Field Instruments for Real Time In-Situ Crude Oil Concentration Measurements

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Near-shore Environments

- Major changes in near-shore ecosystems occur as pulses during stochastic events
- Sampling frequency must be greater than inherent frequency of the system
- Punctual sampling generally will miss environmental activity in pulsed systems
  - Currently: sampling occurs at regular intervals (1-2 times per year)
  - High frequency (traditional) sampling very expensive.
- Must use new concept of “smart sampling”
- Proposed
  - continuous monitoring
    - both remote and in-situ
    - baseline and transition periods
  - discrete studies
    - during key transition periods
    - detailed sampling
  - integrate information from all technical disciplines
  - transfer knowledge to stakeholders

Preliminary Study

- Crude oil emulsions of varying concentrations were analyzed using five instruments
- The implications of potential interferences and instrument limits are investigated
  - as to their importance for real-time monitoring of crude oil spills.

The Five Instruments

- LISST-100 (Sequoia Instruments)
  - A submersible multi-angle laser scattering instrument
- AU-10 field fluorometer (Turner Designs)
  - an *ex-situ* single wavelength fluorometer
- Flashlamp (WET Labs, Inc.)
  - an *in-situ* single-wavelength fluorometer
- two *in-situ* multiple-wavelength fluorometers
  - ECO-FL3 (WET Labs, Inc.)
  - SAFire (WET Labs, Inc.)
- Instruments evaluated for sensitivity and bias

Sensor Instrumentation

SAFire by WET Labs

LISST-100 by Sequoia

Photos from manufacturers' websites

Sensor Instrumentation

ECO-FL3 by WET Labs

10-AU Field Fluorometer by Turner Designs

FlashLamp by WET Labs

Photos from manufacturers' websites

Methods/Materials (Reactor Set-up)

- The Reactor Set-up
  - derivative of standard jar test apparatus
  - agitated using a stainless steel mixing impeller
  - instrument installation (for oil concentration monitoring)
    - LISST-100 -- installed through one end of reactor wall
    - ECO-FL3 -- suspended directly in the reactor
    - Flashlamp -- suspended directly in the reactor
    - SAFire -- used ex-situ with continuous flow analysis
    - 10-AU Field Fluorometer -- ex-situ with continuous flow analysis
  - An electric pump attached to fluorometers
    - water from reactor pulled through polyethylene tubing, SAFire and 10-AU fluorometer, the pump, and back into the reactor.

