Can there be an environmentally 'safe' antifouling paint biocide?

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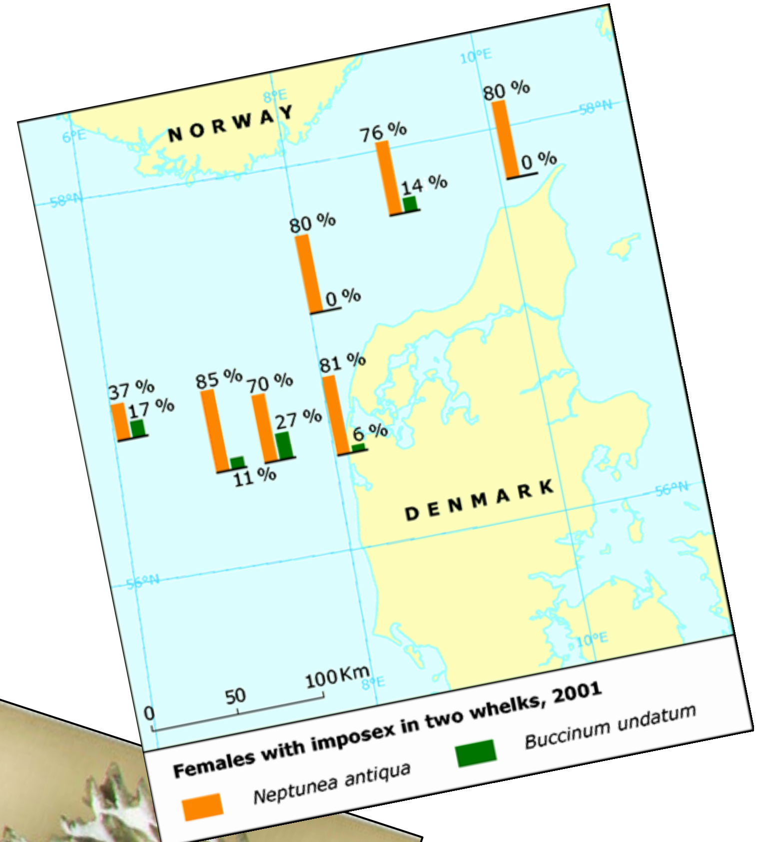
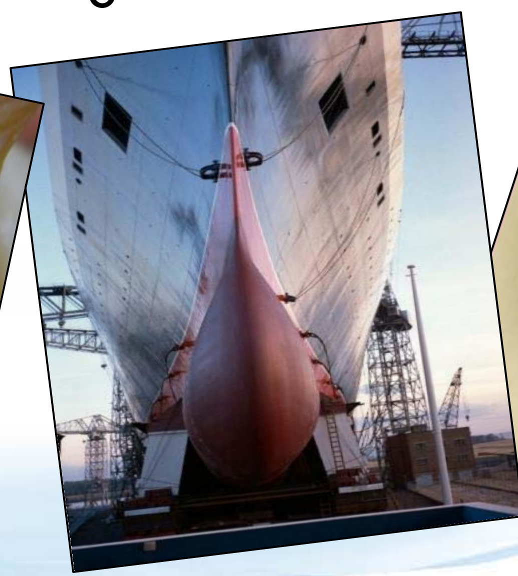
TBT

- 1980's
  - Decline of oyster cultures (Arcachon Bay, France),
  - Imposex in female welks
- 1982 Restriction on boats <25m (Fr.)
- 2008 IMO AFS global TBT ban!





Antifouling paint biocides

Diuron
Irgarol 1051
Zinc/copper pyrithione
Dichlofluanid
Tolyfluanid
SeaNine 211 (DCOIT)
Chlorothalonil
TCMTB
Zineb
TPBP
Medetomidine
Copper thiocyanate
Copper

Regulation

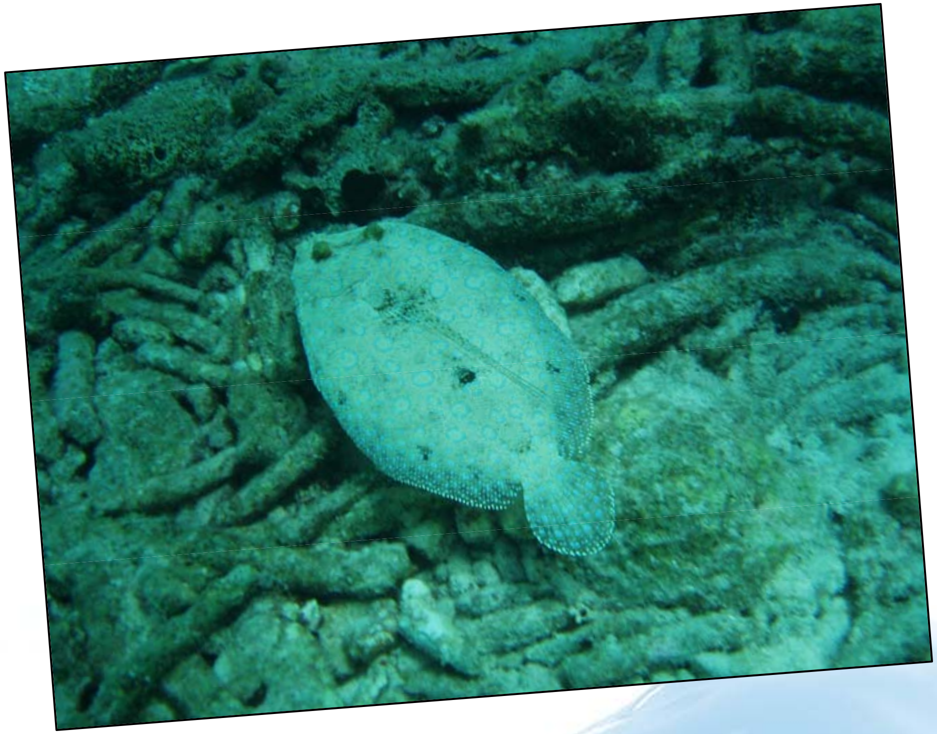
- Europe: State + BPD (98/8/EC)
- USA: Registration with EPA and state
- Canada: Registration with Health Canada
- Japan: 'approved biocides'
- Australia: Registration with NRA


Environmental Fate & Behaviour
Use
S250
Release
Transformation
Bioaccumulation
Occurrence
Bioavailability
Degradation
Sediment/water partitioning

Environmental risk assessment

- Predicted environmental concentration (PEC)
- Predicted no-effect concentration (PNEC)

- Risk quotient= PEC/PNEC
  - >1 risk
  - <1 little risk



Predicting environmental concentrations

- PECs
  - Determined from data relating to
    - Environment
    - Physico-chemical properties
    - Emission scenario
- Examples
  - MAMPEC
  - REMA (UK)
  - Exams

