Corrosion and Copper Release Rates of Selected Copper Alloys in Seawater

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Common Wrought Copper-Nickel Alloys for Seawater Service

- 90-10 CuNi
- 70-30 CuNi
- Ni added primarily for increased strength and erosion-corrosion resistance
- Single-phase solid-solution over full composition range (0 – 100%)

Nominal Compositions (weight %)

Alloy	UNS	Ni	Fe	Mn	Cu	Others
90-10	C70600	9 - 11	1.0 – 1.8	1.0 max.	Bal.	Zn 1.0 max. Pb 0.05 max.
70-30	C71500	29 - 33	0.4 – 1.0	1.0 max.	Bal.	Zn 1 max. Pb 0.05 max.

Examples of Cu-Ni Alloy Applications in Seawater

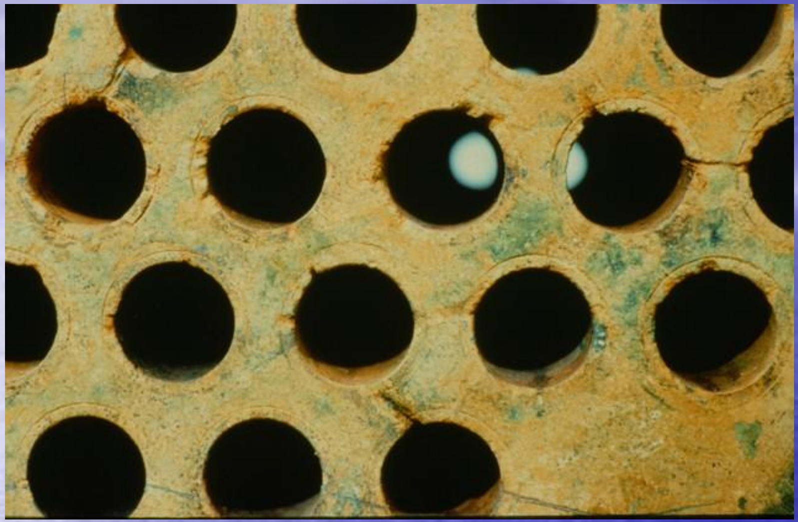
- Heat exchangers
- Piping systems
- Intake screens
- Sheathing or cladding
- Fish-farming cages

Cu-Ni Alloy Advantages

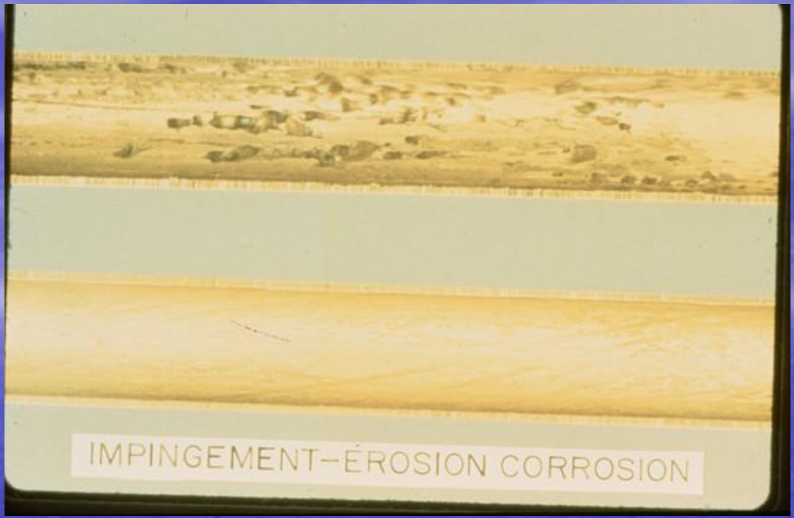
Selected mainly because of

- Excellent heat transfer
- Very good general and localized corrosion resistance;
  - typically ~ order of magnitude << carbon steel
- Improved erosion-corrosion resistance
- Biofouling resistance can be an added benefit
  - Minimal macrofouling attachments - easy to clean
  - Flow not restricted
  - Minimal drag resistance

Application Examples



90-10 CuNi ship condenser ~ 10 years;
Very low general and localized corrosion loss



Al-brass (top), 90-10 CuNi (bottom) ~ 60 days;
90-10 CuNi >> erosion-corrosion resistance

Concrete pipe section internally lined with 90-10 CuNi ~ 5 years;
Excellent biofouling resistance

Application Examples

Offshore platform 90-10 CuNi sheathing for splash and tidal zone protection

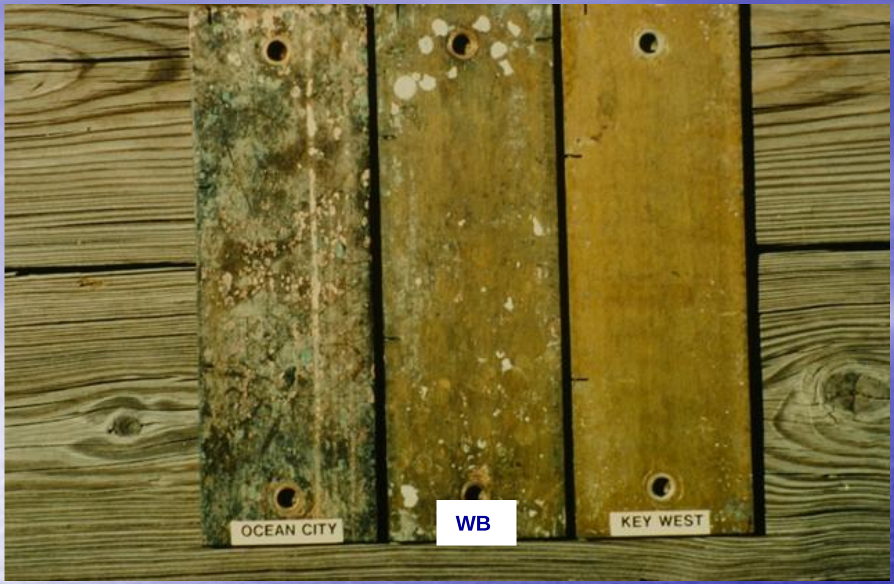
90-10 CuNi boat hull

General Corrosion Rates – Typically reported as

- Thickness loss in mils per year (mpy) or micrometers per year (μm/yr)
- Mass loss, $mg/dm^2/day$ (mdd)
- For biofouling resistance – Cu release rate, as $\mu g/cm^2/day$

Corrosion Data

- Published data from tests in natural seawater reviewed
- Worldwide ASTM 5-year seawater corrosivity study
- Historical data from LaQue Center, North Carolina
- Mostly 90-10 Cu-Ni



100 x 300 x 6 mm mass-loss panels

Exposed for 0.5, 1, 3 and 5 years

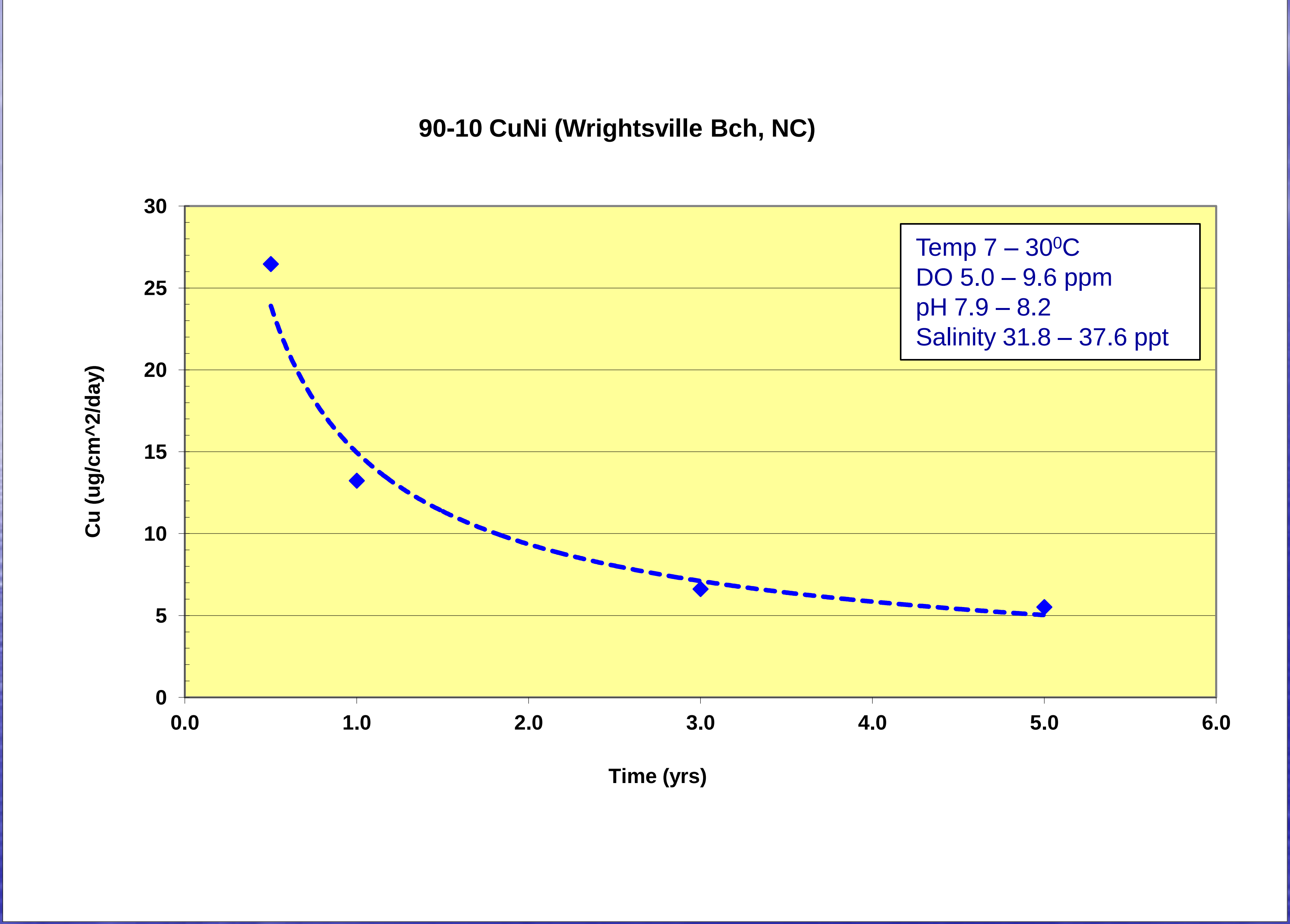
90-10 CuNi 5-yr seawater immersion at 14 worldwide locations

Mass loss determined after removal of corrosion products.

