Distribution of inorganic nanoparticles in a Norwegian fjord

Collaborators: **AM Bienfait, TK Ervik, K Loeschner, S Valdersnes**

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Submarine tailings disposal

Dei skal lenke seg fast for å stoppe dumping i fjorden

Ungdom er klare til kamp for å stanse anleggsmaskinene som kjem til Førdefjorden.

Bergens Tidende

Lokalt

Nå begynner forarbeidet til gruvedeponiet i Førdefjorden. Her har 15 ungdommer flyttet inn, og forbereder seg på sivil ulydighet.

Aksjonistene vil hindre at Nordic Mining får rive 23 bygninger ved Engebøfjellet.

– Engebøprosjektet er et enormt naturinngrep, og det er frustrerende at politikerne ikke tør å ta en ny vurdering, sier Gina Gylver, leder i Natur og ungdom.

Vil stanse gruvedrift – det kan koste staten milliarder

SV lover stans av gruveprosjektet i Repparfjorden etter valget. Hvis nestleder Torgeir Knag Fylkesnes får Stortinget med på det, kan det koste staten flere milliarder kroner i erstatning.

Christian Kråkenes, Journalist

Irmelin Kulbrandstad

Opposisjonen vil forby all dumping i sjøen

SV, Rødt, MDG og Venstre fremjar felles forslag til Stortinget om å forby all dumping av gruveavfall i sjøen.

NRK Nyheter Sport Kultur Humor Distrikt Mer Logg inn Søk

Jakter etter mineraler til flere milliarder

Et selskap mener å ha funnet kvarts for flere titalls milliarder kroner ved Årsnes i Kvinnherad.

Ørjan har aksjonert mot gruvedrift i 15 år – til lita nytte

og aksjonar mot sjødeponi og gruvedrift sidan 1990-
teke at grunnarbeidet til det omstridde anlegget ved

2016, då Ørjan Thingnes og andre aksjonistar vart fjerna av politiet.

Håvard Nyhus, Journalist
Håvard Heggen, Journalist
Benedikte Grov, Journalist

Vi rapporterer frå Sunnfjord

Publisert 17. feb. kl. 21:44

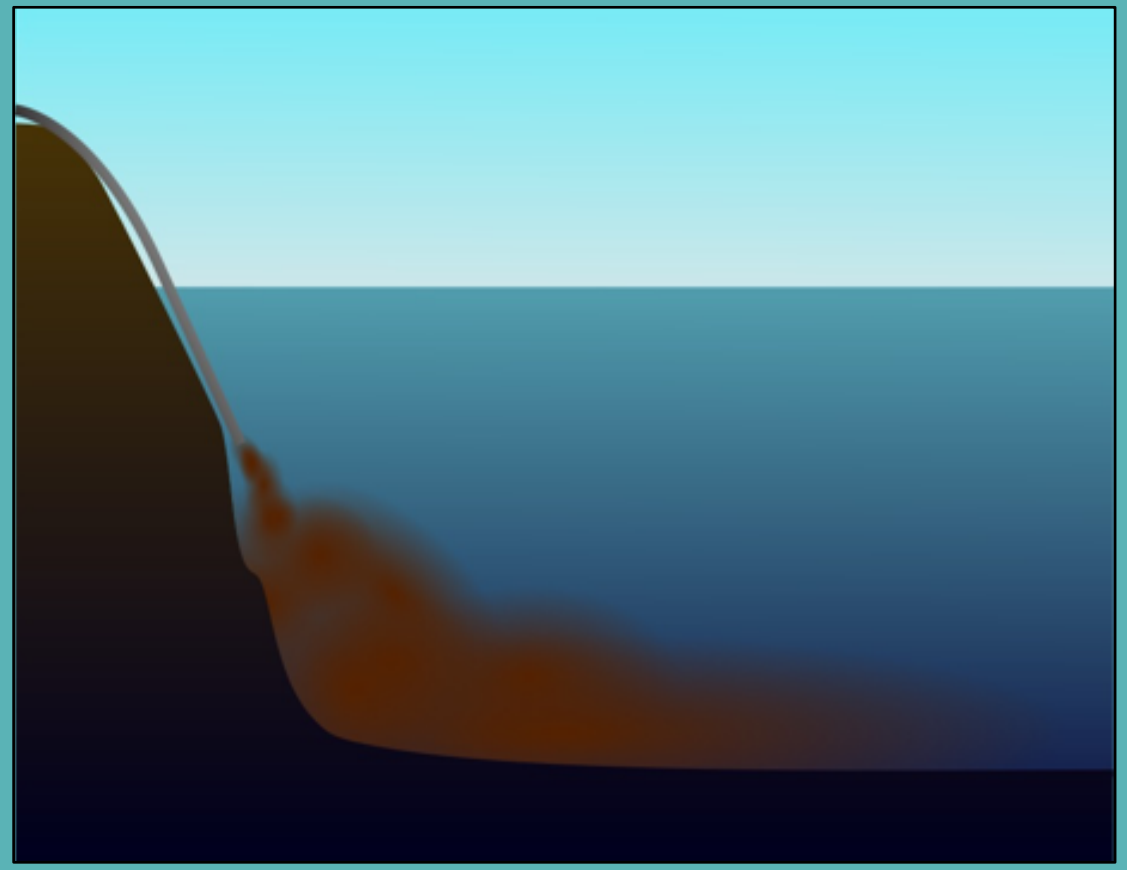
Aftenposten A-magasinet Oslo Sport

Norge | Miljø og klima

Lenker seg fast mot omstridt gruvedrift i Finnmark

Gruveselskapet har ingen planer om å anmelde aksjonistene: – Vi vil løse dette gjennom dialog.

