AARHUS
UNIVERSITY

DCE – DANISH CENTRE FOR ENVIRONMENT AND ENERGY

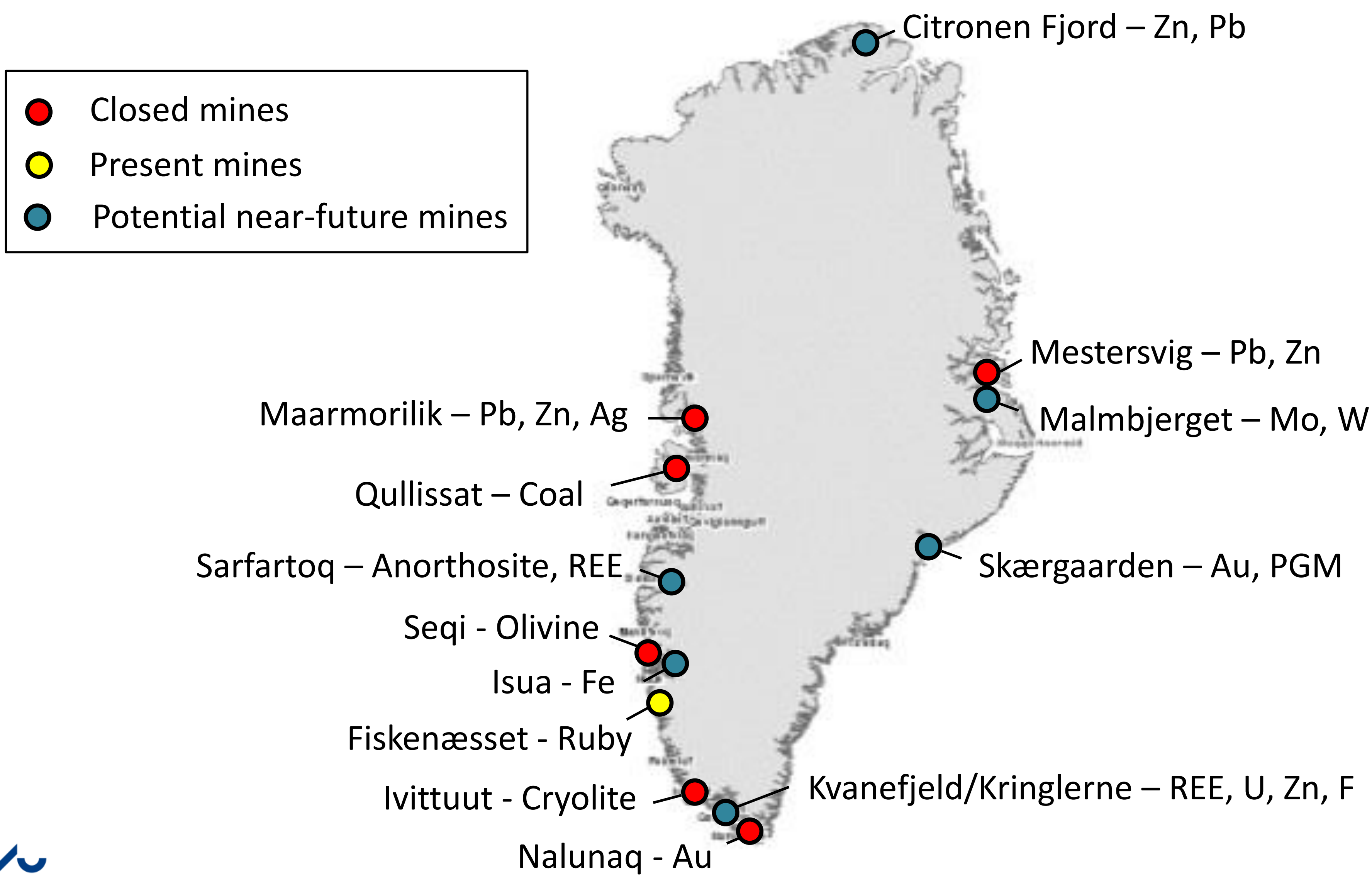
SCIENCE FOR THE ENVIRONMENT CONFERENCE, 1-2 OCTOBER 2015

Application of DGT passive samplers and key monitoring species for measuring bioavailable metal loading in mining-polluted Greenlandic fiords

Jens Søndergaard, Senior Advisor, Geochemist, Ph.D.

Maarmorilik lead-zinc mine, West Greenland

Mines in Greenland



AARHUS UNIVERSITY

Methods for environmental monitoring near mines in Greenland

Sampling:

- Sea- and freshwater
- Sediment
- A range of key monitoring species, typically:
  - Seaweed (*F. vesiculosus*)
  - Mussels (*M. edulis*)
  - Sculpins (*M. scorpius*)
  - Lichens (*F. nivalis*)
- Passive samplers (DGT) – 'bioavailable' metal conc.

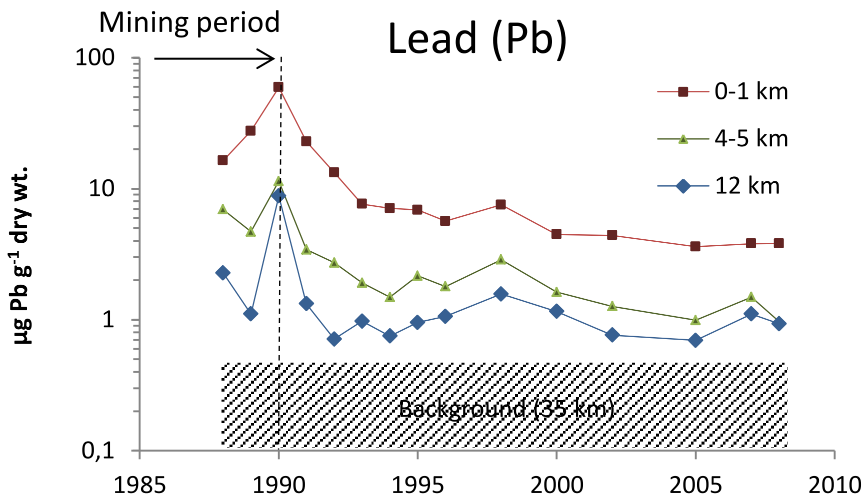
Chemical analyses:

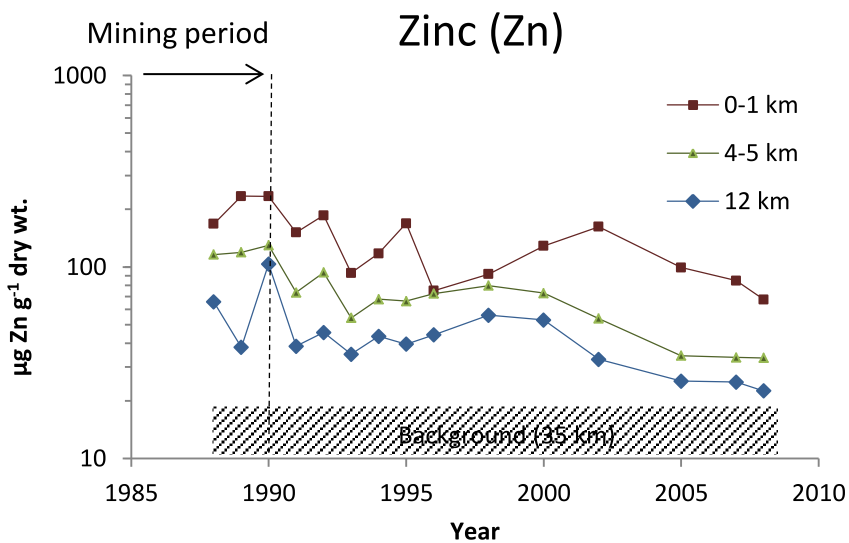
- Element/isotopic composition (ICP-MS, AAS, FIMS, AMA-254, AFS)

Data treatment:

- Comparison with baseline data and reference sites
- Geochemical tracer studies – lead isotopes, element ratios
- Modelling of metal speciation and bioavailability

Seaweed, growth tips, Maarmorilik lead-zinc mine



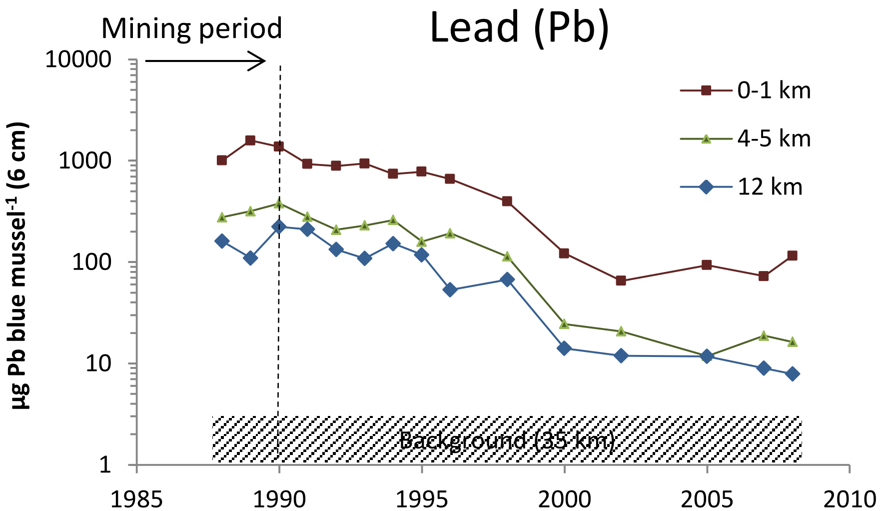


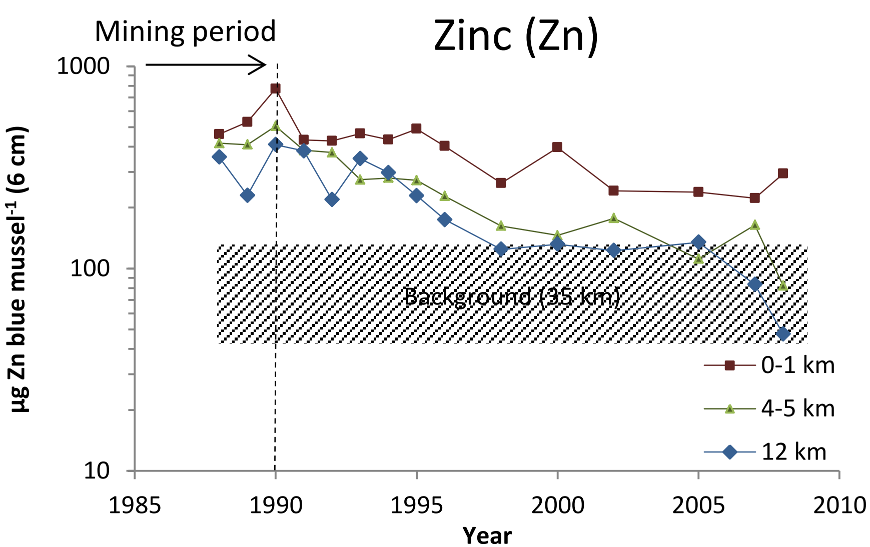
Seaweed (*Fucus distichus*)

AARHUS UNIVERSITY

From Søndergaard et al. 2011. Mar Environ Res 71, 331-41

Blue mussels, resident population, Maarmorilik



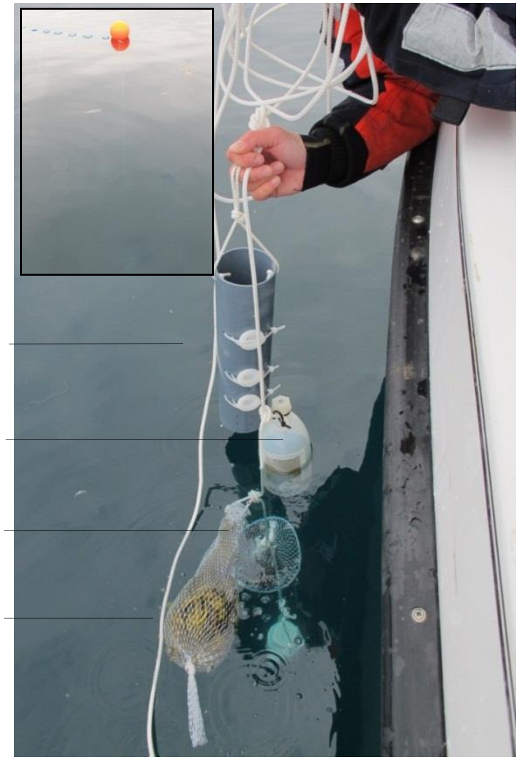


Blue mussels (*Mytilus edulis*)