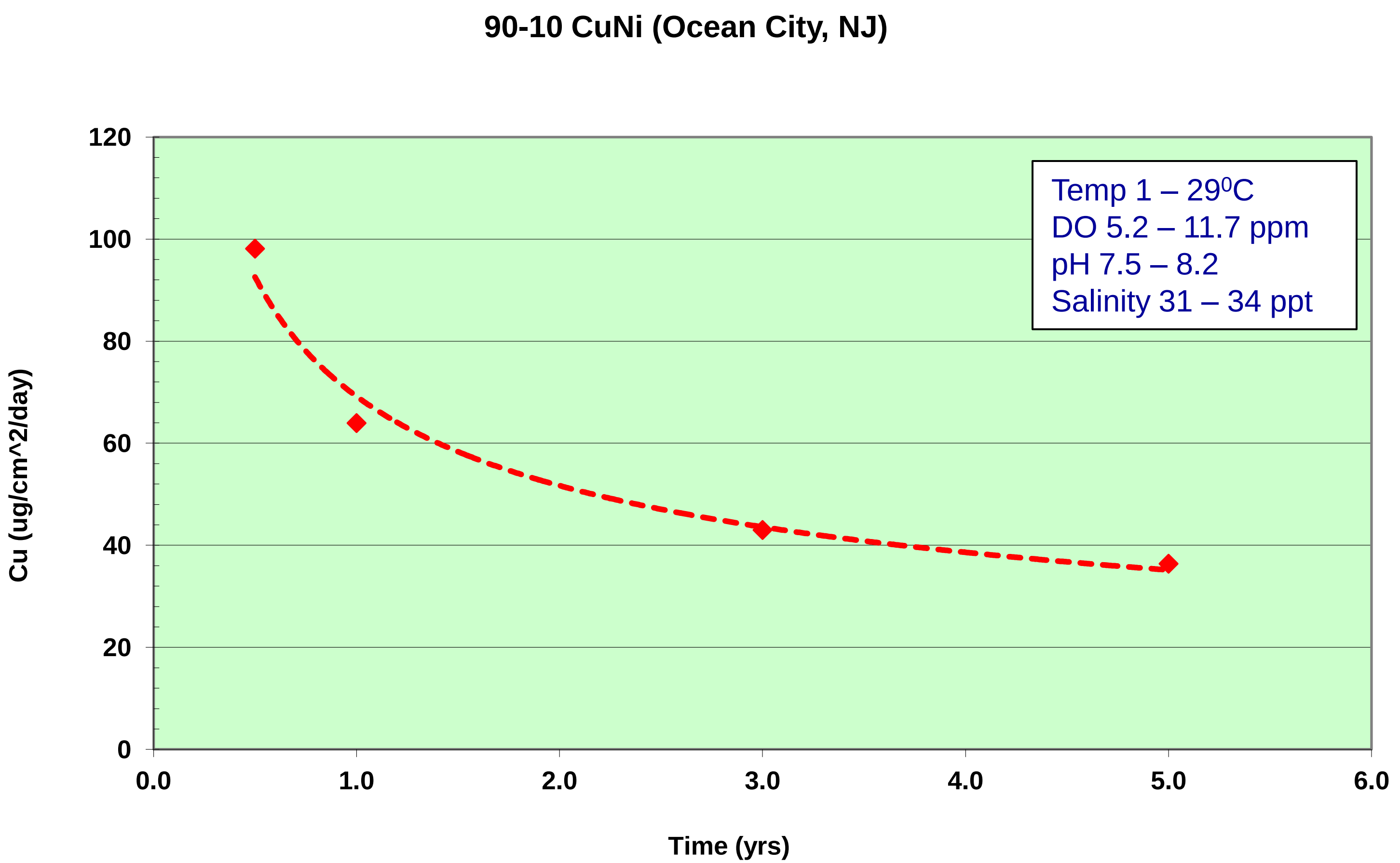
This “overestimates” Cu release rate into seawater

Cu release rate calculation

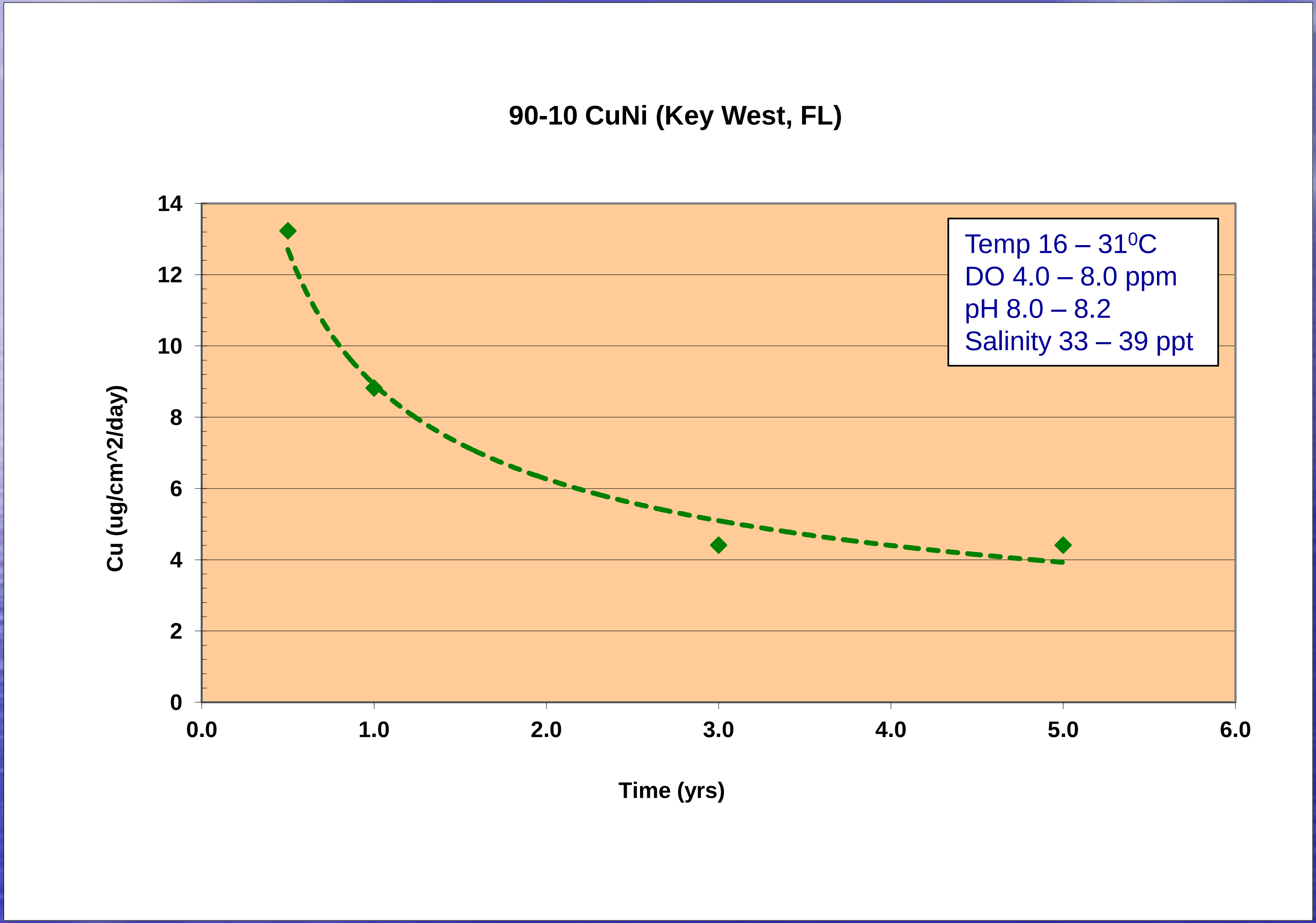
- $\mu g/cm^2/day = (? \ mm/yr \times 10^6) / (10 \times 365) \times \rho \ (g/cm^2)$
- 1 mm/yr = 2449.29 $\mu g/cm^2/day$
- 1 $\mu m/yr$ = 2.45 $\mu g/cm^2/day$ (k)
- Cu release rate ∞ 0.9 x alloy corrosion rate x k
- Corrosion rates - from long-term data in natural seawater

