Toxicity evaluation of waste drilling fluids

R. Żurek + A. Jamrozik** + A. Gonet***

**Institute of Nature Conservation Polish Academy of Sciences*

*** Faculty of Drilling, Oil and Gas,*

AGH - University of Science and Technology, Kraków, Poland

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Why testing of drilling fluids is necessary?

✓still we do not have sufficient knowled

✓the obligation in law:

FWD (2000); Fresh Water Fish Directive (2006) Habitat directive 1992; Drinking water directive 1998 **Directive 2008/99/WE** on the protection of the environment through criminal law

World Oil's Fluids (2002) listed nearly 2400 fluid system additives for drilling

We need to consider the impact on

- terrestrial and
- aquatic ecosystems

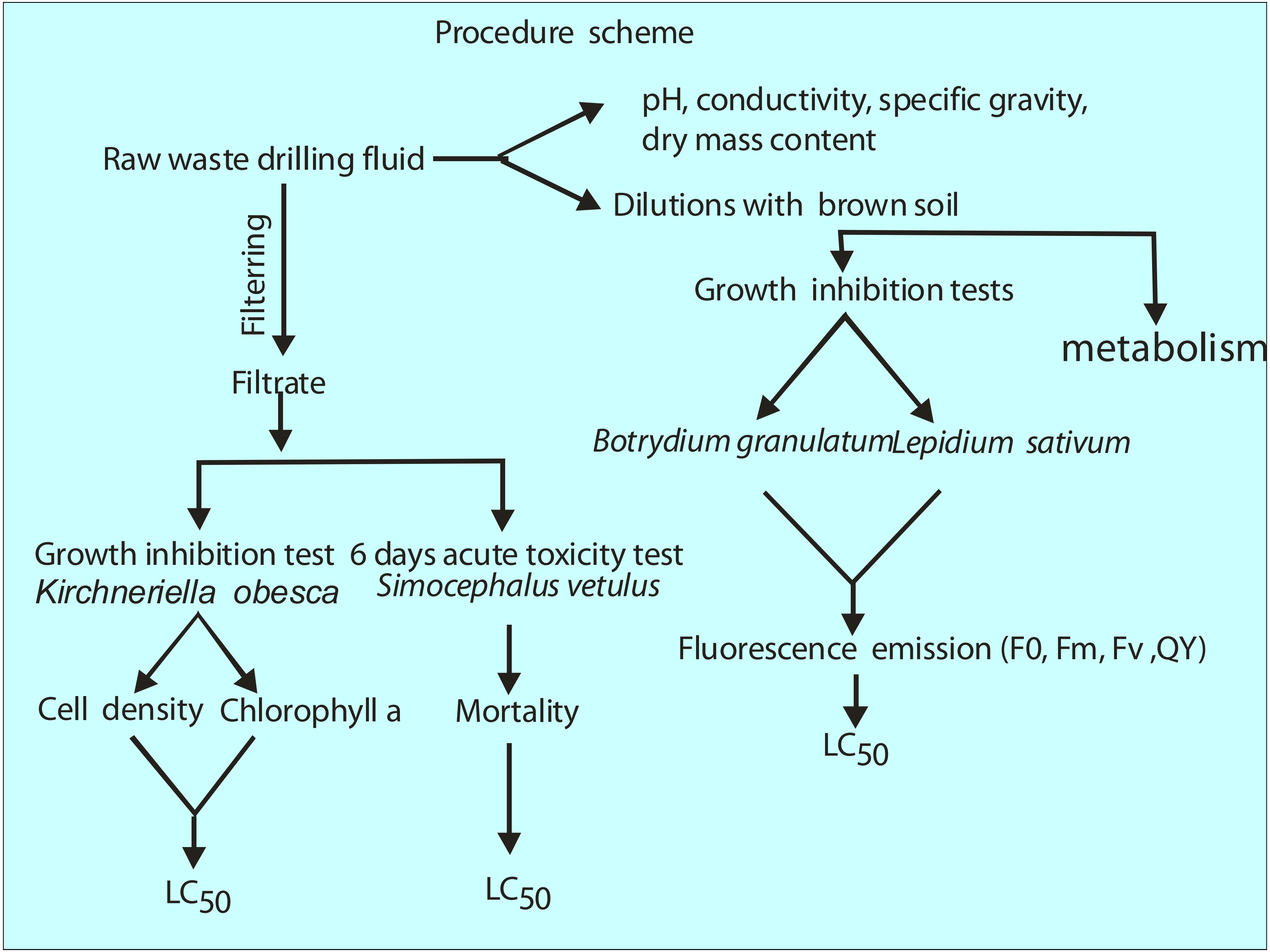
In any ecosysytem we have to evaluate:

- impact of raw drilling fluid
- impact of solid phase
- impact of suspension
- impact of liquid phase
- impact of specific compounds
- impact of cuttings
- impact of processed drilling fluids

And answer the question: how to reduce their harmfulness?

Material. Key to samples

No.	Symbol	Type of drilling fluid
1	**K-1/B**	**Bentonite**
2	**K-1/P-Cl**	**Chloride-polymer**
3	**P-1/K-P**	**Potassium/polymer**
4	**P-2/Dow**	**Non-clay ultradril**
5	**W-1/Cl-P**	**Chloride-polymer-inhibited**
6	**L-1/B**	**bentonite**
7	**KRAM-1/P**	**Potassium**
8	**P-19K**	**Potassium**
9	**L-2K**	**Saline barite**
10	**W-2**	**Polymer**
11	**P-O**	**Oil based**
12	**P-TCC**	**Cuttings after TCC process**


Procedure scheme
Raw waste drilling fluid
pH, conductivity, specific gravity,
dry mass content
Dilutions with brown soil
Filterring
Filtrate
Growth inhibition tests
metabolism
Botrydium granulatum
Lepidium sativum
Growth inhibition test
Kirchneriella obesca
6 days acute toxicity test
Simocephalus vetulus
Fluorescence emission (F0, Fm, Fv ,QY)
Cell density
Chlorophyll a
Mortality
LC50
LC50
LC50

Measuring metabolism naturally contaminated muds

pumps for internal mixing

condensation of moisture

Micro Oxymax respirometer

multiplexer

O_2- measurement

CO_2-measurement

pumps

Thermostatic water bath

Growth inhibition tests were carried out.
Strain origin: CCAP and Univ. of Gdańsk

