UNIL | Université de Lausanne

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

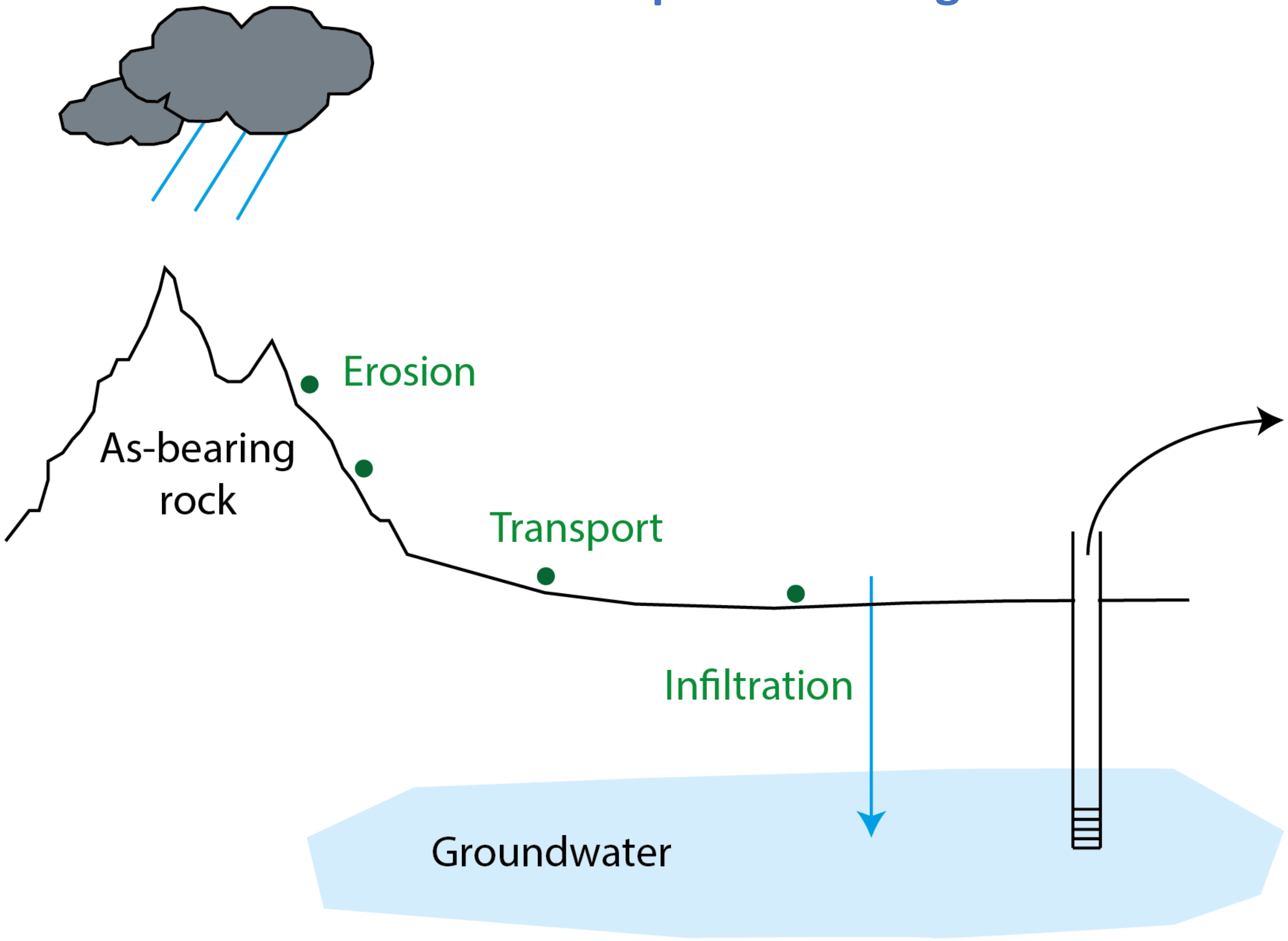
FONDS NATIONAL SUISSE DE LA RECHERCHE SCIENTIFIQUE

Arsenic removal from natural waters using iron(0) electrocoagulation

C. Catrouillet, N. Manetti, L.H., Soegaard Jensen, J. Peña

charlotte.catrouillet@unil.ch
jasquelin.pena@unil.ch

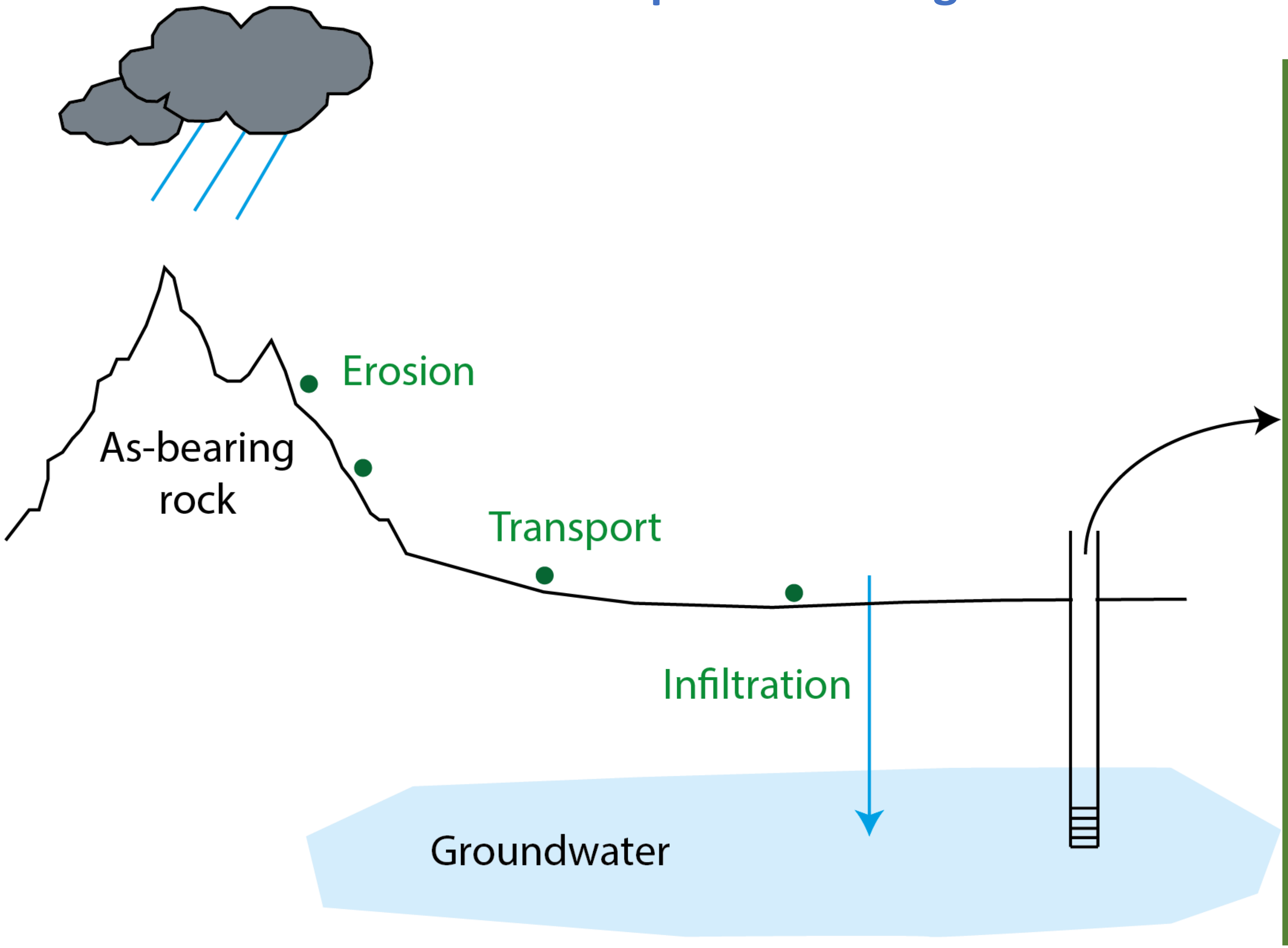
As exposure through contaminated water



Medicalxpress.com

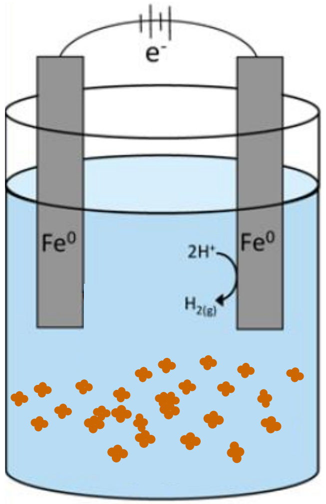
WHO recommendation:
10 µg L^{-1} As (=0.133 µM)

