

Chemical Contaminants Entering Estuaries of the South Atlantic Bight and Determining Their Effects by Bioassays

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Chemical Markers of Land Use and Their Sources

- PAHs – 3 to 5 ringed aromatic compounds of pyrogenic origin whose sources includes vehicles, roads and parking lots and deposition from the atmosphere
- Pesticides – atrazine (herbicide), chlorothalonil (fungicide) and fipronil (insecticide) whose sources include agriculture, golf courses, and domestic/commercial applications

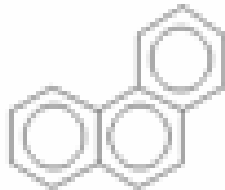
Polycyclic Aromatic Hydrocarbons (PAHs)

- 2-3 ring

Naphthalene



Phenanthrene



1,6,7-trimethyl-

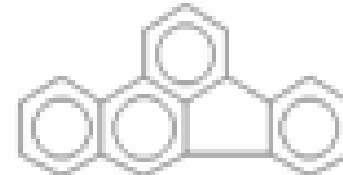


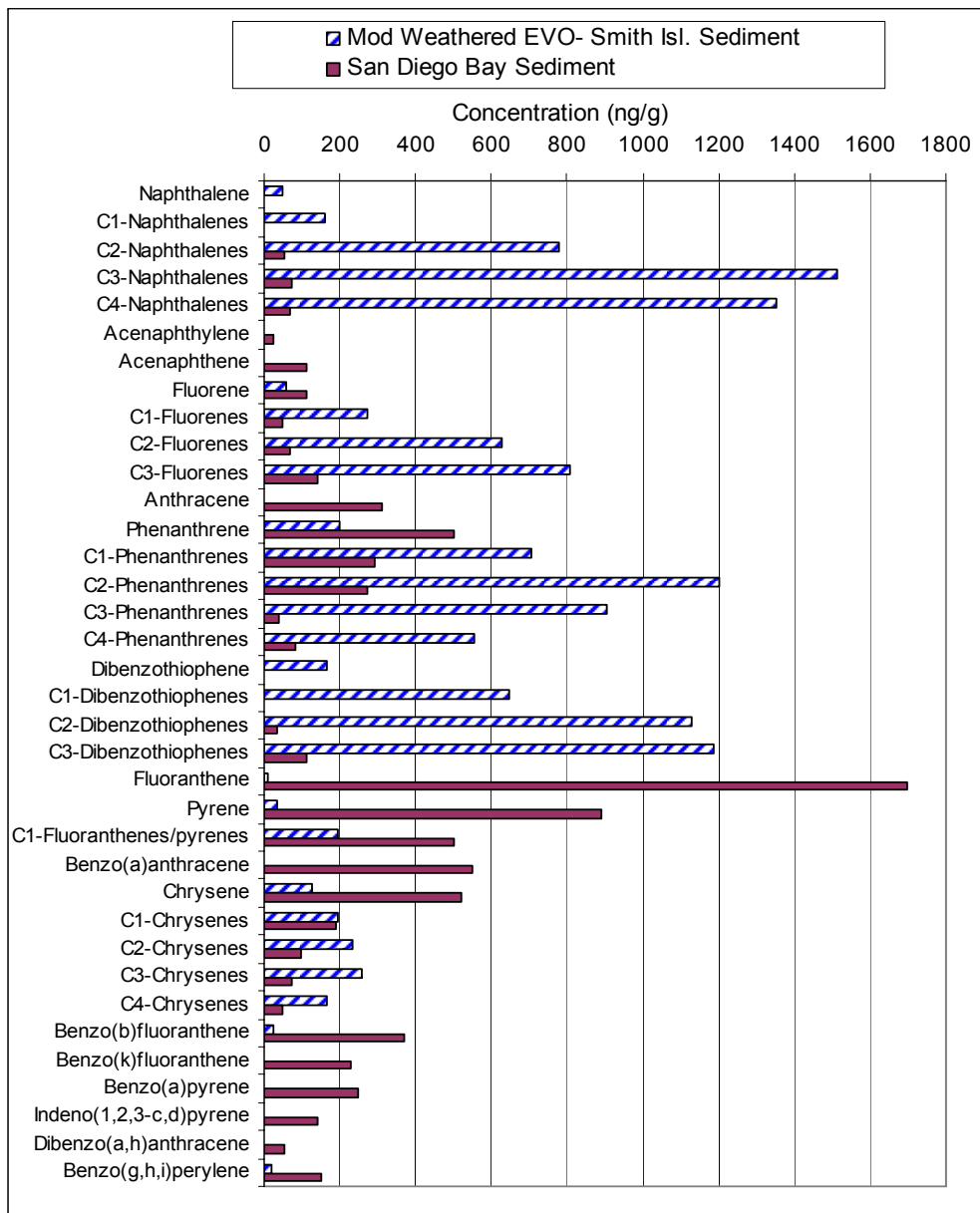
- 4-5 ring

Chrysene

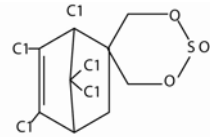


Benzo[b]fluoranthene

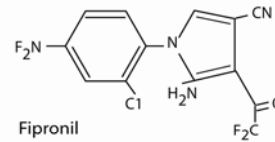




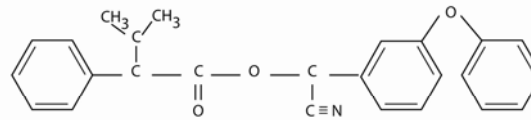
Widely Used Pesticides in Coastal South Atlantic



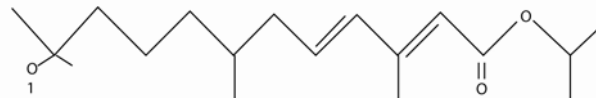
Endosfan
(Organochlorine)



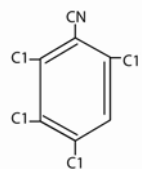
Fipronil



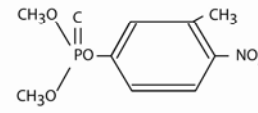
Fenvalerate (Pyrethroid)



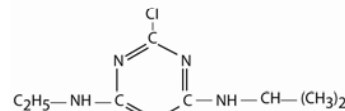
Methoprene (Mosquito control agent)



Chlorothalonil
600,000 lbs/yr in S.E. U.S.
up to 2ppm in leachate
Highest Application Rate:
88kg/hectare



Fenitrothion (Organophosphate)



