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Assessment of bioavailable hydrocarbons in Pribilof Island rock sandpiper fall staging areas and overwintering habitat

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ABSTRACT

At present, significant adverse hydrocarbon influence on the Pribilof Island rock sandpiper (*Calidris ptilocnemis ptilocnemis*) is unlikely. Almost the entire population overwinters in Cook Inlet and breeds on four Bering Sea islands. Passive samplers deployed several times in a three year period and corresponding sediment and soft tissue samples on St. Paul Island and in Cook Inlet generally accumulated small quantities of polycyclic aromatic hydrocarbons (PAHs). Composition was consistent with oil in <15% of the passive samplers and rarely in soft tissue. Total PAH concentrations in corresponding sediment were very low (<42 ng/g dry weight); composition was consistent with oil in 39% of these samples and biomarker composition confirmed this on St. Paul Island. However, composition was dominated by normal alkanes from natural sources.

1. Introduction

The Pribilof Island rock sandpiper (*Calidris ptilocnemis ptilocnemis*) is the nominate subspecies of rock sandpiper with the world's population estimated at approximately 20,000 birds (Ruthrauff et al., 2012). Almost the entire world population of Pribilof Island rock sandpipers overwinters along Cook Inlet, Alaska's mud and sand flats feeding on clams (primarily *Macoma balthica*) and invertebrates exposed by the shifting ice floes (Gill and Tibbitts, 1999; Gill et al., 2002; Ruthrauff et al., 2013). Cook Inlet is located in south-central Alaska, approximately 290 km long, and contains shorefast ice most winters (Fig. 1). In addition to a limited overwinter range, the Pribilof Island rock sandpiper also has a limited breeding range, consisting of only four Bering Sea Islands (St. Matthew, Hall, St. Paul, and St. George Islands) totaling an area of 511 km^2 (Fig. 1; Ruthrauff et al., 2012).

While St. Matthew and Hall Islands are uninhabited, St. Paul and St. George Islands are home to one human settlement each, with St. Paul Island hosting a harbor open to Bering Sea commercial fishing fleets. This harbor is adjacent to a tidally influenced salt lagoon that serves as a fall migratory staging area for Pribilof Island rock sandpipers. Given the proximity of the harbor to the salt lagoon, there is the possibility that inadvertent spills or discharge occurring during activities in the harbor could contaminate the fall staging area of the Pribilof Island rock sandpipers.

Additionally, Cook Inlet hosts marine vessel traffic transiting to and from facilities such as the Port of Anchorage, as well as 16 operating oil and gas platforms. Cook Inlet is also open for further oil and gas development with lease sales occurring yearly (ADNR, 2016). These routine marine vessel operations in Cook Inlet, along with oil and gas operations, present the possibility for inadvertent spills or discharges of hydrocarbons into Pribilof Island rock sandpiper habitat. In 2009 the M/V *Monarch*, serving as a supply vessel to an oil platform, sunk when it was pinned to the platform by sea ice (ADEC, 2009). At the time of loss, the M/V *Monarch* was estimated to contain 35,000 to 38,000 gal of diesel fuel, as well as unknown quantities of oil and other chemicals. Given the limited overwinter distribution and small population size of the Pribilof Island rock sandpiper, instances such as the M/V *Monarch* sinking, or other accidents related to human activity, can put this subspecies at risk of exposure to contaminants and oil spills. In fact, an oil-vulnerability index created by King and Sanger (1979) ranked the rock sandpiper as the second most vulnerable among all North American shorebirds.

Oil pollution has the potential to negatively affect birds through external contamination and ingestion resulting in systemic toxicity and/or mortality (Leighton, 1993). External contamination of feathers can lead to loss of thermal properties and water repellency, while embryos are susceptible to mortality from oiling of eggshells

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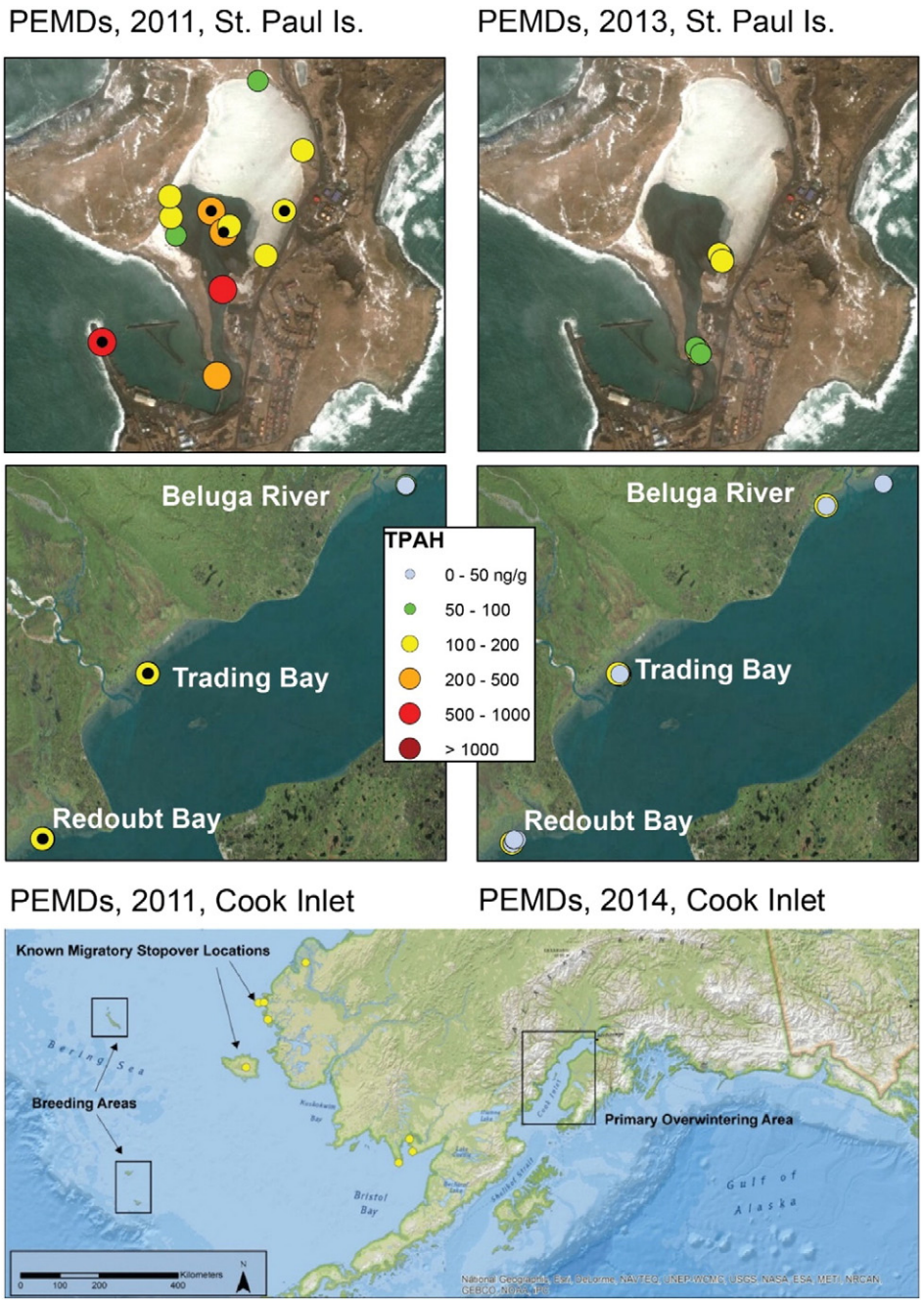