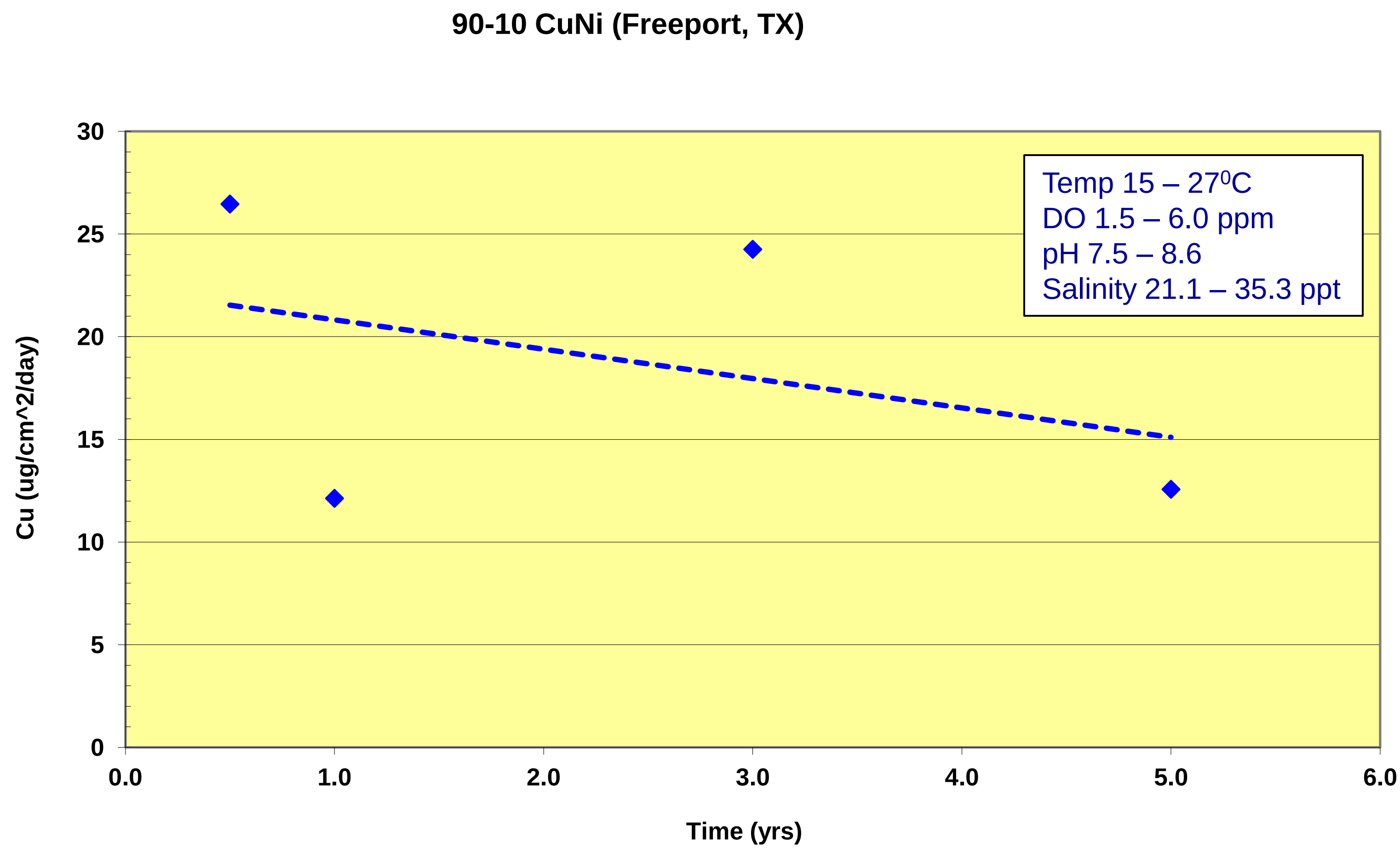


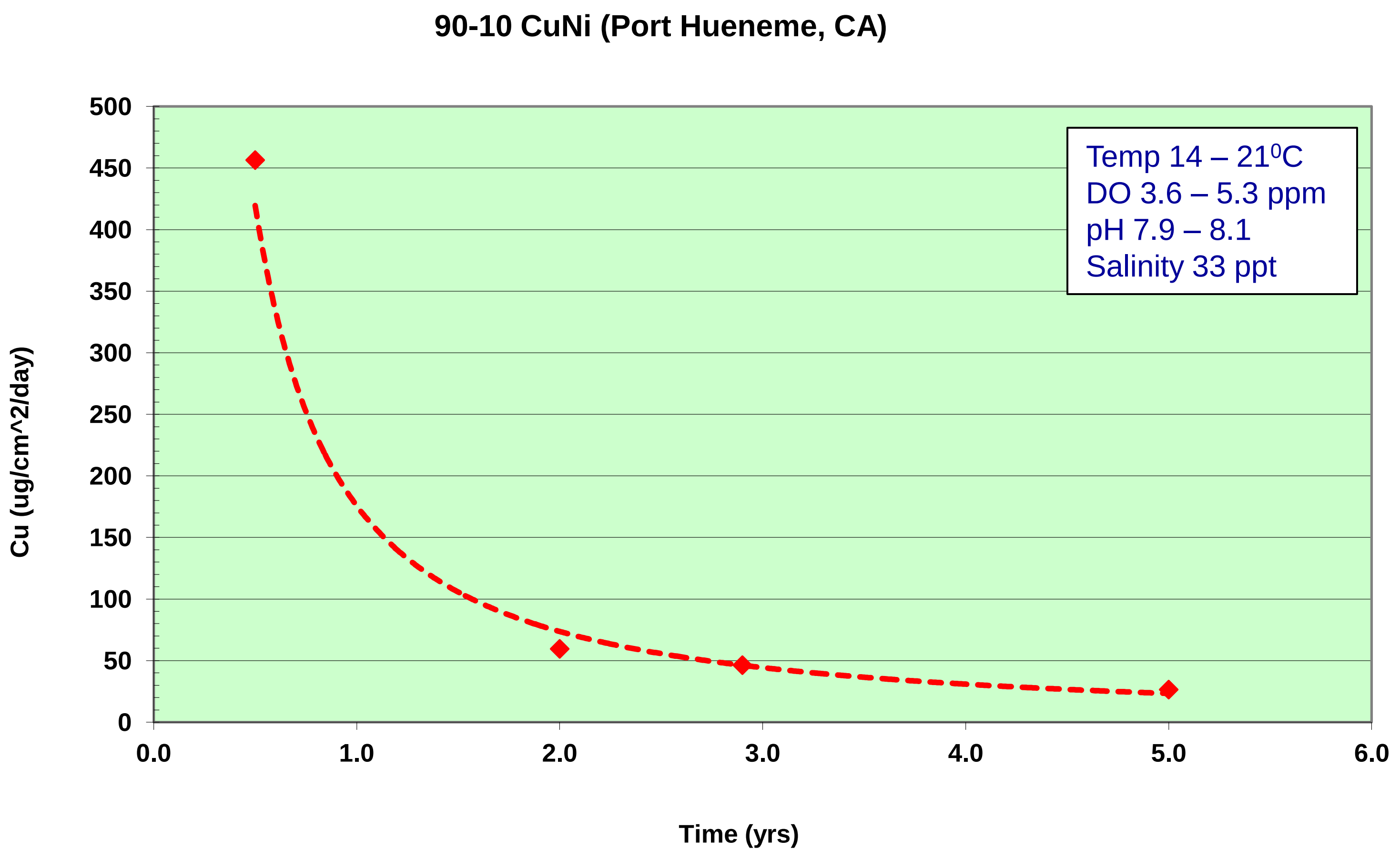
90-10 CuNi (Wrightsville Bch, NC)
Temp 7 – 30^{0}C
DO 5.0 – 9.6 ppm
pH 7.9 – 8.2
Salinity 31.8 – 37.6 ppt
Cu (ug/cm^2/day)
0
5
10
15
20
25
30
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)