www.antifoulingpaint.com/downloads/mampec.asp

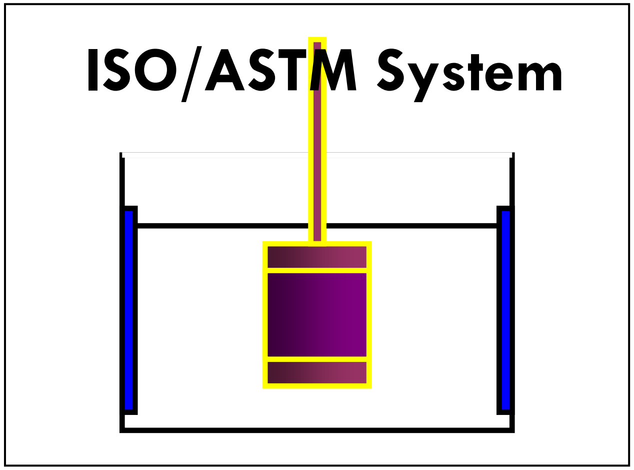
Analysis: Extraction

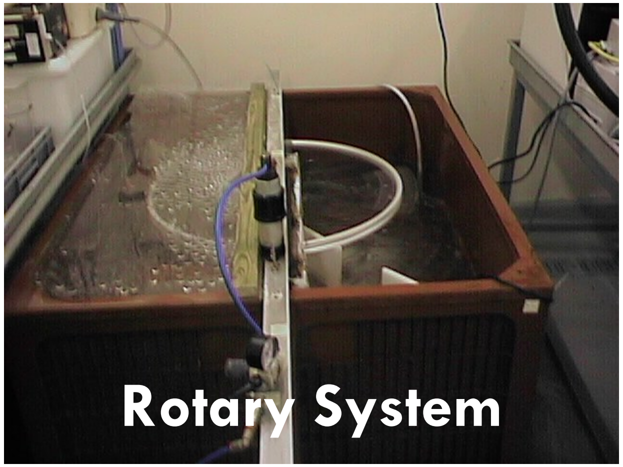
	Extraction phase	Recovery (%)	LOD (ng/L)	Reference
Irgarol	C18 Sep-Pak	81-107	11	(Gatidou *et al.* 2005)
	C18	95		(Ferrer *et al.* 1999)
	C18	93	4	(Biselli *et al.* 2000)
	C18	80-100	1	(Bowman *et al.* 2003)
	ENV+	93-96	11	(Gatidou *et al.* 2005)
	Eni-Chrom P	71-85	11	(Gatidou *et al.* 2005)
	Polymeric	95	2	(Ferrer *et al.* 2001)
	Polymeric	84	10-20	(Pocurull *et al.* 2000)
	Polymeric	106	5	(Ferrer *et al.* 1999)
	Polymeric	89-93		(Cai *et al.* 2006)
	LiChrolute EN	91-95	5	(Gimeno *et al.* 2001)
	SPME - polydimethylsiloxane		50	(Lam *et al.* 2005)
M1	C18 Sep-Pak	79-101	26	(Gatidou *et al.* 2005)
	ENV+	77-110	26	(Gatidou *et al.* 2005)
	Polymeric	87-90		(Cai *et al.* 2006)
	Eni-Chrom P	71-110	26	(Gatidou *et al.* 2005)
	SPME - polydimethylsiloxane		100	(Lam *et al.* 2005)
Diuron	C18 Sep-Pak	98-111	7	(Gatidou *et al.* 2005)
	C18	89		(Ferrer *et al.* 1999)
	ENV+	89-100	7	(Gatidou *et al.* 2005)
	Eni-Chrom P	88-107	7	(Gatidou *et al.* 2005)
	Polymeric	99	10	(Ferrer *et al.* 1999)
	LiChrolute EN	97-99	5	(Gimeno, Aguilar et al. 2001
Dichlofluanid	LiChrolute EN	87-89	5	(Gimeno, Aguilar et al. 2001
	Polymeric	67	10-20	(Pocurull *et al.* 2000)
	Polymeric	<10		(Ferrer *et al.* 1999)
	Divinylbenzene disc	72-87	3	(Hamwijk *et al.* 2005)
	C18	<10		(Ferrer *et al.* 1999)
	SPME - PDMS	103-118	2	(Lambropoulou *et al.* 2000)
	SPME - polyacrylate		200	(Penalva *et al.* 1999)
Chlorothalonil	Polymeric	96	2	(Ferrer *et al.* 1999)
	SPME - PDMS	103-124	5	(Lambropoulou *et al.* 2000)
	C18	63		(Ferrer *et al.* 1999)
TCMTB	Polymeric	111	8	(Ferrer *et al.* 1999)
	C18	98		(Ferrer *et al.* 1999)

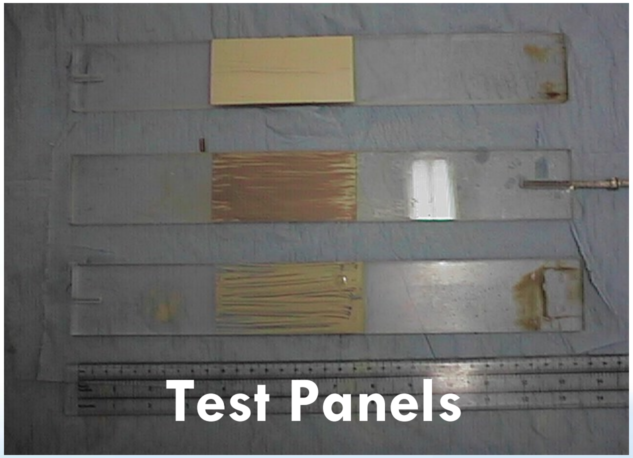
Analysis

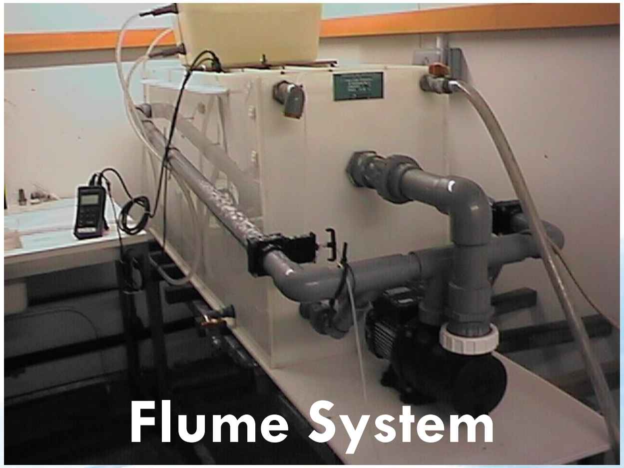
Compound	Instrument	Mode	Molecular Ion	Fragment Ions	Daughter Ion
Irgarol 1052	GC/MS	EI +ve	253	238/182	196
	LC/MS	ESI/APCI +ve	254		198
M1	GC/MS	EI +ve	213	198/157	
Diuron	LC/MS	ESI/APCI +ve	233		72/46
DCOIT	GC/MS	EI -ve/NCI	246	182/169	
		EI -ve/NCI			
	GC/MS	MS/MS	282		170
	LC/MS	APCI +ve	284/282		
Chlorothalonil	GC/MS	EI +ve/NCI		266/264/268/270	
	LC/MS	APCI -ve	264	245	
Dichlofluanid	GC/MS	EI +ve	224	167/123	
	LC/MS	APCI -ve	199	155	
DMSA	GC/MS	EI +ve	200	92/108	
TCMTB	GC/MS	EI +ve	238	180/136/108	
	GC/MS	CI -ve	166	58	
	GC/MS	CI +ve	222	182/210/136	
	LC/MS	APCI -ve	238	166	
TCMS-					
pyridine	LC/MS	APCI -ve		230/232/234/236	
ZPT	LC/MS	APCI	317	221/319	
TPBP	HPLC	UV	220 nm		

Leach/release rates









Biocide Release

Biocide	Alternative trade name	Release Rate ($\mu g\ cm^{-2}\ day^{-1}$)	
		ISO test system	Flume system
Cuprous oxide		25-40[a]	18.6±6.5
TBT		1.5-4.0[a]	1.6
Irgarol 1051		5.0	2.6[b]
Diuron		3.3	0.8
Dichlofluanid	Euparen	0.6	1.7
Zinc pyrithione	Zinc omadine	3.3	-[c]
Kathon 5287	Sea-Nine 211	2.9	3.0
TCMTB	Busan	-[c]	0.9
TCMS pyridine	Densil S	0.6	3.8

Occurrence

- Good occurrence data for:
  - Irgarol 1051
  - Diuron
  - Labile and total copper
- Not so good for:
  - DCOIT
  - Dichlofluanid
- Little or no data for:
  - Zn/CuPT
  - TPBP
  - Zineb
  - Tolyfluanid

Summary of occurrence: Irgarol 1051

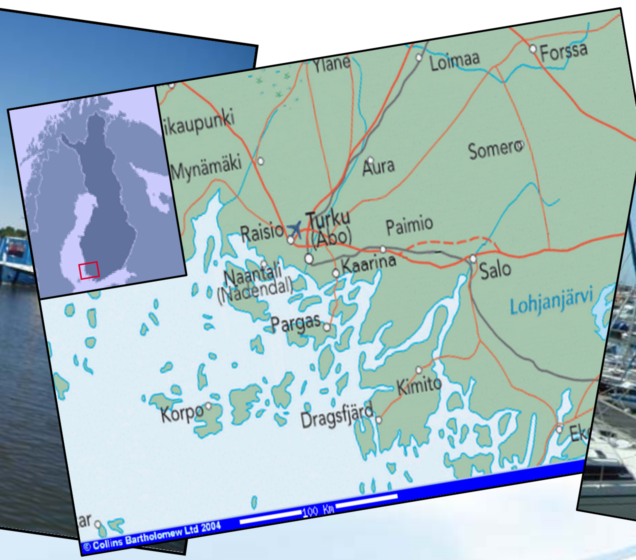
Marina, port and estuary surface waters, inland water ways and lakes, sediments and macrophytes.	Marinas- <1-670 Coastal- <1-92 Lakes- In-land waterways- Sediments-	Europe (Norway, Sweden, Denmark, The Netherlands, UK, Spain, Italy, France, Greece), Australia, North America (USA, Canada, Bermuda), Caribbean, Asia (Japan, Singapore, Thailand, Vietnam)	Found ubiquitously in areas where Irgarol 1051 containing paint formulations are used

