A Quantitative Ecological Risk Assessment of the Toxicological Risks from *Exxon Valdez* Subsurface Oil Residues to Sea Otters at Northern Knight Island, Prince William Sound, Alaska

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ABSTRACT

A comprehensive, quantitative risk assessment is presented of the toxicological risks from buried *Exxon Valdez* subsurface oil residues (SSOR) to a subpopulation of sea otters (*Enhydra lutris*) at Northern Knight Island (NKI) in Prince William Sound, Alaska, as it has been asserted that this subpopulation of sea otters may be experiencing adverse effects from the SSOR. The central questions in this study are: could the risk to NKI sea otters from exposure to polycyclic aromatic hydrocarbons (PAHs) in SSOR, as characterized in 2001–2003, result in individual health effects, and, if so, could that exposure cause subpopulation-level effects? We follow the U.S. Environmental Protection Agency (USEPA) risk paradigm by: (a) identifying potential routes of exposure to PAHs from SSOR; (b) developing a quantitative simulation model of exposures using the best available scientific information; (c) developing scenarios based on calculated probabilities of sea otter exposures to SSOR; (d) simulating exposures for 500,000 modeled sea otters and extracting the 99.9% quantile most highly exposed individuals; and (e) comparing projected exposures to chronic toxicity reference values. Results indicate that, even under conservative assumptions in the model, maximum-exposed sea otters would not receive a dose of PAHs sufficient to cause any health effects; consequently, no plausible toxicological risk exists from SSOR to the sea otter subpopulation at NKI.

Received 7 November 2008; manuscript accepted 3 May 2009.

Funding provided by ExxonMobil; however, the opinions and conclusions expressed herein are strictly those of the authors and do not necessarily represent the opinions of ExxonMobil. Additionally, the Minnesota Department of Natural Resources (MDNR) is listed to identify a co-author's affiliation only, and MDNR had no role in the work herein.

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Key Words: ecological risk assessment, sea otter, *Enhydra lutris*, Exxon Valdez oil spill, subsurface oil residues, stochastic simulation modeling, conceptual exposure modeling, polycyclic aromatic hydrocarbons.

INTRODUCTION

The *Exxon Valdez* oil spill (EVOS) in March 1989 released more than 250,000 barrels of crude oil into Prince William Sound (PWS) (Figure 1) (NOAA 1992; Leschine *et al.* 1993); 782 km of the PWS shoreline (about 16%) was oiled to some degree (Neff *et al.* 1995). Four stressors to the PWS biota resulted from EVOS: (1) volatile organic chemicals (VOCs), which may have posed an early inhalation risk but dissipated quickly; (2) physical oiling, which caused loss of thermoregulation capacity in the cold PWS waters, leading to most of the observed mortality to seabirds and sea otters (*Enhydra lutris*); (3) polycyclic aromatic hydrocarbons (PAHs), which

Figure 1. Oiled shoreline of Prince William Sound from the *Exxon Valdez* oil spill based on the Shoreline Cleanup Assessment Team (SCAT) survey (from Neff *et al.* 1995).

present a longer-term toxicity risk to exposed organisms; and (4) clean-up activities, with extensive human presence and associated noise, likely causing disturbance to some wildlife.

PWS is a highly dynamic system, experiencing extreme storms, waves, and tidal action; consequently, the Exxon Valdez oil (EVO) was largely eliminated from shorelines by natural processes and clean-up activities in the initial months to few years after the spill (NOAA 1992; Neff *et al.* 1995). Boehm *et al.* (1996) concluded that only minimal risk to mussel-foraging wildlife remained within one year of the spill. The quantity of residual oil decreased rapidly, at degradation rates of ~25% per year during 1992–2001 (Short *et al.* 2004, 2007). By 2001 the extent of intertidal shoreline with remnant surface oil residues (SOR) and subsurface oil residues (SSOR) had decreased by more than 99%, estimated at 11.3 ha ($\leq 0.05\%$ of the PWS shoreline) (Short *et al.* 2004); further reduction from the 2001 estimates would be expected by 2009, even at the slower degradation rates estimated by Short *et al.* (2007). The small amount of SOR remaining in 2002 was limited to small patches of asphalt or highly weathered tar “splats” in the upper-middle intertidal to supratidal zones, typically on cobble, boulder, and pebble beaches in low- to moderate-energy wave environments (Taylor and Reimer 2008). Because SOR has little bioavailability and is located on shorelines well above any potential for sea otter exposure (the focus of this assessment), the SOR is not considered here. Likewise, because no subtidal deposits of EVO have been reported since shortly after the spill (O’Clair *et al.* 1996; Boehm *et al.* 1998), subtidal residues are not considered here. By 2002, only small, widely dispersed pockets of subsurface residues remained in the intertidal zone (ITZ), mostly under a boulder and cobble armor in the mid-to-upper ITZ (Short *et al.* 2004; Taylor and Reimer 2008), that is, in locations protected from waves, where physical disturbance of the sediments below the surface armor would occur only rarely (Michel *et al.* 2006; Short *et al.* 2007; Taylor and Reimer 2008).

The composition of the residual constituent PAHs has changed over time, leaving higher-molecular-weight, less-bioavailable compounds, as shown in PAH levels in intertidal animals (*e.g.*, Huggett *et al.* 2003, 2006; Boehm *et al.* 2004; Neff *et al.* 2006). The remaining SSOR has undergone varying degrees of weathering and typically is covered by a 15–25 cm thick layer of clean sediments (Hayes and Michel 1999; Michel *et al.* 2006; Taylor and Reimer 2008). Consequently, PAHs are released into the environment only very slowly (Boehm *et al.* 2004; Neff *et al.* 2006). Further, three of the four stressors from EVOS, VOCs, physical oiling, and clean-up activities, were eliminated many years ago, which leaves exposure to PAHs in buried residues as the sole remaining potential ecological risk.

There has been speculation (*e.g.*, Bodkin *et al.* 2002; Peterson *et al.* 2003; Short *et al.* 2006) that this residual risk of exposure to SSOR is sufficient to cause continuing adverse effects on species that feed in the ITZ, in particular sea otters and seaducks at Northern Knight Island (NKI), an area that was heavily oiled by the spill and contains patches of SSOR. Rice *et al.* (2007) reported that cytochrome P4501A (CYP1A), an exposure biomarker, was elevated in sea otters at NKI, attributing this biochemical response to residual EVO contamination. However, the utility of CYP1A as an indicator of exposure to EVOS-derived PAHs is debatable. Anderson and Lee (2006) noted that CYP1A responds more to pyrogenic than petrogenic hydrocarbons and that biomarker-inducing pyrogenic PAHs (*e.g.*, chrysene and benzo(a)pyrene)

occur throughout the spill zone (*e.g.*, Page *et al.* 1999, 2002, 2004; Huggett *et al.* 2003). CYP1A induction is not specific to PAHs, but can be induced in marine mammals by many other chemicals, such as polychlorinated biphenyls (PCBs) and chlorinated dioxins (*e.g.*, Houde *et al.* 2005). PCBs have been found in seaducks and sea otters in PWS (Thust *et al.* 2000; Ricca *et al.* 2010).

On the effects side of the risk paradigm, sea otters and Harlequin ducks (*Histrionicus histrionicus*) were characterized by the EVOS Trustees Council in 2009 as “recovering” but not yet recovered species (EVOSTC 2009). Bodkin *et al.* (2002) and Dean *et al.* (2002) suggested that the sea otter subpopulation at NKI continued to show effects, potentially attributable to SSOR (no current effects are posited for the sea otters elsewhere in PWS). Short *et al.* (2006) suggested that, when digging in sediments for food, NKI sea otters and seaducks may encounter SSOR in sufficient frequency and quantity to affect their health. Using data from the NOAA 2003 survey of SSOR, Short *et al.* (2006) calculated probabilities of randomly encountering SSOR from digging into intertidal sediments, asserting that “these encounter probabilities are sufficient to ensure that sea otters and ducks that routinely excavate sediments while foraging within the intertidal would likely encounter subsurface oil repeatedly during the course of a year.” However, since the SSOR is located under a 15–25 cm layer of clean sediments, the prospect of seaducks (in PWS, primarily Harlequin ducks, Barrow’s goldeneye [*Bucephala islandica*], and the common goldeneye [*Bucephala clangula*]) excavating sediments to that depth is implausible, because their diet is largely epibenthic and they have no physical capability to dig to that depth (see Robertson and Goudie [1999] and Eadie *et al.* [1995, 2000]). Thus, there is no plausible route of exposure to seaducks from excavating buried SSOR. However, sea otters do excavate sediments to depths of 50 cm while foraging for infauna (primarily clams) in the ITZ (Shimek and Monk 1977; Calkins 1978; Hines and Loughlin 1980; Kvitek *et al.* 1988), so a potential route of exposure exists if a sea otter excavates a pit that intersected SSOR.

To assess the potential toxicological risk that EVOS-derived SSOR poses to NKI sea otters, we conducted a quantitative ecological risk assessment of both exposures and effects of PAHs. We began by developing a conceptual model that illustrates possible exposure pathways of the PAHs in SSOR to sea otters. The variables in each pathway were then quantified and a simulation model was developed to project the doses that might ensue. Toxicity reference values (TRVs) were derived to assess the effects the model-projected doses could have on the health of NKI sea otters. Using this quantitative ecological risk assessment framework, we assess whether NKI sea otters foraging on intertidal infauna could excavate enough SSOR to result in chronic doses of PAHs sufficient to affect the health of maximum-exposed individuals. We then assess qualitatively whether the projected exposures and individual-level toxicological effects could cause effects on the subpopulation of sea otters at NKI.

EXPOSURE PATHWAYS CONCEPTUAL MODEL FOR SEA OTTERS

A central element of the USEPA guidelines for ecological risk assessment (USEPA 1992, 1998; Gentile *et al.* 1993) is the development of a conceptual model delineating all the natural and anthropogenic processes that lead to stressors that may cause effects on ecosystem components. The conceptual model presented here focuses on

Current Risks of Exxon Valdez Subsurface Oil Residues to Sea Otters

Figure 2. Exposure pathways conceptual model for sea otters at Northern Knight Island from PAHs in subsurface oil residues (SSOR).

the potential toxicological risks to the NKI sea otter subpopulation from background and SSOR-derived PAHs (Figure 2).

