# Slightly weathered oil from the Exxon Valdez spill pers Gail V. Irvine<sup>1</sup>, Danie on rocky Gulf of Alaska shores after 23 years Robert K. Nelson<sup>5</sup>, La

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## Introduction:

- Before the Exxon Valdez oil spill (EVOS) in March, 1989, oil persistence had been linked to wave exposure, with longest persistence in low wave-energy environments (e.g, mudflats, tidal marshes; Gundlach and Hayes, 1978).
- But, after EVOS, oil was found to persist on higher-energy armored shores, where a layer of cobbles or boulders overlays finer substrates.
- In 1994 we began our study of 6 Gulf of Alaska rocky beaches distant (240 640 km) from the spill origin, which had been contaminated by Exxon Valdez oil (EVO), in the form of mousse.
- Oil mousse is a viscous water-in-oil emulsion that can be transported long distances with little weathering.
- New in 2012: a) asking whether oil is leaking from the sites, and b) examining the oil with multiple chemical methods to look at weathering and confirm source.





## Does the oil persist?



Subsurface oiling is measured the smaller stones between boulders. These 2012 images show dip stones and/or places they were removed

Result: subsurface oil at 4 sites has not changed for 18 years.

#### How has the oil weathered?

## Is it Exxon Valdez oil?



Six study sites on the Gulf of Alaska coastlines of Kenai Fjords and Katmai National Parks and Preserves were selected in 1992. Five (#2-6) are boulderarmored gravel beaches.



Photos of Cape Douglas site from above (top) and Kiukpalik site partial view (bottom).

#### Questions

- Does oil still persist after 23 years at these sites?
- Is boulder stability correlated with oil persistence?
- Is oil leaking out or being released from the sites, and if so, by what mechanism, given the long-term persistence of this oil?
- Is the oil at the sites Exxon Valdez oil (EVO)?
- How has the oil weathered?



## Does the oil persist?

Surface oil percent cover has continued to decline over time and is now at very low levels (0-3%).



This 3-dimensional view of the GCxGC chromatogram allows visual comparison of quantitative data on the relative abundance of the constituents of different oil samples.

Results: the 2012 samples from Cape Douglas, Kiukpalik Is., Ninagiak Is. and McArthur Pass are clearly similar to EVO and show evaporative loss of the compounds compared to EVO. However, Cape Gull and Kashvik are quite distinct. The signature at Kashvik may represent secondary contamination by a mid-range distillate, such as diesel oil. The Cape Gull sample appears highly biodegraded.

The biomarker region of a GCxGC-FID chromatogram for (a) Exxon Valdez crude, and 2012 site samples. Biomarkers are recalcitrant components of oil that can be used to determine the oil source.

Result: the 2012 samples from Cape Douglas. Kiukpalik Is., Ninagiak Is. and McArthur Pass are quite similar to the reference Exxon Valdez crude oil. The sample from Cape Gull has some different patterns in the biomarkers (abundances of hopanes and relative abundances of triaromatic steranes) that suggest that this either is not EVO, or that it has degraded significantly, in ways not anticipated. The Kashvik sample is distinctly different (Note that no oil was observed at Kashvik in 2012)

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#### References

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Douglas site. The stocking hat measures 22 cm across.

Boulder movements between 1994-2012 at our most exposed site, Cape Douglas (maximum fetch = 880 km). Significant movements (distance) are > 1 meter.

Result: there have been only 3 significant distance

movements by boulders over 18 years at this site. Most changes are smaller and represent boulders rolling or shifting in place, which never completely exposes the embedded oil. Results are similar for other sites.

(degrees)

# Is the oil leaking out?



In 2011 and 2012, we used two methods to test whether oil constituents were being released into the water: 1) **passive samplers** (a plastic strip) inside a protective metal housing deployed at 2 sites and collected after ~ 1 month, and 2) **mussels** collected ~ 30 m from the same sites. **Beault:** - 50% of the same law het

**Results:** ~50% of the samplers had accumulated hydrocarbons consistent with oil, and mussels in 2011 showed contamination by particulate hydrocarbons.



±12 cm

±3cm

±5 degrees

Bolt

Cape Douglas: changing height

Bolt

Cape Douglas: changing azimuth



#### **Major Points**

- Exxon Valdez oil (EVO) has persisted for 23 years on boulder-armored beaches in the Gulf of Alaska up to 500 km from the spill origin.
- In 2012, the most distant (at 640 km) site had no observable oil, and oil was much reduced at the second most distant site.
- Subsurface oil persists at unchanged levels over 18 years at the other 4 sites.
- The boulder armors have been very stable for 18 years, with no significant disruptions which could have led to loss of the subsurface oil.
- Small amounts of oil are leaking out of the sites -- probably due to frequent, small boulder movements (shifting, rolling in place).
- After 23 years oil at four of the sites remains only slightly weathered, similar to 11day old oil
- At only one site (Cape Gull) has the oil weathered considerably; we are still evaluating this puzzle.
- Oil persistence on these beaches is probably due to a combination of initial oiling by weathering-resistant mousse and its subsequent sheltering under stable boulder armors.