CATALOG DOCUMENTATION
VIEQUES FISH TISSUE CONTAMINANTS SUMMARY DATABASE

TABLE OF CONTENTS

1. DATASET IDENTIFICATION

1.1 Title of Catalog document
Vieques, Puerto Rico Fish Tissue Contaminant Database

1.2 Authors of the Catalog entry
David R. Whitall, NOAA Ocean Service,COAST

1.3 Catalog revision date
November 2015

1.4 Dataset name
Vieques, Puerto Rico Fish Tissue Contaminants

1.5 Task Group
Vieques, Puerto Rico Fish Tissue Contaminants

1.6 Dataset identification code
VQS

1.7 Version
001

1.8 Request for Acknowledgment
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2. INVESTIGATOR INFORMATION (for full addresses see Section 13)

2.1 Principal Investigators
David Whitall, NOAA Ocean Service, National Status and Trends Program

2.2 Sample Collection Investigators

David Whitall, Andrew Mason (NCCOS-CCMA), Blaine West (NCCOS-CCEHBR), Antares Ramos (OCM-CRCP)

2.3 Sample Processing Investigators

Nutrient analyses:
: Ed Wirth, Mike Fulton (NCCOS-CCEHBR), Charleston, SC

a. See Methods in Appendix I

3. DATASET ABSTRACT

3.1 Abstract of the Dataset
Worldwide coral reef ecosystems are being threatened by a range of human activities. Sedimentation, overfishing, global climate change, ship groundings, pathogens and pollution are some of the major human-related stressors impacting coral reefs. The eastern half of the island of Vieques (Puerto Rico) was used by the U.S. Navy for live fire exercises for over fifty years, ending in 2003. A variety of compounds associated with military activities have the potential to negatively impact coral reef ecosystems. Despite previous studies on soil and biota which found relatively low levels of pollutants in the environment, there is still public concern about the impact of pollution on the fishery.

This studied assessed tissue concentrations of energetic compounds, DDT and metals in fisheries important species (Queen conch and spiny lobster).

3.2 Keywords for the Dataset
Site, station location, latitude, longitude, date, corals, region, state, parameter, corals, conch, lobster, detection limit

4. OBJECTIVES AND INTRODUCTION

4.1 Program Objective
a) Quantify contaminant levels in species important to the Vieques fishery.
b) Determine spatial differences within the study area.
c) Put findings in a larger context using information available in the scientific literature.

The National Oceanic and Atmospheric Administration was responsible field work, data analysis and for final assembly and data review. Project partners which provided support but did not actual participate in the scientific activities included: U.S. Fish and Wildlife, the Department of the Navy, CH2MHill, and the Vieques Conservation and Historical Trust.

4.2 Dataset Objective
The dataset objective is to report information about the magnitude and spatial variability in contaminants in the tissues of marine organisms in Vieques.

4.3 Dataset Background Discussion
The dataset is composed of seven relational files each listed below.

The “SITES” data file reports information regarding the *planned* sampling locations and the actual locations. The geographical information provided for a sampling site is useful when interpreting the results of other data files.

The “STATION” data file reports the actual location and date of each sampling event. One record is presented per station per sampling event. Each record reports the latitude and longitude recorded for each event along with the date of collection and the collecting organization and personnel.

The “LAB” data file reports information collected in the laboratory about the sample prior to its analysis. Examples include characteristics such as sample weight, sample volume, extraction date, analysis date, and sample identification number.

The “ANALYTE” data file reports the results of analyses for chemical analytes.

The “QA” data file reports information regarding the quality assurance/quality control of the “ANALYTE” data file. It includes results for duplicate analyses, matrix spikes, matrix spike duplicates, sample blanks, and reference materials.

4.4 Summary of Dataset Parameters
See section 4.3

5. DATA ACQUISITION AND PROCESSING METHODS

5.1 Data Acquisition / Field Sampling
See Appendix II.

5.2 Data Preparation and Sample Processing

Sample Type	Container	Field Holding	Lab Storage
Conch Tissue			
Contaminants	HDPE jar	Wet ice (4°C)	Frozen (-40 deg C)
Lobster Tissue			
Contaminants	Aluminum foil/ziplock bag	Wet ice (4°C)	Frozen (-40 deg C)

6. DATA ANALYSIS AND MANIPULATIONS

6.1 Name of New or Modified Values
None.

6.2 Description of Data Manipulation
Not applicable

7. DATA DESCRIPTION

7.1 Description of Parameters
Samples were analyzed for metals (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb, Se, Sn, Tl, U, V, and Zn), DDT and its breakdown products (DDE, DDD) and energetic compounds (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), Tetryl. Nitrobenzene, 2,4,6 trinitrotoluene, 4-Amino-2,6-dinitrotoluene, 2-Amino-2,4-dinitrotoluene, 2-Nitrotoluene, 3-Nitrotoluene, 4-Nitrotoluene, Pentaerythritol tetranitrate (PETN), 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,2’6,6’-tetranitro-4,4’-azoxytoluene). See also section 4.3.