1. With *Kirchneriella obesca*,

2. With *Botrydium granulatum*,

3. With *Lepidium sativum*, *(garden cress)*

4. Toxicity bioassays with *Simocephalus vetulus*.

http://www.discoverlife.org/mp, https://en.wikipedia.org/wiki/Garden_cress

Results
and details of procedures

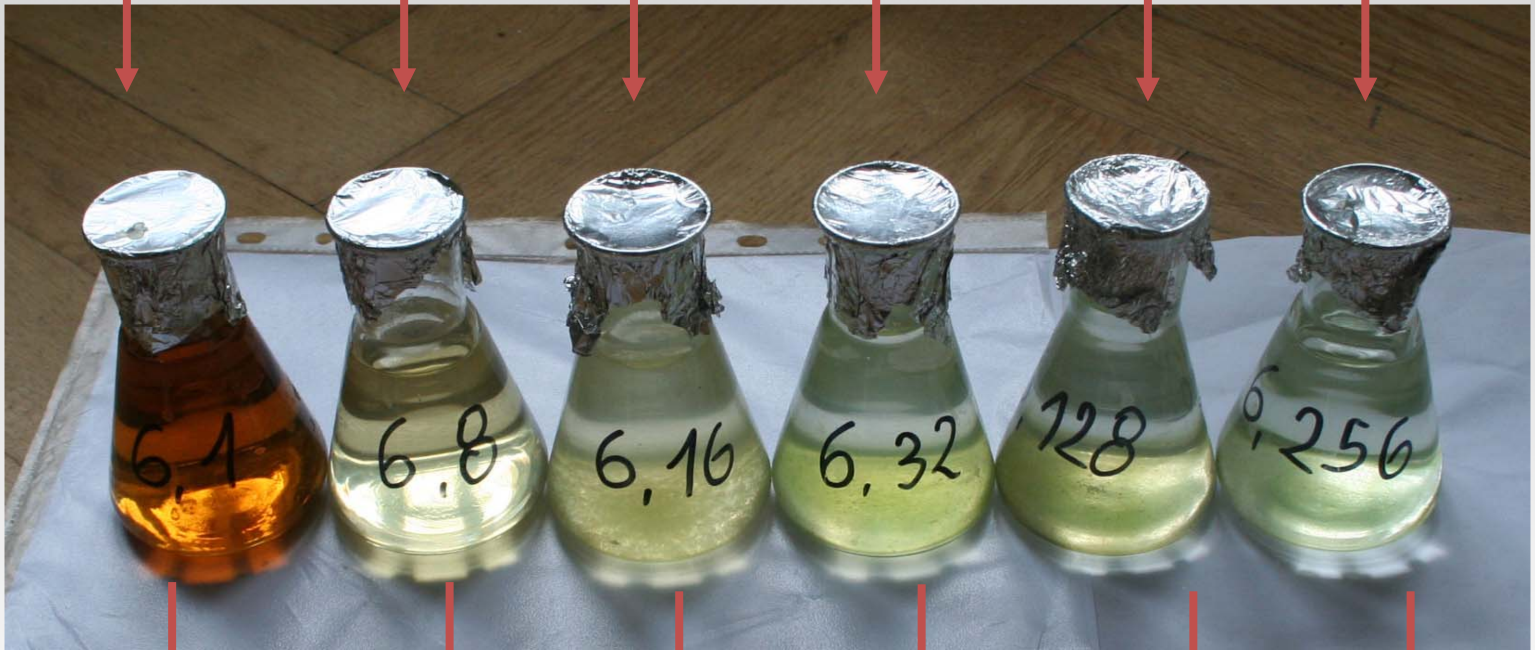
All dilution series: $\mathbf{2^n}$ =1/2, ¼, 1/8, 1/16…. 1/512

Liquid phase. Reaction, pH usually ~ 8,
sample P-1/K-P (Cl/polymer) 9.9
Conductivity [mS cm^{-1}]: usually 100-240 mS cm^{-1},
ex. Sample K-1/B, bentonite, 6.4
TDS [mg/L]: 154 000 -71 700, excludong sample K-1/B: 4 110