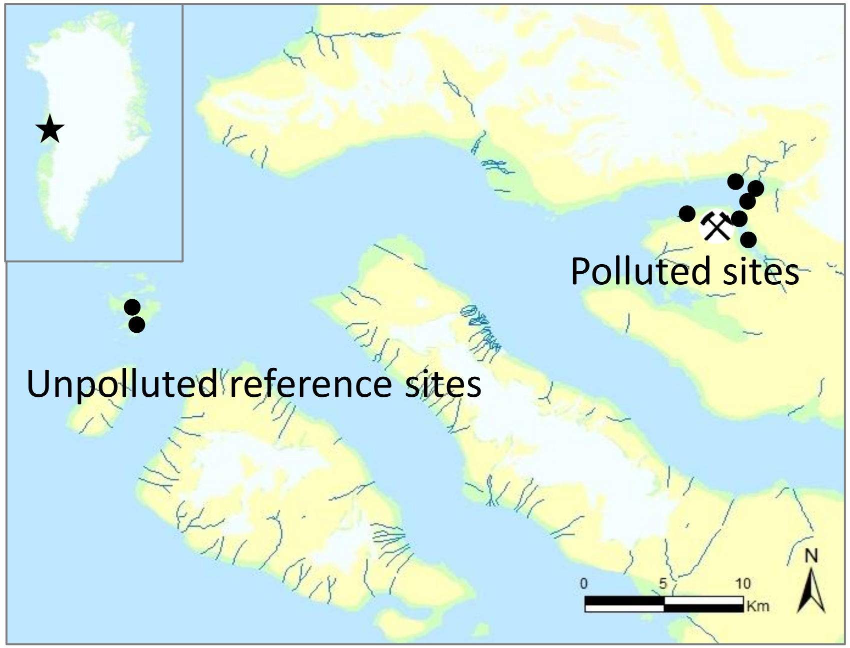
AARHUS UNIVERSITY

From Søndergaard et al. 2011. Mar Environ Res 71, 331-41

Measuring short-term site- and depth-specific metal loading in the marine environment using monitoring bouys (Maarmorilik, 2012-2013)



The monitoring bouy setup, 10 m depth



A total of 8 monitoring bouys were put up during 9 days at the Maarmorilik lead-zinc mine, West Greenland, Aug. 2012,

AARHUS UNIVERSITY

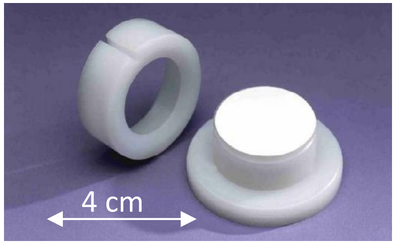
Diffusive gradients in thin films (DGT) – passive samplers

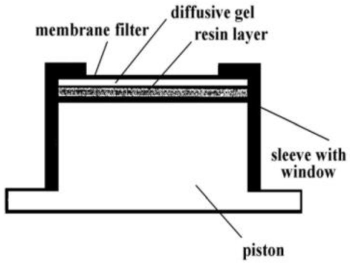
- Samples dissolved small labile ('bioavailable') metal species *in situ* (as opposed to total metal concentrations measured in water samples in the lab)

- Works for typical metals of relevance near mining areas (Cr, Mn, Fe, Ni, Co, Cu, Zn, Ag, Cd, Pb…(Hg))

- Time-integrated concentrations can be measured (hours to weeks) (as opposed to traditional spot water sampling)

- Some analytical advantages compared to analyses of water, especially for seawater analyses (metals pre-concentrated, low salt-interference)





DGT results from the Maarmorilik Pb-Zn mine in 2012

DGT –labile concentrations in µg L^{-1} from the 2 reference sites and 6 polluted sites after 9 days of deployment. The detection limit is calculated as 3 SD on 3 blanks. Underlined results indicate concentrations significantly above the concentration measured at the two reference sites ($p<0.05$).

	Cr		**Mn**		**Fe**		**Ni**		**Co**		**Cu**		**Zn**		**Ag**		**Cd**		**Pb**	
Detection limit (D.l.)	*0.019*		*0.003*		*0.06*		*0.02*		*0.001*		*0.15*		*0.31*		*0.0005*		*0.002*		*0.005*	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Reference Site 1	0.054	0.007	1.678	0.117	2.33	0.15	0.76	0.02	0.077	0.002	0.32	0.10	0.37	0.11	0.0017	0.0026	0.025	0.001	0.013	0.008
Reference Site 2	0.134	0.131	1.480	0.057	2.67	0.06	0.89	0.11	0.080	0.002	0.65	0.26	0.82	0.30	0.0031	0.0031	0.025	0.004	0.031	0.015
Polluted Site 1 (T22)	0.040	0.008	1.195	0.067	2.95	0.47	0.52	0.05	0.045	0.000	0.19	0.06	0.60	0.19	0.0009	0.0011	0.015	0.000	0.135	0.006
Polluted Site 2 (Camp)	0.027	0.003	1.180	0.218	2.87	0.39	0.45	0.06	0.040	0.004	0.17	0.04	0.75	0.55	0.0007	0.0004	0.018	0.003	0.292	0.260
Polluted Site 3 (T17)	0.030	0.008	1.360	0.091	2.86	0.57	0.51	0.04	0.046	0.002	0.30	0.17	1.22	0.56	0.0012	0.0004	0.025	0.004	0.488	0.249
Polluted Site 4 (T3)	0.019	0.000	1.378	0.182	3.41	1.67	0.54	0.03	0.043	0.002	0.22	0.10	1.60	1.70	<D.l.	<D.l.	0.017	0.001	0.280	0.198
Polluted Site 5 (T12W)	0.051	0.003	1.346	0.076	3.47	0.29	0.57	0.03	0.046	0.002	0.26	0.16	1.47	1.09	0.0024	0.0026	0.030	0.009	0.506	0.270
Polluted Site 6 (T12E)	0.106	0.100	1.970	0.368	4.55	1.24	0.66	0.08	0.053	0.004	0.56	0.18	3.09	0.72	0.0007	0.0006	0.036	0.006	0.806	0.220

AARHUS UNIVERSITY

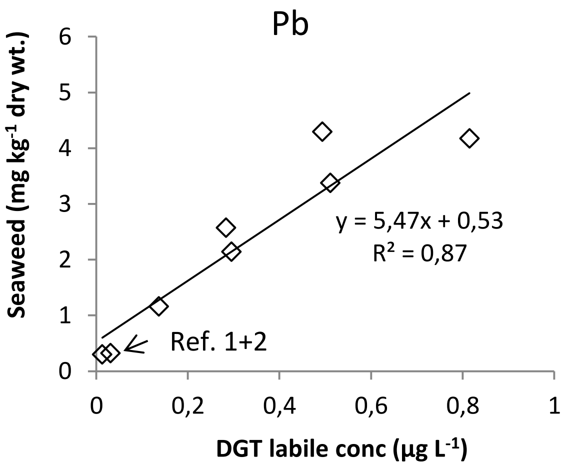
From Søndergaard et al. 2014. Mar Pollut Bull 78, 102-9

Correlation between Pb-, Zn- and Fe concentrations in seaweed, mussels and sea snails after 9 days deployment and DGT labile concentrations at Maarmorilik.