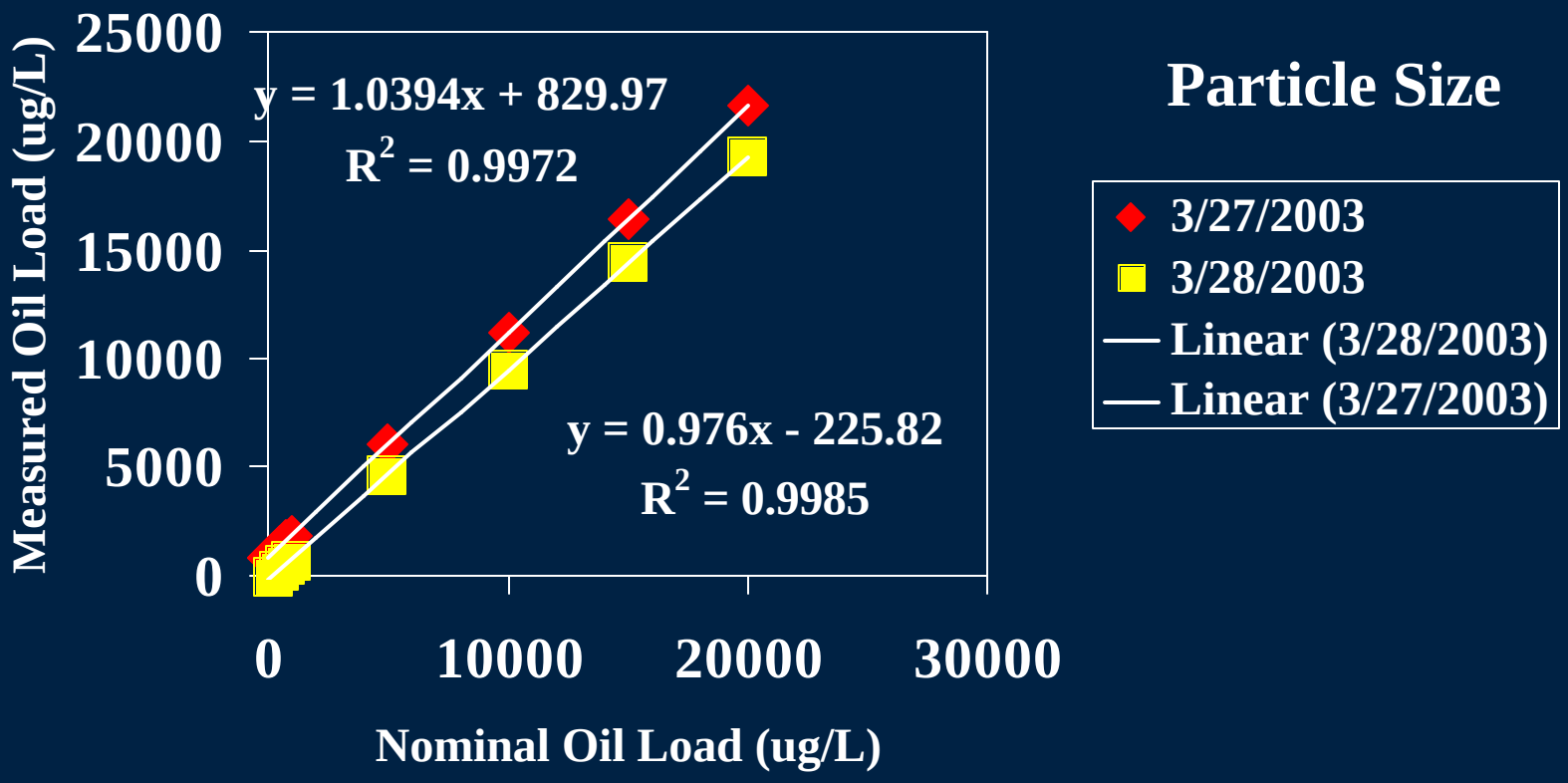
Methods/Materials (Reactor Set-up)

- Stock solution (chemically-dispersed oil in water solution)
  - weathered Medium Arabian crude oil
  - Corexit® 9500 dispersant
  - Synthetic seawater (Instant Ocean)
  - Dispersant-to-oil ratio of 1:10
  - Dispersed-oil-to-synthetic-water ratio of 1:1000
- Reactor Solution
  - 50 liters synthetic seawater
  - Varying amounts of stock solution added to reactor
- Series of experiments
  - nominal oil concentrations were 10, 100, 250, 500, 750, 1000, 5000, and 10000 ppb