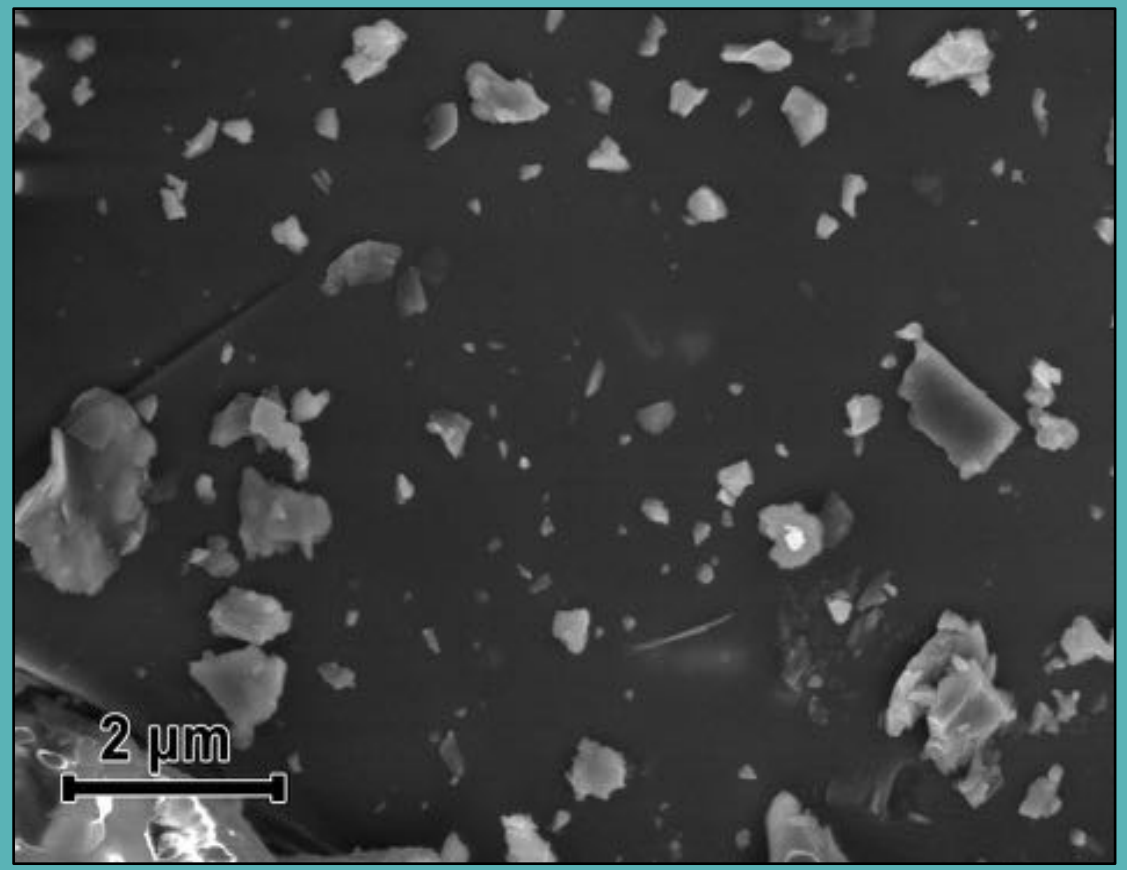
Submarine tailings disposal



- Used in mineral mining
- Millions of tonnes waste per year
- 16 sites **globally**[1] - four **Norway**
- Controversial and poorly understood[2]

1 Vare, L. et al. (2018). Scientific Considerations for the Assessment and Management of Mine Tailings Disposal in the Deep Sea. Front. Mar. Sci. 5. doi: 10.3389/fmars.2018.00017.
2 Ramirez-Llodra et al. (2015). Submarine and deep-sea mine tailing placements: A review of current practices, environmental issues, natural analogs and knowledge gaps in Norway and internationally. Marine Pollution Bulletin 97, 13–35. doi: 10.1016/j.marpolbul.2015.05.062.

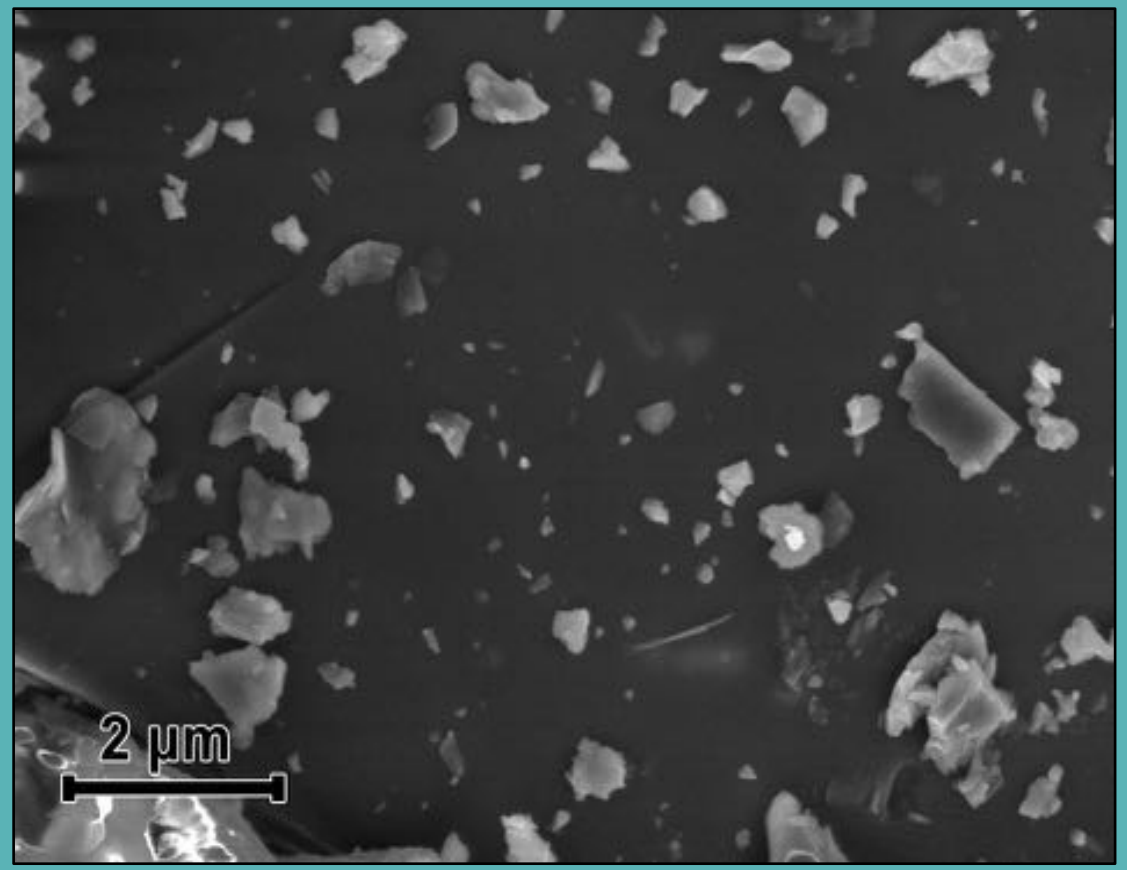
Submarine tailings disposal



- Global **Natural** NP flux:
  - ~ 1000s MT/year[1,2]
  - (Atmospheric, riverine, glacial, hydrothermal)
- **Incidental** NPs from one mine:
  - 4 MT/yr x 30% ≈ 1.2 MT/yr

1 Hochella, M. F. et al. (2019). Natural, incidental, and engineered nanomaterials and their impacts on the Earth system. *Science* 363, eaau8299. doi:10.1126/science.aau8299
2 Barnard, A. S., and Guo, H. eds. (2012). *Nature's nanostructures*. Singapore: Pan Stanford Publications.

Submarine tailings disposal



- Global **Natural** NP flux:
  - ~ 1000s MT/year[1,2]
  - (Atmospheric, riverine, glacial, hydrothermal)
- **Incidental** NPs from **one** mine:

~ 0.1% of GLOBAL total?

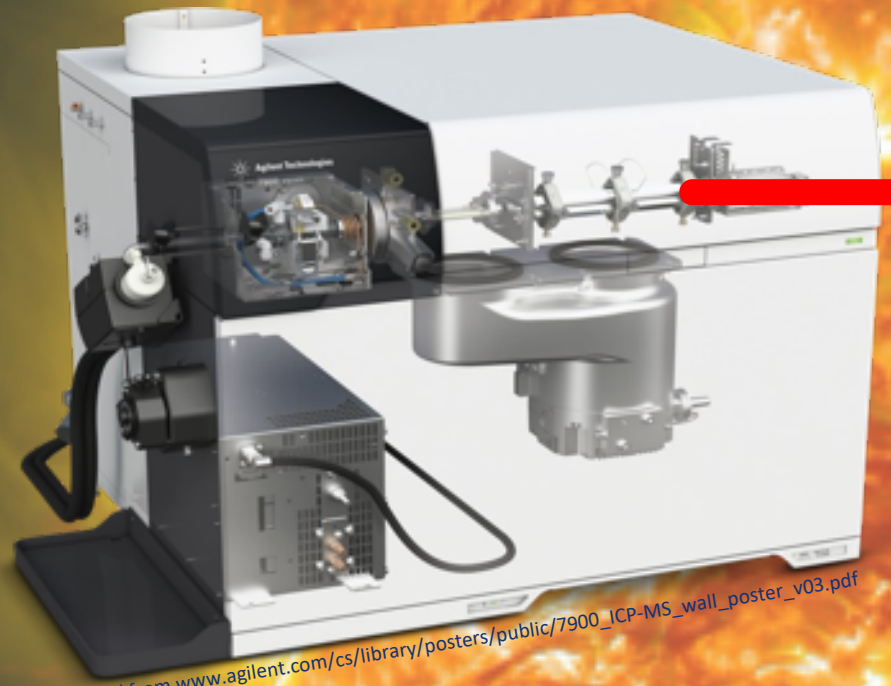
Estimate based on estimates…

1 Hochella, M. F. et al. (2019). Natural, incidental, and engineered nanomaterials and their impacts on the Earth system. *Science* 363, eaau8299. doi:10.1126/science.aau8299
2 Barnard, A. S., and Guo, H. eds. (2012). *Nature's nanostructures*. Singapore: Pan Stanford Publications.