Correlation matrix showing R^2 values between concentrations of Pb, Zn and Fe in seaweed, blue mussels and sea snails and DGT-labile concentrations after the 9-day deployment period. An asterisk (*) indicates a significant linear trend ($p<0.05$).

	Seaweed	Mussels	Sea snails	DGT
Pb				
Seaweed	1			
Mussels	0.94*	1		
Sea snails	0.79*	0.87*	1	
DGT	0.87*	0.88*	0.97*	1
Zn				
Seaweed	1			
Mussels	0.80*	1		
Sea snails	0.69*	0.64*	1	
DGT	0.82*	0.67*	0.78*	1
Fe				
Seaweed	1			
Mussels	0.72*	1		
Sea snails	0.34	0.27	1	
DGT	0.20	0.62*	0.18	1

Example:



Conclusions from the project

- DGT passive samplers offer a convenient method to measure time-integrated dissolved 'bioavailable' metal concentrations *in situ* (days/weeks) in Greenlandic fiords and is a adequate supplement to traditional spot water sampling.

- Monitoring buoys with DGT samplers and transplanted monitoring species such as seaweed, mussels and sea snails can provide a adequate method to assess <u>present</u> (short-term) loads of bioavailable metals e.g. near mine sites.

- Such monitoring buoys can be a valuable supplement to other monitoring techniques, especially if site- and depth-specific information is required (e.g. near outlets from tailings-/waste rock deposits) or if recent environmental impacts have to be evaluated based on a single field trip.

- Correlations between uptake of Pb, Zn and Fe between the species/DGT samples indicate that uptake of Pb is relatively simple with little or no internal body regulation, in contrast to Zn and Fe where mechanisms for accumulation are more complex.

- More than 2 decades after mine closure, there is still a significant load of bioavailable Pb, Zn and Fe near the former Maarmorilik Pb-Zn mine in West Greenland.

Challenges and opportunities…

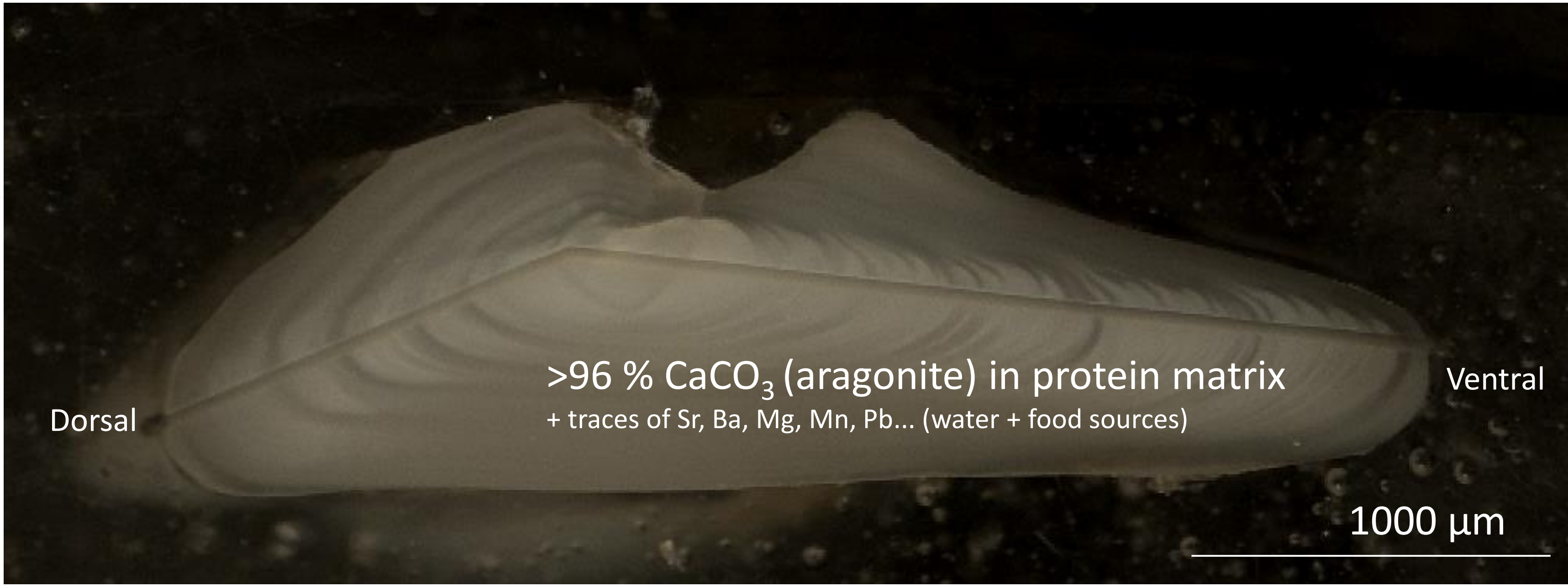
Challenge:

How to estimate the bioavailable metal loading in a mining area back in time?

Opportunities:

?

Otoliths from sculpins as possible new tools to record pollution near mines in Greenland (2013-2015)



