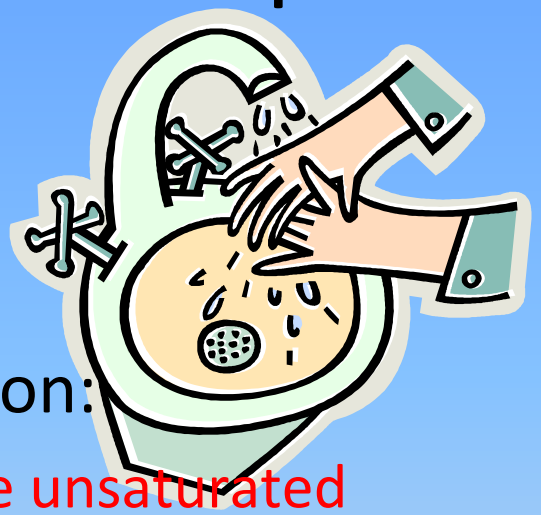
How do surfactants affect soil properties?

Steve Leharne

What effects do surfactants have upon soil properties?



- The purpose of talk is to examine:
  - The effects that surfactants have upon:
    - Drainage and imbibition of water in the unsaturated zone.
      - To understand the effects that surfactants have upon water retention we need to understand how surfactants alter the **surface tension** of water in soil water systems; and
      - How surfactants, through **adsorption**, alter **wetting properties**.
    - Hydraulic conductivity

Surfactants and soils

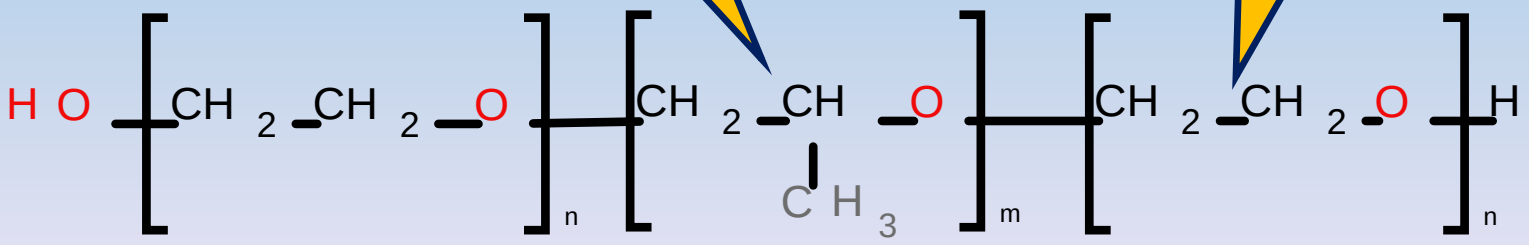
- Surfactants maybe released into soils in a variety of ways.
  - Waste water – in particular grey water
  - Industrial wastes
  - As components of agrochemical formulations

- Their presence in soils can lead to changes in water retention and water transport.

Surfactants used in the investigation were: Pluronics ….

Propylene oxide block: Hydrophobic

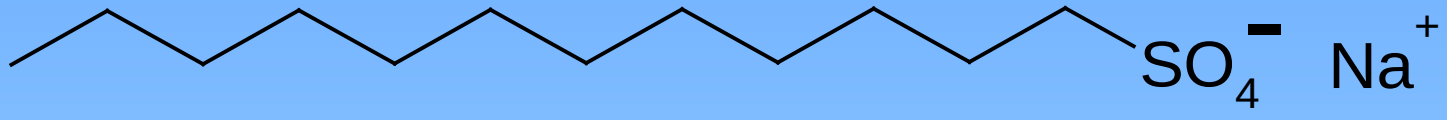
Ethylene oxide block: Hydrophilic

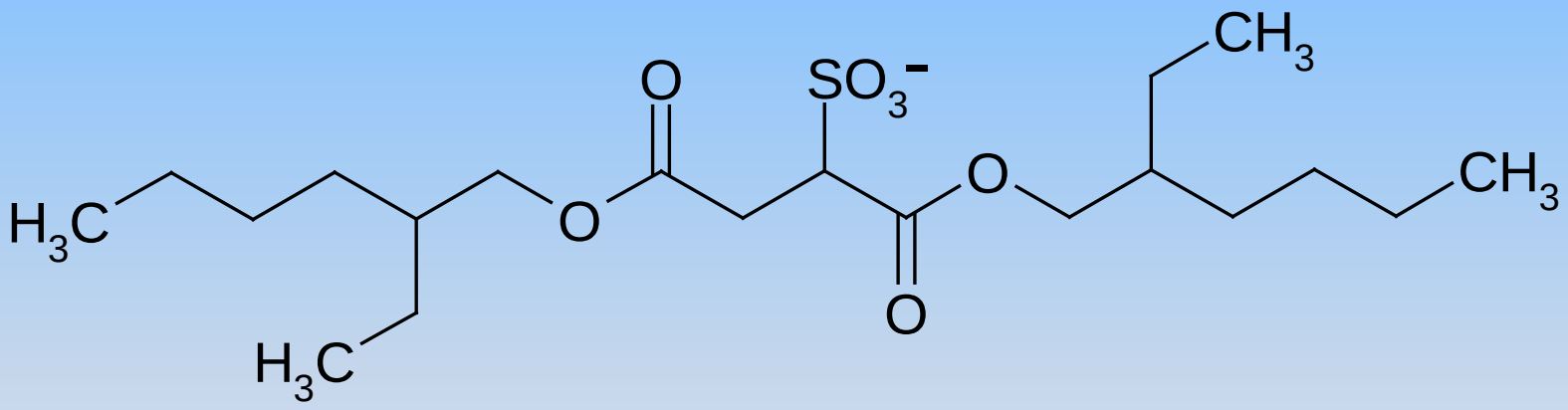


Approximate composition

Copolymer	Molecular Formula	*cmc* (w/v%)
P184	$(EO)_{27}(PO)_{30}(EO)_{27}$	0.8
P188	$(EO)_{80}(PO)_{30}(EO)_{80}$	n.d.
P284	$(EO)_{21}(PO)_{47}(EO)_{21}$	0.05
P288	$(EO)_{125}(PO)_{47}(EO)_{125}$	0.5