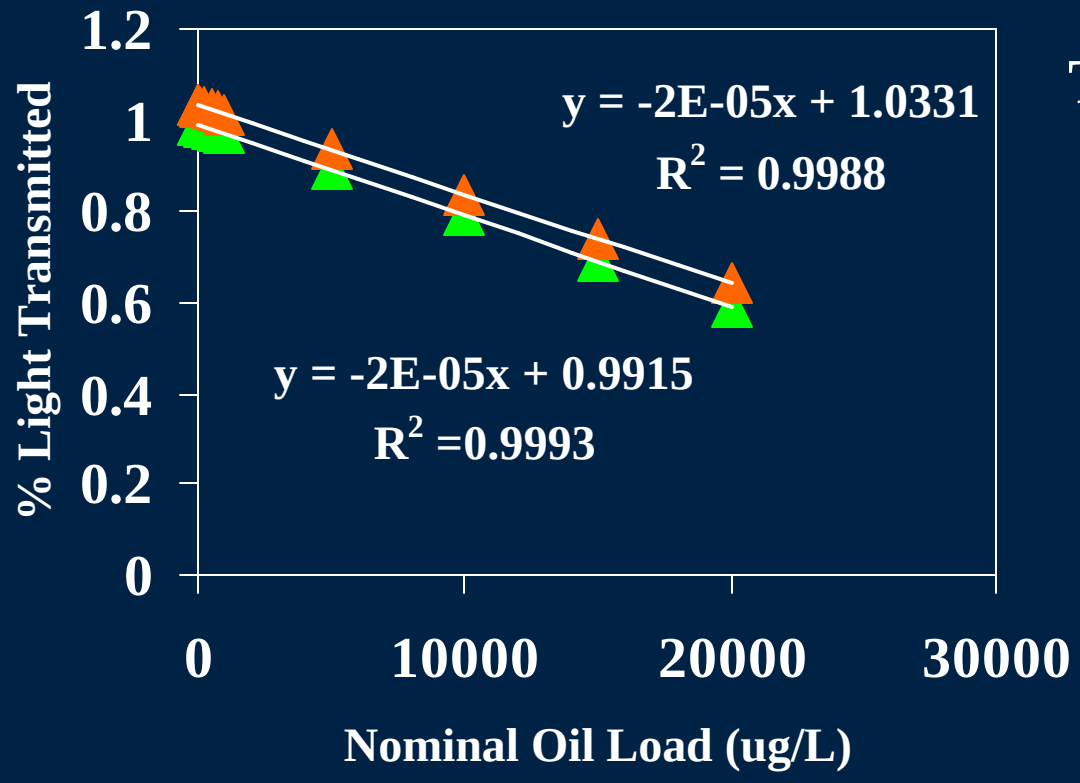
Methods/Materials (Monitoring Oil Concentrations)

- Specified volume of stock solution added to reactor
- Mixing commenced
- Five-minute measurement period
  - A series of dynamic droplet size distributions were measured using the in-situ laser scattering particle sizer (LISST-100) and analyzed using instrument software
  - Raw count data from the Flashlamp and the ECO-FL3 were captured using Windows Hyperterminal software
  - Raw count data from the 10-AU Field Fluorometer were hand recorded from the instrument display window
  - Raw count data from the SAFire were captured using instrument software
- The experiment was conducted twice

