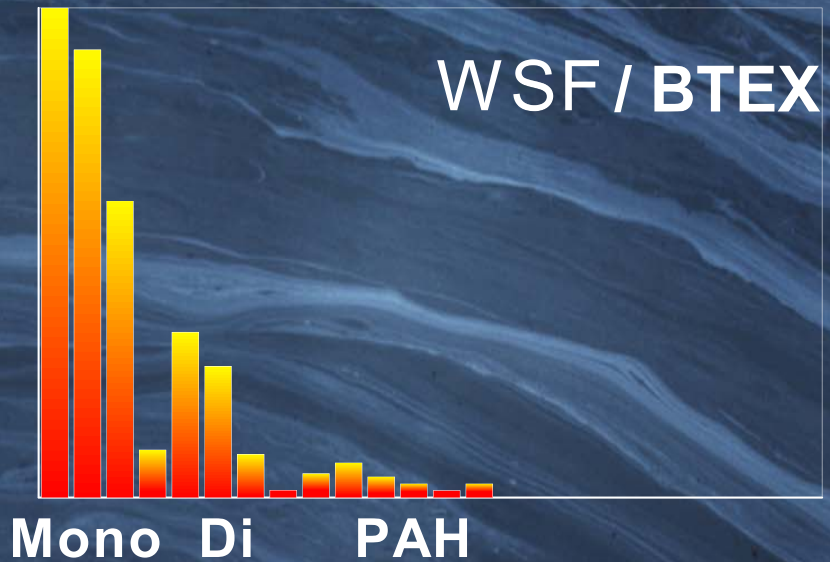
Oil in the environment:

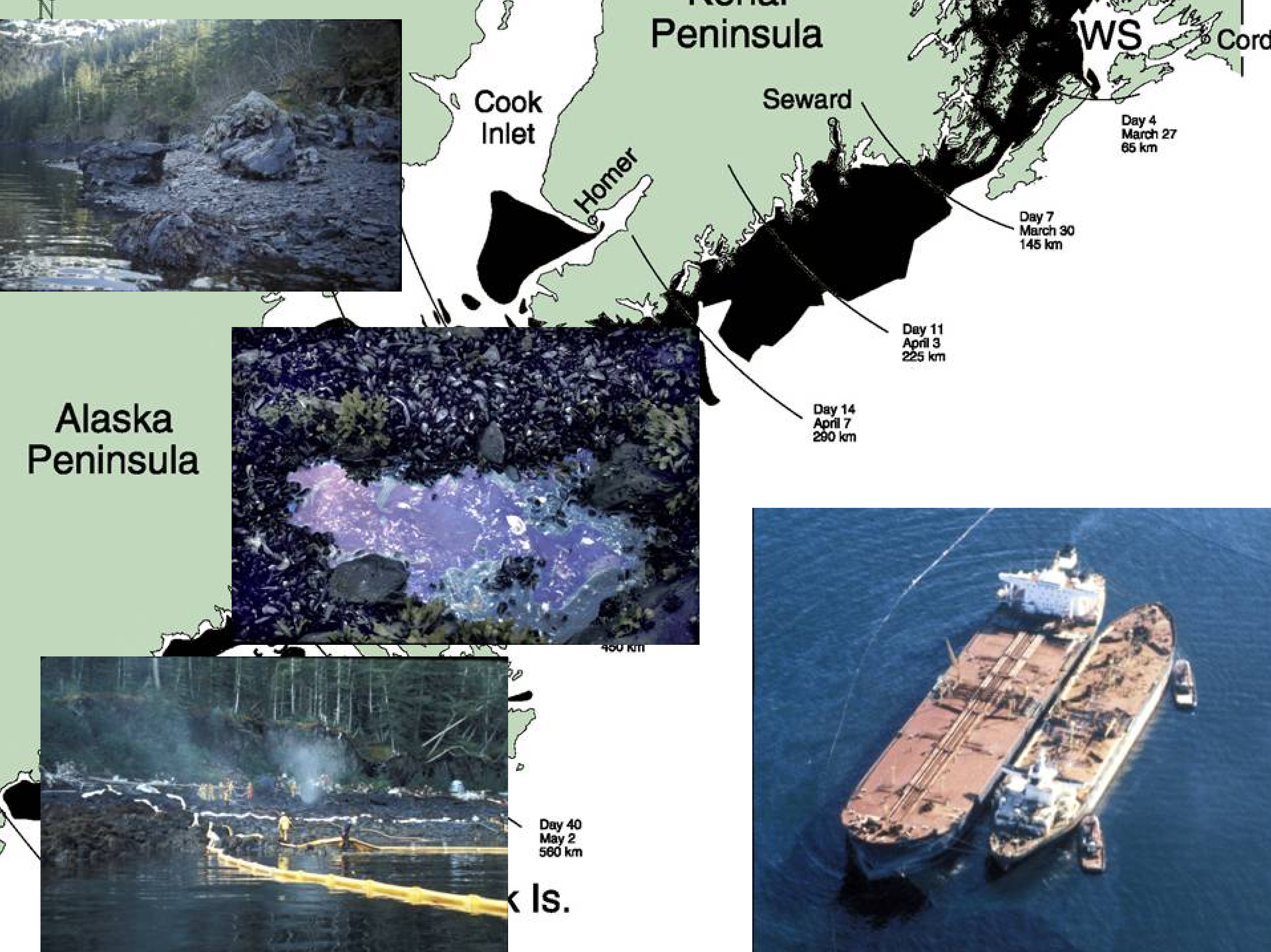
Development of new study tools

Mark G. Carls

History, Auke Bay Lab



- **≤1970's:** Oil is acutely toxic at (ppm) levels

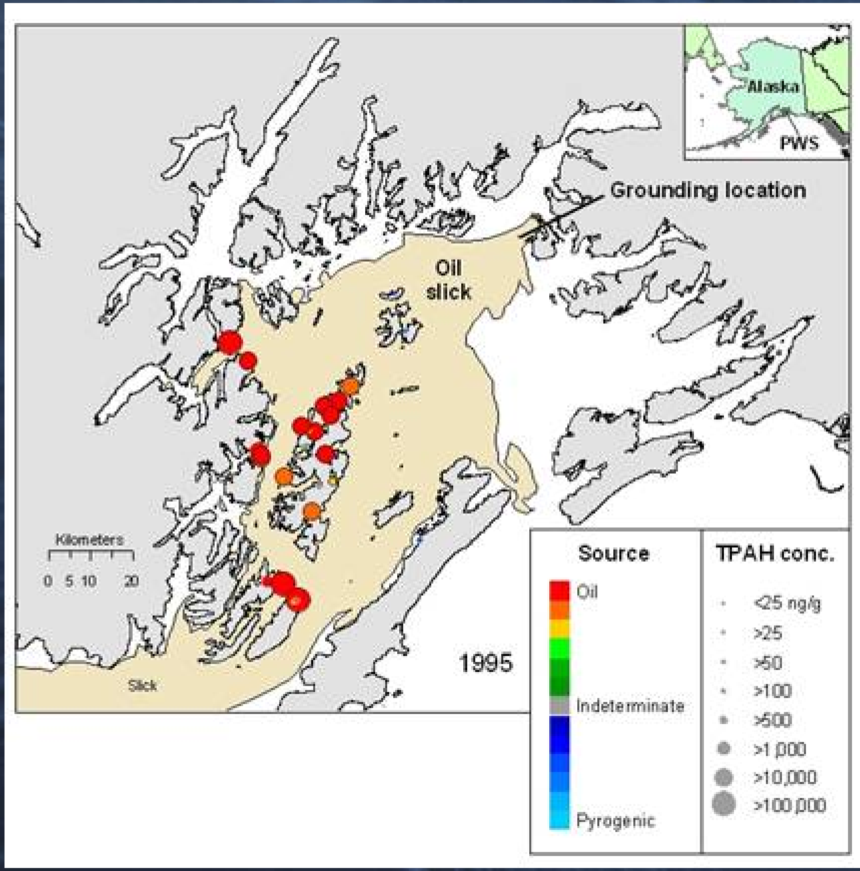

Peninsula
Cook
Inlet
Seward
Homer
Day 4
March 27
65 km
Day 7
March 30
145 km
Day 11
April 3
225 km
Day 14
April 7
290 km
Alaska
Peninsula
Day 40
May 2
560 km

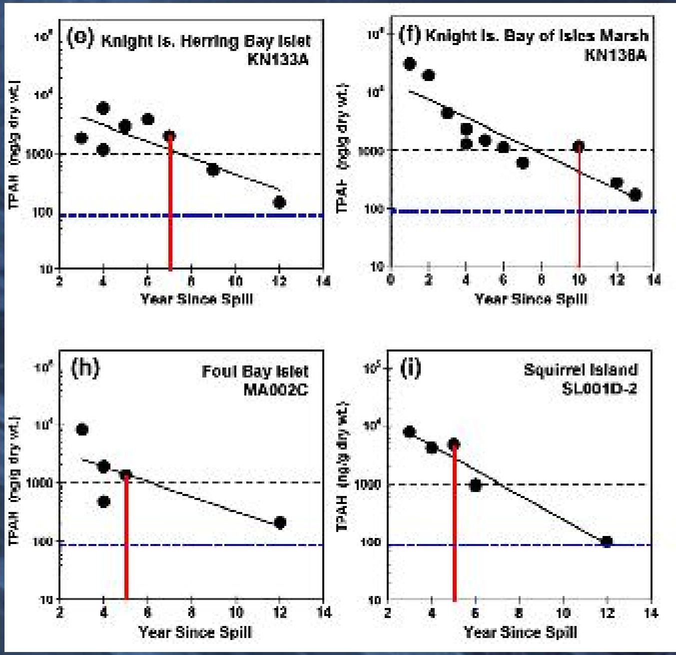
History, Auke Bay Lab

- 1989 *Exxon Valdez* oil spill
  - – Field studies
  - – Lab studies

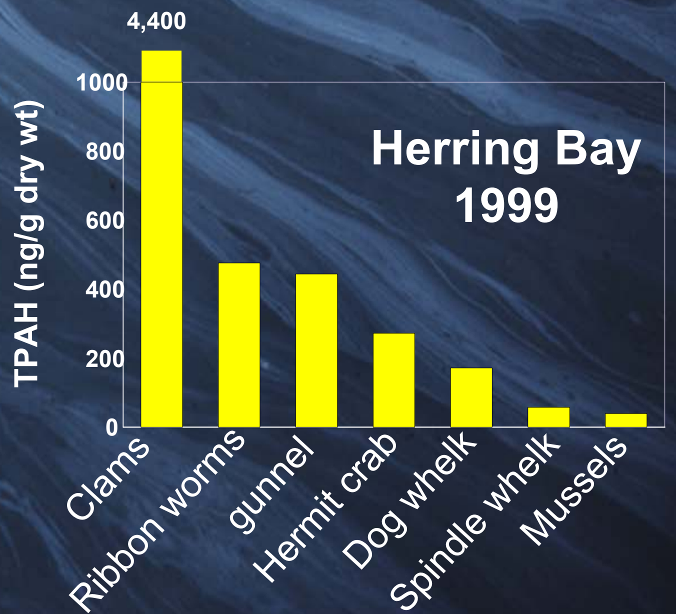
Result

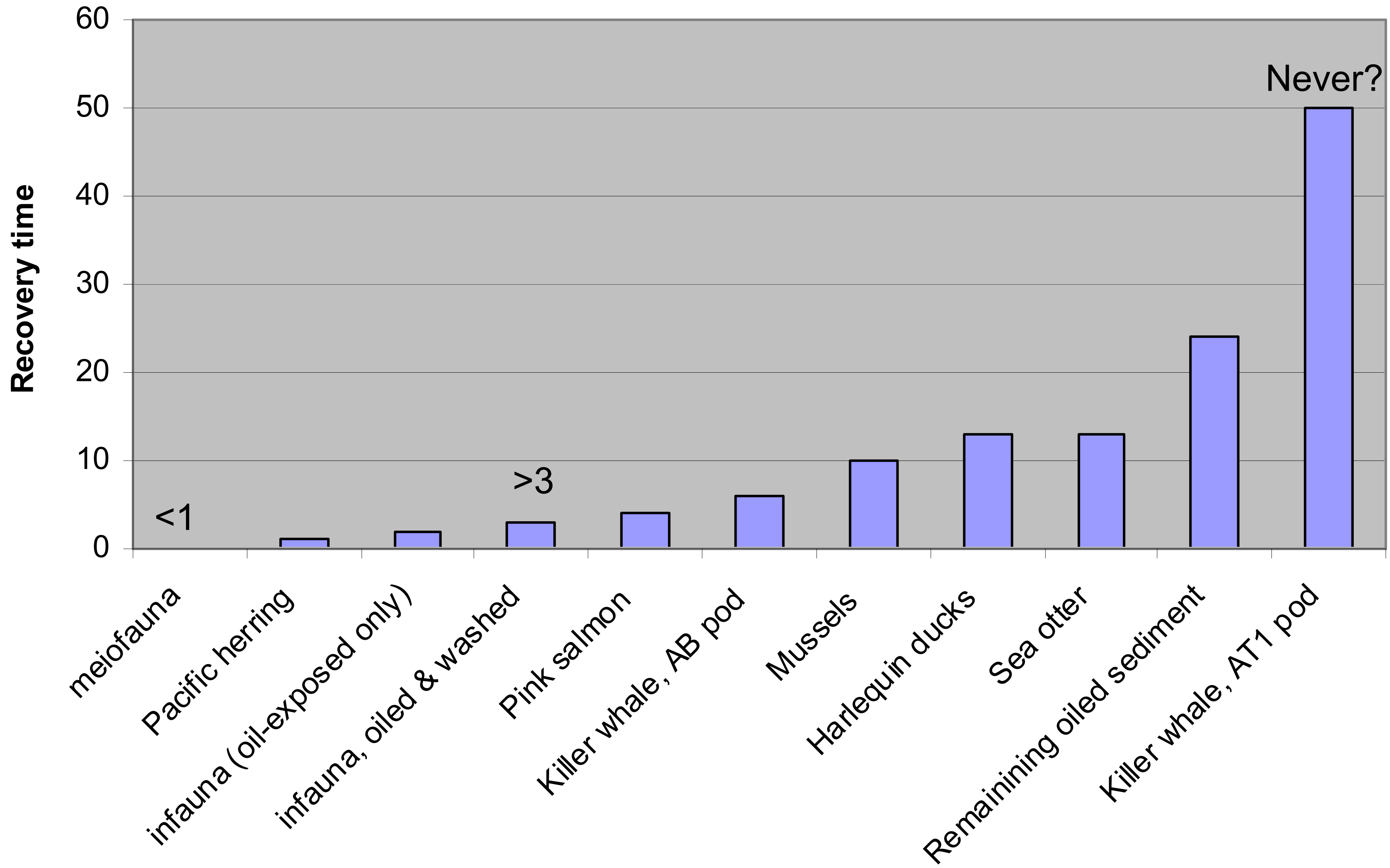
① Biologically available oil can persist for a long time in intertidal sediment





Page et al. 2005




Recovery time
60
50
40
30
20
10
0
Never?
>3
<1
meiofauna
Pacific herring
infauna (oil-exposed only)
infauna, oiled & washed
Pink salmon
Killer whale, AB pod
Mussels
Harlequin ducks
Sea otter
Remainining oiled sediment
Killer whale, AT1 pod

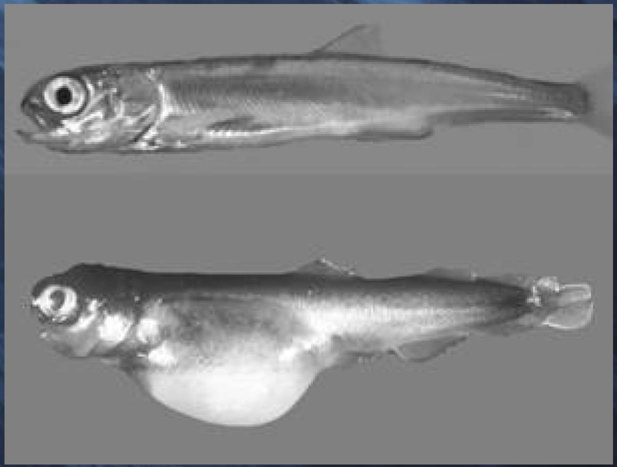
Result

②

PAH are damaging at part per billion levels

(fish embryos & adults)

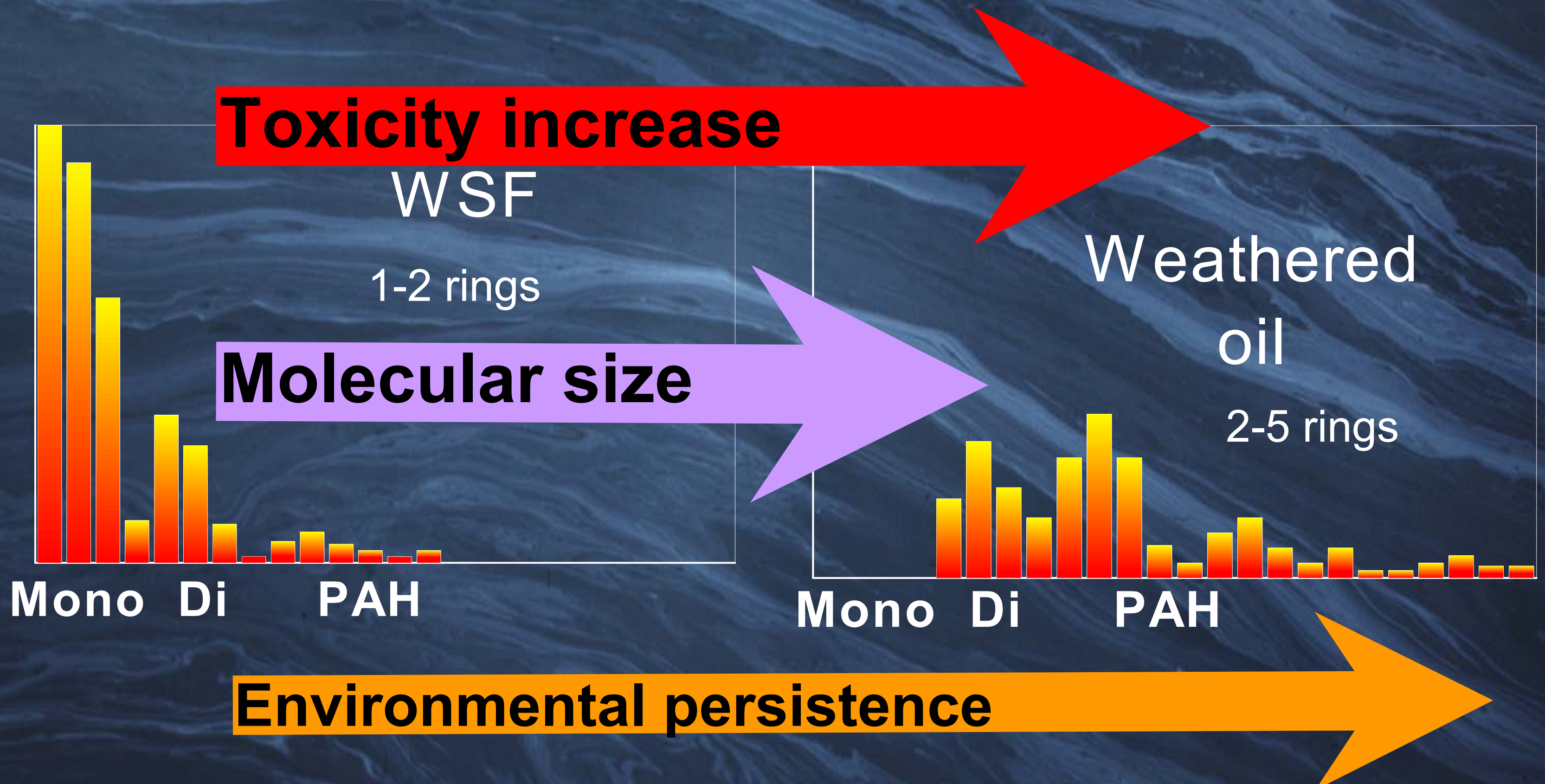
Carls



Heintz

Aromatic composition:

- **≤1970s:** Oil is toxic at (ppm) levels



≥1990s: Oil is toxic at **part per billion (ppb)** levels

Tools

- Passive hydrocarbon samplers (PEMD)
- Oiled rock column assays
- Oil identification models
- Toxicity prediction

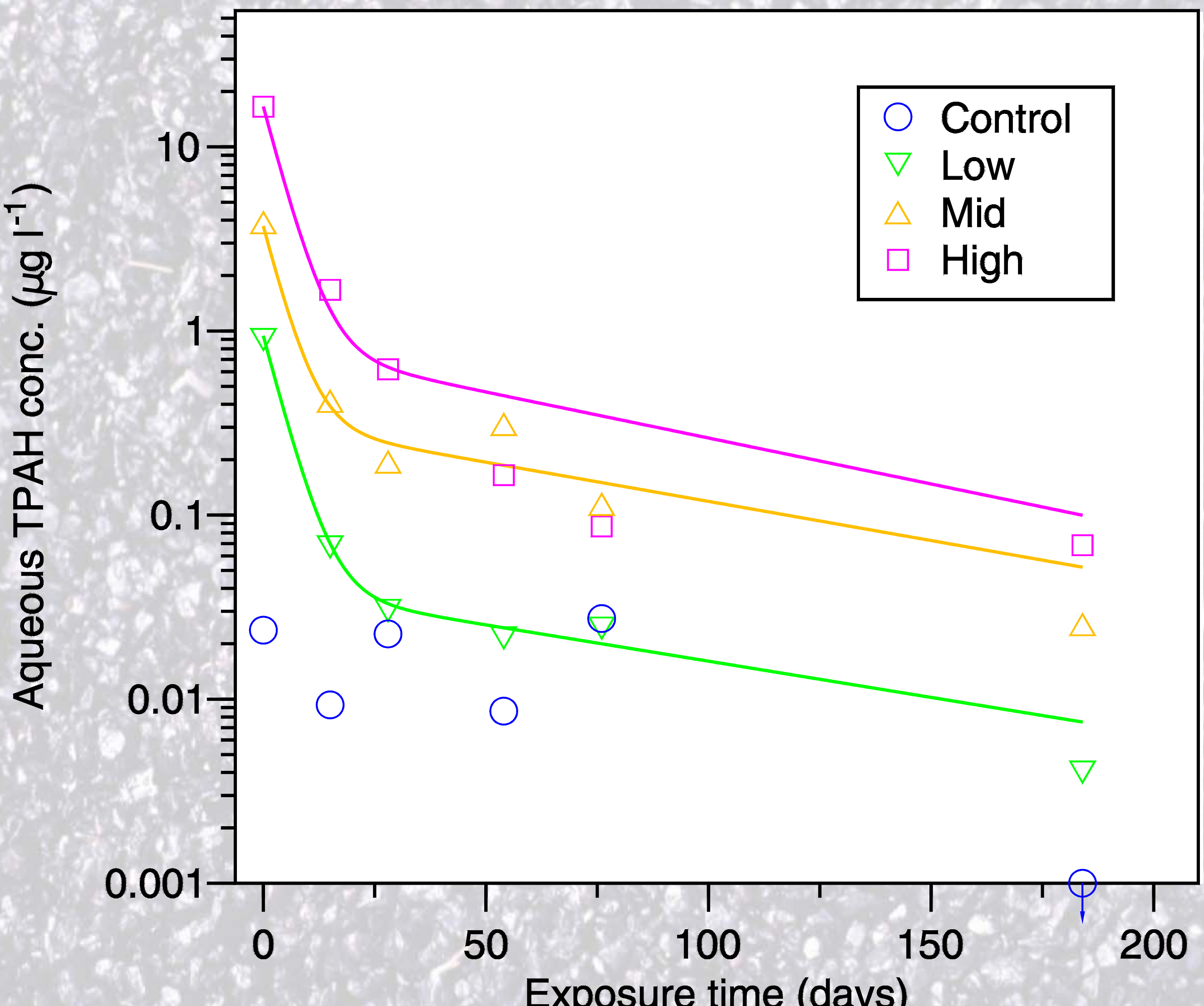
Tools

- Tools developed are highly applicable to urban watershed issues
- Can be applied to insidious, low-level oil leaks.

