural nacional. Aproximadamente 9.300 puertorriqueños viven en la zona residencial de la isla, que se extiende entre los extremos oriental y occidental.

Para la presente investigación, se recolectó muestras de jueyes y de cangrejos violinistas en marismas, manglares, zonas boscosas costeras y áreas arenosas de los extremos oriental y occidental de la Isla de Vieques. Se recolectó jueyes debido a su importancia en la dieta de los residentes isleños. Se recolectó cangrejos violinistas porque viven en hábitats similares, aunque representan una vía ligeramente diferente en la red alimenticia y sirven como especie indicadora adicional de la captación de contaminantes potenciales. Debido a el pequeño tamaño de los cangrejos violinista, una muestra compuesta del cangrejo violinista también representa un número mucho mayor de individuos por estación de muestreo que la posible con el cangrejo terrestre.

Se recolectó entre cinco y seis especimenes de jueyes en cada uno de los 12 sitios de muestreo, los cuales representaron principalmente zonas conocidas o potenciales para la captura, más dos sitios de referencia de hábitat similar. Se recolectó tres muestras compuestas de cangrejos violinistas en cada uno de los 12 sitios de muestreo y en un sitio de referencia: no hubo cangrejos violinistas presentes en el sitio de referencia Blue Horizon en la isla. Tras la recolección de las muestras, los jueyes y los cangrejos violinistas fueron procesados y enviados de acuerdo con los métodos descritos en el *Plan Definitivo de Análisis y Muestreo para el Proyecto de Muestreo Biota en la Isla de Vieques*. Se analizó muestras individuales del cuerpo entero de jueyes y muestras compuestas de cangrejos violinistas para hallar compuestos de explosivos, PCB, pesticidas organoclorados y oligoelementos. Un número limitado de muestras de jueyes se subdividió en muestras de exoesqueleto (es decir, el caparazón y otras partes duras externas) y muestras de tejido blando solamente y se analizaron en forma independiente para hallar oligoelementos. Todos los datos del análisis se revisaron y validaron independientemente para asegurar su efectividad.

Los datos sobre el cangrejo violinista se compararon con puntos de referencia conservadores de comprobación ecológica; tales valores conservadores proporcionan un alto grado de confianza en cuanto a que las concentraciones de contaminantes que no exceden los puntos de referencia no plantean riesgos desfavorables significativos. Por el contrario, las concentraciones de

contaminantes que superan los puntos de referencia conservadores no necesariamente indican problemas, pero señalan la necesidad de evaluaciones más detalladas. Algunos de los puntos de referencia son específicos para la protección del cangrejo; se usó puntos de referencia protectores de la vida silvestre que consume presas contaminadas cuando no hubo disponibilidad de puntos de referencia específicos para crustáceos. Los datos sobre los jueyes también se compararon con los puntos de referencia específicos para crustáceos solamente, los cuales incluyen todos los compuestos orgánicos, cadmio, mercurio y vanadio.

Los resultados en general indican mínima presencia de químicos orgánicos. Las concentraciones de muchos químicos orgánicos estuvieron por debajo de los límites de detección por método específico a la muestra (LDM) y muchas de las detecciones estuvieron apenas ligeramente por encima de los LDM. No se detectó compuestos de explosivos en los jueyes ni en los cangrejos violinista. Se detectó compuestos de PCB en las muestras de una sola área: se descubrió Aroclor 1260 en una sola muestra de juey en Laguna Kiani, mientras se halló Aroclor 1254 en todos los tres compuestos de cangrejos violinistas en ese sitio de muestreo. Sin embargo, las concentraciones de PCB en las muestras de cangrejos estuvieron bien por debajo de los puntos de referencia conservadores ecológica. En el pasado, la Marina de Estados Unidos ha informado acerca de presencia de PCB en las aguas subterráneas de Laguna Kiani.

Se detectó pesticidas organoclorados, predominantemente DDT y sus metabolitos, en muchas muestras de jueyes y de cangrejos violinistas. Los niveles de DDT total fueron generalmente más altos en los cangrejos violinistas que en los jueyes, pero hubo concordancia entre las dos especies en el patrón general de los sitios que tenían las concentraciones promedio más altas. Laguna Kiani, Red Beach, Blue Beach y Bahía Tapón mostraron concentraciones más altas de DDT total tanto en jueyes como en cangrejos violinistas. La constitución de los compuestos de DDT no sugiere emisiones continuas. Estos resultados son similares a los concluidos en investigaciones precedentes.

El segundo pesticida más comúnmente encontrado fue el clordano y sus compuestos relacionados. Se detectó compuestos del clordano cercanos a los LDM en los jueyes de la mitad de las áreas de muestreo, incluyendo el sitio de referencia Blue Horizon en la isla. El clordano total (la suma de sus ocho compuestos) se detectó en concentraciones generalmente cercanas a

los LDM en los cangrejos violinistas de todos los sitios de muestreo, excepto en Mosquito Bay, incluyendo muestras del sitio de referencia Reserva Natural de Humacao, en tierra firme de Puerto Rico. Una vez más, hubo concordancia entre las dos especies, donde Laguna Kiani y Bahía Tapón tuvieron los niveles más altos de clordano total.

La incidencia de otros pesticidas por lo general fue limitada y esporádica. Se detectó aldrino, endrino y dieldrino en uno o dos sitios cada uno. Se observó mirex en la mayoría de muestras de jueyes y en todas las muestras de cangrejos violinistas solamente en la Zona de Tiro. Ninguna concentración de pesticidas en los jueyes o cangrejos violinistas excedió los puntos de referencia ecológica.

Como en investigaciones anteriores, se detectó en todas partes oligoelementos tanto en las muestras de jueyes como en las de cangrejos violinistas en todos los sitios de muestreo. La extensa detección de numerosos oligoelementos en las muestras de cangrejos parece reflejar exposición a elementos que se presentan de forma natural en el suelo, sedimentos, aguas subterráneas y superficiales. Los elevados niveles, especialmente los significativamente mayores al sitio de referencia, tienden a sugerir el potencial para exposición a fuentes antropogénicas. En general, los resultados son variables. Se observó diferencias dentro y entre las áreas de muestreo, de elemento a elemento y entre las dos especies de cangrejos. Sin embargo, hubo observaciones de concordancia entre las dos especies que tienden a sugerir exposiciones constantes.

En los jueyes, las concentraciones promedio de berilio, hierro, mercurio, selenio, talio, uranio, vanadio y zinc no fueron diferentes entre sitios o no fueron significativamente mayores que las concentraciones en los sitios de referencia. Para todos los demás oligoelementos, por lo menos un área tuvo concentraciones significativamente mayores que las que se observaron en un sitio de referencia. Sin embargo, en algunos casos esto ocurrió debido a las elevadas concentraciones medidas en un solo cangrejo.

En su CSP, ATSDR concluyó que los niveles de PCB, pesticidas organoclorados y oligoelementos encontrados en los jueyes fueron mucho más bajos que los reportados en la literatura científica como causantes de efectos perjudiciales para la salud. Por consiguiente, ATSDR no espera que se presenten efectos perjudiciales para la salud en adultos y niños como

resultado del consumo de jueyes en la Isla Vieques. Las concentraciones de DDE también estuvieron por debajo del límite reglamentario de la Administración de Drogas y Alimentos de Estados Unidos para el consumo de mariscos.

También se compararon los datos obtenidos de los jueyes con los s de referencia ecológica en cuanto a cadmio, mercurio y vanadio considerados protectores de otras especies de crustáceos. Todas las concentraciones de mercurio estuvieron por debajo de los puntos de referencia ecológica. Las concentraciones de vanadio estuvieron por debajo de los LDM o por encima del punto de referencia. El vanadio promedio entre áreas no fue diferente de las medias observadas en una u otra referencia, sugiriendo que los niveles de vanadio pueden representar condiciones iniciales. Se excedió el punto de referencia de cadmio en cuatro muestras de tres sitios de muestreo (Boca Quebrada, Laguna Kiani y la Zona de Tiro). Los niveles en los cangrejos de la Zona de Tiro fueron significativamente mayores que los de una u otra referencia. Esta investigación ecológica indica que la posibilidad de impacto desfavorable para el cangrejo terrestre debido a la carga corporal de cadmio, y tale vez vanadio, no puede eliminarse para algunas áreas específicas.

Un juey de cada área de muestreo se diseccionó en exoesqueleto y fracciones de tejido blando, los cuales fueron analizados en forma independiente para hallar oligoelementos. El propósito fue evaluar las dos fracciones en busca de indicadores de bioconcentración preferencial. En general, se detectó más compuestos en el tejido blando del cangrejo que en el exoesqueleto, el cual no contuvo berilio, mercurio ni selenio. Las concentraciones de la mitad de todos los oligoelementos detectados fueron mayores en el exosqueleto que en el tejido blando; las concentraciones de bario, calcio, cromo y magnesio fueron por lo menos un orden de magnitud mayor. Las concentraciones promedio de cadmio, cobre, plata y zinc fueron tres a diez veces más altas en el tejido blando.

Las concentraciones de berilio, manganeso, mercurio, níquel, talio y uranio en el cangrejo violinista no superaron los puntos de referencia ecológica en las muestras. No hubo puntos de referencia ecológica disponibles para cobalto, hierro y plata. Las concentraciones de diez oligoelementos medidos en el cangrejo violinista excedieron los puntos de referencia ecológica en una o más muestras. De éstos, aluminio, arsénico, vanadio y zinc excedieron los puntos de

referencia ecológica de vida silvestre en todas las muestras de todas las áreas de muestreo, incluyendo el sitio de referencia. Las concentraciones de bario, cadmio, cromo, cobre y selenio excedieron los puntos de referencia ecológica a grados variantes y en diversos sitios. Las concentraciones de plomo excedieron el punto de referencia en solo un sitio (Laguna Kiani). Tres de los compuestos que excedieron los puntos de referencia ecológica (cadmio, plomo y selenio) no fueron detectados en las muestras de referencia de la Reserva Natural de Humacao en concentraciones por encima de los puntos de referencia ecológica.

La incidencia de PCB tanto en el juey como en el cangrejo violinista de Laguna Kiani, que coincide con informes anteriores sobre PCB de la Marina de Estados Unidos en aguas subterráneas en este mismo sitio, demuestran que PCB en este lugar es biodisponible y capaz de entrar en la red alimenticia. La copresencia de máximas concentraciones de otros contaminantes en estas mismas muestras para ambas especies sugiere que las emisiones de otros contaminantes se pueden estar presentando también dentro de esta área. Aunque las concentraciones de orgánicos reportadas aquí están por debajo de los puntos de referencia ecológica, el grado limitado de muestreo en este estudio preliminar hace difícil sacar conclusiones firmes e relación con el grado de riesgo que puedan plantear las emisiones en este sitio. Además la definición de la naturaleza y grado de las emisiones en este sitio se recomienda como parte de una investigación correctiva continuada o como monitoreo para verificar la eficacia de las acciones de remoción.

La concordancia observada entre las dos especies en algúnes contaminantes detectado puede indicar trayectorias de exposición en otros sitios también. Los ejemplos incluyen mirex, arsénico y cadmio en la Zona de Tiro y DDT total en Blue Beach, Red Beach y Bahía Tapón. Aunque los valores estuvieron por debajo de los puntos de referencia ecológica, estas observaciones demuestran un mecanismo de exposición para estas áreas.