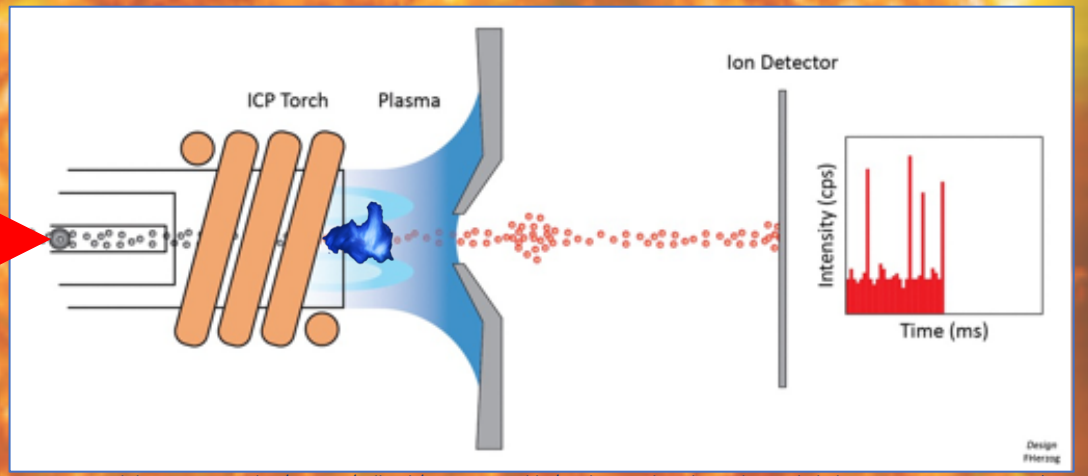
clays – colloids - submicrometer particles – nanoparticles

Keck, C. M., and Müller, R. H. (2008). Size analysis of submicron particles by laser diffractometry—90% of the published measurements are false. International Journal of Pharmaceutics 355, 150–163. doi: 10.1016/j.ijpharm.2007.12.004.
Wilkinson, K. J., and Lead, J. R. (2007). Environmental Colloids and Particles: Behaviour, Separation and Characterisation. John Wiley & Sons, Ltd.

single particle-ICP-MS



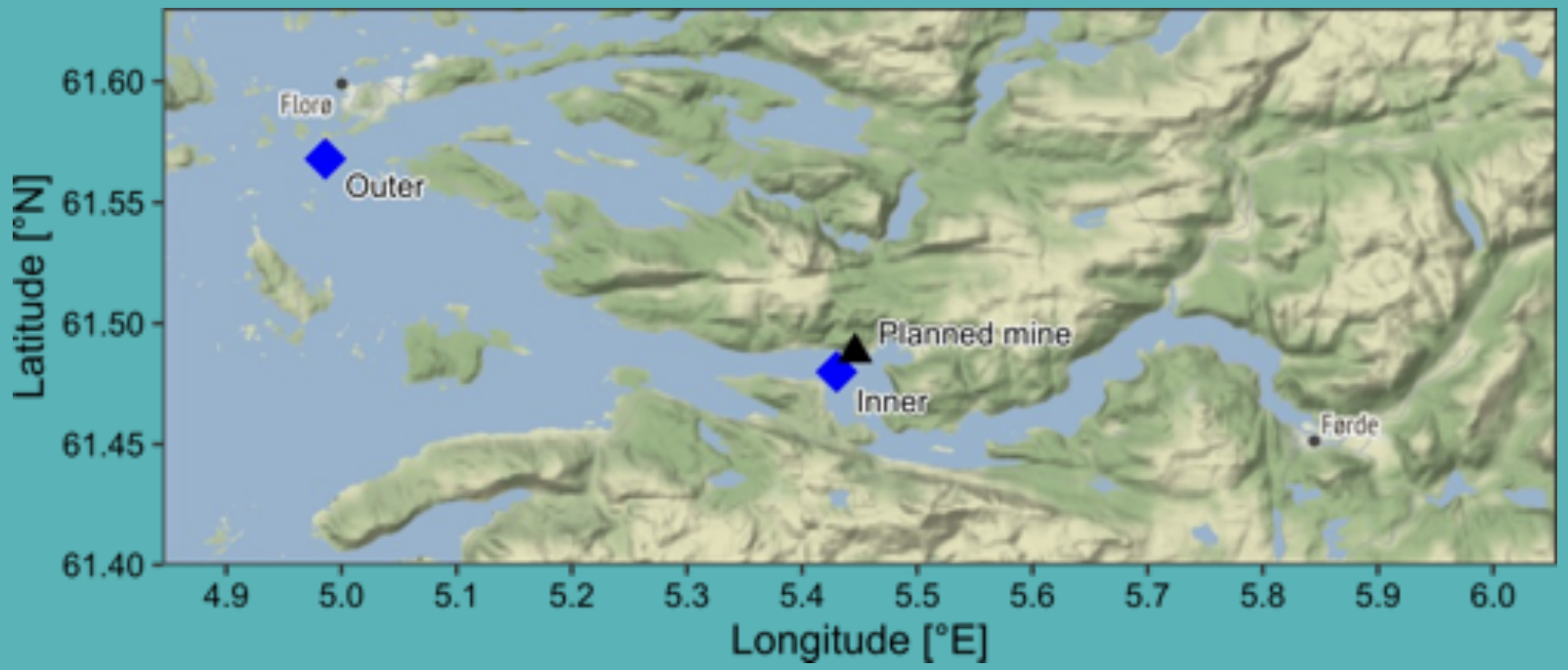
Adapted from www.agilent.com/cs/library/posters/public/7900_ICP-MS_wall_poster_V03.pdf



From www.webdepot.umontreal.ca/Usagers/wilkinsk/MonDepotPublic/single-particle-inductively-coupled-plasma-mass-spectrometry-(sp-icpms).html