Dilutions: distilled water

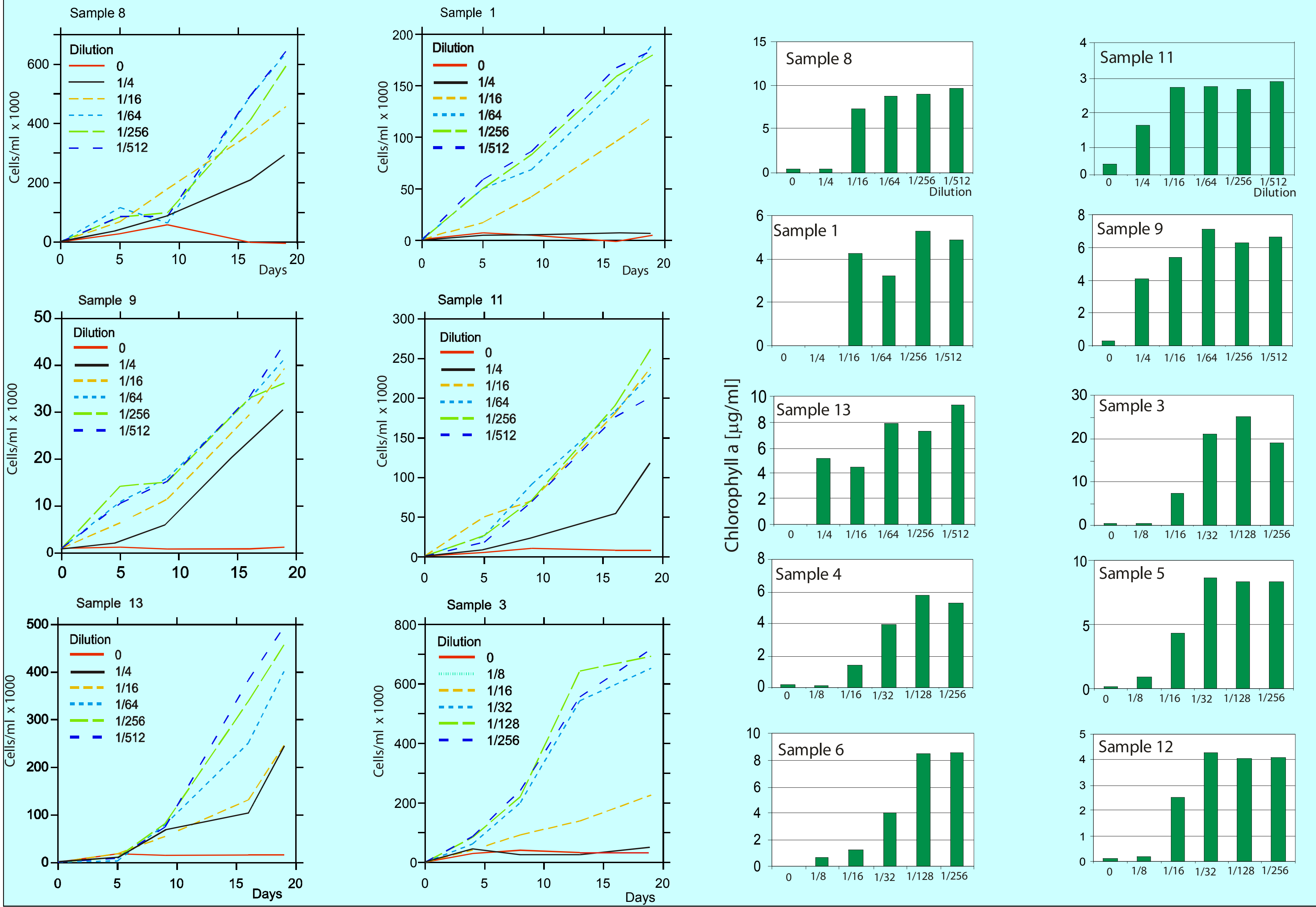
Example of test filtrate

The solution is enriched to a concentration of the culture medium



Counting and finally Chlorophyll *a*

Example of algal growth curves and final chlorophyll *a* concentrations



Cells concentrations and chlorophyll were used to LC_{50} calculation

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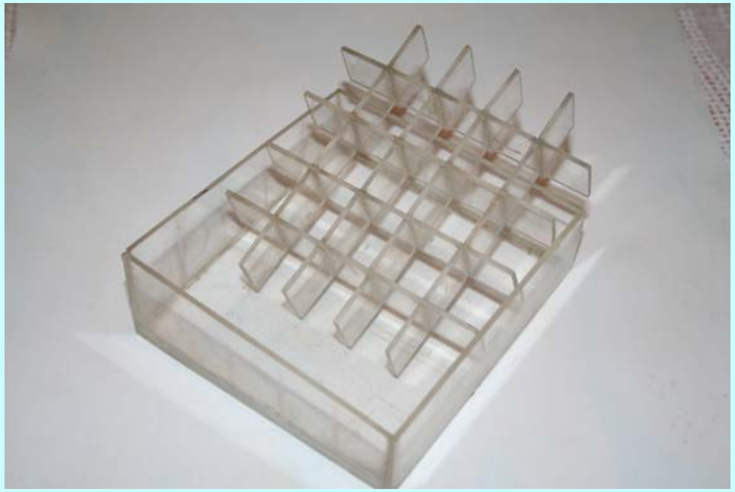
Similar dilutions were used for *Simocephalus vetulus* bioassays

Animals were fed by algal suspension 1.5e6 cells/100ml every 2 days

undiluted liquid phase kills animals within 30 seconds



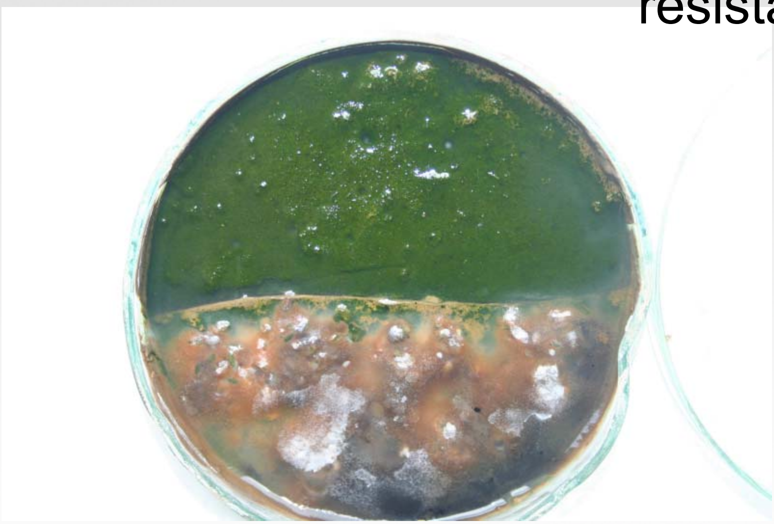
Experiments with solid phase

Dilutions by brown soil

Dilution scheme: 2^n = 1/2, ¼ 1/8 1/16….

Units and proportions as dry mass

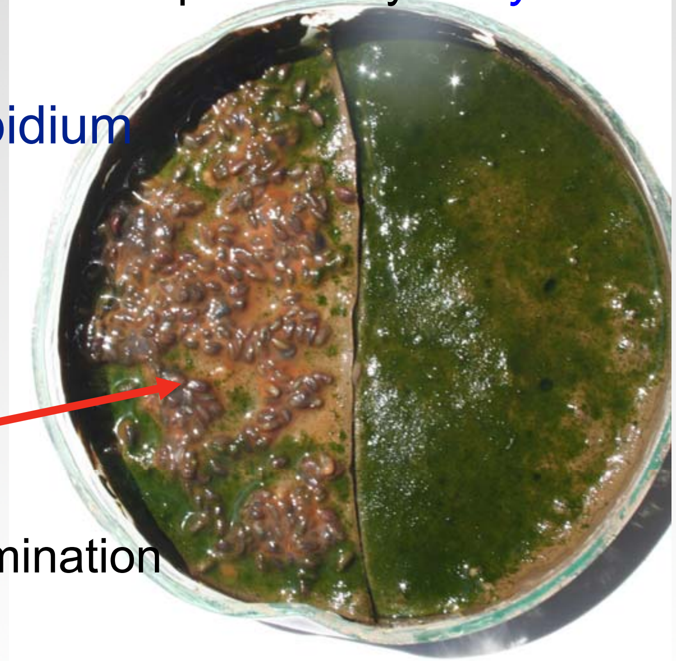
Experiment 2 in 1



Sown *L. sativum* and sprinkled by *Botrydium*

Botrydium more resistant than Lepidium

Seeds,
Without germination



The dilemma: how to measure growth of plants and algae?