La evaluación presentada en este informe no debe considerarse como una evaluación completa de riesgos ecológicos. Esta evaluación aplicó suposiciones conservadoras acerca de la exposición que no son necesariamente reales o adecuadas para definir el riesgo real. Más bien, ofrece un alto nivel de confianza en la determinación de situaciones donde la baja probabilidad de impacto desfavorable está presente, y facilita determinar la necesidad de, y el grado de, más investigación. Este evaluación reconoce que las concentraciones químicas que superan los

valores de referencia conservadores pueden considerarse *potencialmente* peligrosas, aunque no lo sean necesariamente hasta que otras evaluaciones más realistas, específicas al sitio lo determinen. La comprobación preliminar de los residuos de tejido de cangrejo presentes aquí no puede eliminar la posibilidad de que algunos analitos puedan estar presentes en niveles los suficientemente altos para causar impacto desfavorable al cangrejo. Para identificar y definir completamente el riesgo potencial al medio ambiente, se justifica más análisis de las porciones correspondientes de estos datos, como también evaluaciones de otros receptores ecológicos, particularmente con respecto a PCB, DDT total y algunos oligoelementos. La necesidad de evaluación adicional, cuando proceda, debe determinarse en las actividades de evaluación de riesgos para la salud humana y para la ecología requeridas para la investigación correctiva continuada de los sitios en la Isla de Vieques.

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# LIST OF ABBREVIATIONS AND ACRONYMS

AOC Area of Concern

ATSDR Agency for Toxic Substances and Disease Registry

CERCLA Comprehensive Environmental Response, Compensation and Liability Act

EQB Environmental Quality Board (Puerto Rico)

ERED Environmental Residue Effects Database

ESB ecological screening benchmark
FDA Food and Drug Administration

GC gas chromatography

km kilometer

LIA Live Impact Area

MDL method detection limit

mi mile

μg/kg micrograms per kilogram mg/kg milligrams per kilogram

MRL minimal risk level

MS/MSD matrix spike/matrix spike duplicate

NOAA National Oceanic and Atmospheric Administration

NOAEL no observed adverse effects level

NPL National Priorities List

ORR Office of Response and Restoration (NOAA)

PCB polychlorinated biphenyl

PHC Public Health Consultation

PVC polyvinyl chloride

QAPP quality assurance project plan

QA/QC Quality Assurance/Quality Control

RBC risk-based criteria

RCRA Resource Conservation and Recovery Act

RfD reference dose

RI Remedial Investigation

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SAP sampling and analysis plan

SWMU Solid Waste Management Unit

TOXRES Toxicity/Residue (database)

TRV toxicity reference value

USACE U.S. Army Corps of Engineers

USEPA U.S. Environmental Protection Agency

USFWS U.S. Fish and Wildlife Service

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# 1.0 INTRODUCTION

This document describes an investigation of chemical residues in land crab (*Cardisoma guanhumi*) and fiddler crab (*Uca spp.*) tissue samples collected from Vieques Island, Puerto Rico. Crab samples were collected in June 2005 and sent to an analytical laboratory for chemical analysis. The samples were analyzed for explosive compounds, polychlorinated biphenyls (PCBs), organochlorine pesticides, and selected trace elements.

As a natural resource trustee, NOAA provides scientific support to the USFWS, the USEPA, the U.S. Navy, and the EQB for the investigation and cleanup of Vieques Island. Through its participation, NOAA is working to protect coastal resources, mitigate threats to those resources, and restore their ecological function when needed. This investigation was conducted by the National Oceanic and Atmospheric Administration (NOAA) Office of Response and Restoration (ORR) with assistance from the U.S. Fish and Wildlife Service (USFWS), the U.S. Environmental Protection Agency (USEPA), the Puerto Rico Environmental Quality Board (EQB), and RIDOLFI Inc. under contract to NOAA. This study was wholly funded by NOAA.

# 1.1 Purpose of the Investigation

The primary purpose of the investigation was to characterize chemical concentrations in land and fiddler crab from Vieques Island. Although limited crabbing was allowed as a test in an area around Red Beach in June to July 2005 (Diaz pers. comm.), the USFWS currently prohibits the general harvesting of land crab on refuge lands at Vieques Island.

The USFWS will use the data in this report as one factor in deciding whether selected refuge areas can be opened to crab harvesting. In the future, the U.S. Navy, the USEPA, and the Puerto Rico EQB may also use appropriate portions of the land and fiddler crab data as one component of human health and ecological risk assessments for sites on Vieques Island. The land crab data were also provided to the Agency for Toxic Substances and Disease Registry (ATSDR) for use in a Public Health Consultation (PHC). The PHC document is included in the final draft version of this report as Appendix H.

# 1.2 Site Location

Vieques Island is approximately 11 kilometers (km) (7 miles [mi]) southeast of the main island of Puerto Rico (Figure 1-1). The island, which is approximately 34 km (21 mi) long and 5 km (3 mi) wide, is bordered to the north by Vieques Sound and to the south by the Caribbean Sea. Mangrove wetlands, coral reefs, and sea grass beds fringe much of the island. Inland lagoons, streams, and wetland areas provide habitat for crab. The crab samples were collected from a variety of environments, including mostly mud and sand flats, mangrove wetlands, and coastal forested areas on the east and west ends of the island.

# 1.3 Site Characteristics

The habitat types from which samples of land and fiddler crab were collected are briefly described below, as is the geology of Vieques Island. The site geology was reviewed (using information from previous studies) to evaluate whether the minerals in rocks and soils at Vieques Island could contribute to the trace elements observed in crab samples.

# 1.3.1 Habitat Description

Land crab were collected from coastal habitat types, including mangrove wetlands, mud and sand flats, and wet forested/shrub areas. The mangrove wetlands from which some of the land and fiddler crab were collected are composed primarily of red, black, or white mangrove trees or a combination of these species. The mangrove wetlands generally occur as dense thickets along tidal shores that are sheltered from high-energy waves. The coastal forested areas, where additional land crab were collected, are near lagoons or beaches; the dominant tree species in this habitat type is often mesquite. Additional fiddler crab were collected from mud and sand flats near the forested areas where land crab were collected.

# 1.3.2 Site Geology

The bedrock geology of Vieques Island consists primarily of volcanic and volcanoclastic rocks that were intruded by plutonic rocks (igneous rock that has solidified beneath the Earth's surface). Limestone is found along the coastal margin of the island (Torres-Gonzáles 1989). Alluvial sediments, which were deposited by flowing water, are found in the valleys and along

the coastal fringe; beach/dune deposits are also found along the coastal fringe. The mineral composition of these deposits can be expected to reflect their volcanic origin.

Upland soil on Vieques Island ranges from shallow to deep and is well drained. Soil that developed on terraces and alluvial fans is deep and well drained. Volcanically derived soils predominate on the east end of the island, while plutonic- and alluvial-derived soils predominate on the west end of the island. Very poorly drained soils are present on the coastal plain within swamps and marshes (Soil Conservation Service and University of Puerto Rico 1977).

A geochemical reconnaissance of soils on Vieques Island found locally anomalous concentrations of copper, primarily along and attributed to a plutonic/volcanic contact zone that trend southeast from Isabel Segunda and in hydrothermally altered volcanic rocks along the northern coast (Learned et al. 1973). Additional site investigations have been conducted on the west end of Vieques Island to establish background concentrations of explosives, PCBs, and trace elements in abiotic media such as groundwater, soil, surface water, and sediment (CH2M Hill 2002a); details of those investigations are not included in this report.

Unlike the man-made organic chemicals observed during this study, trace elements can have both natural sources. In general, many, if not all, of trace elements can be found in natural materials (e.g., soil, sea salt), and several trace elements are essential nutrients. Analyses from mainland Puerto Rico indicate that nearly all the trace elements analyzed for in this study have been observed in various volcanic soils on the mainland (USGS 2001). However, some trace element levels may sources may be related to human activities. It is often difficult, however, to proportionately attribute chemical body burdens in animals between the potential natural and anthropogenic sources. Evaluation of spatial patterns is one simple approach often used to gain some preliminary insight about potential anthropogenic influences, but such attribution is beyond the scope of this study. At sites where a screening level assessment indicates the potential for exposure and adverse impacts, analysis of the surrounding soil sampled at the same time as tissue sampling is a common subsequent investigational approach to address the causes of elevated tissue concentrations.

# 1.4 Site History

During the early 1940s, the U.S. Navy acquired approximately 10,000 hectares (25,000 acres) on the west and east ends of Vieques Island. From the 1940s until 2003, the U.S. Navy used Vieques Island for munitions storage and military training exercises, which included naval gunfire and aerial bombing. In 2001, the U.S. Navy transferred ownership of approximately 3,000 hectares (7,500 acres) of land on the west end of the island to the municipality of Vieques, the Puerto Rico Conservation Trust, and the USFWS (USEPA 2004). On May 1, 2003, the U.S. Navy ceased all military operations on and around the island and transferred its property on the east end of the island to the USFWS (USEPA 2004). The land on the east end of the island and the land controlled by the USFWS on the west end of the island were then designated a National Wildlife Refuge (some of the land has also been designated as a wilderness area). Any potential for releases of hazardous substances on these refuge lands is related to their history.

Approximately 9,300 civilian Puerto Ricans live in the residential section of the island, which is between the two (west and east) refuge sections (USEPA 2005a).

Since 2000, the U.S. Navy has been working with the USEPA to complete an environmental investigation of the east end of the island under the guidelines of the Resource Conservation and Recovery Act (RCRA). The investigations are organized by areas associated with particular historical activities where releases of hazardous waste or hazardous constituents potentially occurred. These areas are known as Solid Waste Management Units (SWMUs) or Areas of Concern (AOCs).

Investigations of the west end of the island have been and continue to be conducted by the U.S. Navy and the USEPA under the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Certain areas of Vieques Island that have been impacted by military activities plus some of the surrounding waters were placed on the National Priorities List (NPL) in February 2005 (USEPA 2005b). Subsequently, further environmental investigation of both the east and west ends of the island began under CERCLA guidance.

# 1.5 Previous Biological Investigations

The ATSDR, the USFWS, and individuals from the University of Puerto Rico have all conducted limited studies to determine contaminant concentrations in biota from Vieques Island. All of these studies could be considered preliminary screening efforts because of their limited sampling areas, small sample sizes, or other factors. All of these studies examined only tissue residues; none of them examined co-located soils. This section briefly summarizes the methods and results of these previous investigations. For further details regarding any individual study, the reader is referred to the original publication of each study.

# 1.5.1 University of Puerto Rico Study (Deya and Dias 1999)

In November 1999, researchers from the University of Puerto Rico collected approximately 35 fiddler crab from Icacos Lagoon in the Live Impact Area (LIA) on the east end of the island, as well as 35 fiddler crab from a reference location at Puerto Mosquito (Mosquito Bay) on the south side of the island. According to the report, the main objective of the study was "to assess the potential transport of pollutants from the LIA to other ecosystems through the food chain."

The samples were divided into two portions representing the extremities (legs and levers) and the bodies; each portion was analyzed for cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc. Average concentrations of cadmium (8.05 milligrams per kilogram [mg/kg]) and cobalt (35.69 mg/kg) in the Icacos Lagoon crab body sample were 3.5 times greater than averages from the reference sample. The average copper concentration (499.91 mg/kg) in the crab body sample from Icacos Lagoon slightly exceeded the concentrations detected in the reference samples. Conversely, manganese, nickel, and zinc were all detected at greater concentrations in crab bodies from the reference location than from Icacos Lagoon. Average manganese and zinc concentrations in the reference samples were approximately twice the average concentrations of these trace elements in the Icacos Lagoon samples. Chromium concentrations were similar in both the body and the extremities samples and for both the sampling and the reference areas Lead was not detected in any sample; the detection limit was not provided.

In the crab body samples, the only statistically significant differences appear to be the greater manganese and zinc concentrations in the reference sample and the greater cadmium concentration in the Icacos Lagoon body sample. In the crab extremities samples, the only statistically significant differences appear to be greater concentrations of manganese and nickel in the reference sample.