Fig. 1. Pribilof Island rock sandpiper distribution map (bottom) and TPAH concentration in PEMDs (top). Pribilof Island rock sandpiper breeding areas and primary overwintering area shown in boxes; known migratory stopover locations are shown as yellow circles, indicating known distribution (data from Alaska Natural Heritage Programs Biotics database). Regarding TPAH concentrations, each point represents a single sample, except replicate samples can overlap and may not always be visible. Black dots indicate samples with petrogenic characteristics.

(Leighton, 1993). Ingestion of large quantities of oil has acute negative effects on seabirds, while chronic effects may be noticed with longer-term exposure to lower concentrations of oil. Chemically, polycyclic aromatic hydrocarbons (PAHs) are the toxic compounds in oil of concern to biological organisms, and are capable of bioaccumulation that can produce many deleterious effects (Zedeck, 1980; Leighton, 1993; Meador et al., 1995).

Given the Pribilof Island rock sandpiper's small population size, restricted annual distribution, and proclivity for gathering in large flocks, this subspecies is particularly vulnerable to population-level impacts due to possible habitat contamination from oil and gas development. As such, we designed and implemented a study to assess current concentrations of total polycyclic aromatic hydrocarbons (TPAHs) and composition of PAHs to determine abundance and source of these compounds in Pribilof Island rock sandpiper overwinter habitat in Cook Inlet as well as a fall migratory staging area on St. Paul Island. We sampled the St. Paul Island migratory staging areas during late summer to coincide with the timing of use of the areas by Pribilof Island rock sandpipers. We sampled Cook Inlet three times, once in early winter, spring, and fall to assess PAH abundance during the primary period of use by Pribilof Island rock sandpipers as well as the seasons before and after use. Such a study will not only serve to identify current

potential risks, but will also serve as a reference point to develop appropriate mitigation measures of potential future oil spills.

2. Methods

2.1. Passive samplers

Bioavailability of PAHs was assessed with low-density polyethylene membrane sampling devices (PEMDs) as well as associated sediment and soft tissue samples from a variety of marine invertebrates including mussels, snails, and clams (Carls et al., 2004). Sampling on St. Paul Island contained marine sites located in the city harbor area and intertidal sites within a salt lagoon in 2011 (Fig. 1). A total of 13 PEMDs were deployed in July 2011 on St. Paul Island with corresponding sediment ($n = 6$) and tissue ($n = 5$) samples collected (SM 1). One additional PEMD field blank was deployed with the 2011 St. Paul Island sampling event. In 2013, sampling sites on St. Paul Island consisted of the salt lagoon and associated channel leading from the harbor to the lagoon (Fig. 1). A total of 11 PEMDs were deployed in August 2013 and 6 associated sediment samples were collected, as well as 2 tissue samples. Four additional field blanks and one trip blank were also used for this sampling event.

Cook Inlet sampling sites were located in 3 lower intertidal areas along the western shore at Redoubt Bay, Trading Bay, and the outlet of the Beluga River, all sites where the Pribilof Island rock sandpipers are known to overwinter (Fig. 1; Ruthrauff et al., 2013). Sampling at Cook Inlet occurred during November 2011 (winter), May/June 2014 (spring), and August 2014 (fall; SM 1). Seven PEMDs per site were deployed in winter 2011 with 3 sediments samples collected at each site. In 2014, 6 PEMDs were deployed and 3 sediment samples were collected during spring and 6 PEMDs were deployed in fall. Tissue samples were also collected during spring 2014 but quantities were not sufficient for analysis. One field blank was deployed during Cook Inlet sampling in 2011, while the spring 2014 sampling event had 6 field blanks and 3 trip blanks. The fall 2014 sampling event had 3 field blanks and 2 trip blanks.