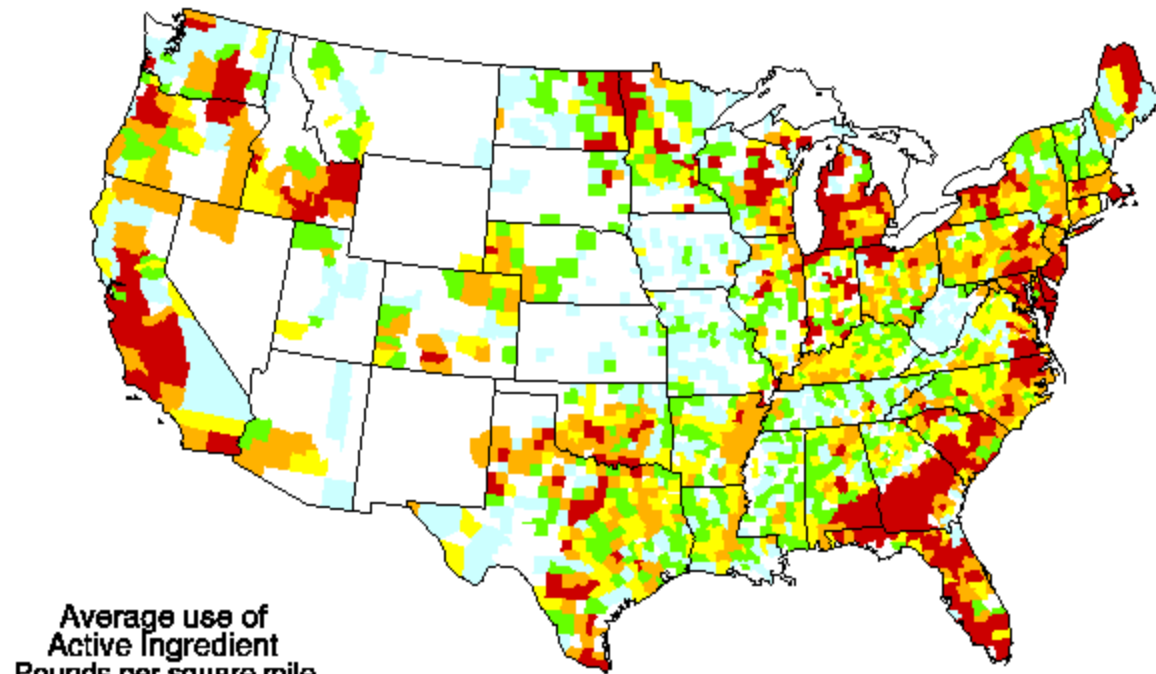
Atrazine



Chlorpyrifos

CHLOROTHALONIL

ESTIMATED ANNUAL AGRICULTURAL USE

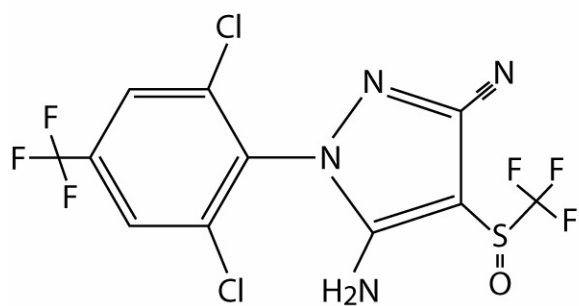


Average use of
Active Ingredient
Pounds per square mile
of county per year

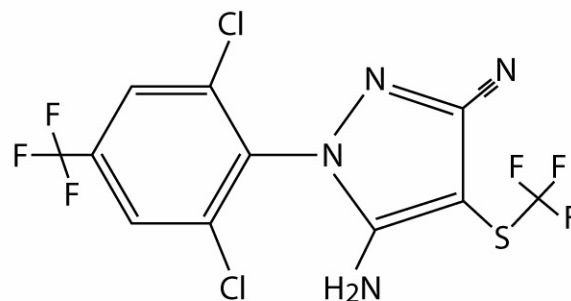
- No Estimated Use
- < 0.033
- 0.033 - 0.162
- 0.163 - 0.765
- 0.766 - 4.052
- ≥ 4.053

Crops	Total Pounds Applied	Percent National Use
peanuts	5,926,168	46.29
potatoes	2,790,349	21.80
tomatoes	1,230,116	9.61
watermelons	423,300	3.31
onions	294,317	2.30
squash	257,804	2.01
cucumbers	239,026	1.87
peaches	213,755	1.67
celery	208,396	1.63
cherries	149,218	1.17

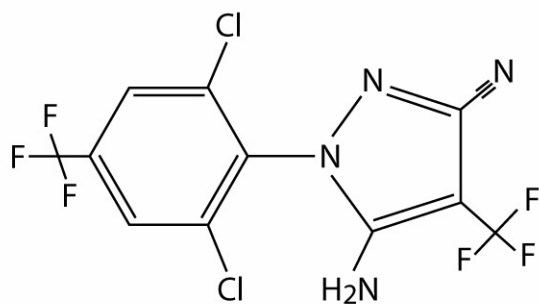
Fipronil and its metabolites



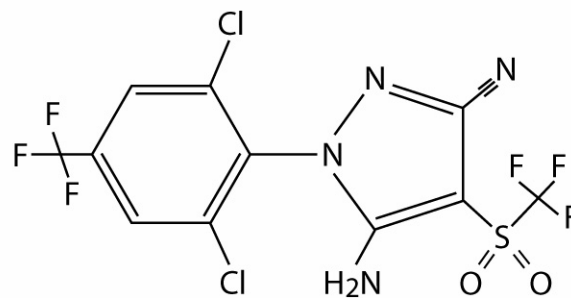
Fipronil



Fipronil sulfide
(anaerobic sediments)



Fipronil desulfinyl
(photodegradation product)



Fipronil sulfone
(oxidative environment)

Stations - Two Different Land Uses

- I Highway Runoff Station – Hilton Head, SC
High conc. of PAHs adjacent to storm drains emptying into estuaries with loading proportional to population/vehicular traffic

- II Watershed from Okatee River
Receives pesticides from Sun City. Linkages to nutrient input.

Bioassays Used to Assess Effects of Contaminated Sediments

- Mortality of Juvenile Clams – Exposure via water
- Reproductive Endpoints of Grass Shrimp - Epibenthic
- Reproductive Endpoints of Benthic Copepods - Meiofauna



Harbor Town

Outer Marsh Station (C)



drain → → →

Estuarine Creek

Mid-Marsh Station (B)

Runoff Station (A)