With the exception of cobalt in the reference sample, all trace elements were detected at greater concentrations in the body portion of the fiddler crab samples than in the extremities.

# 1.5.2 **USFWS Study (Lopez 2002)**

In 2002, one composite fiddler crab and two individual land crab samples were collected from mangrove wetlands at Punta Boca Quebrada near SWMU 4, and one composite fiddler crab and two individual land crab samples were collected from SWMU 6 near Laguna Arenas. Both SWMUs are on the west end of the island (Figure 1-1). Three individual land crab samples were also collected from a reference location at Sandy Point National Wildlife Refuge on St. Croix, U.S. Virgin Islands.

The purpose of this investigation was to collect preliminary data about the level of contamination in the prey base for some aquatic birds present on the island. Whole body samples were analyzed for PCBs, organochlorine pesticides, and trace elements.

DDT compounds were detected in one land crab sample and the composite fiddler crab sample collected at SWMU 6. The maximum concentrations of the pesticides p,p'-DDE and p,p'-DDT<sup>i</sup> were 0.130 and 0.028 mg/kg, wet weight, respectively. PCBs and other organochlorine pesticides were not detected in any of the SWMU 4, SWMU 6, or reference crab samples.

Cadmium, lead, and vanadium were detected in crab samples collected from SWMU 4, SWMU 6, and the Sandy Point reference location. The maximum cadmium concentration (0.656 mg/kg, wet weight) was detected in a land crab sample collected at SWMU 6. The maximum

ip,p'-DDE and p,p'DDT are referred to in this report as 4,4'-DDE and 4,4'-DDT.

concentrations of lead (4.07 mg/kg, wet weight) and vanadium (0.915 mg/kg, wet weight) were detected in the composite fiddler crab sample collected from SWMU 6. The report concluded that the crab collected from SWMU 6 contained DDT and trace elements, including lead and cadmium.

## **1.5.3** ATSDR Study (ATSDR 2003)

In 2001, the ATSDR collected fish and shellfish samples from six sites on Vieques Island as part of a public health assessment. The purpose of the public health assessment was to determine whether the muscle tissue from commonly consumed fish and shellfish contained levels of heavy metals and explosive compounds that would adversely affect public health. During this study, five land crab samples were collected from the north end of the LIA; five were collected adjacent to the west side of Bahia Salina del Sur; and two were collected from Laguna Kiani on the west end of the island. In addition, two composite fiddler crab samples were collected from the north end of the LIA and two were collected from the shore on the west side of Bahia Salina del Sur. The crab samples were analyzed for explosive compounds and trace elements.

In their study, the ATSDR averaged analyte concentrations detected in the land crab samples with concentrations detected in other types of shellfish. The study reported the following results:

- Explosive compounds were not detected in the shellfish samples.
- Calcium, chromium, magnesium, potassium, selenium, and sodium were detected in all
  of the shellfish samples.
- Aluminum, arsenic, barium, iron, and manganese were detected in 64% to 89% of the shellfish samples.
- Cadmium, mercury, silver, and vanadium were detected in 34% to 55% of the shellfish samples.

The ATSDR study concluded that although trace elements were detected in shellfish, the concentrations were too low to pose a human health concern.

### 2.0 DESCRIPTION OF THE STUDY

# 2.1 Study Design

This section describes the study design for the June 2005 investigation of Vieques Island land crab and fiddler crab.

### 2.1.1 Species Selection

### Land Crab

Land crab were collected for this study because of their importance in the diet of the people of Vieques Island. Land crab live in mangrove wetlands and other coastal wetlands and forests, building individual burrows in the soil to protect against predators and warm temperatures (Taissoun 1974). The poorly drained soil in wetlands and other coastal areas is a habitat requirement for land crab, because the water retained in their burrows serves as their water source. If they do not have access to water, land crab will live approximately only three days (Taissoun 1974). Land crab are primarily vegetarians and become carnivorous only if vegetation, including leaves, flowers, and fruit, is not available. Crab generally come out to feed at night when temperatures are cooler, and land crab generally feed within a 100-meter (approximately 330-foot) radius of their burrows (SMS 2001).

Land crab change morphologically and in color as they mature. Juvenile land crab are dark brown and grey, and it is difficult to distinguish between the sexes (Taissoun 1974). During the transitional stage from juvenile to adult, land crab are purple and orange. During this stage, males can be distinguished from females because one of the front claws on the males is larger than the other and the shape of the abdomen becomes distinct between the sexes (Taissoun 1974). Adult crab are blue-lavender in color; in the adults, the features that distinguish the sexes in the transitional stage become more prominent (Taissoun 1974).

Land crab generally require four years to reach maturity (Hostetler et al. 2003). On Vieques Island, the spawning season is generally from mid-July to mid-October. The female lays her eggs and then carries them in her abdomen for approximately two weeks before migrating to shallow nearshore ocean waters, where she releases the eggs (Hostetler et al. 2003). After releasing her

eggs, the female returns to a burrow. Female land crab can release multiple clutches of eggs during one spawning season (Taissoun 1974). The eggs hatch in the nearshore water and the larvae are then carried to deeper water, where they float for approximately one month until they mature into juvenile crab. The currents then carry the juvenile crab back to shore, often to an area different from where the female released them (Hostetler et al. 2003).

### Fiddler Crab

Fiddler crab were selected for this study because they live in habitats adjacent to the land crab, represent a slightly different pathway in the food web, and serve as an additional indicator species for the potential uptake of contaminants of concern. Because of the fiddler crab's small size, a composite sample of fiddler crabs also represents a far greater number of individuals per sampling station than is possible with the land crab. Fiddler crab live in soft sand or mud in mangrove and other coastal intertidal wetlands. Although fiddler crab are not consumed by the people of Vieques Island, they are important in the diets of birds, fish, and other animals present on the island.

At low tide, fiddler crab emerge from their burrows to feed (Grimes et al. 1989). The diet of a fiddler crab is generally composed of detritus and other organic particles. Fiddler crab mate, sleep, and hide from predators in burrows that they dig in the mud or sand. After mating, the female fiddler crab will stay in the burrow for two weeks. The female will then emerge and release her hatched eggs into nearby coastal waters (Grimes et al. 1989).

### 2.1.2 Sample Location Selection

Fourteen locations were sampled for land crab and fiddler crab (Figure 1-1): six locations on the west end of Vieques Island, six locations on the east side of Vieques Island, plus two reference locations, one on Vieques Island and one on the main island of Puerto Rico. Sample locations were selected in close coordination with the USFWS and with input from the federal and commonwealth partners, as well as the community. The sampling locations were selected primarily to represent a balance of:

- Areas where land crab are actively being harvested; and
- Areas where the USFWS may open refuge property to land crab harvesting in the future.

The reference location on Vieques Island was selected because it represents an area of similar habitat, but where exposure to substances released from past military or other activities is considered unlikely. The reference location on the main island of Puerto Rico was sited in the Humacao Wildlife Reserve because of its reserve status; because the geology of the reserve is similar to that of Vieques Island; plus, the location was recommended by the USFWS and the Puerto Rico Department of Natural Resources. Although the Humacao Wildlife Reserve is in the general vicinity of the former Frontera Creek Superfund site, that proximity is not expected to be a factor in this study, because the Frontera Creek Superfund site is part of a separate watershed drainage area. The contaminants of concern at the former Frontera Creek Superfund site were mercury and lindane<sup>ii</sup>. In 1995, approximately 600 cubic meters (800 cubic yards) of contaminated soil and sediment were removed from the site (USEPA 2002). In 1998, the Frontera Creek site was removed from the NPL (USEPA 2002).

The Vieques Island sampling locations and associated figures depicting the locations are:

## West End of Vieques Island

Area 1 (Figure 2-1): Downgradient from SWMU 7

Area 2 (Figure 2-2): Downgradient from AOCs J and R

Area 3 (Figure 2-3): Laguna Kiani

Area 4 (Figure 2-4): Laguna Kiani South

Area 5 (Figure 2-5): Boca Quebrada

Area 6 (Figure 2-6): Laguna Playa Grande

### • East End of Viegues Island

Area 7 (Figure 2-7): Mosquito Bay

Area 8 (Figure 2-8): Puerto Ferro

Area 9 (Figure 2-9): Red Beach

Area 10 (Figure 2-10): Blue Beach

Area 11 (Figure 2-11): Bahia Tapon

Area 12 (Figure 2-12): Live Impact Area

ii Lindane was not detected in any land crab samples; mercury was detected, but at an average level that is indistinguishable from any other site.

The reference sampling locations and associated figures depicting the locations are:

# • Vieques Island

Area 13 (Figure 2-13): Blue Horizon Reference

### Mainland Puerto Rico

Area 14 (Figure 2-14): Humacao Wildlife Reserve, Main Island Reference

### 2.1.3 Contaminants of Potential Concern

Concentrations of DDE, DDT, and trace elements have been detected in crab samples collected from the island during previous investigations (Deya and Dias 1999; Lopez 2002; ATSDR 2003). Explosive compounds and PCBs have been measured in groundwater in some areas where full Remedial Investigations (RIs) have been conducted (CH2M Hill 2002b). In addition, trace elements, including aluminum, antimony, arsenic, barium, chromium, copper, lead, manganese, mercury, nickel, selenium, silver, thallium, vanadium, and zinc, have been detected in soil, sediment, groundwater, or surface water at several sites throughout Vieques Island (CH2M Hill 2002a). These trace elements likely have natural as well as anthropogenic sources.

A target analyte list was developed for this study based on results from the limited prior studies and giving broad consideration to areas where releases of hazardous substances may have occurred. The target analyte list included explosive compounds, PCBs, organochlorine pesticides, and trace elements. Uranium is of interest because depleted uranium rounds have been used within the LIA. Anticipated laboratory detection limits for the target analytes were prescreened to confirm that the analyses would yield data capable of being evaluated against accepted ecological screening benchmarks.

Lipid content was also determined in the tissue samples; however, because the data were not lipid-normalized, those results are discussed only in the quality assurance report (Appendix D), not in the main body of this data report.

Section 3 details the number of samples analyzed and the analytes determined in each sample.

## 2.2 Sample Collection

Land crab and fiddler crab were collected according to the methods described in the *Final Sampling and Analysis Plan for the Vieques Island Biota Sampling Project* (RIDOLFI Inc. and NOAA 2005). The field methods used for sample collection and processing are summarized in Sections 2.2.1 and 2.2.2 of this report. The sample analyses are discussed in Section 2.2.3 and deviations from the sampling and analysis plan (SAP) are described in Section 2.2.4.

#### 2.2.1 Field Methods

Land crab and fiddler crab samples were collected from adjacent habitat types using several methods. The fiddler crab samples were composited to obtain sufficient sample mass for the chemical analyses. Global positioning system coordinates were recorded near the center of each sample location. Table 2-1 summarizes the sample identifications and descriptions. Each sampling area was photographed during the fieldwork; selected photographs representing the different habitat types and collection methods are included in Appendix A.

### Land Crab Collection Methods

Land crab were collected with traps and by hand from 14 locations. Between nine and 14 wood or polyvinyl chloride (PVC) traps were baited with fruit and placed in the entrances of active burrows at each sample area. Active burrows were identified by the presence of feces and freshly piled dirt. The traps were left in place until they were tripped or until sufficient samples had been collected from other burrows. In general, the traps were tripped after one to two hours. Traps that were not tripped within several hours were moved to a different burrow. This process was repeated until six to seven land crabs with carapaces longer than approximately 6.4 centimeters (2.5 inches) were collected. Additional sample mass was collected at some sites for use in matrix spike/matrix spike duplicate (MS/MSD) analyses performed at the laboratory for the purpose of quality assurance/quality control (QA/QC). Occasionally, the field crew collected the crabs by hand if land crab were observed outside of, or in the entrances of, their burrows. Following collection, the land crab were sexed and their carapaces were measured in the field. When possible, a ratio of three females to three males was collected at each sample area.