The PEMDs were low-density polyethylene plastic strips (~98 μm × 4.9 cm × 50 cm) housed in aluminum canisters (11.5 cm diameter × 6.6 cm) with perforated aluminum endplates (3 mm holes spaced 4.8 mm apart). They were deployed for 28 to 34 days at all sites. PEMD field blanks were opened in each area for about 3 min during deployment and/or retrieval. Unopened PEMDs served as trip blanks for the 2013 St. Paul Island sampling event, as well as both 2014 Cook Inlet sampling events; additional laboratory blanks were never shipped.

The PEMDS were usually deployed in lower intertidal areas using hydrocarbon-free 45 cm auger anchors screwed into the sediment and shackles to tie the PEMDs to the anchors. The PEMDs were placed in 2 parallel transects 10 m apart with 3 PEMDs per transect spaced 10 m apart. Exceptions were deployment of PEMDs in the harbor infrastructure in 2011 ($n = 5$) on St. Paul Island. Shortly after arrival at the laboratory, the aluminum canisters were opened and the PEMDs were transferred to hydrocarbon-free glass jars with Teflon lined lids and frozen for chemical analysis.

2.2. Tissue sampling

Tissue samples were collected at all sites each year of the study. However, quantities were not sufficient for processing from any Cook Inlet site. Five tissue samples were processed from St. Paul Island in 2011 and 2 samples were processed from the channel site on St. Paul Island in 2013. Samples were collected via sieving substrate or collecting directly from rocky intertidal substrate. Samples consisted primarily of marine gastropods, *Macoma* sp., and mussels of Family Mytilidae; dry weight equaled 1.0 to 2.2 g for each sample. Tissue samples were placed in hydrocarbon-free jars and frozen pending analysis.

2.3. Sediment sampling

Sediment samples were collected in the same areas as the PEMDs in 2011 and 2013 on St. Paul Island ($n = 14$) and in winter 2011 and spring 2014 in Cook Inlet ($n = 18$). Sediment was collected from the top 2 cm of intertidal substrate using hydrocarbon free utensils. Sediment samples were placed in hydrocarbon-free jars and frozen pending analysis. Dry weight equaled 7.9 g to 18.7 g for each sample.

2.4. Sample processing and extraction

Passive samplers were wiped clean to remove gross surface contamination, placed in centrifuge tubes, and spiked with 500 μl of a solution equivalent to half the concentration of the deuterated surrogate recovery standard, PAHs only (Table 1). The spike solvent (hexane) was allowed to evaporate and the PEMDs were extracted in a sonic bath with 100 ml of 80:20 mixture of pentane:dichloromethane for 120 min (three 20 min sonications with a 30 min rest between each sonication). The PEMDs were immediately rinsed with pentane as they were removed after the final sonication. The extracts were dried with sodium sulfate and concentrated to 1 ml hexane. The extracts were purified on a chromatography column (1.5 g of 5% deactivated silica gel). Samples were eluted with 22 ml of a 1:1 mixture of pentane and dichloromethane. Extracts were spiked with the internal standard, hexamethylbenzene, and stored at −20 °C pending analysis.

Hydrocarbons were extracted from tissue and sediment with dichloromethane, dried, fractionated, purified, and processed by gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectroscopy (GC–MS). Samples were spiked with 500 μl of deuterated surrogate recovery standard (Table 1), and then extracted with dichloromethane using a Dionex accelerated solvent extractor (Larsen et al., 2008). Extracts were dried with sodium sulfate and concentrated to 1 ml in hexane. The extracts were applied to a chromatography column (20 g of 5% deactivated silica gel over 10 g of 2% deactivated alumina) and separated into aliphatic and aromatic fractions. The aliphatic compounds were eluted with 50 ml pentane, and aromatic compounds were eluted with 250 ml of a 1:1 mixture of pentane and dichloromethane. Tissue aromatic fractions were further purified by a high performance liquid chromatograph equipped with size-exclusion columns (22.5 mm × 250 mm phenogel, 100 Å pore size). Both the aliphatic and the aromatic fractions were reduced to 1 ml in hexane, spiked with internal standards (dodecylcyclohexane and hexamethylbenzene, respectively) and stored at −20 °C pending GC analysis.

2.5. Hydrocarbon measurement

Aromatic fractions in PEMD, sediment, and tissue extracts were analyzed for PAHs by GC–MS. Data were acquired in selected ion monitoring (SIM) mode and concentrations were determined by the internal

Table 1
Deuterated surrogate PAH standards and concentrations in spike solvent used for tissue and sediment. Spike volumes were 500 μl for tissue and sediments. The spike solvent was hexane.

(μg/ml)	Surrogate
2.0	Naphthalene-d_8
2.0	Acenaphthene-d_{10}
2.0	Phenanthrene-d_{10}
2.0	Chrysene-d_{12}
2.0	Perylene-d_{12}
2.0	Benzo[*a*]pyrene-d_{12}
9.9	n-Dodecane-d_{26}
9.7	n-Hexadecane-d_{34}
9.7	n-Eicosane-d_{42}
9.8	n-Tetracosane-d_{50}
9.7	n-Triacontane-d_{62}

standard method (Short et al., 1996). Experimentally determined method detection limits were about 0.04 ng/g in sediment. The accuracy of the PAH analyses was about ±5% based on comparison with National Institute of Standards and Technology values (SRM 1944), and precision expressed as coefficient of variation was about 5%. Surrogate recoveries were typically 96% (range 6% to 159%), excluding one blank with poor recoveries. There were two recoveries <26% (perylene) and two >150% (benzo(a)pyrene). Measured PAHs were naphthalenes (N0 to N4), biphenyl (BPH), acenaphthylene (ACN), acenaphthene (ACE), fluorenes (F0 to *F*4), dibenzothiophenes (D0 to D4), phenanthrenes (P0 to *P*4), anthracene (ANT), fluoranthene (FLU), pyrene (PYR), fluoranthene/pyrenes (FP1 to FP4) benzo(a)anthracene (BAA), chrysenes (C0 to *C*4), benzo(b)fluoranthene (BBF), benzo(k)fluoranthene (BKF), benzo(e)pyrene (BEP), benzo(a)pyrene (BAP), perylene (PER), indeno(1,2,3-cd)pyrene (ICP), dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene (BZP). Concentrations below method detection limits were set to zero. Total PAH concentrations were calculated by summing concentrations of these PAHs excluding perylene because the latter is often produced by natural biological activity (Venkatesan, 1988). Concentrations are reported as ng/g dry weight.