Summary of occurrence: Zn/CuPT

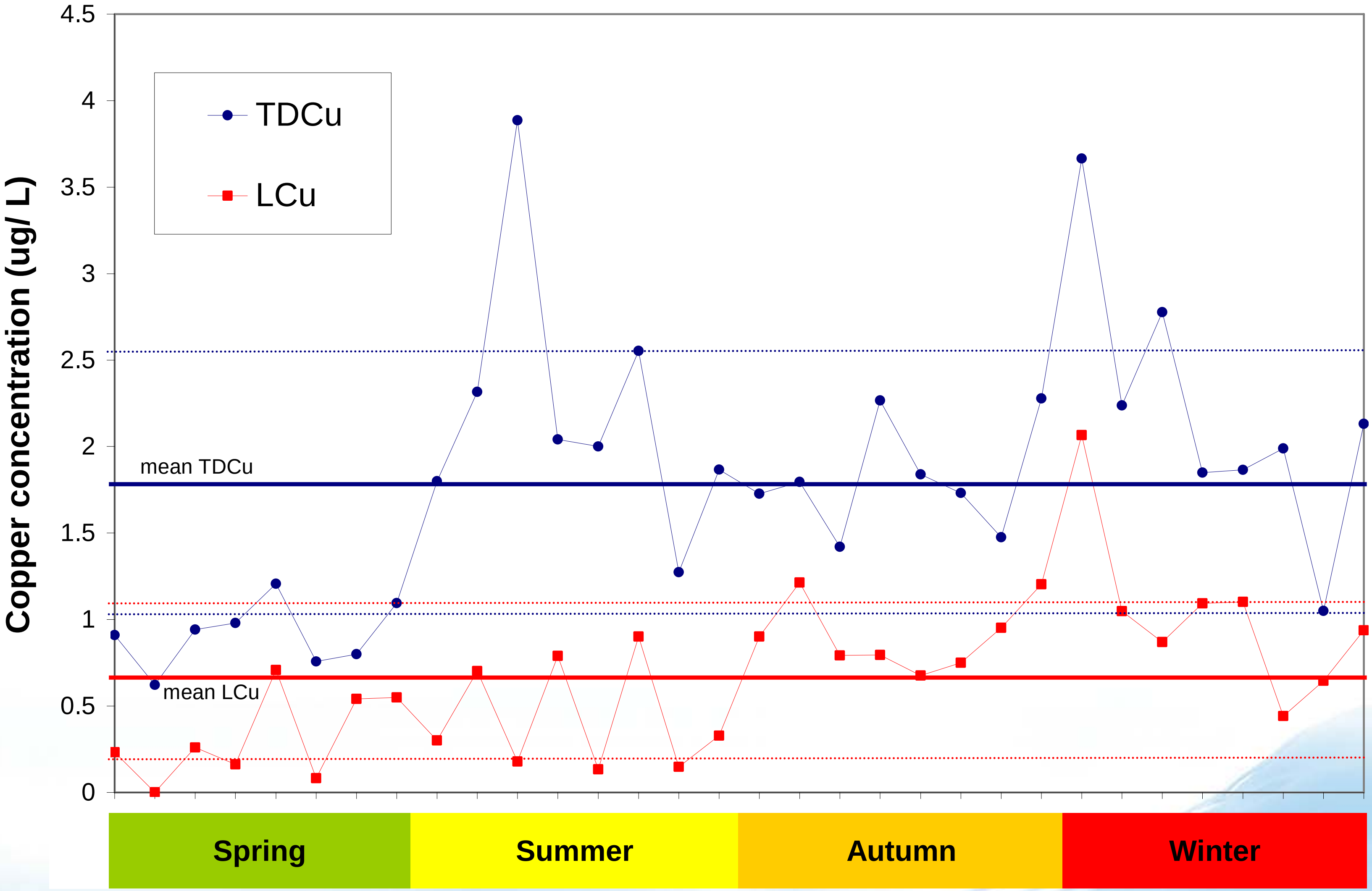
Marinas, ports, coastal waters and sediments	Generally below detection limits although 1 report of 100 nm	Europe (UK), and Asia (Japan)	Very few surveys performed

Copper monitoring

- Measurements of copper (TDCu and LCu) in marinas, ports and harbours
- Other measurements: DOC, SPM
- Seasons, depths
- UK and Finland

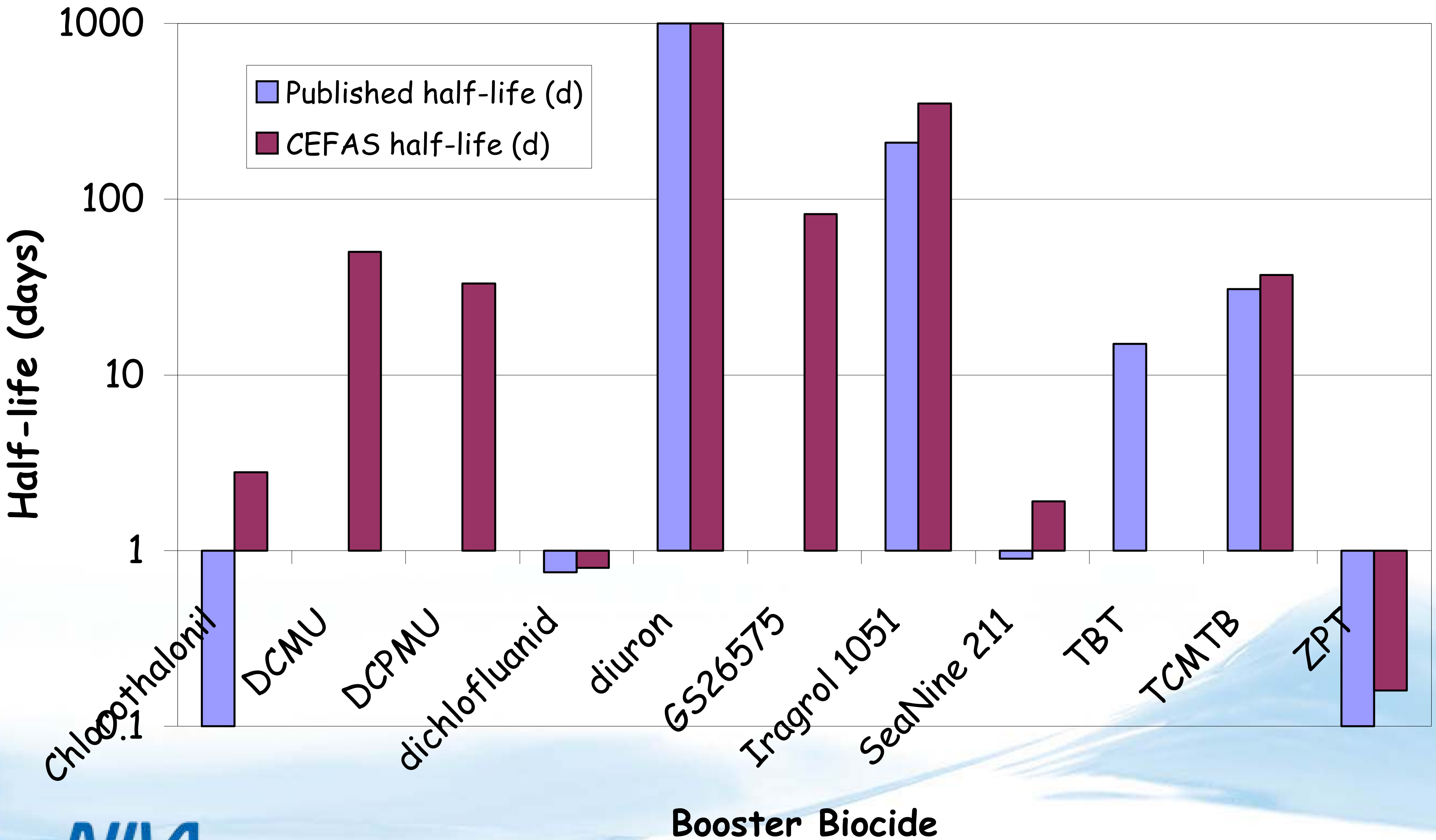


Finnish marina: Copper



Brooks et al., 2007

Persistence in seawater



Sediment/water partitioning

Biocide	K_d (Kg l^{-1})	Log K_{OC}*
Irgarol 1051	141	3.9
Diuron	4 ± 1	2.4 ± 0.2
Sea-Nine 211	253	4.2
chlorothalonil	37	3.3
TCMTB	8	2.7
GS26575	< 1	1.3-1.7
DCPMU	Not measurable	
DCPU	Not measurable	

* Sediment TOC 1.7 %.