LISST Results



LISST Results



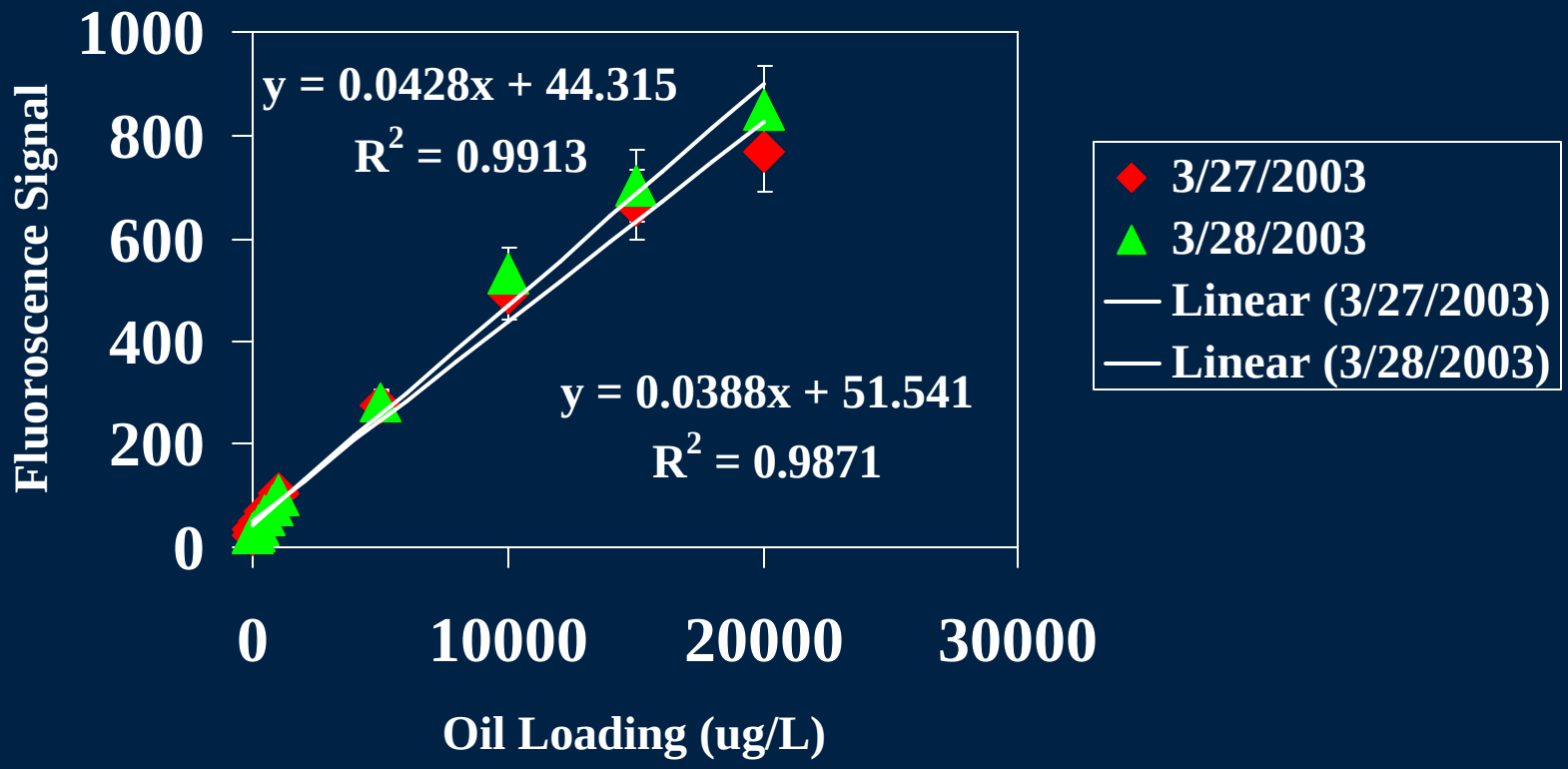
Transmissometry

- 3/27/2003
- 3/28/2003
- Linear (3/28/2003)
- Linear (3/27/2003)

LISST Results (Comments)

- both data sets are linear ($r^2 > 0.999$)
- reproducibility of the curve is high
- For concentrations < 100 ppb, data noise greater than the measurement
  - due to the high transmissivity of the water
- LISST does not require a specific chemical or oil calibration for absolute volume quantification
- presence of bubbles or suspended sediment will impair accurate oil quantification as these also produce significant light scatter