Oiled Rock Column Assays

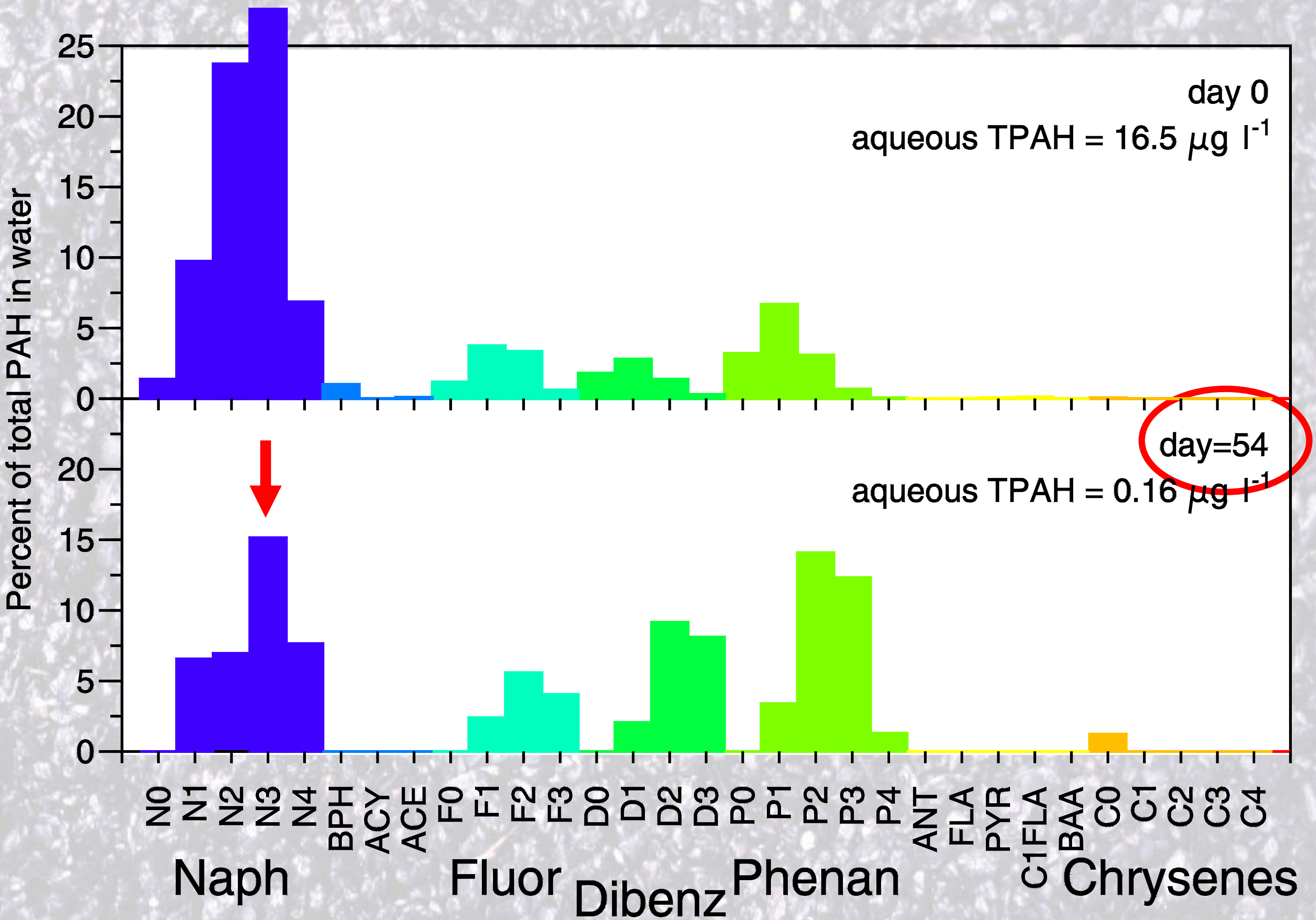
- Emulate spill conditions
- Produce dissolved PAH
  - [tPAH] declines exponentially
  - Oil weathers (PAH composition changes)
  - little or no particulate oil is present
- No competing chemical effects
  - no significant ammonia or sulfides
  - oxygen remains near saturation
- No meaningful microbial interference

Effluent contains dissolved PAH



Carls et al. 2005

Typical dissolved PAH composition & weathering



Oil droplets are scarce or absent in effluent

- [Phytane] in ORC effluent:

  mean = 0.04 µg/L (n = 168)

  0.03 to 0.05 µg/L (95% confidence bounds)

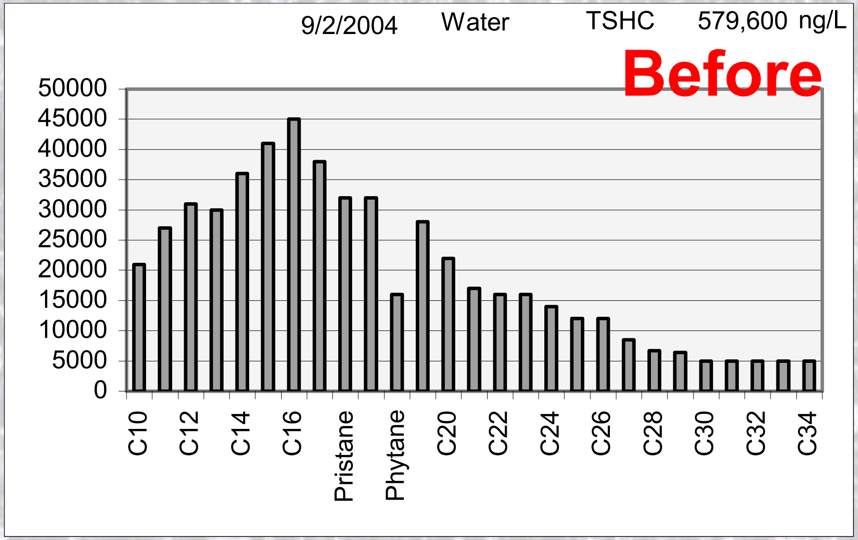
- Contrast with WAF (oil particles present)

  mean = 2.50 µg/L

  range 0.19 to 10.59 µg/L, dose-dependent

Little or no microbial metabolism in ORC

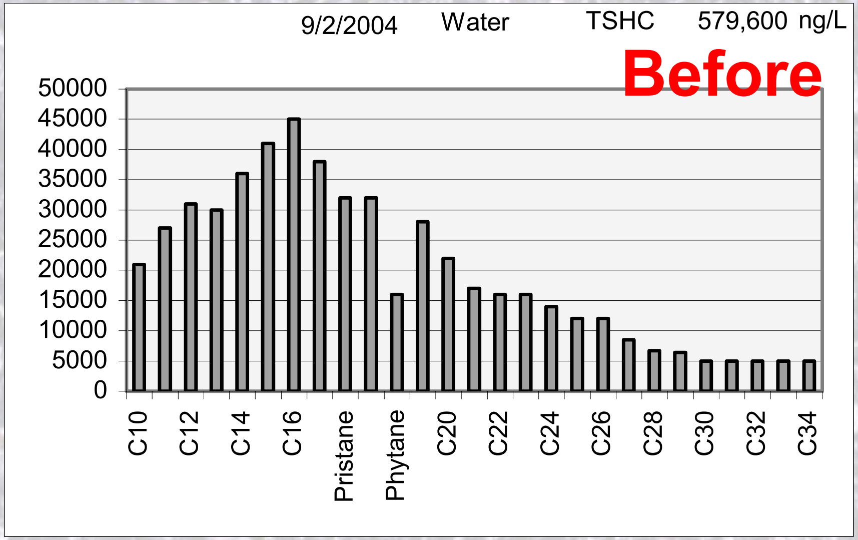
Microbial growth in a treatment facility

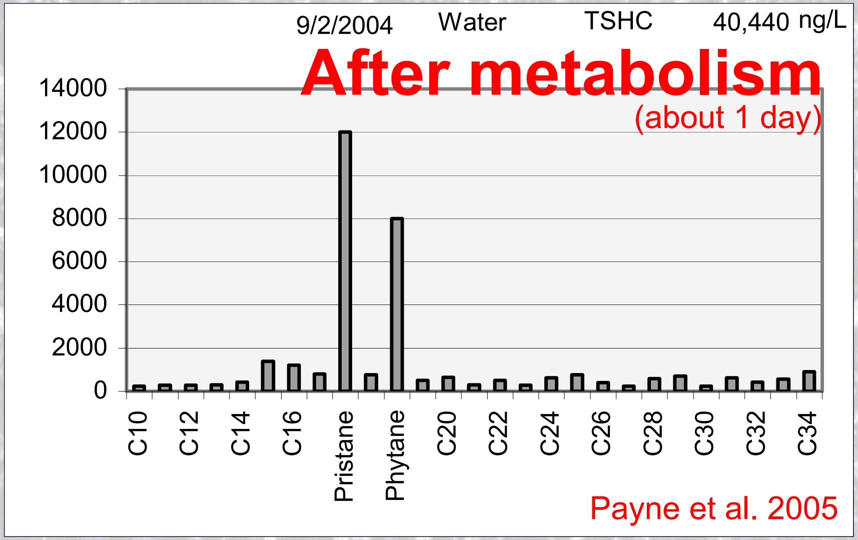


Payne et al. 2005

Little or no microbial metabolism in ORC

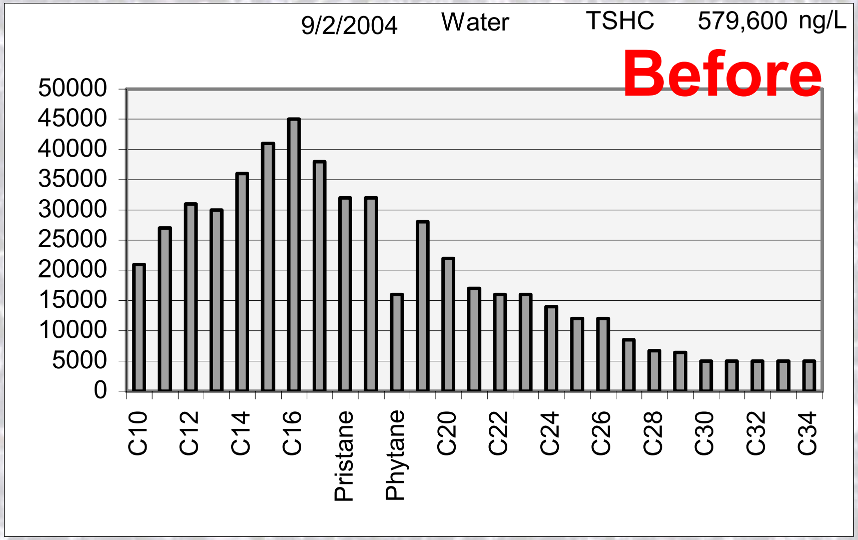
Microbial growth in a treatment facility

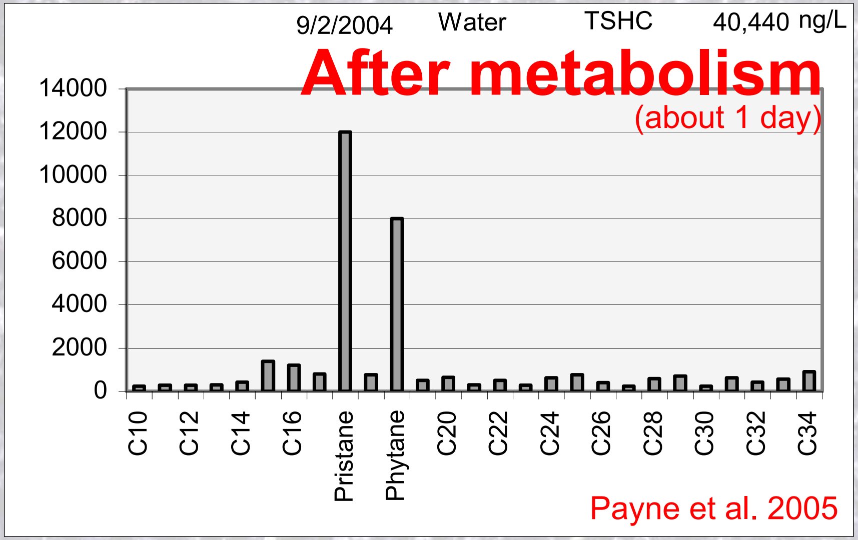




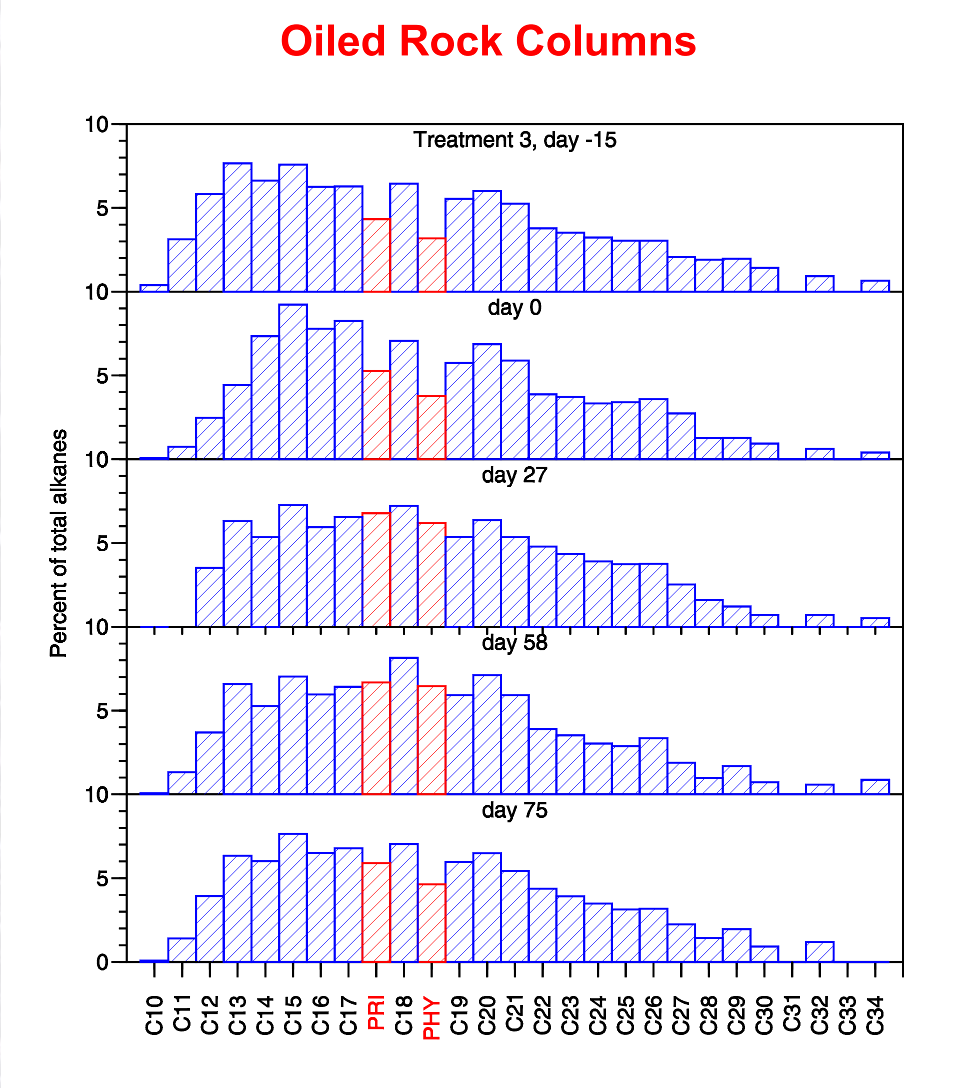
Little or no microbial metabolism in ORC

Microbial growth in a treatment facility





Oiled rock column data



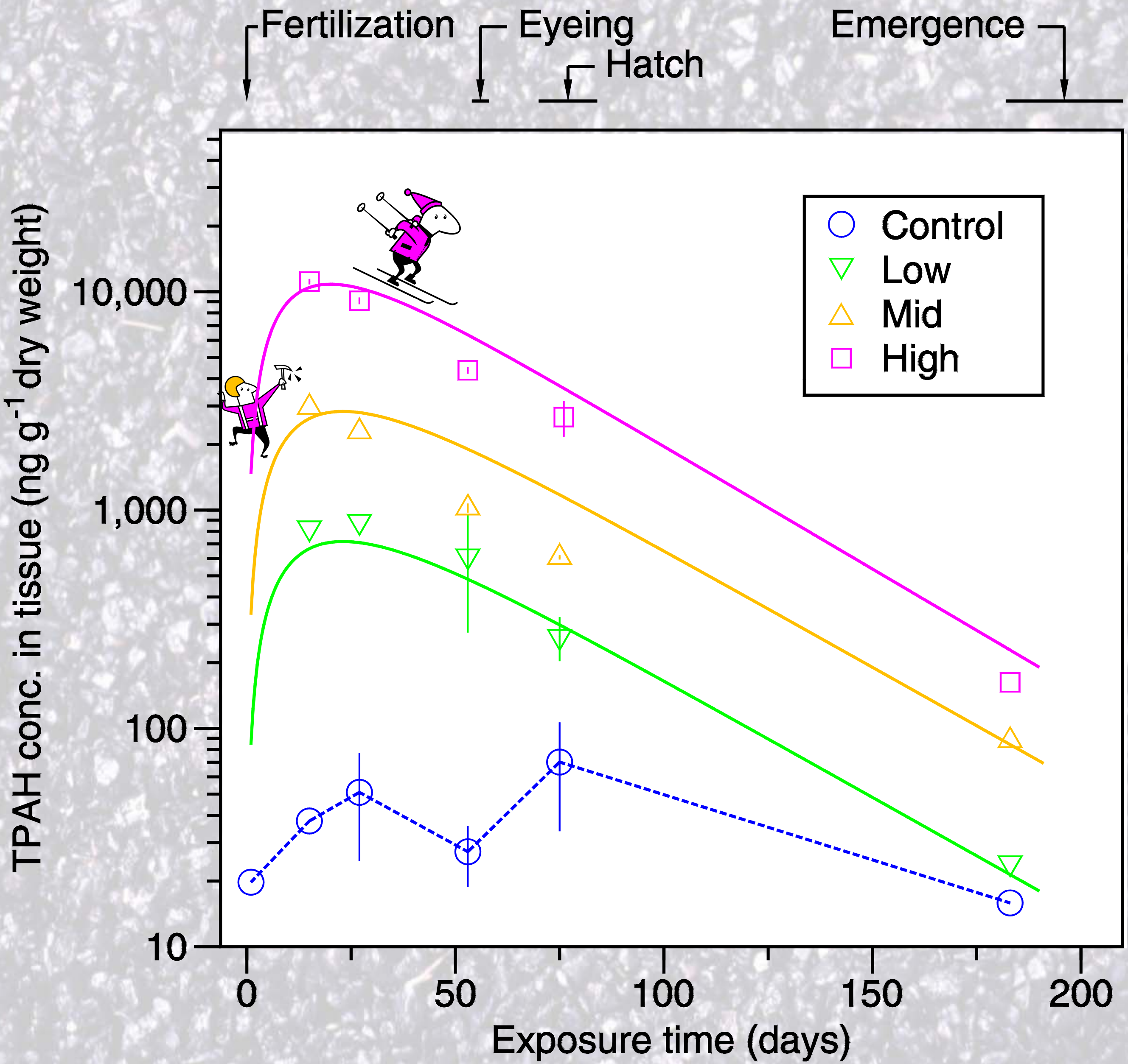
ORC Assay Method

- Oil is typically applied to rock to create a large oil – water contact surface.
- Glass beads also work
- Column sizes & flows can be adjusted to suit experimental conditions