IMG BY NASA

Methods: data acquisition



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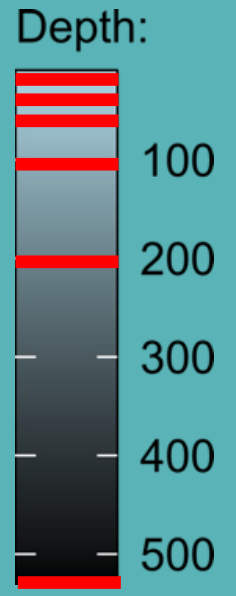
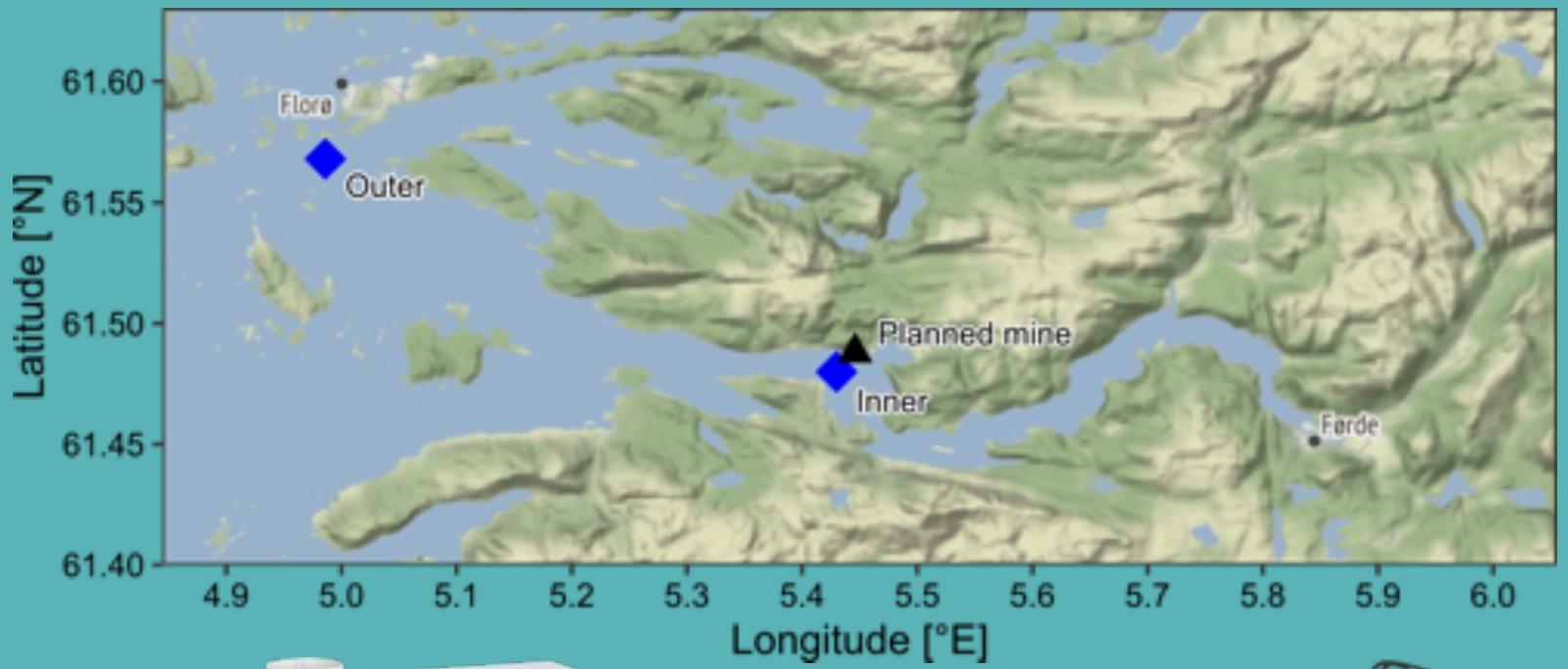


Methods: data acquisition



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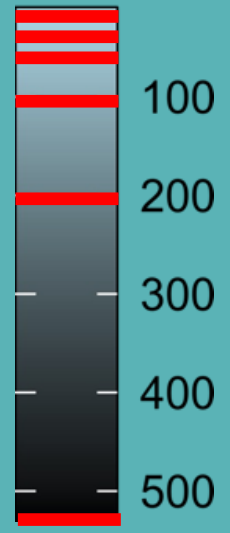
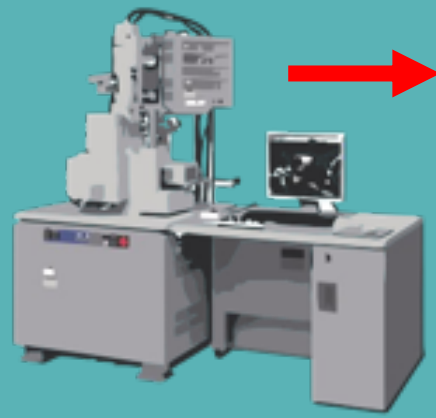


ICP-MS
- Single particle
- Total metals



Scanning electron microscopy
- Confirmative
- Particle speciation

Adapted from www.agilent.com/cs/library/posters/public/7900_ICP-MS_wall_poster_v03.pdf

Methods: instrumentation

Agilent 8900

Acq. time 30/60 s

Dwell time 100 µs

~6x Aerosol gas dilution

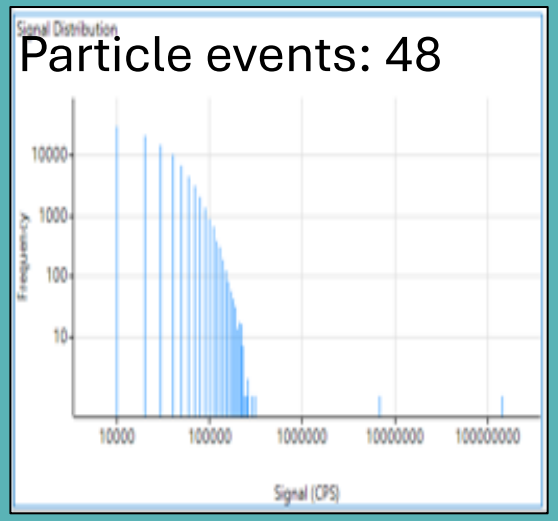
Element	Al	Au	Ba	Cd	Ce	Co	Cr	Cu	Fe	Mn	Ni	Pb	Si	Ti	Zn	Zr
Isotopes monitored [m/z]	27	197	137	111	140	59	52	63	56	55	60	208	28	48>64	66	90
Rx gas [gas, L/min]		-	-	-	-	-	-	-	H_2: 5.0		-	-	H_2: 2.0	H_2: 7.0, O_2: 0.15	-	-

> LOD

Methods: processing

- **Commercial signal processing:**
  - Not transparent
  - Type I & II errors

    -> subjective manual thresholds[1,2,3,4]



Monodisperse NPs, no noise (n papers 100++):

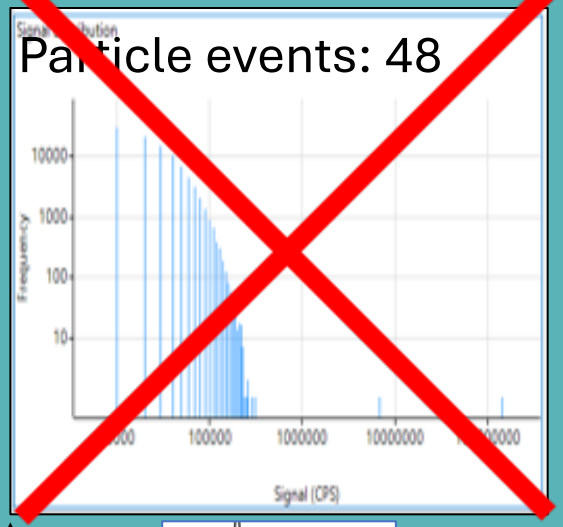
Seawater, polydisperse NPs, high matrix/noise (n papers 2):

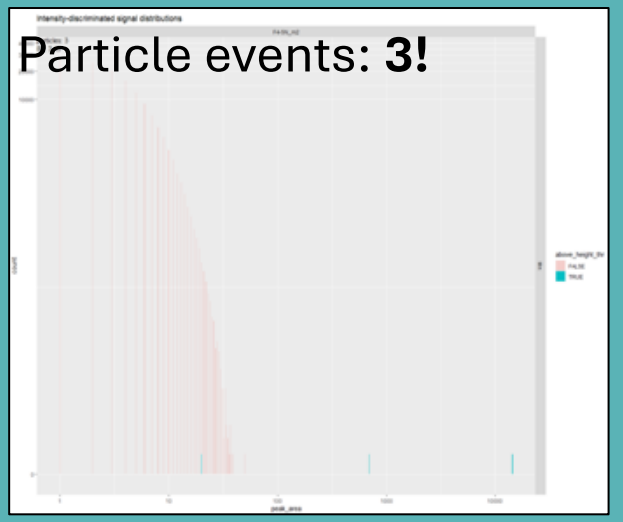
1. Kinnunen, V., Perämäki, S., and Matilainen, R. (2021). Optimization of instrumental parameters for improving sensitivity of single particle inductively-coupled plasma mass spectrometry analysis of gold. Spectrochimica Acta Part B: Atomic Spectroscopy 177, 106104. doi:10.1016/j.sab.2021.106104.
2. Vidmar, J., Hässmann, L., and Loeschner, K. (2021). Single-Particle ICP–MS as a Screening Technique for the Presence of Potential Inorganic Nanoparticles in Food. J. Agric. Food Chem. 69, 9979–9990. doi:10.1021/acs.jafc.0c07363.
3. Rand, L. N., Flores, K., Sharma, N., Gardea-Torresdey, J., and Westerhoff, P. (2021). Quantifying Nanoparticle Associated Ti, Ce, Au, and Pd Occurrence in 35 U.S. Surface Waters. ACS EST Water 1, 2242–2250. doi:10.1021/acsestwater.1c00206.
4. Azimzada, A., Jreije, I., Hadioui, M., Shaw, P., Farner, J. M., and Wilkinson, K. J. (2021). Quantification and Characterization of Ti-, Ce-, and Ag-Nanoparticles in Global Surface Waters and Precipitation. Environ. Sci. Technol. 55, 9836–9844. doi:10.1021/acs.est.1c00488.