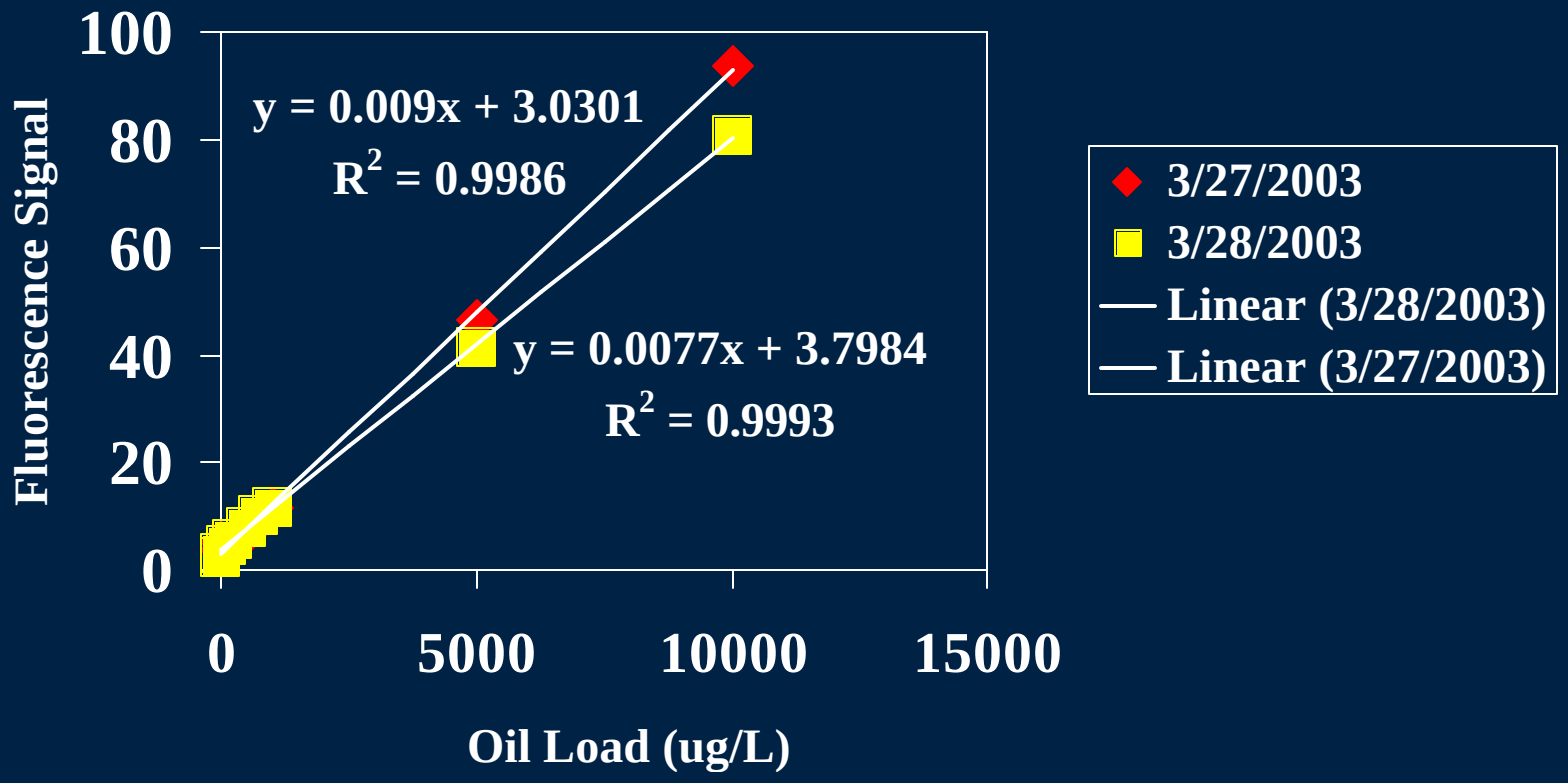
FlashLamp Results



FlashLamp (Comments)

- For both experiments, response was linear ($r^2 > 0.98$)
- For both experiments, response was consistent
  - slope values agree within 10%
- For the entire measured range, the response values were greater than the noise
  - Flashlamp can detect changes in oil concentration throughout the measured range
- Calibration with the oil is required to related fluorescence counts to oil concentration (ppb)
- Instrument is less susceptible to physical interferences such as bubbles or suspended sediments