…. and SDS and AOT



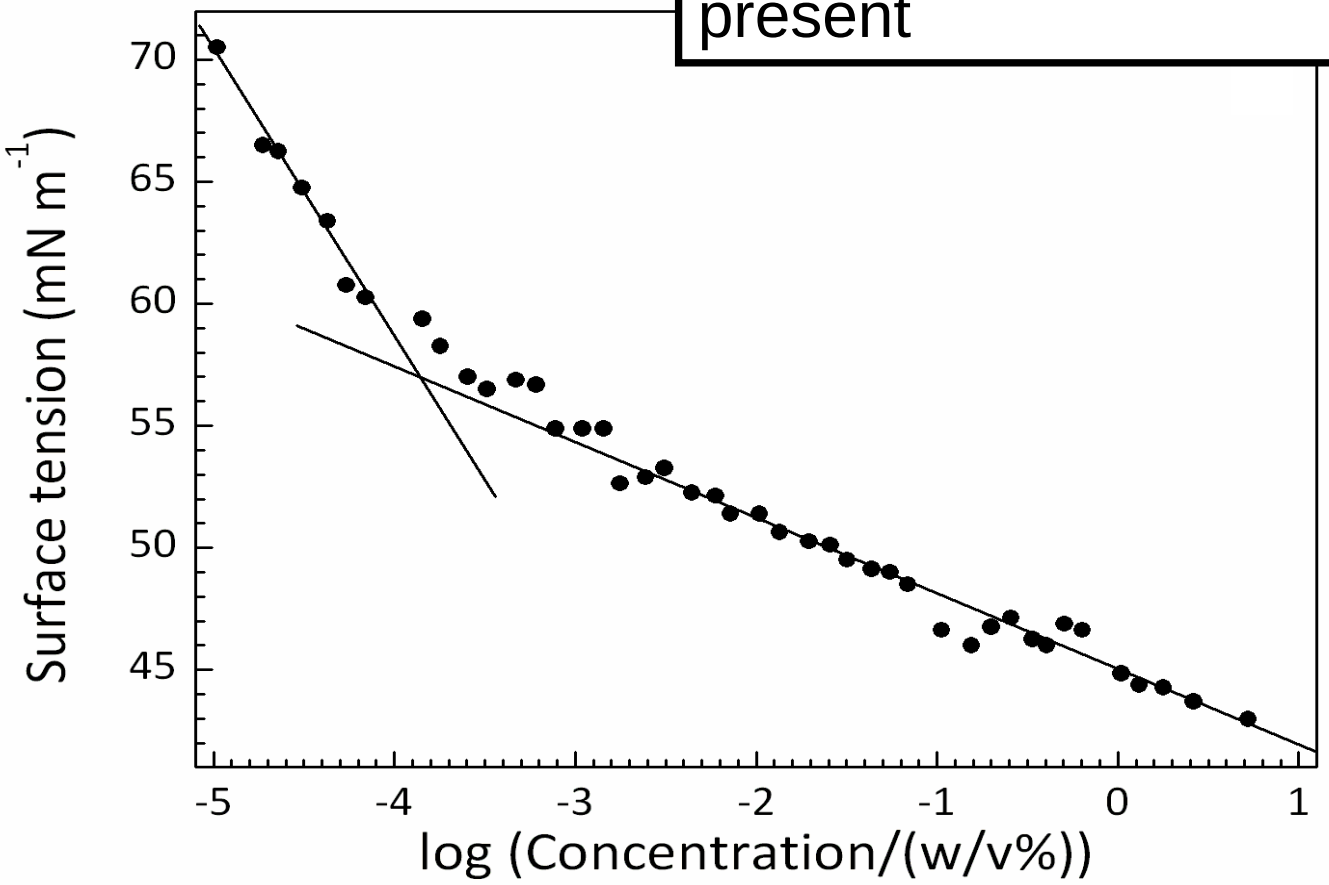


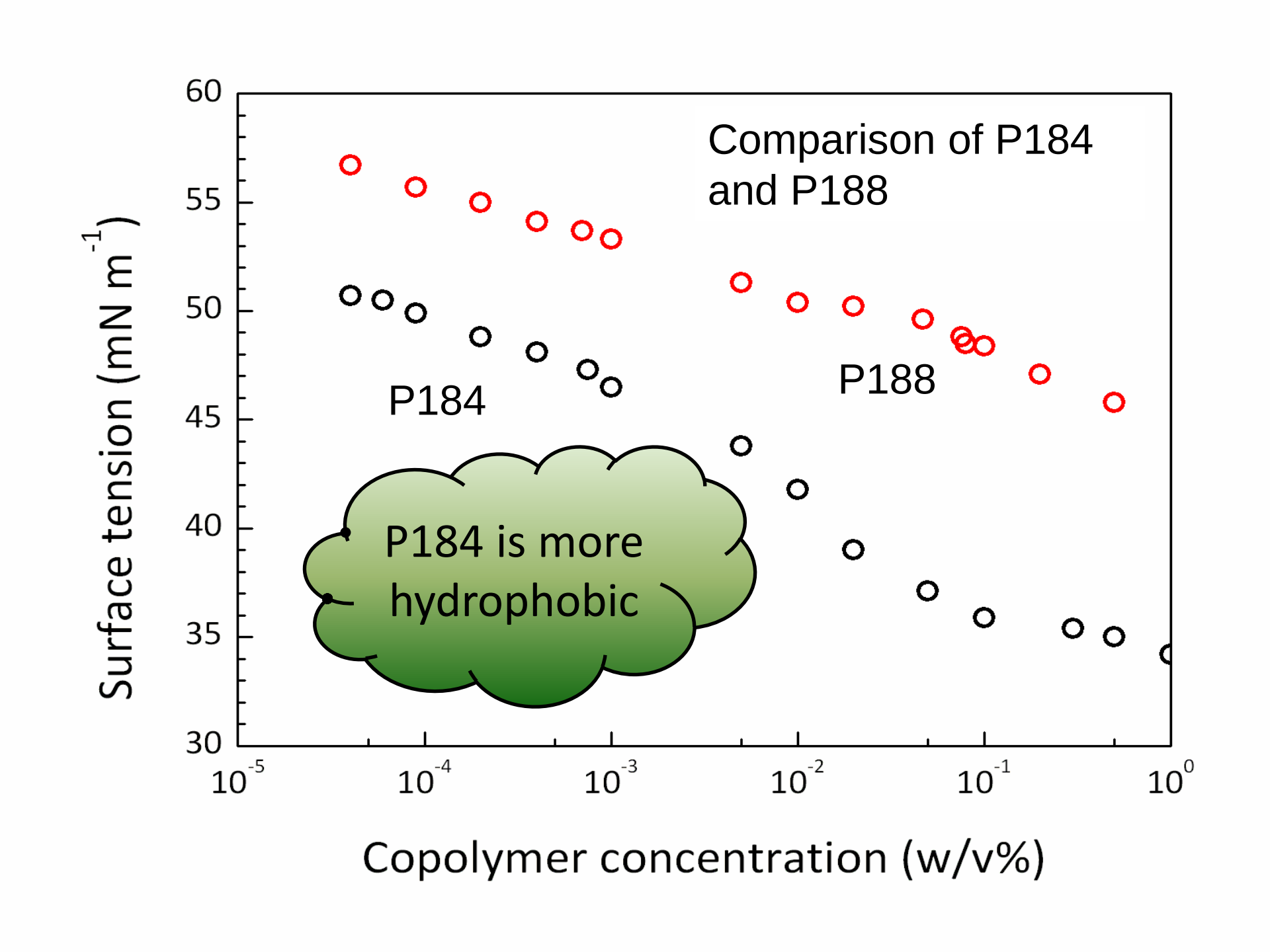
The Soils Used

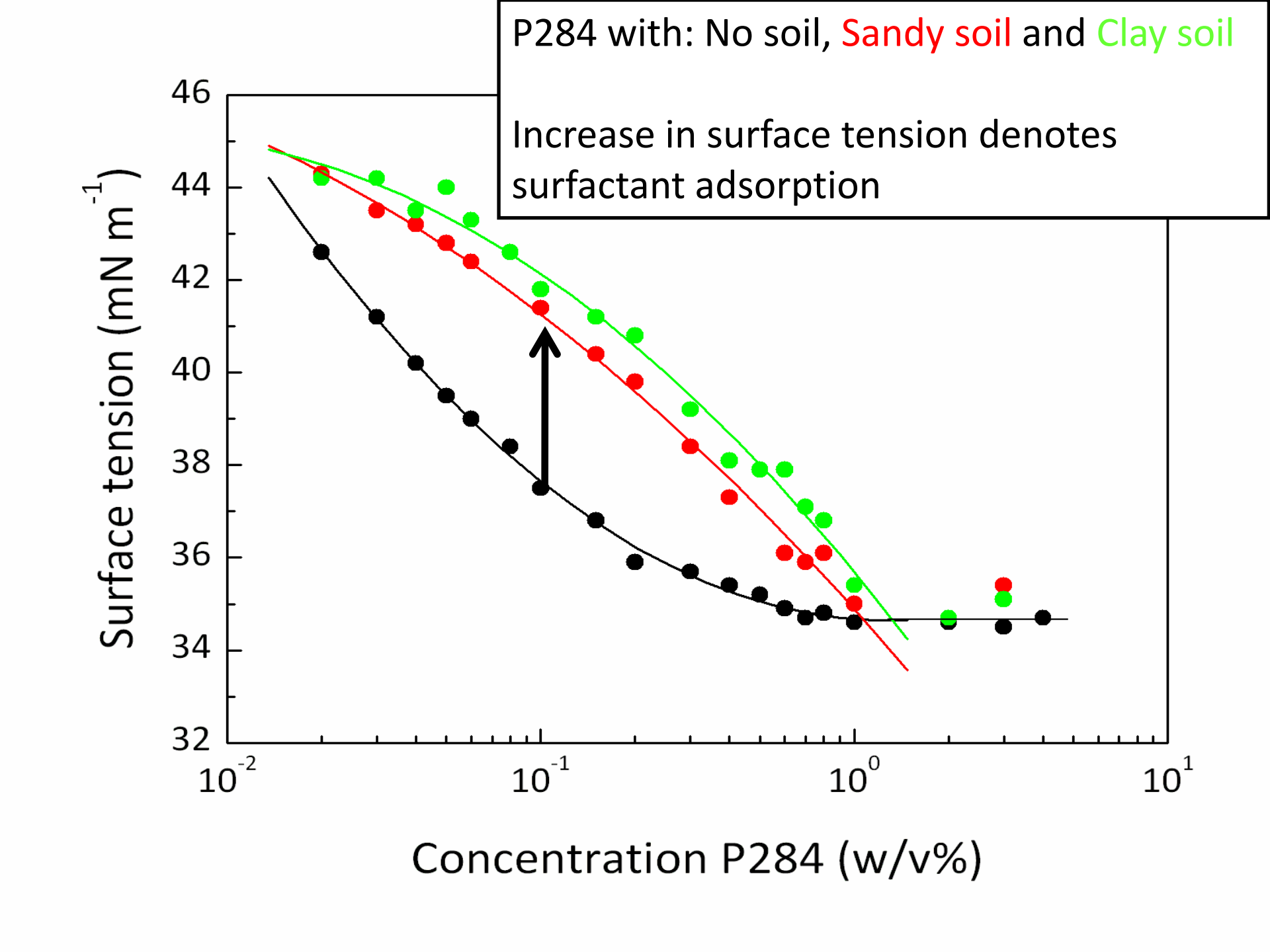
	% Composition	
	Clay Soil	Sandy Soil
Particle Size (µm)		
200-2000	7.3	47.1
60-200	0.9	18.9
20-60	21.8	19.4
2-20	19.5	9.7
<2	50.5	4.9
Texture class	Silty clay	Loam
pH (1:2.5 extract in water)	7.1	6.9
Soil organic matter	4.8%	0.9%

Surface tension pluronics

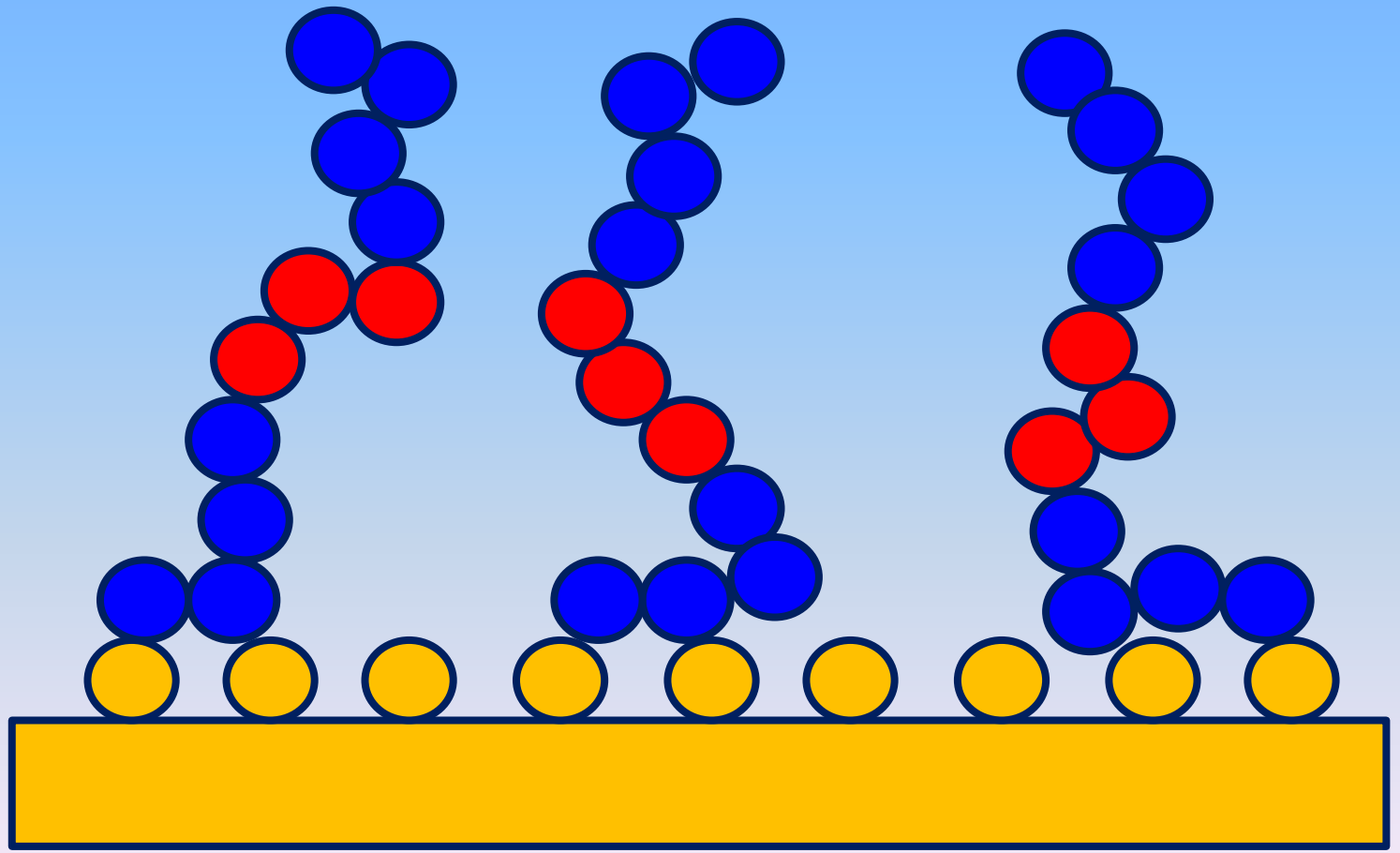
P188 in water – no soil present



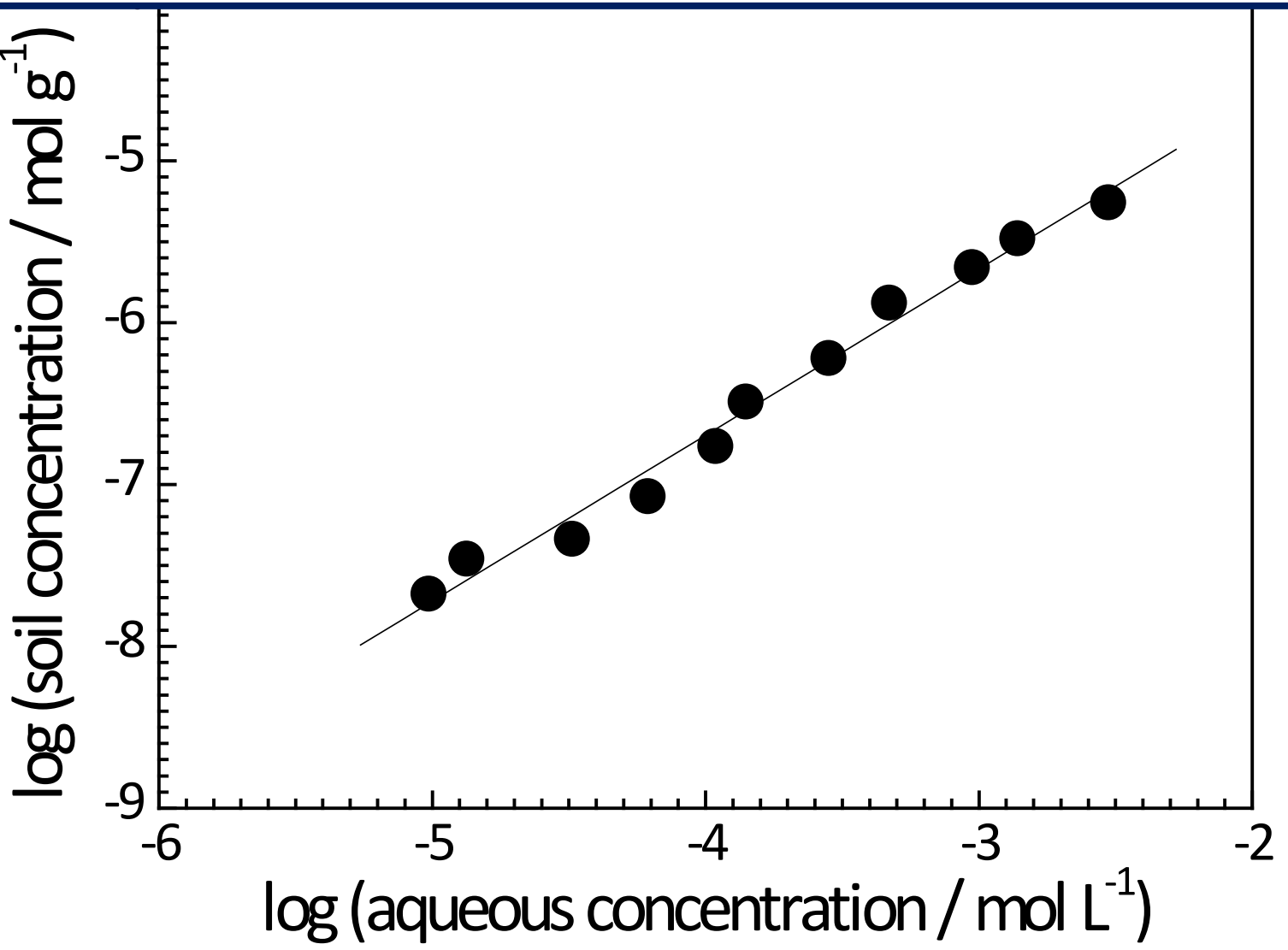

Comparison of P184 and P188
P184
P188
P184 is more hydrophobic
Surface tension (mN m-1)
Copolymer concentration (w/v%)
60
55
50
45
40
35
30
10-5
10-4
10-3
10-2
10-1
100

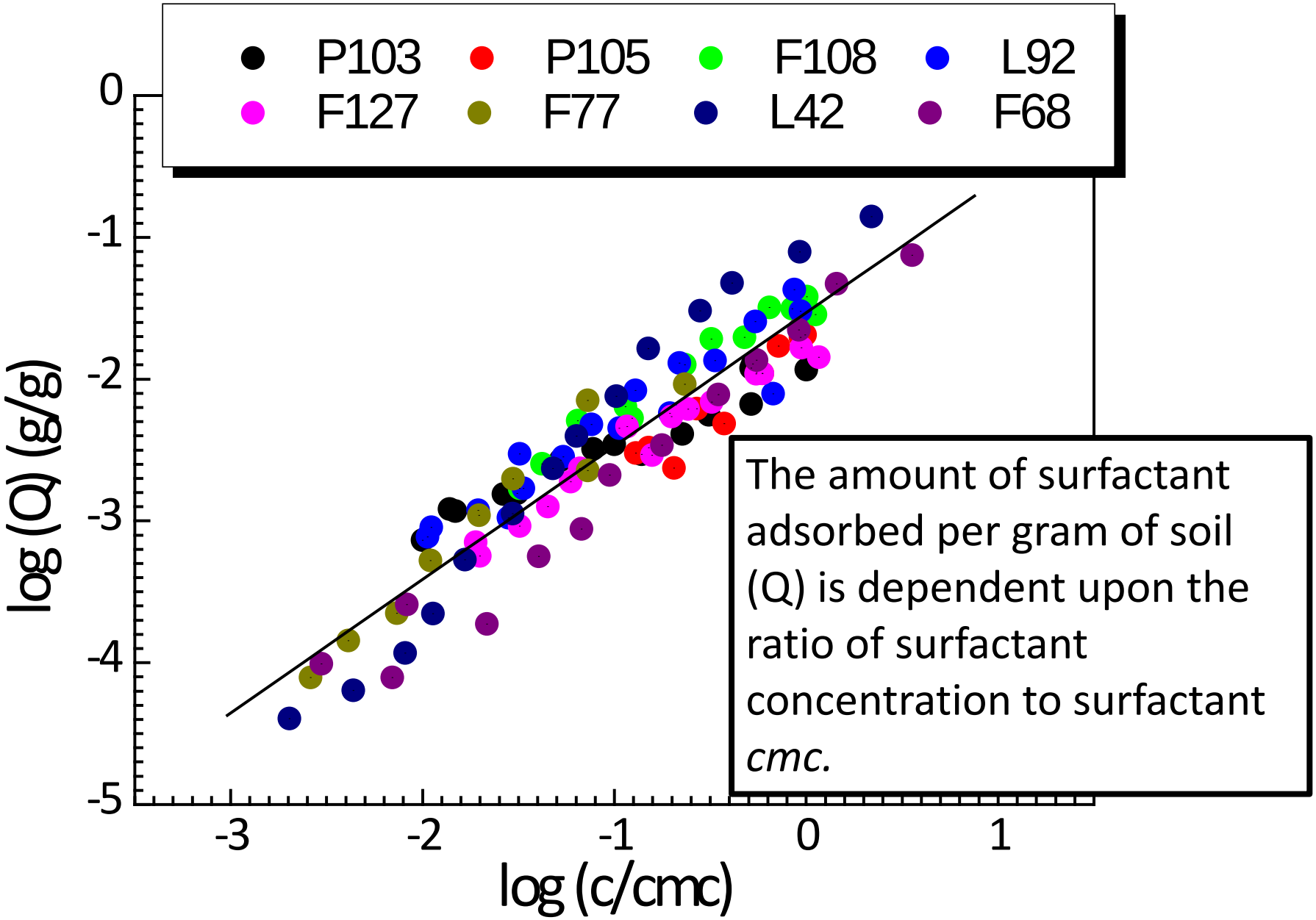

P284 with: No soil, Sandy soil and Clay soil
Increase in surface tension denotes surfactant adsorption
Surface tension (mN m-1)
46
44
42
40
38
36
34
32
10-2
10-1
100
101
Concentration P284 (w/v%)

Possible adsorption mechanism: EO blocks are adsorbed to surface silanol groups. The attached PO and EO blocks are then extended into the aqueous phase.