Homes & Condos

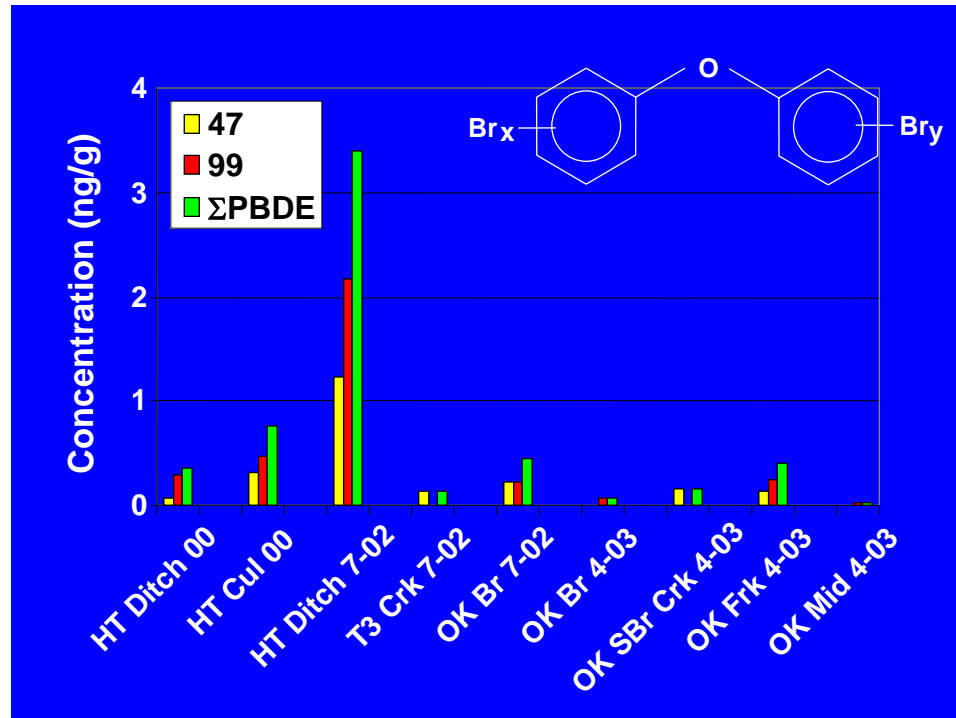


Homes

Sampling Stations -
Hilton Head Island, SC, USA

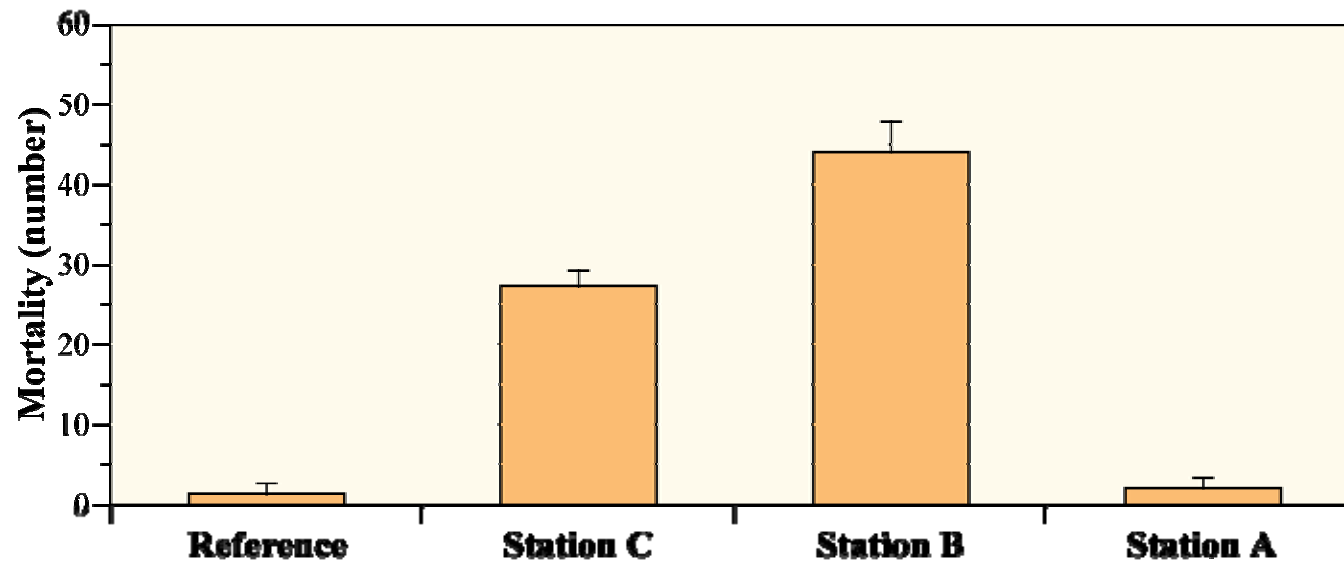
CONCENTRATIONS OF PAH ANALYTES (PPM) IN ESTUARINE SEDIMENTS NEAR HIGHWAY

Analytes	Storm Drain (A)	Mid-Marsh (B)	Outer Marsh (C)
Naphthalene	16	n.d.	n.d.
MeNaphthalene	12	n.d.	n.d.
Fluorene	220	n.d.	n.d.
Phenanthrene	3100	68	15
MePhenanthrene	155	16	n.d.
Fluoranthene	4780	233	27
Pyrene	3800	192	35
Benz(a)anthracene	2300	92	14
Chrysene	2300	110	15
Benzo(a)pyrene	1300	83	n.d.