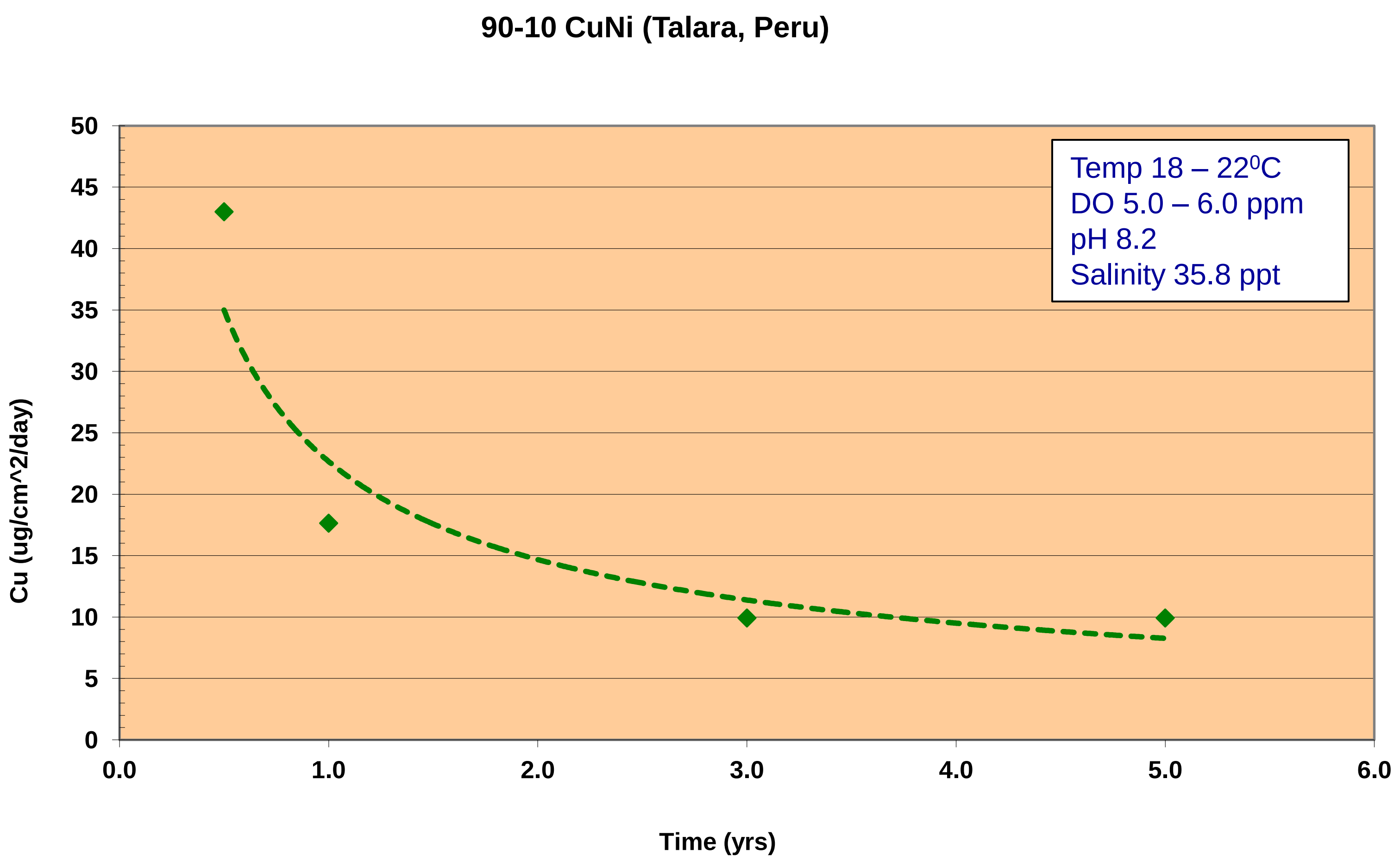


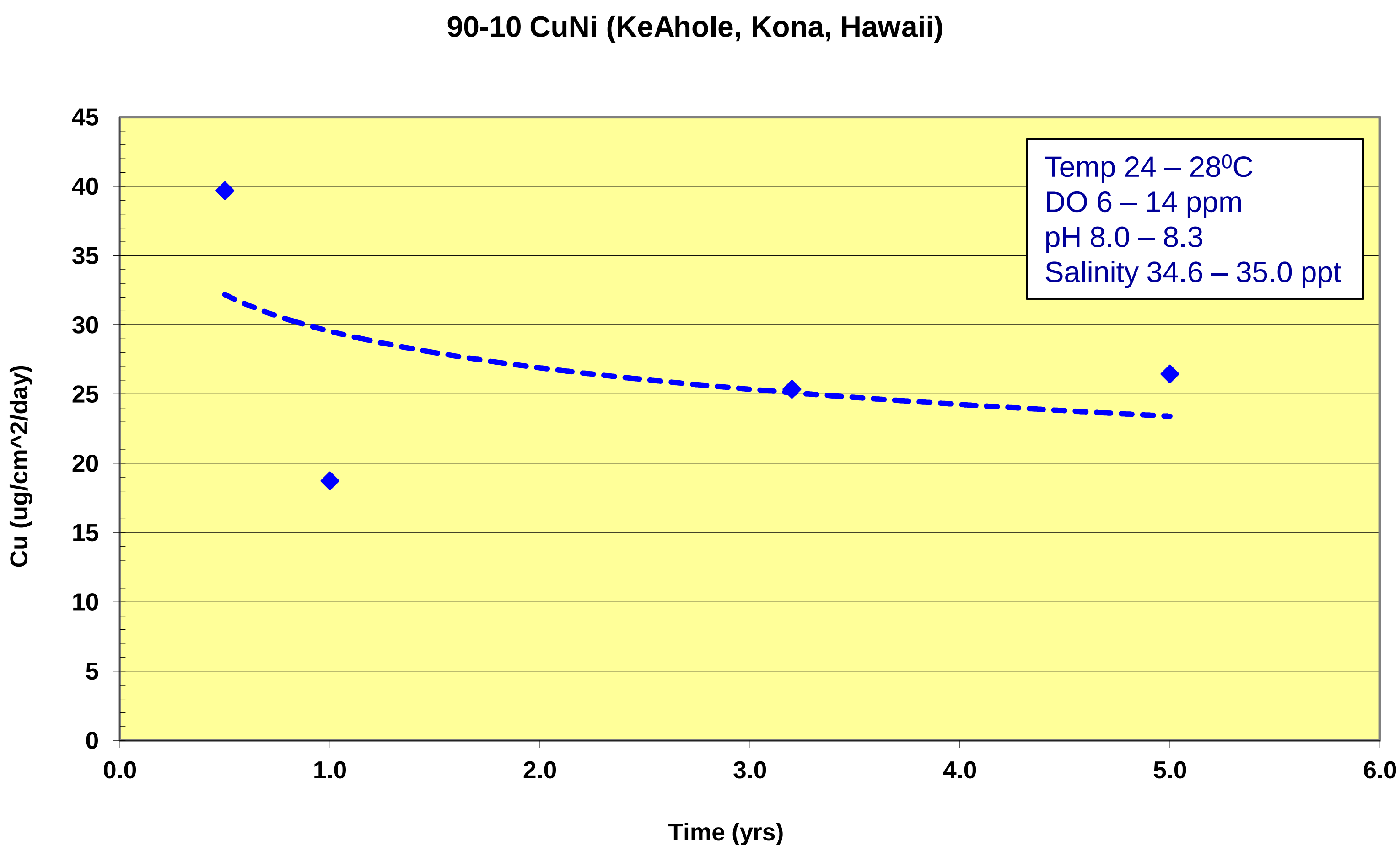
90-10 CuNi (Ocean City, NJ)
Temp 1 – 29^{0}C
DO 5.2 – 11.7 ppm
pH 7.5 – 8.2
Salinity 31 – 34 ppt
Cu (ug/cm^2/day)
120
100
80
60
40
20
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)

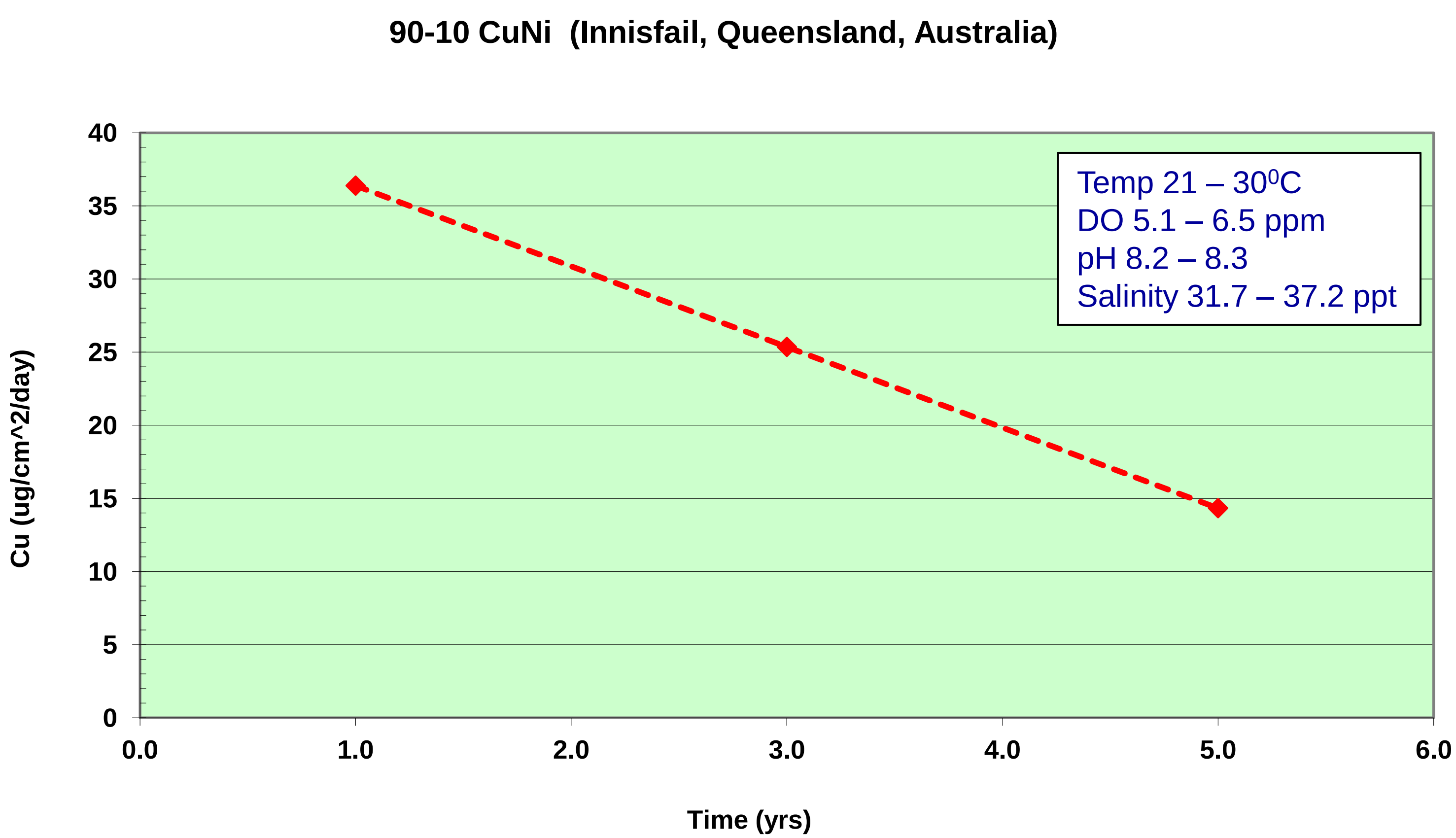

90-10 CuNi (Key West, FL)
Temp 16 – 31⁰C
DO 4.0 – 8.0 ppm
pH 8.0 – 8.2
Salinity 33 – 39 ppt
Cu (ug/cm^2/day)
14
12
10
8
6
4
2
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)


90-10 CuNi (Freeport, TX)
Temp 15 – 27⁰C
DO 1.5 – 6.0 ppm
pH 7.5 – 8.6
Salinity 21.1 – 35.3 ppt
Cu (ug/cm^2/day)
30
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)

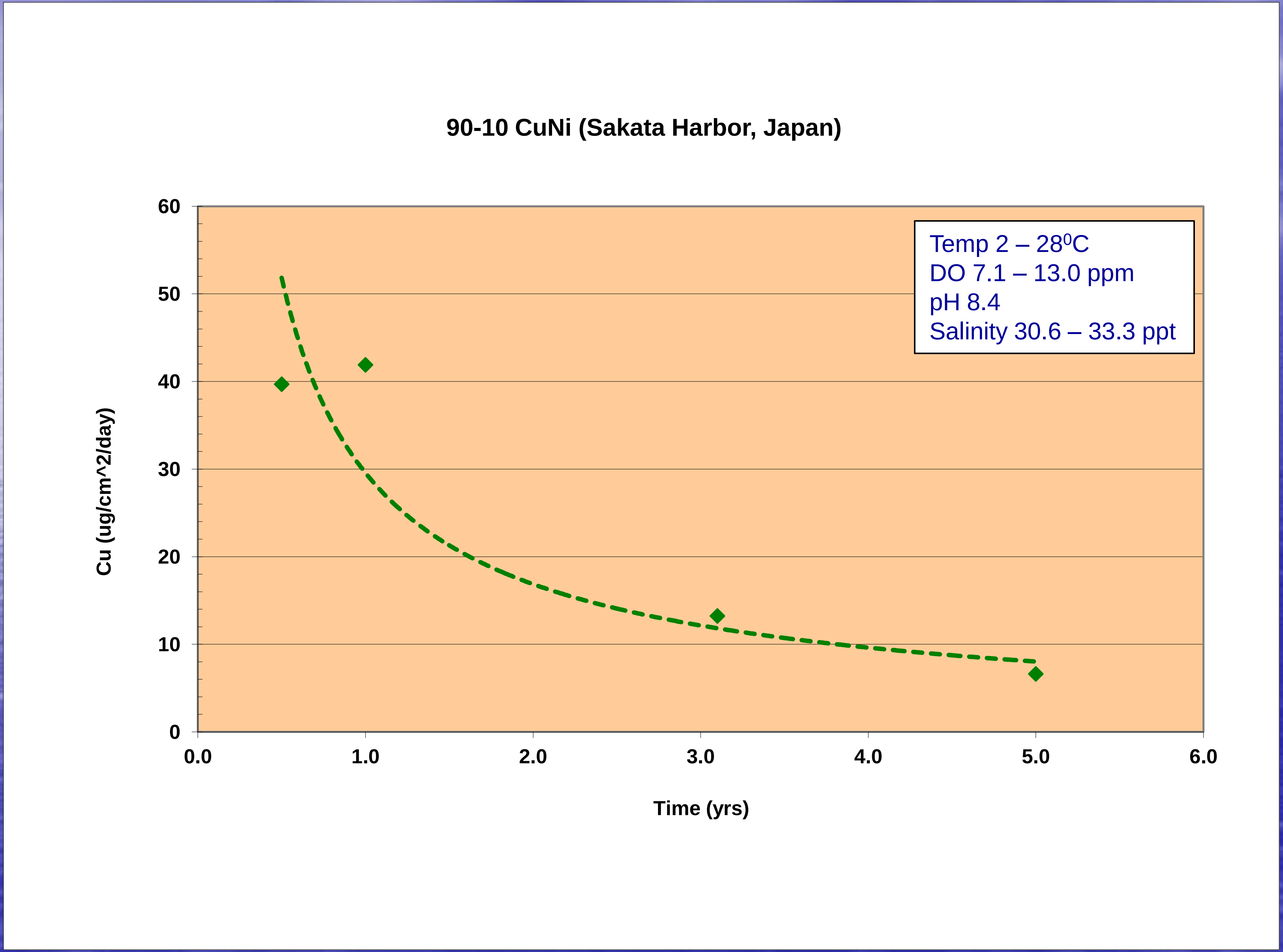

90-10 CuNi (Port Hueneme, CA)
Temp 14 – 21⁰C
DO 3.6 – 5.3 ppm
pH 7.9 – 8.1
Salinity 33 ppt
Cu (ug/cm^2/day)
500
450
400
350
300
250
200
150
100
50
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)