7.1.1 Components of the Dataset
See section 4.3.

7.1.2 Precision of Reported Values

All chemical contaminant values have been rounded to three significant digits. To accommodate the wide range of values, all concentration values have been formatted to the thousandth unit (0.001). The actual precision is listed in Appendix I.

7.2 Data Record Example

7.2.1 Column Names for Example Records
See section 4.3

8. GEOGRAPHIC AND SPATIAL INFORMATION

8.1 Minimum Longitude (Westernmost)
-65.5039325 decimal degrees

8.2 Maximum Longitude (Easternmost)
-65.295939167 decimal degrees

8.3 Minimum Latitude (Southernmost)
18.14773167 decimal degrees

8.4 Maximum Latitude (Northernmost)
18.1027579722 decimal degrees

8.5 Name of Region
Vieques, Puerto Rico

9. QUALITY CONTROL AND QUALITY ASSURANCE

9.1 Measure Quality Objective

Site location -
Sampling sites are located by GPS with a manufacturer reported position accuracy of better than 3 meters in DGPS mode. Coordinates are expressed in units to the nearest 0.00001 decimal degree. In the event the vessel cannot navigate to the site (i.e., too shallow) or the bottom type is not appropriate (i.e., rock or shellfish bed) then the first alternate site will be substituted. In the event the first alternate can not be sampled then the second alternate site will be sampled.

9.2 Data Quality Assurance Procedures

QA procedures include blanks, spiked samples, and standard reference materials with each batch of samples.

10. DATA ACCESS

10.1 Data Access Procedures
Contact Dr. David Whitall (dave.whitall@noaa.gov)

10.2 Data Access Restrictions
None

10.3 Data Access Contact Persons
David Whitall
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10.4 Dataset Format

ASCII (CSV)

11. REFERENCES

12. TABLE OF ACRONYMS

km	Kilometer
NOAA	National Oceanic and Atmospheric Administration
NOS	National Ocean Service
CCMA	Center for Coastal Monitoring and Assessment
NCCOS	National Centers for Coastal Ocean Science
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan

13. PERSONNEL INFORMATION

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Appendix I: Lab Methods

Conch and lobster were received at the laboratory in Charleston, SC and stored at -40°C prior to preparation for analysis. Briefly, tissues were prepared after thawing by homogenizing each conch in a Teflon container using a titanium handheld probe homogenizer (ProScientific, Inc.). Only the edible lobster tissue (tail meat) was homogenized for analysis. Homogenized samples were sub-sampled for organic contaminant analysis (energetics, DDTs) and trace metals analysis (Balthis et al., 2012). Moisture content was determined by drying in an oven at 85°C (>24 hr) until constant mass was achieved. All data were validated by comparison with blanks, spikes (matrix and reagent spikes), and certified reference materials.

Trace metal determination used methods described in Reed et al. (2015). Briefly, homogenized tissue was microwave digested in nitric acid followed by peroxide addition. Analysis for 21 elements (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sb, Se, Sn, Tl, U, V, and Zn) was achieved using ICP-MS (Perkin Elmer Elan 6100), while Hg was determined by direct mercury analysis (DMA-80, Milestone Inc.).

DDTs were determined by GC/MS (Kimbrough et al, 2006) with slight modifications to the protocols. Briefly, samples were prepared for Accelerated Solvent Extraction (ASE) by grinding the sample homogenate with ~28 g anhydrous sodium sulfate in a mortar. Internal standards were added to the samples prior to extraction by ASE. Post extraction clean-up was achieved using gel permeation chromatography, and collected fractions were further processed using activated alumina. Final extracts were analyzed using an Aglient 6890 Gas chromatograph paired with an Agilent 5973 MS.