Aliphatic fractions in tissue and sediment extracts were analyzed for *n*-alkanes using GC-FID. Analyte concentrations were determined by the internal standard method. Experimentally determined method detection limits were about 5 ng/g in tissue and <1 ng/g in sediment. The accuracy of the alkane analyses was ±15% based on a spiked blank processed with each set of samples, and precision expressed as coefficient of variation was usually less than about 10%. Typical surrogate recoveries were 71% (range 29% to 123%). Measured normal alkanes ranged from *n*–C9 through *n*–C36 plus pristane and phytane. Concentrations below method detection limits were set to zero. Total alkane concentrations were calculated by summing these concentrations. The unresolved complex mixture (UCM) concentration was determined from the difference between the total FID response area and resolved peak areas. Concentrations are reported as ng/g dry weight.

The aliphatic fractions of sediment were analyzed for biomarkers by GC–MS. The data were acquired in a selected-ion monitoring mode, and concentrations were determined by the internal standard method with response factors (RF) based on two representative compounds, 17α(H), 21β(H)-hopane (*H*30) and 5α(H),14α(H),17α(H)-cholestane. The accuracy of the biomarker analyses was about ±15% based on a spiked blank processed with each set of samples, and precision expressed as coefficient of variation was about 10%, depending on the biomarker. Biomarker concentrations were not corrected for recovery; typical surrogate recovery was 96% (range 83% to 101%). Biomarker analytes are reported in Table 2. Total biomarker concentrations were calculated separately for the isoprenoids versus all other biomarkers because the isoprenoids weather relatively quickly compared to the triterpanes, hopanes, and steranes.

2.6. Measurement interpretation

Composition of PAH was modeled to characterize source attributes (petrogenic or pyrogenic) using revised methods of Carls (2006); potential values range from −1 (pyrogenic) to +1 (petrogenic). In brief, the model relies on pattern recognition; parent homologues in petrogenic sources are less abundant than alkylated counterparts, and concentrations frequently form a rounded 'hump,' lower or lowest for the parent compound and peaking somewhere in the alkylated compounds within each homologous group. In contrast, abundance of parent compounds in pyrogenic sources is greatest and concentrations decline with increasing alkylation. Weathering, which is differential molecular weight-dependent compound loss, influences these patterns, yet they generally remain discernable. Six homologous families, naphthalenes (N0–N4), fluorenes (F0–*F*4), dibenzothiophenes (D0–D4), phenanthrenes (P0–*P*4), fluoranthene-pyrenes (FL, PY, FP1–FP4), and chrysenes (C0–*C*4) are assessed. Scores within any given homologous family range from −1 (pyrogenic) to +1 (petrogenic). The midpoint (0) indicates there was no discernible source. The model also reports individual homologue results and flags samples with mixed results (i.e., those with both pyrogenic and petrogenic characteristics), thus allowing a detailed view of model function and opportunity to focus on promising subsets where results may otherwise be complicated. Model results ≥0.50 were accepted as petrogenic in this study.

3. Results

3.1. Passive samplers (PEMDs)

Total PAH concentrations on St. Paul Island were elevated above blank concentrations in some PEMDs in 2011 but not in 2013. Maximum TPAH concentrations reached 819 ng/g device in 2011, substantially greater than the median blank concentration of 27 ng/g device. However, only 2 of these 13 PEMDs had concentrations >500 ng/g device (SM 2); one was near the southern drainage of the lagoon site and one was located at the harbor site (Fig. 1). One harbor sample and 3 lagoon samples had petrogenic signatures (Fig. 1). Total PAH concentrations were <140 ng/g in 91% of the blanks; the remaining two blanks were compromised by a contamination artifact (212 ng/g device and 336 ng/g device; SM 3).

Median TPAH concentrations for PEMDs in Cook Inlet were less than on St. Paul Island but several samples had petrogenic characteristics in the winter of 2011 (Fig. 1; source model values greater than or equal to 0.60). Median concentrations were lowest at the Beluga River site and no petrogenic signatures were observed (Fig. 1). In contrast, petrogenic sources were detected in Trading and Redoubt Bays but at low TPAH concentrations (141 to 178 ng/g device). All PEMDs with petrogenic signatures had TPAH concentrations greater than in the corresponding field blank (129 ng/g device). No PEMDs from Cook Inlet exhibited petrogenic signatures in 2014.

3.2. Tissue

Total PAH concentrations were above typical background levels (~100 ng/g dry weight; Boehm et al., 1995; Short and Babcock, 1996; Carls et al., 2001) in 4 out of the 5 samples collected on St. Paul Island in 2011 (range 158 to 651 ng/g dry weight; SM 4) but only one of those had evidence of a petrogenic source (Fig. 2; source model value was 0.55). The observed TPAH concentration range in tissue was similar to that in PEMDs from the same area. Soft tissue samples from St. Paul Island in 2013 were below 100 ng/g dry weight (SM 4).