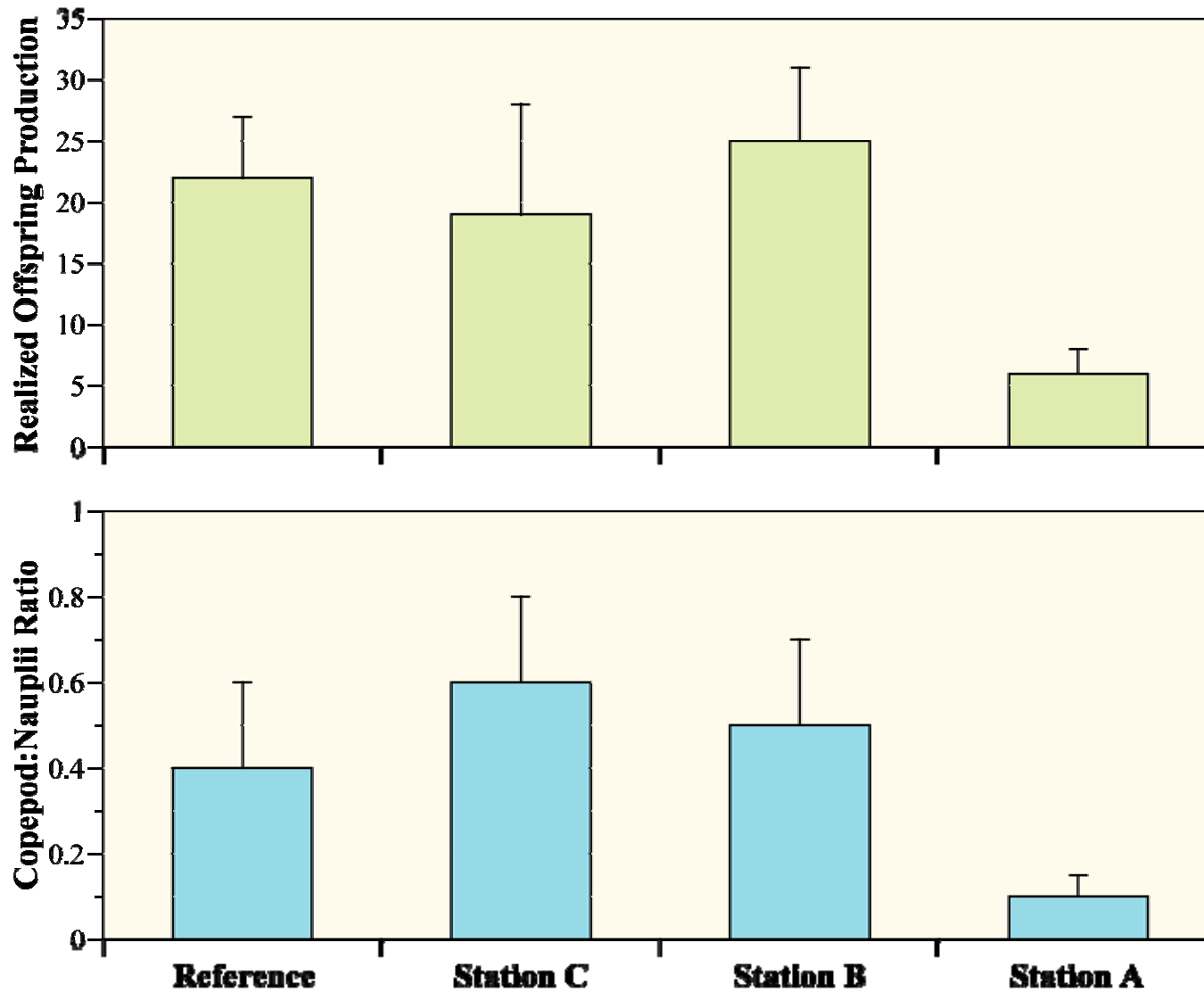


FIRE RETARDENTS IN ESTUARINE SEDIMENTS

Mortality in juvenile clams exposed to estuarine sediments from different stations. Stations located at different distances from highway storm drain (A - 0 m; B - 100 m; C - 500 m).