As exposure through contaminated water



Treatment

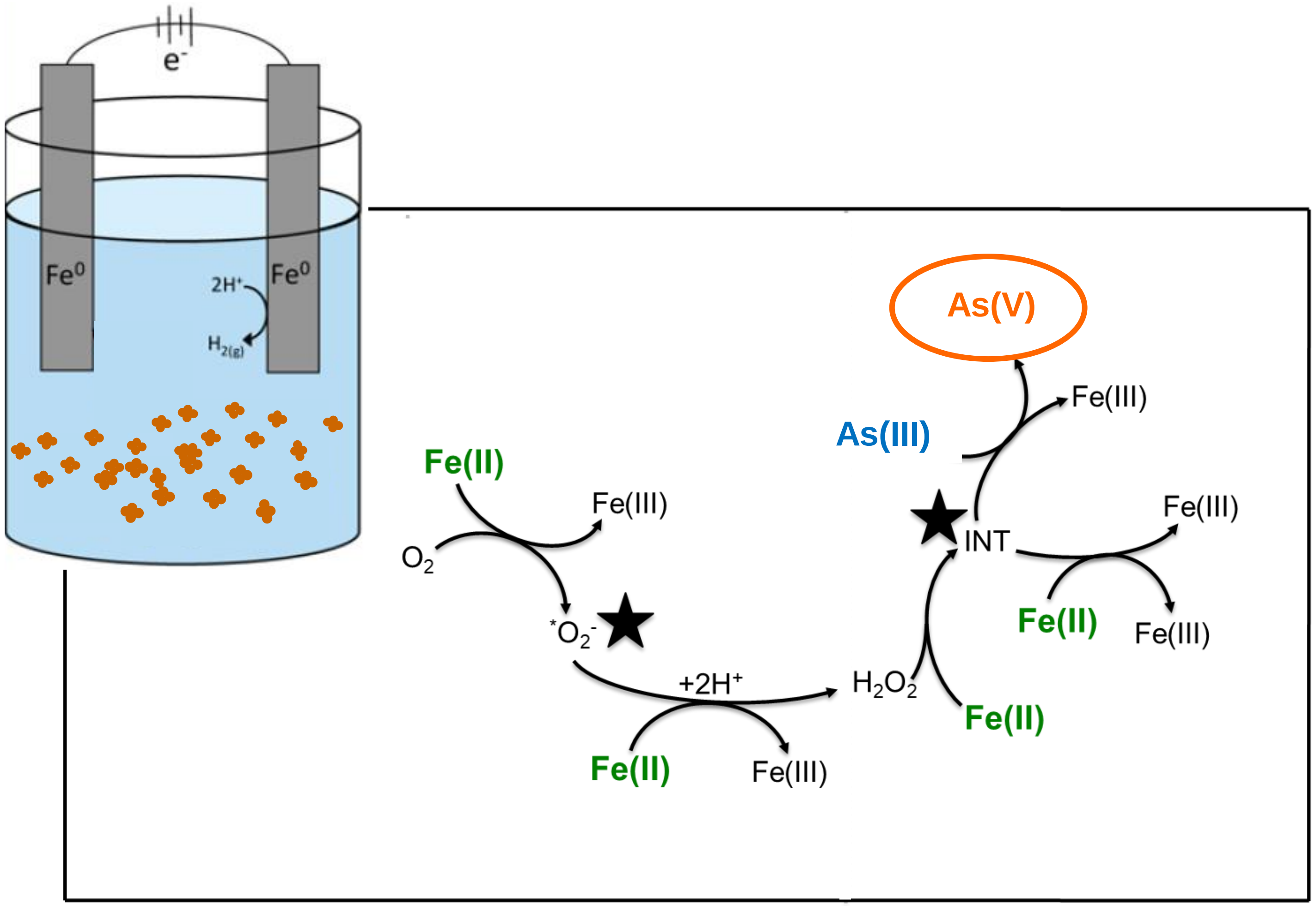
Electro-coagulation



C. van Genuchten

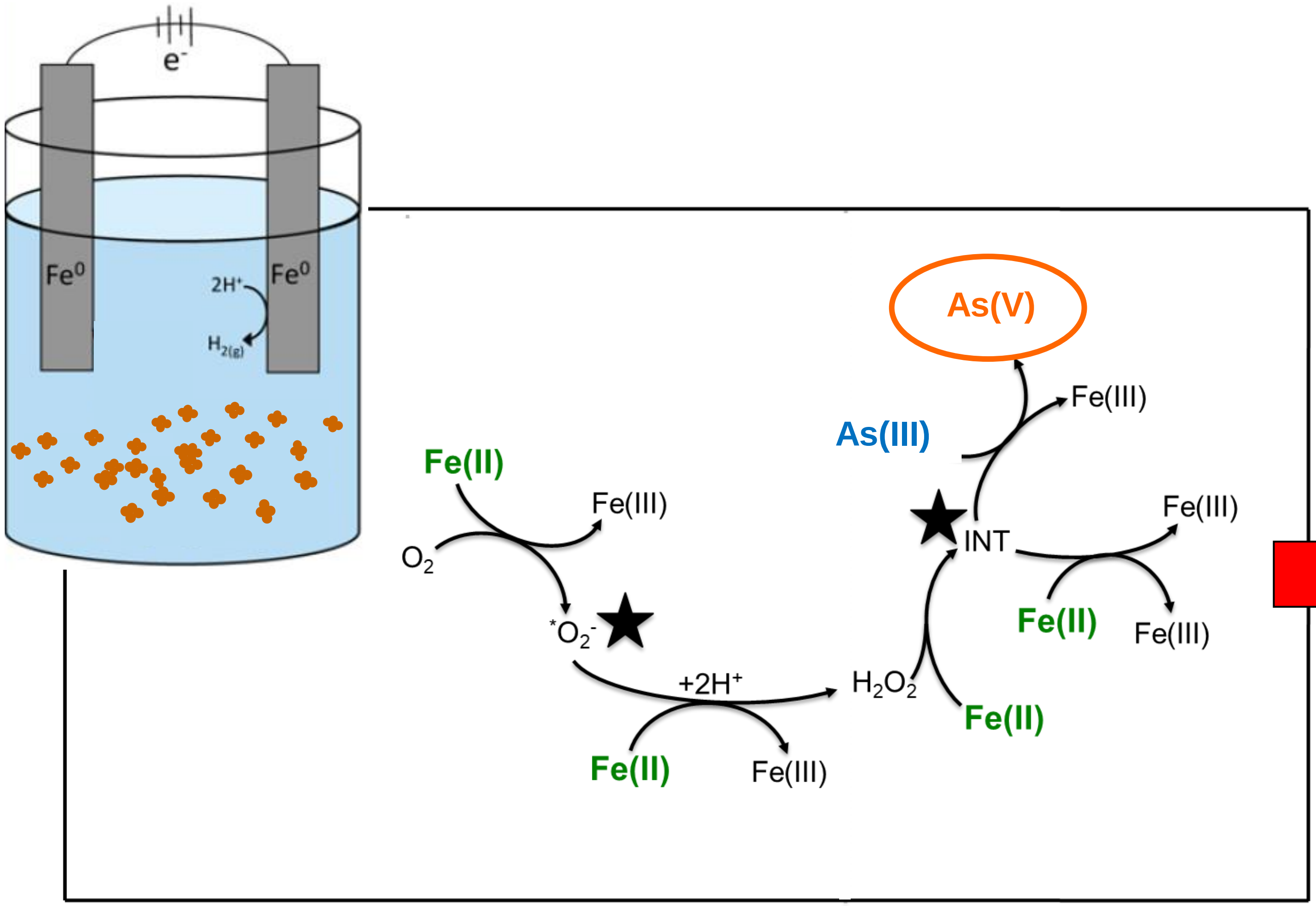
https://fssai.gov.in

Fe(0) electrocoagulation: removal mechanism based on oxidation and sorption



1 As(III) & Fe(II) oxidation by Fenton-like reactions

Fe(0) electrocoagulation: removal mechanism based on oxidation and sorption



van Genuchten et al., 2012

1 As(III) & Fe(II) oxidation by Fenton-like reactions

2 Sorption of As to Fe(III) precipitates

As exposure through contaminated water

Microorganisms (pathogens)

Na^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, HCO_3^{-}, SO_4^{2-}

Nitrates

Phosphates

Organic matter

Arsenic: As(III), As(V)

Metals: iron, manganese
Fe(II,III), Mn(II,III, IV)

Medicalxpress.com

Which elements limit/enhance As removal in natural waters? And how?

Approach – 3 waters from UNIL campus tested

1) Lake (Geneva)
2) River (Chamberonne)
3) Ground water (UNIL Dorigny)

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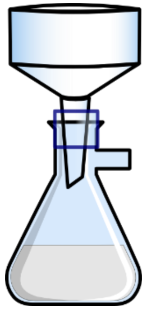
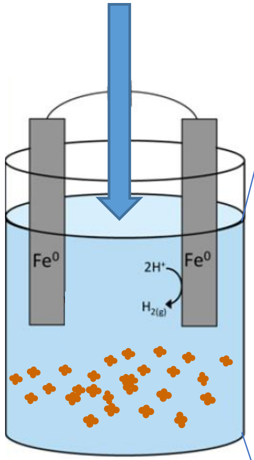


Filtration at 0.2 µm

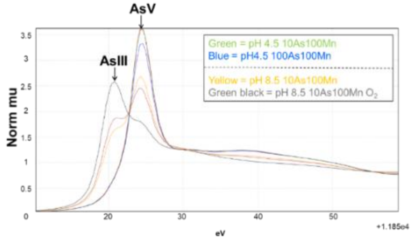
IC, ICP-OES, TIC and TOC
Electro-coagulation

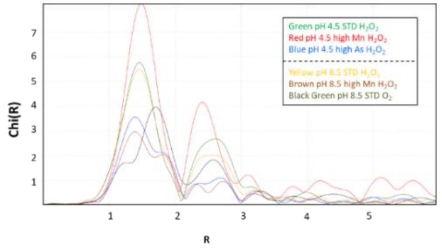
Approach

10 μM As(III)



Aqueous phase (<0.2 μm)	*Solid phase (>0.2 μm)*		
HG-ICP-OES, TOC-TIC, IC	SEM	XANES	EXAFS





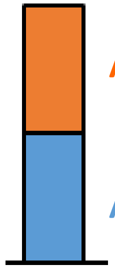
As redox state and water chem.