90-10 CuNi (Talara, Peru)
Temp 18 – 22⁰C
DO 5.0 – 6.0 ppm
pH 8.2
Salinity 35.8 ppt
Cu (ug/cm^2/day)
Time (yrs)
0
5
10
15
20
25
30
35
40
45
50
0.0
1.0
2.0
3.0
4.0
5.0
6.0

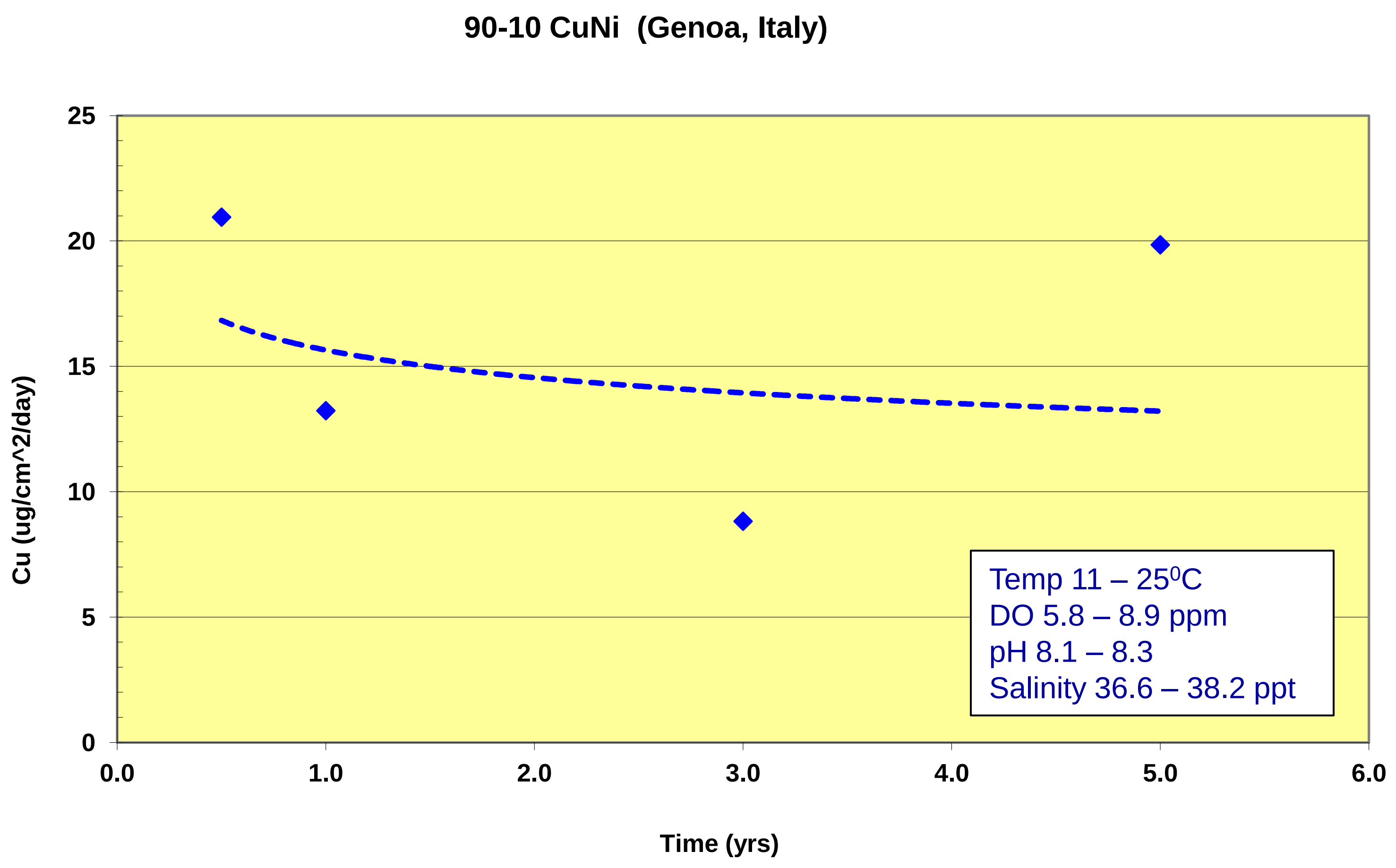

90-10 CuNi (KeAhole, Kona, Hawaii)
Temp 24 – 28⁰C
DO 6 – 14 ppm
pH 8.0 – 8.3
Salinity 34.6 – 35.0 ppt
Cu (ug/cm^2/day)
45
40
35
30
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)