Persistence in sediments

Compound	Free biocide		
	k_h (h^{-1})	$t_{1/2}$ (days)	RSD (%)
CPDU	0.02	35	50.1
chlorothalonil	-	< 0.5	-
DCPMU	0.68	1.0	11.7
DCPU	0.23	3.0	17.1
dichlofluanid	-	< 0.5	-
diuron	0.05	14	1.7
GS26575	0.065	226	70.0
Irgarol 1051	-	No Deg.	-
SeaNine 211	-	< 0.5	-
TCMTB	0.46	1.5	24.0

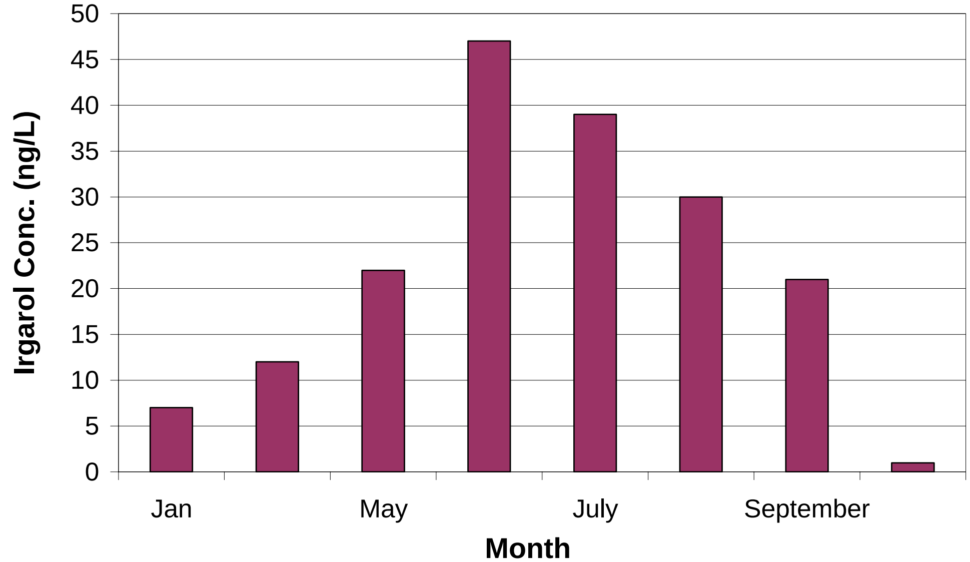
Paint particles/chips

- Hosing and scraping of small boat hulls is often unregulated and occurs on the foreshore and marina hard standings.

Pressure hosing inputs

Run-off from 5 boats

(3 Irgarol 1051, 2 diuron)



Biocide	Concentration (µg l^{-1}) Total	Dissolved	Estimated input† (mg/boat)
Irgarol 1051	81	17 (21 %)	50.6
GS26575	51	15 (29 %)	31.9
diuron	55	13 (24 %)	51.5

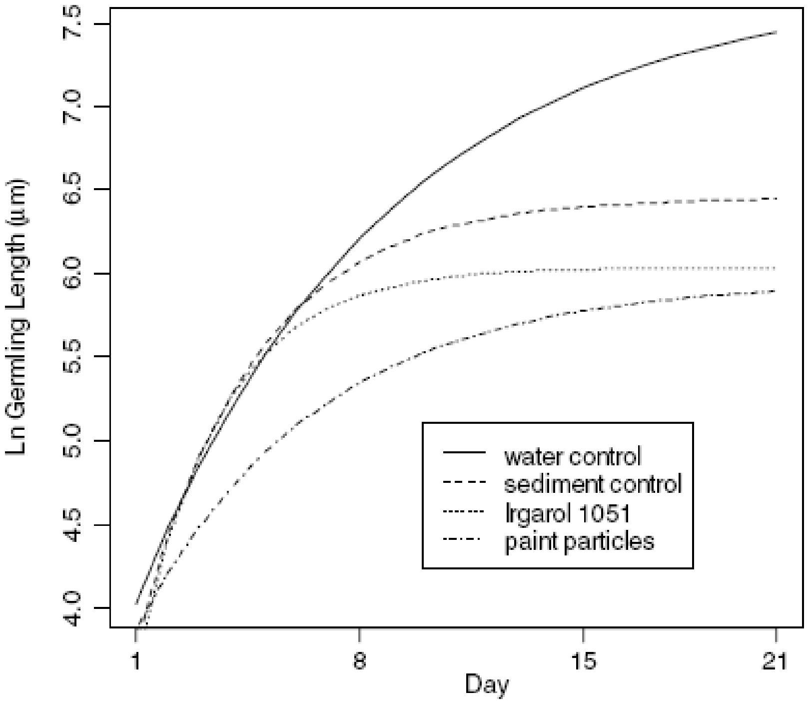
† Estimated from 375 L of water used to hose down 1 boat.

Pseudo-first order degradation rate constants and half-lives (sediments)

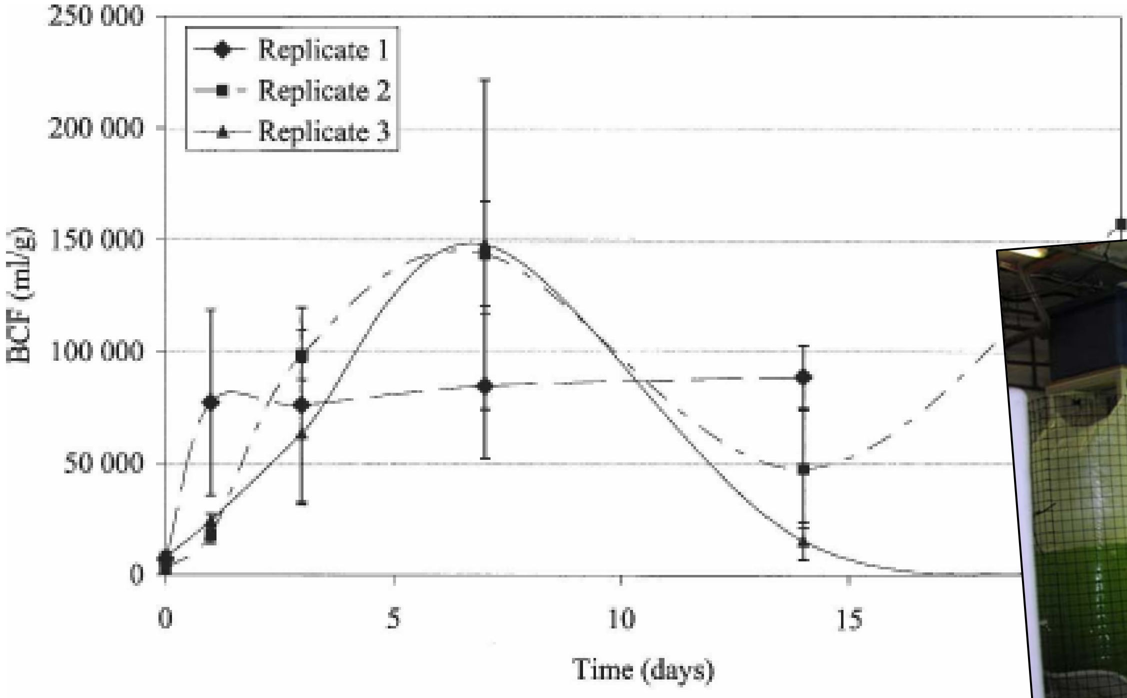
Compound	Free biocide			Paint particle bound		
	k_h (h^{-1})	$t_{½}$ (days)	RSD (%)	k_h (h^{-1})	$t_{½}$ (days)	RSD (%)
CPDU	0.02	35	50.1	-	-	-
chlorothalonil	-	< 0.5	-	-	-	-
DCPMU	0.68	1.0	11.7	-	-	-
DCPU	0.23	3.0	17.1	-	-	-
dichlofluanid	-	< 0.5	-	0.48	14	9.1
diuron	0.05	14	1.7	6.3×10^{-3}	110	23.8
GS26575	0.065	226	70.0	-	-	-
Irgarol 1051	-	No Deg.	-	-	No Deg.	-
SeaNine 211	-	< 0.5	-	0.07	9.9	29.3
TCMTB	0.46	1.5	24.0	-	-	-

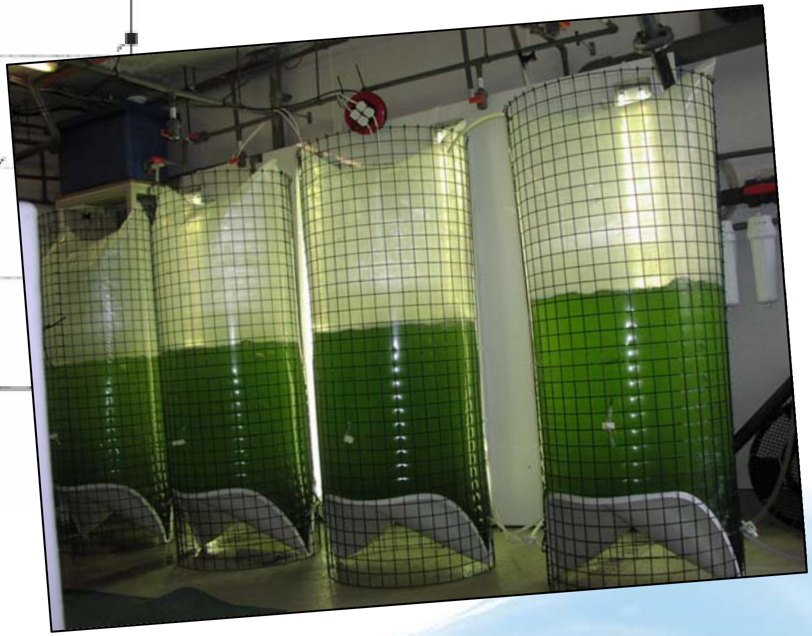
Disturbance of paint chips

- Effects of resuspending Irgarol 1051 contaminated sediment:
  - 60 mg Kg^{-1} paint
  - 0.3 µg L^{-1} aqueous conc.