Morphology

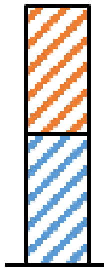
As redox state

Structure of the particles

-o- Aqueous As



TIC, Na, Cl, Ca, Mg, Na, $Si(OH)_4$, etc.



in the solid phase

Different compositions of the waters

	LAKE (Geneva)	RIVER (Chamberonne)	GROUNDWATER (UNIL-Dorigny)
	www.unil.ch 	www.wikipedia.com 	
µM			
Ca^{2+} + Mg^{2+}	895 + 244	1543 + 330	2733 + 531
HCO_3^- (TIC)	1084 (1134)	2173 (2307)	5312 (5765)
$Si(OH)_4$ + Cl^-	9 + 280.5	72 + 593	196 + 2735
NO_3^-	7.6	117	60
pH	8.1-8.3	8.2-8.4	7.7

∑Ions

As(III)

[As solution] depends on the water treated

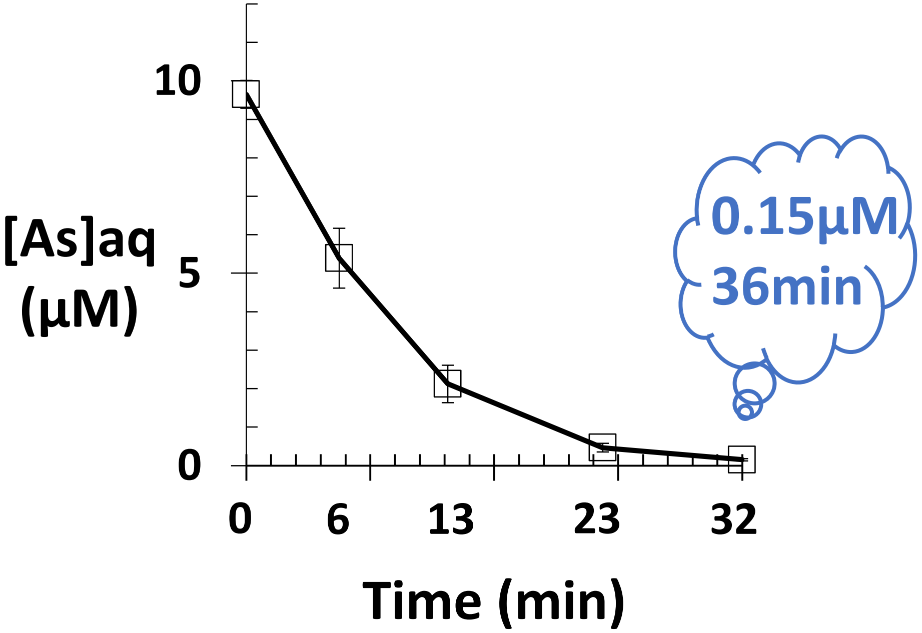
LAKE (Geneva)

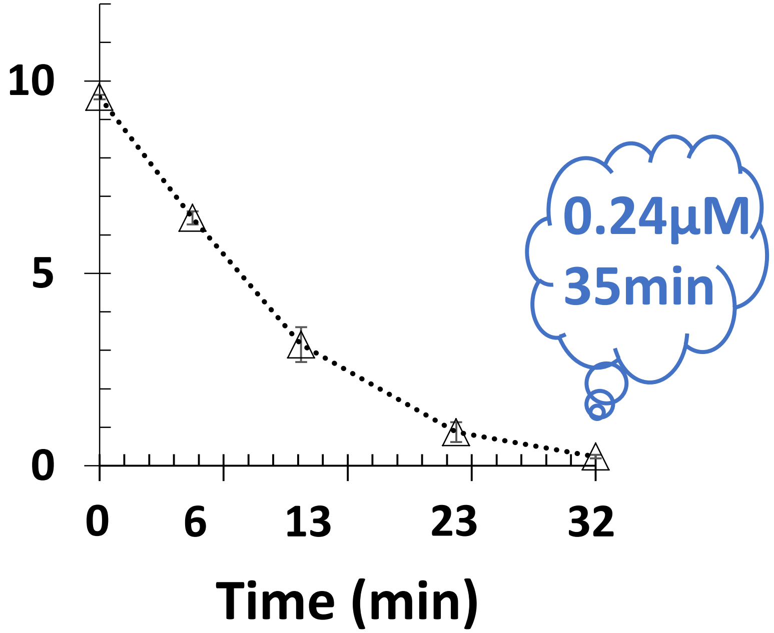
www.unil.ch

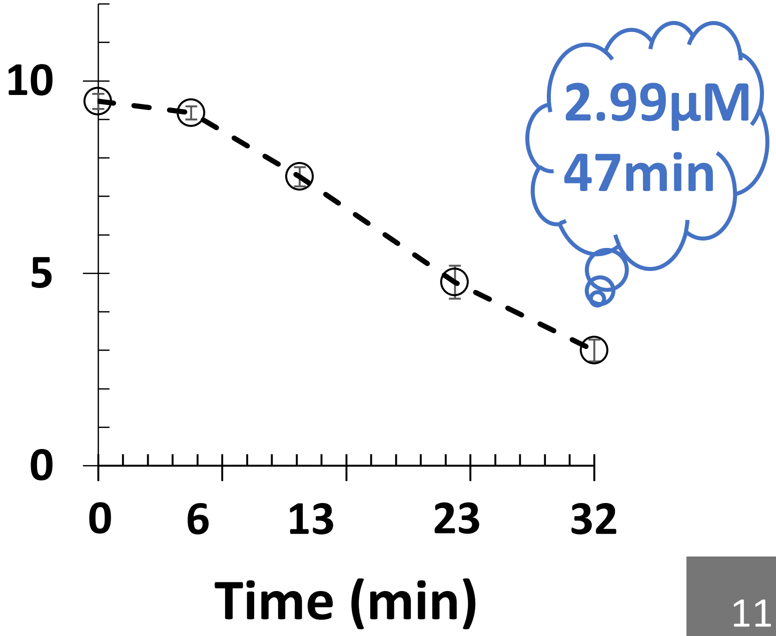
RIVER (Chamberonne)

www.wikipedia.com

GROUNDWATER (UNIL-Dorigny)



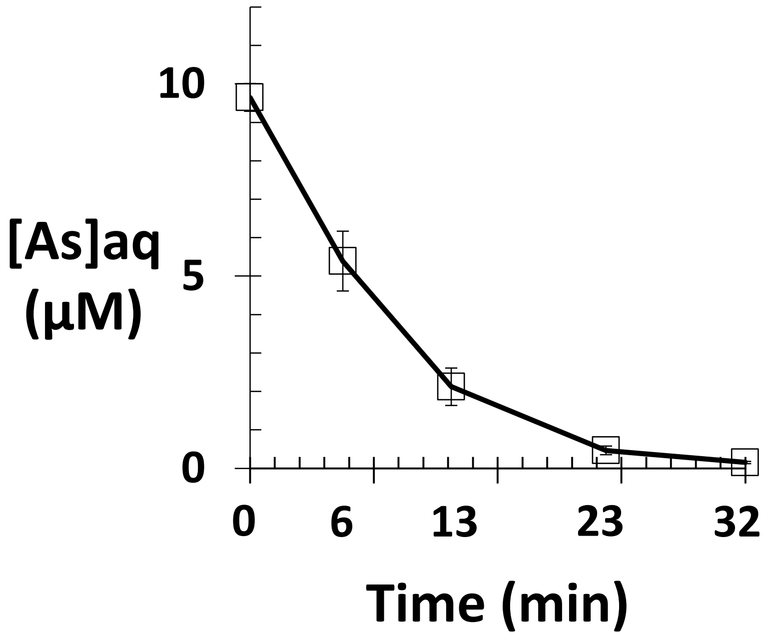




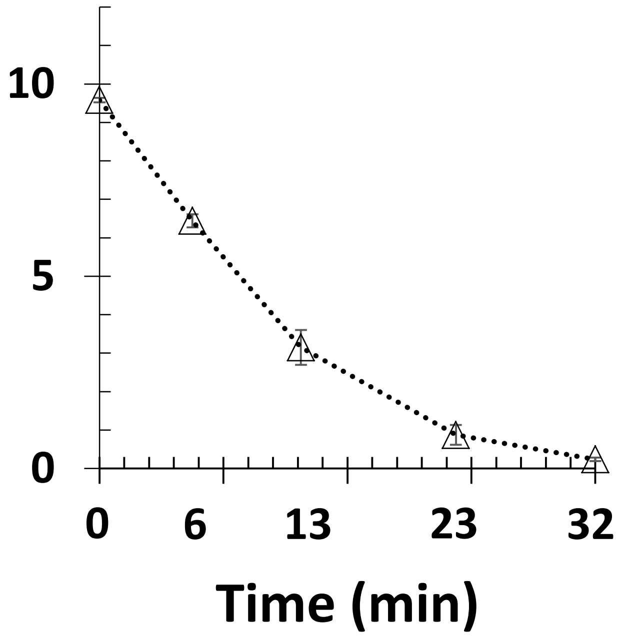
As(III)

Increasing the ∑Ions of the water increases [As solution]

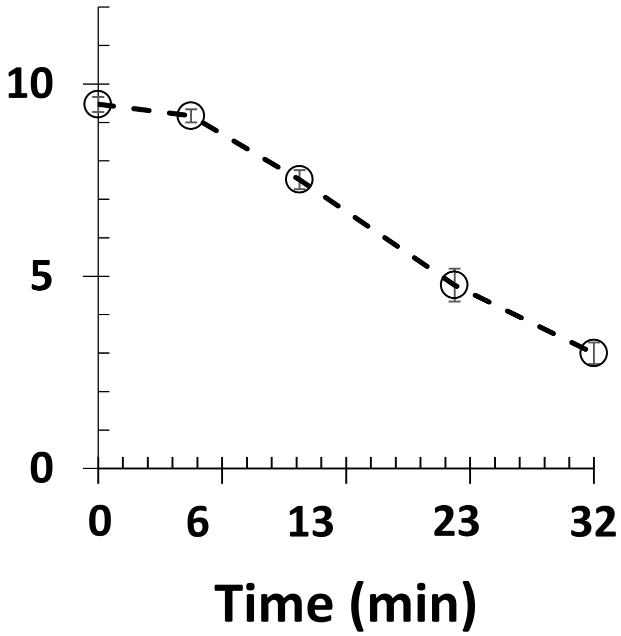
LAKE (Geneva)



RIVER (Chamberonne)



GROUNDWATER (UNIL-Dorigny)



µM				
As (aq)	9.0 (0.15)	9.3 (0.24)	6.3 (2.99)	**Removal**
HCO_3^-	18	193	424	**ions**
$Si(OH)_4$	1	16	29	
Ca^{2+}	28	95	No Ca	

What solid phase do we form?