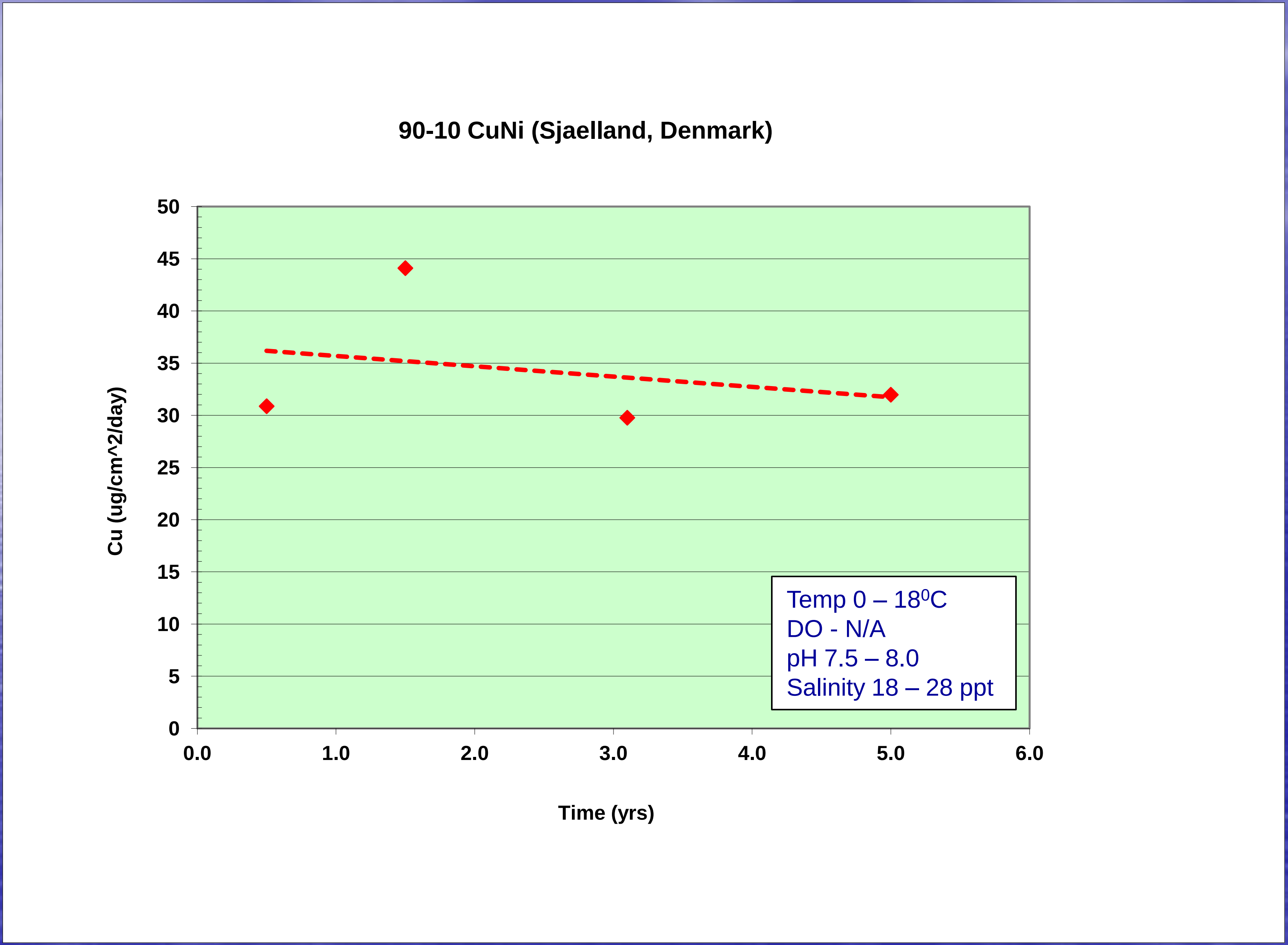


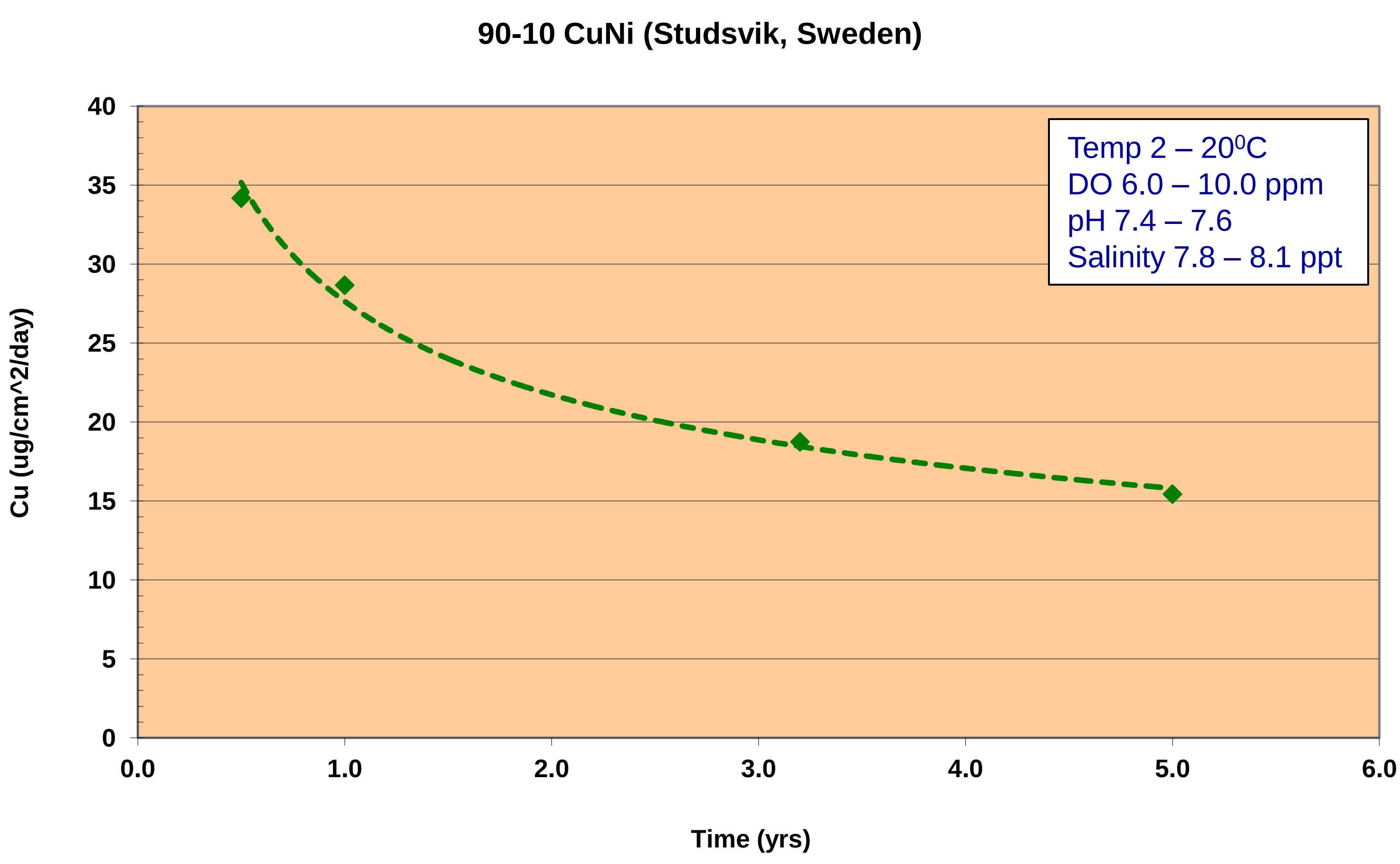
90-10 CuNi (Innisfail, Queensland, Australia)
Temp 21 – 30⁰C
DO 5.1 – 6.5 ppm
pH 8.2 – 8.3
Salinity 31.7 – 37.2 ppt
Cu (ug/cm^2/day)
40
35
30
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)



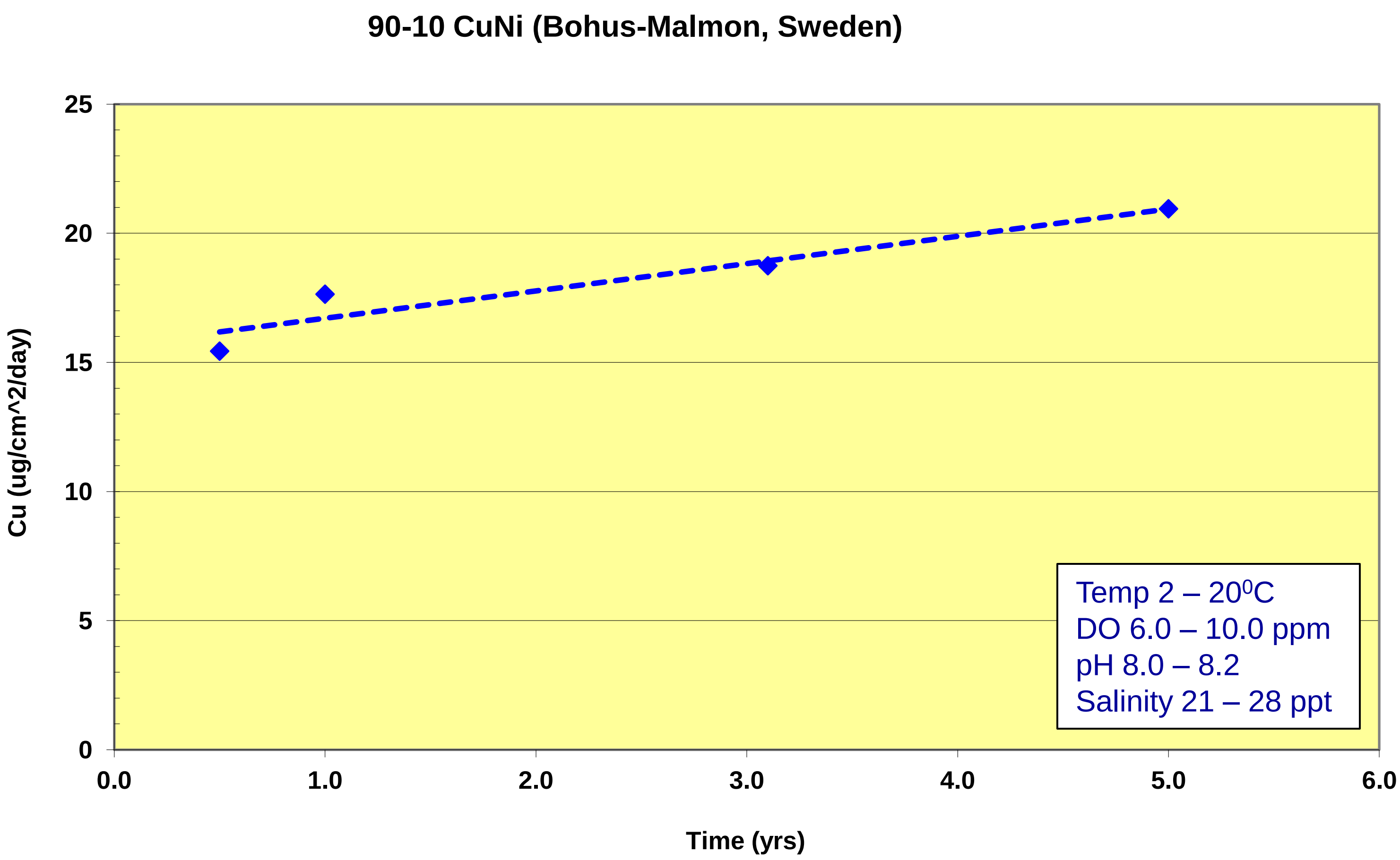
90-10 CuNi (Sakata Harbor, Japan)
Temp 2 – 28⁰C
DO 7.1 – 13.0 ppm
pH 8.4
Salinity 30.6 – 33.3 ppt
Cu (ug/cm^2/day)
60
50
40
30
20
10
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)

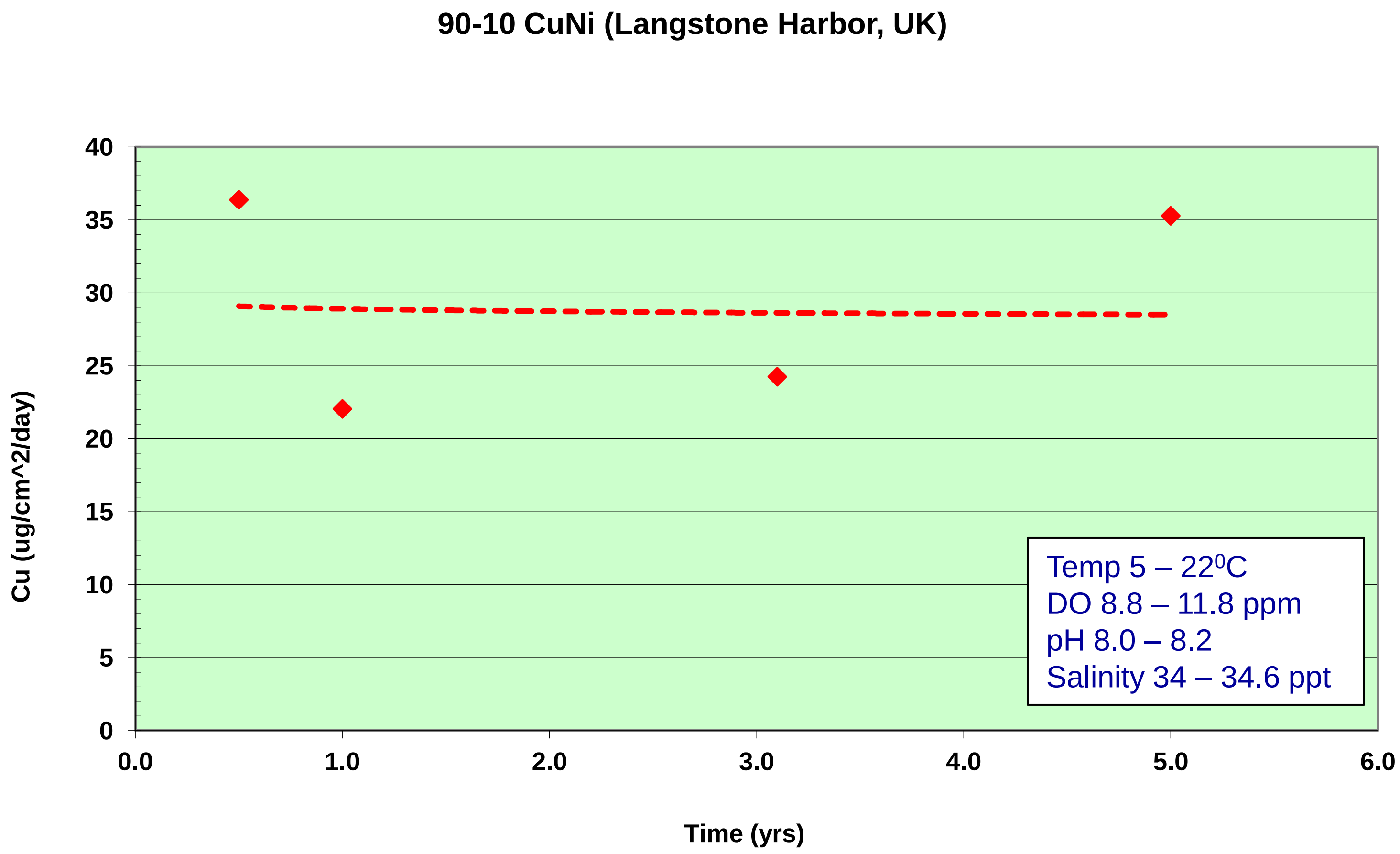

90-10 CuNi (Genoa, Italy)
Cu (ug/cm^2/day)
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)
Temp 11 – 25⁰C
DO 5.8 – 8.9 ppm
pH 8.1 – 8.3
Salinity 36.6 – 38.2 ppt