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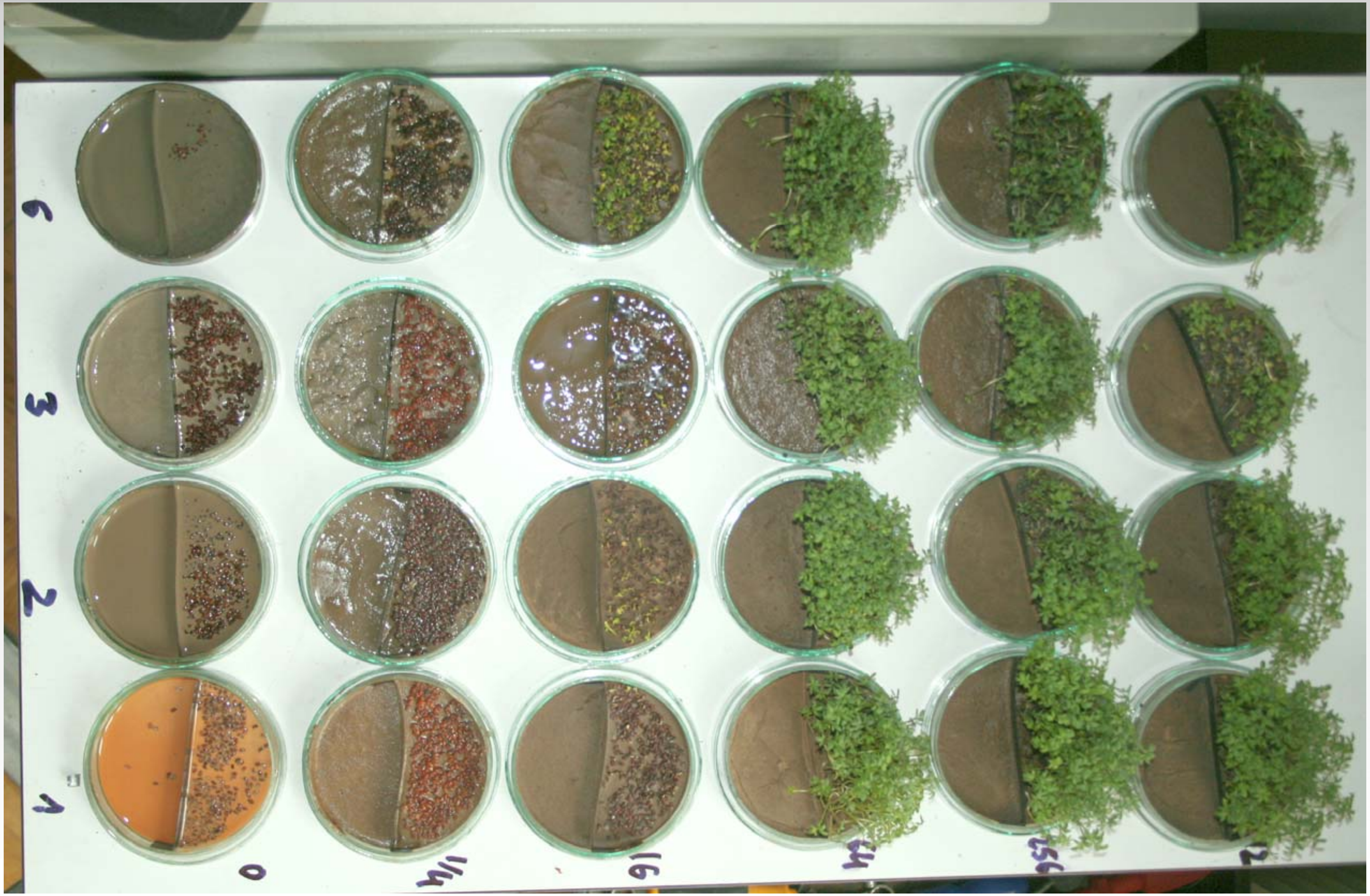


Chlorophyll fluorescence was analyzed to assess the state of photosystem II both for Botrydium and *L. sativum* test. FluorCam FC-800-C of Photon Systems Instruments

Following parameters were measured:

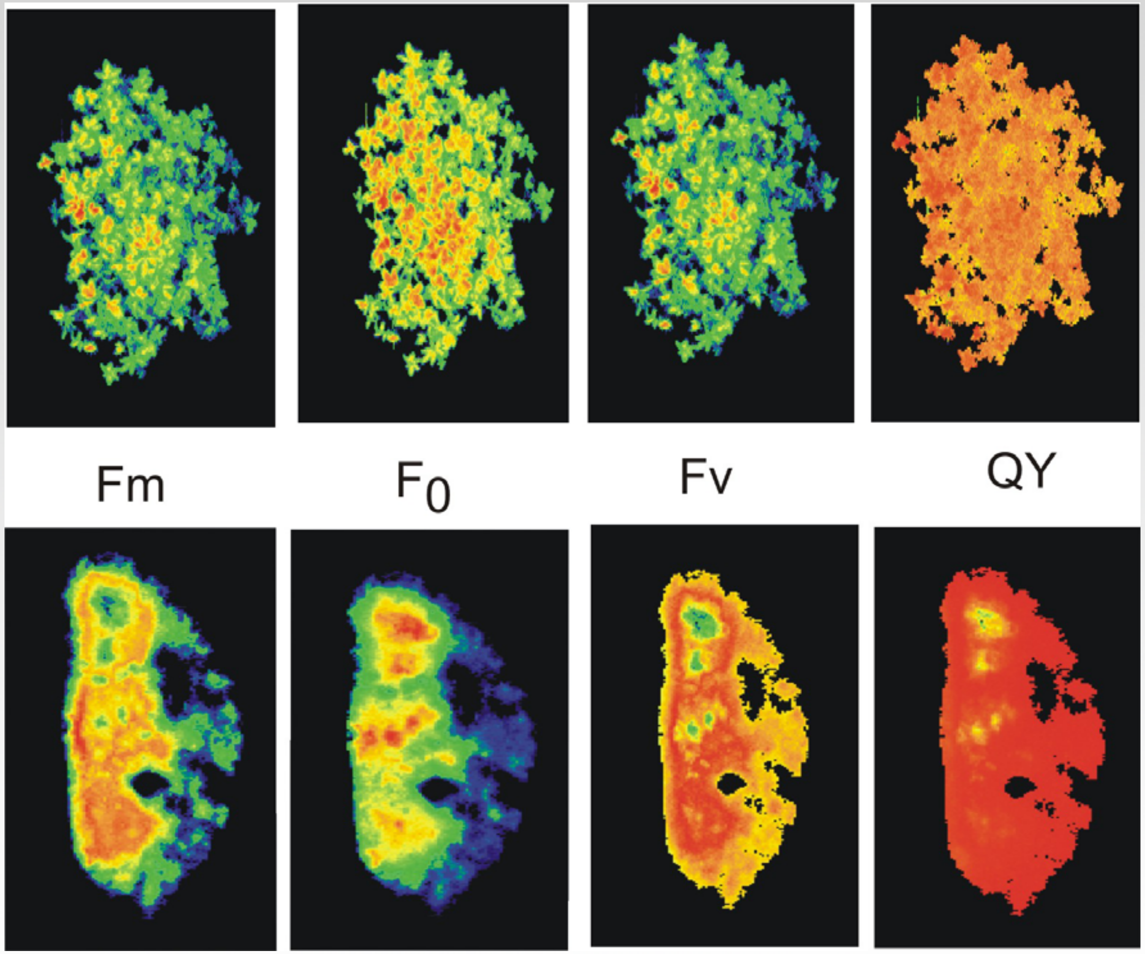
F0 − Minimal fluorescence (arbitrary units). antenna pigment associated with the photosystem II are assumed to be open = dark adapted.