Distribution of SSOR

The Study Area for this ecological risk assessment includes the shorelines of Herring Bay (HB), Lower Passage (LP), and Bay of Isles (BI) (Figure 3), identical to the NKI area defined by Short *et al.* (2006). The NKI Study Area was divided into shoreline subdivisions during the 1991 joint Federal, State of Alaska, and Exxon May Shoreline Assessment Program (MAYSAP) survey as part of the Shoreline Cleanup Assessment Team (SCAT) program (Neff *et al.* 1995). Within these subdivisions, specific sites, identified as having SSOR from prior surveys, were surveyed by NOAA in 2001 and 2003 (Michel *et al.* 2006; Short *et al.* 2006). Each SCAT shoreline subdivision consists of a mosaic of different sediment types, each with differing affinities for entrapping SSOR and for harboring foods accessible to sea otters.

The definitions of particle size used in the SCAT surveys and here (based on Wentworth 1922) are: bedrock outcrops; boulder (>256 mm in diameter); cobble (64–256 mm); pebble (4–64 mm); granule (2–4 mm); sand (0.06–2 mm); and mud (silt and clay <0.06 mm). These particle sizes were aggregated into substrate categories for mapping in the field: (1) bedrock—solid, cracked, or fissured but

Figure 3. Boundaries and shorelines of the Northern Knight Island Study Area, showing the three bays in the risk assessment model: Herring Bay (HB), Lower Passage (LP), and Bay of Isles (BI) (adapted from Short *et al.* 2006).

lacking loose particles; (2) bedrock-boulder—bedrock base topped with varying amounts of boulders; (3) cobble-mixed—cobble or cobble with boulders or bedrock outcroppings; and (4) clam habitat—pebble, granule, sand, or mud substrates (*i.e.*, the only substrates that could support clams). A representation of the sediment distribution shown in Figure 4 is based on our boat-based survey (discussed later) of the entire NKI Study Area. SSOR cannot occur under bedrock; rather, the patches of SSOR exist primarily under areas of stable armor of cobble-mix (*i.e.*, coarse gravel, cobble, and boulders) (Michel *et al.* 2006; Taylor and Reimer 2008), but not typically in finer-grained sediments (Figure 5).

Short *et al.* (2006) and Michel *et al.* (2006) reported on the 2003 NOAA survey sites that were intensively sampled for SSOR, involving 29 non-bedrock shorelines at tide elevations between -0.2 m to $+4.8$ m above mean lower low water (MLLW).

Figure 4. Example of shoreline sediment types (Bedrock, Bedrock-Boulder, Cobble-Mixed, and Fine-Grain [clam habitat]) in the southeastern corner of Herring Bay based on the authors' boat-based survey that covered all of the Northern Knight Island Study Area at low tide. Figure created for this article by Allison Zusi-Cobb, ABR Inc., Environmental Research & Services, Fairbanks, AK, USA.

More than 1100 excavations were made, each covering an area $\sim 0.25 \text{ m}^2$, of which 5.3% had visual oiling. The patches of SSOR occurred primarily in the middle and upper intertidal zones (MITZ and UITZ, respectively), with 88.3% of the SSOR found at locations $\geq +0.8 \text{ m MLLW}$ (Zones MVD1-MVD4 in Table 1) (Short *et al.* 2006). The SSOR was assigned to visual oiling categories: heavy oil residue (HOR), medium oil residue (MOR), light oil residue (LOR), and oil film/trace (OF/TR). The SSOR was located in a layer of sediments often 1–5 cm thick (but for a few patches up to 40 cm), covered by a ~ 15 –25 cm or more layer of clean sediments (Hayes and Michel 1999; Michel *et al.* 2006). Michel *et al.* (2006) also reported on the 2001 NOAA survey of SSOR, in which only the MITZ and UITZ ($\geq +1.8 \text{ m MLLW}$) were surveyed; from these data the median thickness ($\sim 6 \text{ cm}$), median patch size ($\sim 36 \text{ m}^2$), and median areal coverage of SSOR ($< 5\%$) on the surveyed beaches can be calculated. We conservatively assigned a total of 97 of the 157 SCAT shoreline subdivisions as having one or more patches of SSOR (labeled *SSOR subdivisions*)

Figure 5. Schematic cross-section of a representative area of SSOR on Northern Knight Island, showing typical armored (boulder and cobble) sediments in which SSOR occurs, tidal zones, and typical distribution of benthic community (Reprinted with permission from Elsevier from Marine Pollution Bulletin 56(3), E Taylor and D Reimer, “Oil persistence on beaches in Prince William Sound – A review of SCAT surveys conducted from 1989 to 2002,” 17 pages, copyright 2008). Note that if these were finer-grained sediments, clams would occur in the two habitats in the lower intertidal zone labeled here “Rockweed” and “Seagrass and Kelp.”

even if it had not been surveyed since 1991 and, thus, its current SSOR status is unknown. However, it is important to note that the known SSOR patches occupy only a small fraction of each subdivision length.

Direct Exposure Pathways to Sea Otters

Several potential routes of PAH exposures to sea otters at NKI are captured in the conceptual model (Figure 2). For direct exposure to the PAHs in SSOR to occur, the sea otter would have to excavate a pit in the ITZ that directly intersects a patch of SSOR (right side of the conceptual model). Our PWS observational data, discussed later, indicate that 10–35% of the foraging dives occur in the ITZ (the rest in the subtidal zone [STZ]), so this does present a plausible pathway that warrants careful quantification. Four factors affect the probability of a sea otter’s digging a pit that intersects SSOR: (1) the distribution of SSOR patches across tidal zones and shoreline subdivisions; (2) the distribution of clam habitat across tidal zones; (3) the co-occurrence of clam habitat and SSOR; and (4) the number of pits excavated per sea otter per day in the ITZ (which varies by age and gender).

Table 1. Frequency distribution of SSOR across tidal zones.

Zone designation ⁱ	Relative to MLLW ⁱⁱ	Relative frequency of occurrence of SSOR ⁱⁱⁱ
MVD5	−0.2 to + 0.8 m	0.117
MVD4	+0.8 to + 1.8 m	0.267
MVD3	+1.8 to + 2.8 m	0.433
MVD2	+2.8 to + 3.8 m	0.150
MVD1	+3.8 to + 4.8 m	0.033
All zones	−0.2 to + 4.8 m	1.000

ⁱFrom Short *et al.* (2006).ⁱⁱMLLW = Mean Lower Low Water.ⁱⁱⁱSSOR = Subsurface Oil Residues.

Sea otters in PWS feed primarily on infauna excavated from sediments (clams and occasionally worms) or on epibenthic invertebrates (particularly crabs, mussels, urchins, octopus, worms, or snails) (Calkins 1978; Doroff and Bodkin 1994; Johnson and Garshelis 1995; Dean *et al.* 2002; this study). Foraging in the ITZ occurs only at the high part of the tidal cycle, when the benthos is underwater (sea otters do not feed on shore). A sea otter excavates a pit by digging several centimeters into the substrate until clams are encountered. One to several clams may be collected from a pit during one or several dives. Consumption of food occurs at the water surface. From our observational database, discussed later, the average sea otter's ITZ diet in the oil-affected part of PWS is about 50% clams and 40% mussels (compared to ~75% clams in the STZ). PWS clams are restricted to the LITZ and STZ, primarily $\leq +0.5$ m MLLW (Paul and Feder 1973; Nickerson 1977; Dean *et al.* 2002; Boehm *et al.* 2007a). Consequently, a sea otter's potential to encounter SSOR is limited to the LITZ (MVD5 in Table 1).

If SSOR is encountered, exposure could involve direct contact on the sea otter's paws and fur. The conceptual model distinguishes this as either oil-phase SSOR (*i.e.*, a thin film or small droplets) that contains PAHs or as sediments with particulate-bound PAHs, each with different exposure pathways and bioavailability (Figure 2). Sea otters rely on frequent grooming to maintain the insulative capacity of their fur (Kenyon 1969) and typically groom after feeding, using the paws and mouth to clean and aerate the fur. Thus, oil-phase SSOR from an excavated pit could stick to the fur or paws and then be ingested during grooming. Similarly, a thin coating of oil-phase SSOR on the surface of any collected clam could subsequently transfer to the mouth when feeding or grooming. Another potential route of exposure is oil-phase SSOR being released from a pit, rising to form a thin sea-surface film or sheen, sticking to the sea otter's fur when it surfaces, and subsequently being ingested during grooming. Finally, oil could be dispersed into the water column and ingested by the sea otter when drinking seawater. All ingested oil-phase PAHs are assumed to be completely bioavailable to the sea otter.

Particulate-bound PAHs could be present in the plume of fine suspended particles generated during sediment excavation (related to the clay/silt fraction). A sea otter remains underwater for 0.1–3 minutes while digging a pit (this study; see also Calkins 1978; Garshelis 1983). Consequently, exposure to sediment-bound PAHs in

the plume could occur if some fraction of the plume were attached to the fur and subsequently transferred to the mouth during grooming. Particulate-bound PAHs are sorbed onto particles as a function of PAH-specific oil–water partitioning coefficients (K_{ow} ; from Durrell *et al.* 2006) and only those PAHs released from particulates in the gut would be bioavailable, the remainder passing through the gastrointestinal tract without assimilation.

Indirect Exposure Pathways: Ingestion of Contaminated Prey

The potential indirect exposure pathways involve the sea otter's food web (left side of the conceptual model, Figure 2). For most prey, this requires the release of the PAHs into the water column and uptake by filter-feeders; however, a small portion of the diet is the tube-dwelling fat innkeeper worm (*Echiurus echiurus alaskensis*), which potentially could intersect SSOR and directly incorporate PAHs into its tissues. The potential release mechanisms for PAHs to get from subsurface deposits into the water-column include: (1) diffusion through the overlying sediments; (2) resuspension by extreme storm events (the mechanism by which most sediments have already released SSOR); and (3) bioturbation (*i.e.*, biological activity that disturbs the sediments, most likely by previous sea otter pits). Once in the water column, PAHs could be taken up by benthos, either directly to filter-feeders (*e.g.*, clams and mussels) or indirectly through the food web (*e.g.*, crabs).