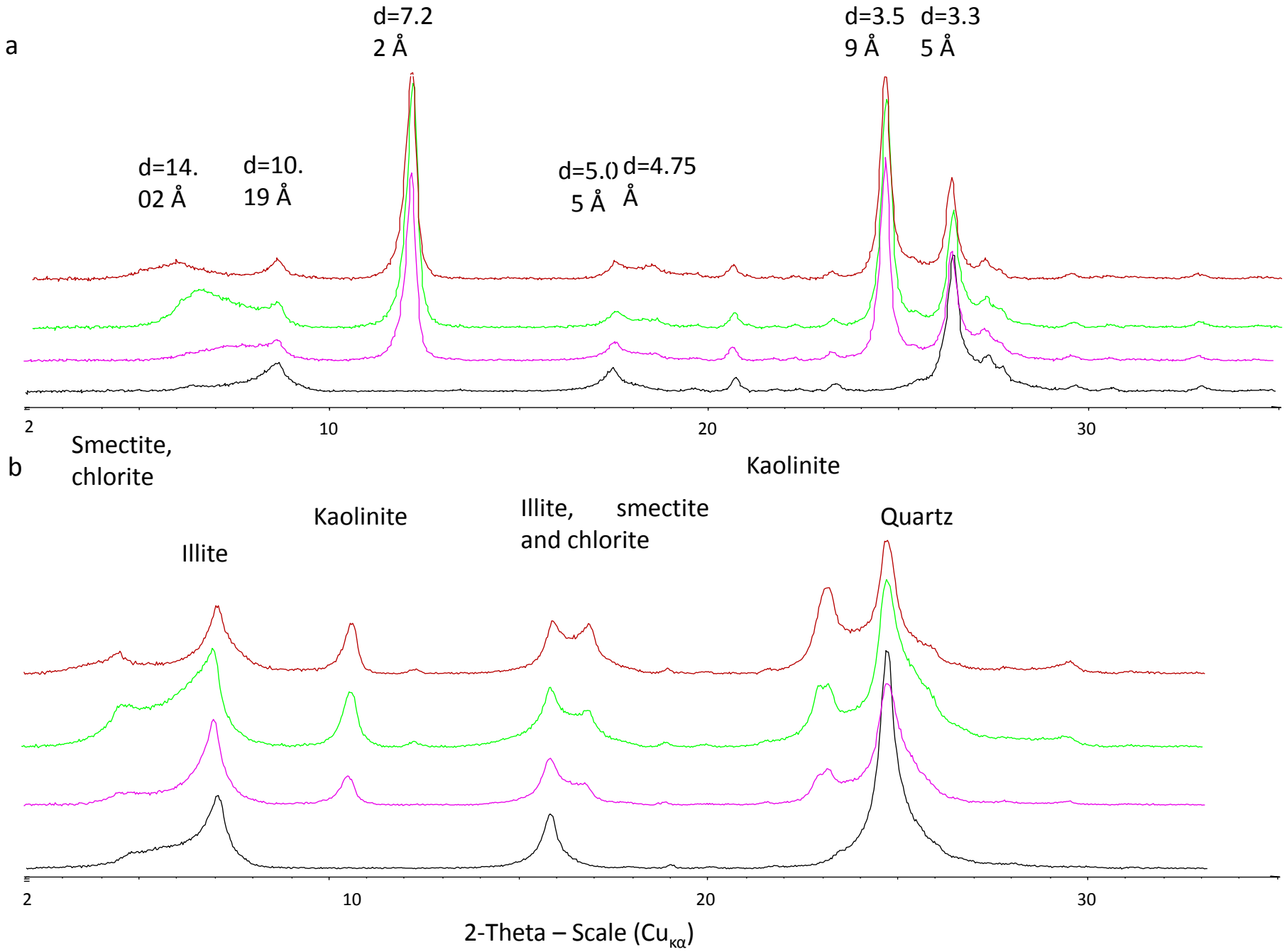
The surfactant adsorption isotherm can be determined using the surface tension data.

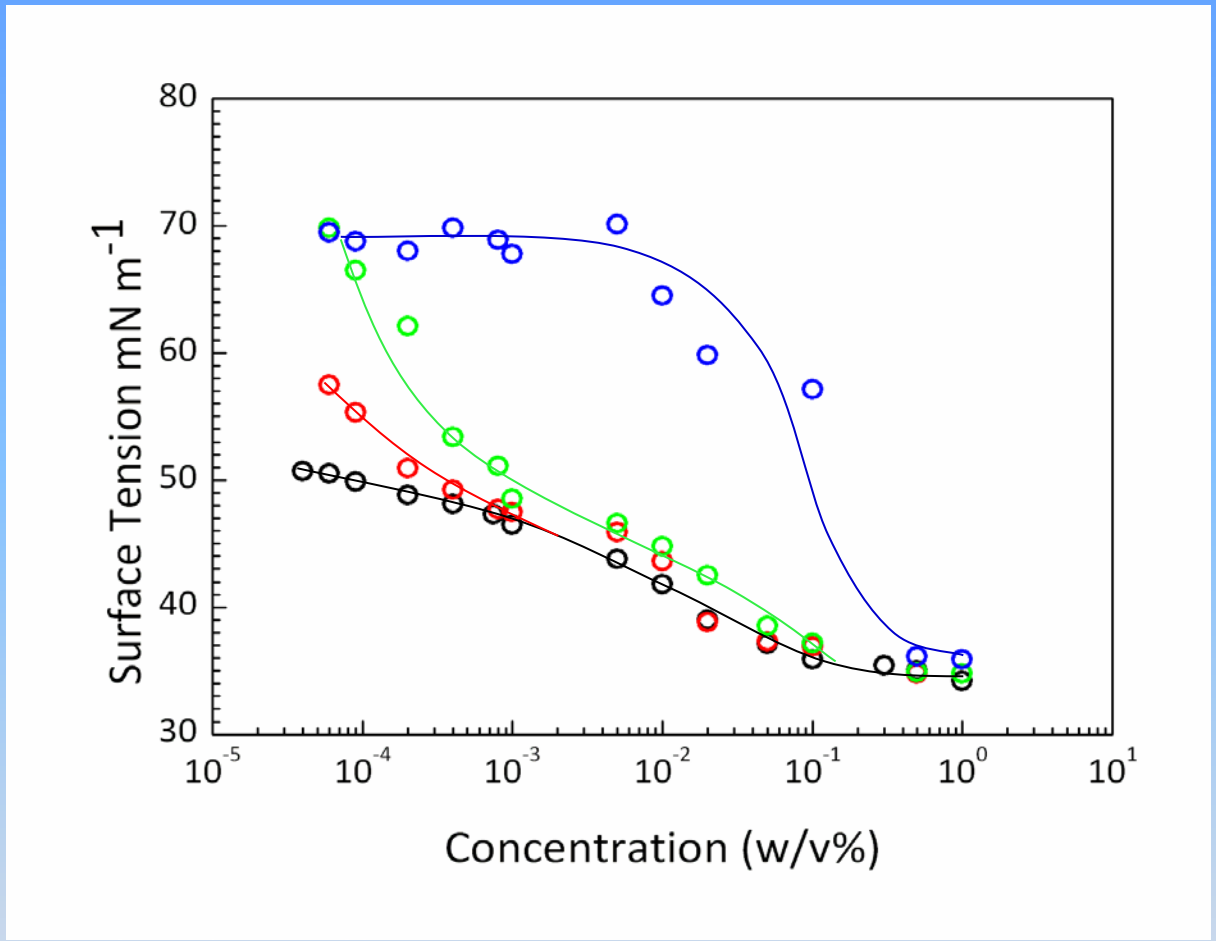



P103
P105
F108
L92
F127
F77
L42
F68
0
-1
-2
-3
-4
-5
log (Q) (g/g)
-3
-2
-1
0
1
log (c/cmc)
The amount of surfactant adsorbed per gram of soil (Q) is dependent upon the ratio of surfactant concentration to surfactant *cmc.*

Soil heterogeneity

- The data clearly indicate that pluronics in soil-water-air systems are adsorbed to the soil surfaces.
- The soils used are heterogeneous. How do individual minerals affect surface tension?


a
d=7.2
2 Å
d=3.5
9 Å
d=3.3
5 Å
d=14.
02 Å
d=10.
19 Å
d=5.0
5 Å
d=4.75
Å
2
10
20
30
b
Smectite,
chlorite
Illite
Kaolinite
Illite, smectite
and chlorite
Kaolinite
Quartz
2
10
20
30
2-Theta – Scale (Cu$_{k\alpha}$)



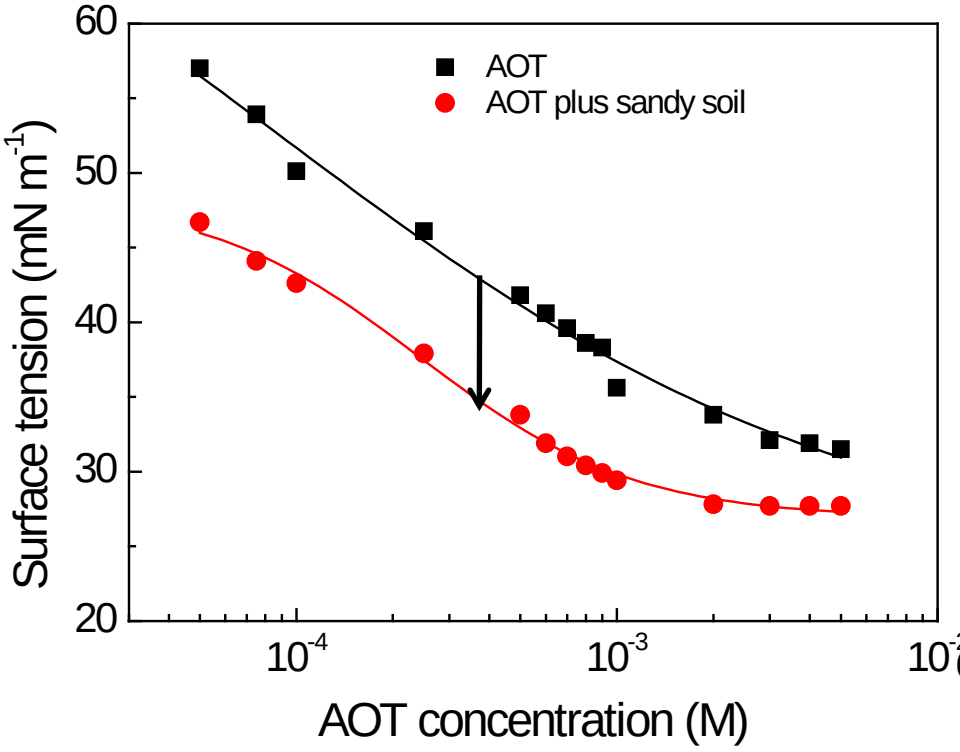
The surface tension of various aqueous systems comprising aqueous solutions of P184 mixed with silica sand (O); kaolinite (O); bentonite (O) and in the absence of any mineral (O).

Pluronic adsorption to mineral and soil surfaces

- The relatively hydrophobic pluronics are less well adsorbed.
- **Adsorption to mineral surfaces can and often does alter surface wetting properties.**

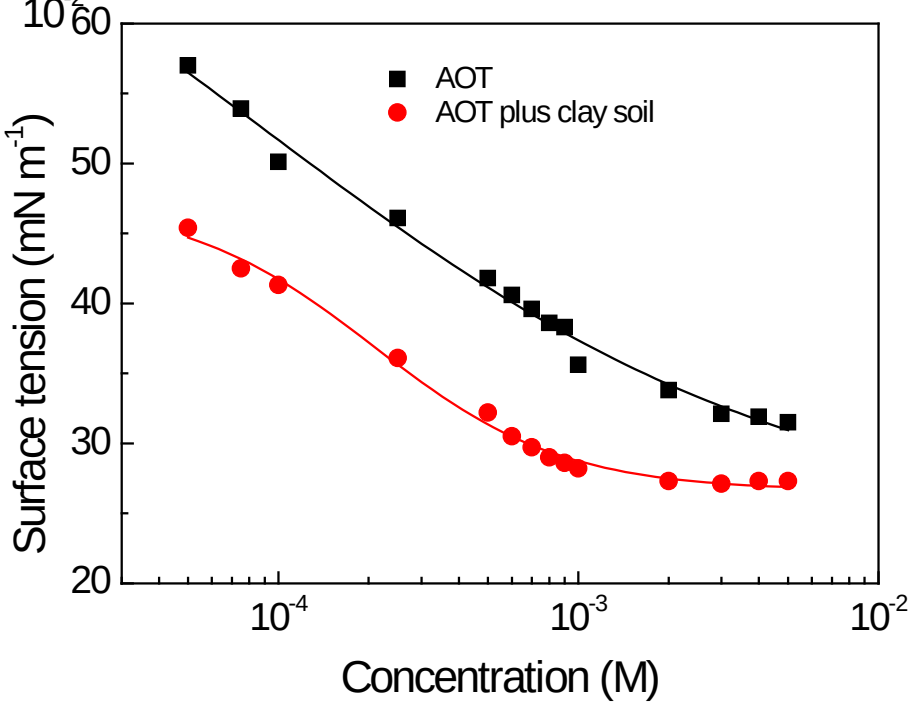
SDS, AOT and soils

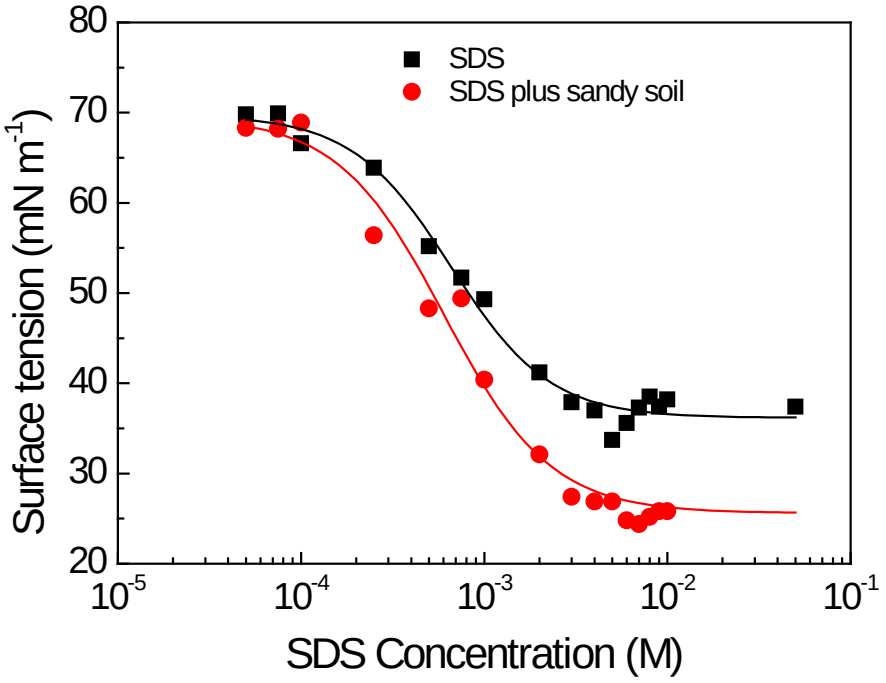
- SDS and AOT are anionic surfactants so they shouldn’t be adsorbed by soils.
- As a consequence surface tension should be unaffected by the presence of soils.