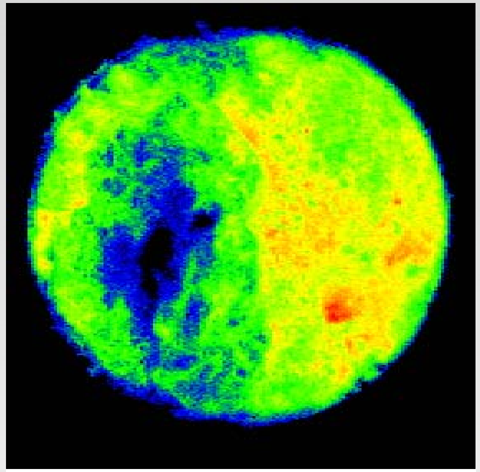
Fm − Maximal fluorescence (arbitrary level) when a high intensity flash has been applied. All antenna sites are assumed to be closed.

Fv − is variable fluorescence, calculated as Fv=Fm −F0

QY − maximum quantum efficiency. Calculated as Fv/Fm=(Fm-F0)/Fm.

Example of image analysis for the activity of photosystem II





Example of photosynthesis parameters of *B. granulatum* on drilling fluids.
Values F0, Fm, Fv/Fm

input data for the calculation LC

Sample code		1:16	1:32	1:64	1:128	1: 1
1	F_0	0,19	0,092	0,059	0,049	0,179
	Fm	0,381	0,024	0,122	0,125	0,036
	Fv/Fm	0,501	0,617	0,516	0,608	0,507
2	F0	0,086	0,008	0,05	0,077	0,009
	Fm	0,162	0,199	0,099	0,163	0,018
	Fv/Fm	0,469	0,558	0,495	0,528	0,5
3		0,089	0,078	0,069	0,076	00
		0,190	0,179	0,157	0,184	00
		0,532	0,564	0,561	0,587	0,008

etc.

Brown soil	Fv/Fm				0,754

Results of LC_{50} calculations for algal tests for solid and liguid phase.

Sample no.	*Name of drilling fluid*	*L. sativum*	*Botrydium granulatum*	*Kirchneriella obesca*
1	**L-2K** saline-barytic	0.039	0.156	0.11
2	**K-1/P-Cl, Chloride-polymer**	0.039	0.156	0.053
3	**P-1/K-P potassium polymer**	0.039	0.156	0.061
4	**P-1/K-P KCl- polymer**	0.094	0.094	0.029
5	**P-2/Dow Non-clay ultradril**	0.094	0.094	0.094
6	**W-1/Cl-P chloride - polymer inhibited**	0.039	0.156	0.019
11	**K-1/P-Cl KCl_polymer**	0.25	0.56	0.60
12	**K-1/P-Cl KCl_polymer**	0.25	0.56	0.073
13	**P-2/Dow clayless with blockers**	0.25	0.56	0.21

Simocephalus vetulus after 6 days

For calculation the LC50 or EC50 the modified source code of program *Spearman* obtained from EPA was used and ToxCalc.

No	Code	type	LC50
1	**L-2K**	saline-barytic	0.0078
2	**W-2**	**Polymer**	0.0073
3	**P-2/Dow**	clayless with blockers	0.0078
5	**KRAM-1/P**	**Potassium**	0.0036
6	W-1/Cl-P	**Chloride-polymer-inhibited**	0.0118
8	P-1/K-P	**Potassium/polymer**	0.0078
9	L-1/B	**bentonite**	0.125
11	S-4	Potassium-polymer	0.0078
12	S-5K	Polymer	0.0313
13	S-7	Clayless with blockers	0.0042

Sample P-O (Oil based)

LC50 for *L. sativum* is 21.2 % of dry mass of drilling mud

50 g soil + X g of drilling fluid , [dry mass]

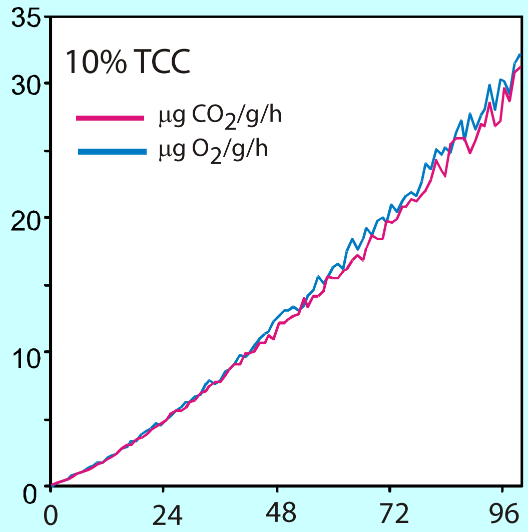
Soil, control	50+10	50+25
		
0%	16,6%	33%

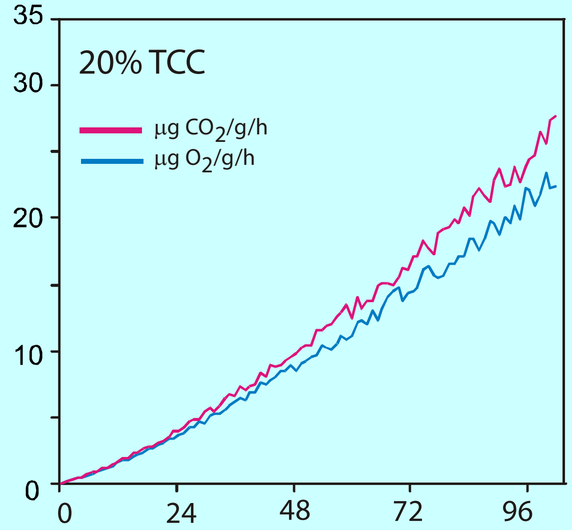
Equivalent conc. of drilling fluid %

untreated oil based drilling mud is more toxic for growth *L. sativum* (LC50) than treated, 21.2 % and 29% relatively.