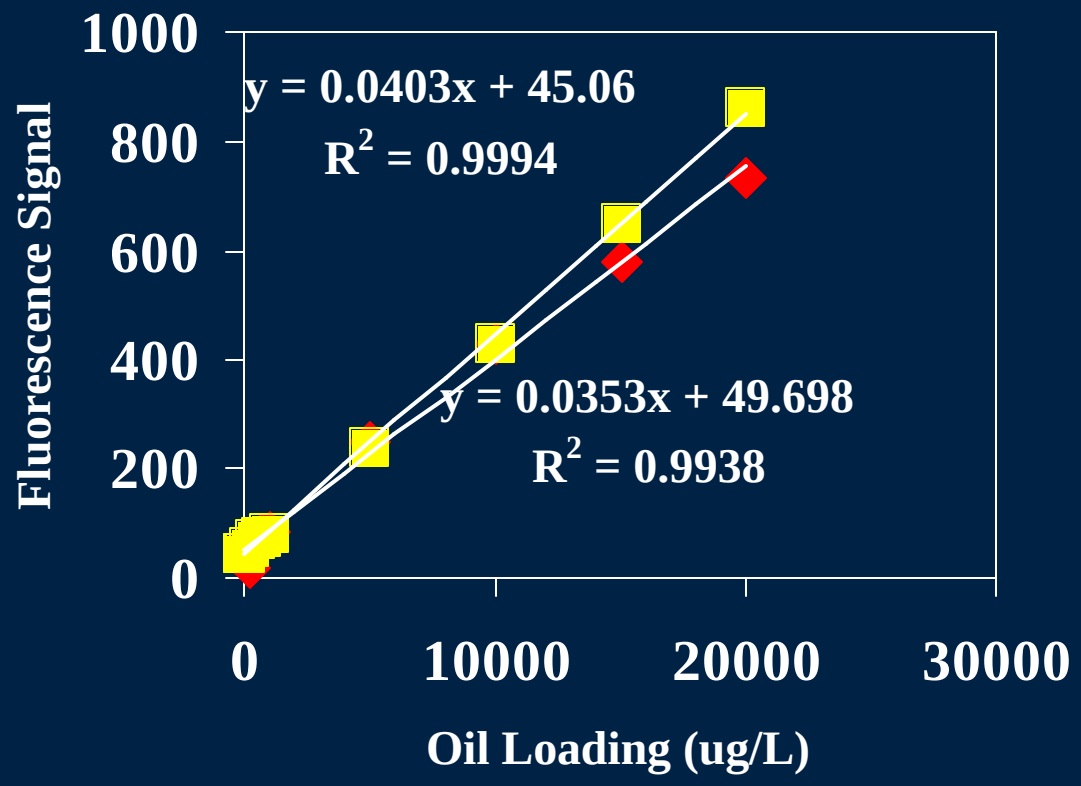
Turner Fluorometer Results



Turner Fluorometer (Comments)

- Response linear ($r^2 > 0.999$) for both experiments
- Response values slightly less consistent compared with the previous instruments, (difference ~ 15%)
- At 15,000 and 20,000 ppb, concentrations above measurement range of the Turner fluorometer
- As with Flashlamp, calibration with the oil required to relate fluorescence counts to oil concentration (ppb)

ECO-FL3 Results

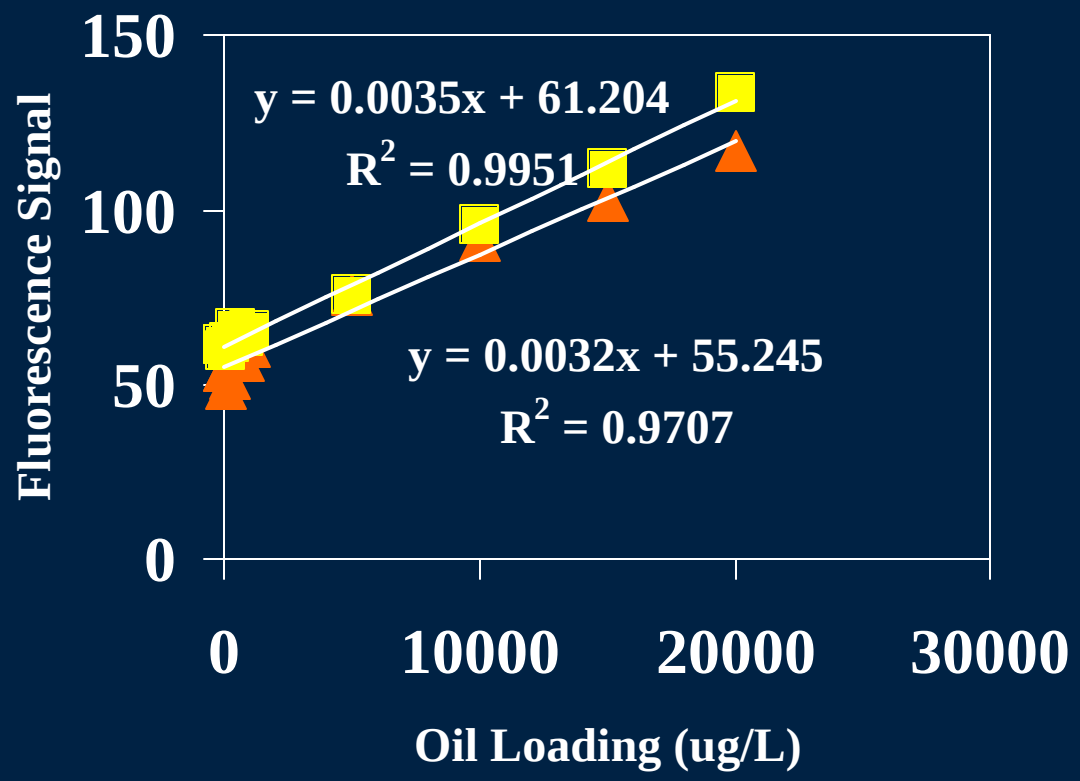


470nm/ex & 695nm/em

“chlorophyll a”