ORC Assays

- Aqueous [tPAH] output is controlled by
  - Amount of oil applied
  - Amount of rock
  - weathering
  - Grain size
  - flow rate

PAH uptake by tissue



ORC Assays

- Published studies include:
  - Marty et al. 1997
  - Carls et al. 1998, 1999, 2005
  - Heintz et al. 1999, 2000
  - Incardona et al. 2005
- Species include:
  - pink salmon -- Pacific herring
  - zebrafish

ORC Assays

- Contribution to scientific literature:
  - dissolved [tPAH] are toxic

    0.4 to 18 µg / L

- Verification by other laboratories:
  - fathead minnows: death at <23 µg/L (Colavecchia et al. 2004)
  - Medaka: hatch length reduced at 2.2 µg/L (Rhodes et al. 2005)
  - Pink salmon: morphologic lesions at 25 to 54 µg/L (Brand et al. 2001)

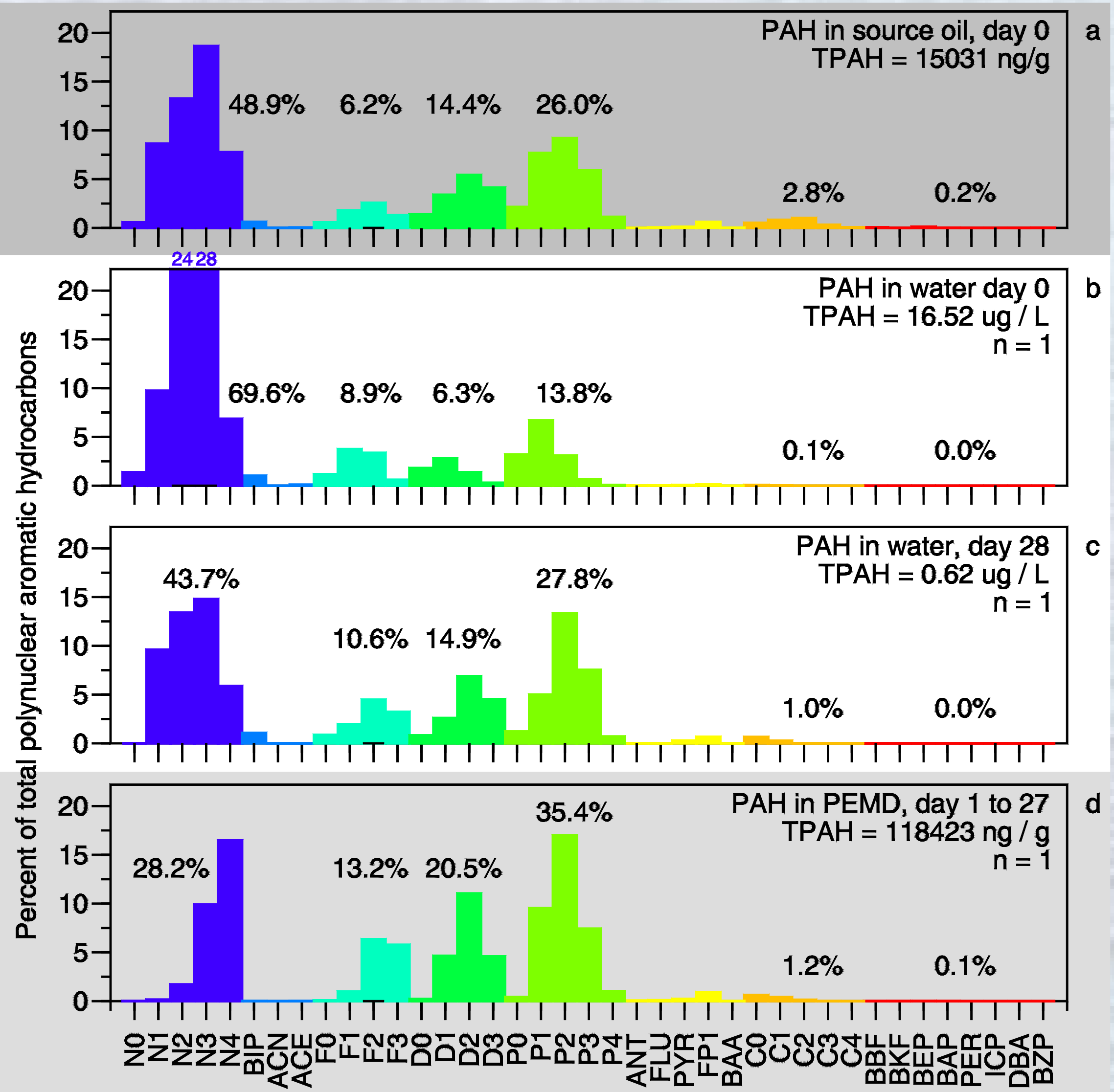
PEMDs:

- Polyethylene membrane devices
- Passive hydrocarbon samplers.

Oil on rock

Collected after 26 d

Oil on rock

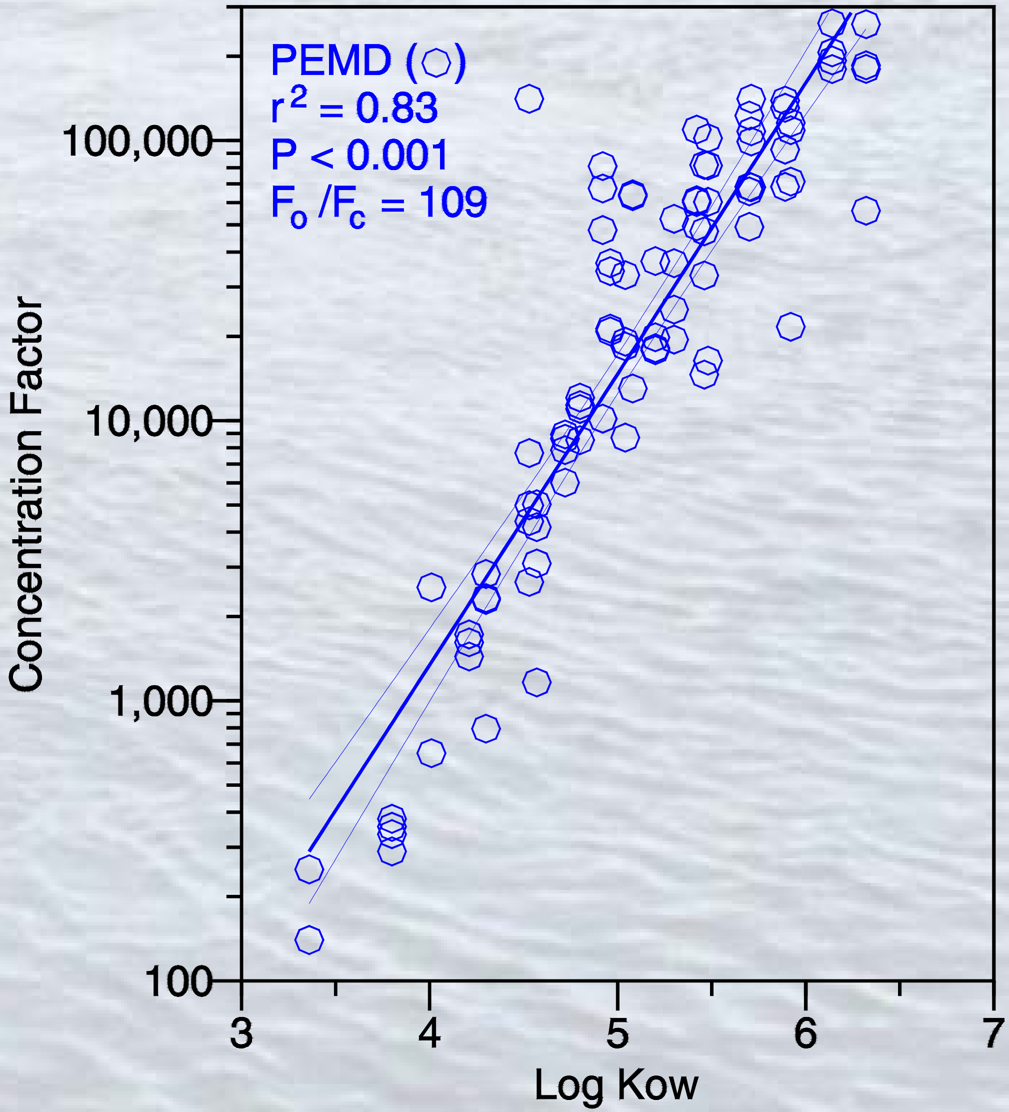


Passage through water

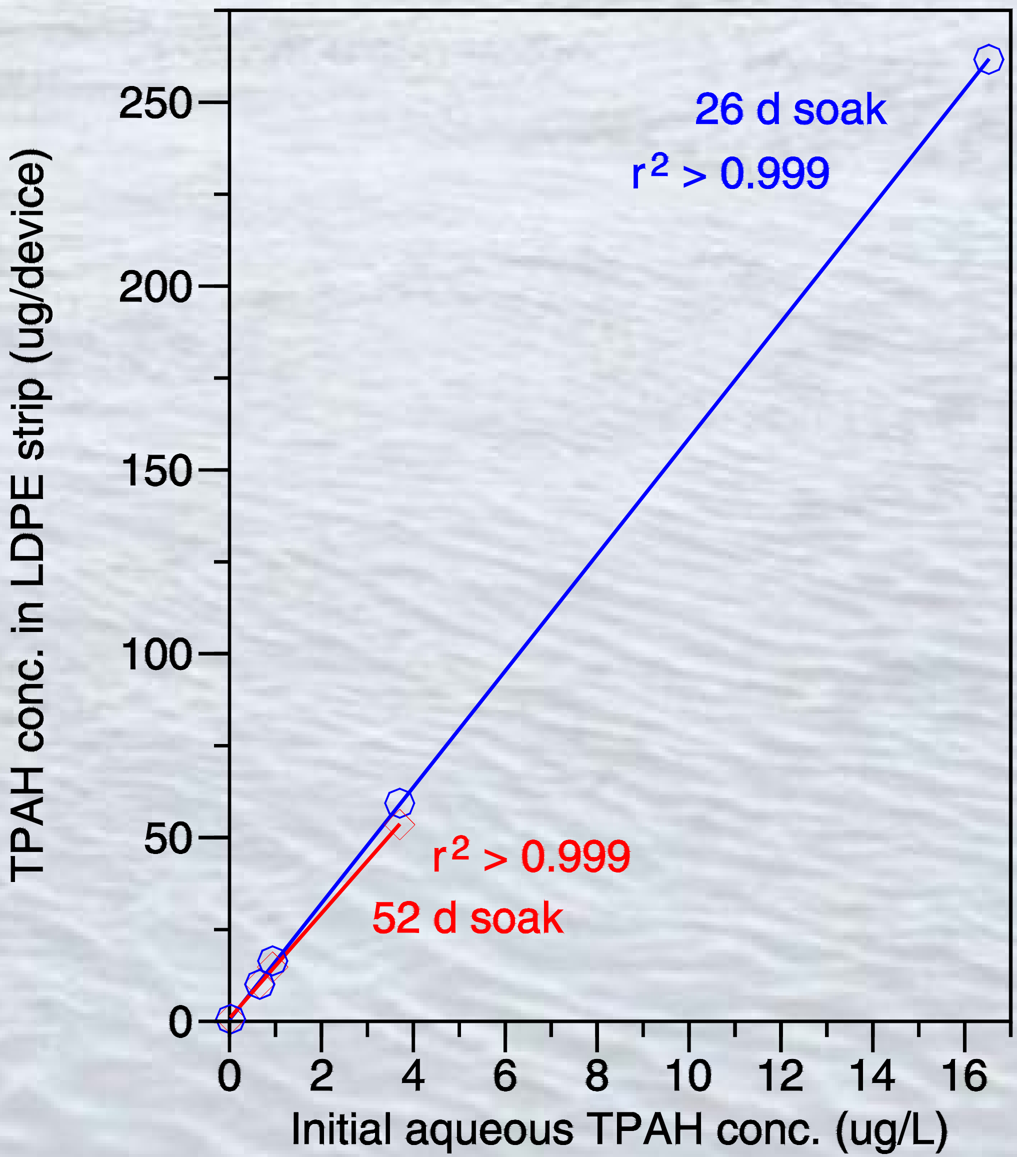
Collected after 26 d

PAH composition in PEMDs ≈ source composition

PAH accumulation increased with molecular size

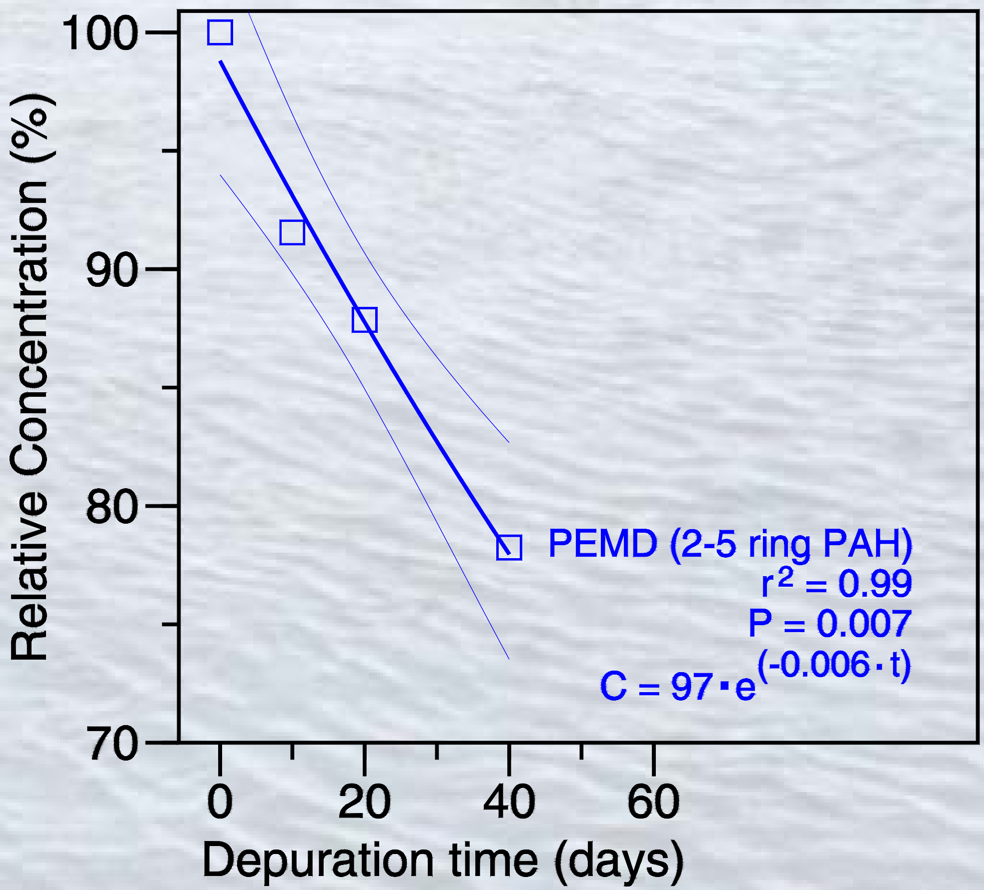


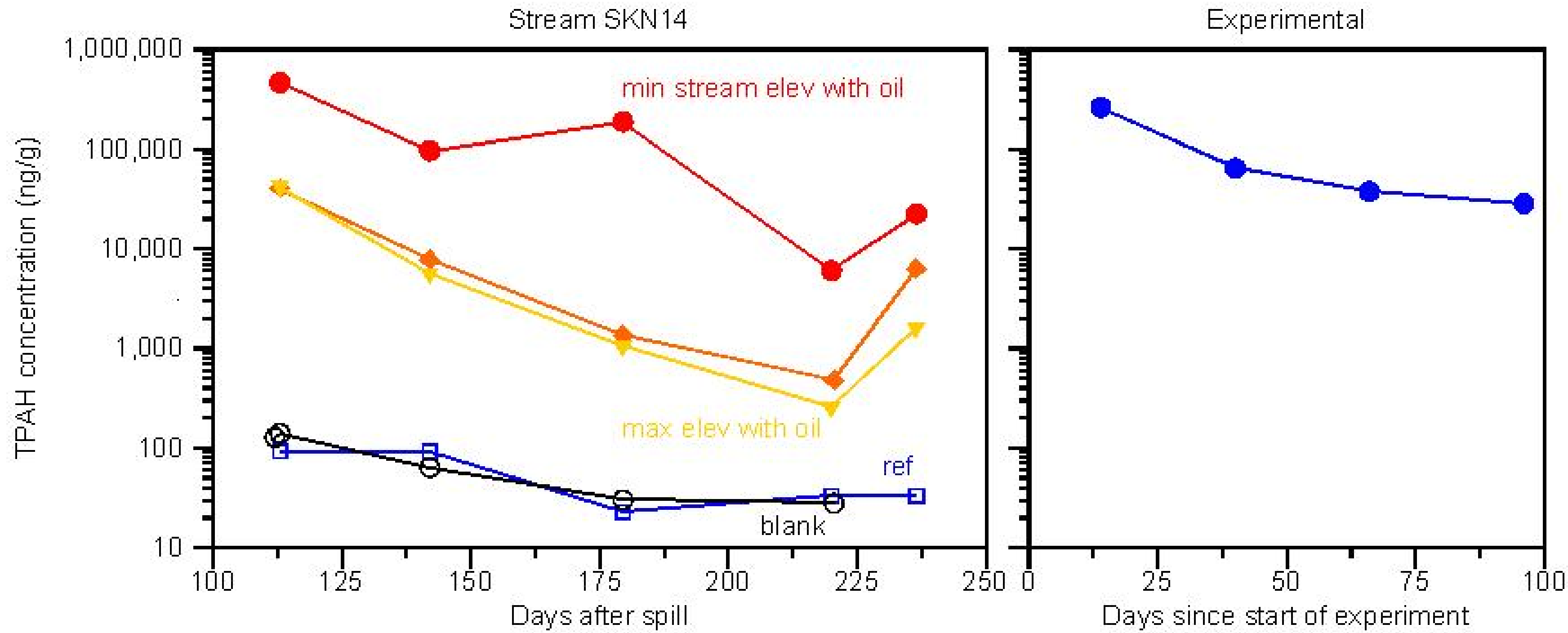
Correlation between TPAH conc. in water & PEMDs



Divide ug/device by 2.2 to get ug/g (ppm)

PAH retention is good





Stream SKN14
Experimental
TPAH concentration (ng/g)
1,000,000
100,000
10,000
1,000
100
10
min stream elev with oil
max elev with oil
ref
blank
100
125
150
175
200
225
250
Days after spill
0
25
50
75
100
Days since start of experiment

Conclusions

- PEMDs are:
  - reliable time-integrated samplers of hydrocarbons
  - [PAH] highly correlated with aqueous [PAH]
  - Uptake was linear over test range (0-17 µg/L)
  - Preferentially accumulated higher molecular mass PAH
  - Accumulations were ≈ to those in SPMDs
  - ~78% TPAH retained 40 d in clean water

Recommended for environmental monitoring

Source Identification

in Environmental Samples

- First-order loss rate kinetic model
  (Short & Heintz 1997)
- Nonparametric models
  (Carls 2006)
- Oil Fingerprint model
  (Bence & Burns 1995)

First-order loss-rate model (FORLM)

(Short & Heintz 1997)