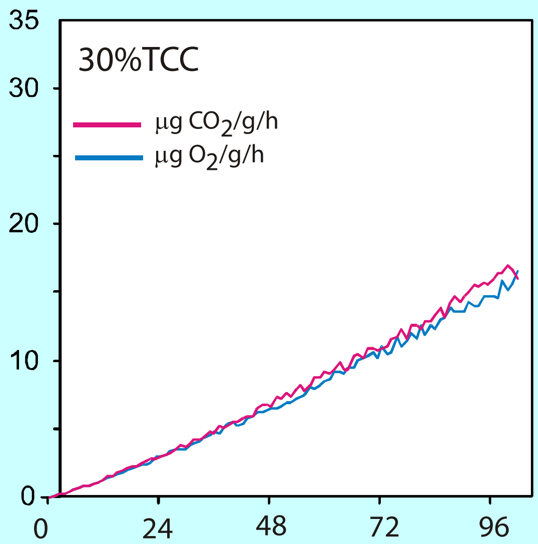
The oil drilling fluid after thermal desorption

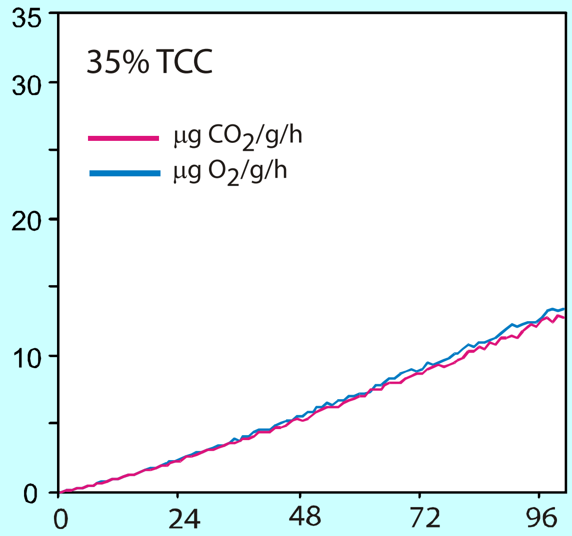
Admixture up to 20 % of dry mass has no apparent effect on the germination and growth of *L. sativum*



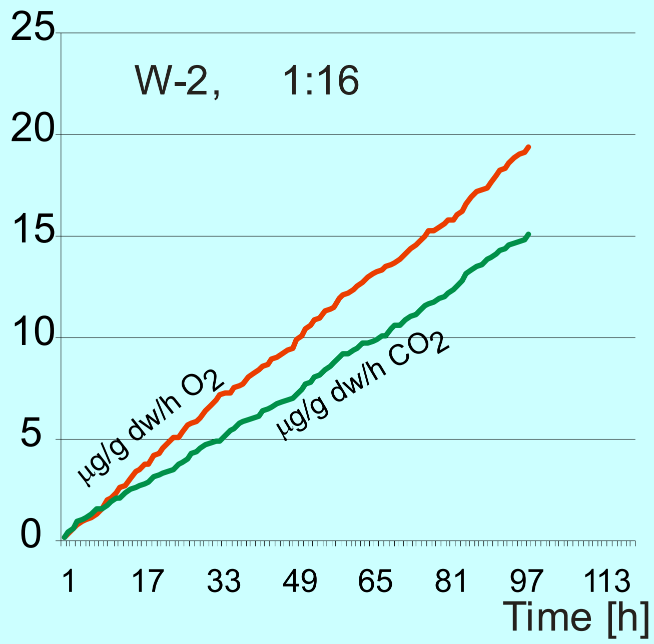


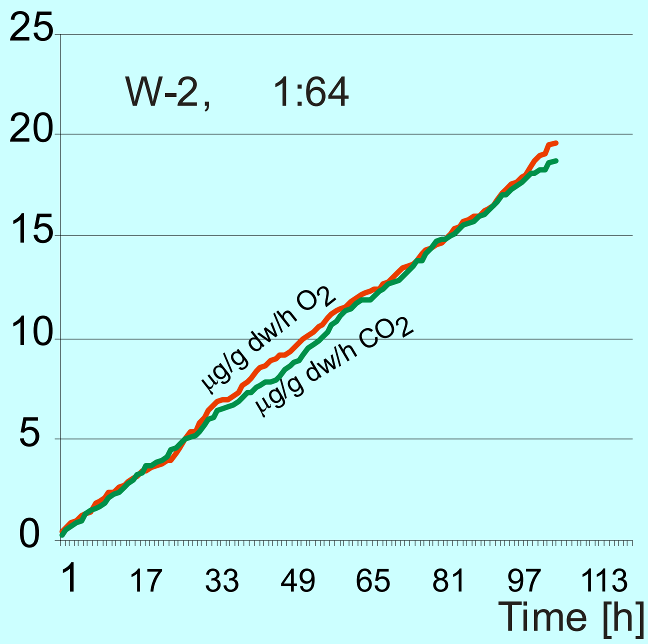
Addition 30 and 35 % of desorbed drilling fluids diminish microorganisms' activity to about 50 percent.