Bioaccumulation: Irgarol 1051

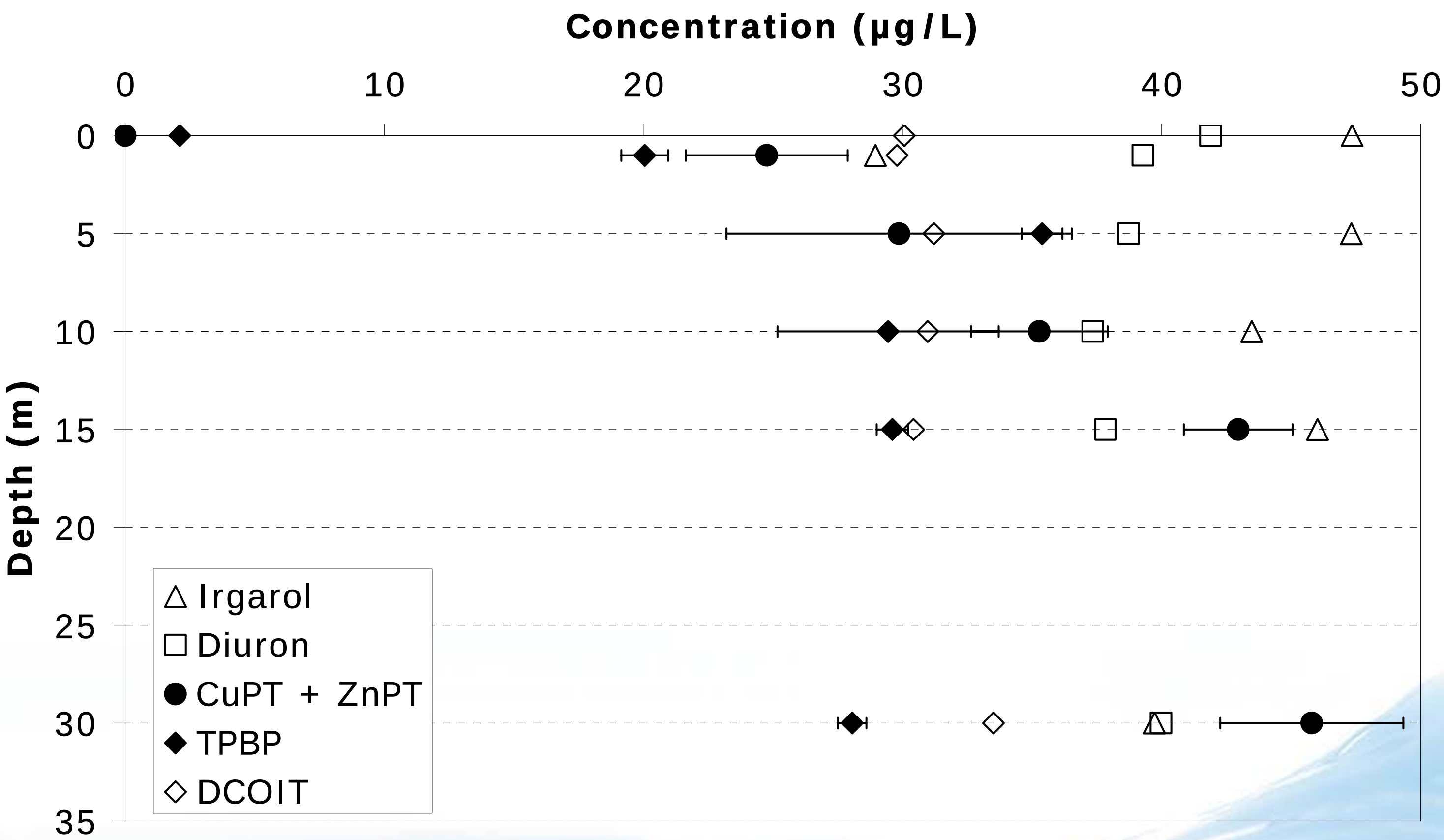




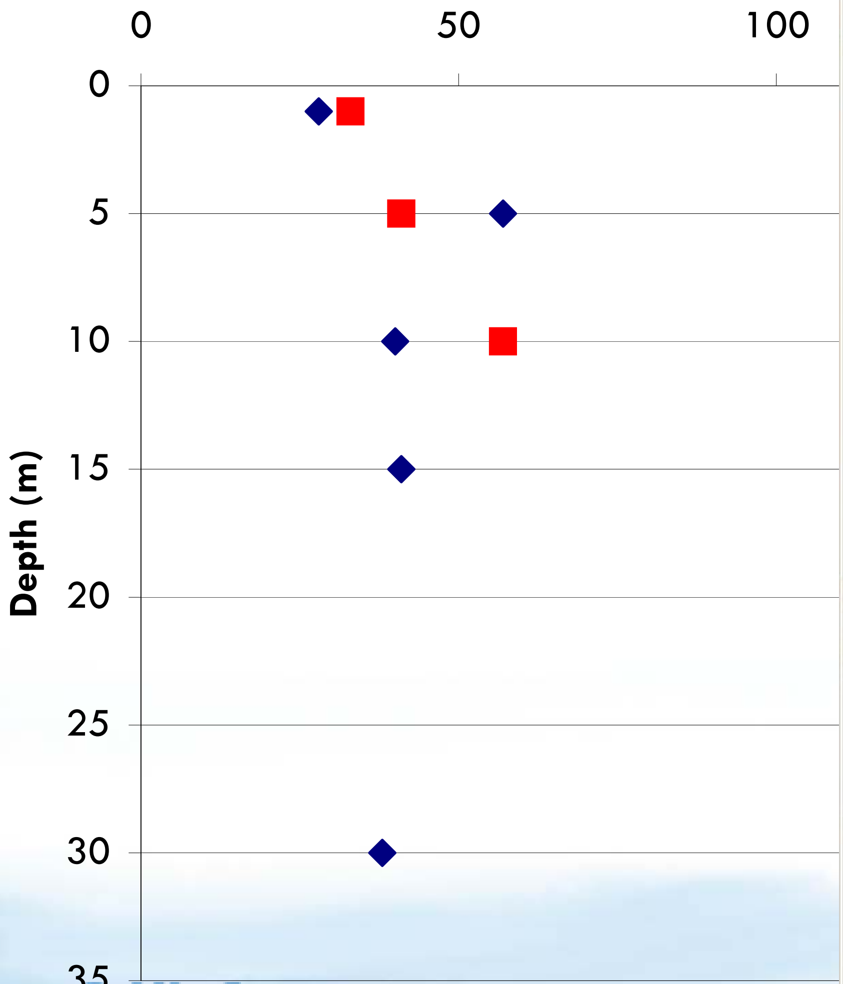
Photolysis: Lab vs. field

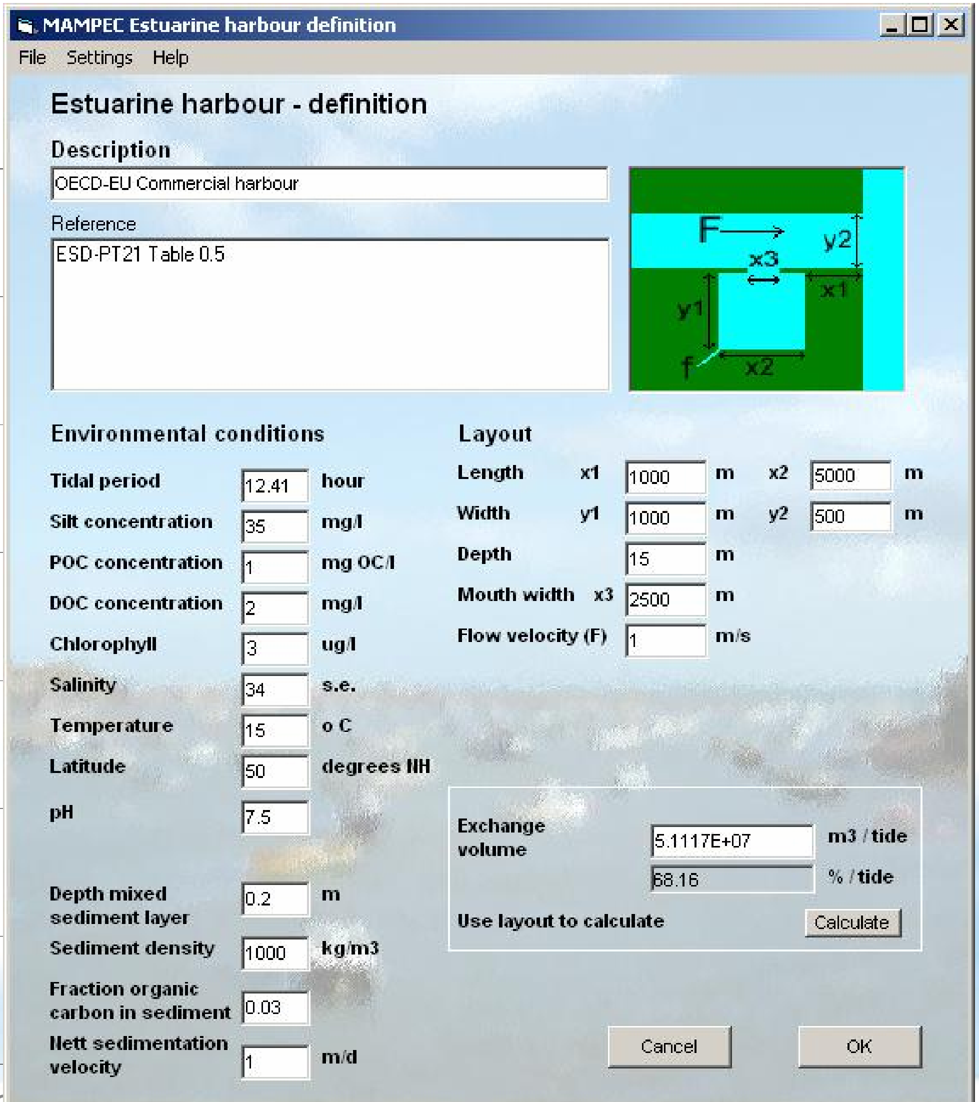
- Comparison of photlysis rates of photolabile biocides with depth