Using the actual measurements of PAH levels in the sea otter's prey, as we do here, obviates the need to model the pathways by which PAHs are incorporated into the prey tissues. Thus, factors included in the indirect pathway assessment are the ITZ and STZ food items and their PAH concentrations, whether associated with SSOR or background sources. Since the PAHs are already incorporated into prey tissues, all dietary PAHs are assumed to be bioavailable to the sea otter. All prey tissues in PWS contain some level of PAHs (Boehm *et al.* 2004; Neff *et al.* 2006); thus the risk assessment compares the dose to a sea otter from the vicinity of SSOR sources with the dose from background levels of PAHs in the environment. (Note that *background*, as used here, does not include point-sources of PAHs, such as abandoned human activity sites in PWS like former mines and canneries, or transient-sources, such as vessel discharges [Boehm *et al.* 2004; Page *et al.* 1999, 2004]).

PAHs are readily metabolized and consequently do not biomagnify through the food web (Eisler 1987; Neff 2002). Broman (1990) and Broman *et al.* (1990) showed that all PAH concentrations decreased up a simple marine food web, from phytoplankton through blue mussels (*Mytilus edulis*) to the common eider duck (*Somateria mollissima*). These authors demonstrated bioconcentration of the PAHs in plankton (*i.e.*, concentrations exceeding that of the surrounding seawater) and subsequent trophic transfer of PAHs. However, because the PAHs are metabolized, this trophic transfer actually led to biodiminution (a lipid-normalized concentration decrease of about two orders of magnitude from the phytoplankton to the duck liver) rather than biomagnification (see also Neff 2002). This contrasts significantly, for instance, with PCBs, which present a serious trophic biomagnification risk, such as seen in high levels of PCBs in top predators like killer whales (*e.g.*, Ross *et al.* 2000).

OBSERVATIONS OF FORAGING SEA OTTERS

The authors made observations of foraging sea otters in western PWS during 1980–1982 and 1990–1991, primarily during May–Oct (Garshelis 1983; Johnson and Garshelis 1995; Garshelis and Johnson 2001). Foraging sea otters were selected opportunistically near Gibbon Anchorage, Green Island, and various locations around Knight Island. We representatively sampled sea otters of each gender (ascertained by presence of a penile bulge or mammary glands) and age class (ascertained by color, appearance, and behavior) (Garshelis 1983). Subadults and newly independent pups were identified by their size, dark heads, and behavior (*e.g.*, tail breaking the surface when diving). Solitary females were distinguished from females with a pup, with the latter differentiated by whether the pup could feed independently (older than ~6–8 weeks); females accompanied by older pups were more restricted to shallower (often ITZ) feeding areas to enhance independent foraging by the pup. Foraging observations were conducted on either the female or the pup, but generally not both at the same time.

Observations were made during daylight hours from shore with a 50–80× *Questar*® telescope. One foraging sea otter at a time was continually observed during a 30-minute period or until the sea otter stopped feeding or moved out of view. Each series of consecutive dives by one sea otter constituted one foraging bout; 210 foraging bouts, comprising 3034 dives, were observed. The duration of each foraging dive and surface interval was recorded to the second. Captured prey were identified to species when possible, otherwise to higher taxonomic groups: clams, mussels, crabs, urchins, octopuses, sea stars, and worm-like organisms (primarily fat innkeepers). Dive locations were recorded, and the water depth was subsequently measured to the nearest meter with a sounding rope from a skiff; three measurements were made within ~5 m of the dive locations and averaged to assign the depth to each set of dives at that location. If the sea otter moved among different locations during a foraging bout, separate measurements were made for distinct groups of dives. Depths were corrected for the hourly tide level to distinguish ITZ dives (tide level–dive depth ≥ -0.2 m) from STZ dives (tide level–dive depth < -0.2 m), using published tide tables from: (<http://tidesandcurrents.noaa.gov/data.menu.shtml?type=Historic+Tide+Data&mstn=9454050>).

We calculated the mean fraction of ITZ and STZ dives for each of five classes of sea otters: adult males, solitary adult females, adult females with dependent pup, subadults, and pups that were old enough to dive for food themselves but not yet independent. For each sea otter class and separately for the ITZ and the STZ, we calculated the mean dives·hr⁻¹ when foraging and the fraction of foraging dives resulting in a pit (defined as dives collecting infauna, *i.e.*, clams, cockles, or fat innkeepers, with conservative assumption that each such dive resulted in one new pit). Dives with unidentifiable prey were excluded. To derive mean parameter estimates, data from all areas and years were pooled, with bouts rather than dives as the sample unit. Each sample was weighted by the duration (min) of the bout, and means and standard errors were calculated.

We used daily activity budgets from a companion study in the same area (Garshelis *et al.* 1986) to estimate the total time the five classes of otters spent feeding each day. Year-round, 24-h activity data were obtained by recording signals received at

remote tracking stations from radio-transmitters attached to the rear flippers of 101 sea otters in PWS and later interpreting the recorded patterns. When a sea otter dove for food, its radio signal was interrupted continuously for >30 s, followed by uninterrupted transmissions for 15–120 s as the sea otter consumed prey at the surface. Foraging activity was readily identified by this consistent pattern of alternating sequences of interrupted and uninterrupted signals. Interpretations of transmitter data were verified with visual observations of sea otters. Estimates from the transmitter data of the amount of time spent foraging each day were used in combination with the sea otter class-specific rates of pit excavation to estimate the total number of intertidal and subtidal pits dug per feeding hour as inputs to the quantitative model.

QUANTITATIVE ECOLOGICAL RISK ASSESSMENT MODEL

The ecological risk conceptual model was converted into a simulation model that quantifies the toxicological risks to NKI sea otters from potential exposure to remnant EVOS-SSOR. The quantitative model simulates the co-occurrence of sea otter pits and SSOR based on realistic spatial relationships. We used the object-oriented simulation language *Stella*TM (ver. 9.0.2; copyright isee systems, inc. [www.iseesystems.com]) to simulate each exposure pathway in the conceptual model. Six primary sources of empirical data were used in the model: (1) our observational data on foraging, diving, and dietary attributes of each class of PWS sea otters, discussed above (Table 2A), supplemented with other data on sea otter characteristics (Table 2B); (2) characterization of the spatial distribution of sediment and habitat types of the NKI Study Area (Table 2C) based on our shoreline survey, which was conducted by skiff following the shoreline ~50 m offshore at low tides in June 2008; (3) the most recent NOAA survey data on the spatial distribution of SSOR on the shorelines of NKI (Michel *et al.* 2006; Short *et al.* 2006); (4) the chemical characterization by NOAA of 41 PAHs in the SSOR on the shorelines of NKI (EVOSTC 2008); (5) the survey in summer 2006 by Boehm *et al.* (2007a) of sea otter pits on shorelines of NKI during particularly low tides; and (6) chemical characterization of 41 PAHs in prey based on mussels collected in 1998–2002 (Boehm *et al.* 2004); clams collected in 2002–2004 (Neff *et al.* 2006); crabs, whelks, and worms collected in 2002–2004 (Neff *et al.* 2006); and seawater collected in 2005 (Boehm *et al.* 2007b). Note that in all cases, measured PAH concentrations reported as 0 or non-detected were assigned here the value of $\frac{1}{2}$ Method Detection Limit.

For a few parameters in the model, no empirical data exist, requiring those parameterizations to be based on informed expert judgment (see Acknowledgments for list of expert participants in modeling workshops). These parameters included: (a) grooming efficiency for removing particles (75% for HOR); (b) fraction of sediment particles sticking to fur (5% for HOR); and (c) thickness of SSOR-coating on paws and clams ($33\times$ thickness of HOR oil film [characterized as dark colors film; see HAZMAT 1996]). Each of the expert-judgment-based parameters were assigned conservatively and were either subject to parameter-sensitivity analyses (discussed later) or were assigned the most conservative possible number (*e.g.*, 100% efficiency for ingestion of oil-phase SSOR coating on paws and clams; zero dilution of oil-phase

Table 2. Model Parameterization for Simulating Co-occurrence of Sea Otter Pit and SSOR

Sea Otter Class	Younger Pup	Older Pup	Juvenile	Subadult	Adult Male	Adult Female without Pup	Adult Female with Pup
<i>A) Summary of Sea Otter Data in Model from Authors' Observational Database</i>							
Feeding Period (Hr □ Day ⁻¹)	12.8	12.2	12.2	11.3	11.3	12.8	
Intertidal Zone (ITZ) Dives							
Rel. Frequency Dives in ITZ	—	0.35	0.28	0.28	0.15	0.10	0.23
# Dives Per Hr	—	49.5	50.0	50.0	33.7	60.5	51.2
Rel. Frequency Dives for Pits	—	0.42	0.80	0.80	0.54	0.75	0.32
Relative Frequency of Diet							
Clams	—	0.57	0.67	0.67	0.53	0.51	0.33
Mussels	—	0.43	0.27	0.27	0.3	0.42	0.53
Crabs	—	0	0	0	0	0	0.08
Fat Innkeepers	—	0	0.06	0.06	0	0.07	0.04
Other	—	0	0.01	0.01	0.16	0	0.02
Subtidal Zone (STZ) Dives							
Rel. Frequency Dives in STZ	—	0.65	0.72	0.72	0.85	0.90	0.77
# Dives Per Hr	—	40.8	36.8	36.8	30.8	34.4	34.2
Rel. Frequency Dives for Pits	—	0.43	0.80	0.80	0.70	0.79	0.43
Relative Frequency of Diet							
Clams	—	0.38	0.77	0.77	0.74	0.81	0.49
Mussels	—	0.45	0.01	0.01	0.05	0.01	0.13
Crabs	—	0	0.15	0.15	0.05	0.07	0.29
Fat Innkeepers	—	0	0.05	0.05	0.03	0.01	0.01
Other	—	0.17	0.02	0.02	0.12	0.10	0.09
<i>B) Additional Sea Otter Parameters in Model</i>							
	0–2	2–6	6–12	1–3			
Ages	month	months	months	yr	>3yr	>3yr	>3yr
Simulation Period (days)	—	120	180	180	180	180	180
Weight (kg)	9.2	10.4	18.0	19.4	33.0	23.0	23.0
Notes	i	ii	ii, iii	i, iv	i, v	i, ii, v	i, v
Data Sources	a	b, c	b, c	a, d	a, e	a, b, c, e	a, b, c, e

*(Continued on next page)***Notes:**

- i) Weight data from Green Island in 1980–1981
- ii) Weight data from Knight, Montague, and Green Islands in mid-1980s
- iii) Weight data after independence from mid-July
- iv) Weight data from Northern Knight Island 1996–98
- v) Weight data from Green, Knight, Chenega, Prince of Wales Islands 1992–93