- 3/27/2003
- 3/28/2003
- Linear (3/28/2003)
- Linear (3/27/2003)

ECO-FL3 Results



390nm/ex & 460nm/em

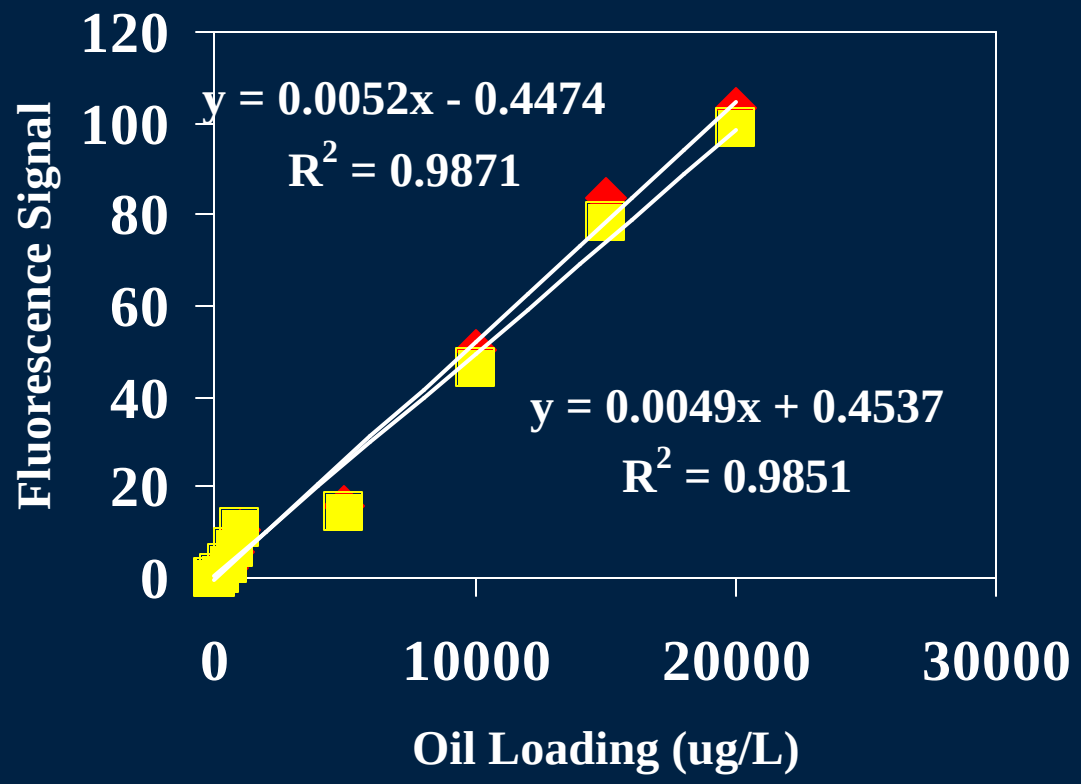
"CDOM"

- 3/27/2003
- 3/28/2003
- Linear (3/28/2003)
- Linear (3/27/2003)

ECO-FL3 (Comments)

- Most significant response on chlorophyll A wavelength (nm)
  - only minimal responses on CDOM or fluorescein (nm) wavelengths
- The chlorophyll A response linear ($r^2 > 0.99$)
- Response reproducibility similar to that of the Turner 10-AU Field Fluorometer (within 15%)
- Data noise at concentrations < 1000 ppb was greater than the mean response values
  - ECO-FL3 would have problems quantitatively detecting changes in oil concentration below this threshold value
- Calibration with the crude oil is required to relate fluorescence counts to oil concentration (ppb)