Data obtained for AOT

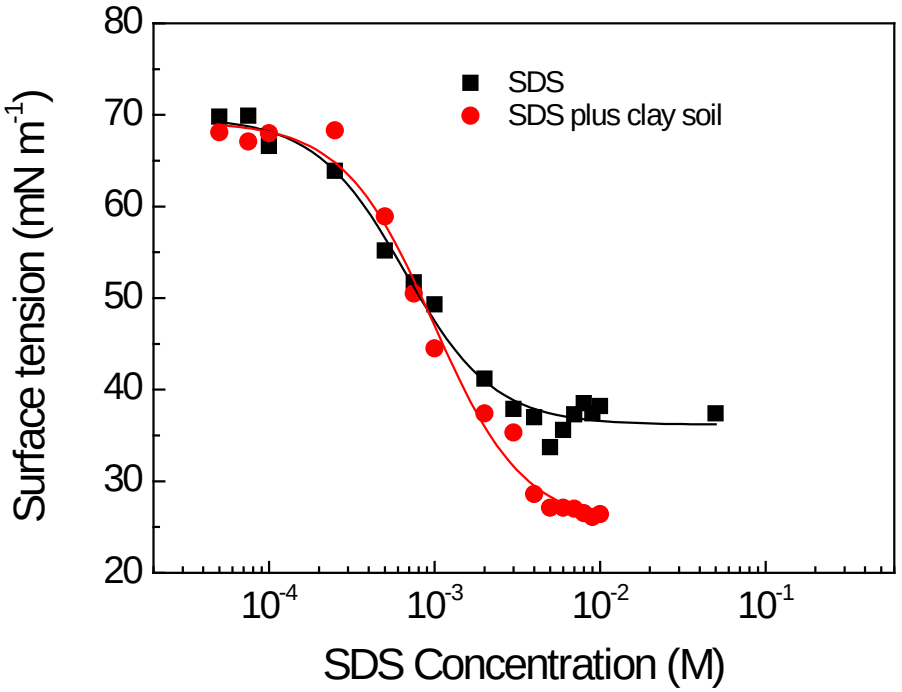
Surface tension decreases in the presence of soil



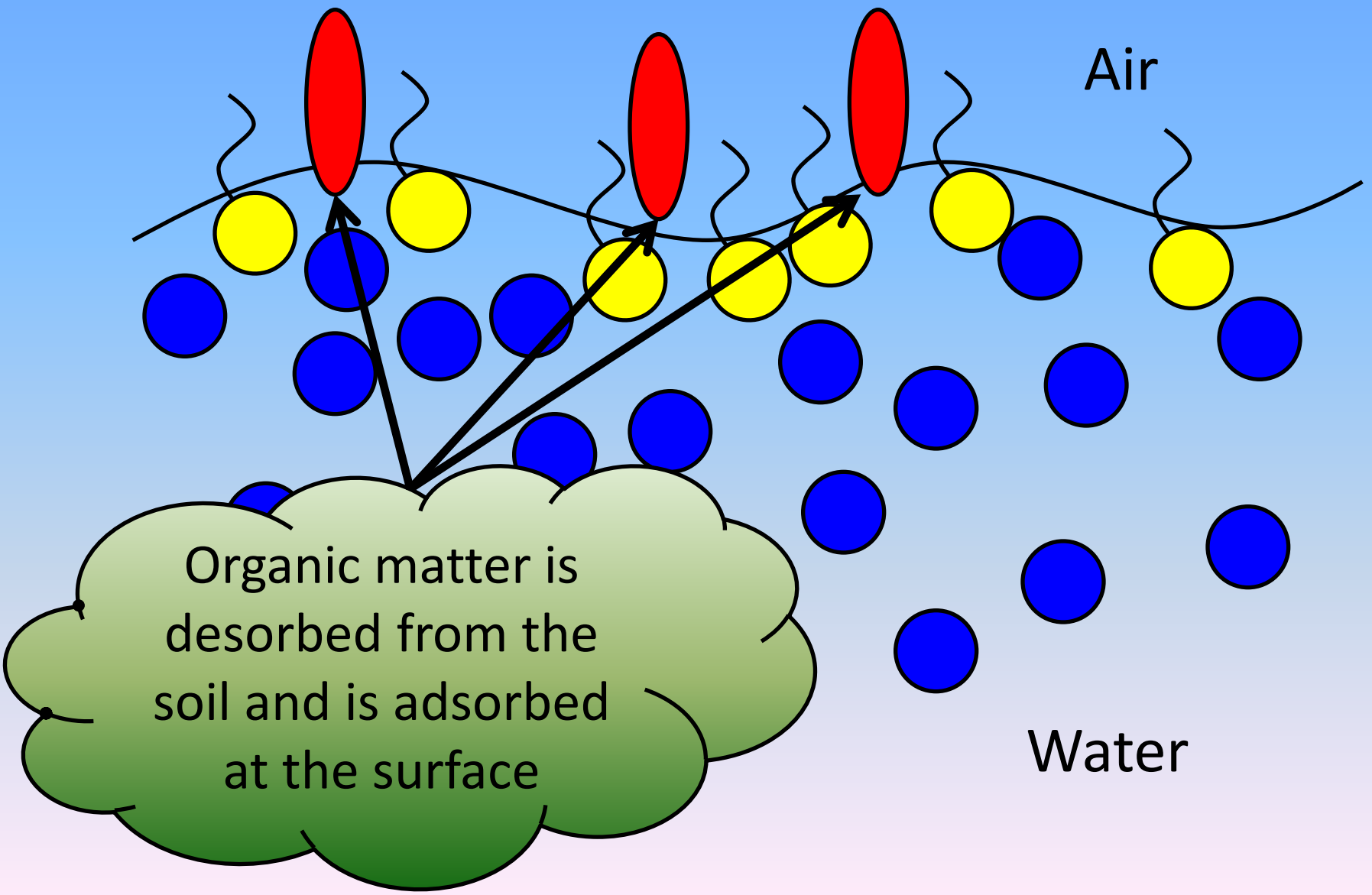


SDS

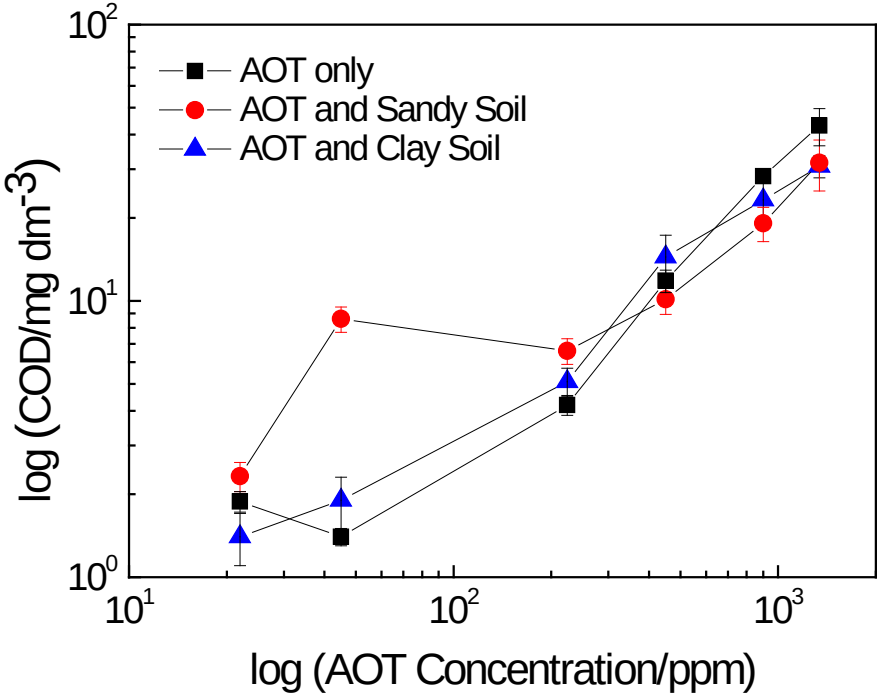
Surface tension decreases in the presence of soil

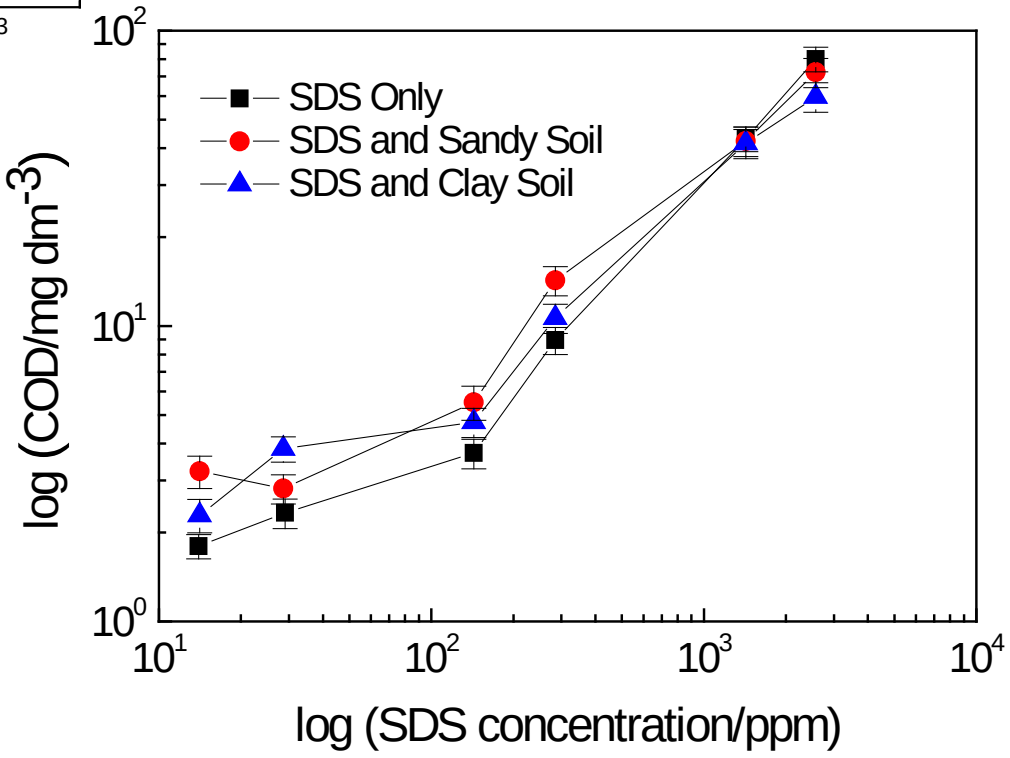


Hypothesis


Air
Organic matter is desorbed from the soil and is adsorbed at the surface
Water

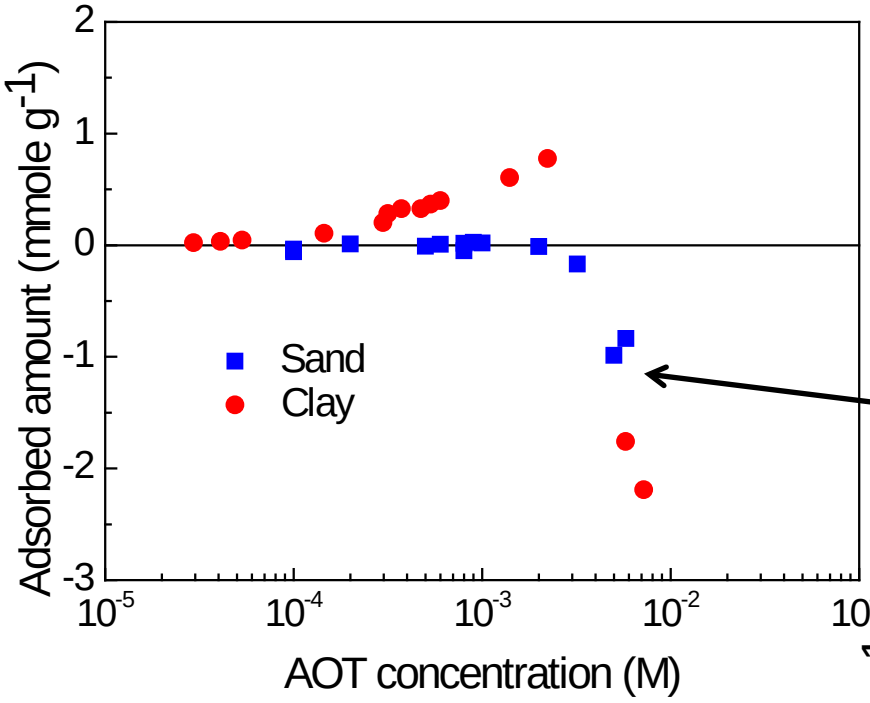
Chemical Oxygen Demand





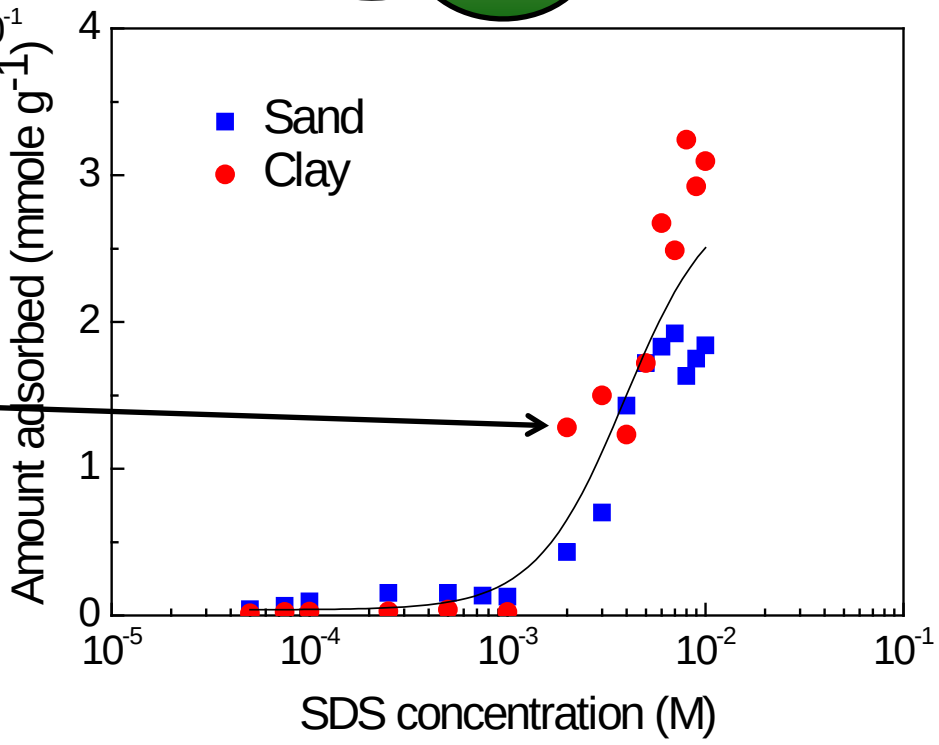
Some evidence that surfactants desorb organic matter; but not conclusive.