Reproductive endpoint for copepods exposed to estuarine sediments from different stations. Stations located at different distances from highway storm drain (A - 0 m; B - 100 m; C - 500 m).



Grass Shrimp Used for Bioassays on Contaminated Sediments



- Reproduction –
 1. Percent females producing mature ovaries
 2. Percent females producing embryos
- Embryo Development
 1. Hatching percent
 2. Percent of abnormal embryos
- Mortality

Closeup of Grass Shrimp Embryos



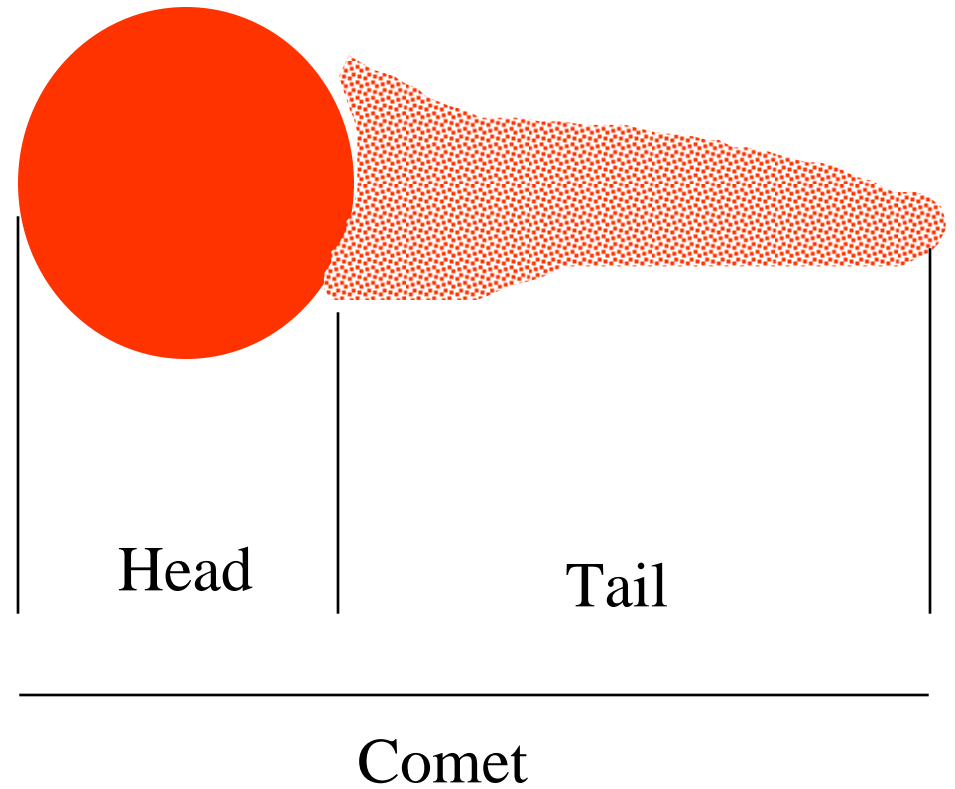
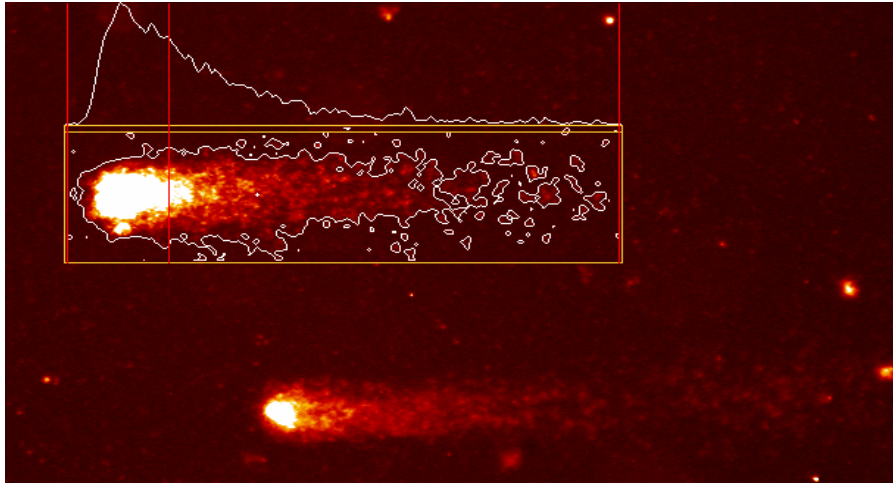
STATION (distance from storm drain)	REPROD (% females producing embryos)	EMBRYO DEVELOP (% females producing embryos)	HATCHING RATE (% embryos hatching into zoea)	DNA STRAND DAMAGE (% DNA in Tail)
A(0 m)	62 ± 13	42 ± 8*	35 ± 5*	25.7 ± 4.7*
B(100m)	67 ± 9	53 ± 6	46 ± 13*	14.1 ± 3.9
C(500m)	73 ± 7	65 ± 12	88 ± 5	10.1 ± 2.7
Controls	70 ± 9	71 ± 14	93 ± 7	9.2 ± 1.8