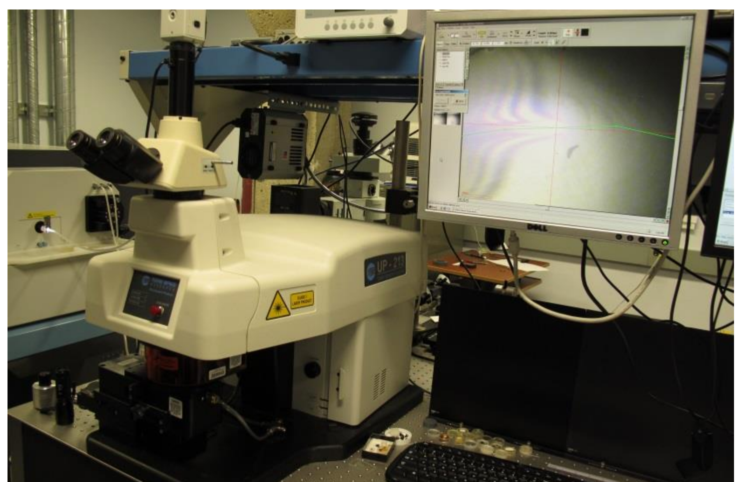
Laser scan through a sculpin otolith

Laser parameters

Beam width: 40 µm

Beam depth ≈ 20 µm

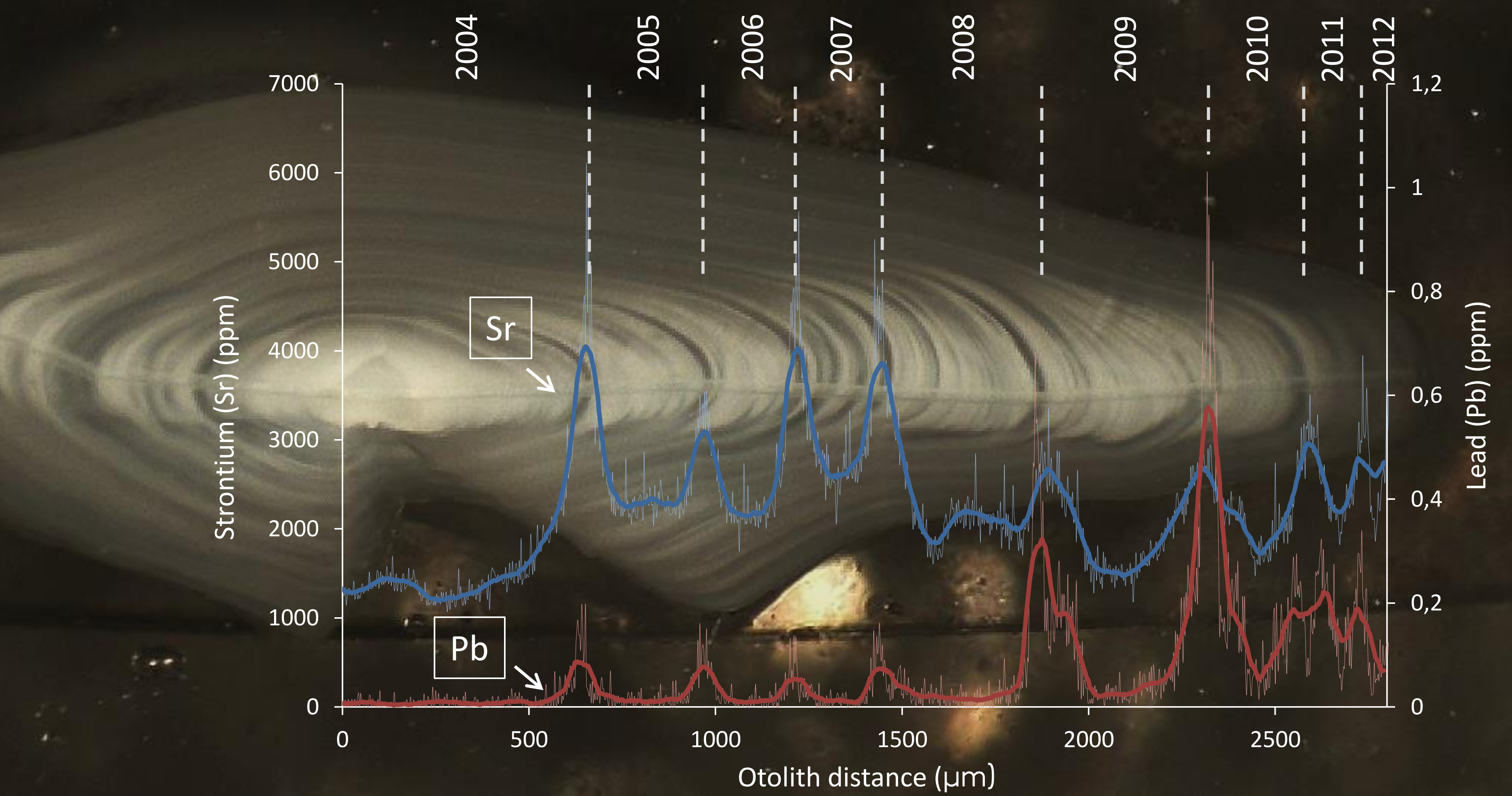
Scan speed: 3 µm s^{-1}



Mechantek LUV 213 Nd:YAG laser at University of Manitoba, Canada

AARHUS UNIVERSITY

Common sculpin, Maarmorilik lead-zinc mine, West Greenland
(#46572, Female, 460 g, c. 8 years)