Adsorption experiments with methylene blue



Desorption

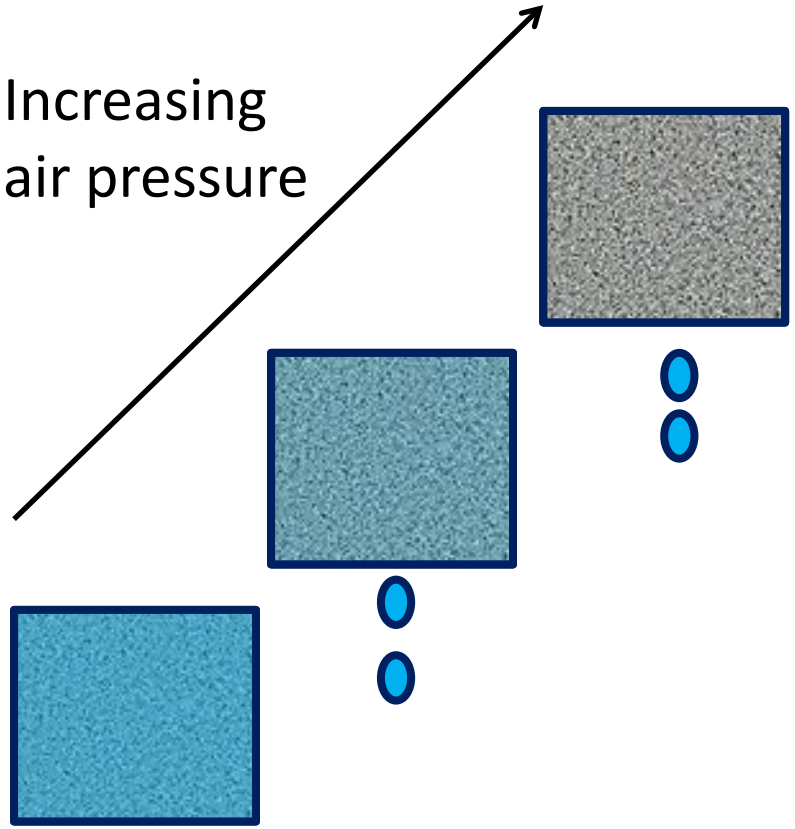
Adsorption

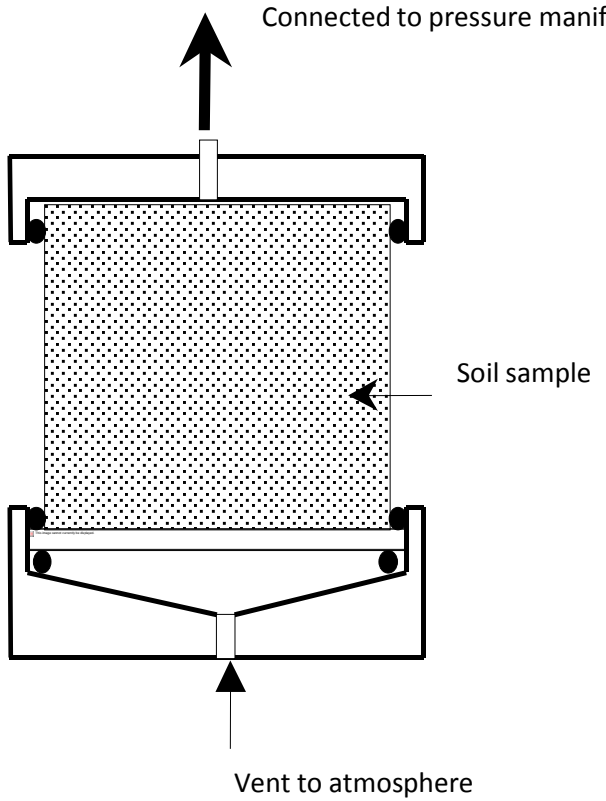


Hydraulic Conductivity

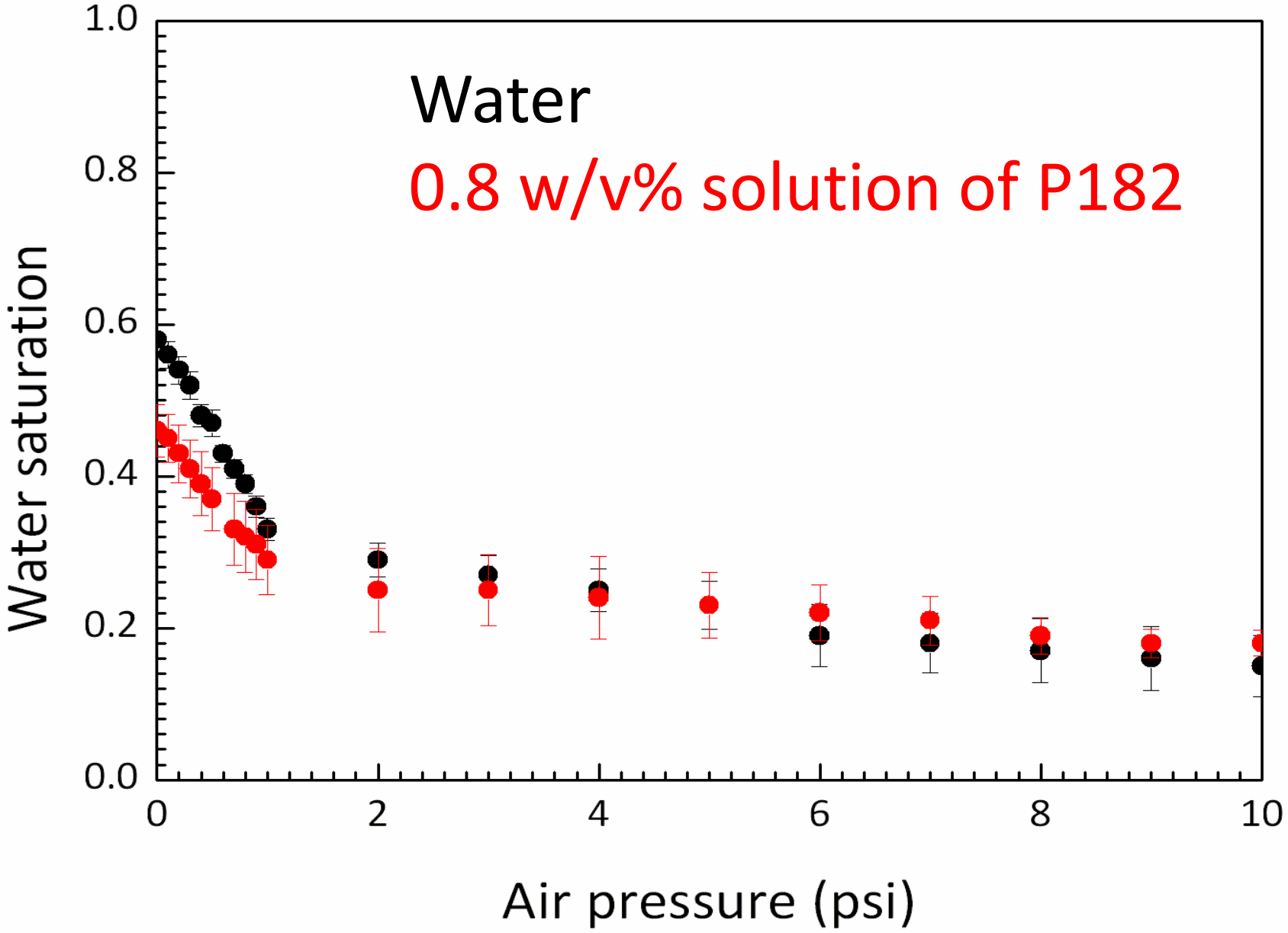
Treatment	PEO/PPO	K_{sat} (m/sec)	K_{sat} (m/day)	Standard deviation (m/day)
Water	–	1.8×10^{-4}	15.86	0.38
P124	0.83	1.5×10^{-4}	12.90	1.71
P105	1.00	1.4×10^{-4}	11.90	0.83
P184	0.66	1.2×10^{-4}	10.00	4.09
P188	3.77	1.1×10^{-4}	9.50	0.24
P284	0.67	1.1×10^{-4}	9.10	0.47

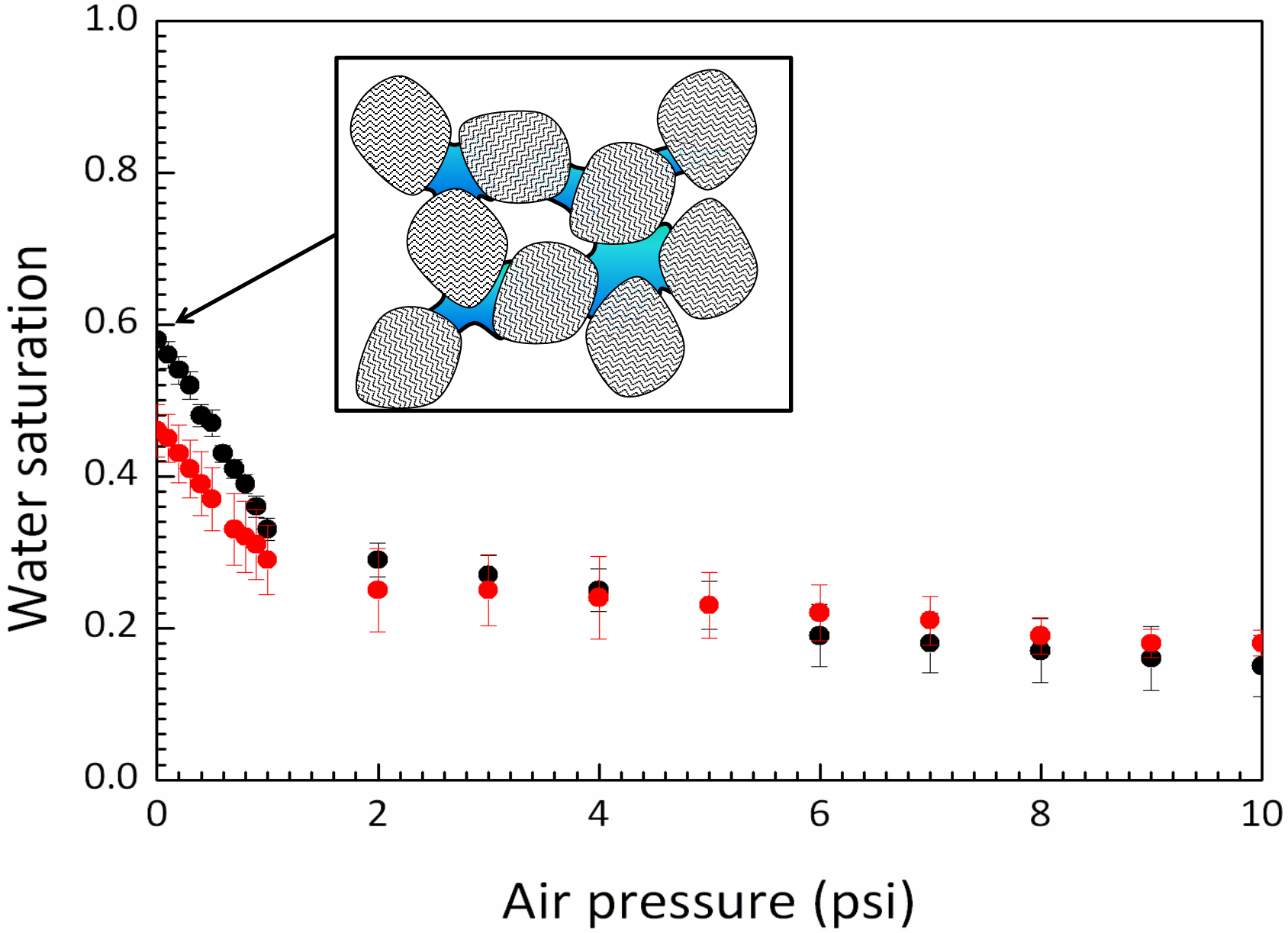
Changes in soil water characteristics: Drainage and imbibition