Grass Shrimp Bioassays on Estuarine Sediments (Highway)

Examples of DNA Lesions Produced After Genotoxicant Exposure

- Strand Breaks (double and single)
- Modified Bases (e.g. 8-hydroxyguanosine)
- DNA-DNA Crosslinks
- DNA-Protein Crosslinks

Persistent DNA lesions can cause transcriptional errors, mutagenesis and cell death



Parameter Determined: %DNA in Tail

Assessing Sediment Toxicity by Determination of DNA Strand Breaks (Comet Assay) and Embryo Hatching Rates after Pore Water Exposure

Station (meters from storm drain)	DNA Strand Breaks (% DNA in tail)	Embryo Hatching Rate (% embryos hatching into zoea)
A (0 m)	27.2 ± 3.1*	22 ± 12*
B (100m)	18.9 ± 3.8*	39 ± 16*
C (500m)	8.8 ± 5.1	89 ± 14
Reference	9.3 ± 4.4	94 ± 8

*Significantly different from reference station and station C





Pesticides in the Upper Okatee River – April 2003

Station	Chlorothalonil	Atrazine	Fipronil	Chlorpyrifos
Creek draining from Sun City into Okatee R.	n.d.	1.6 µg/L	0.065 ng/L	n.d.
Okatee R source	n.d.	0.8 µg/L	n.d.	n.d.
Mid-point in upper Okatee	n.d.	0.6 µg/L	n.d.	n.d.
Lower part of upper Okatee	n.d.	0.6 µg/L	n.d.	n.d.

Pesticides in the Upper Okatee River - April, 2004

Station	Chlorothalonil	Atrazine	Fipronil	Chlorpyrifos
Creek draining from Sun City into Okatee R.	14 ng/L	7.3 µg/L	11ng/L	14 ng/L
Okatee R. source	n.d.	7.2 µg/L	n.d.	n.d.
Mid-point in upper Okatee	n.d.	1µg/L	n.d.	n.d.
Lower part of upper Okatee	n.d.	0.5 µg/L	n.d	n.d.