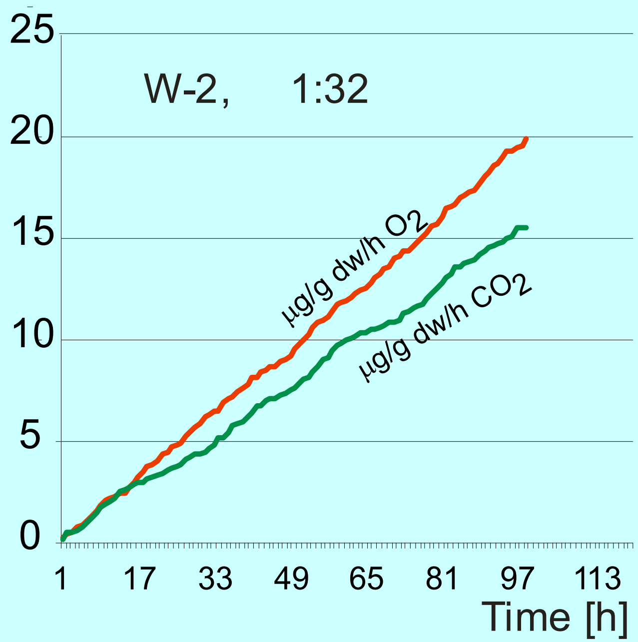


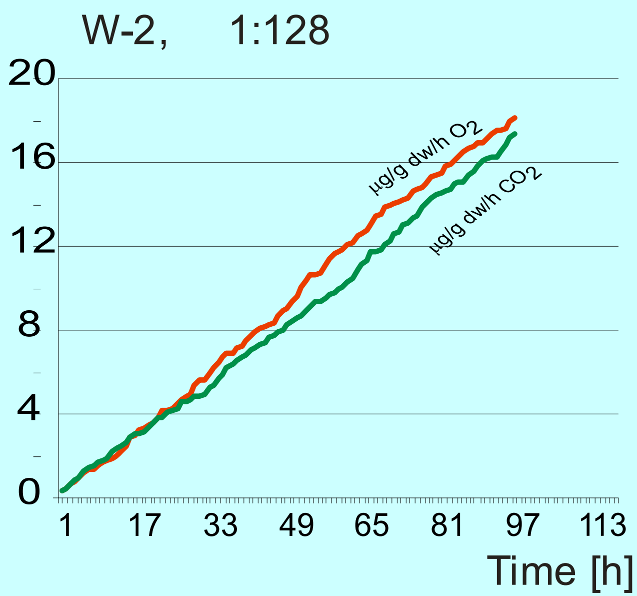


Polymer

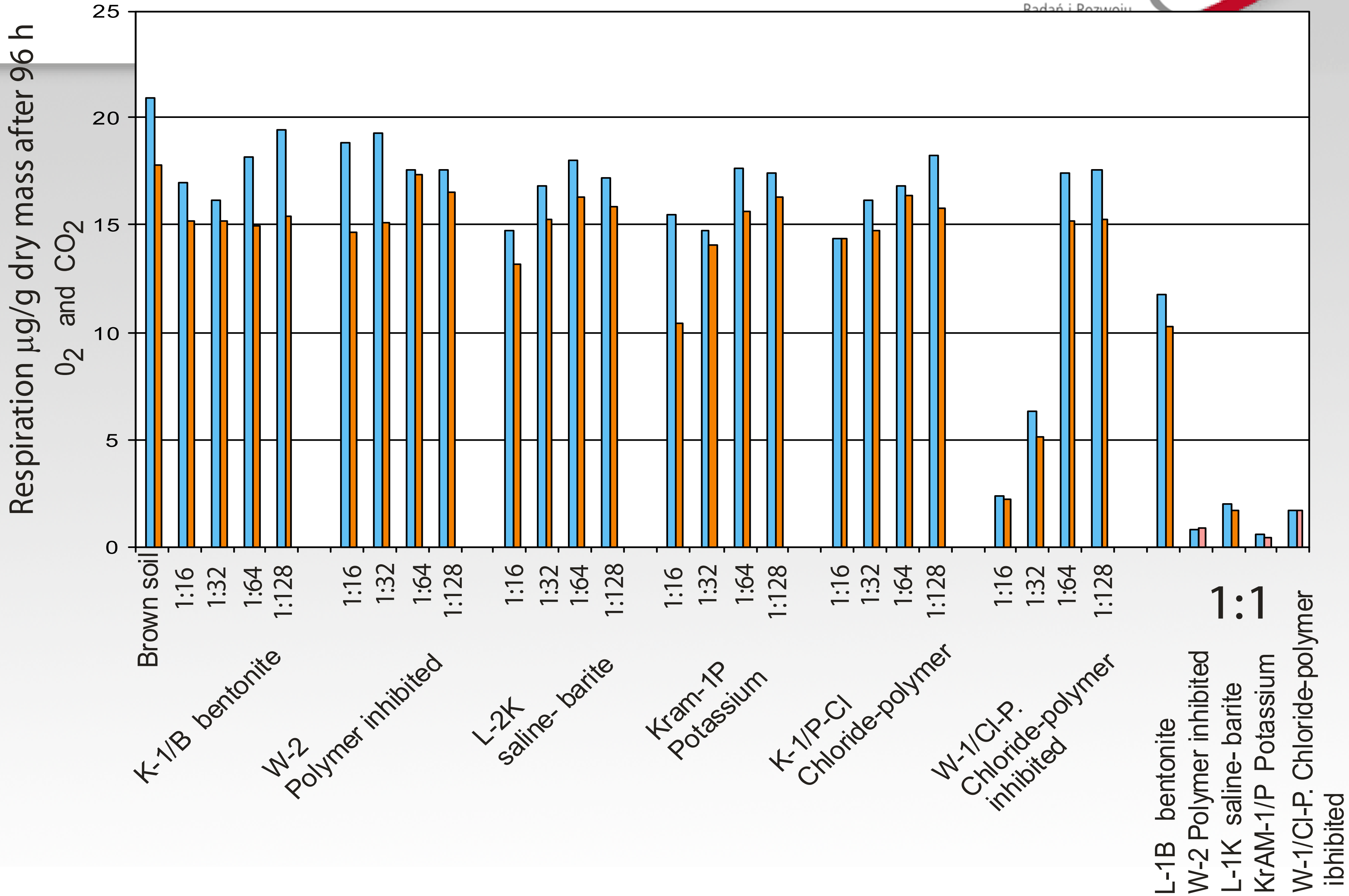

W-2, 1:16
25
20
15
10
5
0
1 17 33 49 65 81 97 113
Time [h]
µg/g dw/h O2
µg/g dw/h CO2


W-2, 1:64
25
20
15
10
5
0
1 17 33 49 65 81 97 113
Time [h]
µg/g dw/h O2
µg/g dw/h CO2