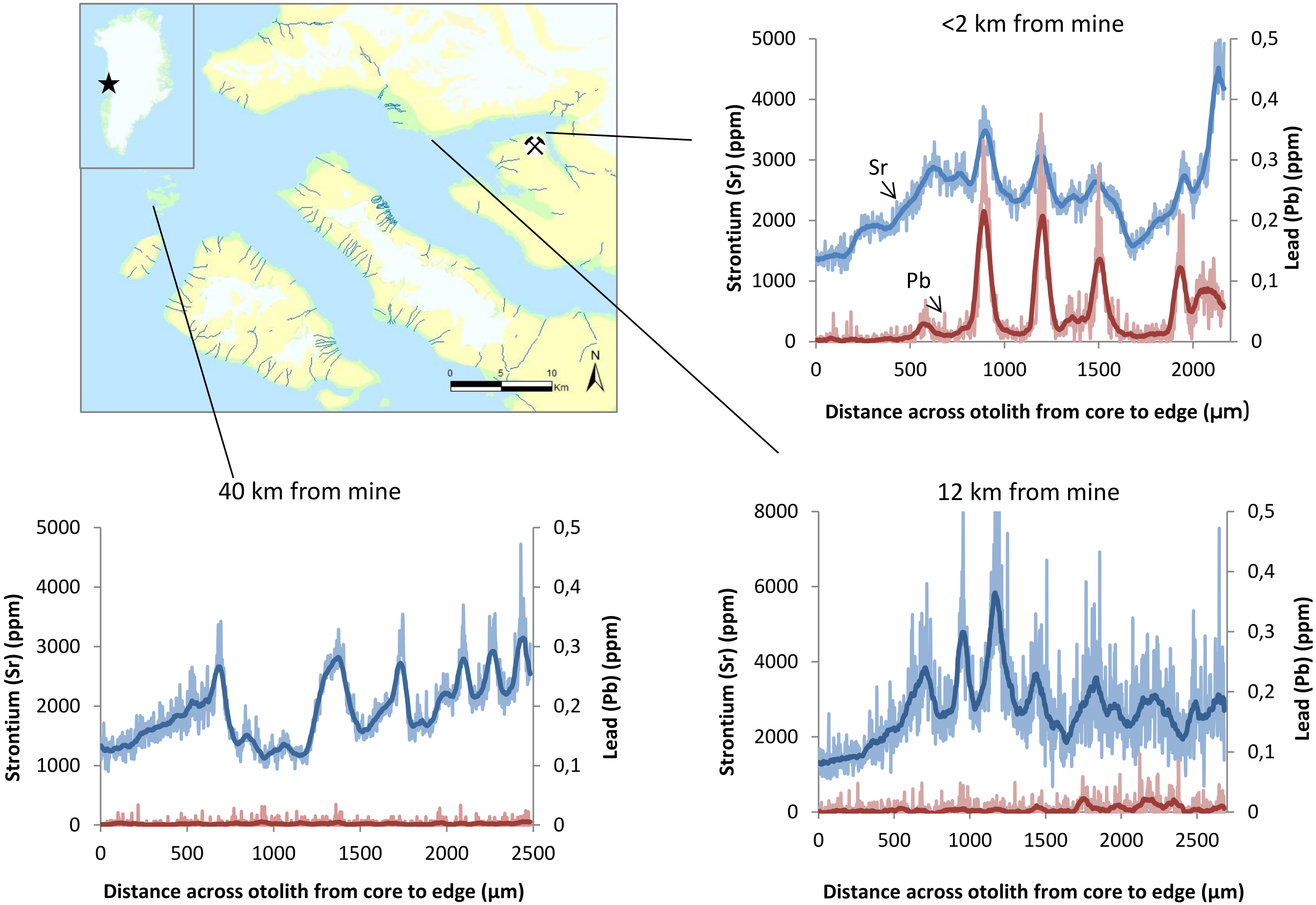


Søndergaard et al. 2015. Water Air Soil Poll., in press

Thank you for your attention!

Questions?

Sculpin otolith chemistry, Maarmorilik lead-zinc mine



From Søndergaard et al., 2015. Water Air Soil Pollut 226, 336-47

Table 1
Element concentrations in transplanted mussels, seaweed and sea snails and in DGT samplers after a 9-day deployment period at 6 monitoring sites and two reference sites in Maarmorilik. Results for biota are in mg kg^{-1} dry wt. DGT results are in μg L^{-1}. Underlined results indicate a concentration above the mean + 3 standard deviations (SD) of concentrations measured at the two reference sites (Ref. St. 1 + 2). d.l. = detection limit determined as 3 SD on blanks. ND = Not determined.

		Cr	Fe	Ni	Cu	Zn	As	Ag	Cd	Hg	Pb
d.l. (biota)		0.05	3	0.08	0.1	0.05	0.2	0.01	0.02	0.03	0.03
Ref. St. 1	Seaweed	0.29	93	2.09	9.7	26	52	0.18	0.94	<d.l.	0.32
Ref. St. 2		0.24	85	2.21	5.4	26	51	0.19	0.96	<d.l.	0.30
St. 22		0.23	102	1.54	4.8	28	52	0.21	0.94	<d.l.	1.16
St. 17B		0.32	162	1.96	11.3	35	43	0.17	0.91	<d.l.	4.29
St. 12E		0.52	233	1.94	7.0	40	55	0.19	1.04	<d.l.	4.18
St. 12SW		0.31	174	1.70	4.6	31	47	0.17	0.82	<d.l.	3.37
Tailings outlet		0.60	332	2.20	4.3	27	43	0.16	0.84	<d.l.	2.14
St. 3		0.51	268	2.52	27.5	31	47	0.18	0.88	<d.l.	2.57
Ref. St. 1	Mussels	1.40	267	3.67	25.7	145	15	0.04	2.53	0.101	1.96
Ref. St. 2		1.26	267	4.08	8.9	138	15	0.04	2.60	0.100	2.16
St. 22		1.50	496	3.70	30.1	194	15	0.10	2.74	0.097	5.57
St. 17B		1.91	864	3.20	9.5	165	15	0.09	2.69	0.097	12.78
St. 12E		2.65	1292	3.98	9.7	172	16	0.08	2.72	0.104	12.98
St. 12SW		1.97	813	4.02	10.2	165	16	0.10	3.03	0.114	9.24
Tailings outlet		2.25	1029	4.18	14.4	142	14	0.08	2.73	0.097	7.21
St. 3		2.16	1043	9.44	10.3	151	14	0.06	2.44	0.102	5.88
Ref. St. 1	Sea snails	0.78	353	2.41	31.1	52	13	1.43	3.28	0.049	0.65
Ref. St. 2		0.96	414	2.76	27.4	50	11	1.16	2.06	<d.l.	0.63
St. 22		0.41	296	2.32	27.7	55	11	1.08	2.43	0.046	1.15
St. 17B		0.75	355	2.33	38.0	58	14	1.35	3.11	0.041	2.74
St. 12E		0.80	474	2.67	24.0	87	14	1.14	3.41	0.047	4.34
St. 12SW		1.08	617	3.08	25.1	63	12	1.16	2.14	0.048	2.47
Tailings outlet		0.78	516	3.21	75.6	53	12	1.10	2.36	0.051	1.63
St. 3		0.69	474	2.01	27.3	50	11	1.18	2.26	0.045	1.26
d.l. (DGT)	DGT	0.019	0.1	0.02	0.15	0.31	ND	0.0005	0.002	ND	0.01
Ref. St. 1		0.135	2.7	0.90	0.66	0.83	ND	0.0032	0.025	ND	0.03
Ref. St. 2		0.054	2.4	0.77	0.32	0.37	ND	0.0017	0.025	ND	0.01
St. 22		0.040	3.0	0.52	0.19	0.61	ND	0.0009	0.015	ND	0.14
St. 17B		0.030	2.9	0.52	0.30	1.23	ND	0.0012	0.025	ND	0.49
St. 12E		0.107	4.6	0.67	0.57	3.12	ND	0.0007	0.037	ND	0.81
St. 12SW		0.052	3.5	0.57	0.27	1.49	ND	0.0024	0.031	ND	0.51
Tailings outlet		0.027	2.9	0.46	0.17	0.76	ND	0.0007	0.018	ND	0.30
St. 3		0.019	3.4	0.54	0.22	1.62	ND	0.0000	0.018	ND	0.28