### Fiddler Crab Collection Methods

Fiddler crab were collected at 13 locations. The samples were collected using dip nets or by digging fiddler crabs from their burrows with stainless steel shovels or trowels. Between 33 and 223 fiddler crabs were collected from each sample location and placed in precleaned glass jars to make one composite sample. The number of individuals per composite sample depended on the size of the fiddler crabs. Individuals were collected until the target minimum mass required for chemical analysis was reached. Each fiddler crab composite sample weighed approximately 60 to 100 grams (approximately 2 to 3.5 ounces).

Three composite samples were collected from each sample location, with the exception of the Blue Horizon (Area 13) reference location on Vieques Island. Although this reference location was searched extensively, no fiddler crab were present<sup>iii</sup>. Mosquito Bay, which is sampling Area 7 in this study, has been used previously as a reference location. For over 20 years, the Mosquito Bay area has been managed by Puerto Rico as a natural resource (for example, gasoline-powered boats are banned). Like some other sample locations, no activities that would have led to substantial contaminant releases are known to have occurred in the Mosquito Bay area. For these reasons, the Mosquito Bay sampling area shares many of the characteristics of a reference location. However, the Mosquito Bay area was selected because of its implications for land crab harvesting: it is believed to be an area that provides land crab for the replenishment of adjacent areas. Mosquito Bay was not designated as a reference location in the original study design, and it was deemed inappropriate to make that designation retroactively.

### 2.2.2 Sample Processing

# **Land Crab Processing**

The land crab samples were rinsed in the field with distilled water to remove sand and other debris. The samples were measured, sexed, tagged, and placed in a cooler. The land crab were

iii The exact locale originally evaluated and chosen for the on-island reference location had, by the time of sampling, been bulldozed, so no land crab were present there. In consultation with local partners, and after considerable discussion of alternatives, it was concluded that the Blue Horizon locale offered the best likelihood of representing an area with minimal anthropogenic impacts. Because of this, and the fact that land crab were the primary target of this study, an adjacent location within the Blue Horizon region was retained as the on-island reference.

then placed in a freezer at the USFWS headquarters. After several hours, the land crab samples were removed from the freezer, rinsed, measured, and sexed again. They were then double-bagged in clean freezer-style polyethylene bags. Both the inner and outer sample bags were marked in indelible ink with the sample identification number and other sample information. A custody seal was placed over the opening of each outer bag. The land crab samples were then stored in a freezer at the USFWS headquarters until frozen. Once the samples were frozen, the bags were wrapped in bubble wrap, placed in coolers with blue ice, and shipped by courier to the laboratory under chain-of-custody procedures.

### Fiddler Crab Processing

The composite fiddler crab samples were placed in a freezer at the USFWS headquarters. After several hours, the samples were rinsed over a sieve with distilled water to remove sand and other debris. The fiddler crabs were counted, sexed, and then placed in new, precleaned glass jars. For each composite sample, the sample identification number and other sample information were written in indelible ink on a label that was affixed to the jar, and the labels were covered with clear tape. A custody seal was placed across the opening of each jar. The sample jars were stored in a freezer at USFWS headquarters until they were shipped. Prior to shipping, the sample jars were wrapped in bubble wrap, double-bagged in clean polyethylene bags, and placed in coolers with blue ice, then shipped by courier to the laboratory under chain-of-custody procedures.

### 2.2.3 Sample Analyses

The land crab and fiddler crab samples were sent to Columbia Analytical Services, Inc. of Kelso, Washington, for chemical analysis. At the laboratory, whole bodies of five to six land crab from each sample location were individually homogenized and analyzed for explosive compounds, PCBs, organochlorine pesticides, and trace elements. The land crab were analyzed as whole body samples because the residents of Vieques Island consume the majority of the land crab, including parts of the shell.

In addition to the whole body analyses, one land crab from each sample location was dissected to separate the soft tissue from the exoskeleton (which includes the carapace and all other parts of the shell). The soft tissue and the exoskeleton fractions were weighed and analyzed separately

for trace elements. These samples were analyzed to determine whether concentrations of trace elements in the whole body crab samples may be due to elevated concentrations sequestered in the exoskeletons.

The whole body fiddler crab composite samples were homogenized and analyzed for explosive compounds, PCBs, organochlorine pesticides, and trace elements.

A list of all compounds for which crab samples were analyzed can be found in Section 3 with the discussion of results

## 2.2.4 Deviations from the Sampling and Analysis Plan

To accommodate conditions encountered in the field, some changes were made to the sampling and processing methods described in the final SAP (RIDOLFI Inc. and NOAA 2005). These changes do not compromise the integrity of the samples or the quality of the analytical data generated from the samples. Deviations from the SAP are described below:

- An overview photograph of each sampling area and some individual traps and crabs was taken, instead of photographing each individual trap and crab.
- An attempt was made to place the land crab traps at regular distance intervals, but this
  was not always possible due to habitat constraints. At some locations, the traps were
  placed wherever active burrows were present so that enough sample material could be
  collected to complete the sample for that location.
- Several of the land crab were collected by hand, instead of with a trap, because of the
  ease of capture and because at least six land crab specimens were needed from every
  sample location.
- Individual fiddler crabs were not identified by species.
- The first attempt to collect land crab at the Humacao Wildlife Reserve (Area 14) reference location was not successful<sup>iv</sup>. As a result, the reference crab samples from this

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iv The area originally targeted had recently active burrows, but crab within this area had been completely harvested.

location were collected two weeks after the other samples. Such temporal adjustments are slight and are not expected to affect the analytical results.

- The land crab generally were collected over a span of several hours rather than overnight.
- Although the sampling effort was extended, fiddler crab were not collected at the Blue Horizon (Area 13) reference location because suitable habitat was lacking.
- Mosquito Bay (Area 7) was sampled instead of Sun Bay because of permitting issues.
   The Mosquito Bay sample location is believed to be similar to Sun Bay and a recruiting habitat for land crab.
- The sample area referred to in the SAP as Laguna Arenas was moved to the south end of Laguna Kiani at the request of the USFWS; the name of the sample area was therefore changed to Laguna Kiani South (Area 4).

## 2.3 Quality Assurance Summary

Analytical data quality was evaluated both by the laboratory and independently, as specified in the quality assurance project plan (QAPP). The independent review and the validation of laboratory data packages were performed by Validata, LLC, of Seattle, Washington. An additional review of explosive compounds data was performed by D.M.D., Inc., of Vashon, Washington. The validated laboratory data appear in Appendix B. Data validation reports and associated memoranda are included as Appendix C. A summary quality assurance report is included as Appendix D.

Laboratory results were either accepted as received (unqualified) or were qualified. No results were rejected. Unqualified results are considered valid with respect to the specified procedures and QA/QC measures and may be used as intended. Results qualified with a J flag are considered usable with the understanding that the associated values are estimates because they are so near the sample-specific method detection limit (MDL). Certain pesticide and PCB results were flagged by the laboratory as JP, indicating that the result is less than the method reporting limit and that the gas chromatography (GC) confirmation criteria were not met. Data with the JP flag have more associated uncertainty and should be used with caution. The data validation report (Appendix C) defines the data qualifiers.

The principal measures associated with data quality are precision, accuracy, representativeness, completeness, and comparability. An evaluation of each of these measures determined that overall analytical performance and data quality are acceptable (see Appendix D for more detail).

During data evaluation, it became evident that trace element analyses associated with one preparation batch of land crab exoskeletons actually represented crab soft tissue, not the exoskeleton. Archived samples from this batch were reprepared and reanalyzed; the revised results are consistent with other exoskeleton results. Details regarding reanalysis of the land crab exoskeleton samples are provided in Appendix G.

### 3.0 DATA SUMMARY

This section discusses the results of the chemical analysis of Vieques Island land crab and fiddler crab samples. The analytical results are presented in milligrams per kilogram (mg/kg) or micrograms per kilogram ( $\mu$ g/kg) on a wet weight basis. Summary tables are provided in this section, and the complete laboratory analytical data are provided in several tables in Appendix B. Statistical analyses of trace element and total DDT data are provided in Appendix E for land crab and Appendix F for fiddler crab.

It's important to note that in comparing analytical results, use of the word "significant" has a particular meaning within the context of the statistical analyses conducted for land crab (Appendix E) and fiddler crab (Appendix F). An alpha of 0.05 was applied for significant findings (a p value lower than this indicates a statistically significant difference exists among some sites). Therefore, a concentration described as, for instance, "significantly greater" is one that exhibits a *statistically* significant difference from the value to which it is being compared.

In this section, the results of this study are briefly compared to the results from previous biological investigations where possible, although often data comparability is lacking. The land crab results presented here were screened for human health effects by the ATSDR in a PHC (Appendix H). In addition, this report provides limited screening of the land crab data against conservative ecological risk benchmarks intended to protect the crab themselves (as opposed to consumers of crab). The fiddler crab results presented here are also screened against conservative ecological risk benchmarks.

In addition to the toxicological evaluation of the data, a spatial evaluation was conducted to provide further insight into any patterns associated with potentially hazardous substances.

## 3.1 Development of Screening Benchmark Values

The analytical results were screened against highly conservative benchmark values to establish whether any compounds could *potentially* pose a threat to human or ecological receptors. The benchmark values used in this screening were identified from various published sources. Although this screening-level assessment should not be treated as a human health and ecological

risk assessment, it does offer "a high level of confidence in determining a low probability of adverse risk" (Suter 1993) to facilitate a determination regarding the need for, and degree of, further investigation. A screening-level assessment acknowledges that chemical concentrations in excess of the conservative benchmark values may be considered *potentially* hazardous. However, concentrations that exceed the benchmark values are not *necessarily* hazardous. To make that determination, further, more realistic, site-specific assessment is required (USEPA 2001). Ultimately, potential risks can be identified and characterized only after consideration of site-specific exposure parameters, pathways, endpoints, and other assumptions.

Land crab are a food resource for residents of Vieques Island. Therefore, the analytical results for land crab were compared to human health screening benchmarks in accordance with values used by the ATSDR in its PHC and assessments that involve fish and shellfish consumption (ATSDR 2003). These human health consumption guidelines are based on the ATSDR's Minimal Risk Levels (MRLs), the USEPA's reference dose (RfD) levels, and USEPA regional risk-based criteria (RBC) for the protection of human health. An MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure. These substance-specific estimates, which are intended to serve as screening levels, are used by ATSDR health assessors and others to identify contaminants and potential health effects that may be of concern at hazardous waste sites and that deserve further evaluation. Human health screening benchmarks and results of the land crab screening-level evaluation are provided in the ATSDR PHC (Appendix H). For the current study, land crab data were also screened against selected ecological benchmarks for cadmium, mercury, and vanadium that are specifically protective for crustacean species.

Fiddler crab are a common intertidal species important in the ecological food web of Vieques Island. Therefore, the analytical results for fiddler crab were compared to conservative ecological threshold values. Consistent with the philosophy of a screening-level assessment, the lowest available tissue residue limits identified in the literature for the protection of crustacean (specifically crab, when available) survival, growth, and reproduction were selected (Table 3-1). Tissue concentration limits, based on no observed adverse effects levels (NOAELs), were compiled from the USEPA Toxicity/Residue (TOXRES) database (Jarvinen and Ankley 1999)

and the U.S. Army Corps of Engineers (USACE) Environmental Residue Effects Database (ERED) (USACE 2005).