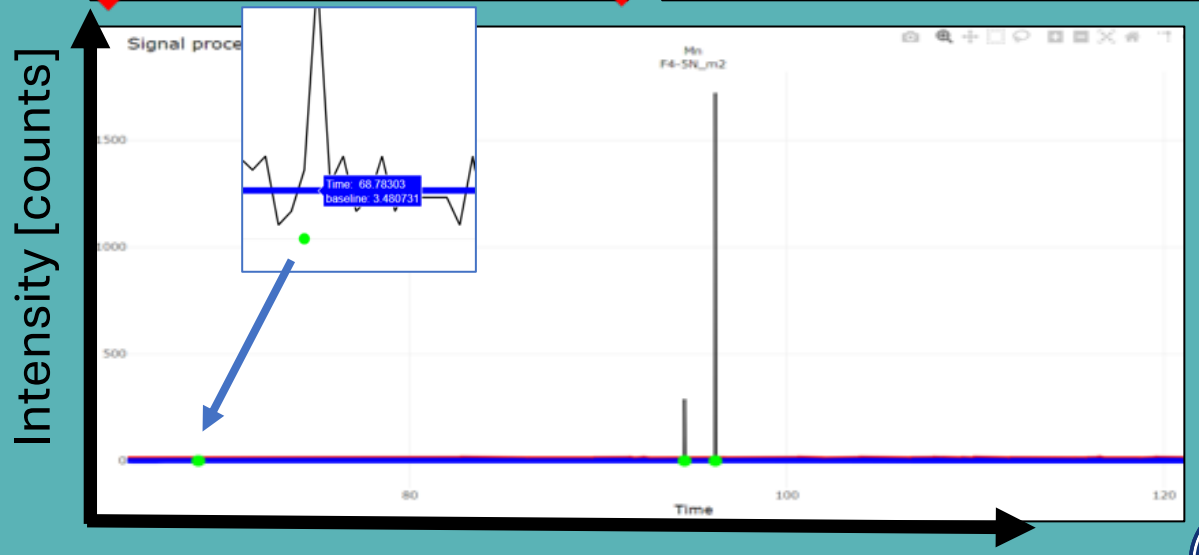
Methods: processing

- **Novel signal processing:**
  - Open source/ transparent
  - **Minimizes** errors type I & II
  - Statistically defined critical level **(α)**
  - Additional & flexible parameters

/arebruvold/fordefjorden_distribution







Monodisperse NPs, no noise (n papers 100++):

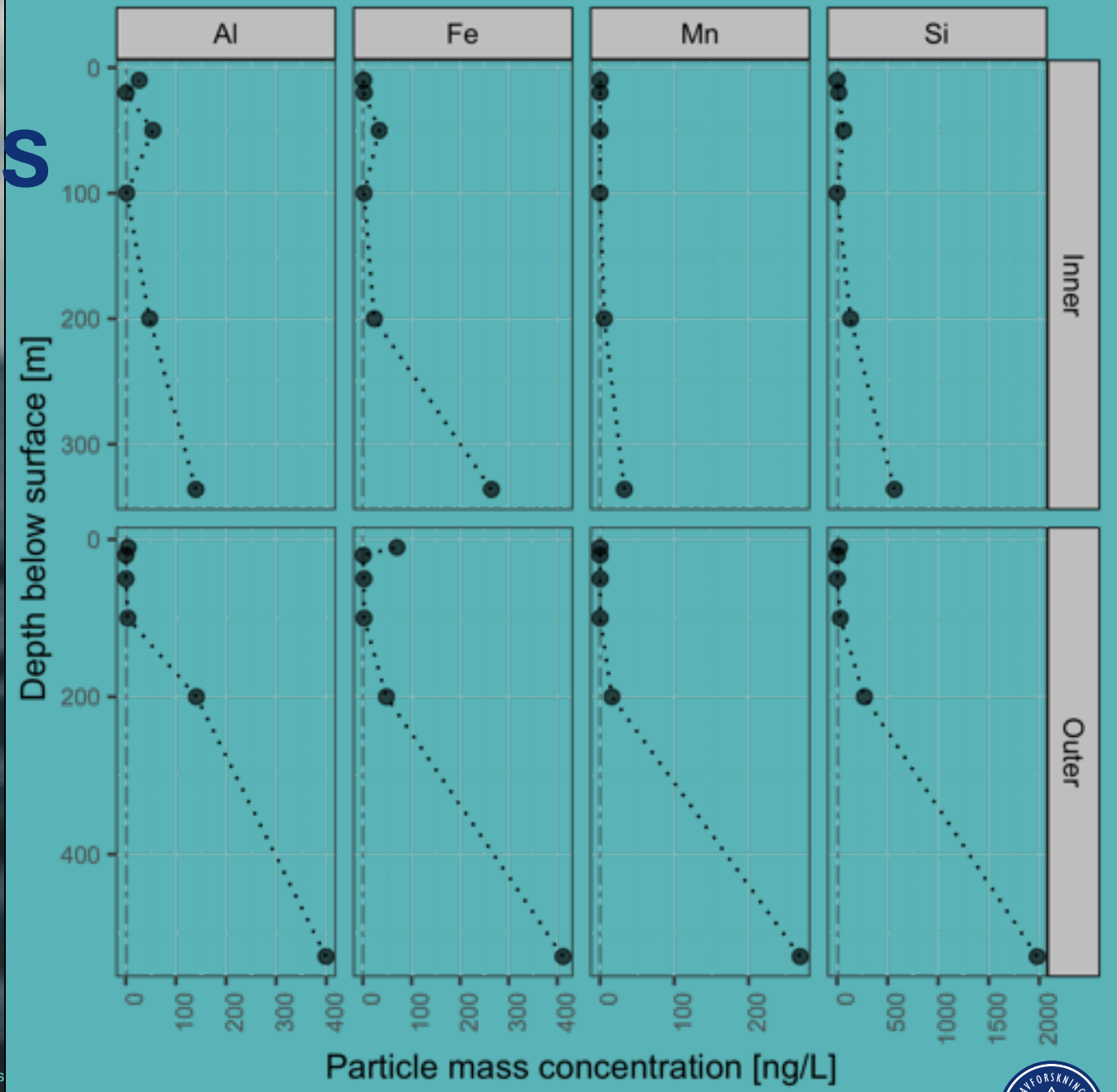
Seawater, polydisperse NPs, high matrix/noise (n papers 2):