From Søndergaard et al. 2014. Mar Pollut Bull 78, 102-9

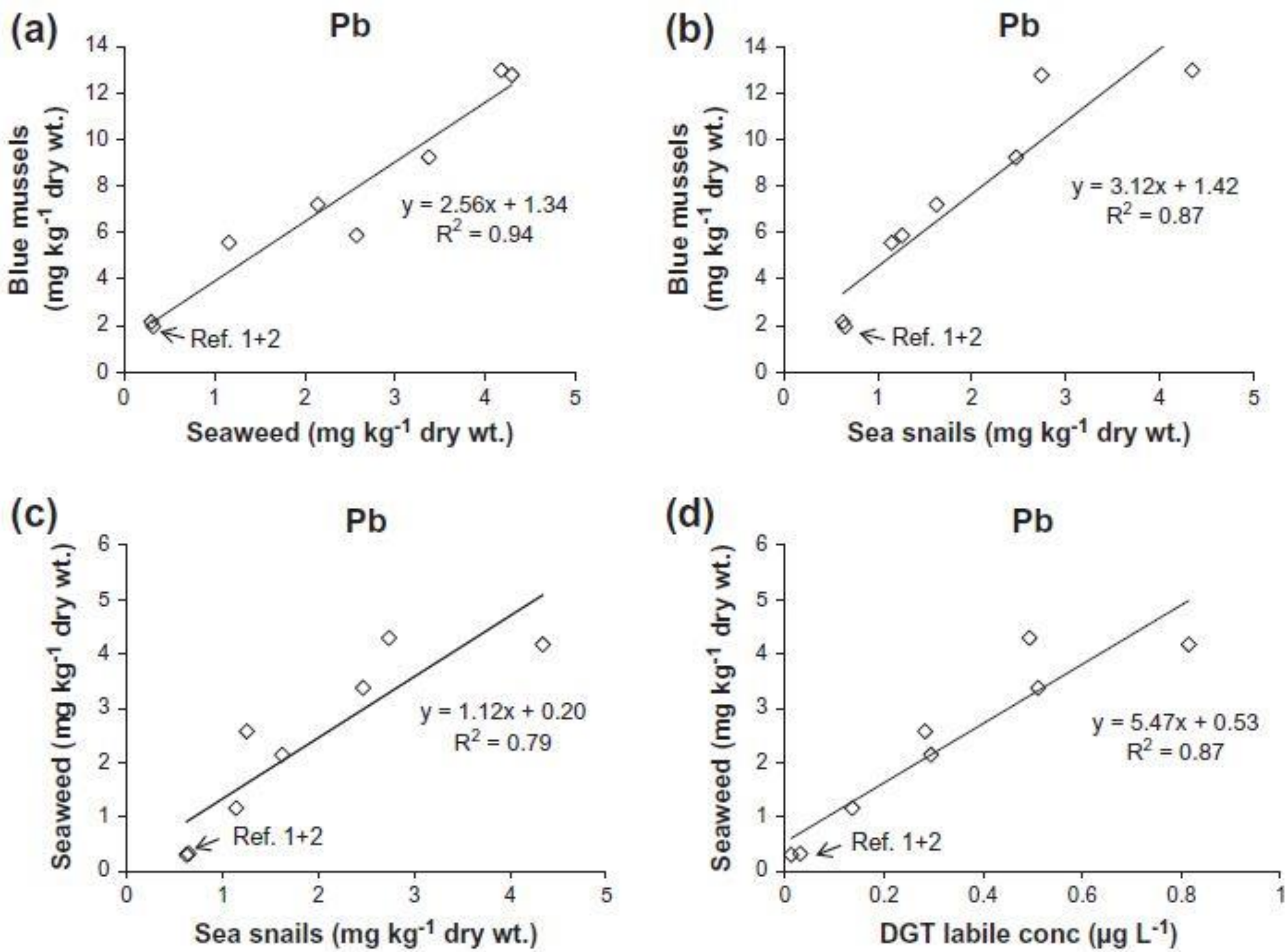


Fig. 2. Selected correlations between Pb concentrations in transplanted mussels, seaweed and sea snails at six monitoring sites and two reference sites after a 9-day deployment period (a, b and c). Figure d shows the correlation between Pb concentrations in seaweed and the DGT labile metal concentrations. The points representing the two reference sites are marked and linear trend lines are shown.