Data sources:

- a) Garshelis, unpub data
- b) Rotterman and Monnett (2002)
- c) Monnett *et al.* (1991)
- d) Dean *et al.* (2002)
- e) Ballachey *et al.* (2003)

Table 2. Model Parameterization for Simulating Co-occurrence of Sea Otter Pit and SSOR (*Continued*)

	Herring Bay (HB)	Lower Passage (LP)	Bay of Isles (BI)
<i>C) Shoreline Lengths (in m) from Authors' NKI Study Area Shoreline Survey</i>			
Total Shoreline Length	64,486	61,970	43,617
SSOR Subdivisions Length	41,372	44,762	29,054
Non-SSOR Subdivisions Length	23,114	17,208	14,563
SSOR-Potential Sediments	17,627	14,525	14,142
Clam-Potential Sediments	4,186	4,153	3,288
<i>D) Spatial Probabilities Calculated in Model</i>			
Probability Bay (i)	0.379	0.364	0.256
Probability SSOR Subdivision (ii)	0.624	0.722	0.666
Probability SSOR-Potential Sediments (iii)	0.426	0.324	0.487
Probability Clam-Potential Sediments (iv)	0.237	0.286	0.232

Notes:

- i) $P_{\text{Bay}} = \text{Bay Shoreline Length} \div \text{NKI Study Area Shoreline Length}$
- ii) $P_{\text{SSOR subdivision}} = \text{SSOR Subdivision Lengths} \div \text{Bay Shoreline Length}$
- iii) $P_{\text{SSOR-potential sediments}} = \text{SSOR Potential Sediments Lengths} \div \text{SSOR Subdivision Lengths}$
- iv) $P_{\text{clam-potential sediments}} = \text{Fine-Grained Sediment Lengths} \div \text{SSOR Potential Sediment Lengths}$

SSOR released from pits as it floats to become surface film, 100% of which coats the sea otter's fur).

The quantitative model predicts daily doses of each of 41 PAH analytes assimilated by an individual sea otter subject to specific activities each hour of the day, utilizing the individual-based modeling (IBM) approach (DeAngelis and Gross 1992), in which environmental constraints parameterized by empirical data provide the framework in which sea otter behavior occurs. The model predicts exposures and effects on an individual sea otter under the paired situation of: (1) an *at-risk sea otter*, which has potential direct PAH exposure from excavating a pit that intersects SSOR, consumption of diet and exposure to sediments in the vicinity of SSOR, and exposure to background levels of PAHs in diet, drinking water, and sediments from areas separate from the SSOR; and (2) a *not-at-risk sea otter*, which experiences identical situations except exposure is only to background levels of PAHs in diet, drinking water, and sediments. Many model parameters are age- or gender-specific; consequently, separate models simulate each of seven classes of sea otters: (1) older pups (ages 2–6 months); (2) juveniles (ages 6–12 months); (3) subadults (ages 1–3 years); (4) adult males in the territorial phase (limited to a single bay, BI); (5) adult males in the non-territorial phase (allowed to roam over all three bays); (6) adult females with dependent pups (also limited to a single bay, BI); and (7) adult females without pups. Each adult phase is assumed to extend over a 6-month period. Dependent pups ≤ 2 months were not modeled separately as they are unable to dig

pits and fully rely on their mother's milk for food (Payne and Jameson 1984), which apparently does not transfer significant quantities of PAHs (*e.g.*, Bulder *et al.* 2006).

A major component of the IBM model is a series of stochastic functions that incorporate variability for the sea otters and the environmental conditions in which they actually live. Each distribution, derived in all cases from empirical data, is sampled using a pseudo-random number generator, that is, meeting all criteria for randomness following a particular sequence initiated by a "seed," thereby allowing reconstruction of specific runs and parameter-sensitivity analyses. The model's stochastic functions assign the sea otter to a specific bay daily, based on the frequency distribution of shoreline lengths (p_{BAY}) from the SCAT maps of NKI, and assign the following parameters hourly (Table 2): (1) assignment to an SSOR-subdivision or a non-SSOR-subdivision, based on the bay-specific frequency distribution of SSOR- and non-SSOR subdivisions ($p_{\text{SSOR subdivision}}$); (2) assignment to the ITZ or the STZ, based on class-specific frequency distributions from our sea otter observational data ($p_{\text{sea otter ITZ}}$); (3) assignment to a site with sediments that potentially could have SSOR (bedrock sediments cannot have SSOR), based on the frequency distribution of sediment types from our shoreline survey discussed earlier ($p_{\text{SSOR-potential sediments}}$); (4) assignment to sediments that potentially support clams and thus could be excavated by sea otters (*i.e.*, fine-grained sediments), based on the same shoreline survey ($p_{\text{clam-potential sediments}}$); (5) assignment to an SSOR field or not, based on the SSOR frequency distribution from the 2003 NOAA intense-survey sites (here the term *field* means an area comparable to the cross-ITZ 12.5 m-wide swath sampled in that survey) (EVOSTC 2008) ($p_{\text{SSOR field}}$); (6) probability of a patch of SSOR being within the LITZ and thus potentially containing sufficient clams that sea otters might dig, based on the frequency distribution from the NOAA SSOR surveys ($p_{\text{SSOR LITZ}}$); (7) assignment of a dive resulting in a pit or not, based on the frequency distributions of infauna prey in the ITZ from our feeding observational database ($p_{\text{sea otter ITZ pit}}$); and (8) probability that the hour is within the feeding period of the day, based on our feeding observational database ($p_{\text{feeding activity}}$). Thus within a particular bay, the effective probability of co-occurrence of a sea otter pit and a patch of SSOR (Table 3) is a product of the individual probabilities, calculated as:

$$\begin{aligned}
 &P_{\text{sea otter pit in SSOR}} \\
 &= p_{\text{SSOR subdivision}} \times p_{\text{SSOR-potential sediments}} \times p_{\text{clam-potential sediments}} \\
 &\quad \times p_{\text{SSOR field}} \times p_{\text{SSOR LITZ}} \times p_{\text{sea otter ITZ}} \times p_{\text{sea otter ITZ pit}} \times p_{\text{feeding activity}} \quad (1)
 \end{aligned}$$

Note that the model does not literally assign this effective probability value (except for some sensitivity analyses, discussed later); rather, co-occurrence emerges from the hour-by-hour assignment of each stochastic parameter based on the data distributions. If a patch of SSOR is intersected during a time-step, then the model assigns the SSOR category (*e.g.*, HOR, MOR) based on the frequency distribution of NKI SSOR from the NOAA surveys. The model then assigns a specific TPAH concentration to that particular SSOR category, randomly sampling from a log-normal distribution fit to the SSOR PAH data (EVOSTC 2008), and the mass of each analyte is calculated based on the relative fraction of TPAH of each analyte. If no co-occurrence occurs during a time-step, the model assigns only PAH concentrations from background sources (*e.g.*, diet, seawater, and STZ and

Table 3. Effective Probability of Co-occurrence of Sea Otter Pit and a Patch of SSOR

	Effective Probability of Co-occurrence (i)		
	Herring Bay (HB)	Lower Passage (LP)	Bay of Isles (BI)
Sea Otter Class			
pup	2.94E-04	3.03E-04	3.42E-04
juvenile	4.48E-04	4.62E-04	5.20E-04
subadult	4.48E-04	4.62E-04	5.20E-04
territorial male	—	—	1.88E-04
non-territorial male	1.62E-04	1.67E-04	1.88E-04
female without pup	1.50E-04	1.55E-04	1.74E-04
female with pup	—	—	1.71E-04

Notes:

i) Equation 1 in text; probabilities on a per-hour basis; territorial males and adult females with pups assigned to BI throughout simulation.

non-SSOR-ITZ sediments). Similarly, for the not-at-risk sea otter, all SSOR co-occurrence algorithms are bypassed.

The diet consumed by a sea otter class is assigned based on our feeding observation data (Table 2A). The foraging values used to parameterize the model are similar to those reported for sea otters occupying similar habitats with similar histories of occupation elsewhere. However, PWS sea otters feed more in the STZ than the ITZ because clams, their primary food in PWS (Calkins 1978; Doroff and Bodkin 1994; Johnson and Garshelis 1995), are more abundant in the large benthic STZ compared with the narrow ITZ (Dean *et al.* 2002). Similar clam-dominated diets have been observed for sea otters in soft-bottomed habitats in Kodiak (Doroff and DeGange 1994) and Washington State (Laidre and Jameson 2006). The estimated daily mean number of foraging dives across sea otter classes in PWS ranged from 348 to 684 dives·day⁻¹ (dives·day⁻¹ = dives·hr⁻¹ * feeding period; Table 2A), 2–5× higher than recorded for sea otters in southeast Alaska (Bodkin *et al.* 2004). This is as expected because dive frequency is inversely related to water depth, and the feeding areas in PWS are shallower than the foraging areas reported in southeast Alaska, where a substantial proportion of dives were >60 m deep (Bodkin *et al.* 2004). Rates or proportions of intertidal foraging by sea otters have not been reported for other areas. However, we recognize that using land-based observations likely biased our data toward foraging in shallower areas and led to higher estimated rates of diving compared with telemetry-based observations (see Ralls *et al.* 1995). Any such bias in the model diving rate parameters would increase the projected exposure of the NKI sea otters to SSOR (because of over-estimated ITZ diving rates), rendering the modeling results more conservative. We used separate estimates of foraging parameters for each sea otter class because numerous studies confirmed our observations of significant gender- and age-specific differences in foraging (Garshelis *et al.* 1986; Johnson and Garshelis 1995; Ralls *et al.* 1995; Bodkin *et al.* 2004; Laidre and Jameson 2006) and even individual variation in prey selection (Estes *et al.* 2003). As will be shown, variations in rates of ITZ foraging and pit excavation are important to the

ecological modeling outcomes because these rates directly affect PAH exposures for the at-risk sea otters.