Changes in half-life with depth

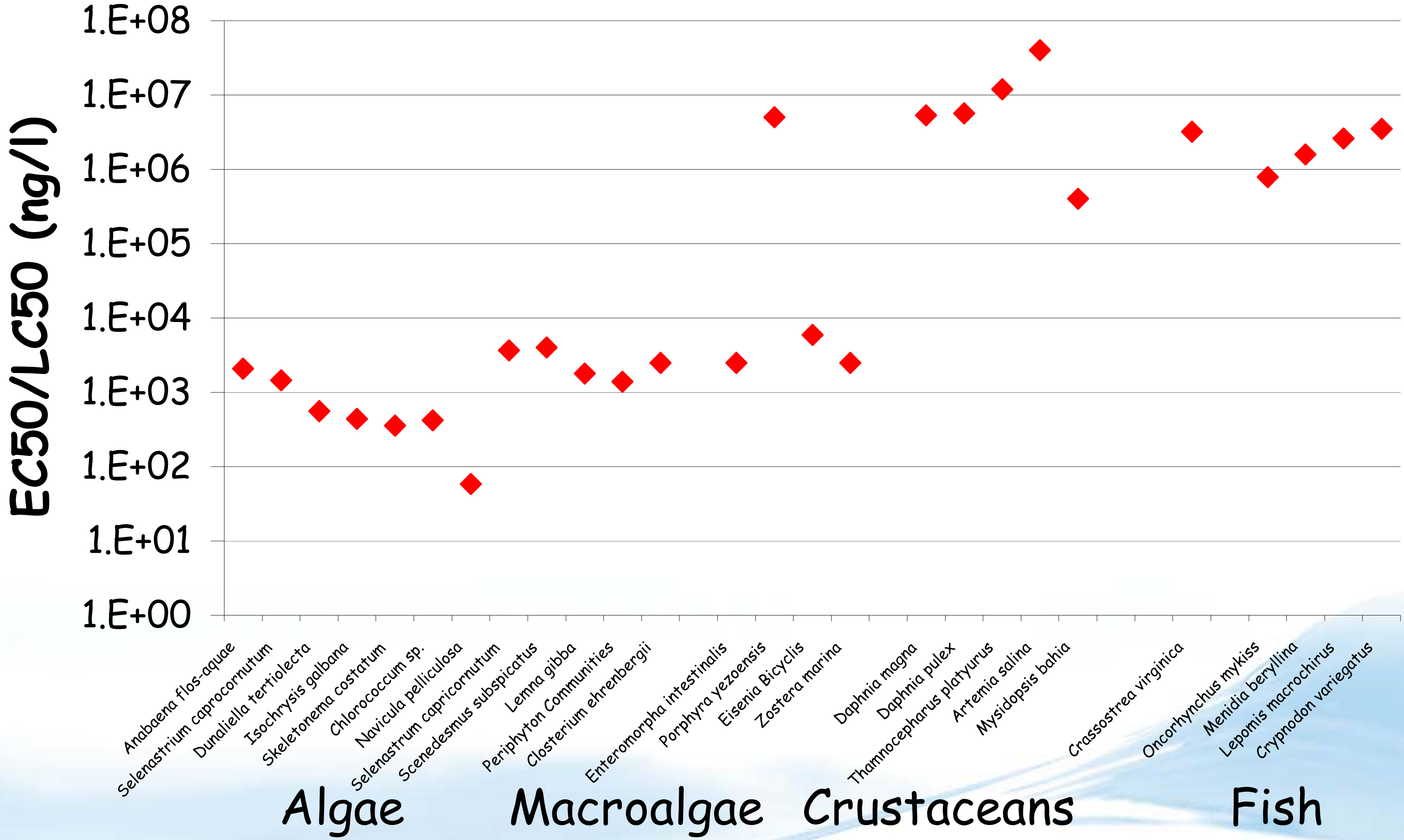


How does this affect half-lives

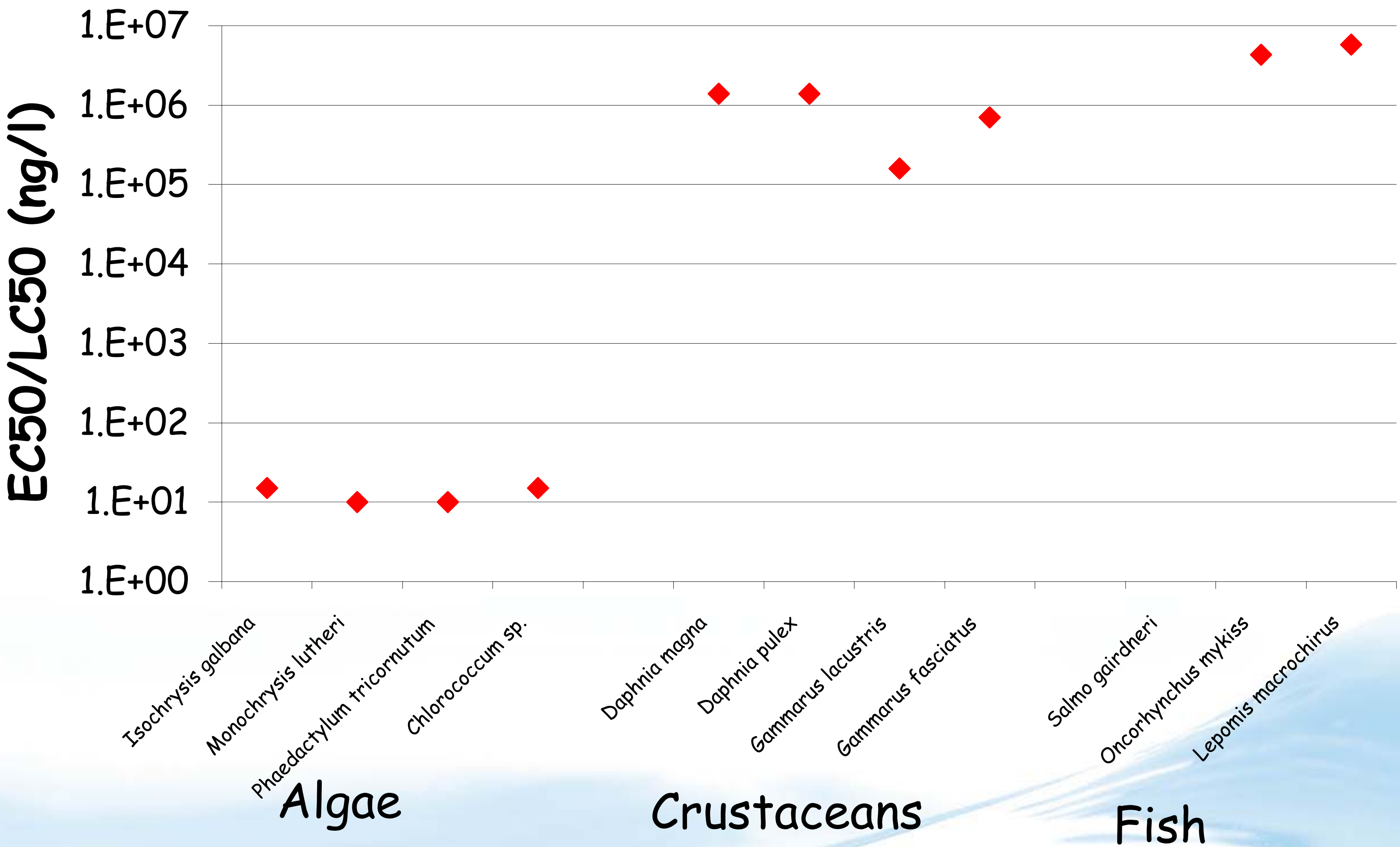




Aquatic toxicology (Irgarol 1051)