From Søndergaard et al. 2014. Mar Pollut Bull 78, 102-9

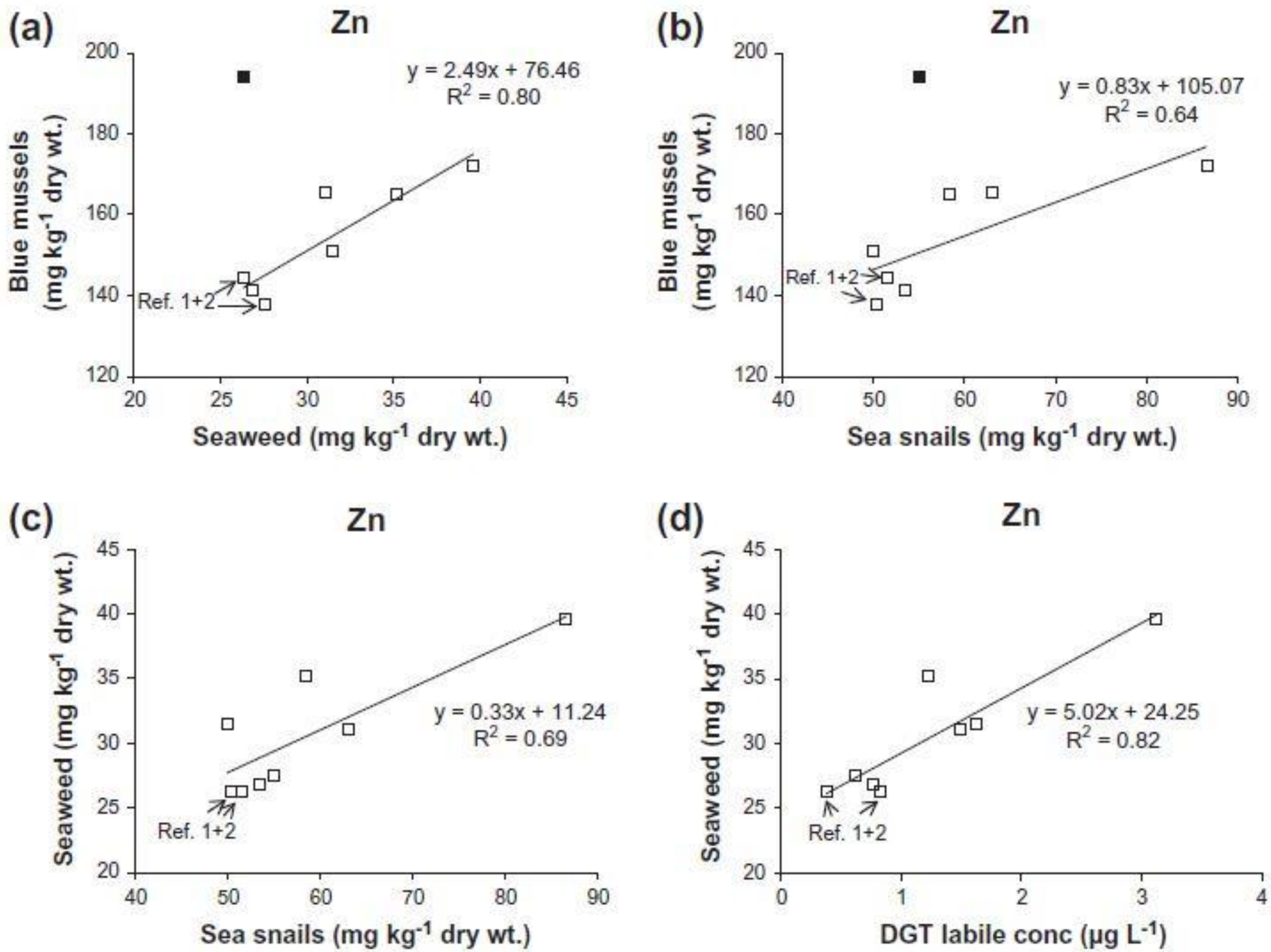


Fig. 3. Selected correlations between Zn concentrations in transplanted mussels, seaweed and sea snails at six monitoring sites and two reference sites after a 9-day deployment period (a, b and c). Figure d shows the correlation between Zn concentrations in seaweed and the DGT labile metal concentrations. The points representing the two reference sites are marked and linear trend lines are shown. The Zn concentration in mussels at St. 22 was abnormally high and not included in the trend line (point shown with solid fill).

From Søndergaard et al. 2014. Mar Pollut Bull 78, 102-9

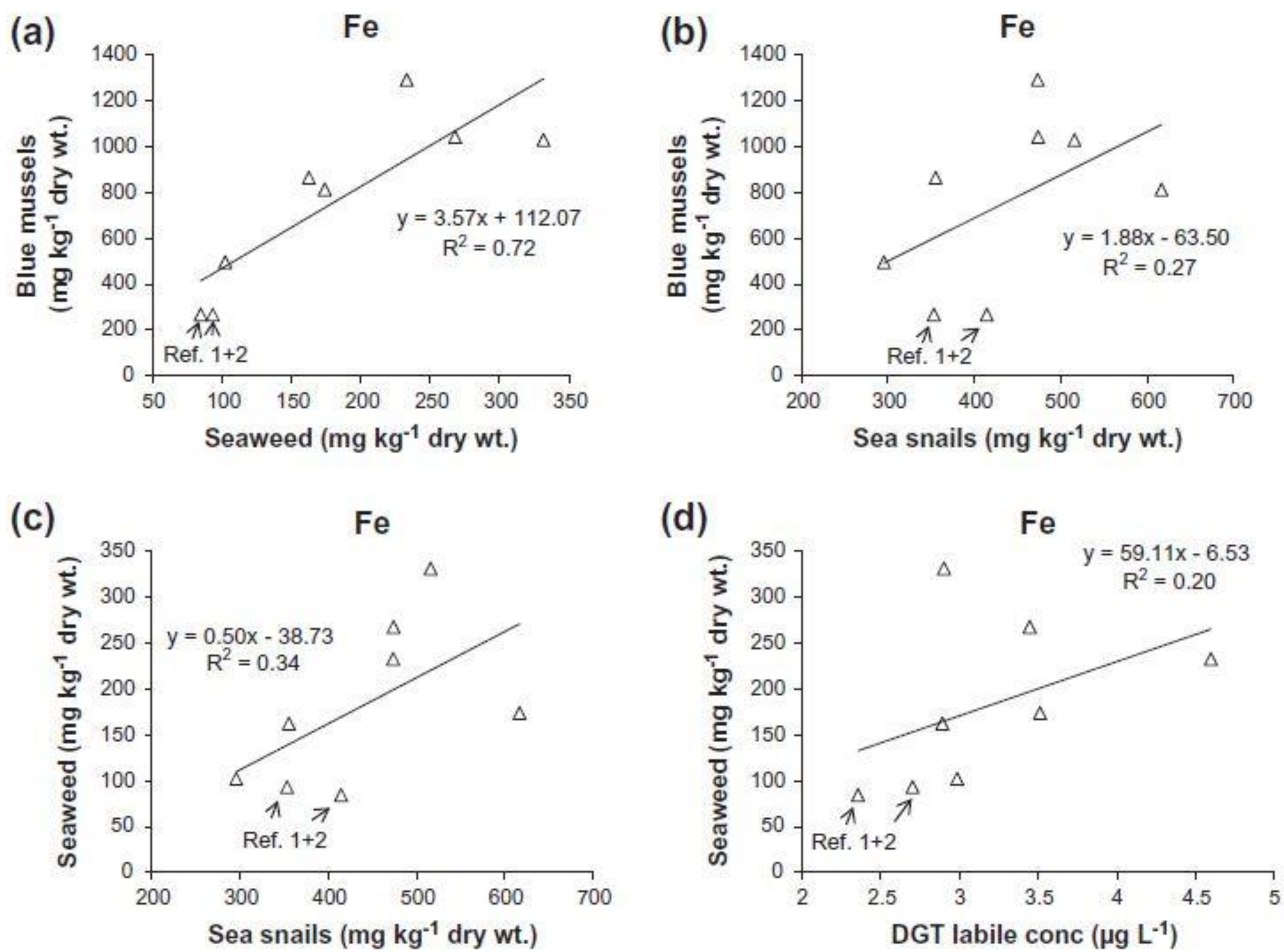


Fig. 4. Selected correlations between Fe concentrations in transplanted mussels, seaweed and sea snails at six monitoring sites and two reference sites after a 9-day deployment period (a, b and c). Figure d shows the correlation between Fe concentrations in seaweed and the DGT labile metal concentrations. The points representing the two reference sites are marked and linear trend lines are shown.

From Søndergaard et al. 2014. Mar Pollut Bull 78, 102-9