As(III)

Different water chemistries lead to Fe precipitates

LAKE (Geneva)

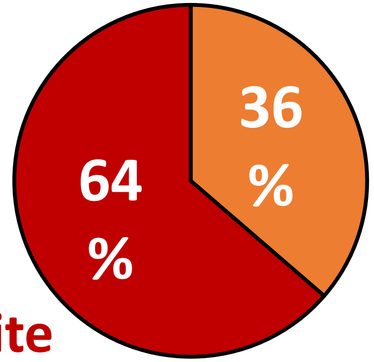
www.unil.ch

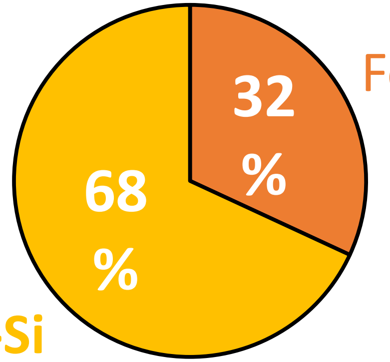
RIVER (Chamberonne)

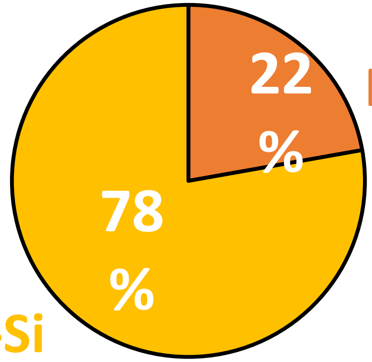
www.wikipedia.com

GROUNDWATER (UNIL-Dorigny)

XAS







As(III)

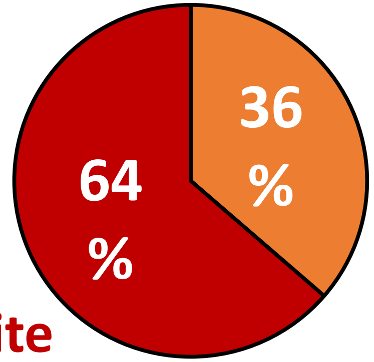
Different water chemistries lead to Fe precipitates

LAKE (Geneva)	RIVER (Chamberonne)	GROUNDWATER (UNIL-Dorigny)

www.unil.ch

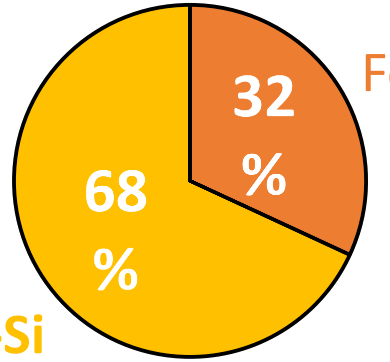
www.wikipedia.com

XAS



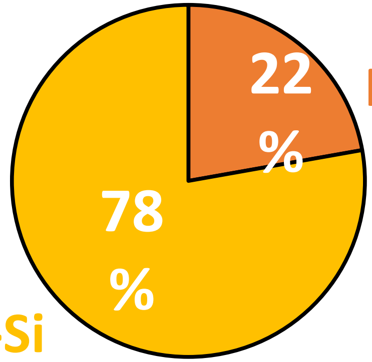
Ferrihydrite

Lepidocrocite



Ferrihydrite

HFO-Si



Ferrihydrite

HFO-Si

	LAKE (Geneva)	RIVER (Chamberonne)	GROUNDWATER (UNIL-Dorigny)
	6min – 32min	6min – 32min	6min – 32min
Si:Fe	**0.2 – 0.04**	**1.7 – 0.3**	**7.7 – 0.9**

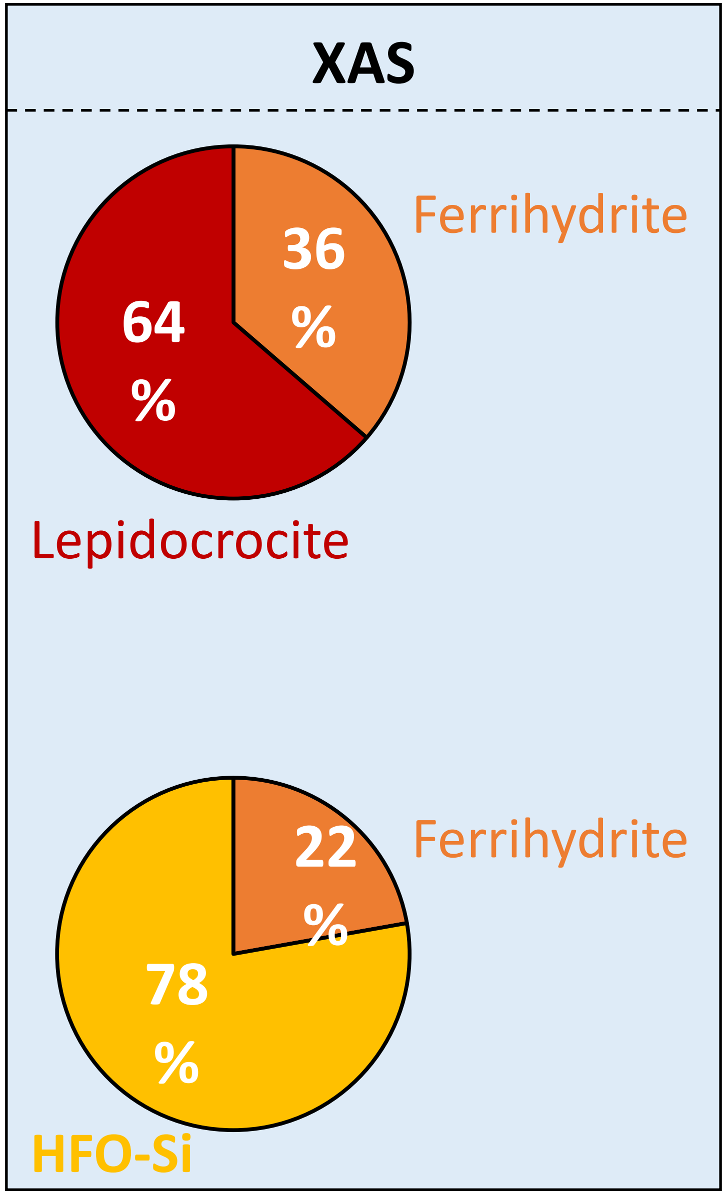
Si:Fe < 0.1-0.2 *Kinsela et al., 2016*

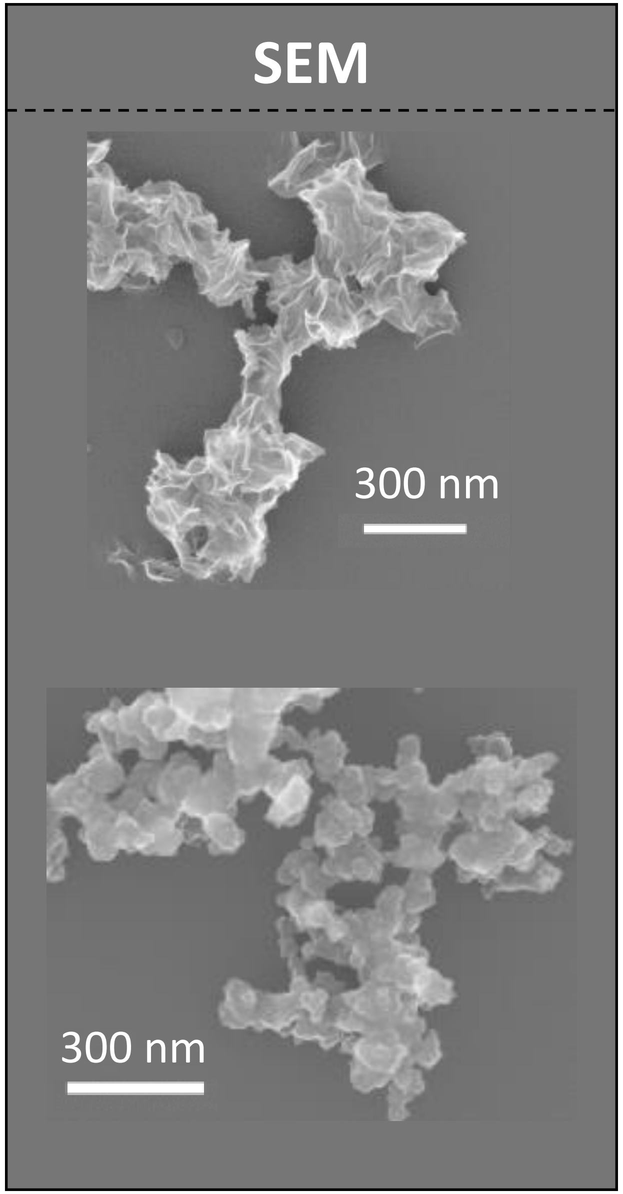
As(III)