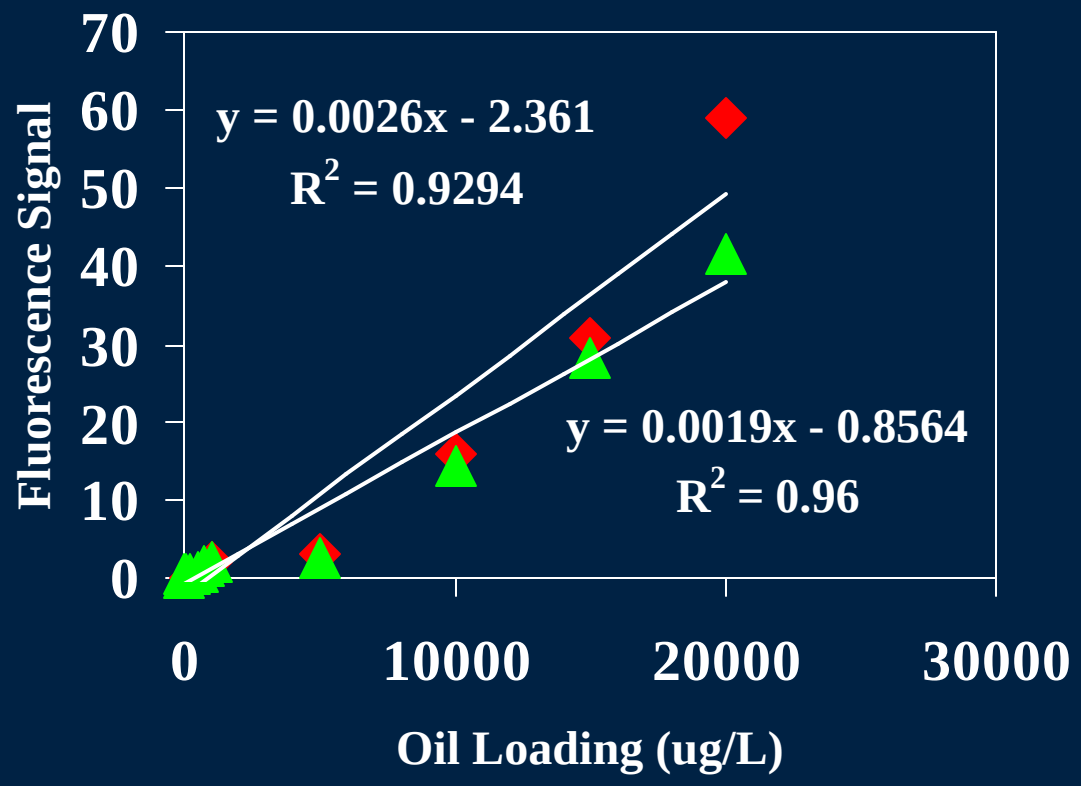
SAFire Results



228nm/ex & 340nm/em

340nm/ex & 460nm/em

SAFire Results



340nm/ex & 460nm/em

- 3/27/2003
- 3/28/2003
- Linear (3/27/2003)
- Linear (3/28/2003)

SAFire (Comments)

- For 228 excitation/340 emission pair (top figure),
  - response linear (r^2>0.98) and consistent
  - Response slope values within 5% of each other
  - For entire range, mean response was greater than the measurement noise
- For the 340 excitation/460 emission pair (lower figure),
  - response less linear (r^2 > 0.92) and less consistent
  - Slope values are within 30% of each other
- This suggests that the 228 nm excitation/340 nm emission on SAFire can detect changes in oil concentration throughout the measured range
- Calibration with the crude oil required to relate fluorescence counts to oil concentration (ppb).

Conclusions

- All tested instruments ollowed a linear response (r^2>0.98) within tested concentration range (10-20000 ppb)
- At the lowest concentrations, LISST-100 not as effective as the fluorometers due to the limited particle volume present for scatter
- For Turner Designs AU-10 Field Fluorometer, highest concentrations tested were above the measurement range of the instrument
- This **preliminary study** indicates the applicability of real-time *in-situ* sensors in the context of oil spill response.
  - Potential benefits include
    - better understanding of cyclical nature of near-shore ecological and physical parameters,
    - building a foundation for quantitative modeling and for oil spill response and designing long-term, cost-effective monitoring strategies,
    - formulating operational tools for environmental managers, and
    - disseminating results in “user-friendly” formats for the general public, educators, and policy makers

Acknowledgements

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