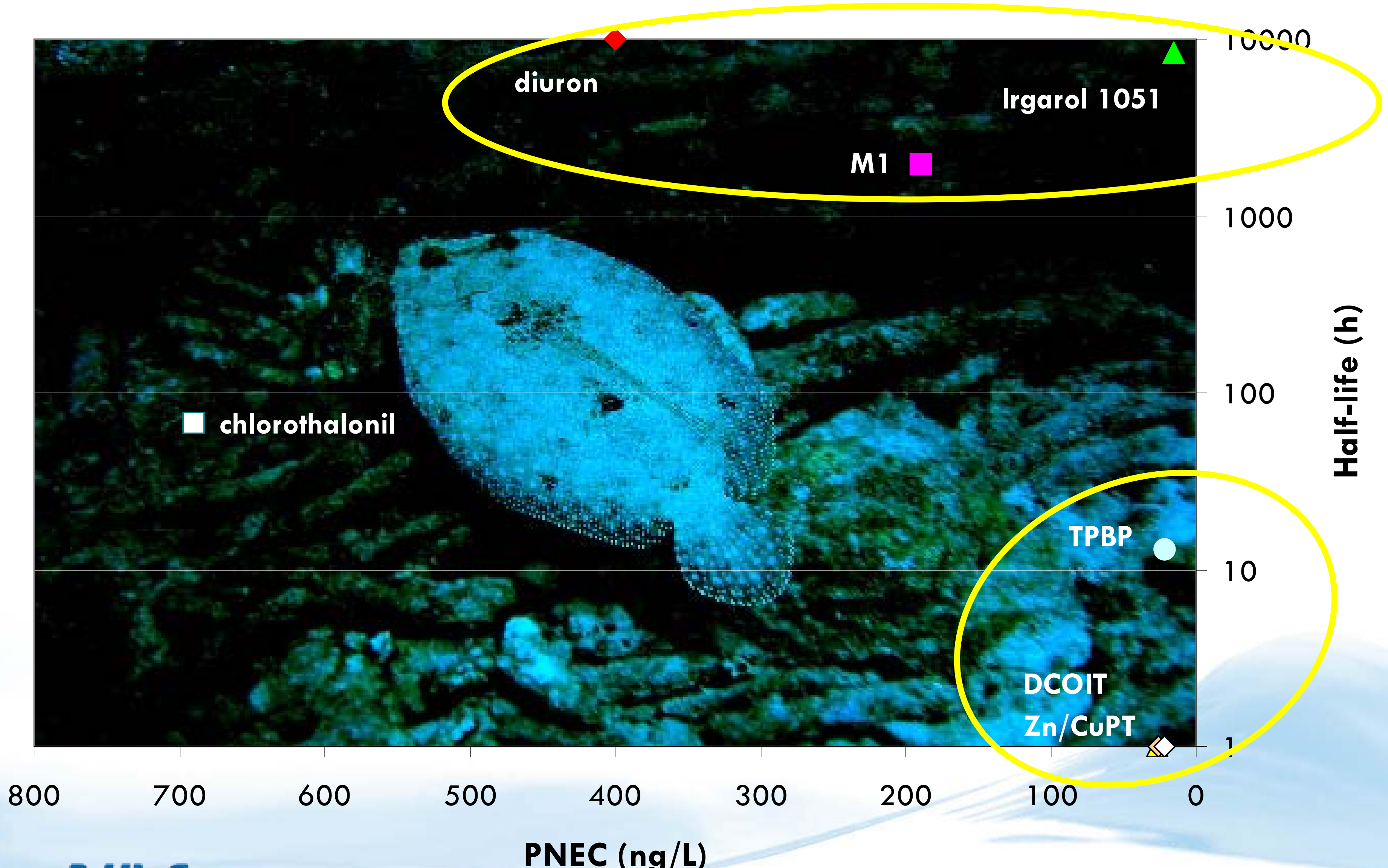
Aquatic toxicology (Diuron)



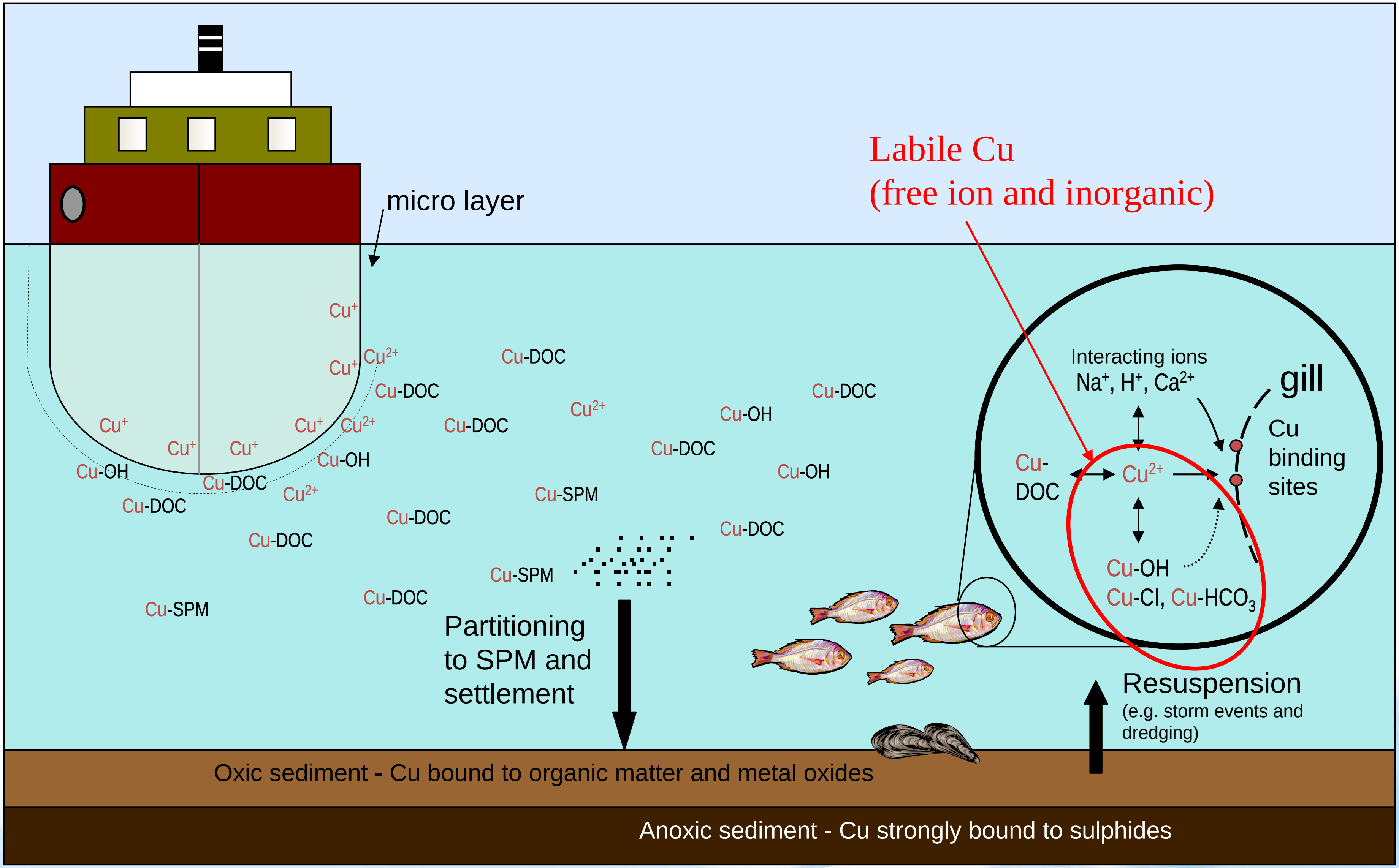
Lets not forget inland waterways!

	Mean MEC (ng l^{-1})			Risk Quotients MEC/NOEC					
				Chara vulgaris			*Apium nodiflorum*		
	Irgarol 1051	GS26575	Diuron	Irgarol 1051	GS26575	Diuron	Irgarol 1051	GS26575	Diuron
Hickling Boat House	170	10	74	**85**	**1**	**2.1**	**1.7**	1.0	0.4
Hickling Boat Channel	545	22	84	**273**	**2.2**	**2.4**	**5**	**2.2**	0.4
Ormesby Little Broad	951	231	67	**475**	**23**	**1.9**	**9**	**23.1**	0.3
Lyonex Marina	24	7	49	**12**	0.7	**1.4**	0.2	0.7	0.2
Landamores Yd	26	17	169	**13**	**2**	**4.8**	0.3	1.7	0.8
Brinks Marina	1256	14		**628**	**1**		**12**	1.4	
Surlingham Broad	52	6	65	**25**	0.6	**1.9**	0.5	0.6	0.3
Rockland Broad	1222	52	107	**611**	**5**	**3.1**	**12.2**	**5**	0.5
Rockland St mary	483	37	249	**241**	**4**	**7.1**	**4.8**	**3**	**1.2**
Gt. Ouse Littleport	85	4	84	**42**	0.4	**2.4**	0.9	0.4	0.4
R.Wissey	497	10		**248**	1		**5**	1.0	
Ouse Cut Off	5	157		**2.5**	**15**		0.1	**15**	