Different water chemistries lead to different precipitate

LAKE

GROUNDWATER





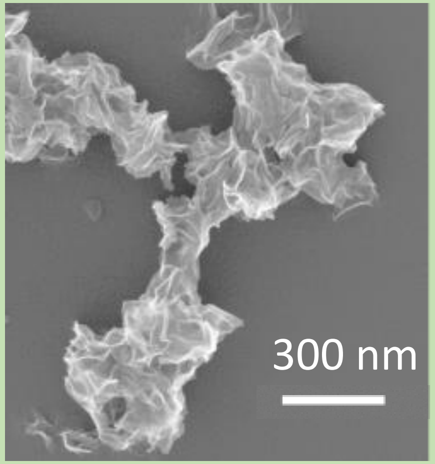
As(III)

Different water chemistries lead to different precipitate morphologies

SEM

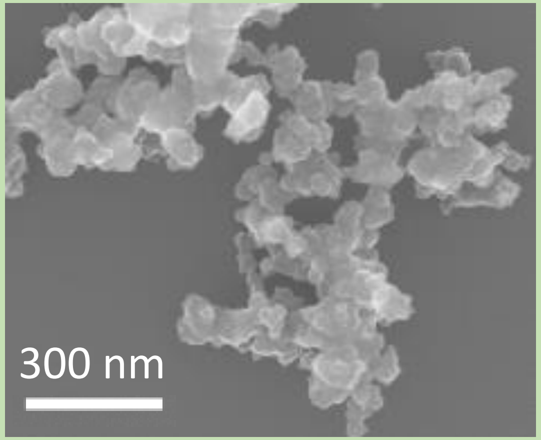
LAKE

0.9 mM Ca
0.009 mM Si
0.04 As/Fe



GROUNDWATER

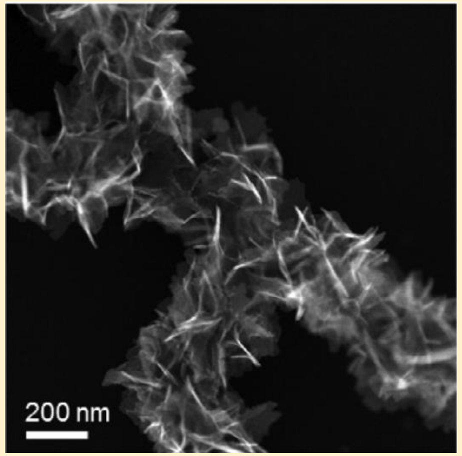
2.7 mM Ca
0.2 mM Si
0.03 As/Fe



STEM

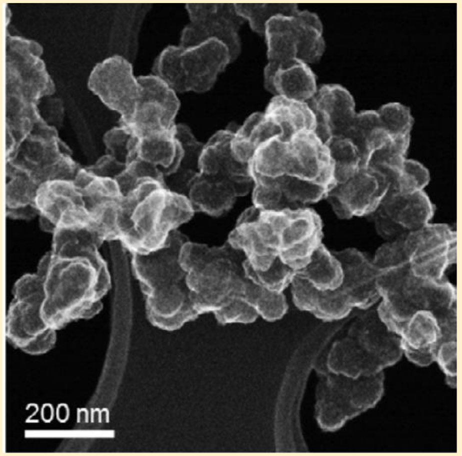
Synthetic water

8 mM Na
0 P/Fe



Synthetic water

4 mM Ca
0.5 mM Si
0.19 P/Fe



Senn et al., 2015

Is As removal limited by its sorption?
Can Si explain our experimental results?

As(III)

[As solution] do not depend only on [Si]

LAKE (Geneva)

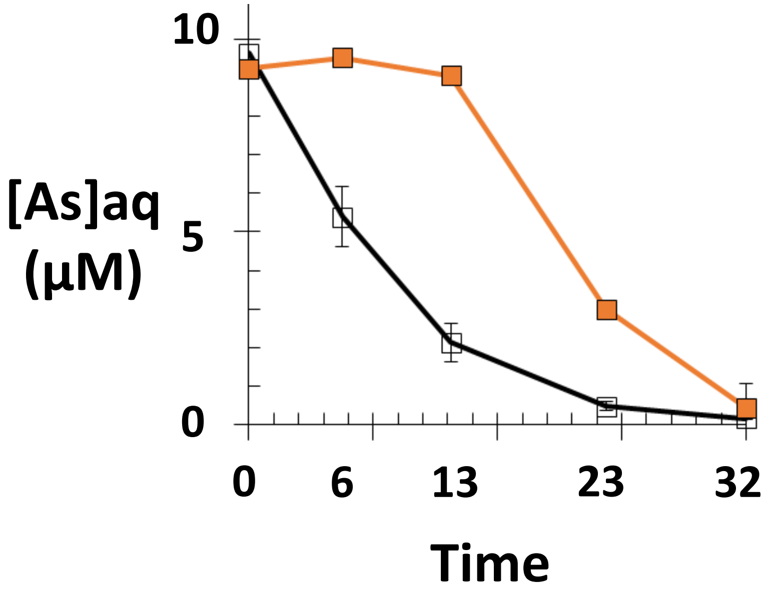
www.unil.ch

RIVER (Chamberonne)

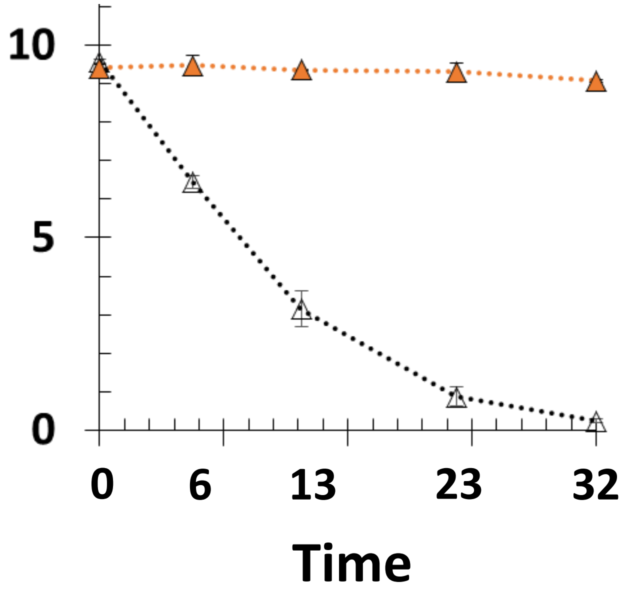
www.wikipedia.com

GROUNDWATER (UNIL-Dorigny)

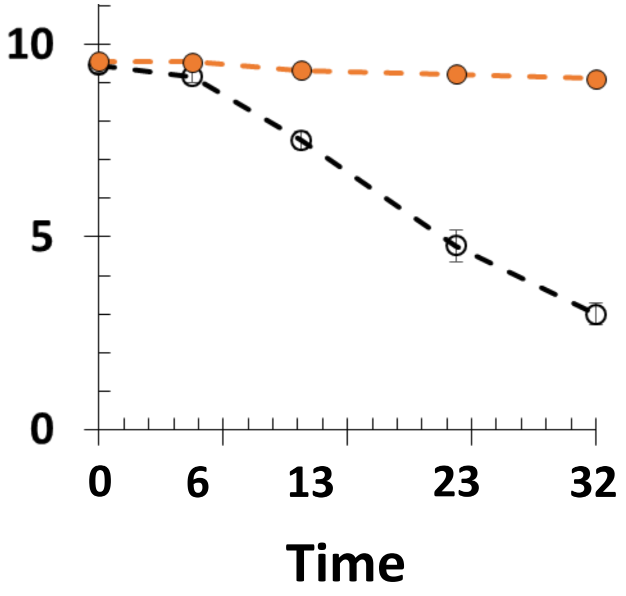
0 µM Si



100 µM Si



200 µM Si



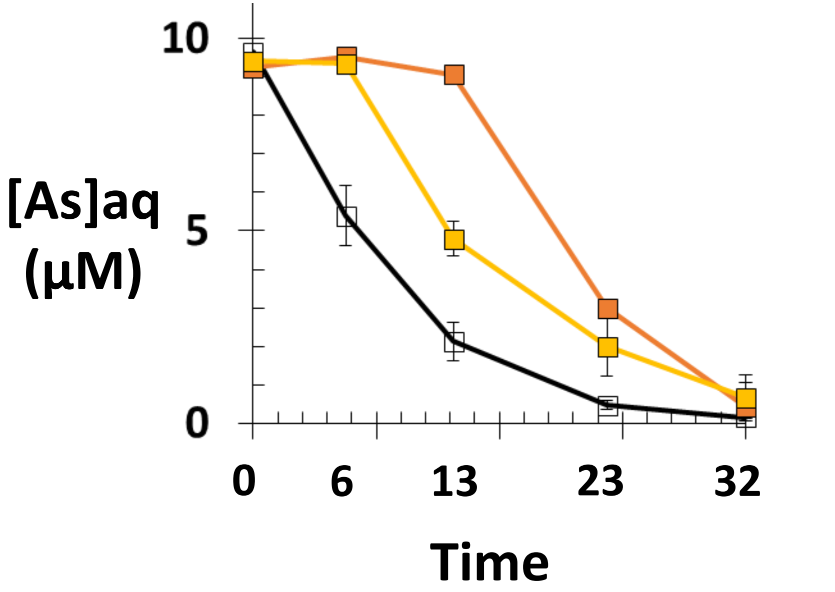
As(III)