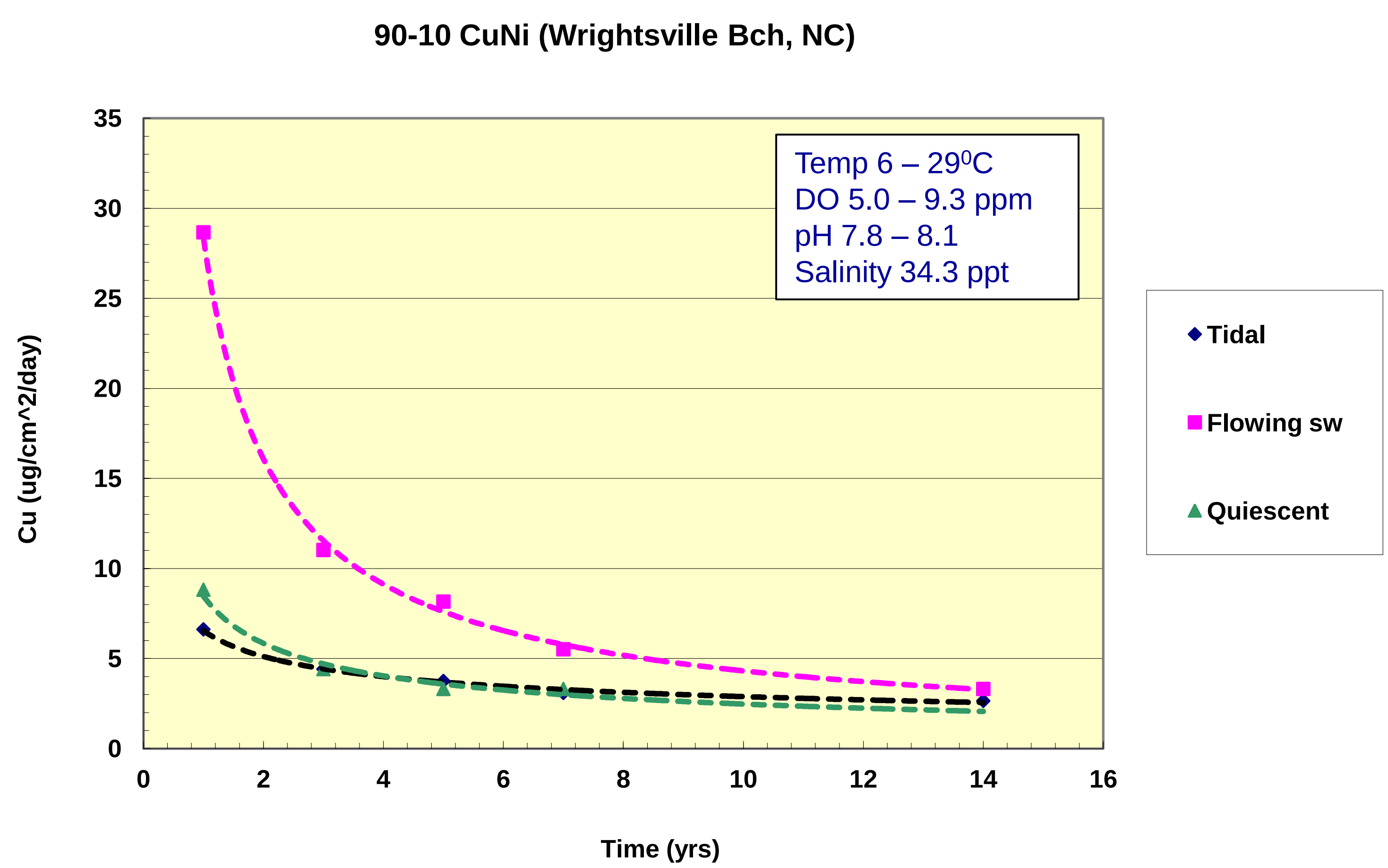

90-10 CuNi (Sjaelland, Denmark)
Cu (ug/cm^2/day)
50
45
40
35
30
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)
Temp 0 – 18⁰C
DO - N/A
pH 7.5 – 8.0
Salinity 18 – 28 ppt

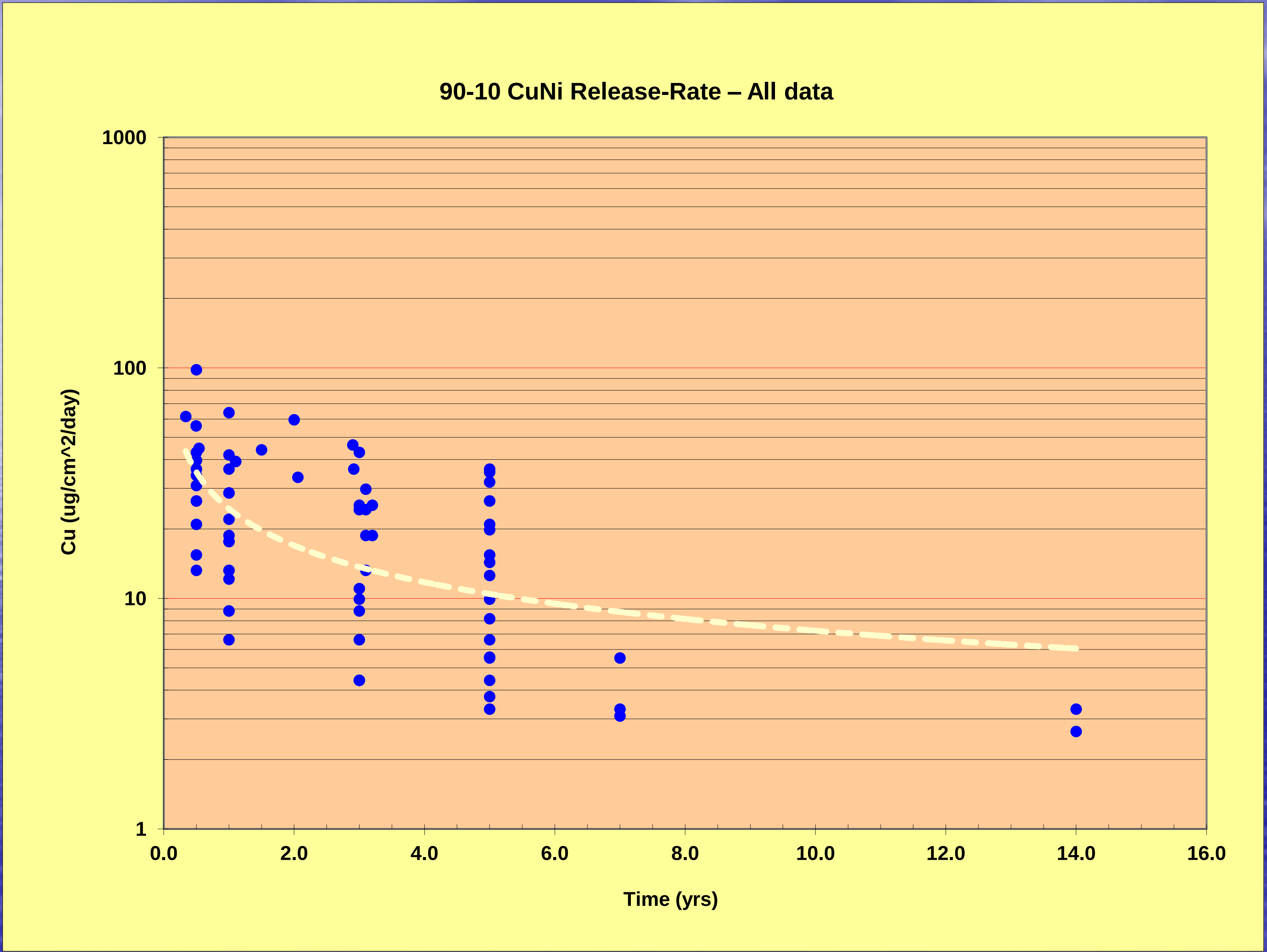


90-10 CuNi (Studsvik, Sweden)
Temp 2 – 20⁰C
DO 6.0 – 10.0 ppm
pH 7.4 – 7.6
Salinity 7.8 – 8.1 ppt
Cu (ug/cm^2/day)
40
35
30
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)