Pesticides in the Upper Okatee River – April 2005

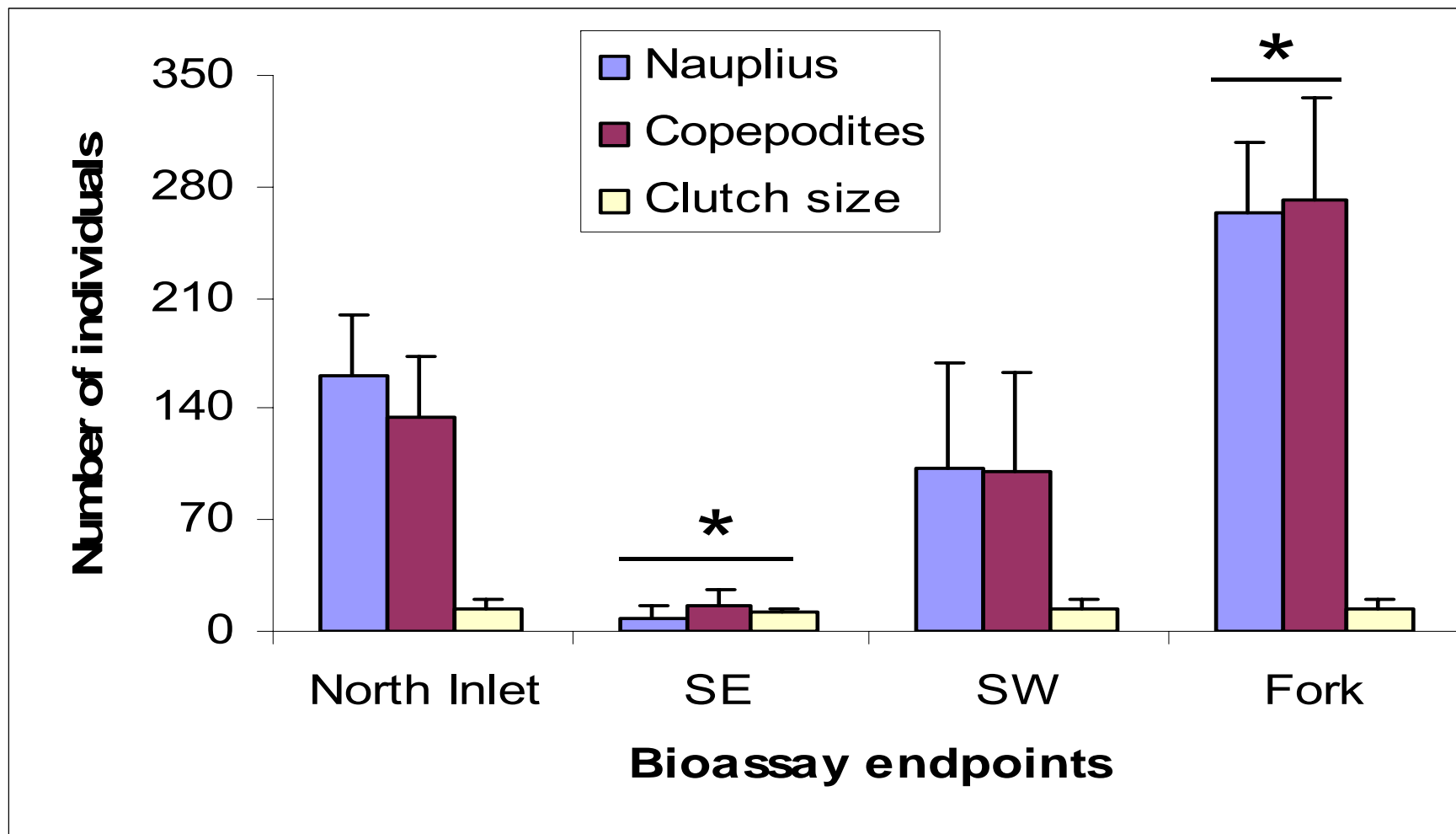
Station	Chlorothalonil	Atrazine	Fipronil	Chlorpyrifos
Creek draining from Sun City into Okatee R.	18 ng/L	12 µg/L	20 ng/L	22 ng/L
Okatee R. source	4 ng/L	9 µg/L	4 ng/L	n.d.
Mid-point in Upper Okatee	n.d.	3 µg/L	n.d.	n.d.
Lower part of Upper Okatee	n.d.	2 µg/L	n.d.	n.d.

Grass Shrimp Bioassay with Upper Okatee River Station Sediments

STATION	MORTALITY (% mortality)	REPROD (% females producing mature ovaries)	EMBRYO DEVELOP (% females producing embryos)	HATCHING RATE (% embryos hatching into zoea)
Upper Okatee at fork	23 ± 8	33 ± 19*	9 ± 9*	88 ± 3
Mid-point Okatee	17 ± 8	78 ± 12	28 ± 7	87 ± 8
Lower part of upper Okatee	42 ± 10	71 ± 17	30 ± 13	82 ± 8
Reference	17 ± 8	79 ± 11	40 ± 2	93 ± 8

Reproductive outputs from copepods chronically exposed to contaminated/reference sediments. (*) Represents significant differences

relative to North Inlet sediments. SW= South West, SE= South East



Summary

Highway Runoff Station

- High PAH conc associated with estuarine sediments adjacent to highway. PAH conc decreased to background levels 500m from highway.
- Exposure of juvenile clams, benthic copepods and grass shrimp to estuarine sediment receiving highway runoff resulted in higher clam mortality, effects on copepod and grass shrimp reproduction parameters
- Grass shrimp embryo pore water bioassay (hatching, DNA strand breaks) gave results comparable to those observed for reproduction effects (reduced embryo production/embryo hatching)

Summary

Suburban Runoff Stations

- Conc. of several pesticides (fipronil, chlorpyrifos, atrazine, chlorothalonil) progressively increased in each year of a 3 year sampling period in the drainage areas of the Okatee River.
- Increased clam mortality, effects on reproductive endpoints of copepod and grass shrimp were noted after exposure to sediments from the drainage area of the upper Okatee River