The majority of hydrocarbons in tissue were *n*-alkanes (77% to 99%). Calibrated *n*-alkane concentrations ranged from about 700 to 3700 ng/g dry weight in 2011 and 23,000 to 25,000 ng/g dry weight in 2013. Alkane composition was generally dominated by odd-chain *n*-alkanes (77% to 100% in 6 of 7 samples; the exception was the sample with the lowest alkane concentration, and where few alkanes were observed). The dominant calibrated *n*-alkane in all samples was *n*-C17 in all except one sample where pristane was dominant. Alkane distributions typically ranged from about *n*-C10 to *n*-C31. Alkane distributions were not consistent with oil contamination and no UCMs were observed.

3.3. Sediment

Total PAH concentrations in sediment were very low (0 to 42 ng/g dry weight), at levels generally considered background, yet several samples had petrogenic characteristics (Fig. 3; SM 5). These oil signatures were confined to sediments with the greatest TPAH concentrations. On St. Paul Island, one harbor sediment sample and one lagoon sample had petrogenic characteristics in 2011 and 2013, respectively (Fig. 3). In Cook Inlet, petrogenic signals were evident at Beluga River and Redoubt

Table 2
Biomarkers and their abbreviations. Asterisks mark analytes used for pattern matching; TR26a and TR26b cannot be resolved with current column settings at our laboratory, thus are combined for modeling. The number of triterpanes, hopanes, and steranes used for modeling were 10, 20, and 15, respectively.

Abbreviation		Biomarker: Isoprenoids	Target Ions
Norprist		Norpristane	57
Prist		2,6,10,14-tetramethylpentadecane (pristane)	57
Phyt		2,6,10,14-tetramethylhexadecane (phytane)	57
Abbreviation		**Biomarker: Triterpanes**	**Target Ions**
TR23	*	C23 tricyclic terpane	191
TR24	*	C24 tricyclic terpane	191
TR25a	*	C25 tricyclic terpane (a)	191
TR25b	*	C25 tricyclic terpane (b)	191
TET24	*	C24 tetracyclic terpane	191
TR26a	*[a]	C26 tricyclic terpane (a)	191
TR26b		C26 tricyclic terpane (b)	191
TR28a	*	C28 tricyclic terpane (a)	191
TR28b	*	C28 tricyclic terpane (b)	191
TR29a	*	C29 tricyclic terpane (a)	191
TR29b	*	C29 tricyclic terpane (b)	191
Abbreviation		**Biomarker: Hopanes**	**Target Ions**
Ts	*	18α(H),21β(H)-22,29,30-trisnorhopane	191
Tm	*	17α(H),21β(H)-22,29,30-trisnorhopane	191
H28	*	17α(H),18α(H),21β(H)-28.30-bisnorhopane	191
NOR25H		17α(H),21β(H)-25-norhopane	191
H29	*	17α(H),21β(H)-30-norhopane	191
C29Ts	*	18α(H),21β(H)-30-norneohopane	191
M29	*	17α(H),21β(H)-30-norhopane (normoretane)	191
OL		18α(H) and 18β(H)-oleanane	191
H30	*	17α(H),21β(H)-hopane	191
NOR30H	*	17α(H)-30-nor-29-homohopane	191
M30	*	17β(H),21α(H)-hopane (moretane)	191
H31S	*	22S-17α(H),21β(H)-30-homohopane	191
H31R	*	22R-17α(H),21β(H)-30-homohopane	191
GAM	*	Gammacerane	191
H32S	*	22S-17α(H),21β(H)-30.31-bishomohopane	191
H32R	*	22R-17α(H),21β(H)-30.31-bishomohopane	191
H33S	*	22S-17α(H),21β(H)-30,31,32-trishomohopane	191
H33R	*	22R-17α(H),21β(H)-30,31,32-trishomohopane	191
H34S	*	22S-17α(H),21β(H)-30,31,32,33-tetrakishomohopane	191
H34R	*	22R-17α(H),21β(H)-30,31,32,33-tetrakishomohopane	191
H35S	*	22S-17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	191
H35R	*	22R-17α(H),21β(H)-30,31,32,33,34-pentakishomohopane	191
Abbreviation		**Biomarker: Steranes**	**Target Ions**
S22	*	C_{22} 5α(H),14β(H),17β(H)-sterane	217,218
DIA27S	*	C_{27} 20S-13β(H),17α(H)-diasterane	217,218
DIA27R	*	C_{27} 20R-13β(H),17α(H)-diasterane	217,218
C27S	*	C_{27} 20S-5α(H),14α(H),17α(H)-cholestane	217,218
C27bbR	*	C_{27} 20R-5α(H),14β(H),17β(H)-cholestane	217,218
C27bbS	*	C_{27} 20S-5α(H),14β(H),17β(H)-cholestane	217,218
C27R	*	C_{27} 20R-5α(H),14α(H),17α(H)-cholestane	217,218
C28S	*	C_{28} 20S-5α(H),14α(H),17α(H)-ergostane	217,218
C28bbR	*	C_{28} 20R-5α(H),14β(H),17β(H)-ergostane	217,218
C28bbS	*	C_{28} 20S-5α(H),14β(H),17β(H)-ergostane	217,218
C28R	*	C_{28} 20R-5α(H),14α(H),17α(H)-ergostane	217,218
C29S	*	C_{29} 20S-5α(H),14α(H),17α(H)-stigmastane	217,218
C29bbR	*	C_{29} 20R-5α(H),14β(H),17β(H)-stigmastane	217,218
C29bbS	*	C_{29} 20S-5α(H),14β(H),17β(H)-stigmastane	217,218
C29R	*	C_{29} 20R-5α(H),14α(H),17α(H)-stigmastane	217,218

Bay. Total PAH concentrations were least at Trading Bay and there was no evidence of contamination in either year (SM 5).