The consumption rate ($1019 \text{ kJ} \cdot \text{kg}^{-1}$ dry weight of sea otter per day) and the energetic value of each prey species ($\text{J} \cdot \text{mg}^{-1}$ dry weight of prey) were taken from Dean *et al.* (2002). The model uses daily dietary energetics needs, prey frequency distribution, and energetic value of each prey species to calculate the required mass of each prey consumed per hour when feeding in order to sustain the sea otter. The prey concentrations of each PAH analyte are assigned to that mass, depending on the source of the prey (ITZ SSOR subdivision, ITZ non-SSOR subdivision, or STZ). Seawater consumption rate is assigned at 23% of total water influx (Costa 1982), or $62 \text{ ml} \cdot \text{kg}^{-1} \cdot \text{day}^{-1}$, converted to quantity per hour for the feeding period of each day. For all dietary, seawater, or oil-phase PAHs, the quantity ingested is assumed to be completely assimilated and contribute to the total daily dose. However, for particulate-bound PAHs in the plume of particles from the pit excavation, a PAH-specific partitioning coefficient controls the amount of each PAH released from the sediment particle and assimilated (data taken from Durrell *et al.* [2006] for each of the 41 PAHs analyzed).

The model calculates the total hourly intake for each of the 41 modeled PAH analytes from each exposure pathway for the at-risk sea otters, with or without co-occurrence with SSOR, and for the not-at-risk sea otters, aggregated to the PAH-ring class (discussed later), and summed at the end of every 24 h to a daily dose that is normalized to the weight of the sea otter (as $\text{mg PAH} \cdot \text{kg}^{-1} \text{ sea otter} \cdot \text{day}^{-1}$). For each class of sea otter, 1000 yr of activity were simulated, resulting in an initial distribution of daily doses of 2–3-ring PAHs, 4–6-ring PAHs, and TPAH for the paired (at-risk and not-at-risk) sea otters. These *daily doses* were converted to *average daily doses* by simulating a sequence of days that could occur in the life of a sea otter in order to derive chronic exposures for comparison with chronic TRVs. To do this, a secondary distribution was created by randomly sampling the initial distribution (with replacement) to select a 180-day sequence (representing the duration of phase of each sea otter class, except that a 120-day sequence was used for the shorter-termed class of older pups) to derive a single average daily dose. This process was repeated 500,000 times, generating the modeled population of NKI sea otters, from which the chronic dose to the 99.9% quantile, maximum-exposed sea otters was calculated.

The model was developed with a consistent bias toward conservative assumptions or data (where *conservative* refers to yielding a higher estimate of risk). Some examples, among many, of this conservatism include: (1) if a simulated sea otter was assigned at random to dig a pit that intersected SSOR, then all the pits dug during that hour were assigned to intersecting SSOR; (2) TRVs are based on the geometric 95% quantile lower confidence interval of the toxicity data within each PAH-ring group; (3) the 4–6-ring PAH TRV is based on toxicity data for the most toxic analyte in the group, benzo(a)pyrene, even though the toxicities of the other PAHs are much lower (*e.g.*, an order-of-magnitude lower for pyrene and fluoranthene; Di Toro *et al.* 2007) and even though benzo(a)pyrene represents $\leq 0.3\%$ of the composition of the modeled assimilated PAHs. On the other hand, the model balances conservatism with common sense and plausibility. For example, the excavations were limited to the tidal zone where sea otters actually forage (99% of ITZ pits occur in the LITZ; Boehm *et al.* 2007a) and in habitats where their infaunal prey

exist and where sea otters can physically dig pits (*i.e.*, the sediments that constitute clam habitat). This contrasts with the assumptions of Short *et al.* (2006), in which probabilities unrealistically included sea otters digging pits in the MITZ and UITZ and in boulder-cobble fields.

Sensitivity Analyses

Two types of sensitivity analyses were conducted: (1) *structural-sensitivity analyses* that examine six alternate model constructs based on different data sources or approaches to assessing co-occurrence; and (2) *parameter-sensitivity analyses* that examine eleven variations in selected base model parameters.

Two structural-sensitivity analyses directly assigned probabilities of co-occurrence of a sea otter pit with SSOR based on two estimates from Short *et al.* (2006): (a) assuming sea otters can dig pits throughout the LITZ, MITZ, and UITZ up to the +4.8 m MLLW tide level (estimated in Short *et al.* [2006], but which does not actually occur); and (b) limiting sea otter pits to the LITZ $\leq +0.8$ m MLLW (the more realistic case derived from the Short *et al.* [2006] data). A third structural-sensitivity analysis assigned the sea otter to foraging only at an SSOR-subdivision throughout the simulation period. The fourth structural-sensitivity analysis used the sea otter diving data for PWS derived from Ballachey and Bodkin (2006), instead of our observational data (except we kept our conservative assumption in the model that sea otters excavated a new pit on each dive rather than those authors' assumption of 2–5 dives per new pit). The final two sets of structural-sensitivity analyses combined the Short *et al.* (2006) parameterization (for probabilities) and the Ballachey and Bodkin (2006) parameterization (for sea otter diving characteristics) as follows: (a) upper-bound (more conservative) parameters, with sea otter pits throughout the ITZ and two dives-pit⁻¹; and (b) lower-bound (more realistic) parameters, with foraging only in the LITZ and five dives-pit⁻¹.

The parameter-sensitivity analyses were conducted on three sea otter classes (older pup, adult male territorial phase, and adult female with pup), chosen to conservatively represent all classes. These sensitivity analyses used identical random-number seeds as the counterpart base models so that any difference between the results is attributable solely to the change in the tested individual parameter. Individual parameters were primarily changed in the direction to increase doses, except for those cases where the parameter was already at its most conservative level in the base model (*e.g.*, 0% dilution for surfaced oil film, and 100% of pits in co-occurrence hour assigned to intercepting SSOR). The parameters examined were: K_{ow} partitioning coefficient for particulate-bound PAHs (all partitioning coefficients were changed to 1.0 to simulate complete bioavailability and assimilation of sediment-bound PAHs); sea otter pit dimensions (width of all pits increased by 10 cm); efficiency of fur grooming to remove particulates (grooming efficiency halved); number of SSOR pits within a co-occurrence hour (reduced by factor of $\frac{1}{4}$); number of sea otter dives per new pit (changed from 1 to 5); dilution of the oil-phase components from the pit to the water surface where feeding occurs near high tide (oil film thickness reduced by 1/10); increased thickness of the oil-phase coating on clams and/or the sea otter paws (doubled); decreased thickness of the oil-phase coating on the sea otter paws; and fraction of sediment particles attaching to the sea otter's fur (doubled).

The model was subject to extensive quality assurance (QA) to examine model structure, equations, parameters, data sources, documentation, and each simulation output, following a USEPA-approved QA plan developed by the authors for a previous model. All models, parameters, QA runs, and simulation outputs have been archived for further analysis and reproducibility. Altogether 126 scenarios were simulated, resulting in a total modeled population of 63 million individual sea otters.

TOXICITY REFERENCE VALUES

The effects component of the ecological risk assessment used the standard USEPA-approved approach to select a chronic reference dose (*i.e.*, the TRV) for PAH exposures to sea otters. The TRV is defined as the dose above which ecologically relevant effects might occur to wildlife species following chronic ingestion exposures and below which it is reasonably expected that such effects would not occur (USEPA 2005). The ratio of the model-simulated exposure to the TRV value is the Hazard Quotient (HQ), where an $HQ \geq 1$ indicates the exposure could lead to chronic effects and $HQ < 1$ indicates no ecologically relevant adverse chronic effect would occur.

TPAH values have often been used for calculating exposures and TRVs. However, as Di Toro *et al.* (2007), among many others, have shown, bioavailability and toxicity of PAHs vary considerably across PAH-ring numbers and the locations and number of alkyl substitution structures: with increasing octanol/water partition coefficients ($\log K_{ow}$), toxicity increases, but solubility decreases even more rapidly. The net result is a reduction in the bioavailability and, therefore, a lower exposure risk for higher-molecular-weight PAHs because in the marine environment solubility effectively limits their bioavailability to below toxic effects levels. In general, higher-molecular-weight PAHs, with their high $\log K_{ow}$ values and low aqueous solubilities, sorb strongly to sediment and suspended particles. Because lower-molecular-weight, higher-aqueous-soluble PAHs are more bioavailable, during weathering in the environment they are lost from oil more rapidly than the higher-molecular-weight, less-bioavailable PAHs. As a result, there is a net reduction in toxicity risk of crude oil over time through weathering (Di Toro *et al.* 2007). To address this issue, the model calculates exposures of each PAH analyte based on the measured PAH composition of the SSOR, sediments, prey, and seawater. Ideally, a TRV would be derived for each analyte to characterize the expected effects from the particular mixture of PAHs assimilated by the sea otter. However, the data available from USEPA-approved toxicity studies relevant to the sea otter are quite limited, with few PAH analytes tested, so USEPA (2007) stated that the best that can be done is to calculate the total doses of lower-molecular-weight PAHs (specifically those PAHs with 2- and 3-ring structures) separately from the higher-molecular-weight PAHs (those with 4-, 5-, or 6-ring structures). TPAH values are also reported for comparison to the literature, but the ring-based values provide the best assessment of toxicological effects.

TRVs were developed for both the “no-observed-adverse-effects level” (NOAEL), that is, the concentration of chronic (time-independent) doses used in toxicity tests at and below which no effects were seen, and for the “lowest-observed-adverse-effects level” (LOAEL), the lowest tested chronic dose concentrations resulting in effects.

Table 4. Chronic Toxicity Reference Values (TRVs) for Sea Otters (i)

	n (iii)	geometric mean	geometric standard deviation	geometric 95% lower CL (iv)
<i>A) Eco-SSL-derived data (ii)</i>				
NOAEL (v)				
2–3-Ring PAHs	27	168.7	2.1	127.0
4–6-Ring PAHs	16	25.3	6.2	9.6
TPAH (vii)	42	83.6	4.7	51.8
LOAEL (vi)				
2–3-Ring PAHs	14	350.5	1.7	254.8
4–6-Ring PAHs	14	63.0	5.1	24.5
TPAH	28	148.6	4.4	83.6
<i>B) TRVs assigned in the model</i>				
	2–3-Ring PAHs	4–6-Ring PAHs	TPAH	
NOAEL	127.0	9.6	51.8	
LOAEL	254.8	24.5	83.6	

Notes:

i) Units $\text{mg PAH} \cdot \text{kg}^{-1} \text{ sea otter weight} \cdot \text{day}^{-1}$

ii) From USEPA (2007)

iii) n = number of relevant, USEPA-approved studies in Eco-SSL database

iv) CL = Confidence Level

v) NOAEL = No Observed Adverse Effects Level

vi) LOAEL = Lowest Observed Adverse Effects Level

vii) TPAH = Total Polycyclic Aromatic Hydrocarbons.