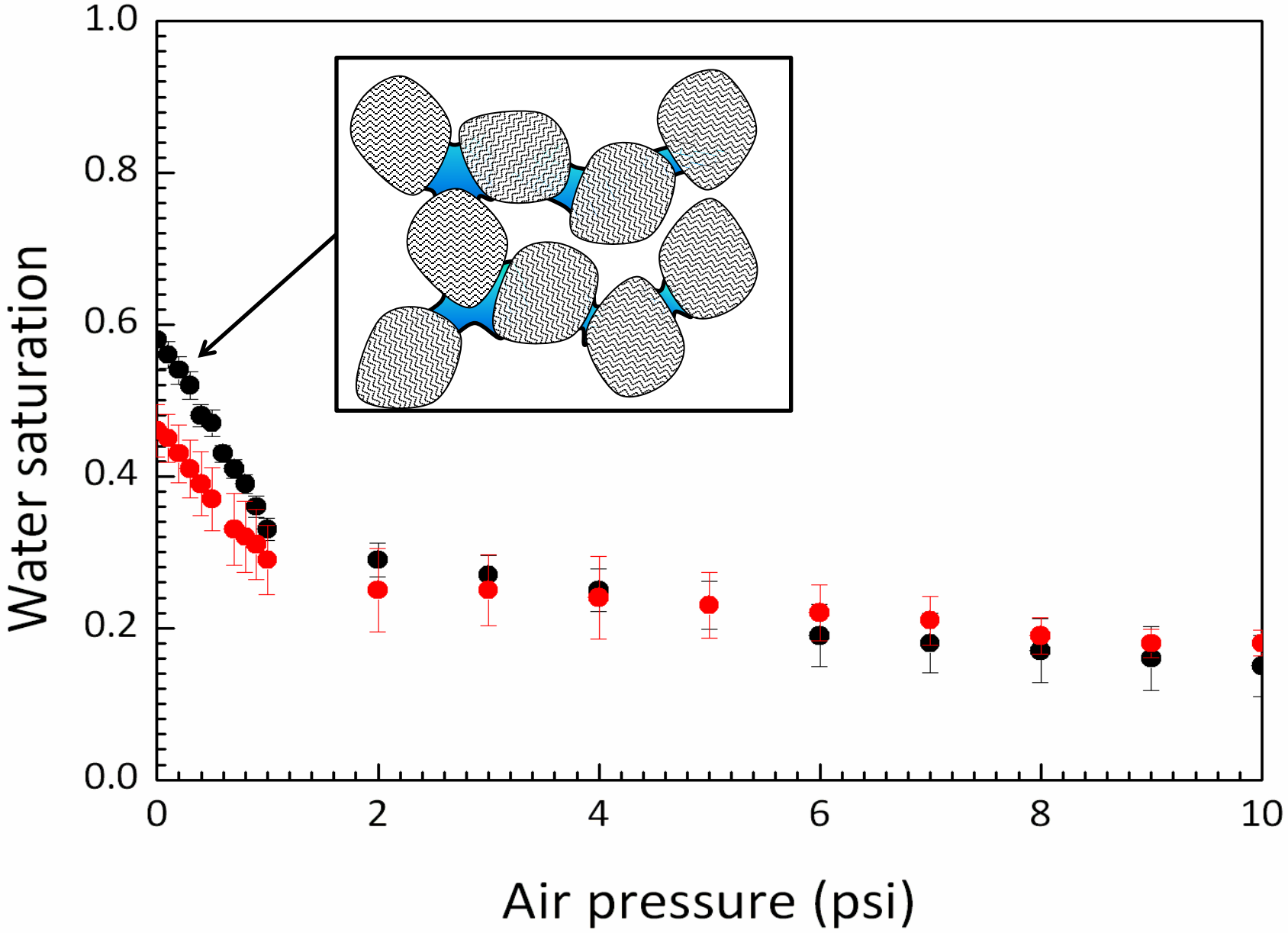


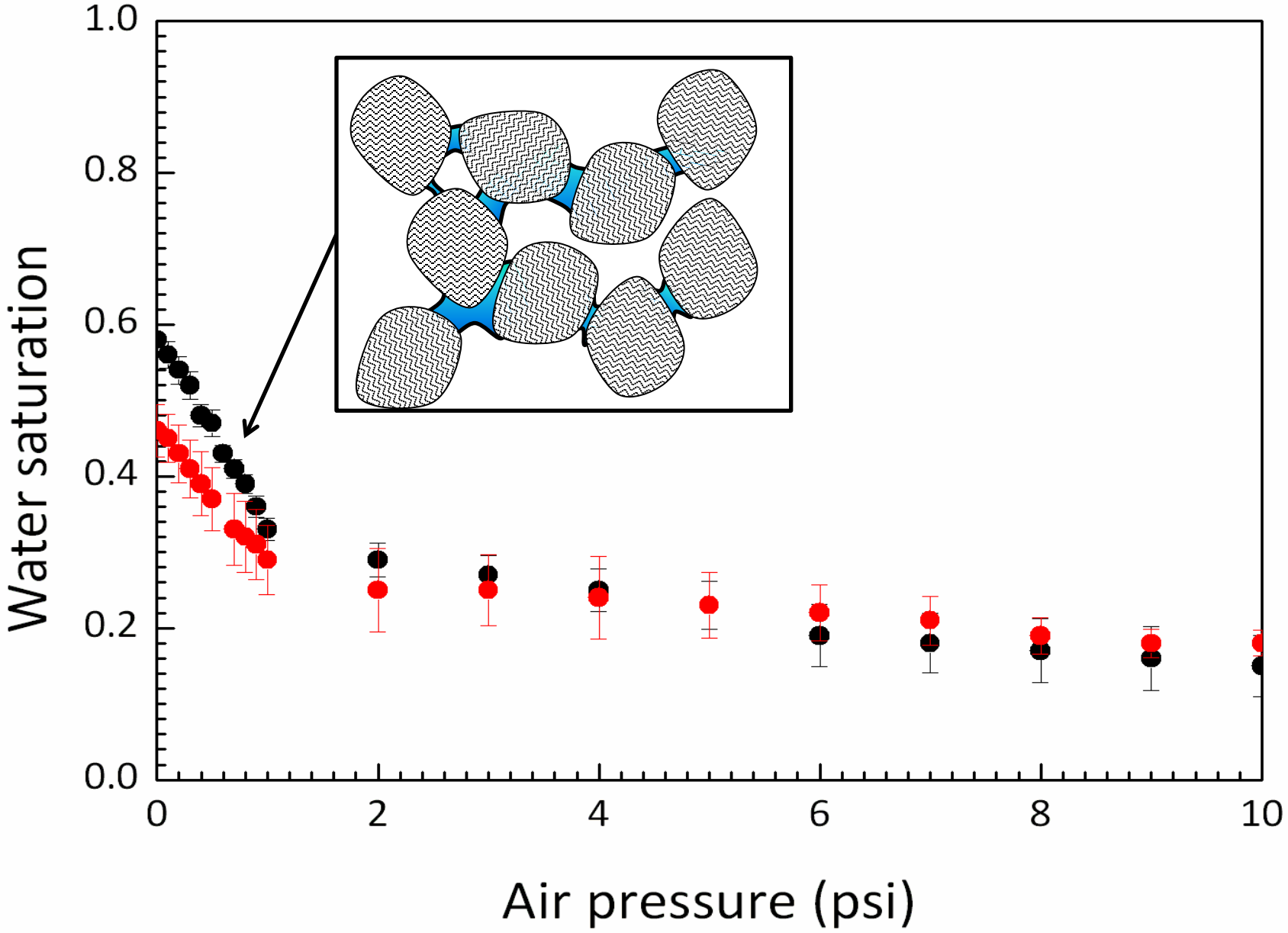


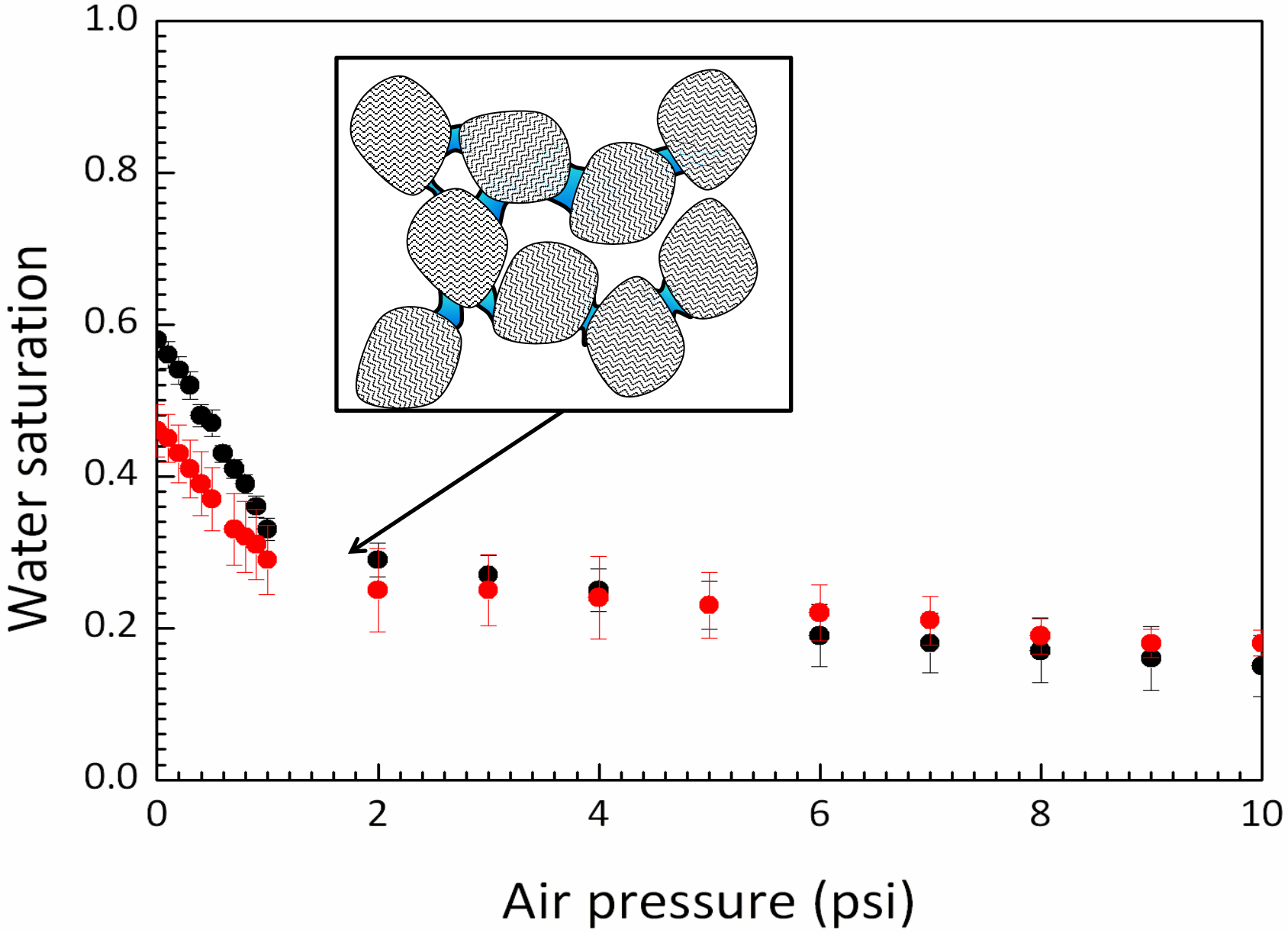
Drainage experiments

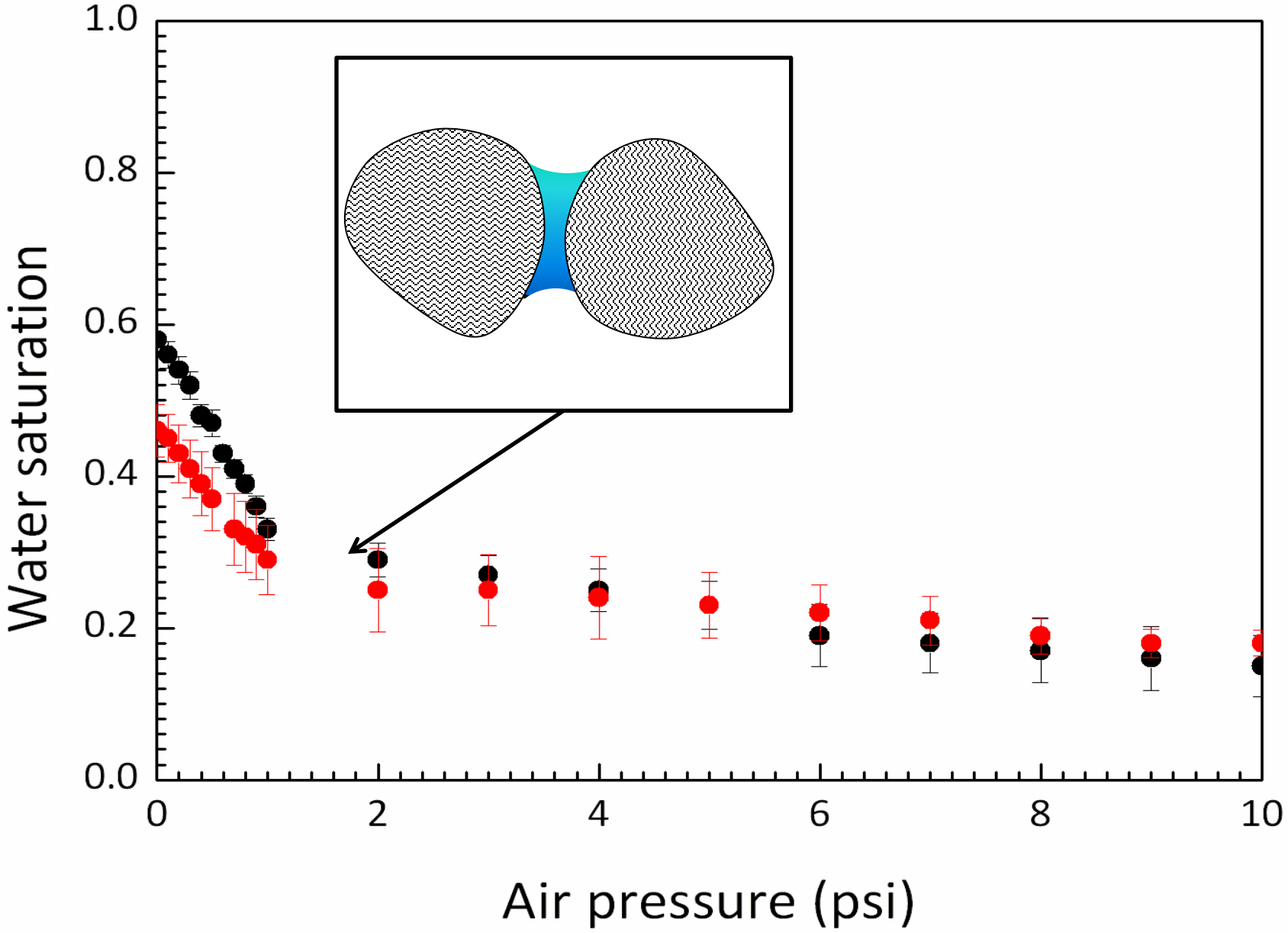

Water
0.8 w/v% solution of P182
Water saturation
Air pressure (psi)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10