The majority of hydrocarbons in sediment were *n*-alkanes (93% to >99% on St. Paul, 49% to 98% in Cook Inlet except they were not detected in two samples). Calibrated *n*-alkane concentrations ranged from 130 to 15,000 ng/g dry weight and were dominated by odd-chain *n*-alkanes (77% to 100%; SM 6). These distributions were consistent with natural plant production (Harji et al., 2008). Calibrated *n*-alkane concentrations were least in Cook Inlet sediment in 2011 and consistently greatest in the St. Paul Island lagoon site (SM 6). Normal-C17 was often dominant in St. Paul Island sediment (11 of 14 samples). Petrogenic alkane sources were not evident and UCMs were absent.

Biomarker residues were distinctly different between Cook Inlet and St. Paul Island (Fig. 4). Many more biomarkers were typically detected in St. Paul Island sediment than in Cook Inlet. Biomarker concentrations in sediment were low, 2 to 45 ng/g dry weight on St. Paul Island and 0 to 6 ng/g dry weight in Cook Inlet (Fig. 5). On St. Paul Island, H30 was dominant in every sample; in Cook Inlet it was only dominant in 29% of the

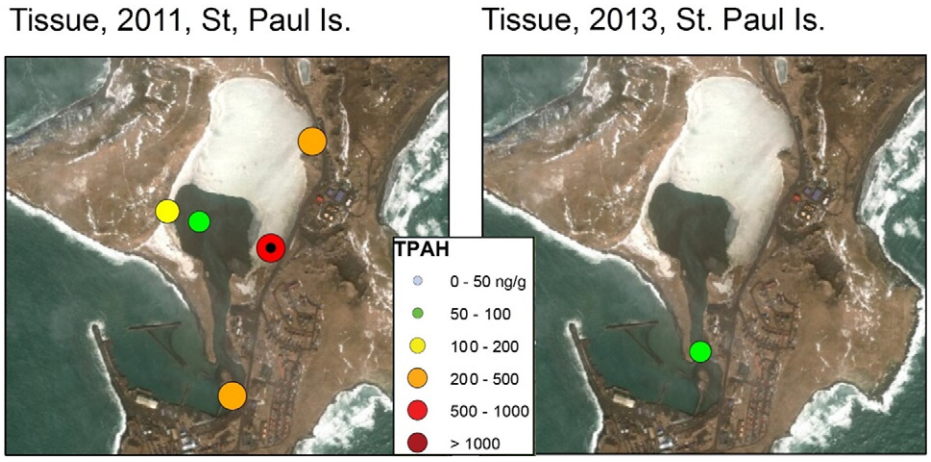

Fig. 2. TPAH in tissue (ng/g dry weight). Each point represents a single sample, except replicate samples can overlap and may not always be visible (e.g., two samples were collected from the same place in 2013). Black dots indicate samples with petrogenic characteristics. Cook Inlet is not represented because tissue samples were not sufficient for analysis.

samples. Biomarker composition on St. Paul Island did not match that in Alaska North Slope crude oil (an example source oil available to us), yet was similar enough that a petrogenic source is plausible.

4. Discussion

There was limited evidence of Pribilof Island rock sandpiper habitat contamination by hydrocarbons on St. Paul Island and in Cook Inlet. Passive samplers (PEMDs) deployed to assess biologically available PAHs, which are considered the primary toxic fraction of oil, generally accumulated small quantities of hydrocarbons. Accumulation in tissue was similar. Furthermore, TPAH concentrations were only substantial in a few PEMDs on St. Paul Island in 2011 and were rarely consistent with oil in tissue. Two- and three-ring PAH composition in PEMDs was consistent with oil in about 14% of all field samples (12 of 84) but four-ring PAH composition was never consistent with either oil or