The expected threshold of effects is somewhere between NOAEL and LOAEL, with NOAEL-based TRVs being more conservative. The USEPA-approved set of experimental data in its Eco-SSL database (USEPA 2007) were used to derive TRVs (Table 4). The USEPA screened several thousand dose–response toxicity experiments on PAHs to select about 40 studies that met all criteria for data quality and applicability to mammalian wildlife. The mammal-relevant NOAEL and LOAEL values were extracted from each USEPA-approved toxicity study, based on mortality, growth, or reproductive effects. Following the USEPA-approved protocol of Sample *et al.* (1996), the ingestion dose data (primarily based on rat or mouse experiments) were normalized on a body-weight basis to apply to sea otters. Using these data across all tests and species, the geometric means and standard deviations, and geometric 95% lower confidence limits (CL) were generated. Geometric statistics are used in USEPA guidance as better representing distribution of toxicity data across experiments and species. Further, the 95% lower CL has been used in ecological risk assessments to address interspecies sensitivity differences for untested species, rather than applying safety factors, as is the common practice in human health risk assessments. The 95% lower CLs were assigned as the TRVs (Table 4B) following the USEPA-issued guidance for establishing water quality criteria (Stephan *et al.* 1985) and sediment quality criteria (USEPA 1993). (See Calabrese and Baldwin [1993] for additional discussion of methodologies for setting TRVs.)

RESULTS AND DISCUSSION

Exposure

The results from the quantitative toxicological risk model focus on the at-risk sea otter (labeled *SSOR*) and the PAH ring-group-based exposures and HQs. The distributions of average daily exposures are reported as mean, median, and 99.9% quantile levels (Table 5A); the latter, representing the exposures to the maximum-exposed individuals, are emphasized here. All coefficients of variability (CVs) for these base model results are $\leq 2\%$, indicating that the number of days simulated is sufficient to capture variability at the 99.9% quantile level.

The exposure data consistently show low doses for the not-at-risk sea otters (labeled *NON*; Table 5B) because exposures to background PAHs in PWS are quite low. Since assimilated doses are weight-normalized, there is little variation in background doses across all sea otter classes. The mean, median, and 99.9% quantile doses for the not-at-risk sea otters are similar within and across classes, indicating a very narrow distribution of background exposures across the millions of simulated sea otter-days. The cumulative frequency distribution of the 4–6-ring-PAH daily exposures for the *NON* pup class has a range of about an order of magnitude across 1000 yr of simulations (Figure 6A), with the variance derived from the lognormal distribution of background PAH concentrations in ITZ and STZ sediments on non-*SSOR*-subdivisions.

By contrast, the at-risk sea otter exposure distributions are highly skewed, with the 99.9% quantiles an order of magnitude or more above the corresponding means and medians. This is because the at-risk doses primarily result from the low-probability interception of *SSOR* in ITZ pits. The at-risk doses have a range of five orders of magnitude, primarily in the tail of the distribution (*i.e.*, only a very few of the simulated days). In all of the at-risk cases, the pup, juvenile, and subadult sea otters have higher assimilated doses than the adults. This is because the three non-adult categories dig similarly high number of ITZ pits per day (~ 100 – 135 compared to 30 – 50 for adults), driven by high dive rates when in the ITZ and the higher proportion of time these animals forage in the ITZ (Table 2A). The pup has the highest assimilated doses of all classes, most apparent in the 99.9% quantile values (Table 5A), because the lower body weight and the $2/3$ -power factor in converting weight to surface area results in a disproportionately high surface area and PAH exposures for smaller sea otters.

Among adults, females with dependent pups are exposed to the highest doses. Their exposure is greater than their counterparts without pups because the pup provides an additional route of exposure through the mother's grooming of the pup's fur. Adult males have the lowest doses because they dig fewer pits per day in the ITZ (~ 30), driven by lower ITZ dive rates and a low proportion of time in the ITZ compared to other classes (Table 2A). The minor difference between the territorial and non-territorial males results from the slightly higher probability of territorial males foraging at an *SSOR* subdivision on clam habitat in the Bay of Isles compared to the other two bays ($p_{\text{SSOR subdivision}} \times p_{\text{SSOR-potential sediments}} \times p_{\text{clam-potential sediments}}$; Table 2D), which the non-territorial male may also visit.

The 2–3-ring-PAH exposures consistently exceed the 4–6-ring-PAH exposures (Table 5A), typically by a factor of $2\times$ or more. This is primarily because the

Table 5. Model-Predicted Average Daily 2-3-Ring PAH, 4-6-Ring PAH, and TPAH Exposures for Northern Knight Island Sea Otters (mg PAH · kg⁻¹ sea otter weight · day⁻¹) (i)

Sea Otter Class	A) SSOR (ii)			B) NON(iii)		
	2-3-Ring (iv)	4-6-Ring (v)	TPAH (vi)	2-3-Ring (iv)	4-6-Ring (v)	TPAH (vi)
Older Pup						
Mean	0.0480	0.0176	0.0654	0.0026	0.0018	0.0043
CV (vii)	0.35 %	0.34 %	0.51 %	0.01 %	0.01 %	0.01 %
Median	0.0292	0.0109	0.0400	0.0026	0.0017	0.0043
CV	0.12 %	0.25 %	0.51 %	0.01 %	0.01 %	0.01 %
99.9% Quantile (viii)	0.6936	0.3252	1.015	0.0028	0.0019	0.0047
CV	0.51 %	0.85 %	1.01 %	0.08 %	0.05 %	0.06 %
Juvenile						
Mean	0.0429	0.0151	0.0581	0.0032	0.0021	0.0054
CV	0.21 %	0.38 %	0.50 %	0.00 %	0.01 %	0.01 %
Median	0.0270	0.0103	0.0374	0.0032	0.0021	0.0054
CV	0.33 %	0.13 %	0.42 %	0.01 %	0.01 %	0.01 %
99.9% Quantile	0.4503	0.1973	0.6204	0.0034	0.0023	0.0057
CV	2.01 %	1.09 %	0.57 %	0.04 %	0.06 %	0.09 %
Subadult						
Mean	0.0416	0.0147	0.0562	0.0032	0.0021	0.0054
CV	0.38 %	0.58 %	0.25 %	0.01 %	0.01 %	0.01 %
Median	0.0265	0.0102	0.0369	0.0032	0.0021	0.0054
CV	0.35 %	0.72 %	0.36 %	0.01 %	0.01 %	0.01 %
99.9% Quantile	0.4383	0.185	0.5932	0.0034	0.0023	0.0057
CV	0.76 %	1.00 %	0.77 %	0.05 %	0.02 %	0.04 %
Adult Male Non-Territorial						
Mean	0.0150	0.0063	0.0212	0.0031	0.0020	0.0051
CV	0.39 %	0.49 %	0.34 %	0.01 %	0.00 %	0.00 %
Median	0.0089	0.0041	0.0129	0.0031	0.0020	0.0051
CV	0.45 %	0.29 %	0.11 %	0.01 %	0.00 %	0.01 %
99.9% Quantile	0.1676	0.0774	0.2468	0.0033	0.0021	0.0054
CV	1.26 %	1.19 %	7.57 %	0.04 %	0.06 %	0.07 %
Adult Male Territorial						
Mean	0.0168	0.0069	0.0238	0.0031	0.002	0.0051
CV	0.24 %	0.29 %	0.39 %	0.00 %	0.01 %	0.00 %
Median	0.0100	0.0044	0.0144	0.0031	0.002	0.0051
CV	0.20 %	0.24 %	0.43 %	0.00 %	0.01 %	0.00 %
99.9% Quantile	0.1769	0.0792	0.2609	0.0033	0.0021	0.0054
CV	2.21 %	1.00 %	0.63 %	0.03 %	0.04 %	0.05 %
Adult Female Without Pup						
Mean	0.0167	0.0063	0.0230	0.0030	0.0020	0.0050
CV	0.75 %	0.33 %	0.46 %	0.01 %	0.01 %	0.00 %
Median	0.0066	0.0033	0.0099	0.0030	0.0020	0.0050
CV	0.82 %	0.21 %	0.81 %	0.01 %	0.00 %	0.01 %
99.9% Quantile	0.2432	0.0868	0.3110	0.0032	0.0021	0.0053
CV	1.11 %	1.13 %	1.86 %	0.07 %	0.04 %	0.04 %

Table 5. Model-Predicted Average Daily 2-3-Ring PAH, 4-6-Ring PAH, and TPAH Exposures for Northern Knight Island Sea Otters (mg PAH · kg⁻¹ sea otter weight · day⁻¹) (i) (*Continued*)

Sea Otter Class	A) SSOR (ii)			B) NON(iii)		
	2-3-Ring (iv)	4-6-Ring (v)	TPAH (vi)	2-3-Ring (iv)	4-6-Ring (v)	TPAH (vi)
Adult Female With Pup						
Mean	0.0316	0.0118	0.0434	0.0032	0.0021	0.0052
CV	0.20%	0.52%	0.30%	0.01%	0.00%	0.01%
Median	0.0204	0.0080	0.0286	0.0031	0.0021	0.0052
CV	0.31%	0.47%	0.26%	0.01%	0.01%	0.01%
99.9% Quantile	0.3421	0.1595	0.5038	0.0033	0.0022	0.0056
CV	1.67%	1.46%	1.45%	0.05%	0.06%	0.05%

Notes:

i) Analysis of 500,000 modeled individuals for each sea otters class

ii) SSOR = at-risk sea otters

iii) NON = not-at-risk sea otters

iv) 2-3 Ring PAHs = sum of 2-ring and 3-ring PAHs among 41 analytes modeled

v) 4-6 Ring PAHs = sum of 4-ring, 5-ring, and 6-ring PAHs among 41 analytes modeled

vi) TPAH = Total PAHs = sum of all 41 analytes modeled

vii) CV = Coefficient of Variability, based on 5 sets of 100,000 modeled individuals

viii) 99.9% Quantile = Maximum-Exposed Sea Otters.

higher-molecular-weight PAHs have reduced aqueous solubility and bioavailability, and they sorb more strongly to sediment and suspended particles.