Suppose the rate of loss to the environment of a PAH (denoted as *P*) dissolved in petroleum follows FOLR kinetics, so that

$$-\frac{d[P]}{dt} = k(t)[P] \quad (1)$$

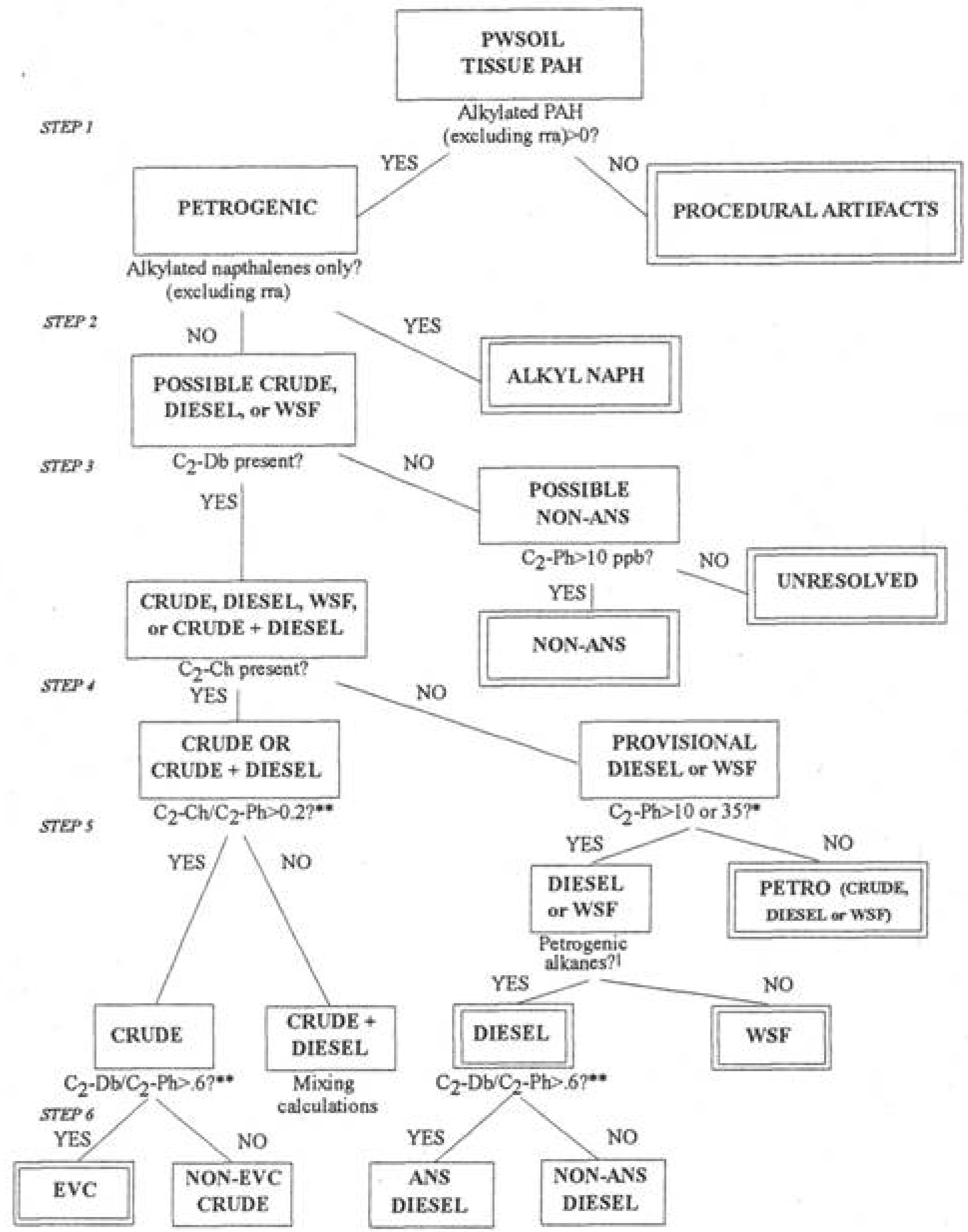
The time dependence of the LR constant, $k(t)$, derives from the variable exposure conditions of the petroleum in the environment. Writing $k(t)$ as $kf(t)$ and integrating eq 1 gives

$$\ln\left(\frac{[P]_0}{[P]}\right) = k\int_0^t f(t)\, dt = kw \quad (2)$$

where the value of the integral in eq 2 is indicated by a weathering parameter, w, which summarizes the exposure history of the petroleum volume element sampled.

Oil Fingerprint Model (OFM)

(Bence & Burns 1995)



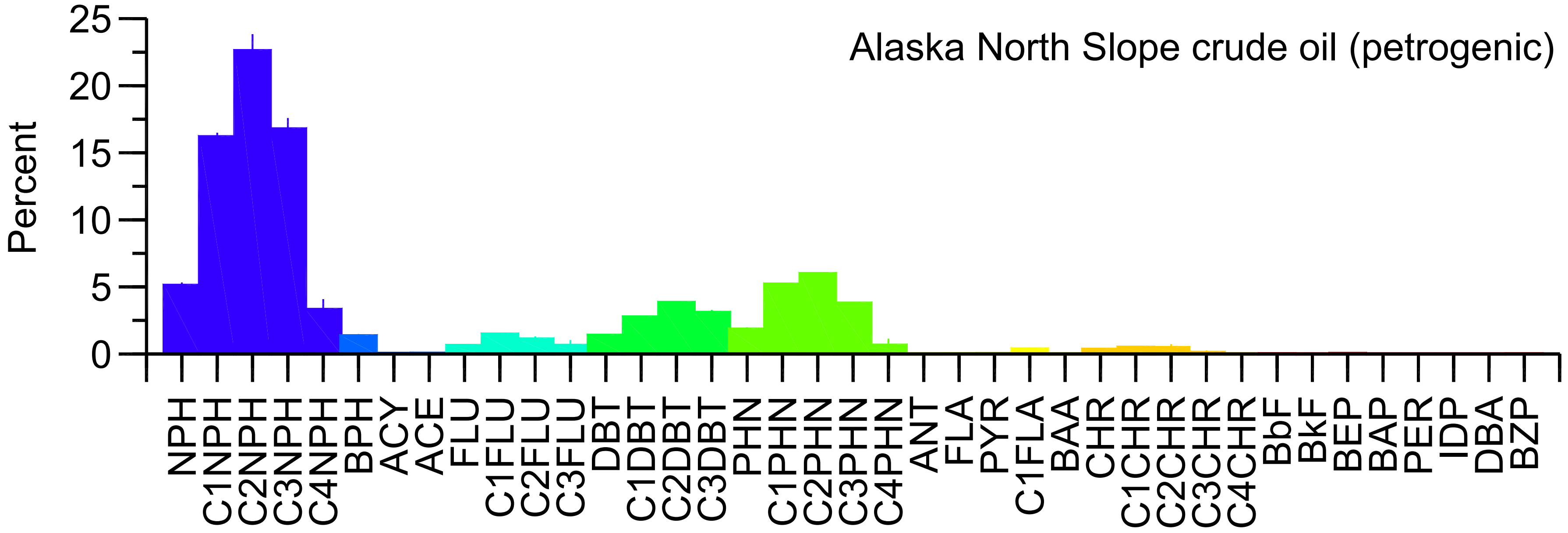
Nonparametric models

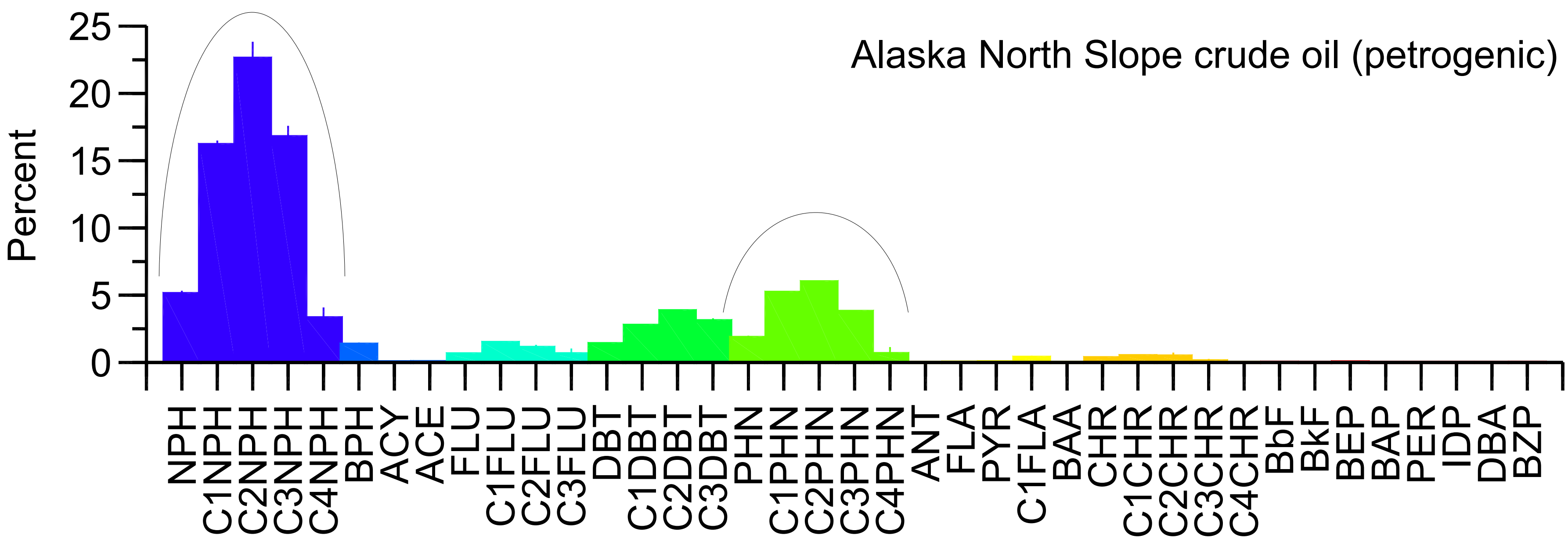
(Carls 2006)

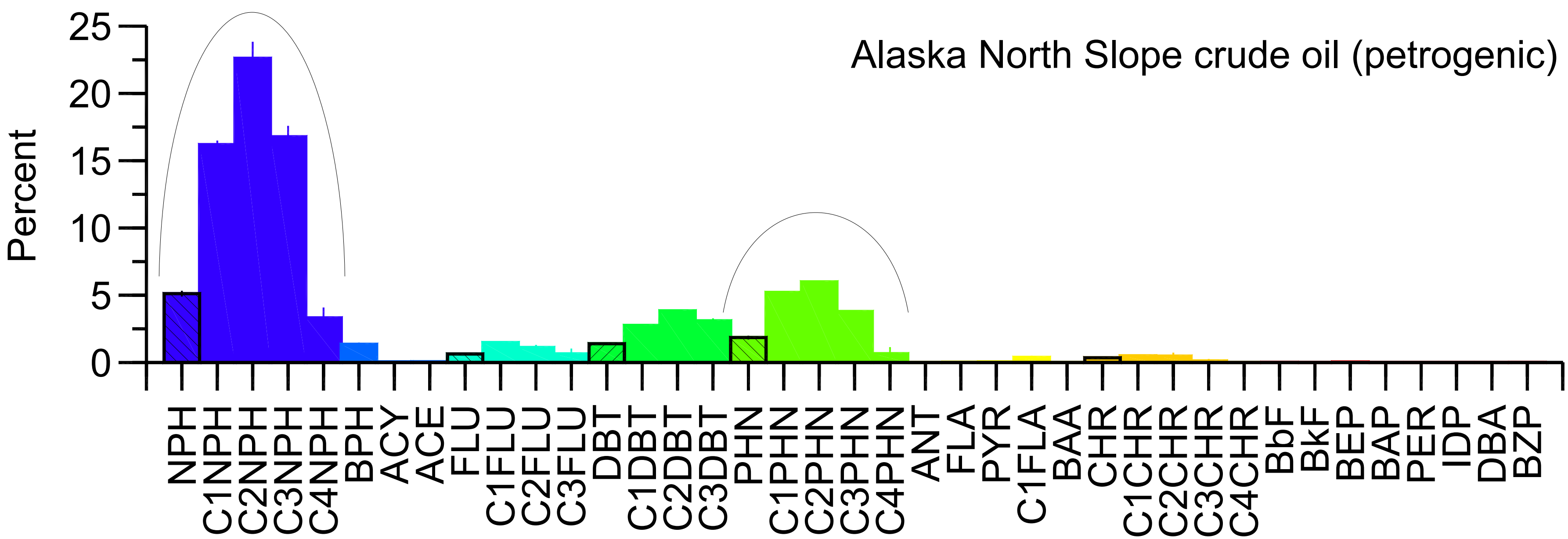
Petrogenic:

the expected relationship among homologs in crude oil is generally

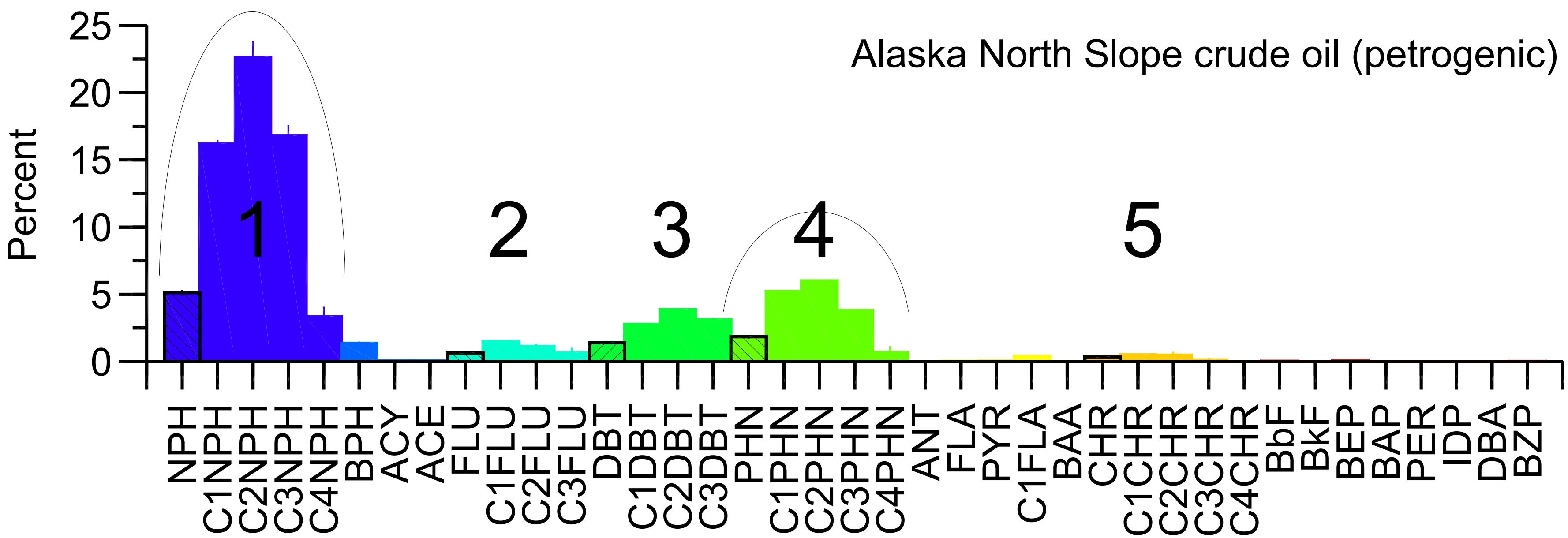
$C0 < C1, C0 < C2, \ldots C0 < \ldots C\mathit{n}$


Alaska North Slope crude oil (petrogenic)
Percent
25
20
15
10
5
0
NPH
C1NPH
C2NPH
C3NPH
C4NPH
BPH
ACY
ACE
FLU
C1FLU
C2FLU
C3FLU
DBT
C1DBT
C2DBT
C3DBT
PHN
C1PHN
C2PHN
C3PHN
C4PHN
ANT
FLA
PYR
C1FLA
BAA
CHR
C1CHR
C2CHR
C3CHR
C4CHR
BbF
BkF
BEP
BAP
PER
IDP
DBA
BZP


Alaska North Slope crude oil (petrogenic)
Percent
0
5
10
15
20
25
NPH
C1NPH
C2NPH
C3NPH
C4NPH
BPH
ACY
ACE
FLU
C1FLU
C2FLU
C3FLU
DBT
C1DBT
C2DBT
C3DBT
PHN
C1PHN
C2PHN
C3PHN
C4PHN
ANT
FLA
PYR
C1FLA
BAA
CHR
C1CHR
C2CHR
C3CHR
C4CHR
BbF
BkF
BEP
BAP
PER
IDP
DBA
BZP



Alaska North Slope crude oil (petrogenic)
Percent
25
20
15
10
5
0
NPH
C1NPH
C2NPH
C3NPH
C4NPH
BPH
ACY
ACE
FLU
C1FLU
C2FLU
C3FLU
DBT
C1DBT
C2DBT
C3DBT
PHN
C1PHN
C2PHN
C3PHN
C4PHN
ANT
FLA
PYR
C1FLA
BAA
CHR
C1CHR
C2CHR
C3CHR
C4CHR
BbF
BkF
BEP
BAP
PER
IDP
DBA
BZP



Alaska North Slope crude oil (petrogenic)
Percent
0
5
10
15
20
25
1
2
3
4
5
NPH
C1NPH
C2NPH
C3NPH
C4NPH
BPH
ACY
ACE
FLU
C1FLU
C2FLU
C3FLU
DBT
C1DBT
C2DBT
C3DBT
PHN
C1PHN
C2PHN
C3PHN
C4PHN
ANT
FLA
PYR
C1FLA
BAA
CHR
C1CHR
C2CHR
C3CHR
C4CHR
BbF
BkF
BEP
BAP
PER
IDP
DBA
BZP

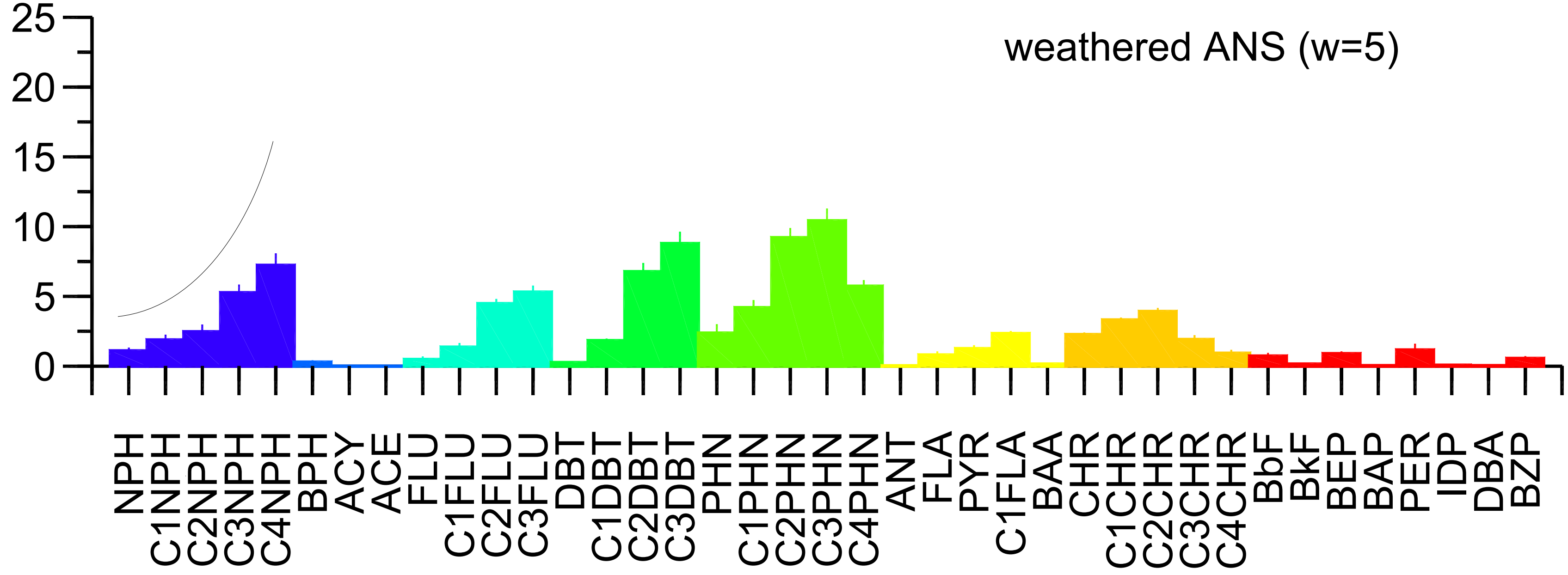
Nonparametric models

(Carls 2006)

Petrogenic:

as weathering occurs, distribution becomes

C0 < C1 < C2 < ... C*n*



weathered ANS (w=5)
25
20
15
10
5
0
NPH
C1NPH
C2NPH
C3NPH
C4NPH
BPH
ACY
ACE
FLU
C1FLU
C2FLU
C3FLU
DBT
C1DBT
C2DBT
C3DBT
PHN
C1PHN
C2PHN
C3PHN
C4PHN
ANT
FLA
PYR
C1FLA
BAA
CHR
C1CHR
C2CHR
C3CHR
C4CHR
BbF
BkF
BEP
BAP
PER
IDP
DBA
BZP

Nonparametric models

(Carls 2006)

Petrogenic:

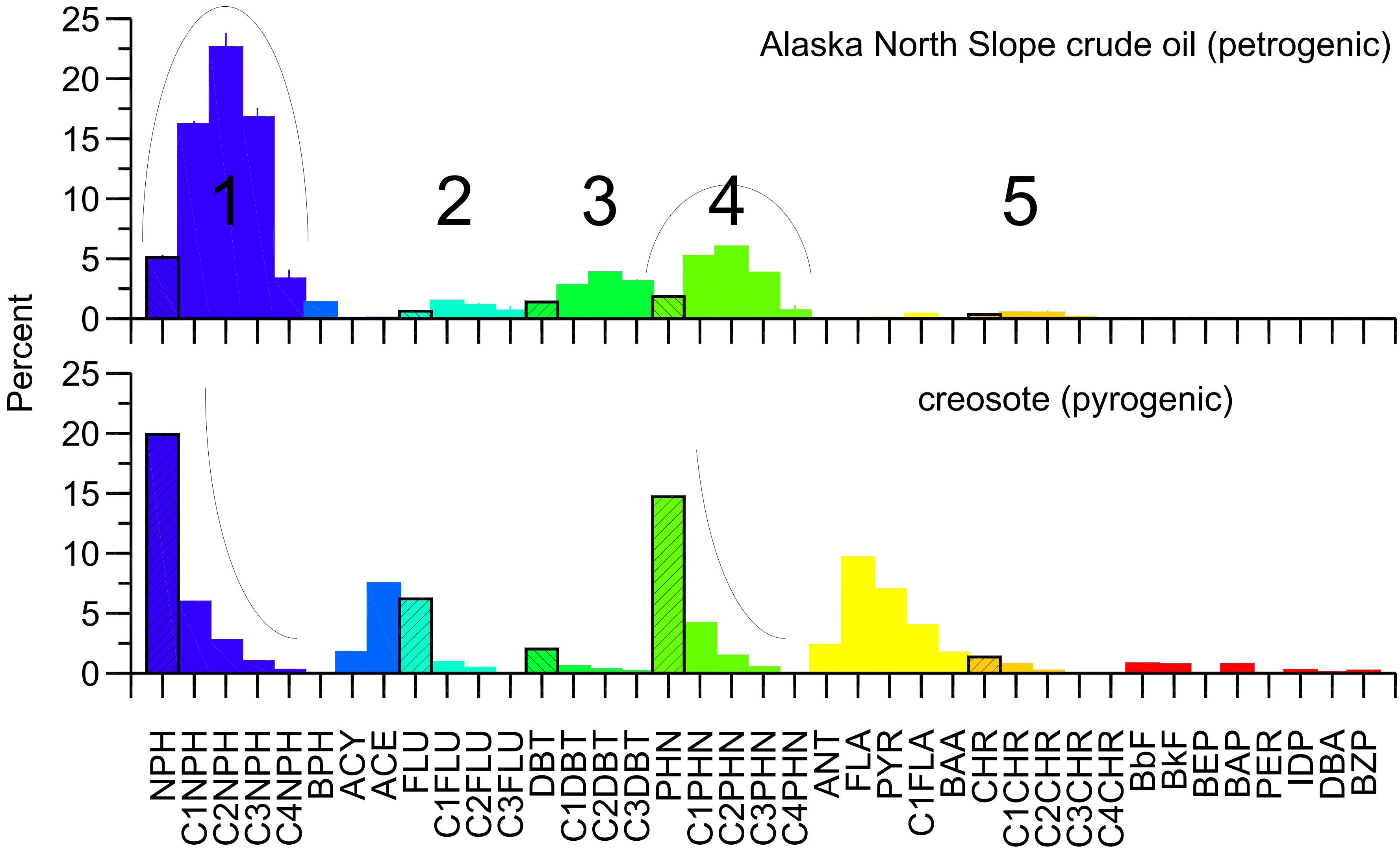
$$X_{0j} < X_{ij}$$

Where i = the i^{th} analyte in the j^{th} homologous family

5 homologous families are examined ($1 \leq j \leq 5$)

The number of alkyl-PAH examined is typically 3 to 4

Score = score + 1/n_j each time $X_{0j} < X_{ij}$ *is true*



Alaska North Slope crude oil (petrogenic)
creosote (pyrogenic)
Percent
0
5
10
15
20
25
1
2
3
4
5
NPH
C1NPH
C2NPH
C3NPH
C4NPH
BPH
ACY
ACE
FLU
C1FLU
C2FLU
C3FLU
DBT
C1DBT
C2DBT
C3DBT
PHN
C1PHN
C2PHN
C3PHN
C4PHN
ANT
FLA
PYR
C1FLA
BAA
CHR
C1CHR
C2CHR
C3CHR
C4CHR
BbF
BkF
BEP
BAP
PER
IDP
DBA
BZP

Nonparametric models

(Carls 2006)

Pyrogenic:

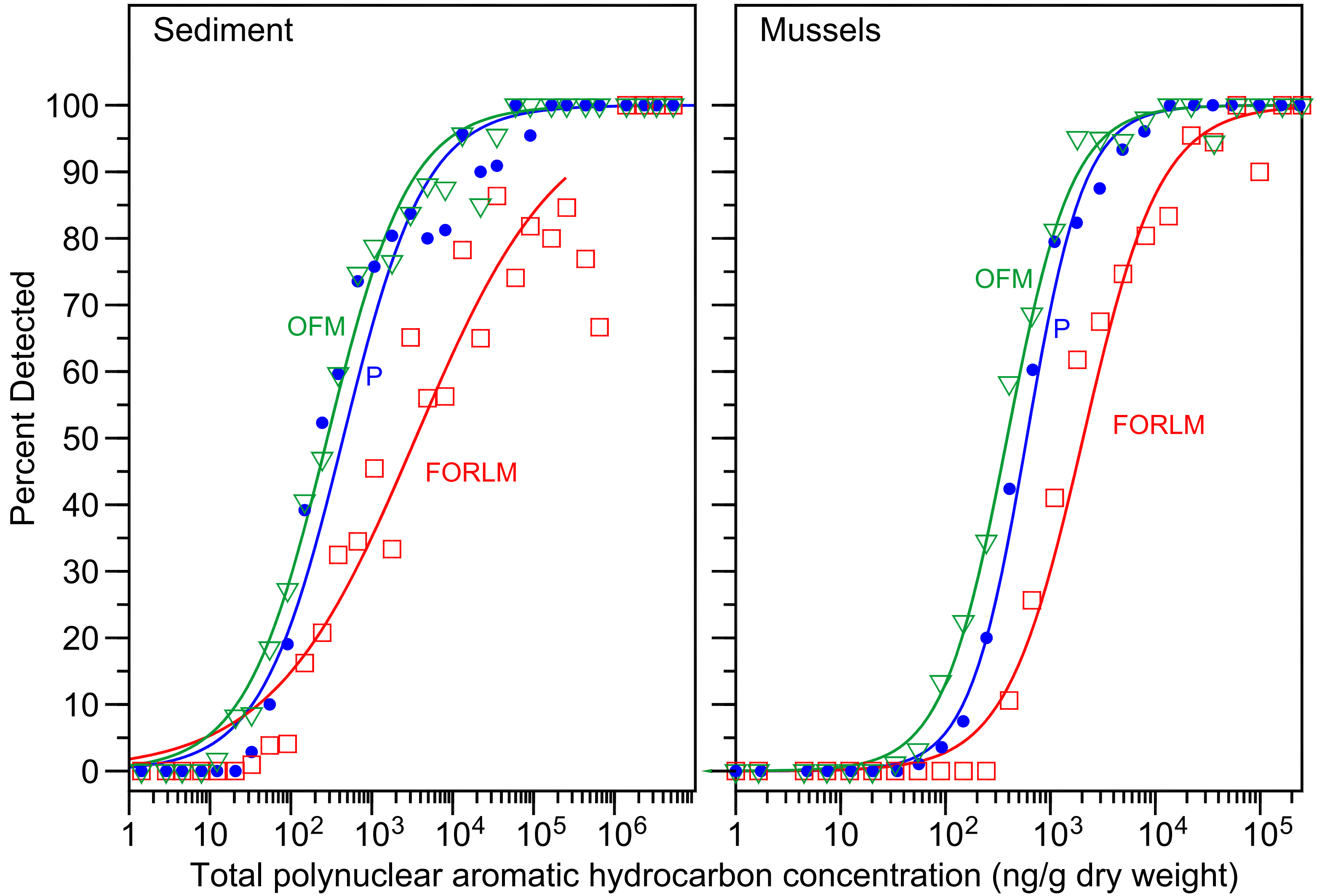
$X_{0j} >> X_{ij}$

Where i = the i^{th} analyte in the j^{th} homologous family

Weighted scores are assigned:

If $X_{0j} > c \cdot X_{ij}$ then $s_{ij} = d/n_j$

c	d
10.0	1.00
5.0	0.50
2.5	0.25
1.0	0.10


Sediment
Mussels
Percent Detected
100
90
80
70
60
50
40
30
20
10
0
OFM
P
FORLM
1
10
10^2
10^3
10^4
10^5
10^6
Total polynuclear aromatic hydrocarbon concentration (ng/g dry weight)

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3

Petrogenic

Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

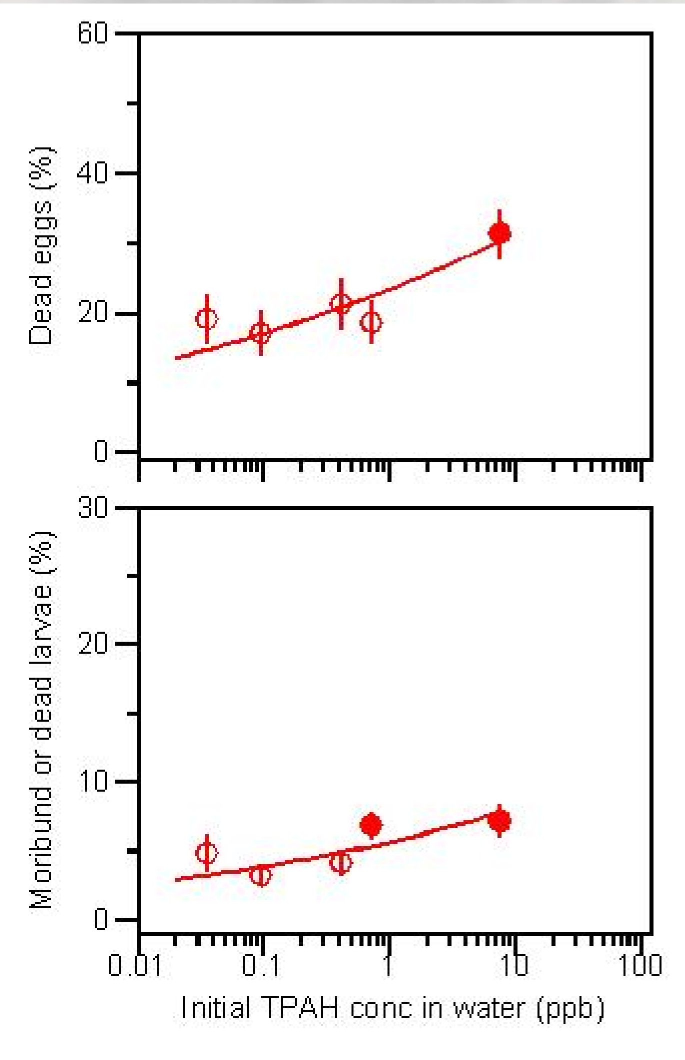
	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
					Pyrogenic
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

Toxicity prediction

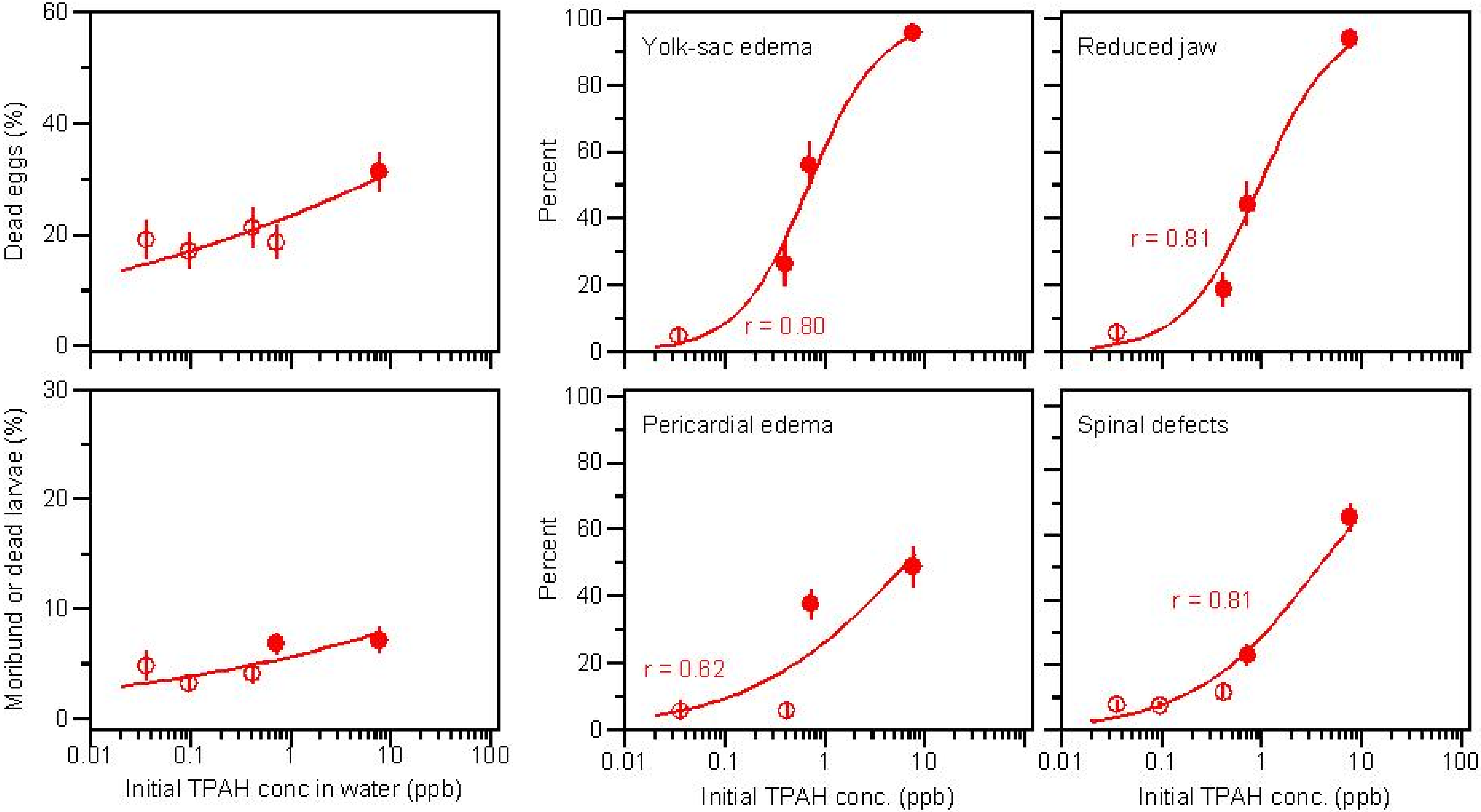
- Do we know enough?

Not all responses are created equal



Example: Pacific herring, more weathered experiment, Carls et al. (1999)

Not all responses are created equal



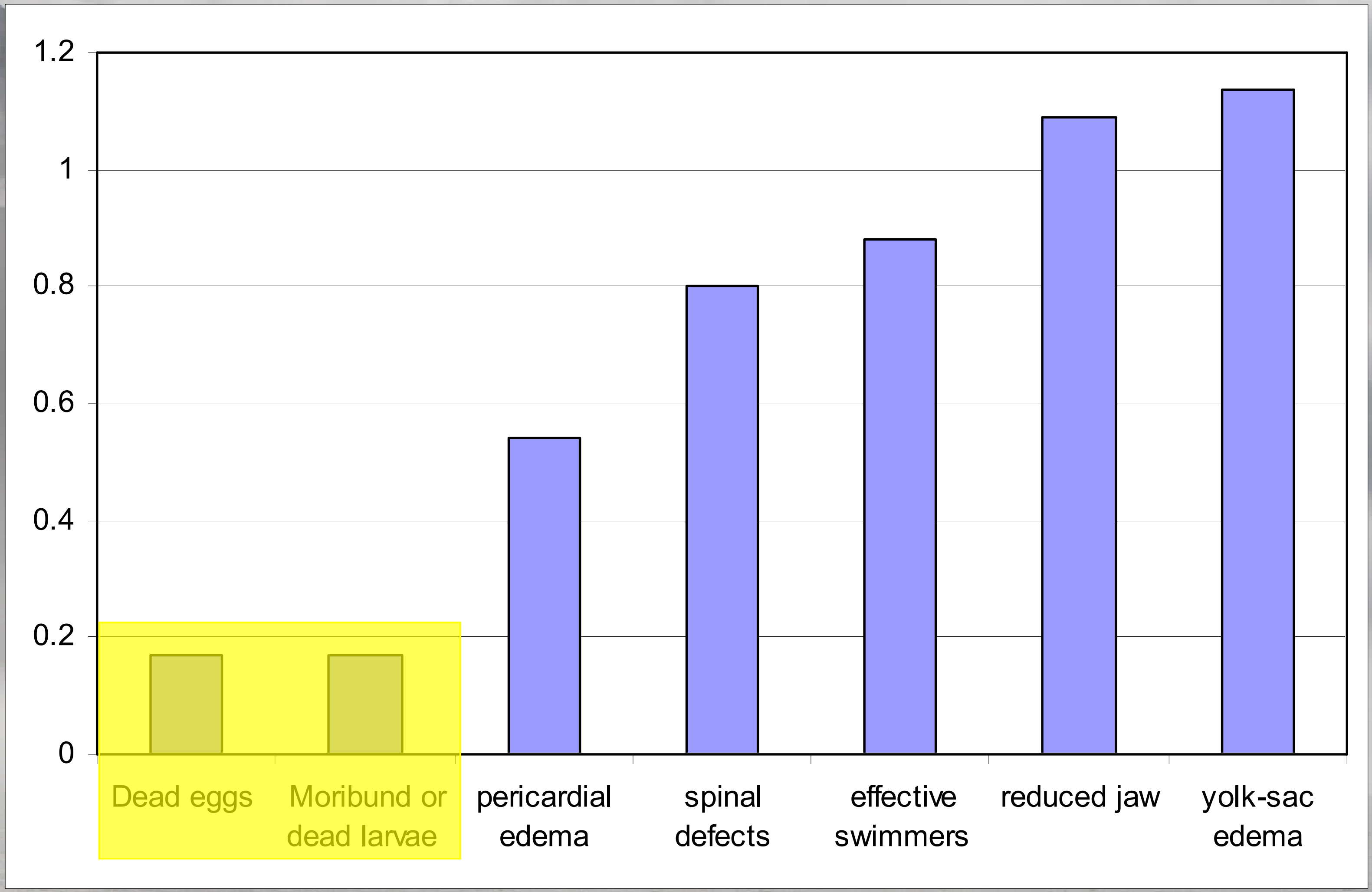
Example: Pacific herring, more weathered experiment, Carls et al. (1999)

Not all responses are created equal

Response differences can be summarized by using β (slope) from the logit regression:

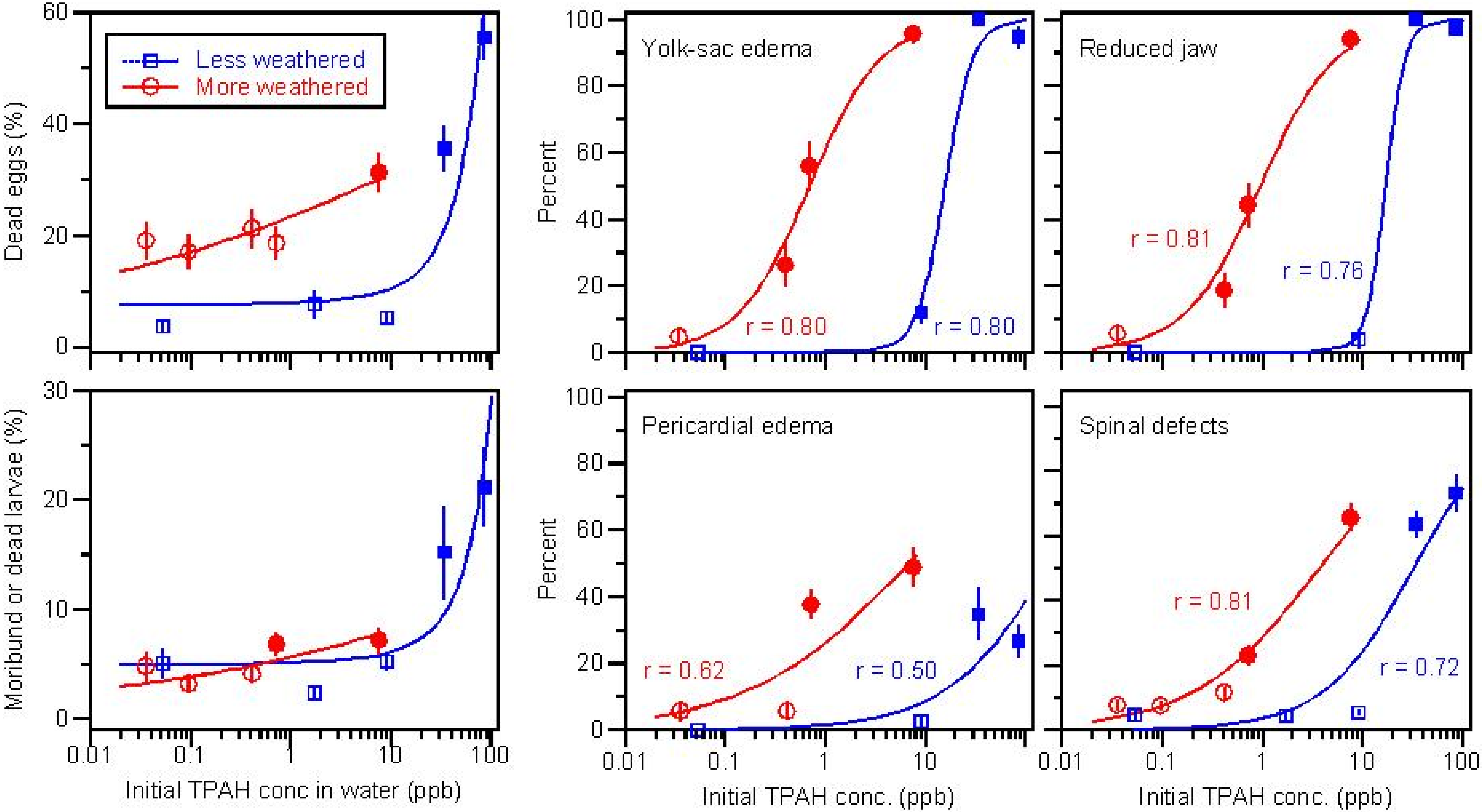
$$P = \frac{1}{1 + e^{-(\alpha + \beta \cdot x)}}$$