[As solution] depends on [Si] and [Ca^{2+}, Mg^{2+}]

LAKE (Geneva)

www.unil.ch

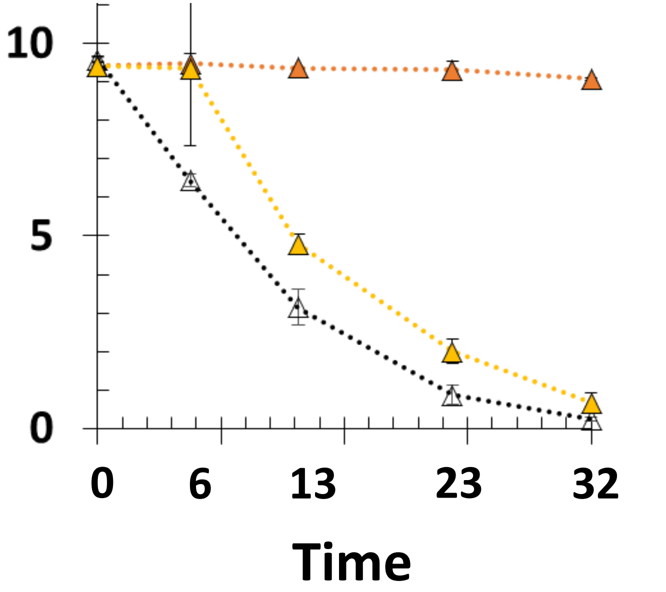
0 µM Si, 2700 µM Ca, 530 µM Mg



RIVER (Chamberonne)

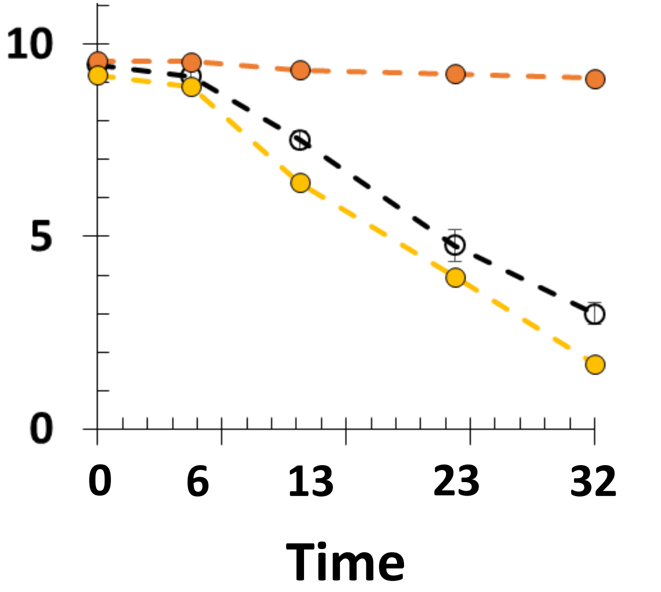
www.wikipedia.com

100 µM Si, 1550 µM Ca, 330 µM Mg



GROUNDWATER (UNIL-Dorigny)

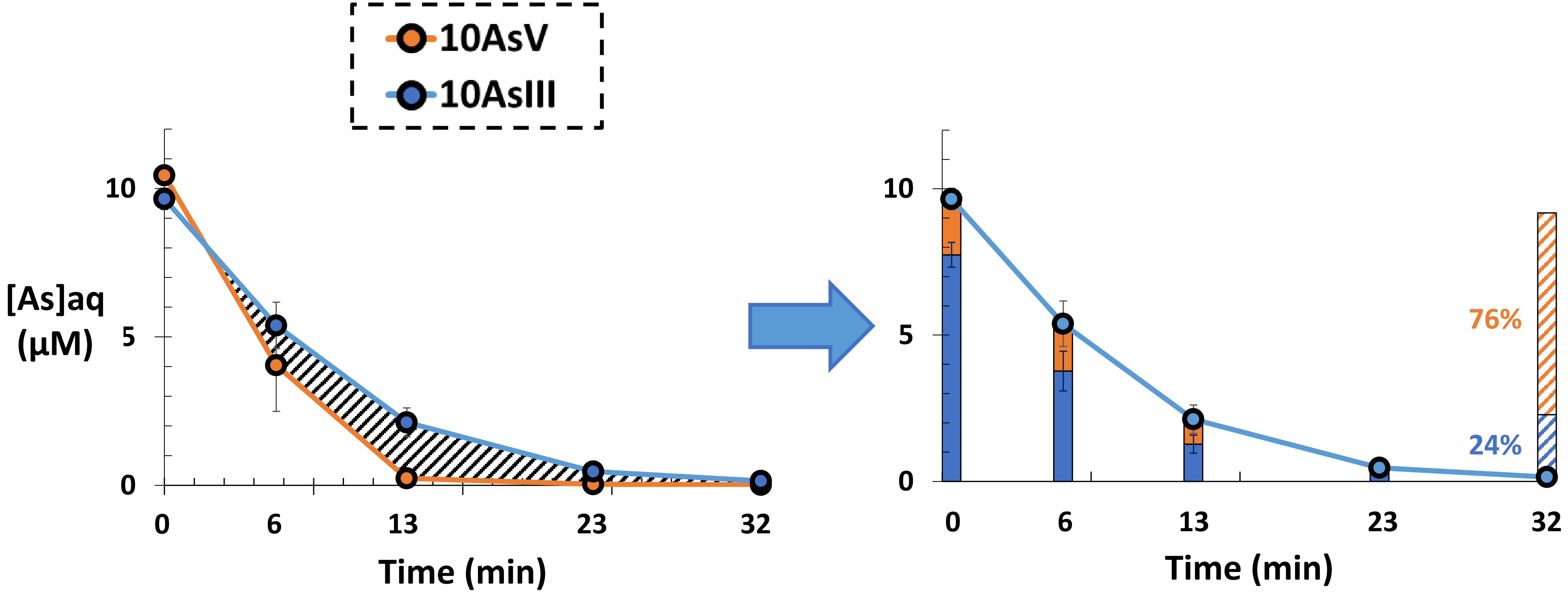
200 µM Si, 2700 µM Ca, 530 µM Mg



Is As removal limited by its oxidation from As(III) to As(V)?

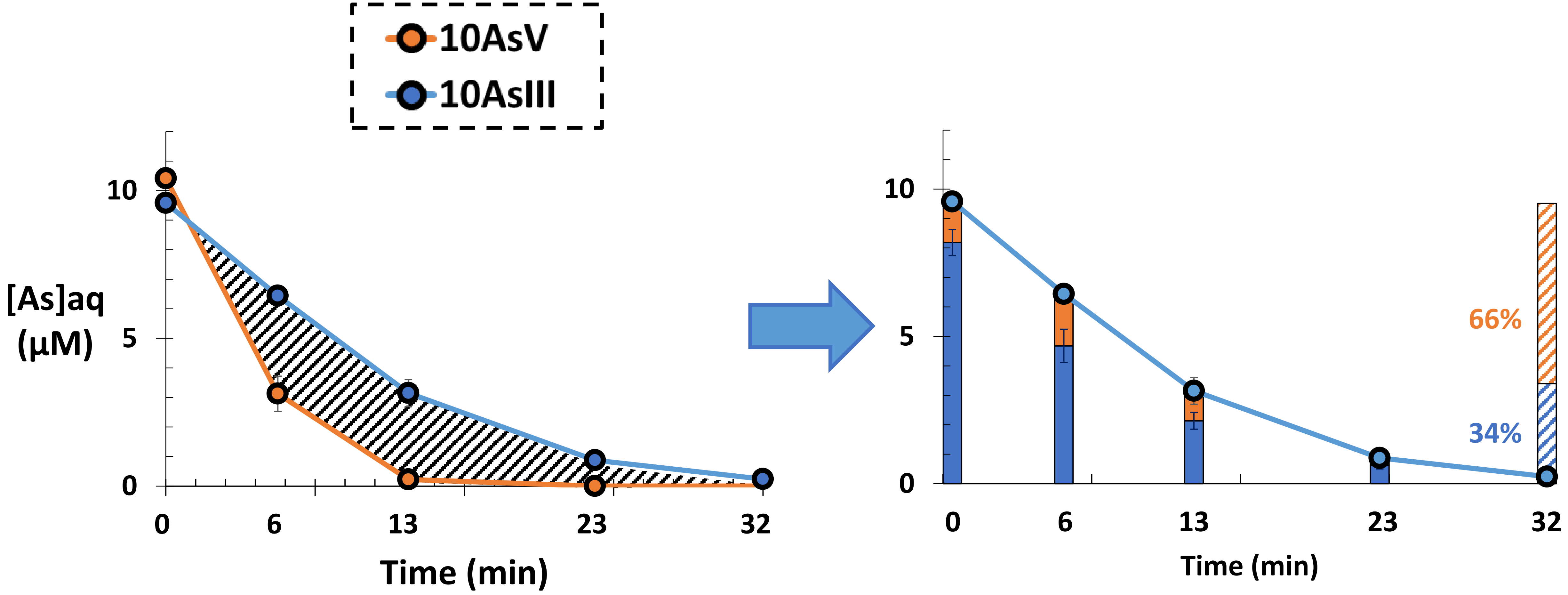
As(III,V)