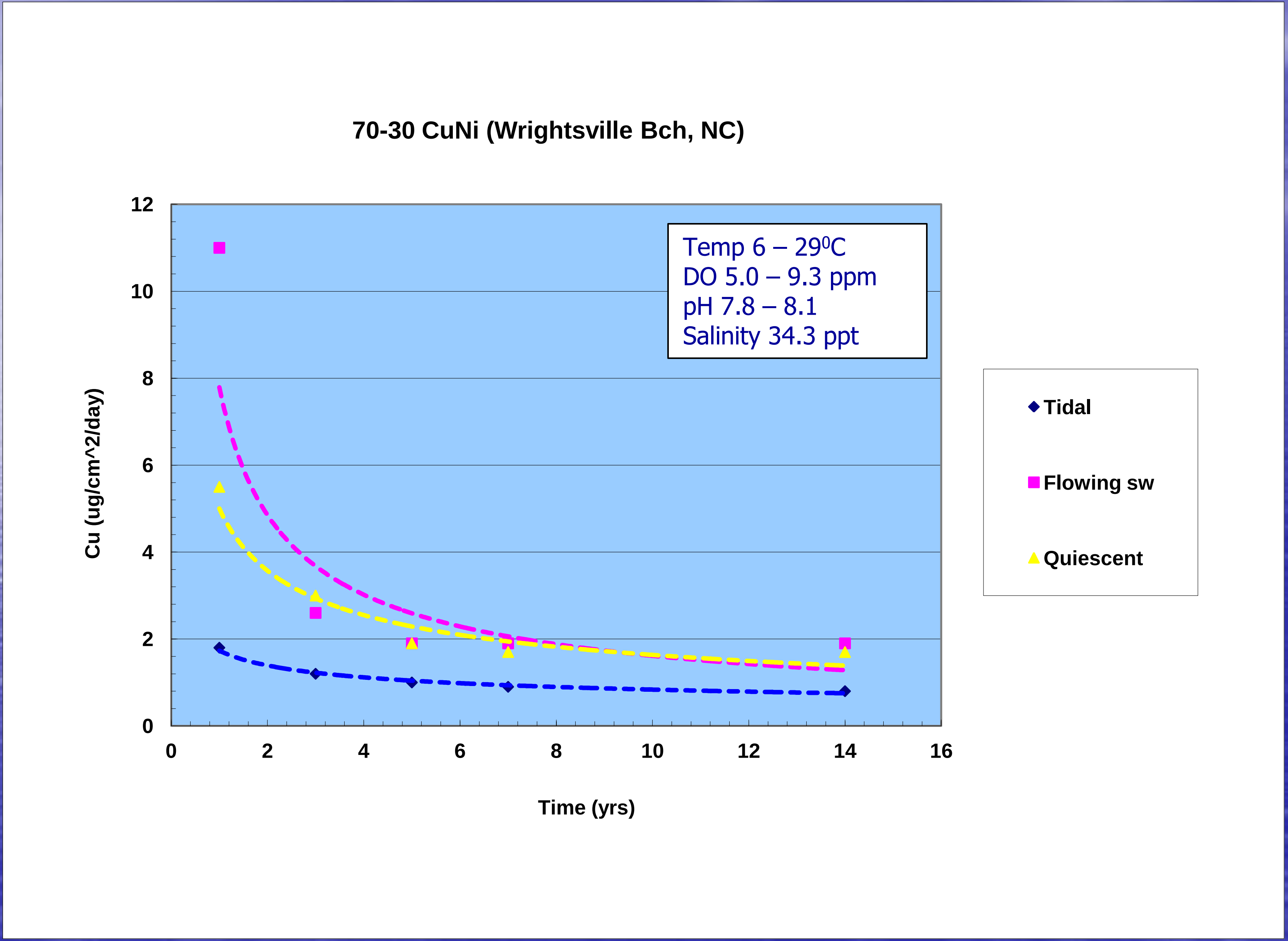

90-10 CuNi (Bohus-Malmon, Sweden)
Cu (ug/cm^2/day)
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)
Temp 2 – 20⁰C
DO 6.0 – 10.0 ppm
pH 8.0 – 8.2
Salinity 21 – 28 ppt


90-10 CuNi (Langstone Harbor, UK)
Cu (ug/cm^2/day)
40
35
30
25
20
15
10
5
0
0.0
1.0
2.0
3.0
4.0
5.0
6.0
Time (yrs)
Temp 5 – 22⁰C
DO 8.8 – 11.8 ppm
pH 8.0 – 8.2
Salinity 34 – 34.6 ppt


90-10 CuNi (Wrightsville Bch, NC)
Temp 6 – 29⁰C
DO 5.0 – 9.3 ppm
pH 7.8 – 8.1
Salinity 34.3 ppt
Tidal
Flowing sw
Quiescent
Cu (ug/cm^2/day)
Time (yrs)
0
5
10
15
20
25
30
35
0
2
4
6
8
10
12
14
16



90-10 CuNi Release-Rate – All data
Cu (ug/cm^2/day)
1000
100
10
1
0.0
2.0
4.0
6.0
8.0
10.0
12.0
14.0
16.0
Time (yrs)



70-30 CuNi (Wrightsville Bch, NC)
Temp 6 – 29°C
DO 5.0 – 9.3 ppm
pH 7.8 – 8.1
Salinity 34.3 ppt
Cu (ug/cm^2/day)
Time (yrs)
0
2
4
6
8
10
12
14
16
Tidal
Flowing sw
Quiescent

Corrosion Rates of CuNi and Cu Release Rates

- Average mass loss corrosion rates for all 14 worldwide locations after 5 years

  < 9 µm/yr (alloy) ≈ 19 µg/cm^2/day (Cu)

- Range: 2.5 – 16.5 µm/yr (alloy) ≈ 6 - 36 µg/cm^2/day (Cu)

- 14-year test: 1.5 µm/yr (alloy) ≈ 3 µg/cm^2/day (Cu)

- Many local factors influence corrosion rate and Cu release rate; e.g. sulfides, temperature, flow

18-months seawater immersion

90-10 CuNi

Macrofouling sloughs off or easily removed

Steel

Heavily fouled

Corrosion rate and Cu release rate after 5 years in quiescent seawater

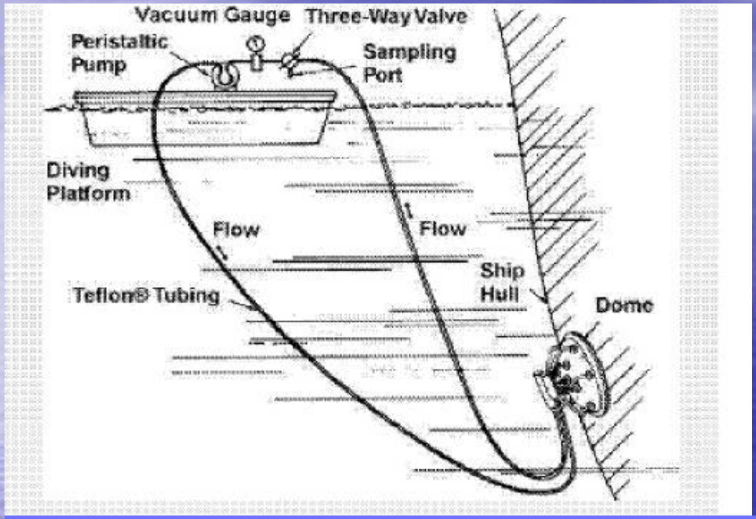
Material	Ave corr rate (µm/yr)	Cu release rate µg/cm²/day	Fouling resistance
Cu	**7.5**	**18.6**	Alternate loss and attainment
90-10 CuNi	**2.5**	**6.2**	Alternate loss and attainment
70-30 CuNi	**2.5**	**6.2**	Alternate loss and attainment

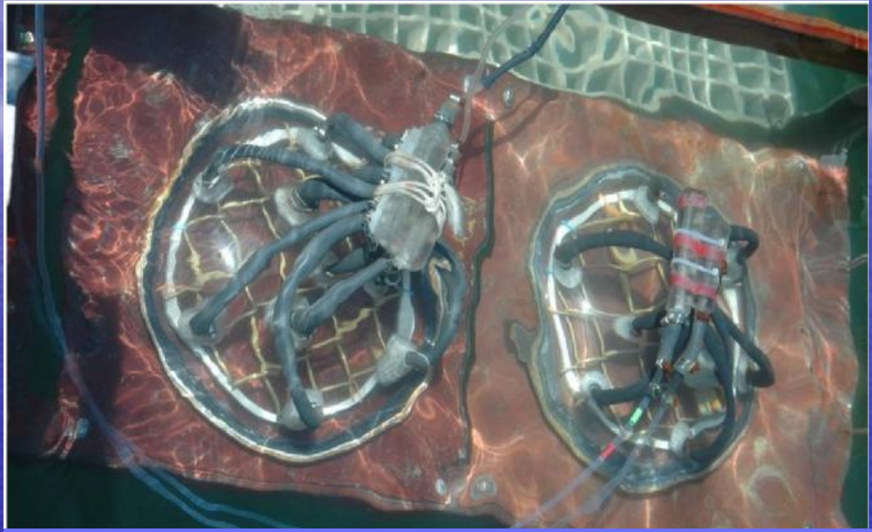
Based on his short-term tests (< 3 months) LaQue calculated Cu release rate ≥ 50 µg/cm²/day, i.e. corrosion rate of ~ 20 µm/yr, required for biofouling resistance. Above long-term data (and other test in Efird study) suggest fouling resistance may not be directly related to Cu^{2+} release rate

Biofouling Resistance Mechanism

- Not well understood; for Cu alloys hypothesized (by Efird) to be as follows:
- Attachment and growth of biofouling organisms
- Duplex nature of corrosion products: Cu_2O and $Cu(OH)_2.3CuCl_3$
- Initial film Cu_2O on substrate surface - resistant to fouling
- Oxidizes over time to green $Cu(OH)_2.3CuCl_3$ - less resistant to fouling; not as tightly adherent to substrate surface
- Alternate loss and attainment of biofouling resistance
- Easy removal and periodic sloughing off biofouling

U.S. Navy Dome Test





Dome attached directly to coated metal surface

Seawater circulated through dome

Circulated seawater analyzed for Cu released

Results of Cu release rates test where surface films have not been removed are nearing completion

Summary

- Average mass-loss corrosion rate of 90-10 CuNi in seawater << carbon steel; typically < 20 vs. 125 µm/yr
- Cu corrosion product generally slows mass-loss corrosion rate and hence Cu release rate significantly over time
- Cu present mostly as insoluble corrosion products
  - Cu_2O and $Cu(OH)_2.3CuCl_2$
- Previous short-term tests (< 3 months) indicated Cu release rate ≥ 50 µg/cm^2/day, i.e. corrosion rate of ~ 20 µm/yr, required for biofouling resistance
- Later long-term (≥ 5-year) tests indicated range of Cu release rates ~ 3 – 36 µg/cm^2/day for similar biofouling resistance
- Mass loss corrosion rates "overestimate" Cu release rates into seawater

Summary ….. continued

- Biofouling resistance of CuNi alloys may not be directly related to corrosion rates, i.e. Cu^{2+} release rates, into seawater
- Biofouling resistance mechanism not well understood; for Cu alloys ascribed to factors such as:
  - Cu_2O film on metal surface
  - Oxidation of Cu_2O oxidized to $Cu(OH)_2.3CuCl_2$ over time
  - $Cu(OH)_2.3CuCl_2$ poorly adherent to metal surface
  - Alternate attachment and sloughing off of biofouling
- Biofouling resistance mechanism of antifouling coatings containing Cu compounds also not well explained

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