Not all responses are created equal



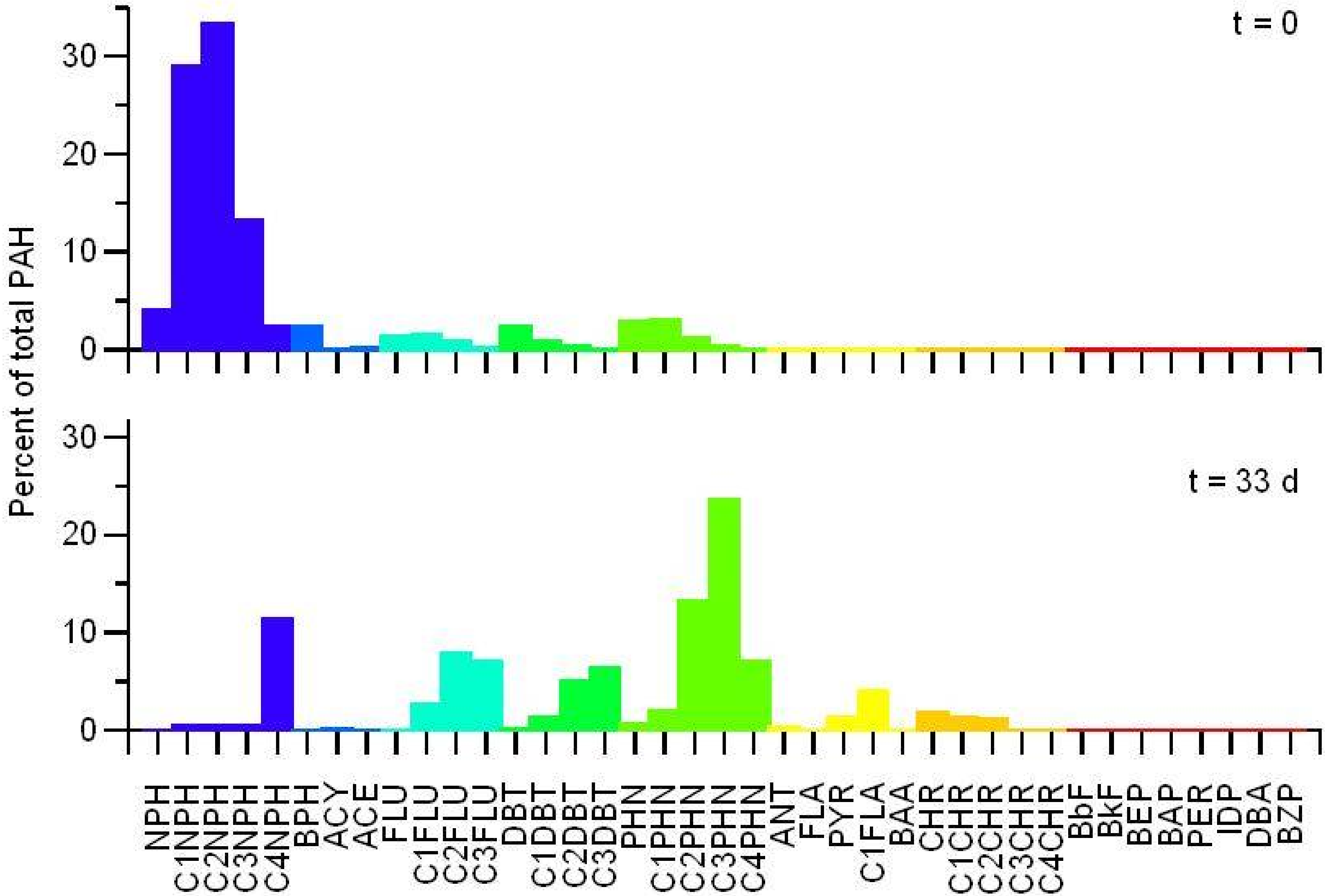
Example: y = absolute slope, Pacific herring, weathered experiment, Carls et al. (1999)

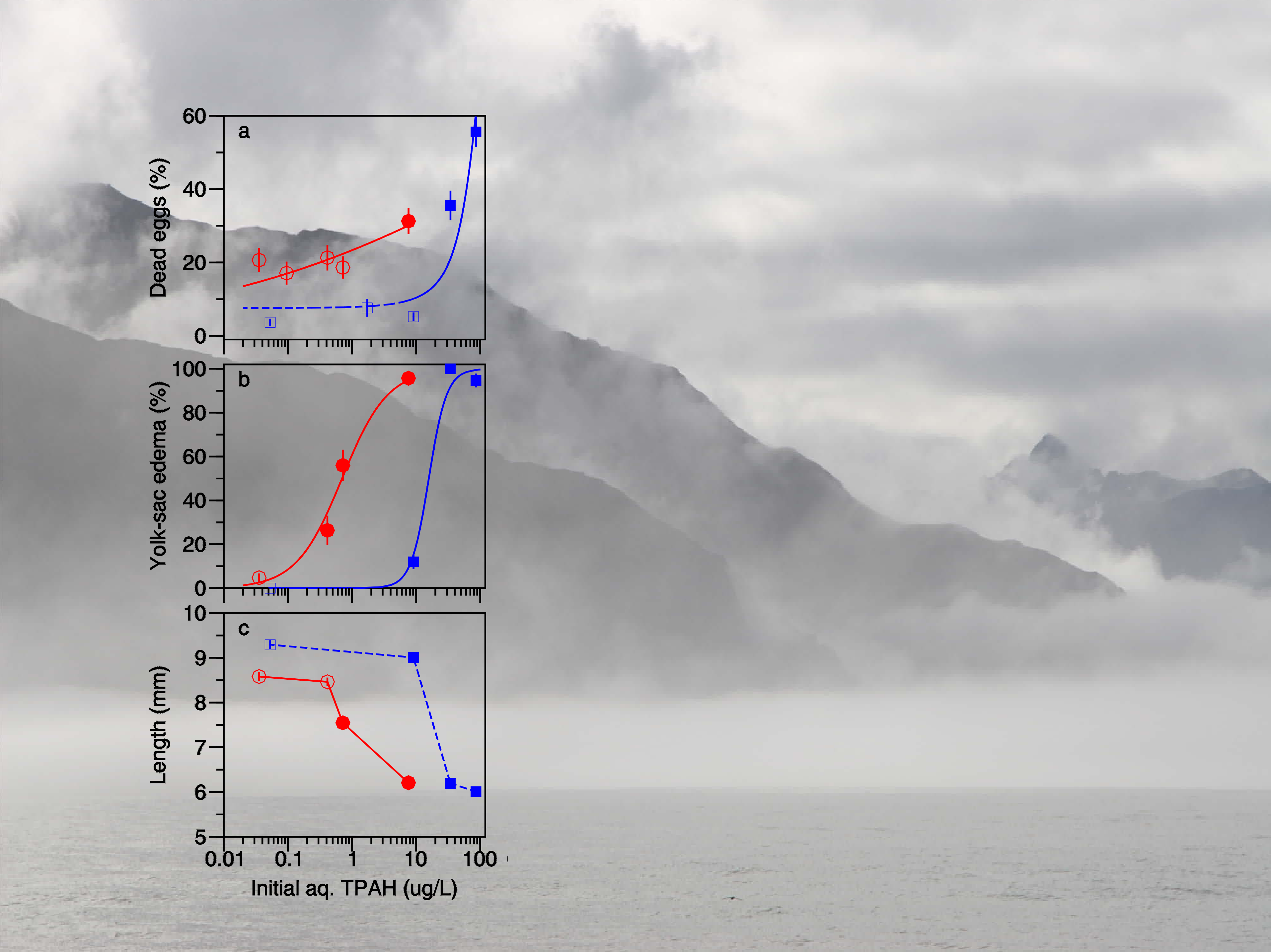
Not all PAH are created equal



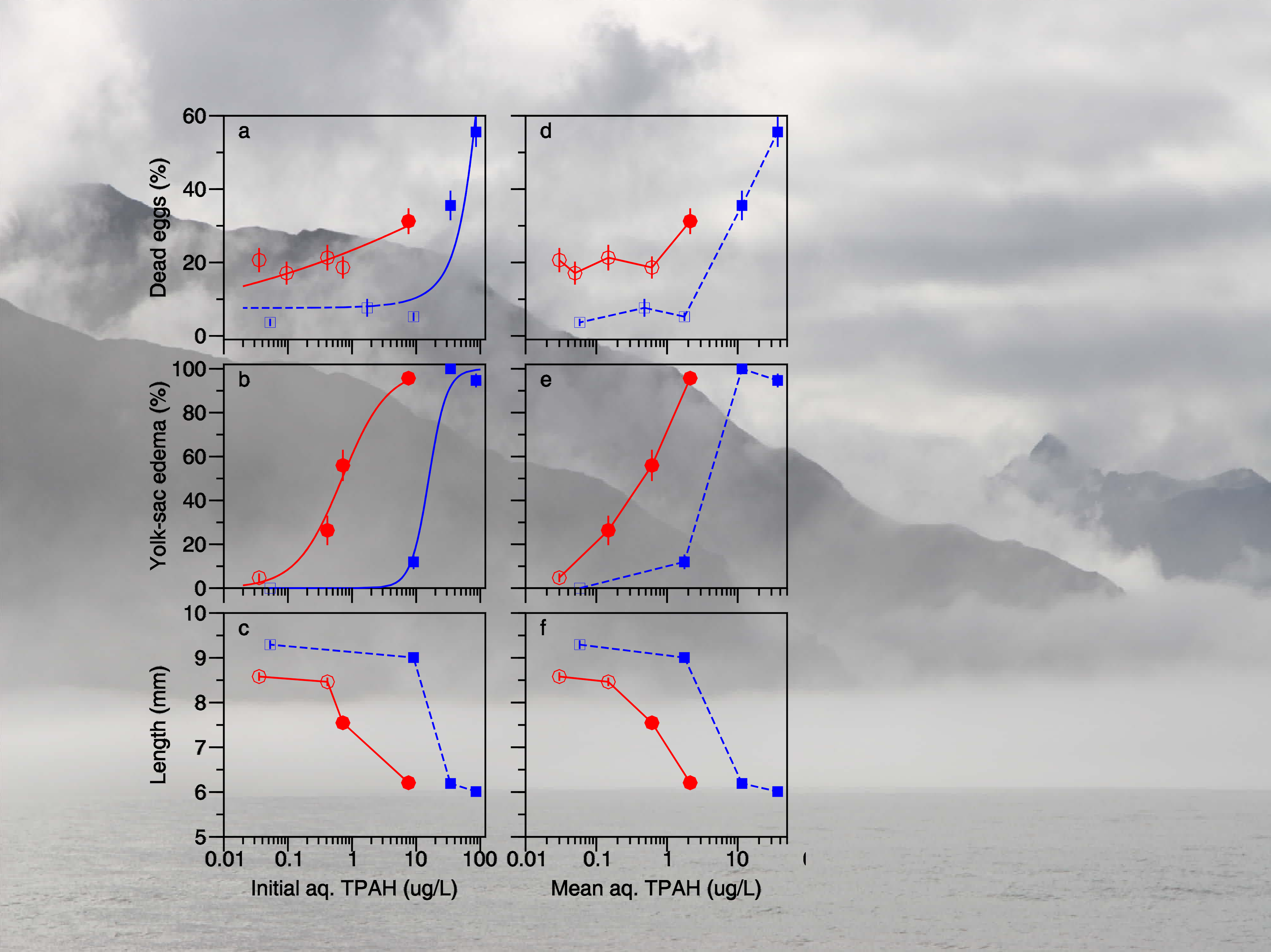
Example: Pacific herring, weathered experiment, Carls et al. (1999)

Not all PAH are created equal

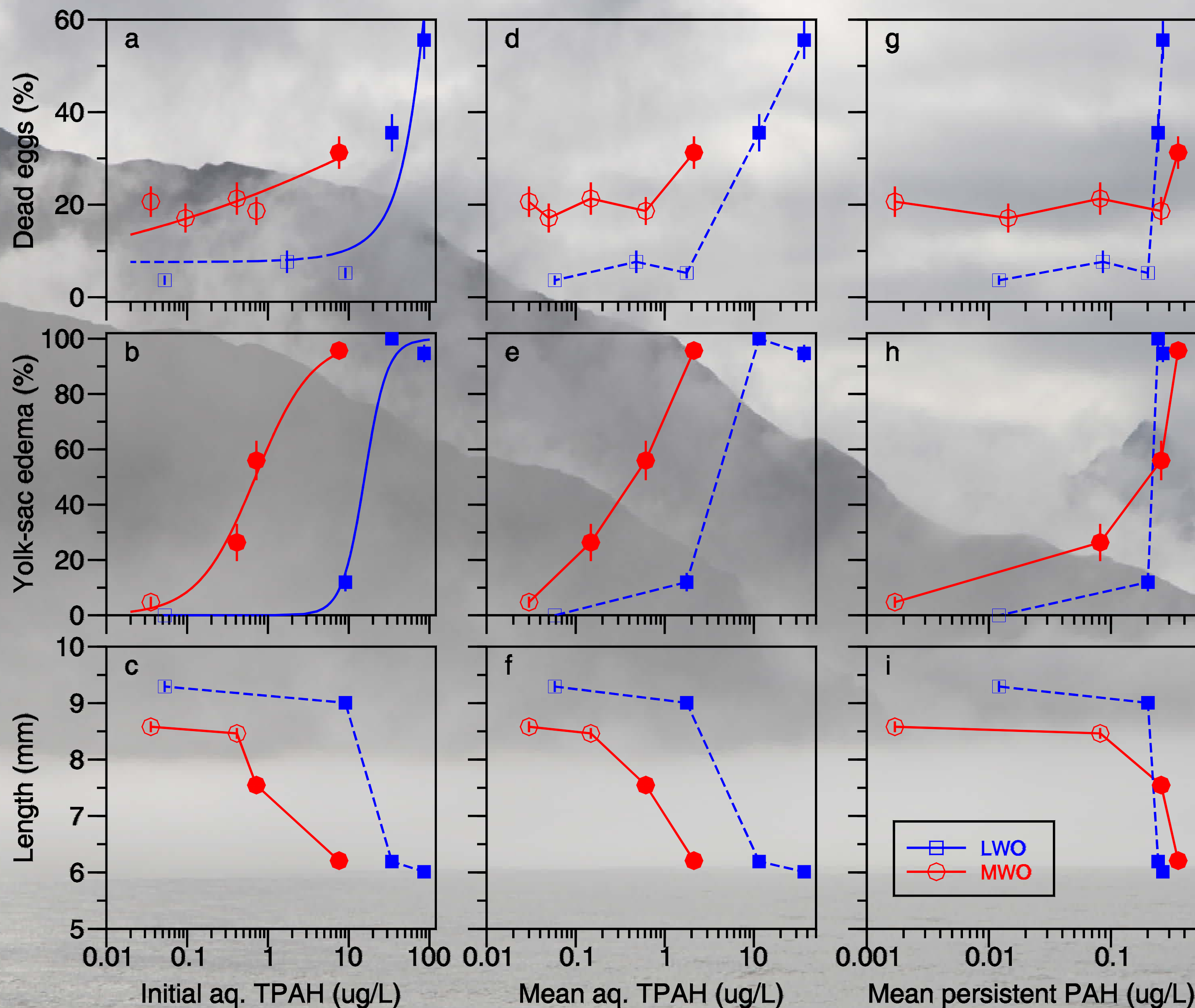




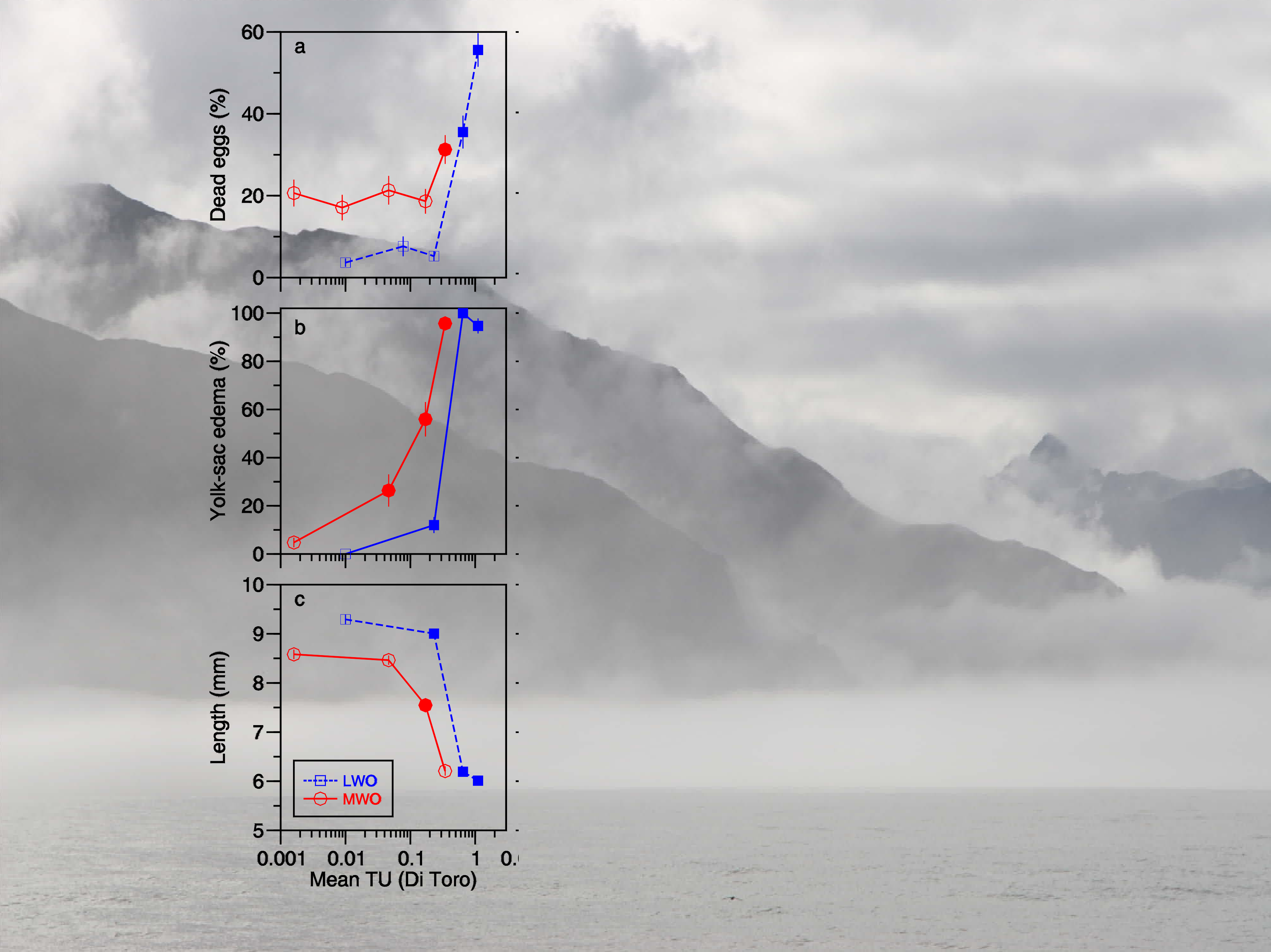
a
b
c
Dead eggs (%)
Yolk-sac edema (%)
Length (mm)
0
20
40
60
80
100
5
6
7
8
9
10
0.01
0.1
1
10
100
Initial aq. TPAH (ug/L)