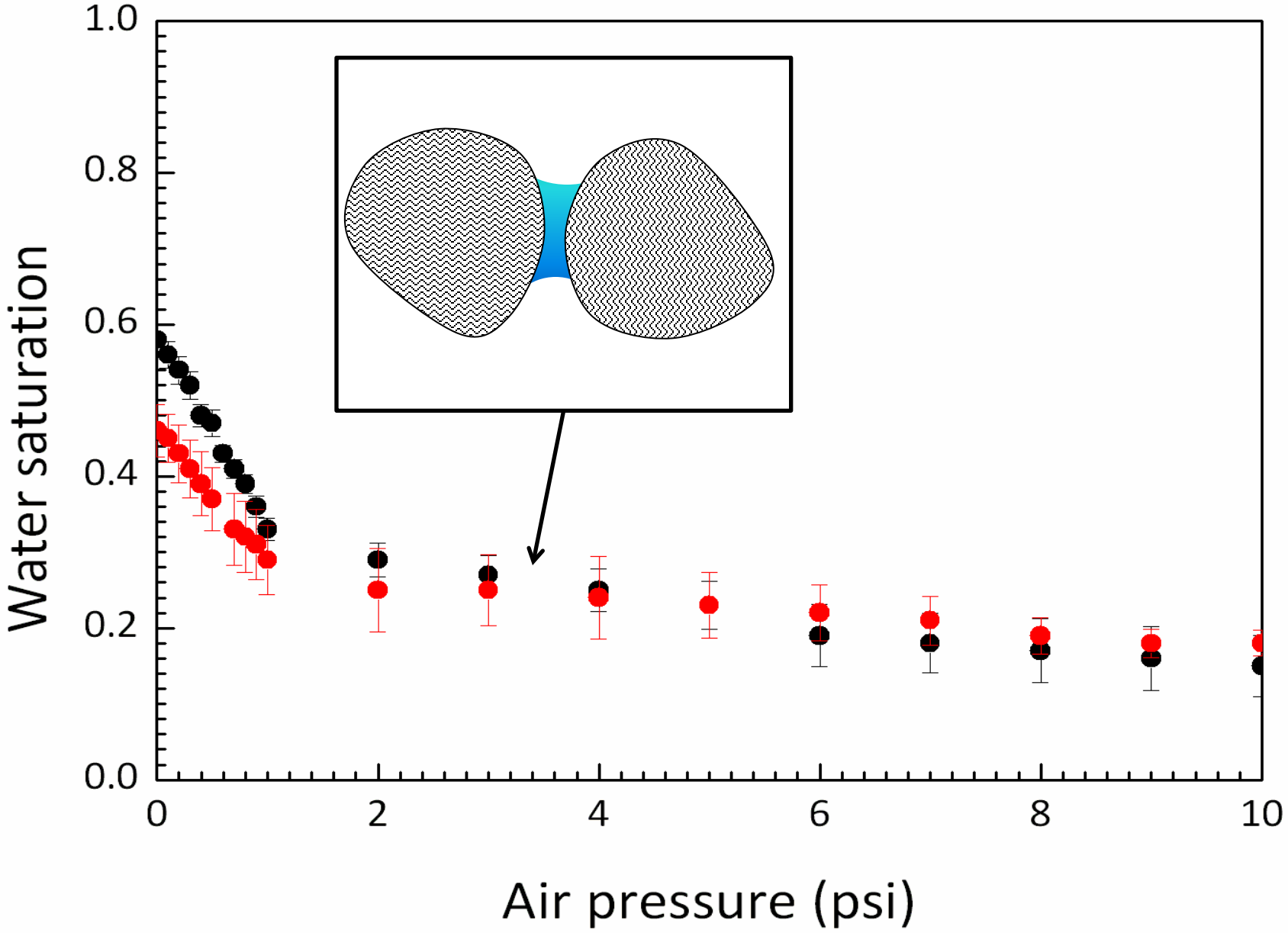

1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)

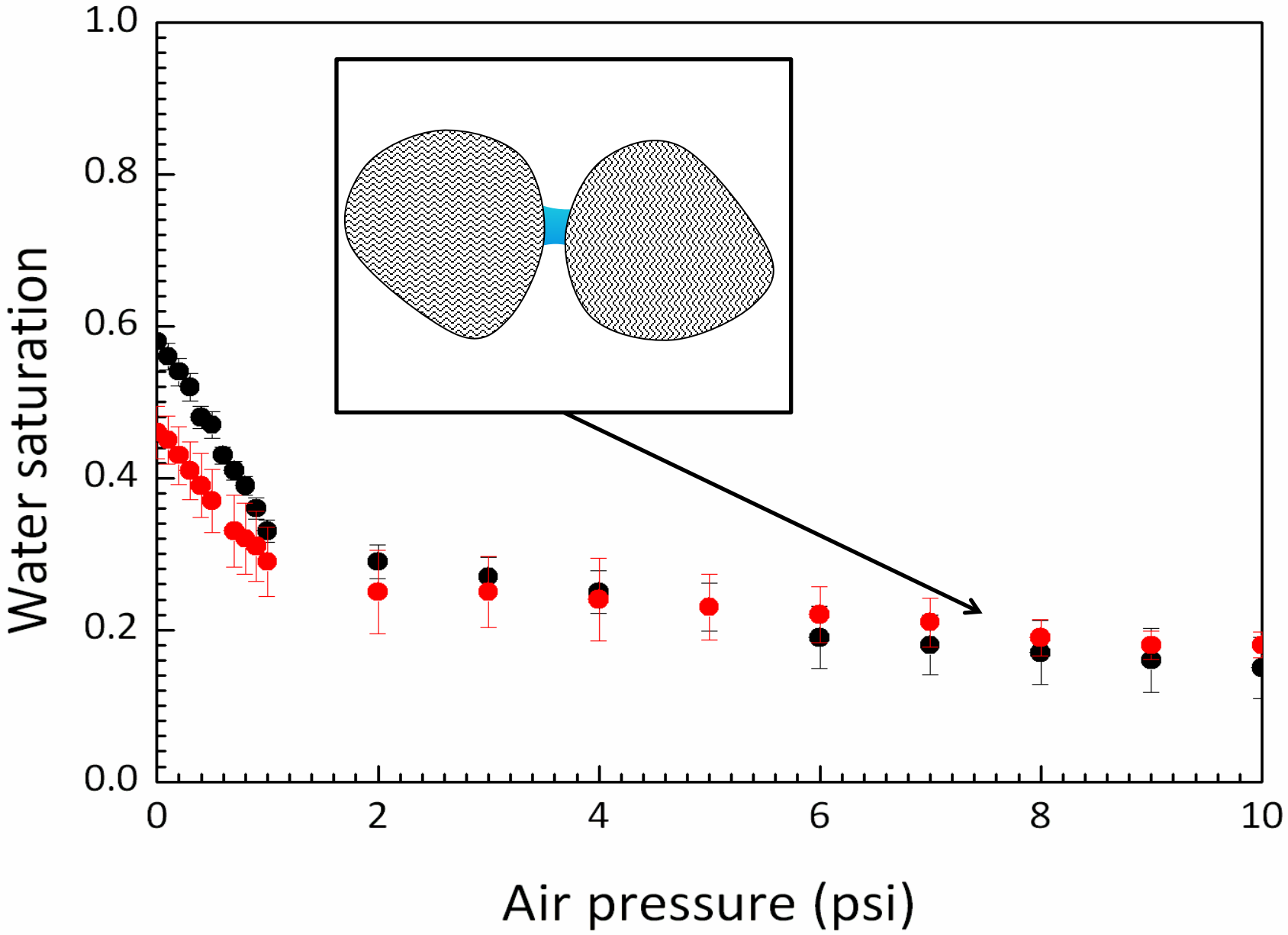

1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)

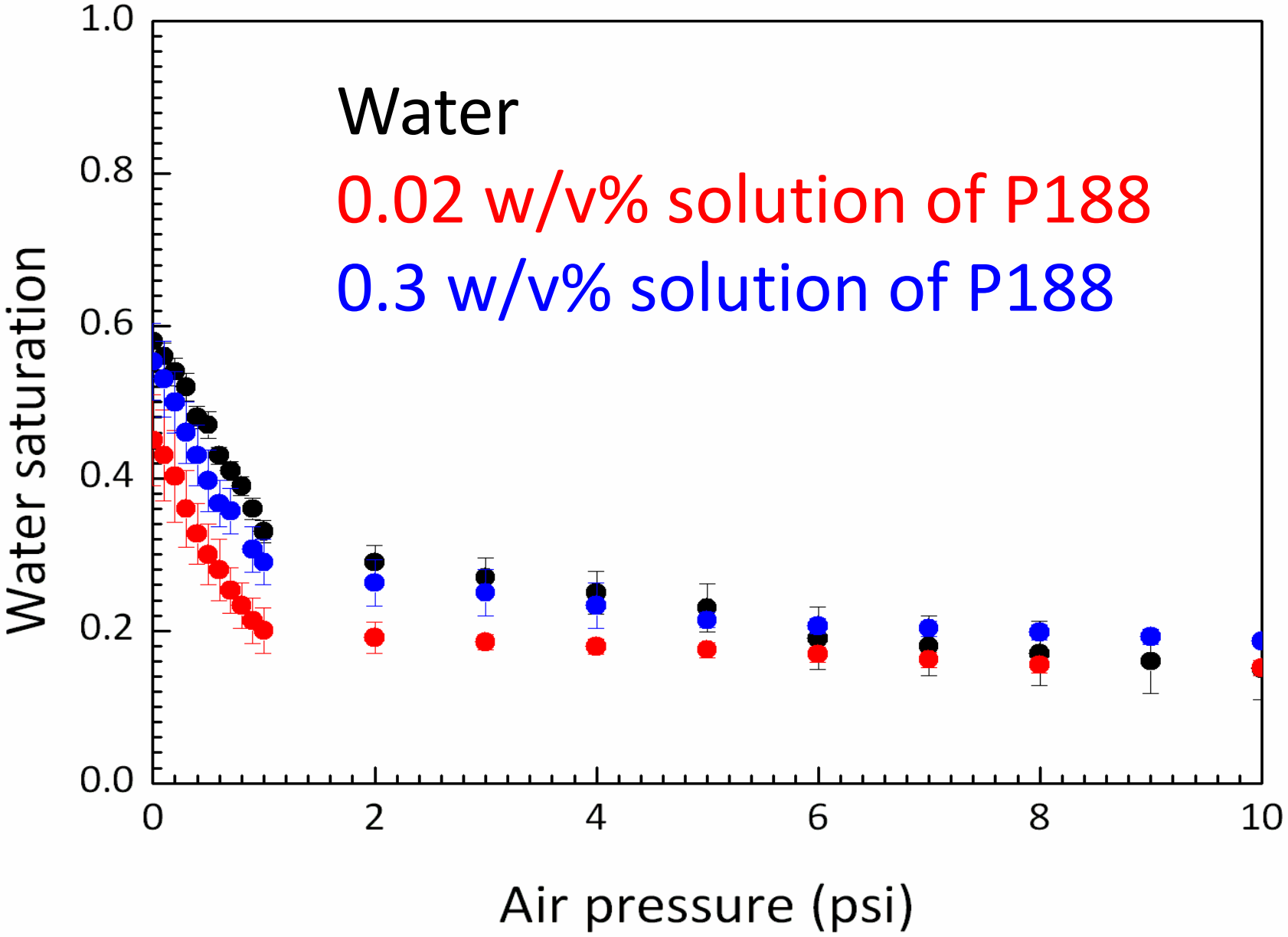

1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)

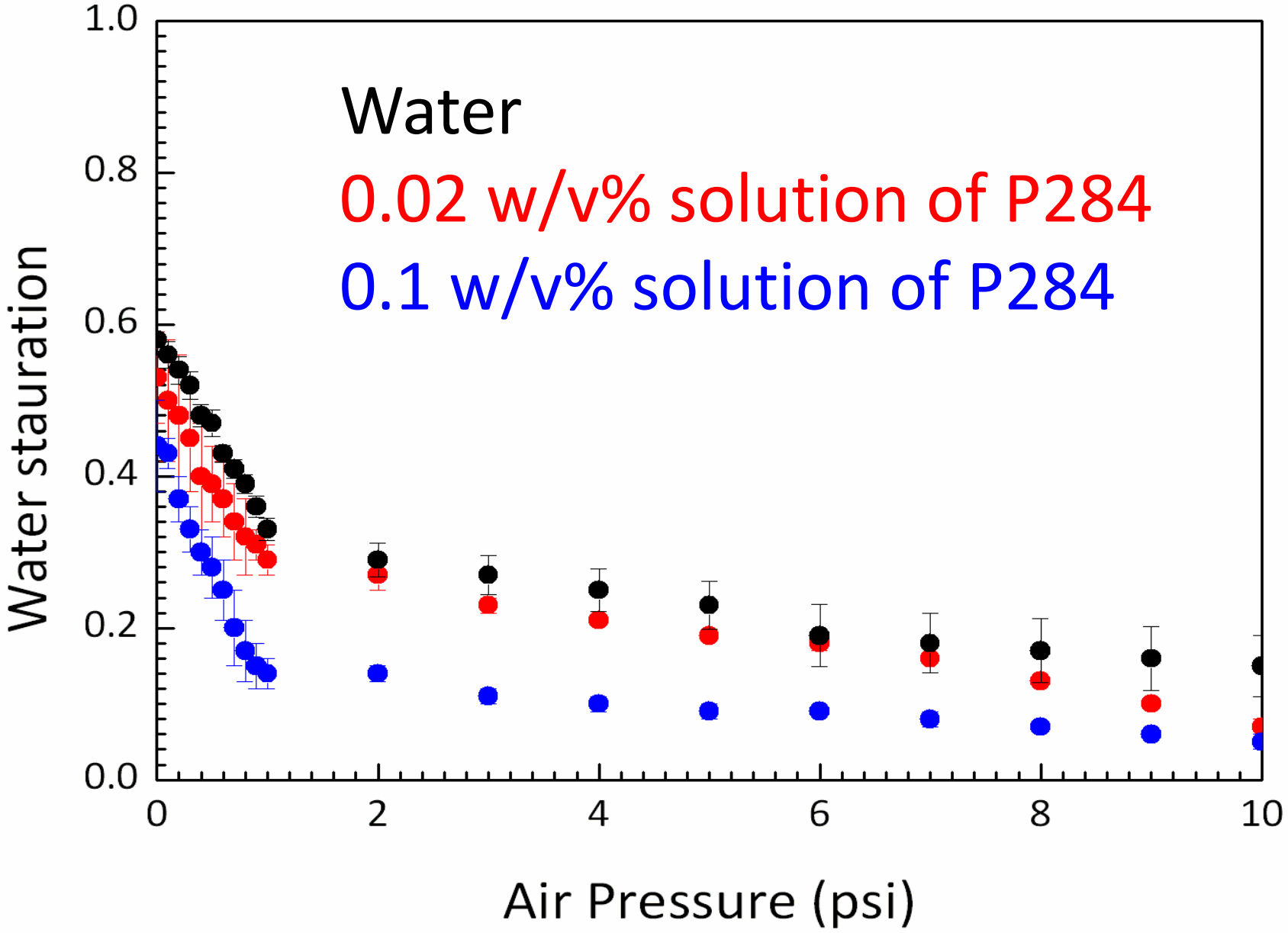

1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)