Results & discussion

Single particle-ICP-MS

Fe Mn Si Al

$n < 10^8$ / liter



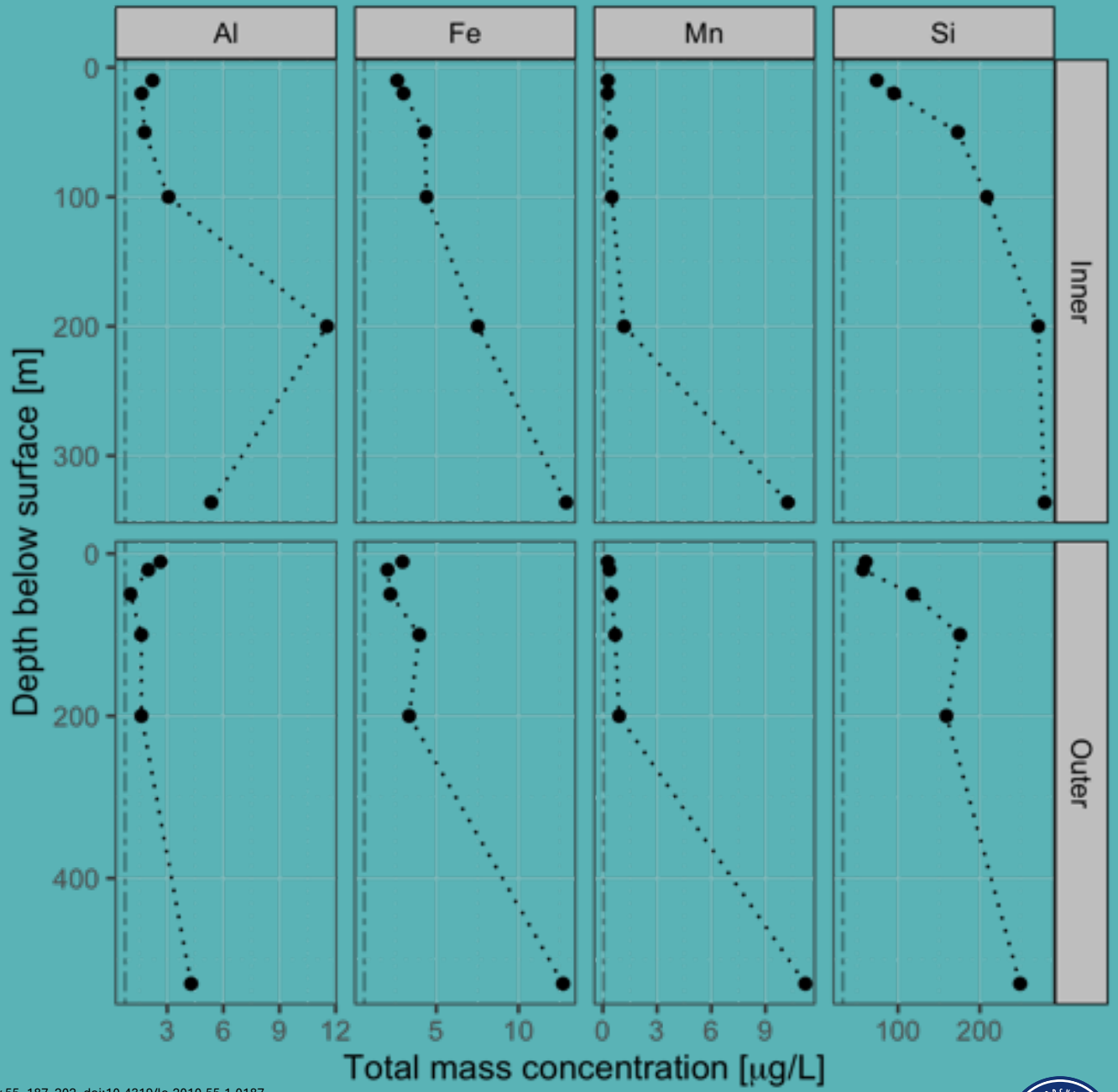
Sanchís et al (2020). Occurrence of Cerium-, Titanium-, and Silver-Bearing Nanoparticles in the Besòs and Ebro Rivers. Environ. Sci. Technol. 54, 3969–3978. doi: 10.1021/acs.est.9b05996.

Azimzada et al(2021). Quantification and Characterization of Ti-, Ce-, and Ag-Nanoparticles in Global Surface Waters and Precipitation. Environ. Sci. Technol. 55, 9836–9844. doi: 10.1021/acs.est.1c00488.

Ohnemus, D. C., Torrie, R., and Twining, B. S. (2019). Exposing the Distributions and Elemental Associations of Scavenged Particulate Phases in the Ocean Using Basin-Scale Multi-Element Data Sets. Global Biogeochem. Cycles 33, 725–748. doi: 10.1029/2018gb006145.

Total metals

- Concentrations ~ as reported[1,2,3,4]
- Fjords: large spatiotemporal variations[3,5,6]
- ~ µg/L (vs ng/L for particles)



Stolpe, B., and Hassellöv, M. (2010). Nanofibrils and other colloidal biopolymers binding trace elements in coastal seawater..., Limnology and Oceanography 55, 187–202. doi:10.4319/lo.2010.55.1.0187.
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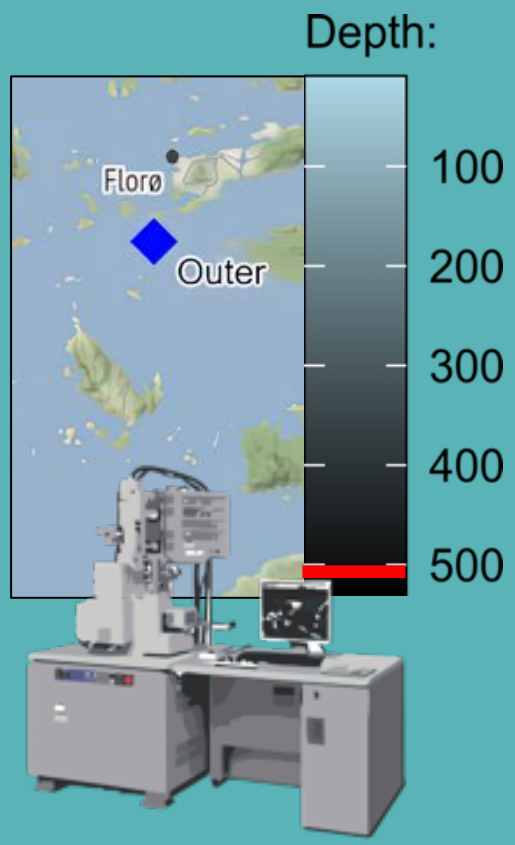
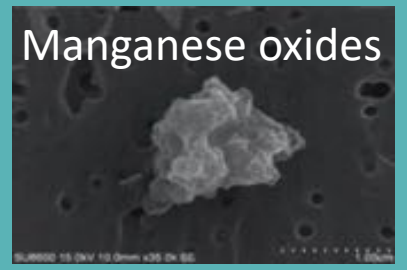
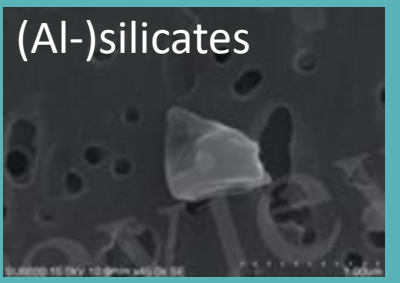
SEM







Heldal, M., Fagerbakke, K., Tuomi, P., and Bratbak, G. (1996). Abundant populations of iron and manganese sequestering bacteria in coastal water. Aquat. Microb. Ecol. 11, 127–133. doi:10.3354/ame011127

