Determination of Dominant Trace Metal Sequestration Processes in Two Vertical Flow Bioreactors Using Modified Tessier Extractions

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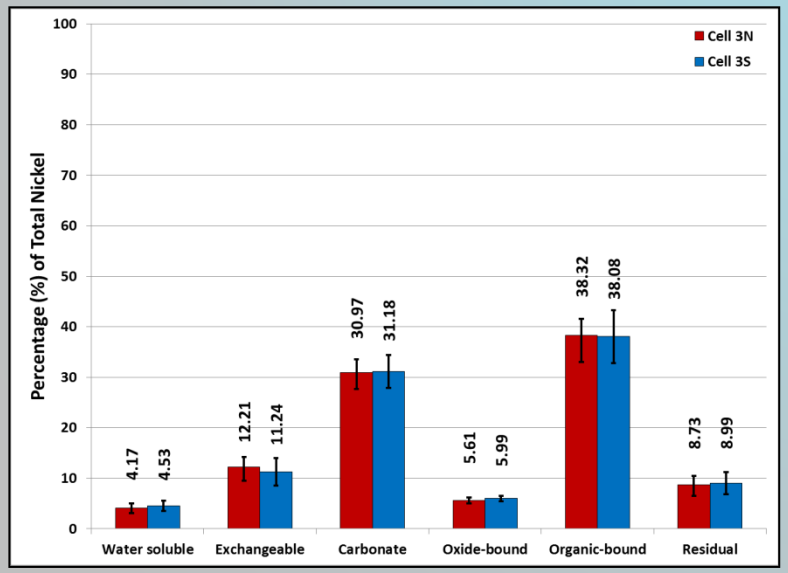
CREW
Center for Restoration of Ecosystems and Watersheds
University of Oklahoma

INTRODUCTION

METHODS

RESULTS



CONCLUSIONS

INTRODUCTION

- Tar Creek Superfund Site
  - Mayer Ranch, Commerce, OK
  - Over 30 years of unabated mine drainage
- Elevated metals (Fe, Cd, Ni, Pb, Zn), mineral acidity, sulfate
- Elevated alkalinity
  - Net-alkaline discharges with circum-neutral pH
- PTS constructed and began operation in 2008

INTRODUCTION

- Vertical flow bioreactors
  - Thick layer of organic carbon substrate
  - Anoxic, reducing conditions
- Goals = generate bicarbonate alkalinity and remove trace metals as sulfides
- Reality = also removed through sorption and exchange and as carbonates and oxides

INTRODUCTION

- Many methods for evaluating removal products
  - Varied success
- Mineralogical analyses
  - XRD, SEM, TEM, XANES, SXRF, etc.
  - High concentrations of crystalline products preferred
- Total metals
  - Lack of speciation
- Acid-volatile sulfides/simultaneously extracted metals
  - Amorphous vs. crystalline

INTRODUCTION

- Sequential extractions
  - Numerous methods
  - Use specific reagents to extract targeted species
  - Species are operationally defined (e.g., acetic acid soluble)

- Tessier et al., 1979
  - Exchangeable – 1 M $MgCl_2$
  - Carbonate – 1 M NaOAc at pH 5
  - Fe-Mn oxides – 0.04 M $NH_2OH{\cdot}HCl$ in 25% HOAc
  - Organic – HNO_3/H_2O_2 then 3.2 M NH_4OAc in 20% HNO_3
  - Residual - $HClO_4/HF$

INTRODUCTION

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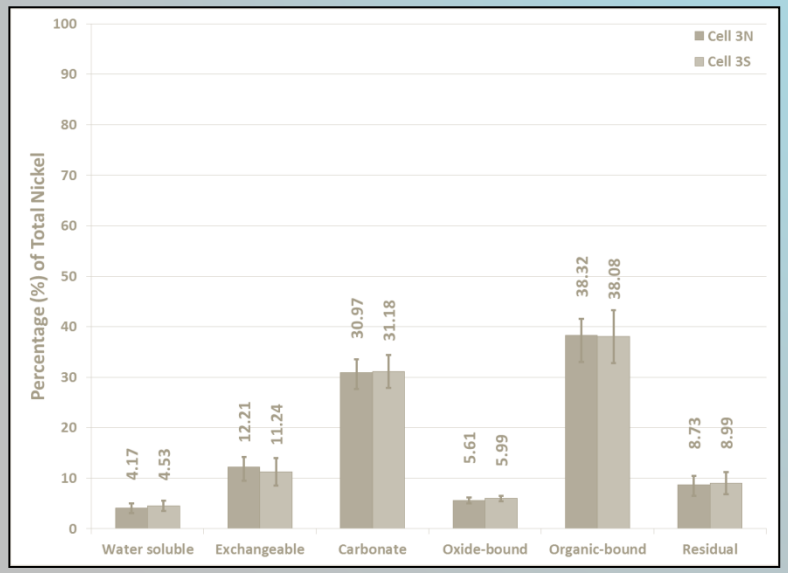