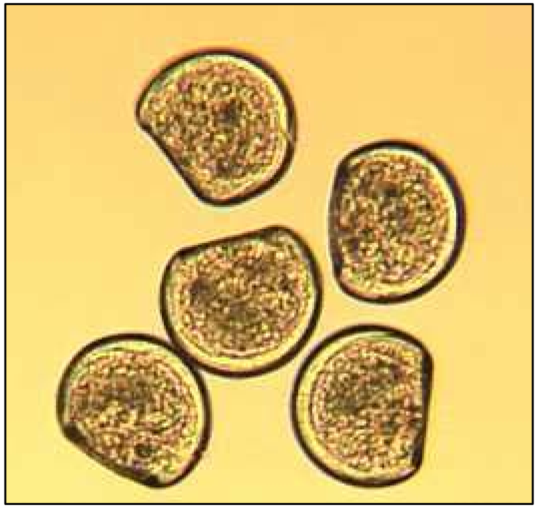
Biocide risk

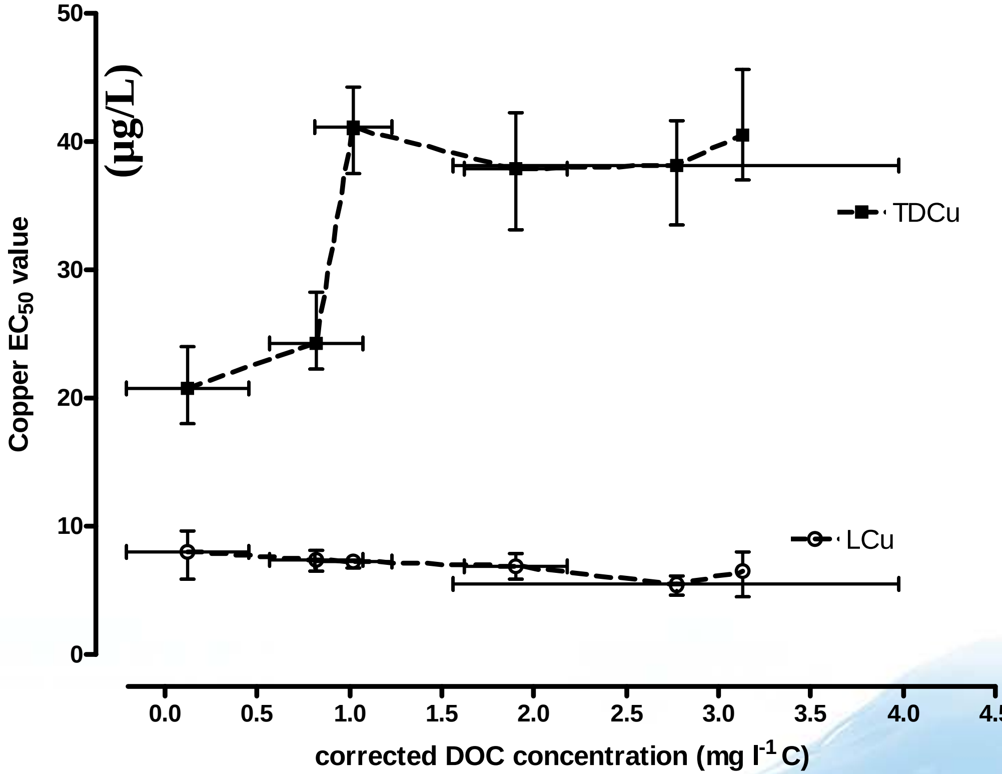


Copper speciation and bioavailability



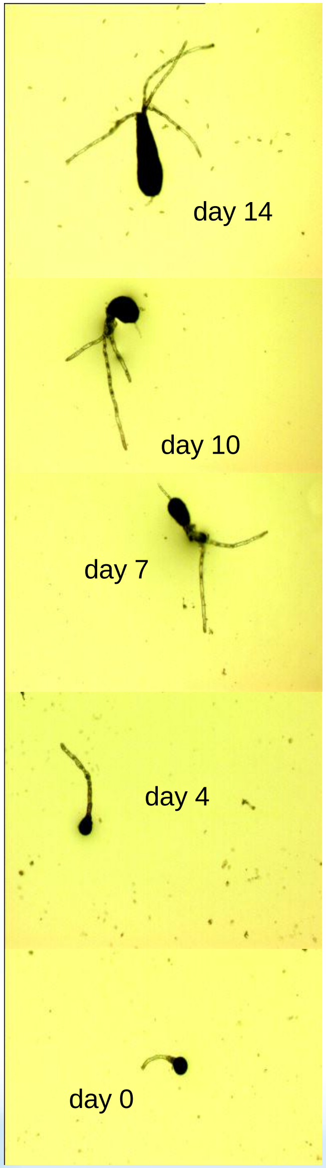
DOC effects on copper toxicity to oyster embryos

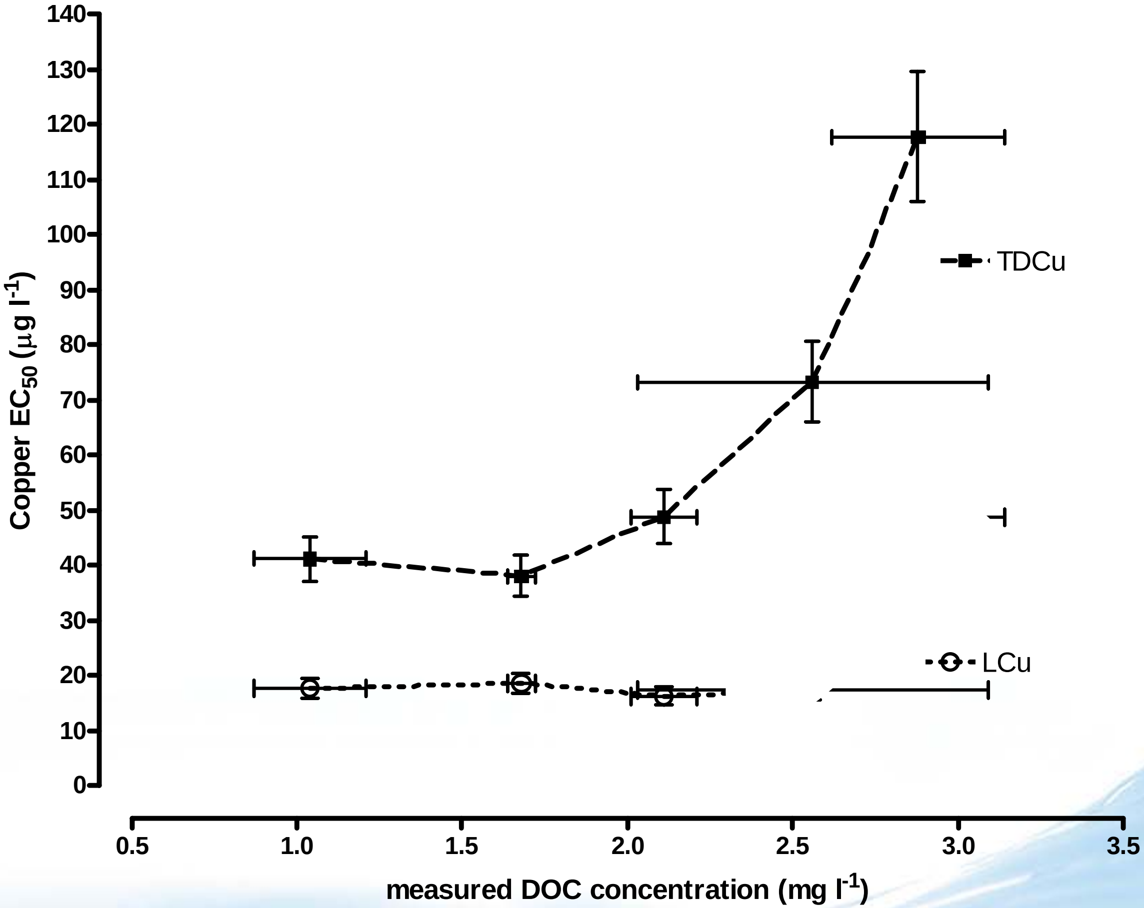




Brooks et al., 2007

DOC effects on copper toxicity to Fucus germlings





Brooks et al., 2008

Simple Copper Risk Assessment

$$\frac{\text{Predicted Environmental Concentration (PEC)}}{\text{Predicted No Effect Concentration (PNEC)}} = >1 \text{ (harm)}$$

Total Dissolved Copper: **worst case**

		In marina	Outside marina
Measured Total Dissolved Copper 6.68 (3.60) / Predicted No Effect Concentration 5	=	1.34	0.72

		In marina	Outside marina
Measured labile copper 2.69 (0.38) / Predicted No Effect Concentration 5	=	0.54	0.08

Summary

- Fully understanding the fate, behaviour and effects of biocides allows thoughough ERA.
- An environmentally safe biocde is one which poses little risk to the environment even when it is missused.

Acknowledgements

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