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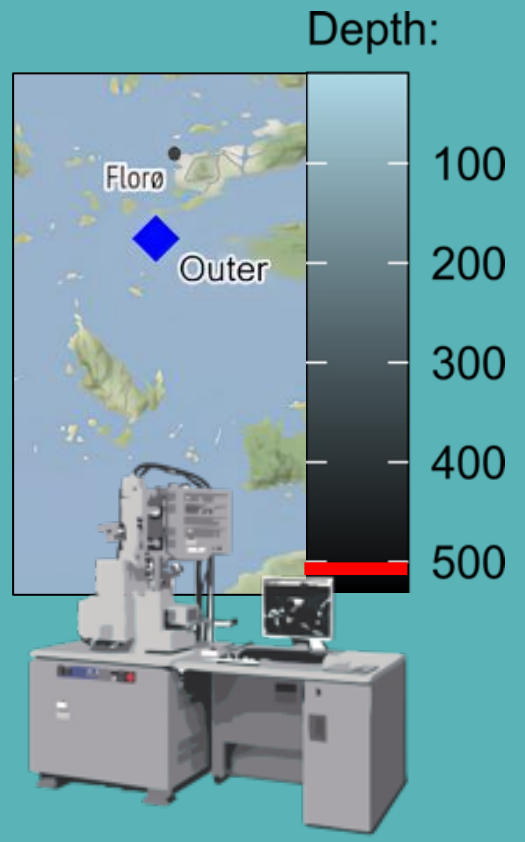
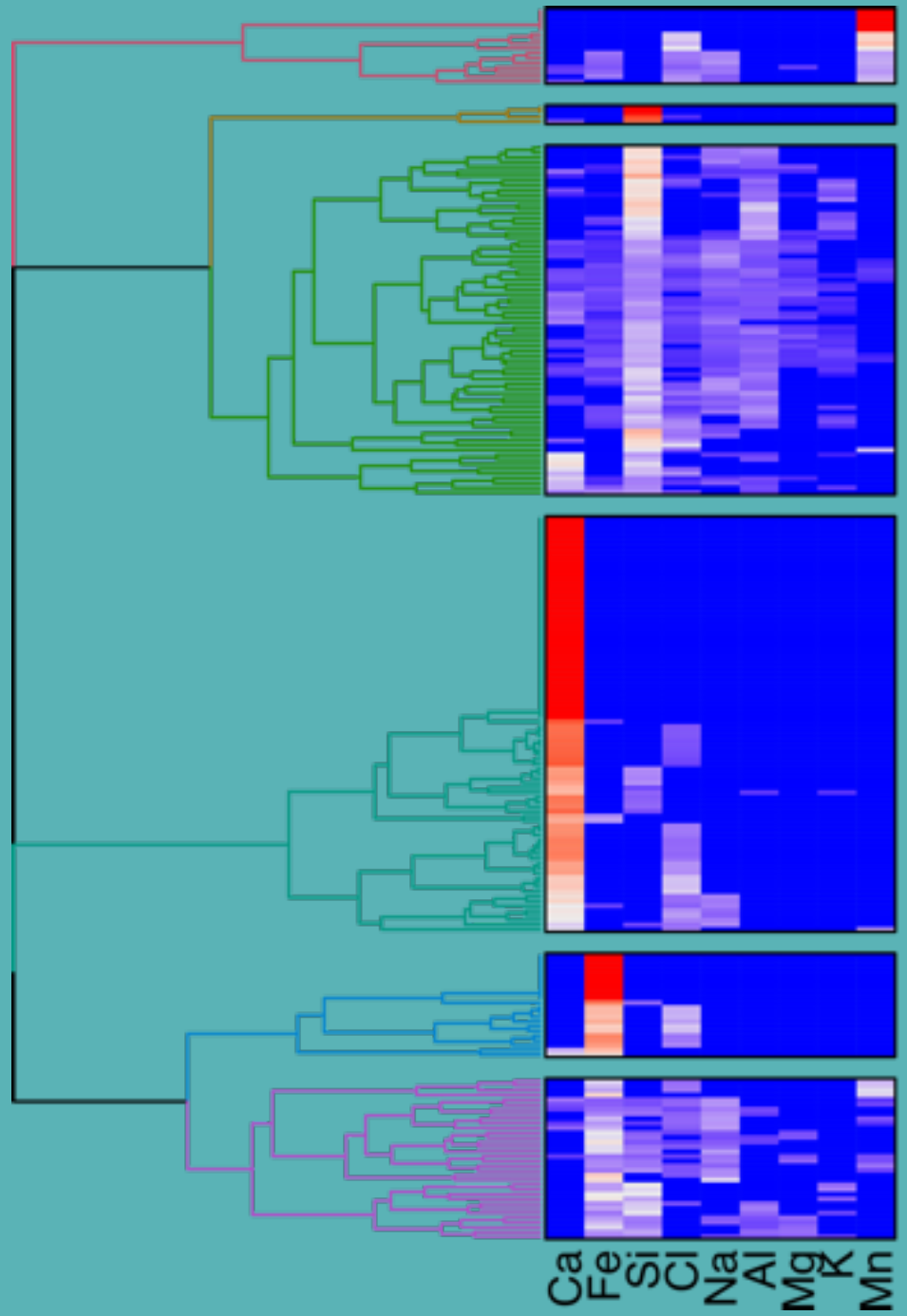
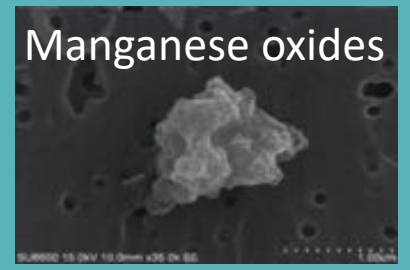
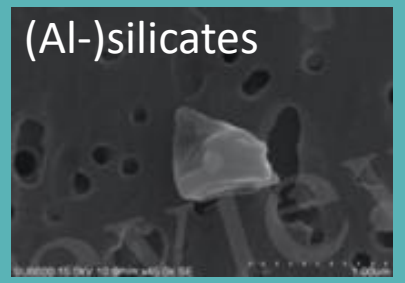
Ohnemus, D. C., Torrie, R., and Twining, B. S. (2019). Exposing the Distributions and Elemental Associations of Scavenged Particulate Phases in the Ocean Using Basin-Scale Multi-Element Data Sets. *Global Biogeochem. Cycles* 33, 725–748. doi: 10.1029/2018gb006145.