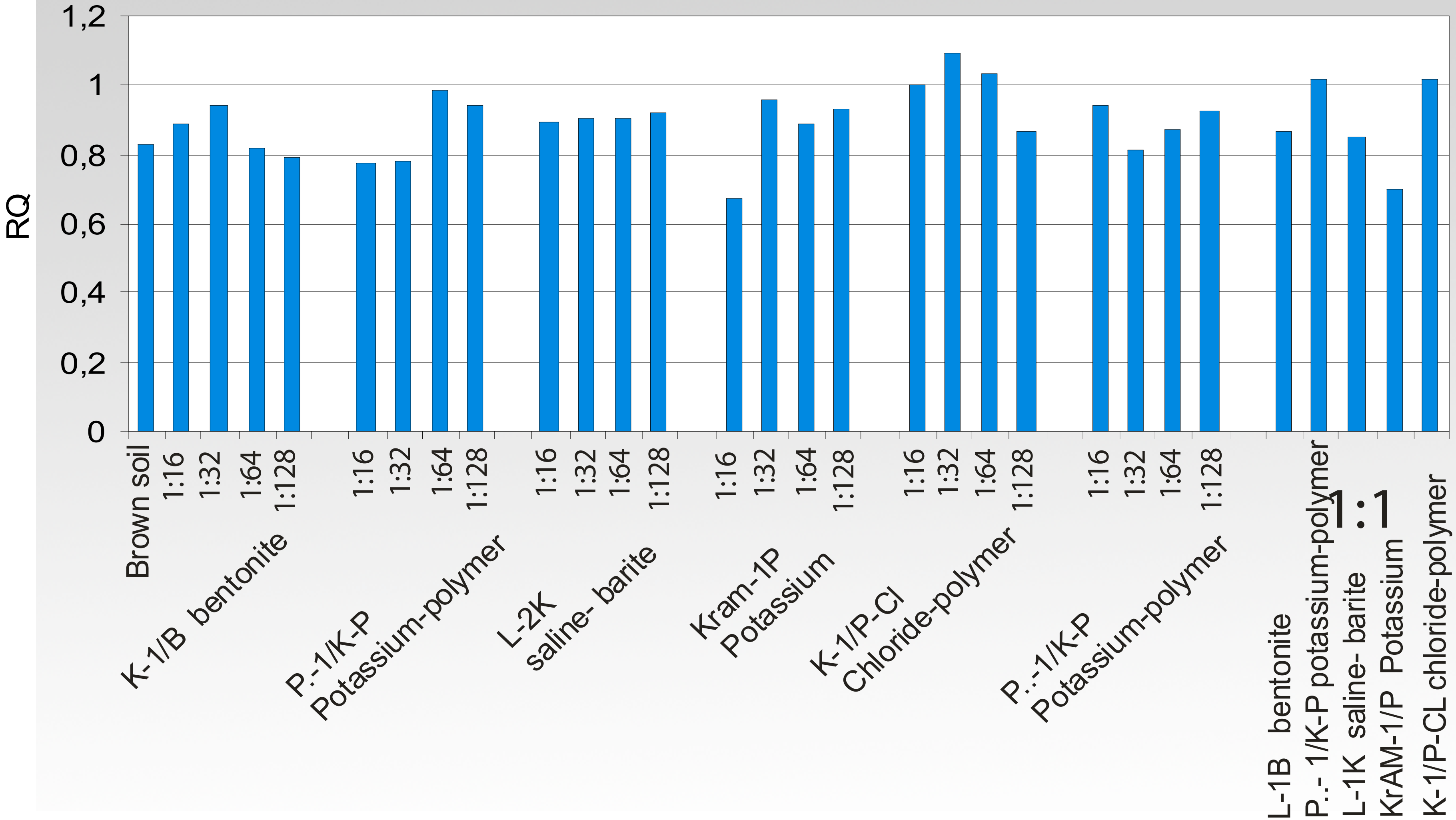

W-2, 1:32
25
20
15
10
5
0
1 17 33 49 65 81 97 113
Time [h]
µg/g dw/h O2
µg/g dw/h CO2


W-2, 1:128
20
16
12
8
4
0
1 17 33 49 65 81 97 113
Time [h]
µg/g dw/h O2
µg/g dw/h CO2

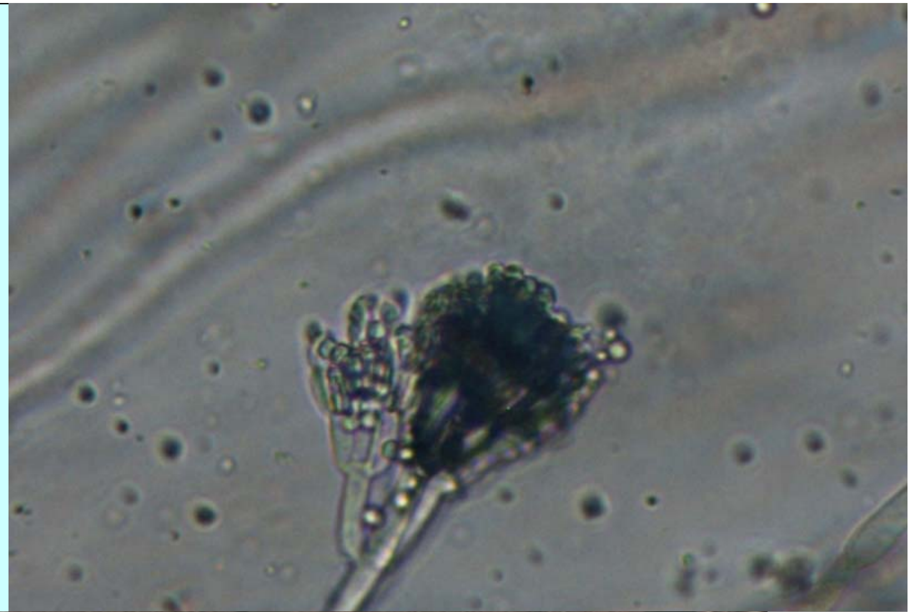
Cumulated O_2 consumption after 96 h, drilling fluid



Cumulated CO_2 exhaled after 96 h, drilling fluid



Penicillum sp.



Conclusions

Investigation showed that:

1. Both for terrestrial and water ecosystems first order problem in toxicity mitigation is very high salt concentration.

2. For mitigation of salinity problem dilution of drilling fluids with natural soil should be recommended. In moderate climate, excess of salinity will be slowly leached by rains.

3. None of the tested drilling fluids not damage the photosystem II of the test plants.

Conclusions

4. The more sensitive organisms were cladocerans is
S. vetulus >
later freshwater planktonic alga *K. obesca*,
>*B. granulatum*
which can be considered as pioneer alga and comparable sensivity of *L. sativum* allow to estimate toxic effect of whole components;

5. Measuring of metabolic activity of naturally contaminated by microflora drilling fluids allow to estimate toxic effect of whole components and simultaneously estimate biodegradation of these organic components like parameter BOD (biochemical oxygen demand).

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http://drillingwaste.eu

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Questions?