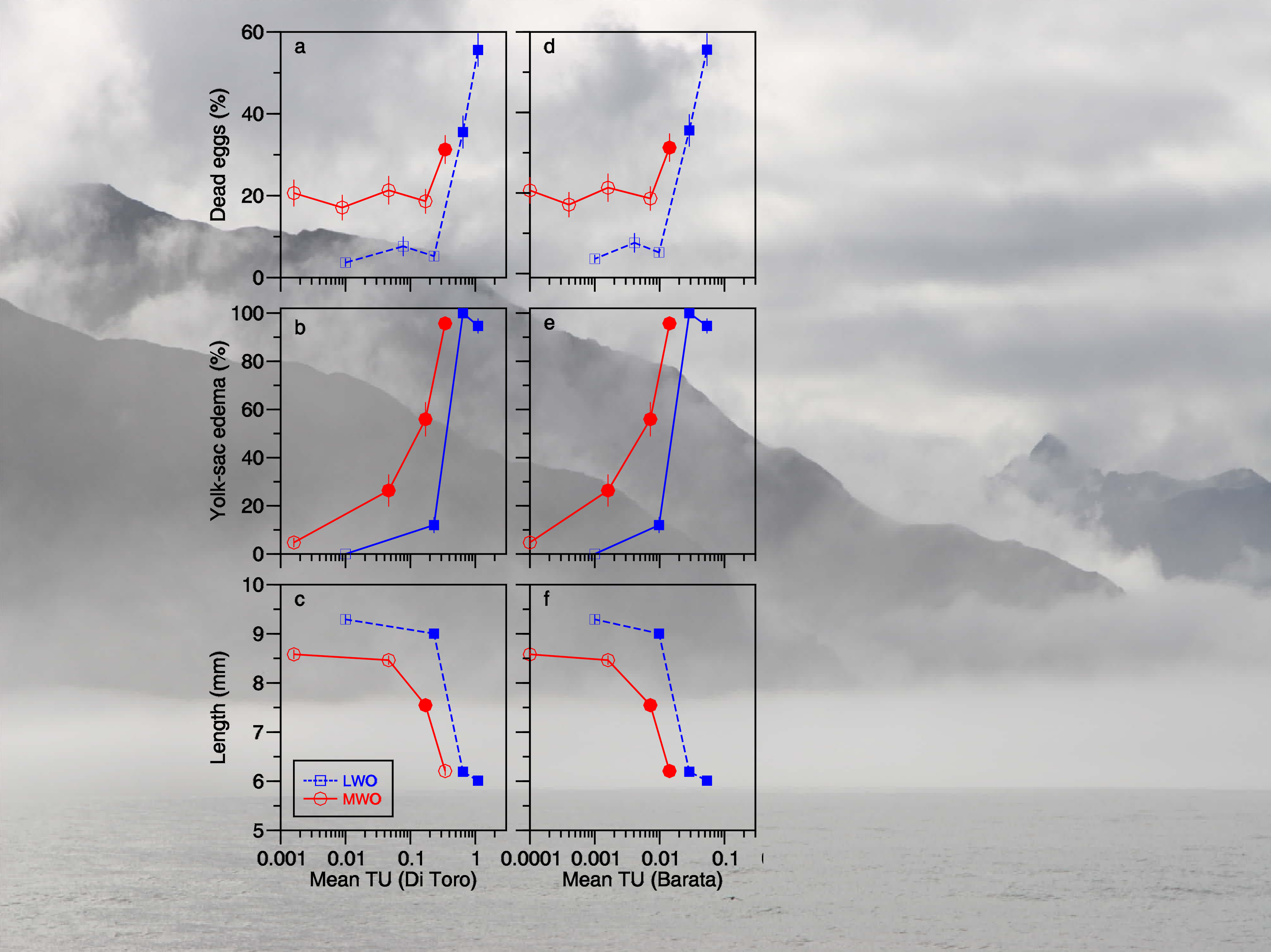
Dead eggs (%)
Yolk-sac edema (%)
Length (mm)
a
b
c
d
e
f
Initial aq. TPAH (ug/L)
Mean aq. TPAH (ug/L)



Dead eggs (%)
Yolk-sac edema (%)
Length (mm)
a
b
c
d
e
f
g
h
i
Initial aq. TPAH (ug/L)
Mean aq. TPAH (ug/L)
Mean persistent PAH (ug/L)
LWO
MWO



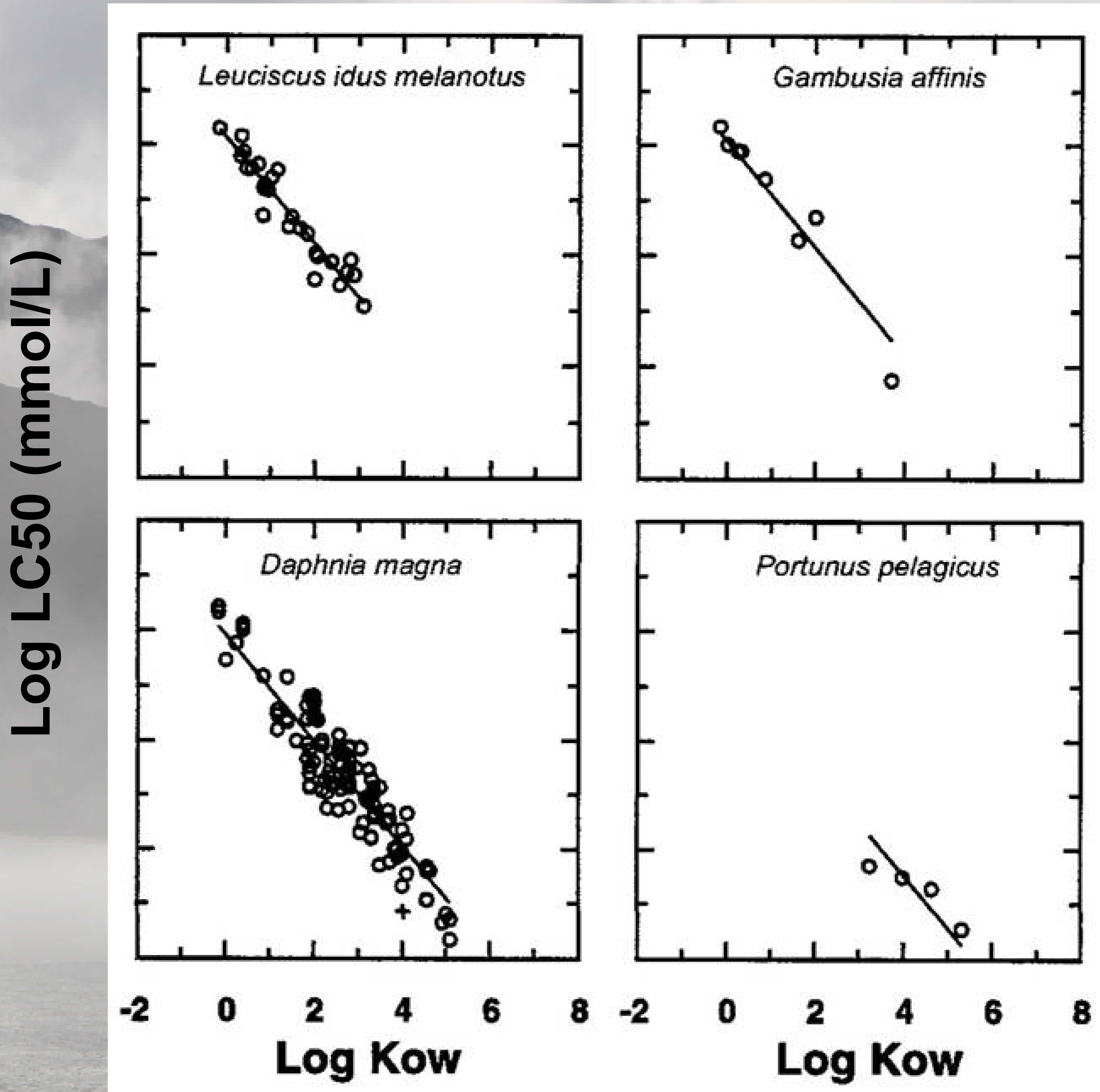
a
b
c
Dead eggs (%)
Yolk-sac edema (%)
Length (mm)
LWO
MWO
Mean TU (Di Toro)
0.001
0.01
0.1
1



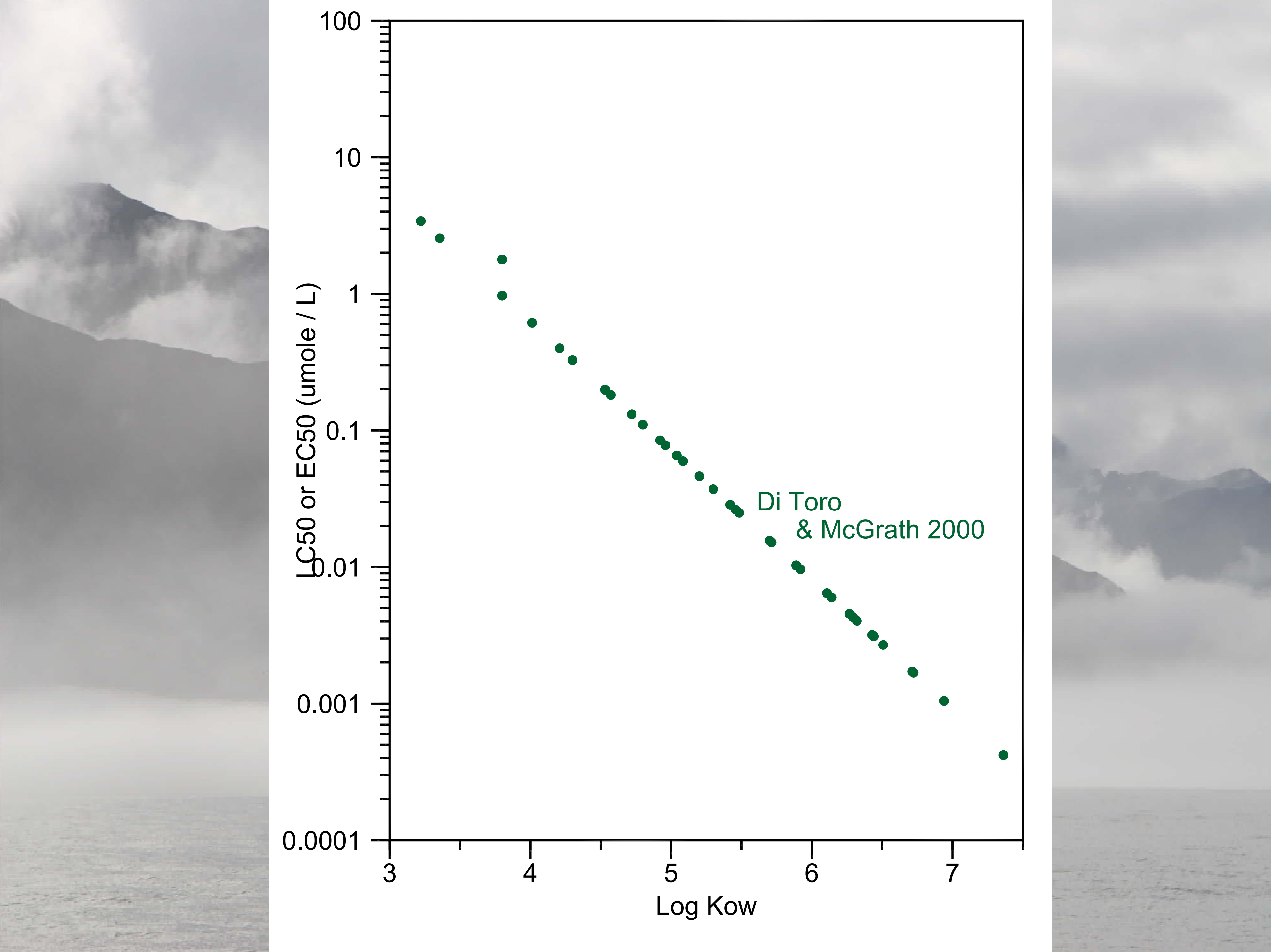
a
b
c
d
e
f
Dead eggs (%)
60
40
20
0
Yolk-sac edema (%)
100
80
60
40
20
0
Length (mm)
10
9
8
7
6
5
LWO
MWO
0.001
0.01
0.1
1
Mean TU (Di Toro)
0.0001
0.001
0.01
0.1
Mean TU (Barata)

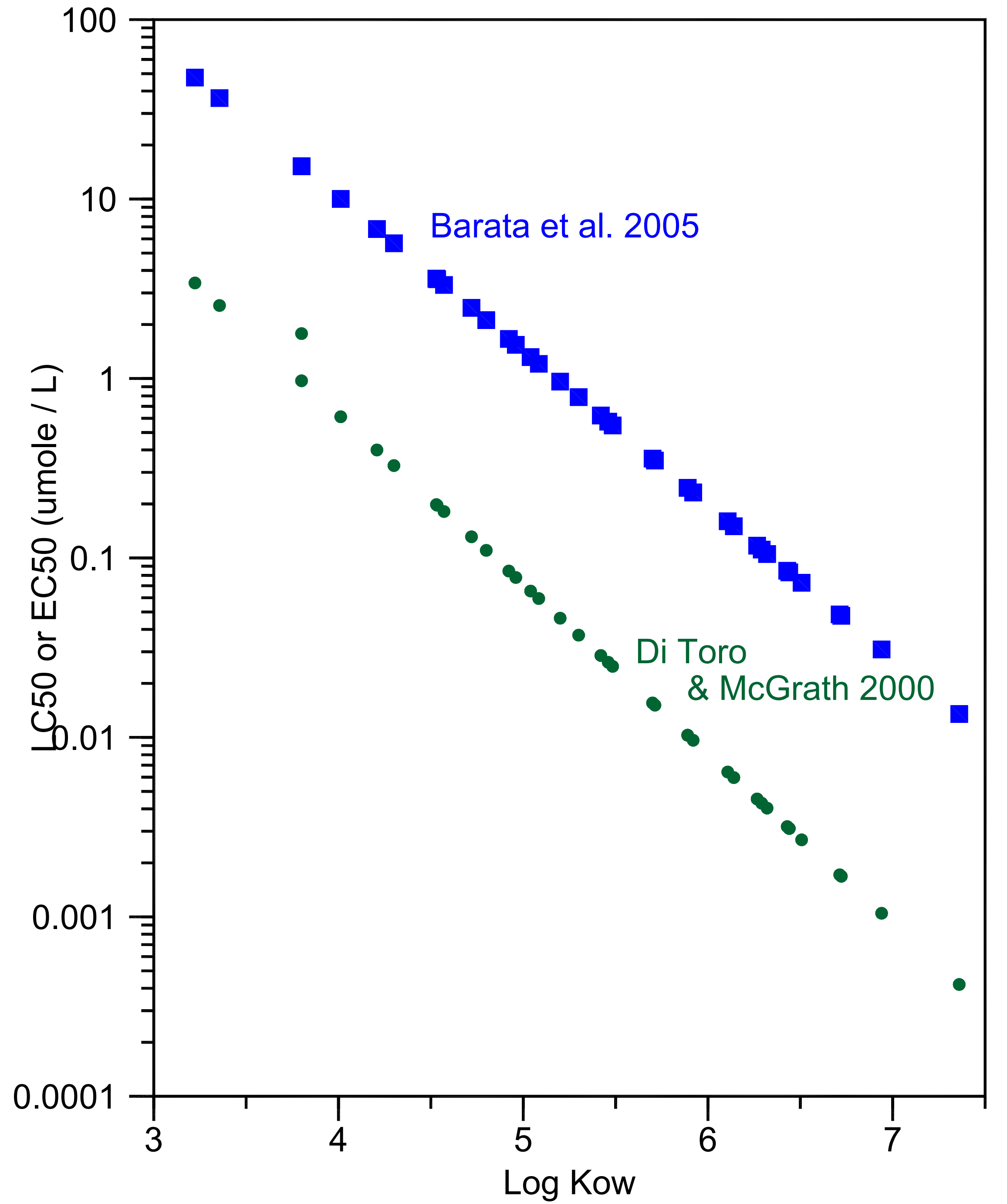
$$TU = \sum_{i=1}^{n} [PAH]_i / LC50_i$$

If TU = 1, expect about half the animals to die

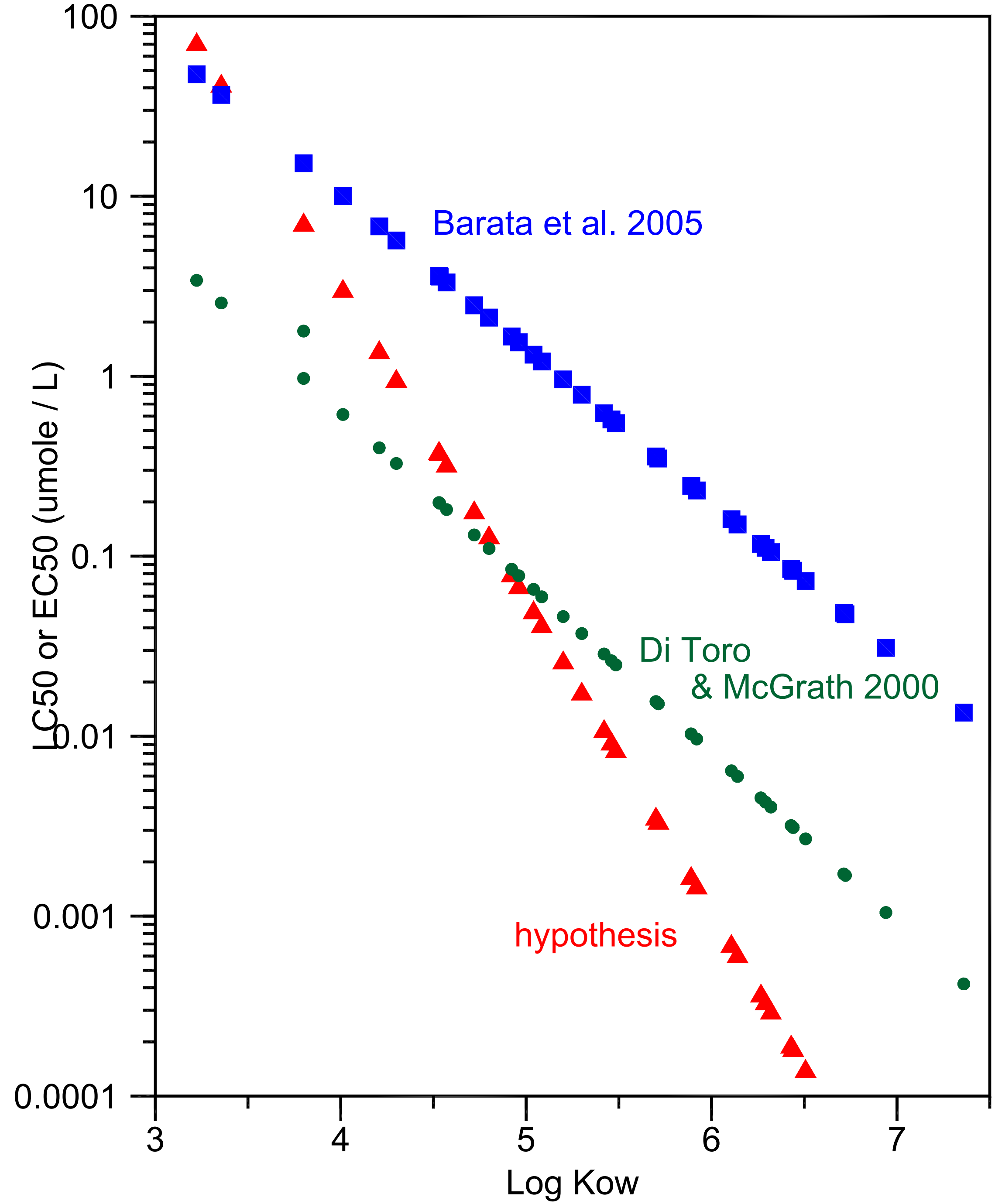


Di Toro & McGrath 2000

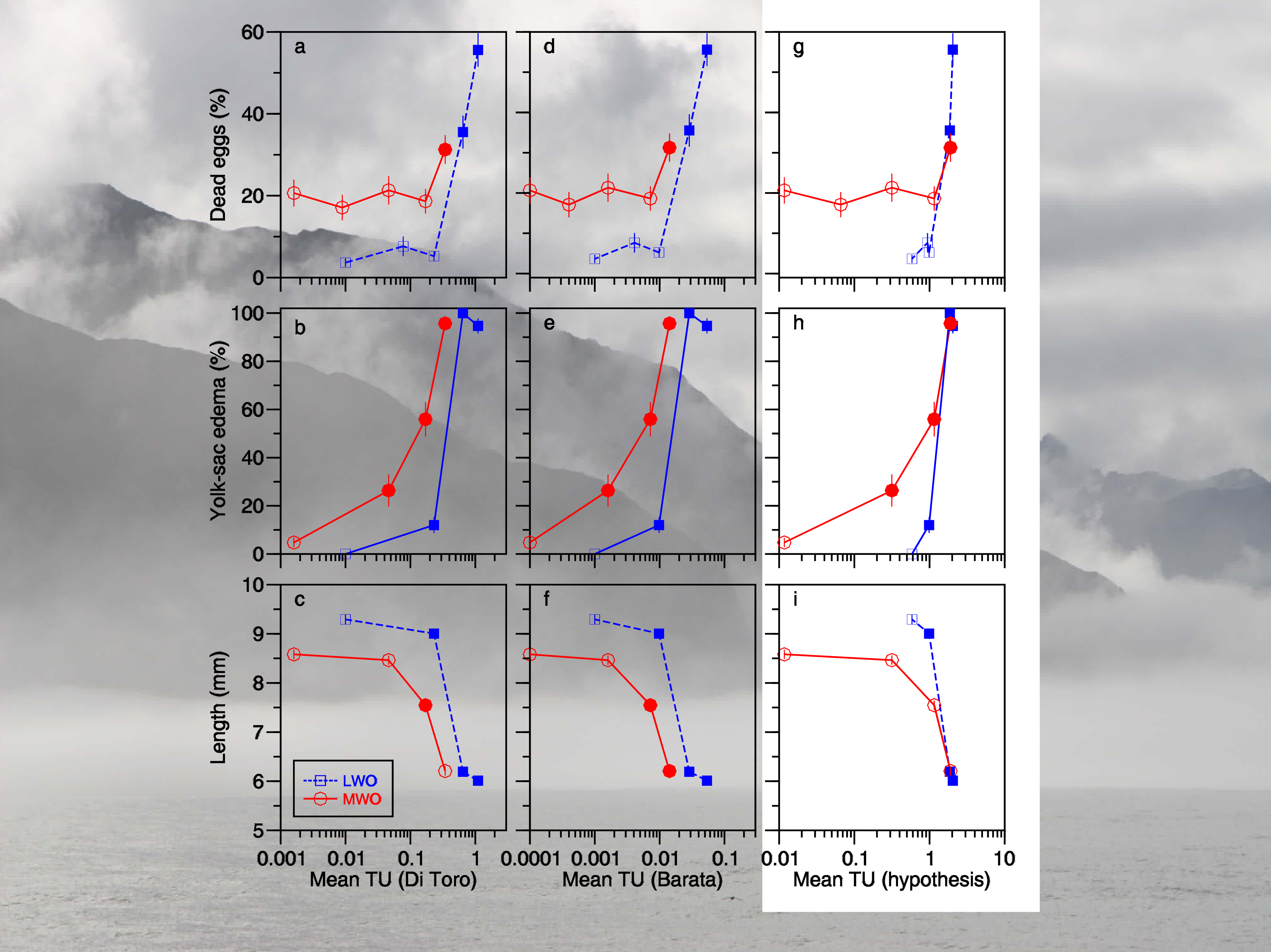

100
10
1
0.1
0.01
0.001
0.0001
LC50 or EC50 (umole / L)
3
4
5
6
7
Log Kow
Di Toro
& McGrath 2000