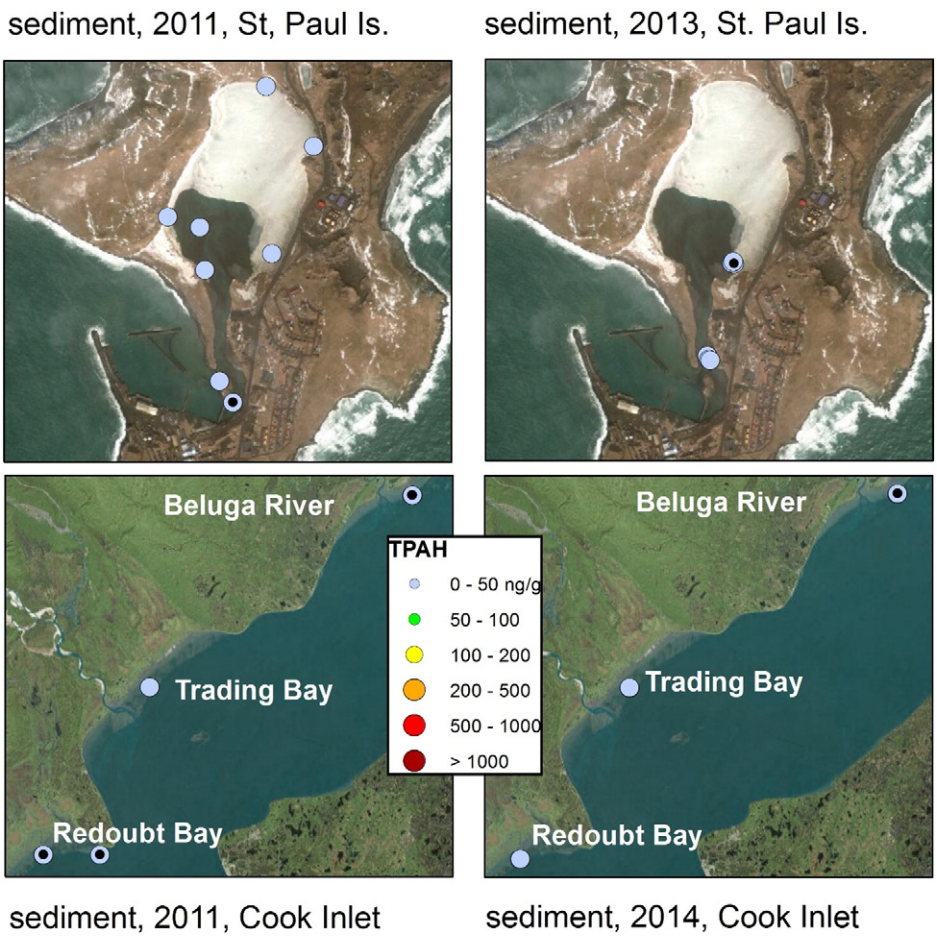

Fig. 3. TPAH concentration in sediment (ng/g dry weight). Each point represents a single sample, except replicate samples can overlap and may not always be visible. Black dots indicate samples with petrogenic characteristics.

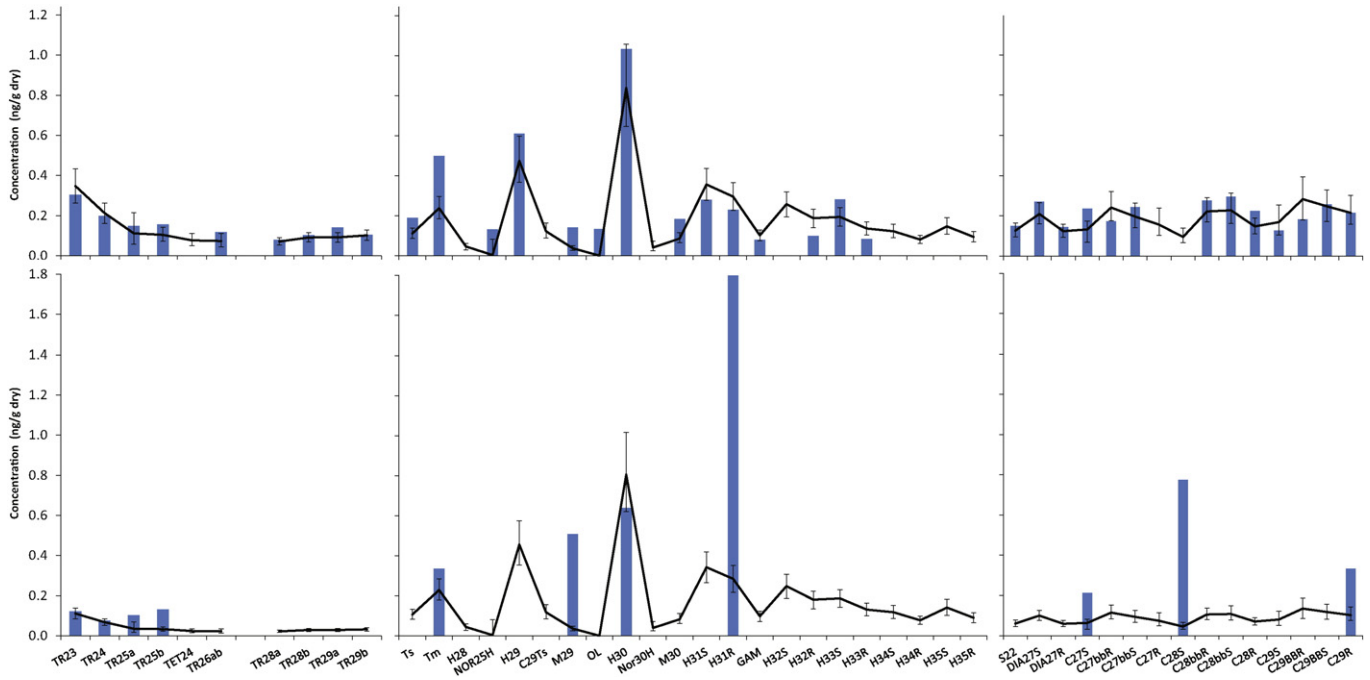

Fig. 4. Example differences in biomarker composition in sediment; St. Paul Island is on top and Cook Inlet is on the bottom. The black line illustrates composition in Alaska North Slope crude oil. Vertical bars indicate model acceptance ranges.