Effects

None of the HQs reaches the NOAEL threshold level (Table 6), meaning that even the maximum-exposed at-risk simulated sea otters (1-in-1000th highest exposed out of the 3.15×10^7 at-risk individuals simulated) would not receive sufficient PAH exposures from SSOR to cause a chronic effect. In fact, the highest NOAEL HQ (NHQ) across all sea otter classes and all PAH groups is 0.034, and the highest LOAEL HQ (LHQ) is 0.0133, so exposures would have to increase by 30 to 75 times over these conservative estimates for a maximum-exposed sea otter to reach the minimal effects thresholds (*i.e.*, HQ = 1) (see Figure 6B). Because the TRVs are weight-normalized, the pattern of the effects results across sea otter classes is similar to that for the exposures, with pups having the highest HQs, followed by juveniles and subadults, and then adult females with pups. There are noticeable differences, however, between the effects from the predicted exposures to the 2-3-ring PAHs and the 4-6-ring PAHs. Even though the predicted 4-6-ring-PAH *exposures* are lower than those for 2-3-ring-PAHs, the 4-6-ring PAH *effects* are considerably higher, by a factor of 3-6×, because of the order-of-magnitude higher toxicity of 4-6-ring PAHs (as indicated by the TRVs in Table 4B).

Figure 6. A. Cumulative frequency (%) distribution of assimilated daily doses of 4-6-ring-PAHs for simulated sea otters in the pup class (primary distribution of model outputs; $n = 365,750$). Shown are the at-risk and not-at-risk sea otter distributions, including selected quantiles of occurrence. The 99.9% quantile is defined here as the Maximum-Exposed Sea Otter.

Sensitivity Analyses

None of the structural- or parameter-sensitivity analysis simulations even approaches the NOAEL threshold level for the maximum-exposed sea otters (Table 7A). The highest NHQ among all sensitivity analyses was 0.1129 (*i.e.*, almost an order of magnitude below the threshold of no effects), which occurred using the unrealistic Short *et al.* (2006) co-occurrence probability based on sea otters digging pits throughout the ITZ, even at tide levels where clams do not exist and where sea otters do not forage. All of the other structural-sensitivity runs have much lower HQs. Comparing the Short *et al.* (2006) total ITZ scenario with the comparable LITZ scenario shows that erroneously assuming that sea otters excavate pits into the MITZ and UITZ doubles to quadruples the estimated risks.

The structural-sensitivity analysis in which a territorial sea otter was assigned to an SSOR-subdivision throughout the simulation period (labeled *Local-Territory Sea Otter* in Table 7A) produced only modest differences in HQs (all differences $\leq 10\%$) compared to base models. The probability of co-occurrence in this case is limited more by the distribution of SSOR-potential sediments, the distribution of SSOR fields within an SSOR subdivision, the distribution of SSOR across tidal levels, and the distribution of clam habitat, than it is by being on an SSOR subdivision itself. This is because within an SSOR subdivision, most of the substrate that potentially could have SSOR (*i.e.*, non-bedrock sediments) and that sea otters might dig into (finer-grained sediments in the LITZ) does not actually contain patches of SSOR.

Figure 6. B. Cumulative frequency (%) distribution of assimilated *average* daily doses of 4–6-ring-PAHs for the simulated at-risk sea otters in the pup class (secondary distribution of model outputs; n = 500,000 simulated sea otters). Shown are selected quantiles of occurrence of assimilated doses; the 99.9% quantile is defined here as the Maximum-Exposed Sea Otter. Also shown are the 4–6-ring-PAH NOAEL and LOAEL toxicity reference value (TRVs), which are more than an order of magnitude greater than the 99.9% quantile of assimilated doses.

Table 6. Model-Predicted LOAEL and NOAEL Hazard Quotients for the Maximum-Exposed Sea Otters (i)

Sea Otter Class	LHQ (ii)			NHQ (Hi)		
	2–3-Ring	4–6-Ring	TPAH	2–3-Ring	4–6-Ring	TPAH
Older Pup	0.0027	0.0133	0.0121	0.0055	0.0340	0.0196
Juvenile	0.0018	0.0080	0.0074	0.0035	0.0206	0.0120
Subadult	0.0017	0.0075	0.0071	0.0035	0.0193	0.0114
Adult Male Non-Territorial	0.0007	0.0032	0.0030	0.0013	0.0081	0.0048
Adult Male Territorial	0.0007	0.0032	0.0031	0.0014	0.0083	0.0050
Adult Female Without Pup	0.0010	0.0035	0.0037	0.0019	0.0091	0.0060
Adult Female With Pup	0.0013	0.0065	0.0060	0.0027	0.0167	0.0097

Notes:
i) Hazard Quotient = Calculated Exposures for 99.9% Quantile Sea Otter ÷ Toxicity Reference Value
i) LHQ = Lowest Observed Adverse Effects Level Hazard Quotient
ii) NHQ = No Observed Adverse Effects Level Hazard Quotient.

Table 7. Summary Results from Sensitivity Analyses for NOAEL Hazard Quotients for 4–6 Ring PAHs for 99.9% Quantile Maximum-Exposed Sea Otters

				Adult Male Non- territorial	Adult Male Territorial	Adult Female without Pup	Adult Female with Pup
	Older Pup	Juvenile	Subadult				
<i>A) Structural Sensitivity Analyses</i>							
Primary Model	0.0340	0.0206	0.0193	0.0081	0.0083	0.0091	0.0167
Short <i>et al.</i> (2006)	0.1129	0.1036	0.0835	0.0411	0.0405	0.0373	0.0486
Total ITZ Probability (i)							
Short <i>et al.</i> (2006)	0.0297	0.0315	0.0268	0.0111	0.0145	0.0183	0.0153
LITZ Probability (ii)							
	Older Pup	Adult Male	Adult Female				
Primary Model	0.0340	0.0083	0.0167				
Local-Territory Sea Otter (iii)	0.0370	0.0087	0.0172				
Ballachey & Bodkin Parameters (iv)	—	0.0076	0.0091				
Combined Upper-Bound Parameters (v)	—	0.0141	0.0229				
Combined Lower-Bound Parameters (vi)	—	0.0028	0.0142				
<i>B) Parameter Sensitivity Analyses</i>							
	Older Pup	Adult Male	Adult Female				
Primary Model	0.0340	0.0083	0.0167				
K _{ow} Coefficient (vii)	0.0603	0.0142	0.0179				
Pit Dimension (viii)	0.0340	0.0082	0.0167				
Grooming Efficiency (ix)	0.0356	0.0084	0.0181				
SSOR Pits per Hour (x)	0.0330	0.0080	0.0163				
Dives per Pit (xi)	0.0330	0.0080	0.0162				
Oil Dilution (xii)	0.0337	0.0081	0.0164				
Coating on Paws and Clams (xiii)	0.0674	0.0160	0.0328				
Coating on Clams (xiv)	0.0347	0.0084	0.0169				
Coating on Paws (xv)	0.0664	0.0162	0.0324				
Reduced Coating on Paws (xvi)	0.0186	0.0044	0.0093				
Particles on Fur (xvii)	0.0340	0.0082	0.0166				

Notes:

- i) Based on Short *et al.* (2006) co-occurrence probability for lower-, mid-, and upper-intertidal zones; 3.7×10^{-3} per pit
- ii) Based for Short *et al.* (2006) co-occurrence probability for lower intertidal zone (MVD5) only, 4.3×10^{-4} per pit
- iii) Sea otter assigned to an SSOR-subdivision throughout simulation
- iv) Based on sea otter diving parameters reported in Ballachey and Bodkin (2006) for adults only, except one dive per pit
- v) Based on Short *et al.* (2006) and Ballachey and Bodkin (2006) upper bound probabilities and diving parameters for adults only including sea otter pits throughout ITZ and 2 dives per pit
- vi) Based on Short *et al.* (2006) and Ballachey and Bodkin (2006) lower bound probabilities and diving parameters for adults only including sea otter pits only in lower ITZ and 5 dives per pit
- vii) All particulate-bound PAHs fully assimilated
- viii) Increased pit radius by 10 cm
- ix) Decreased grooming efficiency by 1/2 (doubled fraction of particles remaining on fur after grooming)
- x) Assigned 1/4 of pits during an SSOR co-occurrence hour to intersect SSOR
- xi) Assigned 5 dives per pit, following Ballachey and Bodkin (2006)
- xii) Decreased thickness of oil film coating sea otter fur by 1/10 to reflect dilution of oil-phase from pit to surface
- xiii) Doubled thickness of SSOR oil-phase coating on sea otter paws and on clams in SSOR pits
- xiv) Doubled thickness of SSOR oil-phase coating on clams in SSOR pits
- xv) Doubled thickness of SSOR oil-phase coating on sea otter paws
- xvi) Halved thickness of SSOR oil-phase coating on sea otter paws
- xvii) Doubled amount of SSOR-bound particles on fur from pit plume.

The structural-sensitivity analysis using the sea otter diving characteristics derived from Ballachey and Bodkin (2006) produced lower estimated risks than our base models (*e.g.*, ~8% lower NHQ for adult females and ~45% lower NHQ for adult males). This is because the Ballachey and Bodkin (2006) data indicate that sea otters feed fewer hours per day and dig fewer pits per hour than indicated by our data.

The combined Short *et al.* (2006) and Ballachey and Bodkin (2006) parameterization scenario for the adult male resulted in an upper-bound NHQ for the 99.9% quantile of 0.014, ~4× below the counterpart scenario based on Short *et al.* (2006) for adult males, and the lower-bound is 0.0028, well under the best estimate of our base model. Similar results are derived for the adult female sea otters. Consequently, the predicted risk values remain ~40–350× lower than the NOAEL threshold for the adult males and ~40–70× below for the adult females.