Several resident avian species on Vieques Island, including herons and egrets, have been reported to feed on fiddler crab, as have small mammals (Deva and Dias 1999). Therefore, when crustacean effects data were not available, the fiddler crab analytical results were compared to toxicity reference values (TRVs) developed by the Oak Ridge National Laboratory for higherorder wildlife. The TRVs are based on NOAELs for the protection of avian and mammalian wildlife species (Sample et al. 1996). These NOAEL-based oral ingestion benchmarks were developed for multiple wildlife species that represent a range of body sizes and diets; however, the value selected for comparison in this report was not based on a particular receptor species, but rather on the lowest available value so as to provide high confidence in the screening. Using the lowest value as a benchmark, even if the animal is not a known predator of fiddlers, helps to ensure that the screening is applicable to the broadest range of actual consumers or predators of fiddler crab. However, chemical concentrations in fiddler crab that exceed these benchmarks do not necessarily indicate a particular risk level. Rather, according to this conservative approach, "concentrations below the benchmarks should not result in significant effects" to predator species (Sample et al. 1996). Exceedance of a TRV does not firmly establish that a risk is present, it merely suggests a *potential* for risk and indicates that further evaluation is warranted. Table 3-1 summarizes the ecological screening benchmarks used in this report for evaluating fiddler crab data.

The maximum detection limits for the data used in this study were below the ecological benchmarks, indicating that the selected benchmarks are sufficiently low to apply to all the data generated.

### 3.2 Land Crab Results

Whole body land crab samples (representing the exoskeleton, soft tissue, and all parts) collected from Areas 1 through 12 and two reference locations (Areas 13 and 14) were analyzed for explosive compounds, PCBs, organochlorine pesticides, and trace elements. Results from these analyses are summarized in Table 3-2 and provided in Appendix B-1. In Table 3-3, mean values

for all analytes that were detected at least once are compared between sample locations to aid in identifying potential spatial patterns. In addition, the exoskeleton and soft tissue fractions of one land crab sample from each area were analyzed separately for trace elements. Those results are provided in Table 3-4. Compounds that were not detected above the sample-specific laboratory MDL are considered non-detects. The MDL is used to represent the non-detects in averaging calculations. Only detected compounds were summed for total DDT and total chlordane.

The results were screened against conservative benchmark values developed for the protection of human health, as discussed in more detail in the ATSDR PHC (Appendix H). In the case of organic compounds, cadmium, mercury, and vanadium, ecological screening benchmarks meant to be protective of the crab themselves are available; therefore, whole body concentrations of these analytes in land crab were also screened against those benchmarks. The results of that screening are discussed in Section 3.2.4.

To gain additional insight into the patterns of occurrence of trace elements and total DDT, the mean levels observed at each area (including reference areas) were tested for statistical difference to identify those areas that exhibited significantly different averages. Details of these statistical tests appear in Appendix E, along with graphical representation of mean trace element and total DDT concentrations for each sample location. The differences are discussed in Section 3.2.5.

### 3.2.1 Explosive Compounds

Seventy-three whole body land crab samples were analyzed for 14 explosive compounds. A 74<sup>th</sup> sample collected in Red Beach (Area 9) was analyzed for all other analyte groups, but was not analyzed for explosive compounds due to an inadvertent error by the laboratory. No explosive compounds were detected at concentrations above the MDLs in any land crab sample.

### 3.2.2 Polychlorinated Biphenyls

Seventy-four whole body land crab samples were analyzed for nine PCB Aroclor mixtures. Aroclor 1260 was detected in one sample from Laguna Kiani (Area 3) at an estimated concentration of 7.6 µg/kg, which is just above the MDL. In a full RI previously conducted at

Laguna Kiani on behalf of the U.S. Navy, PCBs were detected in groundwater (CH2M Hill 2002b). No other PCB Aroclor mixtures were detected in any land crab sample at concentrations above the MDLs.

The ATSDR PHC (Appendix H) discusses human health screening values for PCBs. The estimated concentration of 7.6  $\mu$ g/kg in a single sample from Laguna Kiani is less than the levels reported in the scientific literature as causing harmful health effects.

### 3.2.3 Organochlorine Pesticides

Seventy-four whole body land crab samples were analyzed for 31 individual pesticide compounds (Table 3-2, Appendix B-1). Seventeen of the 31 pesticide compounds were detected in at least one land crab sample, and detections occurred in samples from all areas, including the reference locations. Nearly all of the detections were of DDT and its metabolites or chlordane compounds<sup>v</sup>.

The pesticides 4,4'- and 2,4'-DDT, -DDD, and -DDE were the most ubiquitous of the pesticide compounds; detections ranged from two samples (2,4'-DDE) to 39 samples (4,4'-DDE). DDT and its metabolites were detected in samples from all sample locations except the Blue Horizon (Area 13) reference location at concentrations ranging from  $0.14 \,\mu\text{g/kg}$  to  $190 \,\mu\text{g/kg}$ . 4,4'DDT and -DDE had previously been detected in crab tissue samples from Vieques Island at similar concentrations (Lopez 2002).

Land crab data were statistically tested to determine whether there were differences among the sexes and whether size was an influencing factor. Neither sex nor size was a significant factor to explain differences in total DDT values. The only significant differences were among sampling areas.

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<sup>&</sup>lt;sup>v</sup> Chlordane, especially when applied as a commercial pesticide, is a mixture of dozens of individual compounds. There are about 10 individual compounds that make up the majority of most commercial formulations; the sum of eight compounds has been used in this report to represent total chlordane.

Gamma-chlordane, the most prevalent of the chlordane compounds, was detected in 16 samples representing about half of the sampling areas, including the Blue Horizon reference area. Chlordane compounds were not detected in six areas.

Other pesticide compounds were detected in samples from four areas, including the Humacao Wildlife Reserve (Area 14) reference location. Three cyclo-diene pesticides (aldrin, dieldrin, and endrin) were each detected once at low, estimated concentrations that were just above the MDLs. The samples with these single detections were collected from Bahia Tapon (Area 11) and from the Humacao Wildlife Reserve. Three other pesticides (endosulfan sulfate, methoxychlor, and mirex) were each detected in from two to four samples; many of these detections were also at low, estimated concentrations. These samples were collected from east- and west-end sampling areas, as well as the Blue Horizon reference location. Mirex was detected in land crab only from the LIA (Area 12) (and was also found in fiddler crab only from that same area). Although different compounds were in general detected in different areas, there was a certain degree of concordance in the occurrence of infrequently detected pesticides: Three of the four areas where endosulfan sulfate, methoxychlor, and aldrin were detected are also among the areas with the four highest mean total DDT concentrations. These areas are Laguna Kiani (Area 3), Red Beach (Area 9), and Bahia Tapon. Bahia Tapon and Laguna Kiani also were among the areas with the four highest mean total chlordane concentrations.

The human health screening values for detected pesticides are discussed in the ATSDR PHC (Appendix H). In summary, the concentrations of detected pesticide compounds are less than levels reported in the scientific literature as causing harmful health effects. As reported in the PHC, DDE levels (average of 0.021 mg/kg) were also well below the Food and Drug Administration (FDA) action level of 5 mg/kg for edible portions of fish. Averages from individual areas were also below health effect levels and FDA guidelines.

Pesticide concentrations in land crab data were also screened against the ecological screening benchmarks developed for other crustacean species. All pesticide concentrations were below the available crustacean ecological screening benchmarks.

### 3.2.4 Trace Elements

Seventy-four whole body land crab samples, 14 soft tissue-only samples, and 14 exoskeleton-only samples were analyzed for 23 trace elements, which were ubiquitously detected in samples from all areas, including both reference locations (Tables 3-2 and 3-4, Appendices B-1 and B-2). To compare the concentrations among locations, data from the individual whole body land crab samples were averaged by compound for each location (Table 3-3). For substances that were not detected, the sample-specific laboratory MDL value was used in generating the mean.

More than half of all 23 trace elements were detected in all whole body samples. The widespread detection of numerous trace elements in land crab samples likely reflects exposure to elements naturally occurring in soil, sediment, groundwater, and surface water (CH2M Hill 2002a). Some of these trace elements are in fact essential nutrients (e.g., copper, calcium, magnesium) (Terwilliger and Ryan 2001; van Holde et al. 2001). Extreme values though, such as those significantly greater than values observed from a reference, may indicate potential anthropogenic sources. Certain trace elements had previously been reported in a limited number of land crab tissue samples (Lopez 2002; ATSDR 2003).

Results of the land crab exoskeleton-only and soft tissue-only analyses for trace elements are summarized in Table 3-4 and provided in Appendix B-2. Exoskeletons were analyzed to evaluate whether certain trace elements may be preferentially bioconcentrated in the skeleton. In addition, it was thought that these data might provide additional insight into the levels of whole body residue burdens. In general, more trace elements were detected in the soft crab tissue than in the exoskeleton; the exoskeleton did not contain beryllium, mercury, or selenium. Concentrations of half of all trace elements detected in the exoskeleton were greater in the exoskeleton than in the soft tissue-only samples (ratio greater than 1; see Table 3-4); concentrations of four trace elements (barium, calcium, chromium, and magnesium) were at least an order of magnitude greater in the exoskeleton than in the soft tissue-only samples. Because calcium is one constituent of the carapace, calcium concentrations were, as expected, much greater in the exoskeleton, averaging 105,657 mg/kg compared to the average soft tissue concentration of 3,844 mg/kg. Mean copper concentrations were higher in soft tissue, however, averaging 50.3 mg/kg compared to 6.0 mg/kg in the exoskeleton. This copper result was also expected because

of the biochemistry of crab. A similar pattern of soft tissue concentrations exceeding exoskeleton concentrations was observed for cadmium (0.104 mg/kg vs. 0.012 mg/kg); silver (0.073 mg/kg vs. 0.013 mg/kg), and zinc (48.1 mg/kg vs. 13 mg/kg).

Trace element concentrations in land crab were also screened against screening benchmarks for cadmium, mercury, and vanadium developed for other crustacean species. All concentrations of mercury were below the crustacean ecological screening benchmark. Concentrations of vanadium were either below the MDL or above the ecological screening benchmark derived from shore crab at all areas, except Red Beach (Area 9). Cadmium concentrations exceeded the benchmark in five cases:

- One crab from Boca Quebrada (Area 5) had a cadmium concentration about two times the cadmium benchmark value.
- One crab from Laguna Kiani (Area 3) had a cadmium concentration that just barely exceeded the cadmium benchmark value.
- Three crab from the LIA (Area 12) contained cadmium concentrations about two to four times the cadmium benchmark value.

Although the ATSDR concluded that consumption of these crab is not expected to cause harmful health effects in adults or children, this screening suggests that levels of vanadium and cadmium observed in land crab might affect the health of the crab themselves. Such differences in apparent toxicity (human versus crab) can occur because of variations in sensitivity between species, which can be further related to differences in the biochemistry of specific organisms. Neither the vanadium nor the cadmium benchmark was derived from studies of land crab. Considering species-specific variations in toxicity, it is possible that these benchmarks may under- or overestimate the potential for risk to land crabs.

### 3.2.5 Sample Area Comparisons

This section discusses the spatial pattern and differences observed in concentrations irrespective of their absolute value relative to ecological or human health benchmarks. Spatial evaluations of the data can help raise other insights from the data beyond their toxicological significance.

Table 3-3 presents average concentrations of analytes detected in land crab for Areas 1 through 14. In calculating these averages for the trace elements, the MDL was used to represent any non-detect value. Only detected values were summed to generate total DDT. The means for the trace elements and total DDT were then statistically tested to determine which areas (including the reference locations) were significantly different from each other. Detailed statistics, along with graphical representations of the statistical analysis, are presented in Appendix E. Table 3-5 summarizes the statistical analysis.