Lake Geneva: incomplete As(III) oxidation



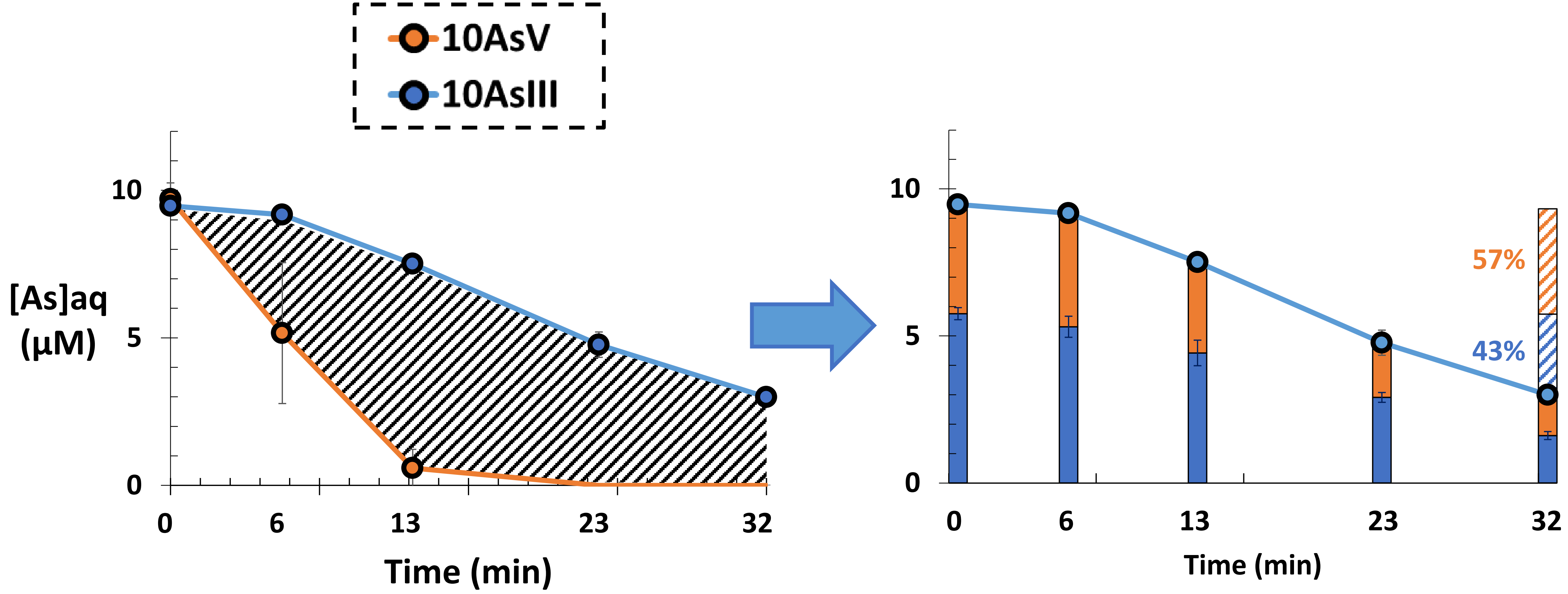
As(III,V)

River: the oxidation step is more limitant than for the lake



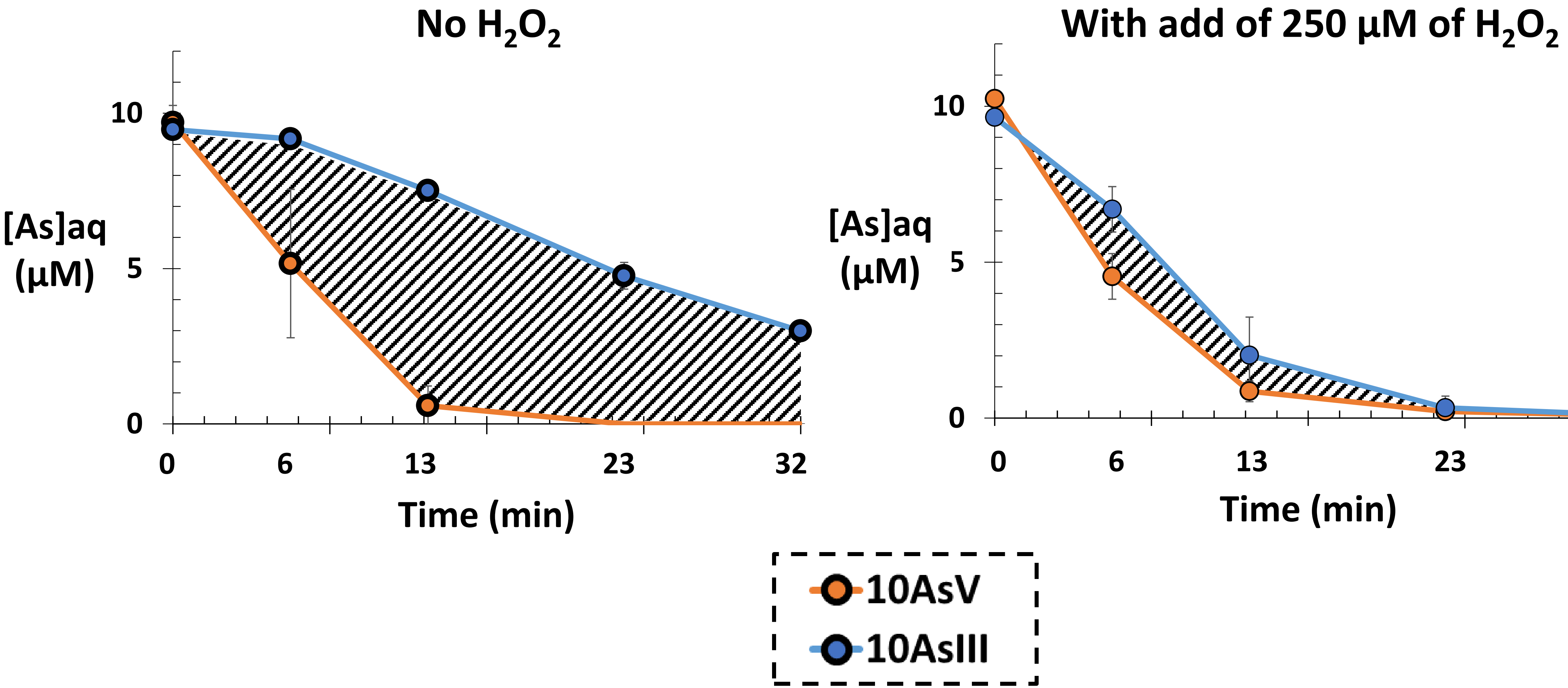
As(III,V)

Groundwater: the oxidation step is kinetically limiting

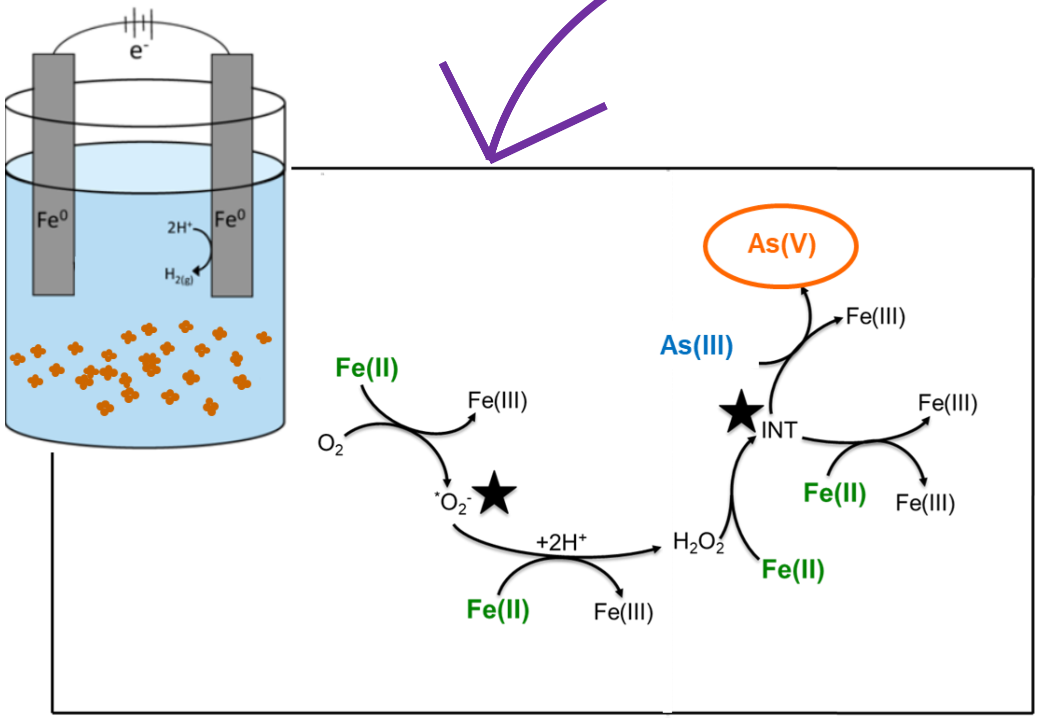


As(III,V)

Groundwater: 100%As removed with addition of a strong oxidant



Which element can influence the oxidation of As(III) (and Fe(II))?