The parameter-sensitivity analyses (Table 7B) for K_{ow} indicate that varying the K_{ow} by 3–6 orders of magnitude (Durrell *et al.* 2006) increase the NHQs by only ~7–77% compared to the respective base models, suggesting particulate-bound PAHs constitute a relatively small component of the total assimilated dose. This is affirmed by the sensitivity analyses that showed small responses to doubling the fraction of particulates sticking to the fur or decreasing the sea otter grooming efficiency by half. The depth of the sea otter pit has no effect on the exposures because the model assigns all of the SSOR under the surface area of the pit to being exposed by the excavation (*i.e.*, exposure is pit-depth-independent). The width of the sea otter pits only minimally affects exposures to the maximum-exposed individuals. The number of pits assigned in the model to intersecting SSOR during a co-occurrence hour does not make a major difference (<3% for 4-fold reduction). The reason for the results of the latter two sensitivity analyses is that the volume of sediments excavated primarily affects the exposure route of particulate-bound PAHs, which, as demonstrated earlier, is not a major route of exposure. Increasing the number of dives-pit⁻¹ from 1 to 5 results in only a small reduction in assimilated doses. Similarly, varying the oil dilution factor makes <3% difference in the exposures because the oil-phase slick contributes a small fraction of the total assimilated dose. However, doubling the thickness of the oil-phase coating on both the paws and claws almost doubles the assimilated doses, indicating this is a sensitive parameter. Additional sensitivity analyses to partition this response, in which the thickness of oil coating on *either* paws or claws was doubled, indicated that the coating on the paws accounts for almost all of this doubling response. As a confirmation, the sensitivity analysis with the thickness of coating on the paws halved results in a reduction in the 4–6-ring PAH NHQ by almost half (Table 7B). This sequence of sensitivity analyses indicate that if a sea otter digs a pit into SSOR, the direct coating of sea otter paws by oil-phase-bound PAHs is the single-most important route of exposure. That exposure route is limited by the surface area of the sea otter's paws.

CONCLUSIONS

EVOS occurred two decades ago. Clearly the oil spill constituted a catastrophic environmental disturbance to the PWS ecosystem in the early months to few years after the spill (Harwell and Gentile 2006). In an extensive review of the literature, based on criteria for determining ecological significance developed for the USEPA

(Gentile and Harwell 1998), Harwell and Gentile (2006) concluded that virtually none of the ecological components of the PWS continued to experience ecologically significant effects 17 years after the spill. A separate review (Integral 2006) reached similar conclusions for most endpoints.

The specific issue addressed here is whether or not the remaining SSOR presents a significant toxicological risk to PWS sea otters, in terms of both the maximum-exposed individual sea otters and the subpopulation of sea otters at Northern Knight Island. The results of this comprehensive, quantitative risk assessment lead to a simple conclusion: there remains no plausible toxicological risk from the SSOR to even the hypothetical maximum-exposed individual sea otters residing at NKI because the assimilated doses are so far below the threshold of effects. This conclusion results from the quantitative simulations across each of seven classes of sea otters that demonstrated there is a 1-to-2 orders-of-magnitude gap between predicted doses to maximum-exposed sea otters and the conservative NOAEL thresholds of individual-level mortality, growth, or reproductive effects.

The residual material from EVOS is at present buried under several centimeters of clean sediments, located in areas protected by surface armoring, such as boulders or cobble fields (Michel *et al.* 2006; Short *et al.* 2007; Taylor and Reimer 2008). This SSOR remains there precisely because it is largely protected from the more frequent and routine physical disturbances of the high-energy wave environment of PWS. A small amount of surface oil residues also remains as highly weathered asphaltic patches in the upper middle to supratidal zones; this SSOR is neither bioavailable nor located where sea otters forage. By 2001 only ~0.1–0.3% of the initial spill volume remained (Short *et al.* 2004); with nine years of subsequent degradation, even less remains in 2010. Over time, the SSOR has been weathered to varying degrees, rendering it significantly less toxic than the original oil. Moreover, the only plausible toxicological risk to biota in the Sound is if SSOR is somehow exposed and thereby becomes bioavailable for uptake. One suggested mechanism for that exposure is excavation of the buried deposits by sea otters when foraging for infaunal prey.

We have presented a conceptual model that describes the multiple pathways by which PAHs from the SSOR could be assimilated by a sea otter. This conceptual model was converted into a quantitative simulation model, parameterized using the best available information about PWS sea otters, the nature and distribution of SSOR at NKI as of 2002, and recent chemical analyses of PAHs in prey tissues, sediments, and seawater, or, in the few cases for which no empirical data exist, using informed expert judgment. Because of the consistent bias towards conservatism, predicted exposures and effects are likely to be over-estimates, in some cases significantly so. The quantitative model simulates the pathways by which a sea otter could be exposed to SSOR by excavating pits when foraging for infauna in the LITZ. This co-occurrence process is simulated in the model using the actual spatial relationships of the habitats of NKI, the distribution of the SSOR as it is presently understood, and the foraging activities of PWS sea otters. Using a stochastic model, we explored the range of plausible events that could occur for an NKI sea otter and the resulting distributions of assimilated doses to the maximum-exposed individuals.

The modeling protocol is conservative, robust, and rigorous, enhancing confidence that the results are scientifically sound and represent over-estimates of the actual exposures to the sea otters of NKI from the current remnant SSOR. These

quantitative projections were conducted for 500,000 simulated sea otters comprising each of seven distinct age and gender classes. Altogether >1 billion sea otter-hours were simulated to capture the environmental, SSOR, and sea otter variability. Defining the maximum-exposed individuals as having the 1-in-1000th greatest assimilated doses adds confidence that the conclusions represent the reasonable upper bound of the toxicological risk from buried remnant oil residues to NKI sea otters.

The results for the effects from the assimilated doses of 4–6-ring PAHs (Table 6) are most useful in understanding the potential for individual sea otter effects, because these results are based on the more conservative NOAEL HQ values for the maximum-exposed individuals for the more toxic component of the PAH mixtures. In the base model, the assimilated dose closest to causing an effect was for the older pup (NHQ = 0.034), although this was still $\sim 30\times$ below the threshold for which no effects were observed in laboratory toxicological studies (Figure 6B). The other sea otter classes were ~ 50 – $120\times$ below the NOAEL threshold. For the LHQs, the picture is even more striking: all assimilated dose values range from $75\times$ to more than $1400\times$ below the threshold at which any effects would be experienced for the maximum-exposed sea otters.

The results of the sensitivity analyses, using alternate model structure or parameterization, further support the conclusion of no significant toxicological risk. The closest to a potential effect results from the co-occurrence scenario presented by Short *et al.* (2006), in which the maximum-exposed older pup reached a factor of $\sim 9\times$ below the NHQ (Table 7A); results from this sensitivity analysis were 10 – $25\times$ below the NHQ for the other sea otter classes. However, this scenario is biologically unrealistic because it allows sea otters to excavate pits in the MITZ and UITZ, where clams do not exist in significant numbers and where sea otters do not dig pits (Boehm *et al.* 2007a). Since the preponderance ($\sim 90\%$) of SSOR occurs in these mid- and upper intertidal zones, the projected results from assumed foraging in these zones are unrealistically high. Nevertheless, it would still require an order-of-magnitude greater assimilated dose for the maximum-exposed individuals to reach the no-effects threshold. When the Short *et al.* (2006) scenario is more appropriately limited to foraging in the LITZ, the results are 30 – $90\times$ below the no-effects threshold (Table 7A). When the sea otter diving characteristics were parameterized based on the Ballachey and Bodkin (2006) data instead of our own observations, the predicted exposures decrease significantly to more than two orders of magnitude below a threshold of no effects. Moreover, when both the Short *et al.* (2006) probabilities and the Ballachey and Bodkin (2006) diving parameters are used in combination, including when the sea otter is assumed to dig pits in the UITZ, the risks remain more than 40 – $70\times$ below thresholds of no effects, and when foraging is more realistically limited to the LITZ, the risks are more than $350\times$ below the no-effects threshold for the maximum-exposed male sea otter. Finally, none of the results of the parameter-sensitivity analyses, including the expert-judgment-based parameters discussed previously, alters the fundamental conclusion of no plausible risk to even the maximum-exposed individual sea otters. This reinforces the characterization of the quantitative risk assessment model and its results as being robust and conservative.

This quantitative risk assessment also definitively answered the question of whether toxicological effects on individuals could possibly rise to the level of causing

subpopulation effects at NKI. Given that our model simulations found no situations in which toxicological exposures would come close to causing individual-level effects on even the 1-in-1000th most-exposed sea otters, it is not possible for there to be any effects on the subpopulation. For a subpopulation effect to occur, several individuals would have to experience adverse effects relatively frequently compared to the time-domain of population dynamics of sea otters. With fewer than 100 sea otters at NKI, on average it would take 10 years for a single individual to attain the maximum-exposed dose level predicted by the model, and that would still be well over an order of magnitude below the no-effects threshold. Such low-frequency and low-consequence exposures could not possibly cause any subpopulation-level effects.

A separate careful analysis would be necessary to assess whether or not there are any effects from any cause on the subpopulation of NKI sea otters compared to the rest of the PWS sea otter population. It is clear that the sea otters of PWS are subject to many environmental stressors, both natural and anthropogenic, that could affect their population levels (*e.g.*, climate regime shifts [Peterson and Schwing 2003; Lees *et al.* 2006]; community trophic-structure shifts [*e.g.*, Mantua *et al.* 1977; Finney *et al.* 2000; Cooney *et al.* 2001]; increased predation by transient killer whales [Estes *et al.* 1998; Doroff *et al.* 2003]; and legal harvesting by Native Alaskans for subsistence [USFWS 2002, 2008]), including some stressors that may vary spatially. Understanding the full suite of risks to PWS sea otters would require an analysis beyond the scope of the present study (see Harwell *et al.*, 2010).

ACKNOWLEDGMENTS

The authors thank the participants in the three workshops that were convened to develop the pathways conceptual model and the data for the parameterization for the quantitative toxicological risk assessment model, including: Drs. Paul Boehm, John Brown, Robert Day, Susan Kane Driscoll, Ray Highsmith, Steve Murphy, Jerry Neff, David Page, and John Wiens. We also acknowledge the comments and suggestions by these scientists and by Dr. Erich Gundlach on drafts of the manuscript. We thank Dr. Elliott Taylor for providing the schematic figure for the distribution of SSOR. Finally, we particularly appreciate the careful reviews and suggestions of the final draft manuscript provided by Drs. Ken Dickson, Terry Young, and David Weinstein, as well as the formal peer reviewers approved by the editors of *Human and Ecological Risk Assessment*, Drs. Donald DeAngelis, Kristin Laidre, and Christopher Teaf.

We acknowledge the financial support provided by ExxonMobil for the time needed to prepare this article.

AUTHOR-DIRECTED PEER REVIEW

This manuscript was prepared under HERA's author-directed peer review process, wherein a manuscript's authors nominate proposed peer reviewers to HERA's Managing Editor for approval or revision. The following persons reviewed and approved the publication of this manuscript:

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