## Organic Compounds

Most of the organic compounds for which land crab were analyzed were either not detected or were detected infrequently. PCB Aroclor 1260 was detected in one land crab sample from Laguna Kiani (Area 3). Endosulfan sulfate, methoxychlor, mirex, and aldrin were each detected in one or two areas. This low number of detections precludes comparison between areas.

Chlordane-related compounds were observed at half of the areas. When detected, chlordane concentrations were just above the detection limit, including at the on-island Blue Horizon (Area 13) reference location.

Low concentrations of the pesticide DDT and its metabolites were observed in land crab from all areas except the Blue Horizon reference location. The greatest average concentrations of total DDT were found in the crab collected from Laguna Kiani on the island's west end and from Red Beach (Area 9) on the east end, followed by Blue Beach (Area 10) and then Bahia Tapon (Area 11). Table 3-5 presents a statistical analysis of areas for which analytical results were significantly different (either lower or greater) from results for the two reference areas. As shown in Table 3-5, mean total DDT concentrations at Laguna Kiani and Red Beach were significantly greater than for both reference areas.

### Trace Elements

Table 3-5 also summarizes the statistical analysis (Appendix E) of average trace element concentrations for each area relative to the reference locations. In calculating these averages, the MDL was used for samples with non-detectable concentrations. Refer to Appendix E for

graphical representations of each trace element that clearly illustrate deviations from the overall average.

The reference locations did not exhibit any difference in trace element concentrations with the exception of barium. Average concentrations of barium in samples from the Humacao Wildlife Reserve (Area 14) were significantly greater than concentrations of barium in samples from the Blue Horizon reference area. In general, mean reference values for trace elements were near an overall average or below. These observations tend to reinforce the appropriateness of the selection of these locales as reference areas.

Average concentrations of several trace elements in land crab (Table 3-3) appear to be elevated (greater than island-wide averages, Table 3-2) at some specific areas. In some cases, however, this apparent difference derives from the analytical results for a single crab. Examples include thallium at Red Beach; silver and chromium at Puerto Ferro (Area 8); copper at Mosquito Bay (Area 7); and lead at Laguna Kiani. It's difficult to determine the significance of a single crab with greater-than-average concentrations. Clearly, consistent results within a given area would be a clearer indication of exposure within that locale. Because of the relatively small sample sizes in this study, however, the singular results should not be immediately dismissed as outliers. For instance, concordance between the results for a given compound in the two species would be a broader indication of significant exposure factors within an area.

Samples from Laguna Kiani, Puerto Ferro, downgradient from AOCs J and R (Area 2), Boca Quebrada (Area 5), and the LIA (Area 12) contained the largest number of trace elements for which average values were greater than the reference values. Land crab from each of these areas had four or more trace elements at concentrations that were significantly greater than concentrations in at least one of the reference locations. SWMU 7 (Area 1) was the only area where no trace elements were detected in samples at concentrations significantly greater than the average reference values.

The spatial distribution of specific trace elements is discussed below:

 Mercury and beryllium display a unique pattern: Apparent statistical differences in these trace elements occurred between samples in which concentrations were below the MDL and those in which concentrations were just above the MDL. Mercury concentrations did not exceed the crustacean-based screening benchmark in any of the areas. Beryllium had the lowest frequency of detection, with a single detection in a sample from downgradient of AOCs J and R (Area 2).

- In the case of selenium, thallium, uranium, and zinc, no apparent spatial pattern in concentrations was observed and the sampling areas did not exhibit significant differences. Uranium was detected in all land crab samples except two at concentrations ranging from 0.0017 mg/kg (Blue Beach) to 0.0375 mg/kg (downgradient of AOCs J and R); however, concentrations across all areas, including the reference locations, are statistically indistinguishable.
- Iron and vanadium also display no apparent spatial pattern: Areas that were different
  from the reference areas had significantly lower concentrations. Mean vanadium
  concentrations from all sampling areas except Red Beach exceeded the crustacean-based
  screening benchmark for vanadium.
- The average cadmium concentration in land crab from the LIA was generally elevated above the other locations, and significantly greater than the reference samples. The LIA was also the only area at which the crustacean-based screening benchmark for cadmium was exceeded.
- Laguna Kiani was the only area with an average lead concentration significantly greater than the reference values.
- Average levels of barium in samples from Laguna Kiani South (Area 4) were significantly greater than the reference values.
- Average levels of nickel in samples from Laguna Playa Grande (Area 6) were significantly greater than the reference values.
- Average levels of arsenic in samples from Red Beach were significantly greater than the reference values.

There was some apparent co-occurrence of maximal levels of both organics and trace elements. The highest average concentrations of arsenic, chromium, iron (on island), lead (detected mostly

in one crab), and magnesium were observed at Laguna Kiani, as were the PCB detection, the second-highest total chlordane result, and the maximum average of total DDT.

### 3.3 Fiddler Crab Results

Fiddler crab composite samples collected from Areas 1 through 12 and Area 14 were analyzed for explosive compounds, PCBs, organochlorine pesticides, and trace elements. The analytical results are summarized in Table 3-6. Mean values shown in Table 3-7 were calculated for all analytes and compared among sampling areas to identify potential spatial patterns. Compounds that were not detected above the laboratory MDLs are considered non-detects. The MDL is used to represent the non-detects in averaging calculations. Only detected compounds were summed for total DDT and total chlordane.

The analytical results are provided in Appendix B-3 and are discussed below. The results were screened against conservative benchmark values (Table 3-1) developed for the protection of ecological receptors. The results of that screening are discussed in Section 3.3.4.

To gain additional insight into the patterns of occurrence of trace elements and total DDT, the mean levels observed at each area (including reference areas) were tested for statistical difference to identify those areas that exhibited extreme averages. Details of these statistical tests appear in Appendix F, along with graphical representation of mean trace element and total DDT concentrations for each sample location. The differences are discussed in Section 3.3.5.

### 3.3.1 Explosive Compounds

Thirty-nine whole body composite fiddler crab samples were analyzed for 14 explosive compounds. No explosive compounds were detected in fiddler crab samples at concentrations above the MDLs.

## 3.3.2 Polychlorinated Biphenyls

Thirty-nine whole body composite fiddler crab samples were analyzed for nine PCB Aroclor mixtures. Aroclor 1254 was detected in three samples from Laguna Kiani (Area 3) at concentrations ranging from 47 to 58  $\mu$ g/kg. None of these concentrations exceeded the

ecological screening benchmark for blue  $crab^{vi}$  of 23,000  $\mu g/kg$  (USEPA 2005c). PCBs had previously been detected in groundwater in this area (CH2M Hill 2002b). No other PCB Aroclor mixtures were detected in fiddler crab samples at levels above the MDLs.

## 3.3.3 Organochlorine Pesticides

Thirty-nine whole body composite fiddler crab samples were analyzed for 31 individual pesticide compounds (Table 3-6). Pesticides were detected in all areas, including the Humacao Wildlife Reserve (Area 14) reference location. Twenty-two of the individual pesticide compounds analyzed for were detected in at least one fiddler crab sample:

- Three pesticides were each detected once at low, estimated concentrations: delta-BHC was detected in a sample from Boca Quebrada (Area 5), while endrin and heptachlor were detected in samples from Laguna Kiani (Area 3).
- Eight individual compounds (aldrin, beta-BHC, cis-nonachlor, endrin aldehyde, endrin ketone, gamma-chlordane, mirex, and trans-nonachlor) were each detected in two or three samples; many of the detections were at low, estimated concentrations. These samples were collected from both east- and west-end sampling areas, as well as from the Humacao Wildlife Reserve.
- Five pesticides (alpha-chlordane, dieldrin, endosulfan sulfate, heptachlor epoxide, and methoxychlor) were each detected in from six to eight samples; these detections represent most of the sampling areas, including the Humacao Wildlife Reserve reference location.
- DDT compounds (4,4'- and 2,4'-DDT, -DDD, and –DDE) were the most ubiquitous of the detected pesticide compounds, occurring in between two samples (2,4'-DDE) and 33 samples (2,4'-DDT). DDT and its metabolites were detected in samples from all areas, including the reference location, at concentrations ranging from 0.27 μg/kg to 270 μg/kg. DDT and DDE had previously been detected in crab tissue samples from Vieques Island (Lopez 2002) at similar concentrations.

vi This is a no observed effects level for survival in juvenile blue crab following a 20-day exposure.

No pesticide compounds were detected at concentrations that exceeded available ecological screening benchmarks<sup>vii</sup>. The remaining pesticide compounds were not detected at levels above the MDLs.

#### 3.3.4 Trace Elements

Thirty-nine whole body composite fiddler crab samples were analyzed for 23 trace elements, which were ubiquitously detected in samples from all areas, including the reference location (Table 3-6). Beryllium was detected in the fewest samples (21), while most other trace elements were detected in all or nearly all 39 samples.

The widespread detection of trace elements in fiddler crab samples likely reflects their exposure to elements naturally occurring in soil, sediment, groundwater, and surface water (CH2M Hill 2002a). Some of these trace elements are in fact essential nutrients (e.g., copper, calcium, magnesium) (Terwilliger and Ryan 2001; van Holde et al. 2001). Extreme values though, such as those significantly greater than values observed from a reference, may indicate potential anthropogenic sources and suggest the need for further evaluation to establish their cause. Certain trace elements had previously been reported in a limited number of fiddler crab tissue samples (Deya and Dias 1999; Lopez 2002).

Uranium was detected in all fiddler crab samples at concentrations ranging from 0.011 mg/kg at the downgradient of SWMU 7 (Area 1) sampling location to 0.115 mg/kg at the Boca Quebrada (Area 5) location. These values do not approach the wildlife TRV screening benchmark for uranium of 5.98 mg/kg. As shown on Table 3-7, which provides average values for each analyte at each location, the highest level of uranium occurred in a sample from Boca Quebrada; however, most locations exhibit concentrations that are relatively consistent. Average concentrations of uranium in samples from Laguna Kiani South (Area 4), Boca Quebrada, and

vii One sample contained 4,4'-DDE at a concentration roughly twice the benchmark for 4,4'-DDT. DDE is known to be generally less toxic than DDT, plus limited data from other crustacean species suggest that DDT may be 10 to up to 200 times more toxic than DDE (Lotufo et al. 2000). Therefore, this single DDE result was not considered significant. This assessment is focused on crabs and does not estimate risk to potential predators, such as birds.

Mosquito Bay (Area 7) were all significantly greater than concentrations at the reference location, but all were well below the screening benchmark.

Ten trace elements (aluminum, arsenic, barium, cadmium, chromium, copper, lead, selenium, vanadium, and zinc) were detected in multiple samples at concentrations that exceeded available ecological screening benchmarks:

- Aluminum concentrations exceeded the ecological screening benchmark of 3.8 mg/kg (wildlife TRV) in all samples; aluminum concentrations ranged from 33.2 mg/kg (Red Beach, Area 9) to 1,100 mg/kg (Blue Beach, Area 10).
- Arsenic concentrations exceeded the ecological screening benchmark of 0.25 mg/kg (wildlife TRV) in all samples; arsenic concentrations ranged from 0.6 mg/kg (downgradient of AOCs J and R, Area 2) to 4.01 mg/kg (Red Beach).
- Barium concentrations exceeded the screening benchmark of 17.2 mg/kg (wildlife TRV) in 29 samples representing all locations except Red Beach and Bahia Tapon (Area 11); barium concentrations ranged from 4.19 mg/kg (Red Beach) to 122 mg/kg (downgradient of AOCs J and R).
- Cadmium concentrations exceeded the screening benchmark of 0.13 mg/kg (lobster NOAEL) in 12 samples from Areas 1, 3, 6, 10, and 12; cadmium concentrations ranged from 0.013 mg/kg (Mosquito Bay) to 0.557 mg/kg (Laguna Kiani, Area 3). However, the average cadmium concentration across all areas (0.118 mg/kg) did not exceed the benchmark.
- Chromium concentrations exceeded the screening benchmark of 0.83 mg/kg (wildlife TRV) in 30 samples representing all locations except downgradient of AOCs J and R; chromium concentrations ranged from 0.27 mg/kg (downgradient of AOCs J and R) to 7.89 mg/kg (Blue Beach).
- Copper concentrations exceeded the screening benchmark of 38.9 mg/kg (wildlife TRV) in 26 samples representing all locations except Areas 1 and 2; copper concentrations ranged from 26.7 mg/kg (downgradient of SWMU 7) to 73.1 mg/kg (Laguna Kiani).