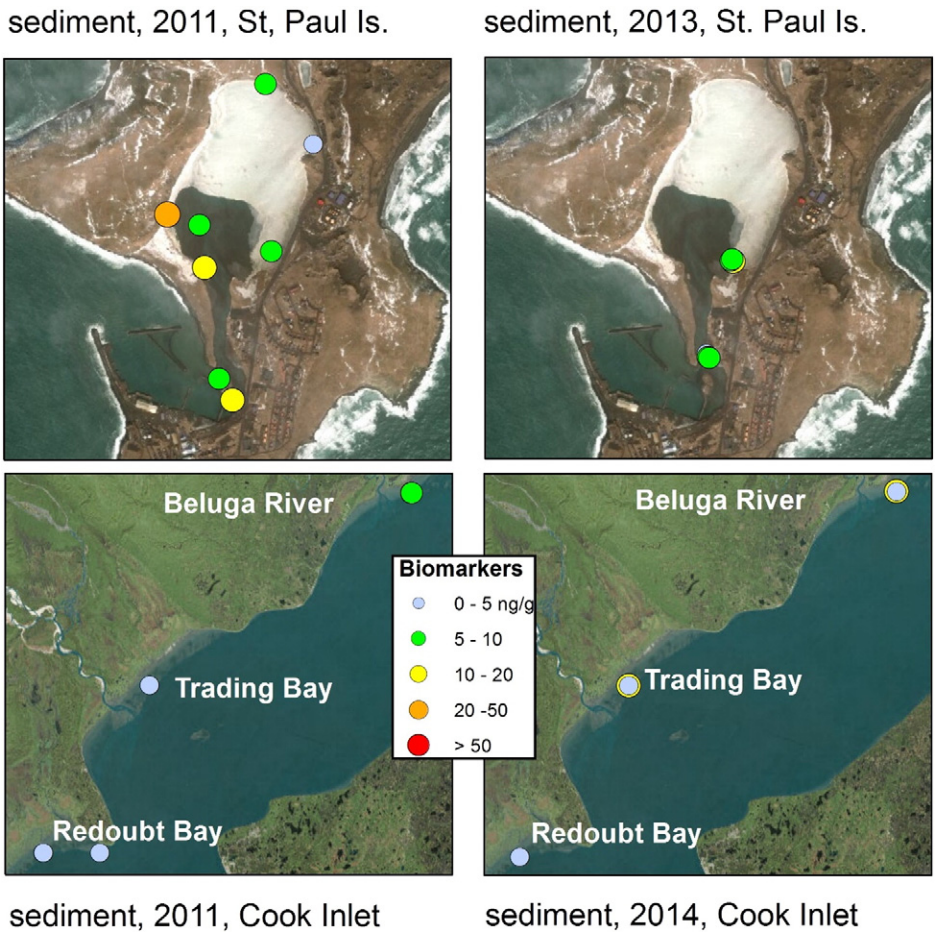

Fig. 5. Total biomarker concentration in sediment (ng/g dry weight). Each point represents a single sample, except replicate samples can overlap and may not always be visible.).

creosote. These passive samplers were designed to accumulate dissolved hydrocarbons, not whole oil, explaining the paucity of highly insoluble four-ring and larger PAHs in them. Unlike PEMDs, soft tissue samples consistently contained higher molecular weight PAHs, similar to those in sediment, thus they likely accumulated at least some of their PAH burden by physical contact and not simply from dissolved sources.

Total PAH concentrations in St. Paul Island and Cook Inlet sediment were very low, yet composition was consistent with oil in 39% of all samples. Composition was never consistent with pyrogenic sources such as creosote. Biomarkers in sediment provided additional evidence of possible low-level petrogenic contamination on St. Paul Island only, by elevated concentration and composition. In contrast, alkane composition in sediment was generally consistent with natural sources and alkane concentrations were unrelated to PAH and biomarker concentrations. Results of this study corroborate previous studies assessing potential hydrocarbon contamination from sediments in lower Cook Inlet showing generally low levels of PAHs and TPAH (Atlas et al., 1983; Saupe et al., 2005).

Additionally, natural influences were evident in the samples. Perylene was frequently prominent or the dominant PAH in sediment and it was present in tissue sample, although typically in relatively smaller quantities. Perylene likely originates from contemporary processes in sediment, hence this substance was not considered as part of PAH totals and assessment of anthropogenic sources (Venkatesan, 1988). Likewise, the dominance of odd-chain n-alkanes was natural. The larger odd *n*-alkanes were likely derived from terrestrial plant lipids (*n*-C25 to *n*-C31) and the smaller *n*-C15 to *n*-C19 likely represents marine algae (Clark and Blumer, 1967; Zhao et al., 2003; Harji et al., 2008).

Significant adverse hydrocarbon influence on the Pribilof Island rock sandpiper from anthropogenic sources in their habitat on St. Paul Island and in Cook Inlet is unlikely because sediment contamination levels were low (TPAH ≤42 ng/g dry weight) and there was generally little potential for bioaccumulation. This situation contrasts with western Prince William Sound, where substantial *Exxon Valdez* oil residues in sediment (Short et al., 2004; Short et al., 2006, 2007) were biologically available to harlequin ducks and reduced winter survival for about 22 years (Esler et al., 2002; Esler and Ballachey, 2014). We recognize that comparison of negative biological effects of oil contamination across studies is difficult due to the varying chemical compositions of differing types of oil as well as the differential weathering that occurs in the environment (Leighton, 1993). However, studies that report negative biological effects cite orders of magnitude greater PAH concentrations in than those in this study (Long et al., 1995; Johnsen et al., 2002; Saupe et al., 2005). Thus we infer that TPAH concentrations in Pribilof Island rock sandpiper habitat are currently not large enough and widespread enough to cause adverse biological effects. This could change rapidly if a spill were to occur, and restoration plans can use these data as baseline information for restoration goals and monitoring of remediation activities. These data span several years of ambient concentrations and sources of TPAHs in Cook Inlet and the St. Paul Island harbor area and reflect the best information to date for potential future restoration activities.

Even though TPAH concentrations in Pribilof Island rock sandpiper habitat are currently low, Rocque and Winker (2004) assessed contaminant levels for Aleutian archipelago avifauna and found support for a west to east long-range transport of organochlorides and mercury and suggested continued monitoring of contaminants in this region is prudent. Moreover, Braune and Noble (2009) suggest that diet composition of Canadian shorebirds may be the best predictor of contaminant exposure among variables such as age, migratory habits, or foraging habits. Specifically, greater ingestion of aquatic invertebrates as opposed to aquatic plants may increase contaminant exposure for shorebirds (Braune and Noble, 2009). Due to the fact Pribilof Island rock sandpipers primarily forage on aquatic invertebrates, they may be additionally susceptible to any larger increases in contaminant concentrations, thus further highlighting the need for continued monitoring.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2016.06.032.

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