The determination of munition compounds in marine tissues was achieved by two separate extraction methods (Table 2), a modification of EPA 8330B (USEPA 2006) and a Dionex ASE 200 Accelerated Solvent Extraction (ASE). Samples were extracted by both methods.

In the modified EPA 8330B method, homogenized sample aliquots (~10 g wet) were lyophilized in amber vials for two days prior for water removal. After lyophilization, samples were transferred to hexane rinsed mortar bowls and ground into a fine powder. Samples were returned to their respective vials and stored in a foil covered desiccator until extraction. Tissues samples of ~1.2 g dry (corresponding to ~4.5 g wet) were placed into 50 ml glass, solvent rinsed centrifuge tubes. The internal standards $^{13}C_7$, $^{15}N_3$-TNT, $^{13}C_4$, $^{15}N_4$-HMX, $^{13}C_3$-RDX, d_5-Nitrobenzene and 3,4-Dinitrotoluene were added followed by 15 mL of 50:50 dichloromethane/acetone. Centrifuge tubes were capped and vortexed for 1 minute then placed into a chilled sonicator bath for 3 hours with temperature controlled not to exceed 30°C.

Roughly 4.2 g of wet tissue sample was placed into a solvent rinsed mortar bowl containing ~27 g of anhydrous sodium sulfate. Samples were ground thoroughly and transferred into 33 mL ASE cells. Samples were spiked with the internal standards and extracted using an ASE 200 using a 50:50 Dichloromethane/Acetone mixture at 1000 psi. Calibration standards, reagent spikes, and matrix spikes were extracted by ASE in addition to the samples (range: 10-250 ng).

After extraction (sonication or ASE) samples were filtered through sodium sulfate into 200 mL TurboVap tubes and concentrated under a stream of nitrogen (pressure did not exceed 1.1 bar, water bath temperature = 25°C).

Samples were concentrated to 0.5 mL and solvent exchanged with dichloromethane once. Samples were again concentrated to 0.5 mL and were transferred to glass culture tubes. TurboVap tubes were rinsed three times with dichloromethane and added to the sample extracts (F_v=2 mL). Samples were then cleaned up using a J2 Scientific Gel Permeation Chromatography (GPC) system (J2 Scientific Biobead column with 100% dichloromethane as the mobile phase). After GPC cleanup samples were concentrated to 0.5 mL and solvent exchanged to methanol twice. Extracts were concentrated to 0.5-1 ml and filtered through 0.45um PTFE filters into amber sample vials. Recovery standards were added prior to instrumental analysis (1,2-Dinitrobenzene and d_4-17β estradiol) .

Sample extracts were analyzed by liquid chromatography tandem mass spectrometry (LC-MS/MS) and gas chromatography mass spectrometry (GC/MS since several analytes would not ionize on the LC-MS/MS platform.) While EPA methods use HPLC-DAD, initial work showed multiple interferences with conch and lobster tissue. For LC-MS/MS, an Agilent 1100 Series HPLC/AB Sciex API 4000 tandem mass spectrometer, operated in negative electrospray ionization with scheduled multiple reaction monitoring, was used. Separation was performed by a Phenomenex Synergi 4u Hydro-RP 80A column using a methanol/water gradient. For GC/MS analysis, an Agilent GC/MS (6890/5973N) operated in selected ion monitoring was used. Samples were injected onto a Restek DB-225ms column (30m x 0.25 um x 0.25 mm) through a split-splitless injector. Calibration curves (10-250 ng) were prepared for each batch of samples (from 8 to 13 samples). For ASE samples, the extracted curve was used, while sonication extracted samples used a calibration curve prepared directly from a stock solution.

All spiking/calibration and internal standard stocks were stored refrigerated in glass amber bottles. Working stocks for spiking and calibration were volumetrically prepared weekly from concentrated stocks in methanol to minimize degradation. Standards for the native compounds were purchased from AccuStandard, while stable isotope-labeled standards were purchased from AccuStandard and Cambridge Isotope Laboratories.

Appendix II: Field Methods

DESCRIPTION

The conch and lobster samples were taken by NCCOS SCUBA divers. Nitrile gloves were worn to prevent cross contamination between samples. Upon surfacing the samples were placed immediately on ice. At the end of each field day, samples were stored frozen at the USFWS facility in Vieques. At the end of the field mission, the samples were shipped on overnight on blue ice to the analytical lab at NCCOS' Center for Coastal Environmental Health and Biomolecular Research in Charleston, SC.

Appendix II: Project related references

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