SEM-EDX





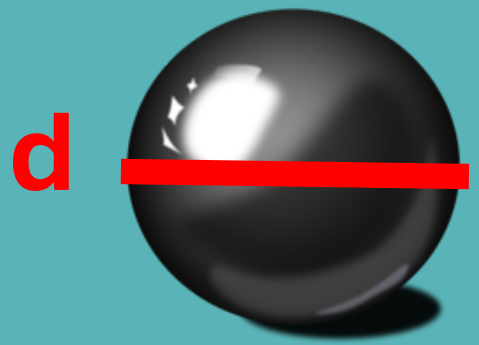


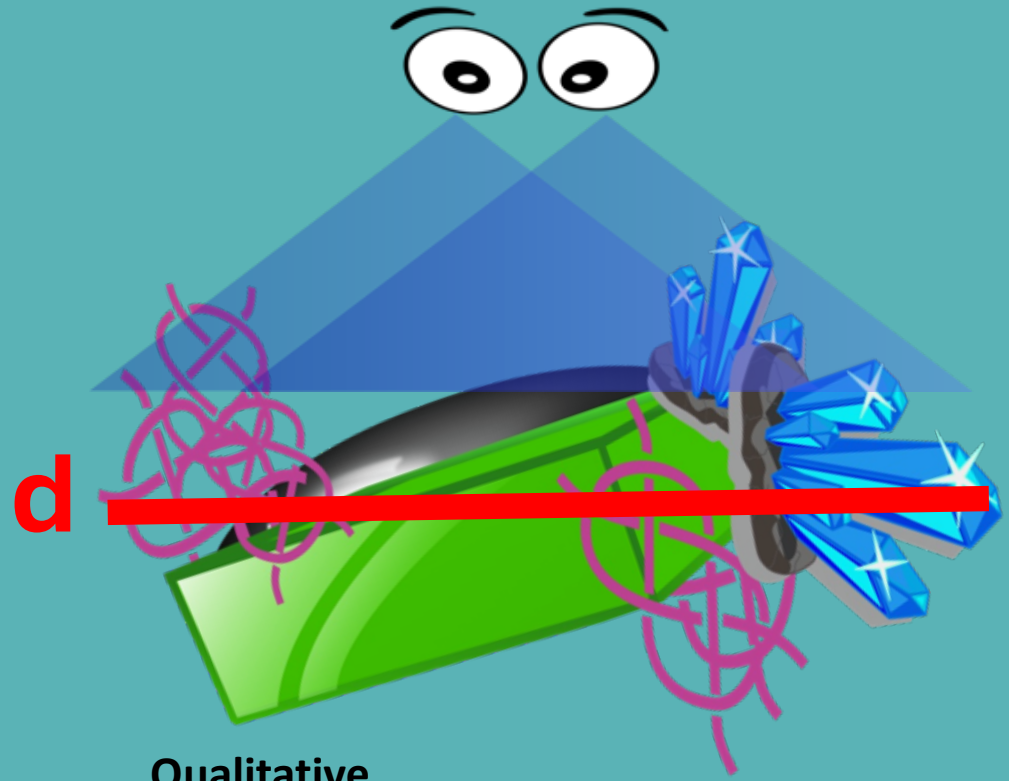


$N_{NP} = 238$

von der Heyden, B. P. et al. (2014). Ubiquitous Presence of Fe(II) in Aquatic Colloids and Its Association with Organic Carbon. Environ. Sci. Technol. Lett. 1, 387–392. doi:10.1021/ez500164v.

SP-ICP-MS + SEM-EDX!

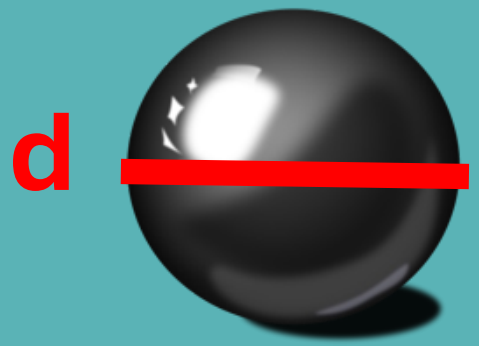


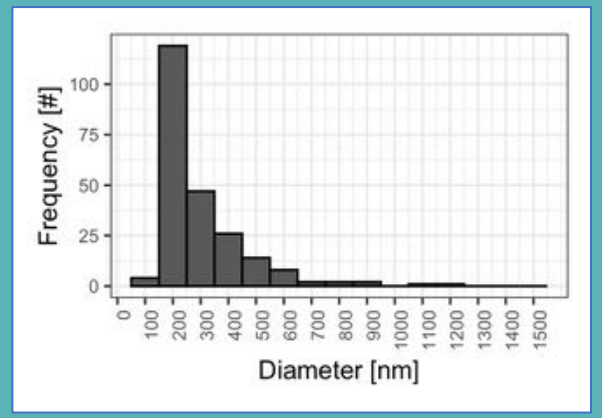


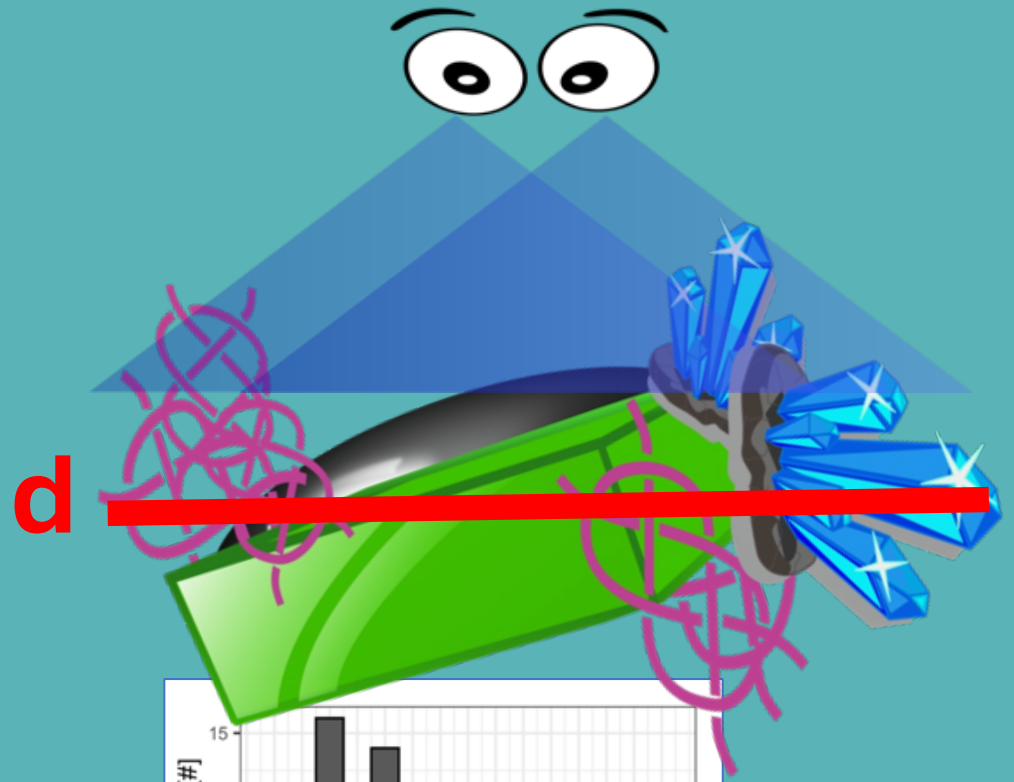
Quantitative data
- Mass/number concentrations
- Hypothesis testing
- Many samples
- Matrix/low conc.

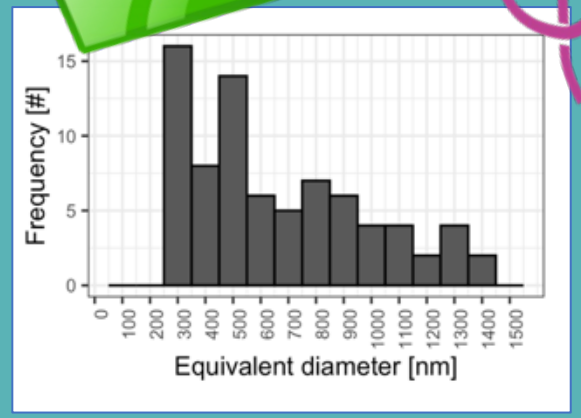
Qualitative
- Select samples
- Morphology and composition
- Low matrix/ high conc.

SP-ICP-MS + SEM-EDX!









Summary and outlook

- NPs mainly: Si, Fe, Al, Mn
  - NPs ~ ng/L vs ~ ug/L total
  - Complex multielement/aggregates
- Suitable for surveillance of inorganic NPs
- Offering insights into:
  - Distribution of incidental NPs (from mining waste)
  - Biogeochemical processes

Thanks!

also to: *AM Bienfait, TK Ervik, K Loeschner, S Valdersnes*

Slides @ arebruvold.com/research.html

Are Sæle Bruvold
PhD student
arebru@pm.me
arebruvold.com

Signal processing

- Rolling window, background approximation using a rolling kernel density estimate.
- Peak discrimination using max peak intensity
- LOD by establishing a critical limit of alpha of 0.05% of observing more than 1 false positive per minute assuming Poisson noise
- Allows investigation of **peak shape**, **autocorrelation** (≈ degree of aggregation) as well as **visual validation**

ADAPTED FROM Tailings Consultants Scandinavia AB, "Submarine tailings placement - Deposition in the fjord Tosen," 27-May-2014.