100
10
1
0.1
0.01
0.001
0.0001
LC50 or EC50 (umole / L)
3
4
5
6
7
Log Kow
Barata et al. 2005
Di Toro
& McGrath 2000



100
10
1
0.1
0.01
0.001
0.0001
LC50 or EC50 (umole / L)
3
4
5
6
7
Log Kow
Barata et al. 2005
Di Toro
& McGrath 2000
hypothesis



a
b
c
d
e
f
g
h
i
Dead eggs (%)
Yolk-sac edema (%)
Length (mm)
LWO
MWO
Mean TU (Di Toro)
Mean TU (Barata)
Mean TU (hypothesis)

Toxicity prediction

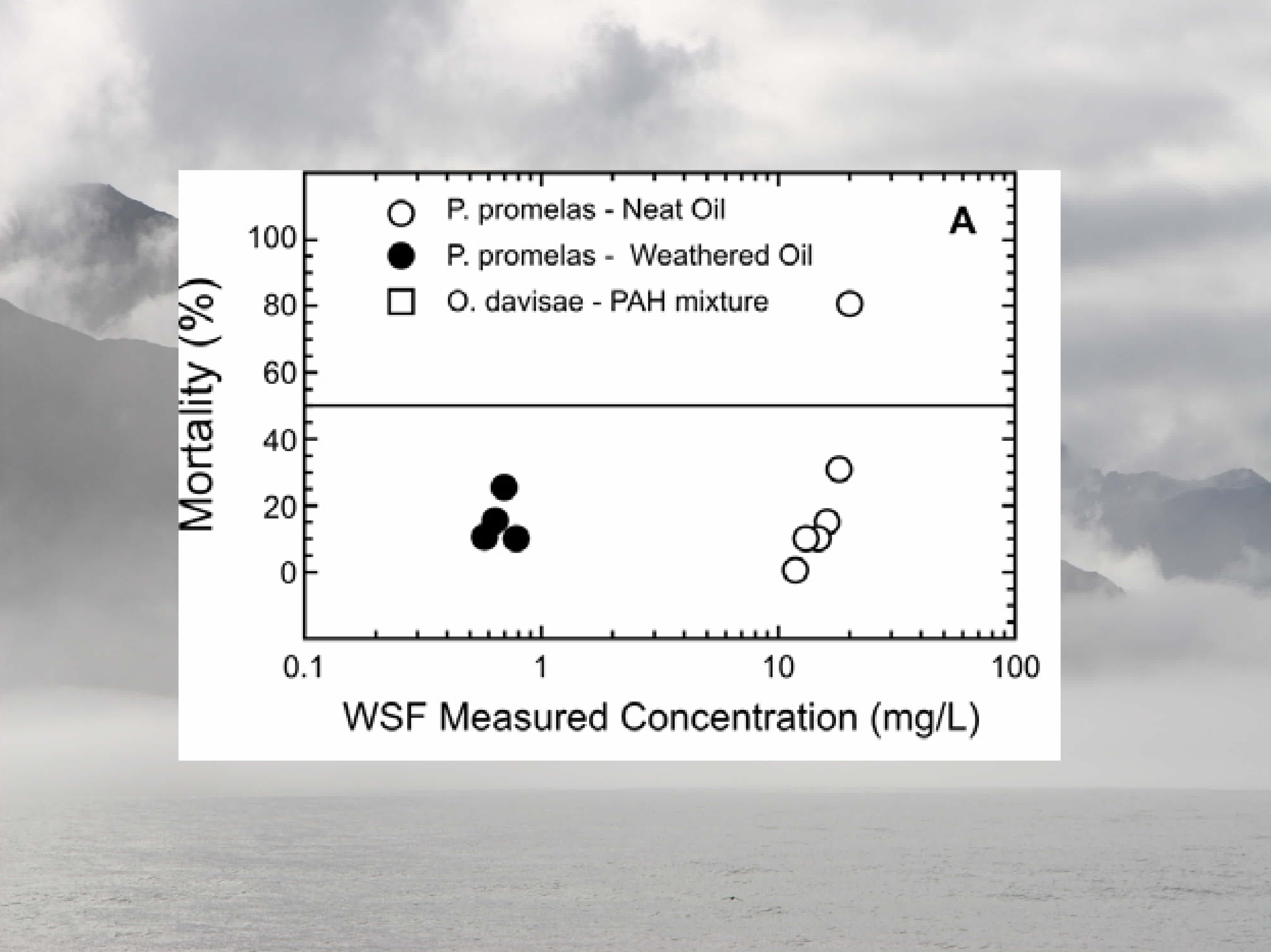
- Do we know enough?

- No
  - Need further research (non-narcotic assays)
  - Need models that work in non-equilibrium conditions
  - Need to examine multiple stressors;
    chemical, physical, pathogens

Safeguards

- Final point:
- Because PAH are highly toxic, safeguards are needed.

- This should take the form of increased regulatory action, and movement away from reliance on fossil fuels.



P. promelas - Neat Oil
P. promelas - Weathered Oil
O. davisae - PAH mixture
A
Mortality (%)
100
80
60
40
20
0
0.1
1
10
100
WSF Measured Concentration (mg/L)

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

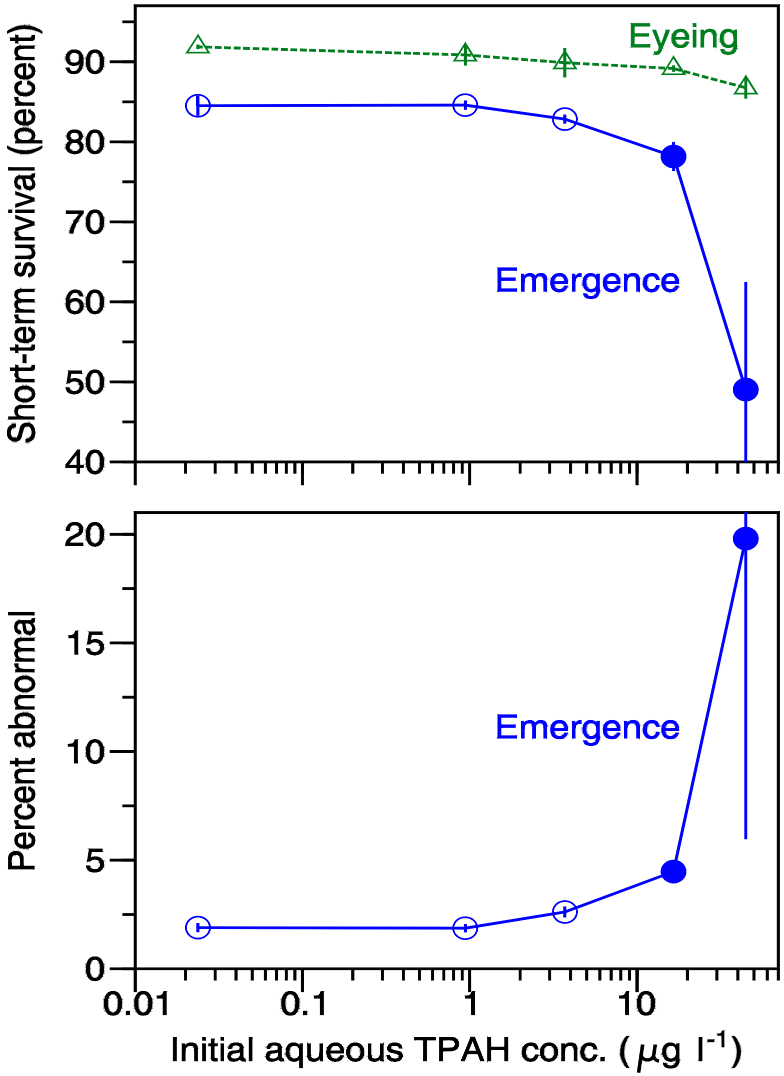
	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
$(FLA+PYR)/\Sigma(P1..P4)$	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

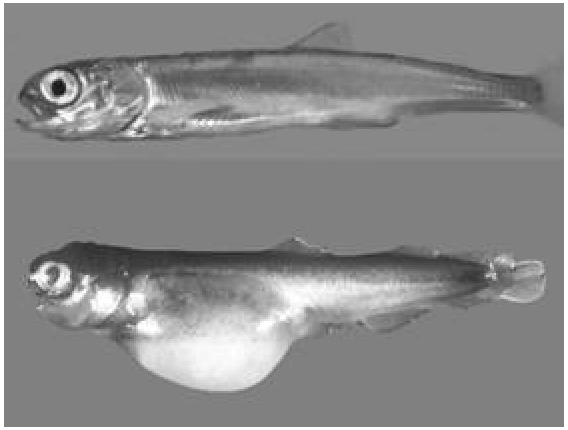
	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
(FLA+PYR)/Σ(P1..P4)	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

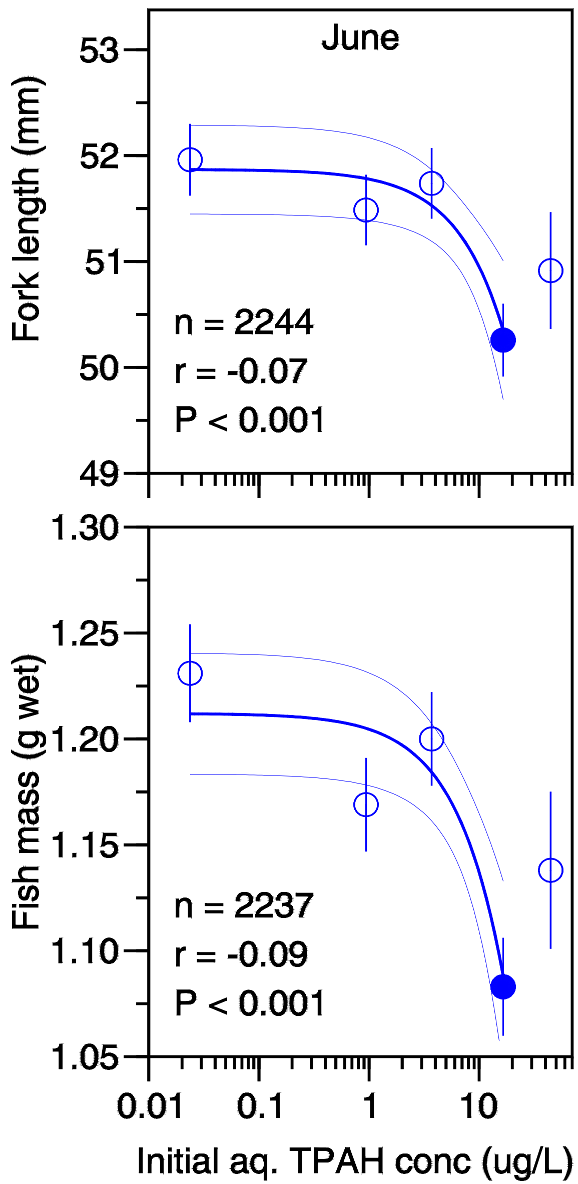
	ANS	Diesel	Constantine	Selendang	creosote
n	5	12	16	26	3
Percent scored as petrogenic (non-specific models)					
$FORLM_{oil}$	100	42	94	58	0
OFM_{oil}	100	100	100	100	100
$PSCORE_{oil}$	100	100	100	100	100
Percent scored as ANS					
$FORLM_{ANS}$	100	17	6	50	0
OFM_{ANS}	100	58	100	58	67
$PSCORE_{ANS}$	100	42	88	96	0
Percent scored as pyrogenic					
Nonpara pyrogenic	0	0	0	0	100
$(FLA+PYR)/\Sigma(P1..P4)$	0	0	0	0	67
Combined model scores (petrogenic & pyrogenic)					
consensus	6	3.8	4.9	5.1	-2.3
nonparametric only	6	4.4	5.8	6	-5

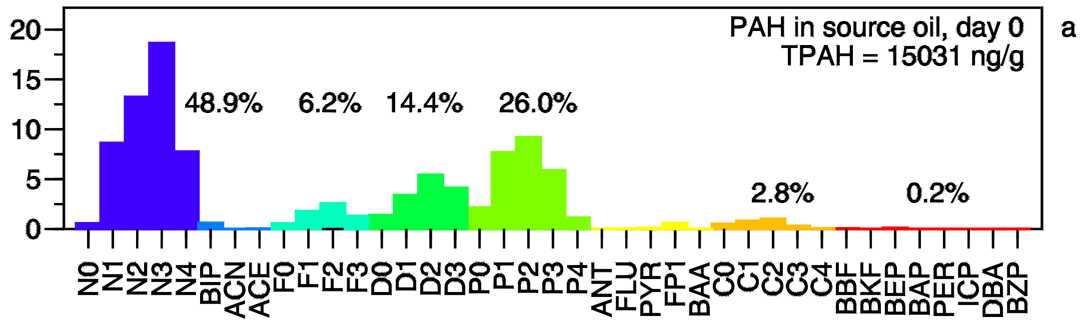
Effects during exposure:



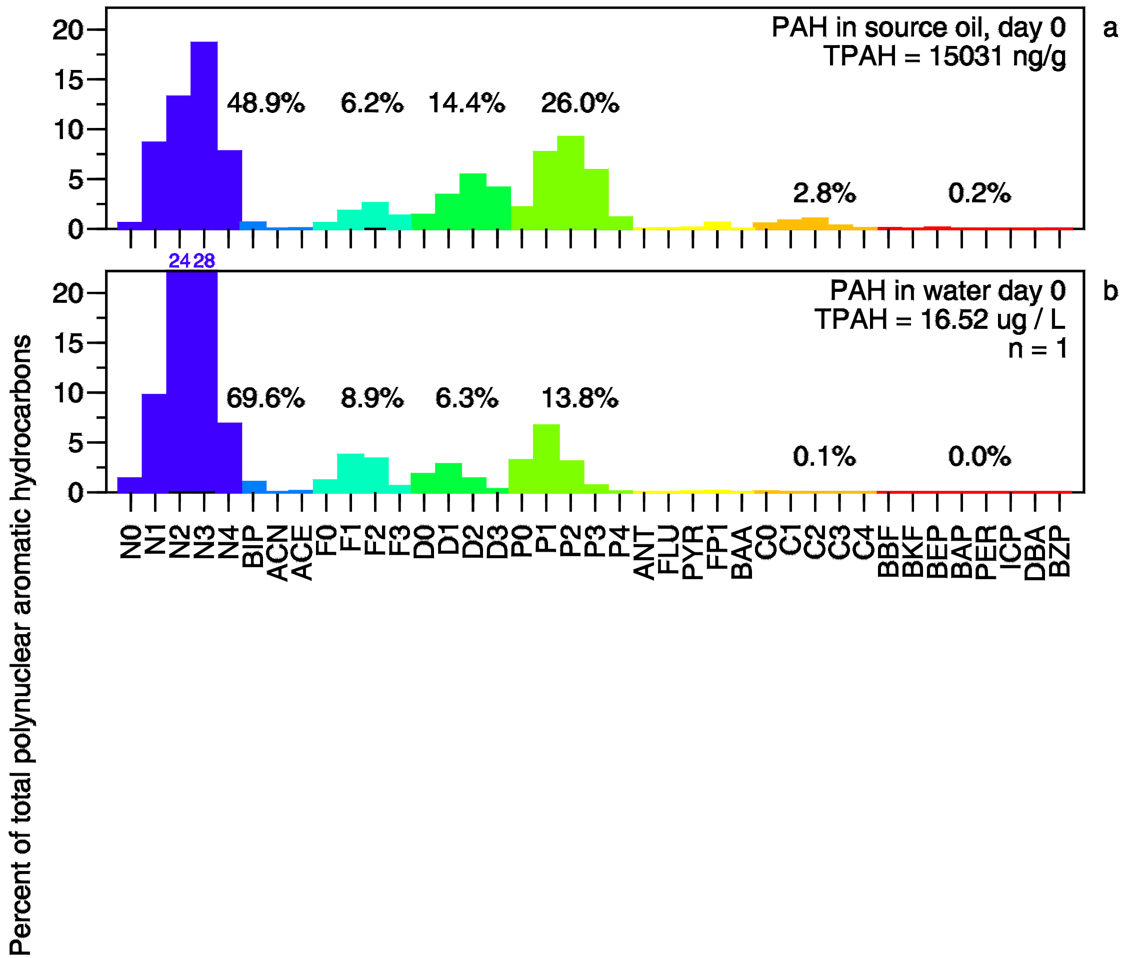


Effects after exposure

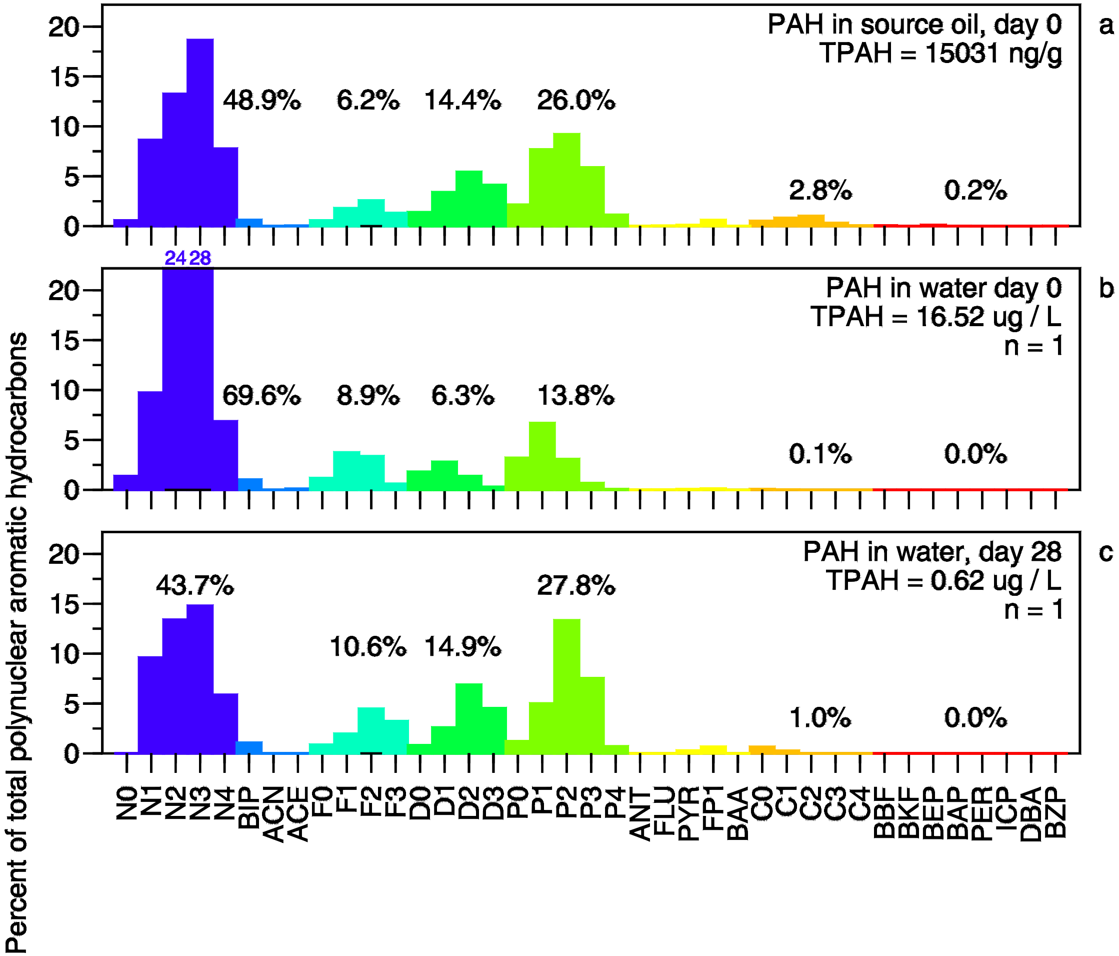




PAH composition in oiled rock



PAH composition in water passed through oiled rock



PAH composition in water passed through oiled rock