- Lead concentrations exceeded the screening benchmark of 0.94 mg/kg in three samples collected from one area, making lead unique among the trace elements with exceedances. Lead concentrations ranged from 0.08 (Mosquito Bay) to 9.72 mg/kg (Laguna Kiani) and exceeded the screening benchmark in the three samples from Laguna Kiani, where the average lead concentration was 8.13 mg/kg; the next highest area average was 0.55 mg/kg.
- Selenium concentrations exceeded the screening benchmark of 0.33 mg/kg (wildlife TRV) in 14 samples representing Areas 5, 6, 9, 10, 11, and 12; selenium concentrations ranged from 0.12 mg/kg (downgradient of AOCs J and R) to 0.83 mg/kg (Laguna Playa Grande, Area 6). However, the average concentration across all areas (0.35 mg/kg) was only slightly greater than the benchmark.
- Vanadium concentrations exceeded the screening benchmark of 0.2 mg/kg (shore crab NOAEL) in all samples but one; vanadium concentrations ranged from 0.2 mg/kg (Red Beach) to 3.2 mg/kg (Blue Beach).
- Zinc concentrations exceeded the screening benchmark of 12 mg/kg (wildlife TRV) in all samples; zinc concentrations ranged from 18.8 mg/kg (Red Beach) to 36.5 mg/kg (Boca Quebrada).

Of the ten trace elements discussed above, all of which exceeded screening benchmarks in multiple samples, only cadmium, lead, and selenium were not detected at concentrations above the screening benchmarks in reference samples from the Humacao Wildlife Reserve (Area 14).

It is important to note that, in the absence of tissue residue screening benchmarks for the protection of crab themselves, the screening benchmark values used for many of these compounds are wildlife TRVs. These TRVs are developed for the protection of avian and mammalian wildlife that may eat contaminated prey. These TRVs represent a dietary benchmark; as applied here, the entire diet is assumed to be fiddler crab, all of the diet is assumed to be contaminated at the maximum analyte concentration detected, and 100% of any contaminant is assumed to be assimilated from the diet. It is recognized that these are overly conservative exposure assumptions. Some trace elements may nonetheless warrant further site-specific evaluation to determine whether they pose a threat to crab and tp other ecological

receptors. Additional data regarding the concentration of trace elements in co-located abiotic media (for example, soil) will also help put these results into context.

## 3.3.5 Sample Area Comparisons

This section discusses the spatial pattern and differences observed in concentrations irrespective of their absolute value relative to ecological or human health benchmarks. Spatial evaluations of the data can help raise other insights from the data beyond their toxicological significance.

Table 3-7 presents average concentrations of analytes detected in fiddler crab for Areas 1 through 12 and 14. In calculating these averages for the trace elements, the MDL was used to represent any non-detect value. Only detected values were summed to generate total DDT. The means for the trace elements and total DDT were then statistically tested to determine which areas (including the reference location) were significantly different from each other. Detailed statistics, along with graphical representations of the statistical analysis, are presented in Appendix F. Table 3-8 summarizes the statistical analysis.

### **Organic Compounds**

Differences in the concentrations of organic substances measured in the fiddler crab were generally similar to those for the land crab, with most substances either not detected or detected at similar concentrations among all locations. As was the case for land crab, PCBs (in this case, Aroclor 1254) were detected in fiddler crab samples collected only from Laguna Kiani (Area 3). The pesticide DDT and its metabolites were detected at more locations than in the land crab samples; however, the greatest concentrations were found at Laguna Kiani, Red Beach (Area 9), and Bahia Tapon (Area 11), similar to the case for land crab. Only concentrations of total DDTs from Bahia Tapon and Red Beach were significantly greater than concentrations in the reference samples.

### **Trace Elements**

Table 3-8 summarizes the results of statistical testing (Appendix F) for trace elements. Figure 3-4 illustrates the mean concentrations identified on Table 3-8 as both significantly greater than concentrations at the reference location and in excess of ecological screening benchmarks. Refer

to Appendix F for graphical representations of each trace element that clearly illustrate deviations from the overall average. Additional data plots in Appendix F also indicate the variability within sampling areas for select trace elements.

Average concentrations of nearly all trace elements (excepting magnesium, mercury, and thallium) determined in samples from Areas 1 through 12 were different from concentrations for the reference location (either greater or lower) for at least one area. However, differences in those trace element concentrations that also exceeded conservative ecological screening benchmarks are of most interest.

Ten trace elements were detected in at least one sample at concentrations that exceeded an ecological screening benchmark:

- Concentrations of aluminum, arsenic, vanadium, and zinc exceeded ecological screening benchmarks in every sample (including the reference sample). Average concentrations of aluminum were significantly greater than the reference mean at Boca Quebrada (Area 5) and Blue Beach (Area 10); average concentrations of arsenic at Laguna Kiani, Red Beach, Bahia Tapon, and the LIA (Area 12) were greater than the reference mean; average concentrations of vanadium at Laguna Playa Grande (Area 6) and Blue Beach were greater than the reference mean; and average concentrations of zinc at Laguna Kiani, Boca Quebrada, Red Beach, and Bahia Tapon were significantly greater than the reference mean
- Concentrations of cadmium, lead, and selenium did not exceed the ecological screening benchmarks at the reference locations, but concentrations detected at one to four sample areas were significantly greater than the reference mean. Concentrations of cadmium, lead, and selenium in land crab and fiddler crab are presented on Figures 3-1, 3-2, and 3-3, respectively, relative to the applicable ecological screening benchmarks. The average selenium concentration exceeded the reference value at Laguna Playa Grande, Blue Beach, Bahia Tapon, and the LIA. The average cadmium concentration was greater than the reference mean at Blue Beach, the LIA, and Laguna Kiani. The average lead concentration at Laguna Kiani was greater than the reference mean and also exceeded the ecological screening benchmark.

 Average concentrations of barium, chromium, and copper exceeded ecological screening benchmarks at one to three sites and were greater than the reference mean. The average concentrations of chromium at Blue Beach; of barium downgradient from SWMU 7 (Area 1) and downgradient from AOCs J and R (Area 2); and copper at Laguna Kiani, Boca Quebrada, and Laguna Playa Grande were all greater than the mean observed at the reference location.

Magnesium, mercury, and thallium were the only trace elements for which no such statistical differences were observed among any of the sampling areas. Cobalt and nickel were the only trace elements for which any significant differences were less than the reference. Cobalt, iron, and silver have no ecological screening benchmark.

Samples from Laguna Kiani, Boca Quebrada, and Blue Beach contained the largest number of trace elements for which average values were greater than the reference values. Land crab from each of these areas had six or more trace elements at concentrations that were significantly greater than concentrations at the reference locations. Puerto Ferro was the only area where no trace elements were detected in samples at concentrations significantly greater than the average reference values.

Overall, three of the sampling areas had samples with trace element concentrations that exceeded ecological screening benchmarks, but the averages for those trace elements were not significantly different from the reference values:

- Laguna Kiani South (Area 4);
- Mosquito Bay (Area 7); and
- Puerto Ferro (Area 8).

Given that these results exceeded ecological screening benchmarks but not the reference values, these results may represent a regional baseline condition.

### 3.4 Comparisons to Previous Studies

Because of differences in sample processing, the results from this study cannot always be directly compared to results from previous studies. Deya and Dias (1999) dissected the fiddler crabs. The fiddler crabs associated with data reported by the ATSDR (2003) were not rinsed of sand and mud, and the land crab results were reported with the results for other shellfish in the ATSDR study. Only the land and fiddler crab data from Lopez (2002) are directly comparable with the data reported here.

Lopez (2002) reported detectable concentrations of DDT compounds and cadmium, lead, and vanadium. The DDT level observed by Lopez (28  $\mu$ g/kg) is comparable to the maximum presented here (25  $\mu$ g/kg), and DDE values in Lopez (130  $\mu$ g/kg in land crab and 54  $\mu$ g/kg in fiddler crab) are also within the range of values presented here. Cadmium data reported by Lopez for fiddler crab are within the range of values reported here. Cadmium concentrations in three of the four land crab samples analyzed by Lopez are lower than the average cadmium values reported here. Lopez reported slightly greater cadmium concentrations in one land crab sample (0.656 mg/kg) than the maximum (0.557 mg/kg) reported here. For lead and vanadium, values reported by Lopez fall within the range of values reported here.

Deya and Dias (1999) focused on selected trace elements (cadmium, chromium, cobalt, copper, lead, manganese, nickel, and zinc). The trace element data presented by Deya and Dias for fiddler crab represent different tissues than the whole body composite data presented here. Deya and Dias generally reported higher levels of trace elements (excepting copper and manganese) and used Mosquito Bay as a reference location for comparison to the values determined in samples taken from the LIA. Similar to the results reported here, no consistent trends were observed in trace element concentrations by sampling area.

### 4.0 CONCLUSIONS

This report summarizes analytical results for Vieques Island land and fiddler crab sampled by NOAA in June 2005. All analytical data were independently reviewed and validated to ensure their usability. Land crab sample results were compared to conservative human health screening values in the ATSDR PHC (Appendix H). Land crab results were also screened in this report against ecological benchmarks meant to be protective of the crab themselves. Fiddler crab sample results were evaluated against conservative ecological screening benchmarks, as summarized in this report. Benchmarks for the protection of crab themselves were used when available. Benchmarks meant to protect wildlife that may prey on fiddler crab were applied when crustacean-based benchmarks were not available.

The ATSDR prepared a PHC using the data reported here to evaluate potential human health impacts from eating land crab. The ATSDR determined that the levels of PCBs, organochlorine pesticides, and trace elements found in land crab are much lower than levels reported to cause harmful health effects. Concentrations were also below appropriate FDA regulatory contaminant limits for shellfish consumption. The ATSDR does not expect that adults or children will experience harmful health effects from eating land crab from Vieques Island.

While the ATSDR's evaluation focused on human health aspects of the land crab data, NOAA used the data to determine whether contaminants could pose a risk to the land crab themselves.

There appears to be little contamination of crab by the organic contaminants analyzed for in this study. No explosive compounds were detected in any land or fiddler crab. Few PCB compounds were detected, and the detections occurred only in samples from Laguna Kiani (Area 3). Aroclor 1260 was detected in one land crab sample while Aroclor 1254 was detected in all fiddler crab composite samples from Laguna Kiani. It is noteworthy that the PCB detections occurred at the same area where PCBs had previously been detected in groundwater (CH2M Hill 2002b). Laguna Kiani is one of the few sampling areas with sufficient assessment data to allow comparisons among various environmental media and the body burdens reported here. Although PCBs were detected in crabs from Laguna Kiani, the results did not exceed the human or ecological screening benchmark values.