Si: (Kinsela et al., 2016)

$Fe^{III} + Fe^{III}$ ➔ LEP + LEP — $k = 5x10^5$

$Fe^{III}Si + Fe^{III}Si$ ➔ SiFHY + SiFHY — $k = 3.5x10^4$

HCO_3^-: (Hug and Leupin, 2003)

Fe^{2+} + Fe(IV) ➔ 2 Fe^{3+} — $k = 1.2x10^3$

$FeOH^+$ + Fe(IV) ➔ 2Fe^{3+} — $k = 8.5x10^7$

$Fe^{II}CO_3$ + Fe(IV) ➔ $Fe^{3+} + Fe^{III}CO_3$ — $k = 4.3x10^6$

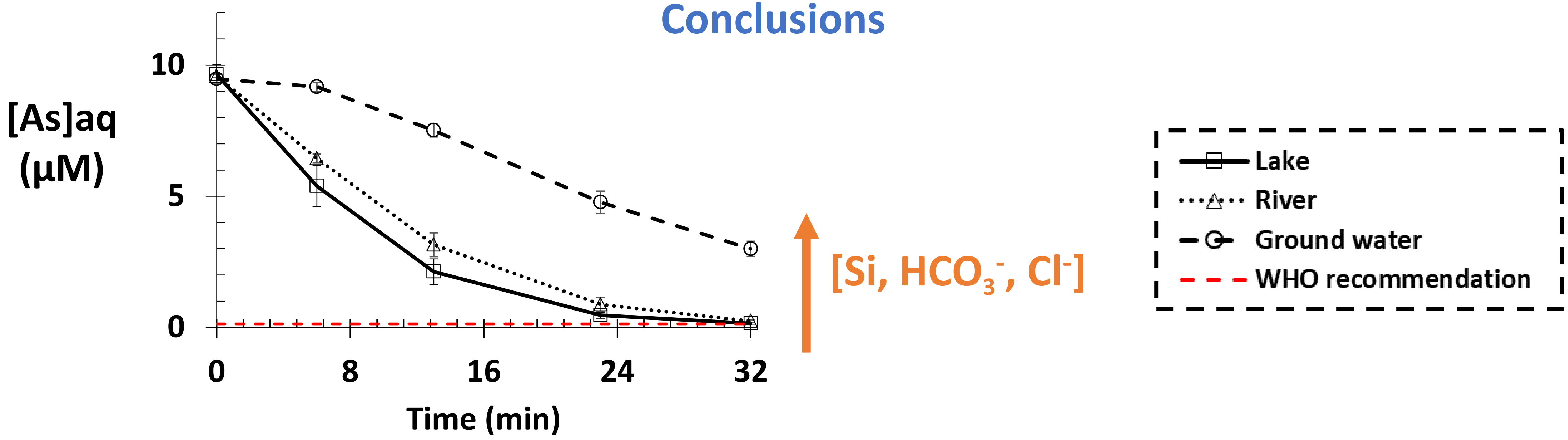
Cl^-: (Pigantello et al., 2007; Sharma et al., 2007)

Inhibition of Fenton reactions by Cl^-: formation of $HOCl^{*-}$

$As(OH)_3 + HOCl^{*-}$ ➔ $AsO_4^{3-} + Cl^- + 4H^+$ — $k = 4.3x10^3$

As(III) + Fe(IV) ➔ As(IV) + Fe(III) — $k = 4.5x10^5$

Conclusions



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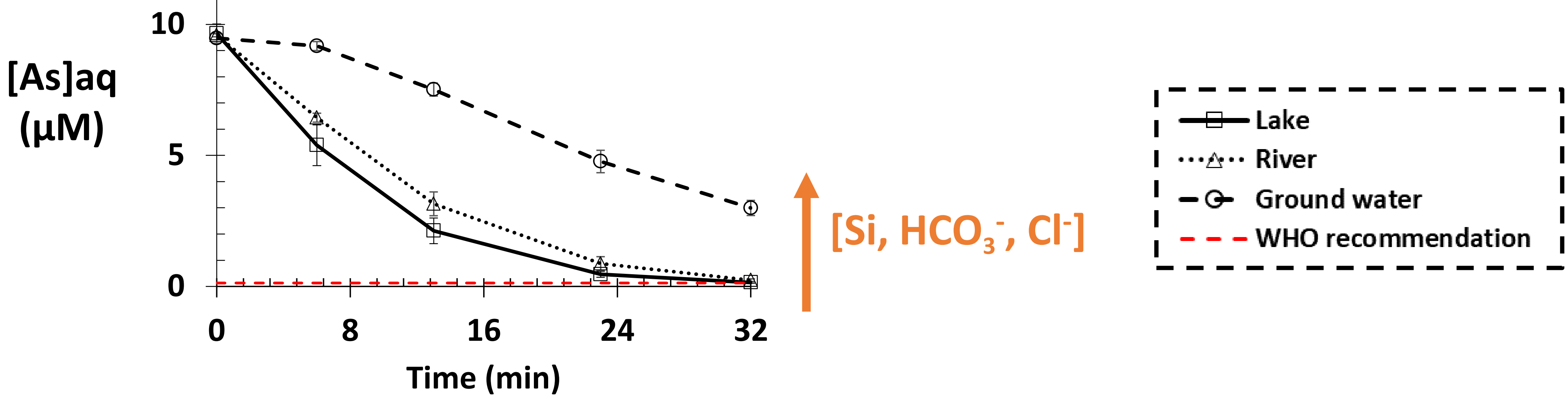
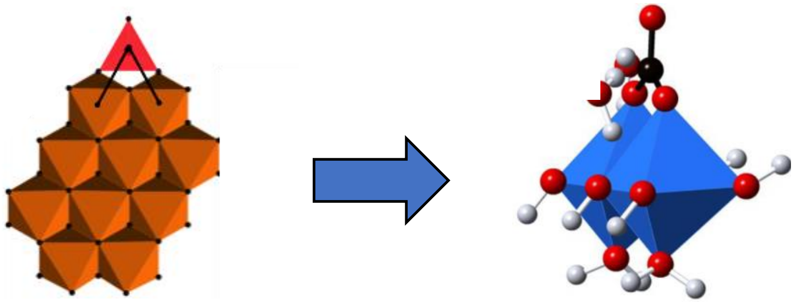
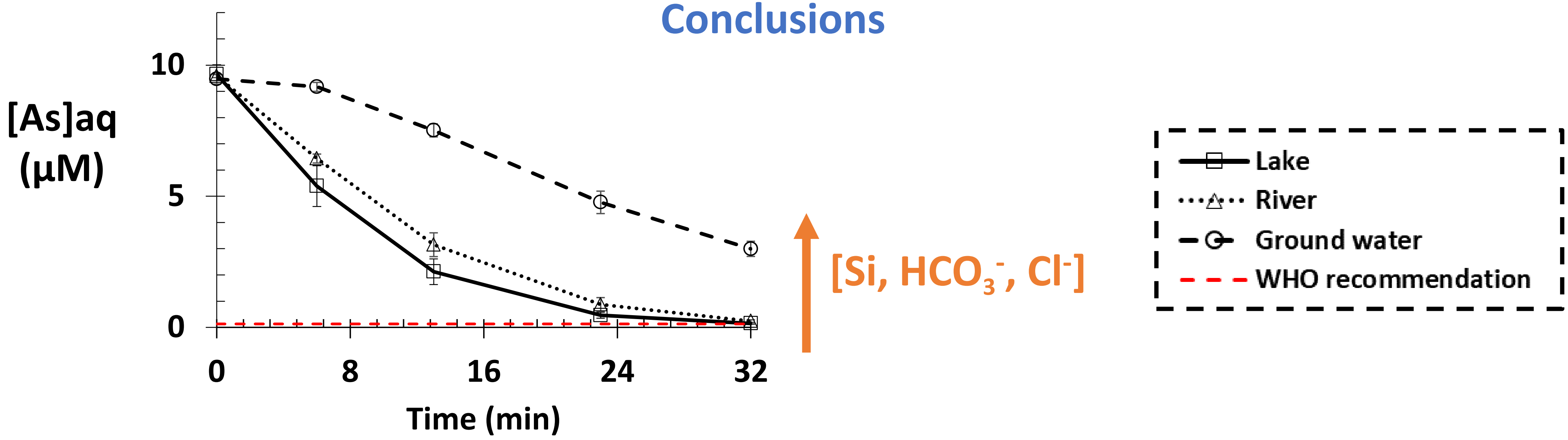


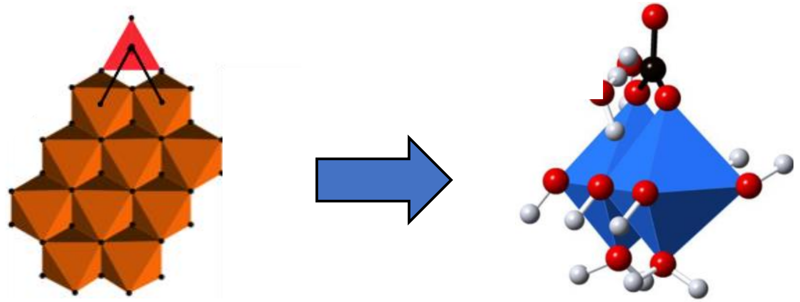


van Genuchten et al., 2012 *Mandez and Hiemstra, 2019*

- Si as modificator of the sorbent (lepidocrocite vs. hydrous ferric oxide) formed and inhibitor of Fe(III) oxides precipitation
- Ca^{2+} and Mg^{2+} as « coagulant »
- Si as competitor for the sorption with As

Conclusions





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- Ca^{2+} and Mg^{2+} as « coagulant »
- Si as competitor for the sorption with As

Competition for the oxidants between $As(OH)_3$, Cl^- and HCO_3^-

Thank you!

- GRUTTEE
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