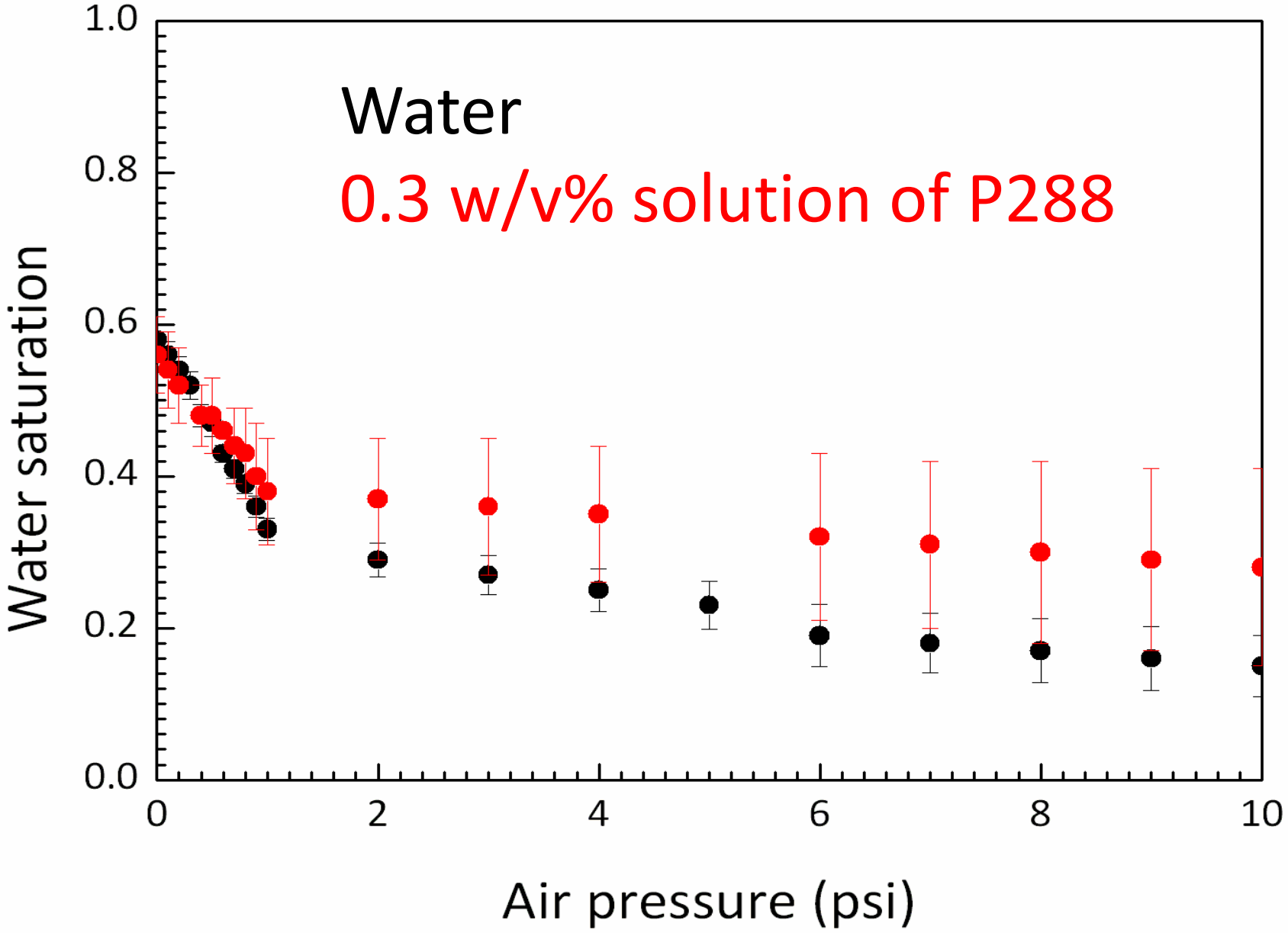

1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)

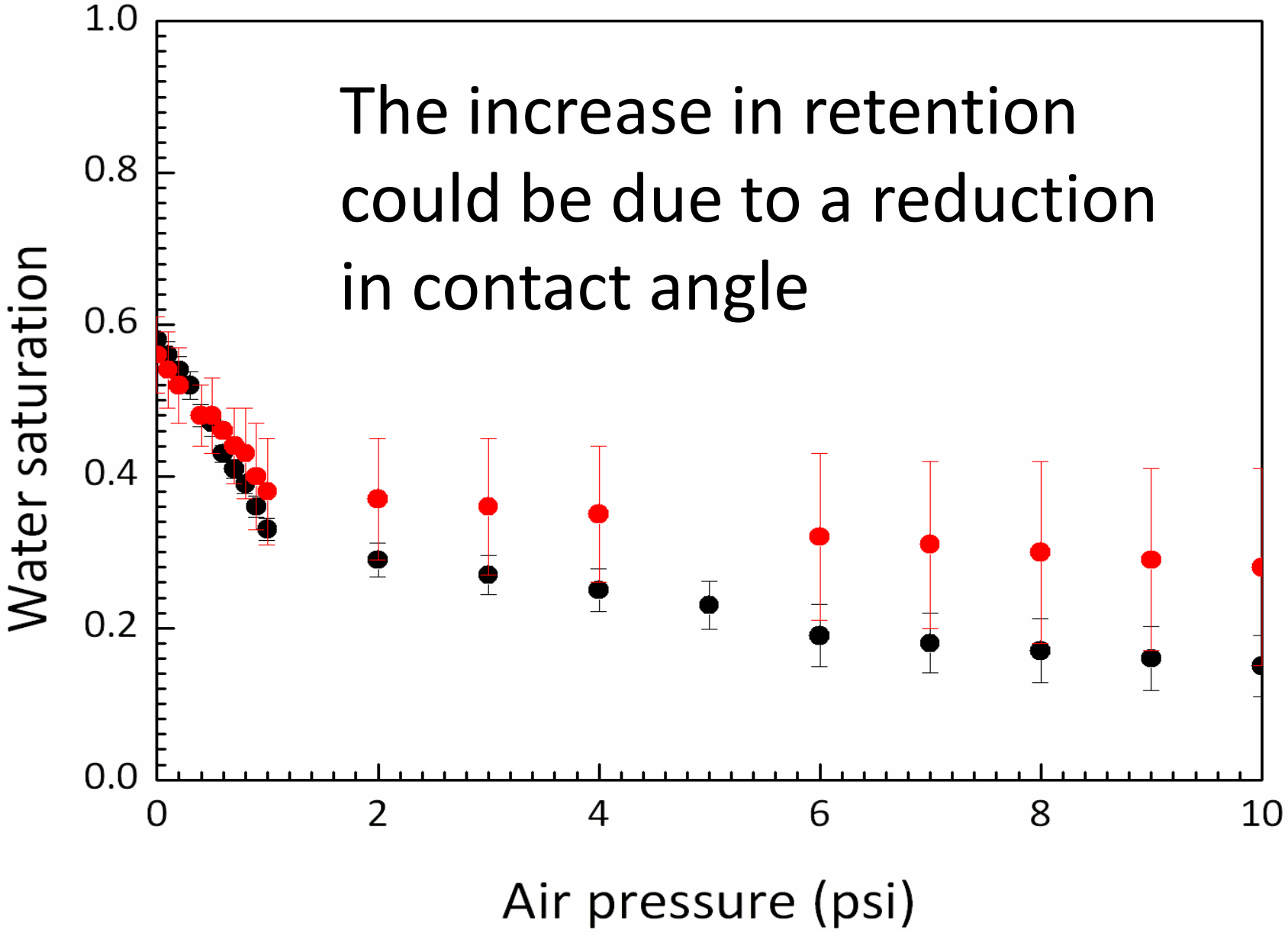

1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)


1.0
0.8
0.6
0.4
0.2
0.0
Water saturation
0
2
4
6
8
10
Air pressure (psi)


Water
0.02 w/v% solution of P188
0.3 w/v% solution of P188
Water saturation
Air pressure (psi)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10


Water
0.02 w/v% solution of P284
0.1 w/v% solution of P284
Water staturation
Air Pressure (psi)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10


Water
0.3 w/v% solution of P288
Water saturation
Air pressure (psi)
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10


The increase in retention could be due to a reduction in contact angle
Water saturation
1.0
0.8
0.6
0.4
0.2
0.0
0
2
4
6
8
10
Air pressure (psi)

Displacement entry pressure

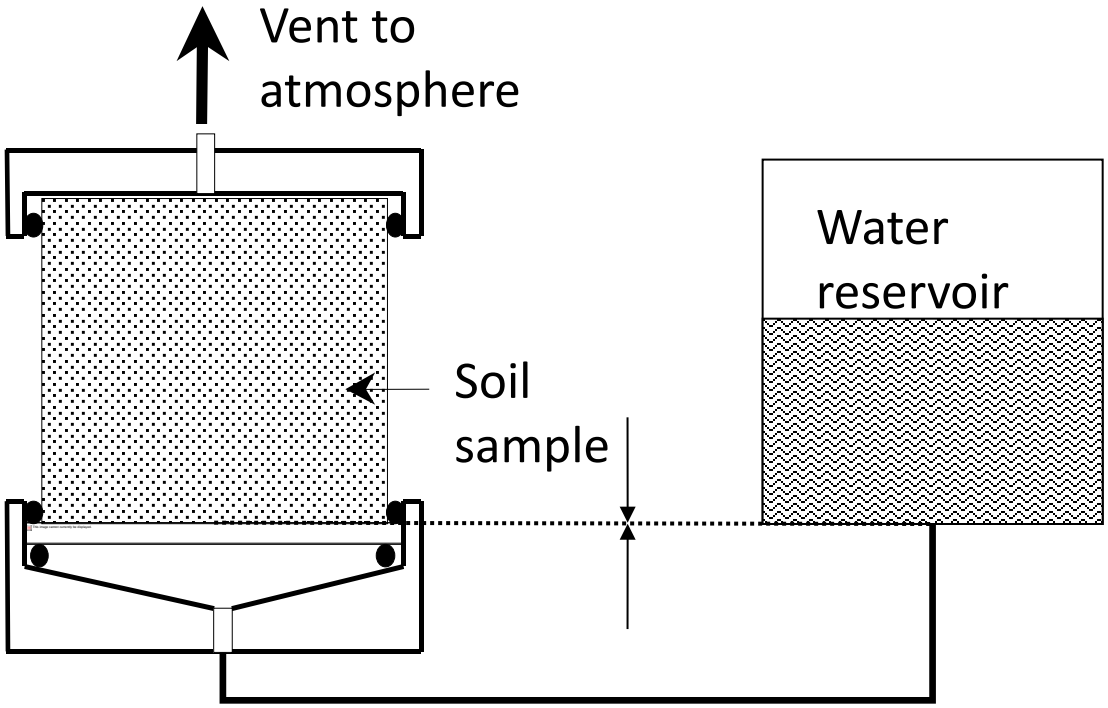
- To remove water from a lens the air pressure must exceed the Laplace pressure.

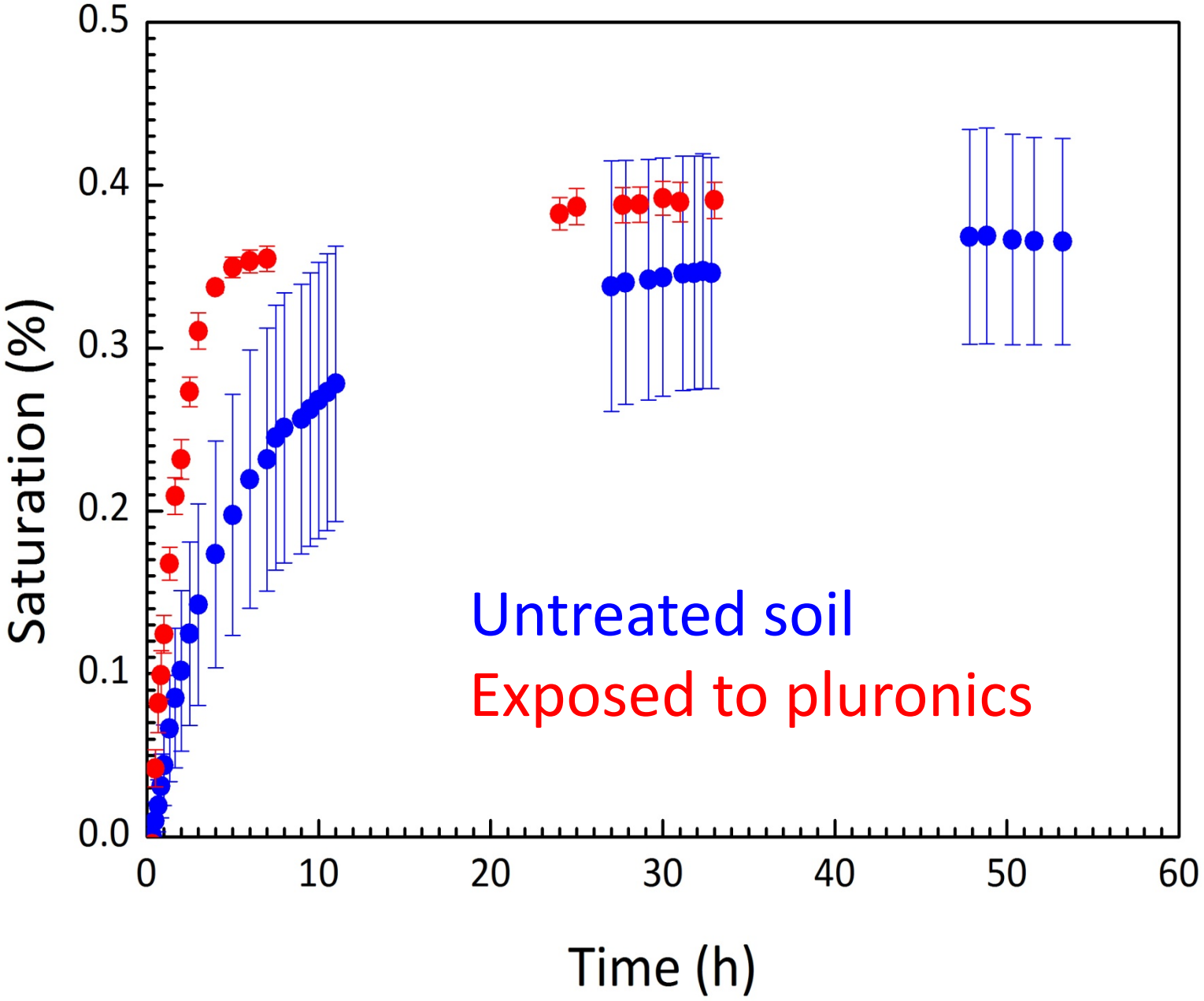
$$P_{air} > P_{water} + \frac{2\sigma\cos\theta}{r}$$

$$\cos\theta \to 1 \quad as \quad \theta \to 0$$

If the contact angle is reduced the air pressure necessary to bring about drainage is increased.

Imbibition




0.5
0.4
0.3
0.2
0.1
0.0
Saturation (%)
0
10
20
30
40
50
60
Time (h)
Untreated soil
Exposed to pluronics

Conclusions

- Surfactants through alterations in contact angle and surface tension affect the physics of water retention and flow in soil systems.