Pesticides were also rarely observed, excepting DDT metabolites and chlordane compounds, which were both detected in multiple land crab and fiddler crab samples. Many of the detections were at low, estimated concentrations just above the MDLs. No pesticide concentrations in crab exceeded ecological screening values intended for the protection of crustaceans. The composition of DDT compounds does not suggest ongoing releases. There was general concordance in the spatial pattern of exposure for the two crab species: The four highest average total DDT concentrations in both land crab and fiddler crab were observed at Laguna Kiani, Red Beach (Area 9), Blue Beach (Area 10), and Bahia Tapon (Area 11). Laguna Kiani and Bahia Tapon also had the highest total chlordane levels. Other pesticides were detected infrequently, at just one or two locations. Mirex, however, was observed in most land crab and all fiddler crab samples from the LIA (Area 12) and was not detected at any other sampling area. Although mirex concentrations in crab were below the crustacean screening benchmark, the co-occurrence of this compound in multiple samples from both species is noteworthy because it demonstrates an exposure pathway in this area.

Trace elements were ubiquitously detected in both land crab and fiddler crab samples. Concentrations were generally greater in fiddler crab than in land crab. In land crab, no differences were observed in average trace element concentrations between the two reference locations (excepting barium). In general, reference values were average or low, indicating that the reference locations were appropriately selected.

In land crab, concentrations of mercury did not exceed the crustacean-based ecological benchmark in any sampling area. Concentrations of vanadium exceeded the crustacean-based ecological benchmark in all areas except Red Beach, but there were no differences among the averages. Cadmium concentrations in samples from the LIA were elevated, were significantly different from cadmium concentrations in the reference samples, and exceeded the ecological benchmark for crustaceans. Average lead concentrations in land crab were significantly greater than the reference values at only one sampling area, Laguna Kiani. No differences were observed in average land crab residues of iron, selenium, thallium, uranium, and zinc among sampling areas, nor were concentrations of these trace elements in land crab significantly greater than in the reference samples.

Ten trace elements exceeded conservative ecological screening benchmarks in fiddler crab: aluminum, arsenic, barium, cadmium, chromium, copper, lead, selenium, vanadium, and zinc. Concentrations of some of these elements exceeded benchmarks at all sampling areas, including the reference location, while others (such as lead at Laguna Kiani) exceeded their respective benchmark at only one sampling area. Concentrations of cadmium, lead, and selenium exceeded benchmarks in some samples, but not at the reference location, and were detected at levels significantly greater than the reference means. These observations tend to suggest that exposure of these trace elements at these sampling areas may include non-natural sources in addition to natural sources. Trace elements exceeded benchmarks but were not different from the reference at three locations: Laguna Kiani South (Area 4), Mosquito Bay (Area 7), and Puerto Ferro (Area 8). Exposures at these sites may represent a regional baseline conditions that results in body burdens greater than the conservative benchmarks applied here.

There were several instances of concordance between trace element levels in the two species; elevated concentrations were observed in both species for lead at Laguna Kiani; cadmium at the LIA; and arsenic at Laguna Kiani, the LIA, and Red Beach. Total DDT was greatest in both species at Laguna Kiani, Red Beach, Blue Beach, and Bahia Tapon. Both species from Laguna Kiani and Bahia Tapon also had the highest total chlordane averages. Concordance between the two species provides a consistent indication of exposure.

This data report includes a screening-level assessment of land and fiddler crab samples from Vieques Island. This preliminary screening indicates that some analytes may be present at levels sufficiently high that the possibility of adverse impacts to crab cannot be eliminated. To fully identify and characterize potential risks to human health and ecological receptors, further analysis of land and fiddler crab, as well as other ecological receptors, may be warranted, particularly with regard to organochlorine pesticides and trace elements. The need for additional analyses should be evaluated as applicable, as part of the ongoing human health and ecological risk assessment activities required for the Remedial Investigations of sites on Vieques Island.

### 5.0 REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR). 2003. Public Health Assessment: Fish and Shellfish Evaluation, Isla de Vieques Bombing Range, Vieques, Puerto Rico. Agency for Toxic Substances and Disease Registry.
- CH2M Hill. 2002a. Final Soil, Groundwater, Surface Water, and Sediment Background Investigation Report. Norfolk, VA: Department of the Navy, Atlantic Division.
- CH2M Hill. 2002b. Final Expanded Preliminary Assessment/Site Investigation Phase II Seven Sites. Norfolk, VA: Department of the Navy, Atlantic Division.
- Deya, A.M., and E. Dias. 1999. Biomagnification of Carcinogenic Metals in Crab Tissue, Vieques, Puerto Rico. University of Puerto Rico. March 1999.
- Diaz, Oscar. 2005. Personal communication with Michael Buchman. 21 Nov 2005.
- Grimes, B.H., M.T. Huish, J.H. Kerby, D. Moran, and E. Pendleton. 1989. Species: Life Histories and Environmental Requirements of Coastal Fishes and Invertebrates (Mid-Atlantic), Atlantic Marsh Fiddler. Vicksburg, MS and Washington D.C.: U.S. Army Corps of Engineers and U.S. Fish and Wildlife Service.
- Hostetler, M.E., F.J. Mazzotti, and A.K. Taylor. 2003. Blue Land Crab (*Cardisoma guanhumi*). Gainesville, Florida: University of Florida, Institute of Food and Agricultural Sciences.
- Jarvinen, A.W., and G.T. Ankley. 1999. Linkage of Effects to Tissue Residues: Development of a Comprehensive Database for Aquatic Organisms Exposed to Inorganic and Organic Chemicals. Published (hard copy) by the Society for Environmental Toxicology and Chemistry (SETAC) and online by the USEPA. Website accessed October 2005: <a href="http://www.epa.gov/med/Prods\_Pubs/tox\_residue.htm">http://www.epa.gov/med/Prods\_Pubs/tox\_residue.htm</a>.
- Learned, Robert E., G.R. Grove, and R. Boissen. 1973. A geochemical reconnaissance of the Island of Vieques, Puerto Rico. US Geological Survey and Puerto Rico Department of Natural Resources. Open-file report 73-155 (order no. 1866).

- Lopez, F. 2002. Contaminant Levels in Crabs from Two Solid Waste Management Units on Vieques National Wildlife Reserve. U.S. Fish and Wildlife Service, Caribbean Field Office, Boqueron, Puerto Rico.
- Lotufo, G.R., et al. 2000. Comparative toxicity and toxicokinetics of DDT and its major metabolites in freshwater amphipods. *Environ. Toxicol. Chem.* 19(2):368-379
- Marsh, Sherman P. 1992. Analytical results for stream sediment and soil samples from the Commonwealth of Puerto Rico, Isla de Culebra, and Isla de Vieques. U.S. Geological Survey Open-File Report 92-353A.
- RIDOLFI Inc. and the National Oceanic and Atmospheric Administration (RIDOLFI Inc. and NOAA). 2005. Final Sampling and Analysis Plan for the Vieques Island Biota Sampling Project. Seattle, WA; NOAA, National Ocean Service, Office of Response and Restoration.
- Sample, B.E., D.M. Opresko, and G.W. Suter II. 1996. Toxicological Benchmarks for Wildlife: 1996 Revision. Oak Ridge National Laboratory (ORNL), Oak Ridge, TN.
- Schellekens, J.H., J. Joyce, A.A. Smith, and D.K. Larue. 1991. Tectonics and mineral deposits of the Caribbean, in Schellekens, J.H., ed., 105h Annual Symposium on Caribbean Geology: Mayaguez University of Puerto Rico, Department of Geology.
- Smithsonian Marine Station (SMS). 2001. Animals of the Indian River Lagoon: *Cardisoma guanhumi* (blue land crab). Available at: Smithsonian Marine Station at Fort Pierce <a href="http://www.sms.si.edu/irlspec/Cardis\_guanhu.htm">http://www.sms.si.edu/irlspec/Cardis\_guanhu.htm</a> (accessed September 23, 2005).
- Soil Conservation Service and University of Puerto Rico. 1977. Soil survey of Humacao Area, Eastern Puerto Rico. January.
- Suter II, G.W. 1993. Ecological Risk Assessment. Lewis Publishers. Chelsea, MI.
- Taissoun, E. 1974. The Land Crab of Venezuela. Maracaibo, Venezuela: University of Zulia, Center for Biological Investigations. 48 pp.
- Terwilliger, N. B., and M. Ryan. 2001. Ontogeny of Crustacean Respiratory Proteins. *Integrative and Comparative Biology* 41(5):1057-1067.

- Torres-Gonzáles, Sigfredo. 1989. Reconnaissance of the Ground-Water Resources of Vieques Island, Puerto Rico. U.S. Geological Survey Water-Resources Investigations, Report 86-4100.
- U.S. Army Corps of Engineers (USACE). 2005. Environmental Residue Effects Database (ERED). Website accessed October 2005: <a href="http://el.erdc.usace.army.mil/ered/">http://el.erdc.usace.army.mil/ered/</a>.
- U.S. Environmental Protection Agency (USEPA). 2001. ECO Update: The Role of Screening-Level Risk Assessments and Refining Contaminants of Concern in Baseline Ecological Risk Assessments. Pub 9345.0-14. EPA 540/F-01/014. June 2001.
- U.S. Environmental Protection Agency (USEPA). 2002. More In-Depth Site Details: Frontera Creek. August 2002. Available at: <a href="http://www.epa.gov/Region2/superfund/npl/0202550c.pdf">http://www.epa.gov/Region2/superfund/npl/0202550c.pdf</a> (accessed October 31, 2005).
- U.S. Environmental Protection Agency (USEPA). 2004. Vieques Island, Puerto Rico Sectors. Available at: USEPA Region 2, Vieques, <a href="http://www.epa.gov/Region2/vieques/sectors.htm">http://www.epa.gov/Region2/vieques/sectors.htm</a> (accessed August 11, 2005).
- U.S. Environmental Protection Agency (USEPA). 2005a. NPL site narrative at listing Atlantic Fleet Weapons Training Area-Vieques. Available at: USEPA National Priorities List, <a href="http://www.epa.gov/superfund/sites/npl/nar1719.htm">http://www.epa.gov/superfund/sites/npl/nar1719.htm</a> (accessed August 11, 2005).
- U.S. Environmental Protection Agency (USEPA). 2005b. EPA proposes the Atlantic Fleet Weapons Training Area on Vieques and Culebra for inclusion on the Superfund National Priorities List. Available at: USEPA Region 2 News & Speeches 2004, <a href="http://www.epa.gov/Region2/news/2004/04129.htm">http://www.epa.gov/Region2/news/2004/04129.htm</a> (accessed August 11, 2005).
- U.S. Environmental Protection Agency (USEPA). 2005c. Toxicity/Residue Database, http://www.epa.gov/med/Prods\_Pubs/tox\_residue.htm (accessed 2005).
- U.S. Navy. 2005. Vieques public website: East Vieques Island. March 2005. Available at: U.S. Navy, Installation Restoration Program, http://public.lantops-ir.org/sites/public/vieques/East%20Site%20Info/about.aspx (accessed August 11, 2005).

- U.S. Geological Survey. 2001. Geology, geochemistry, geophysics, mineral occurrences, and mineral resource assessment for the Commonwealth of Puerto Rico. Walter J Bawiec, ed. USGS Open File Report 98-38 (on CD-ROM).
- Van Holde, K. E., K. I. Miller, and H. Decker. 2001. Hemocyanins and Invertebrate Evolution. *J. Biol. Chem.* 276(19):15563-15566.

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#### **TABLES**

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Fiddler Crab Trace Element and Total DDT Statistical Analysis

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## APPENDIX H

**ATSDR Public Health Consultation** 

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