CONCLUSIONS

METHODS

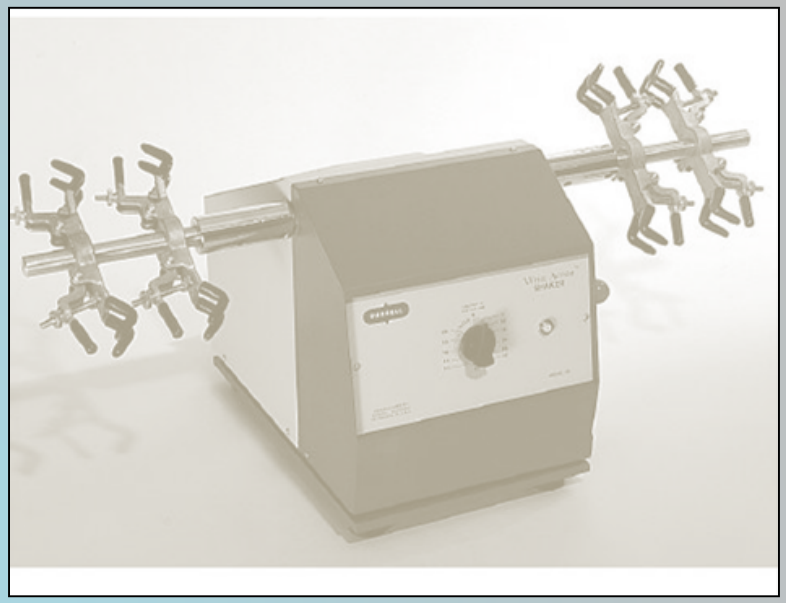
- Two VFBR
  - Approx. 49 m x 22 m
  - 45% SMC, 45% wood chips, 10% man-sand
- Water quality evaluated monthly for 18 months
- Nine substrate cores collected at equidistant points
  - June 2010
  - Placed in Ziploc bags
  - Stored at <4°C
  - Returned to CREW labs

METHODS

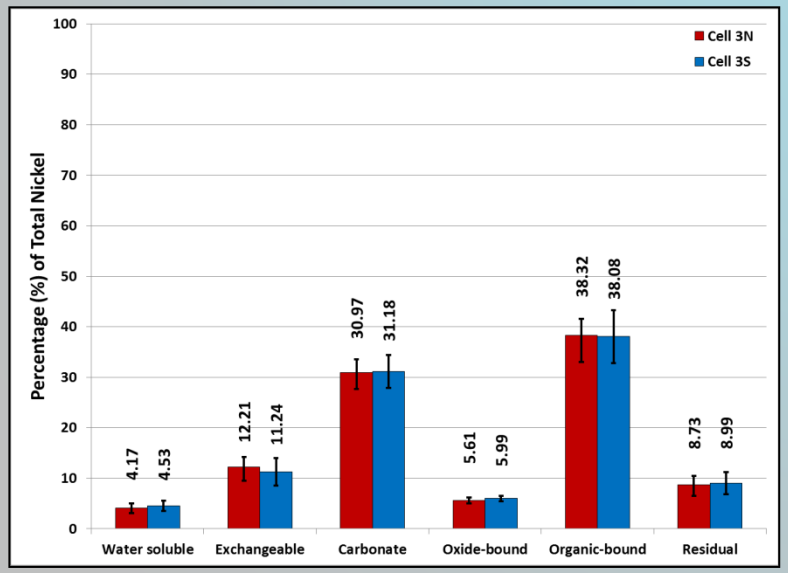
- Samples dried and subsampled
  - TCLP
  - Total metals
  - Sequential extractions
- Modified Tessier method
  - Added water soluble fraction (e.g., Leinz et al., 2000)
  - Microwave assisted HNO_3 digestion for “residual”
- All fractions analyzed with ICP-OES
  - Matrix adjustments
  - Y internal standard

INTRODUCTION

METHODS



RESULTS



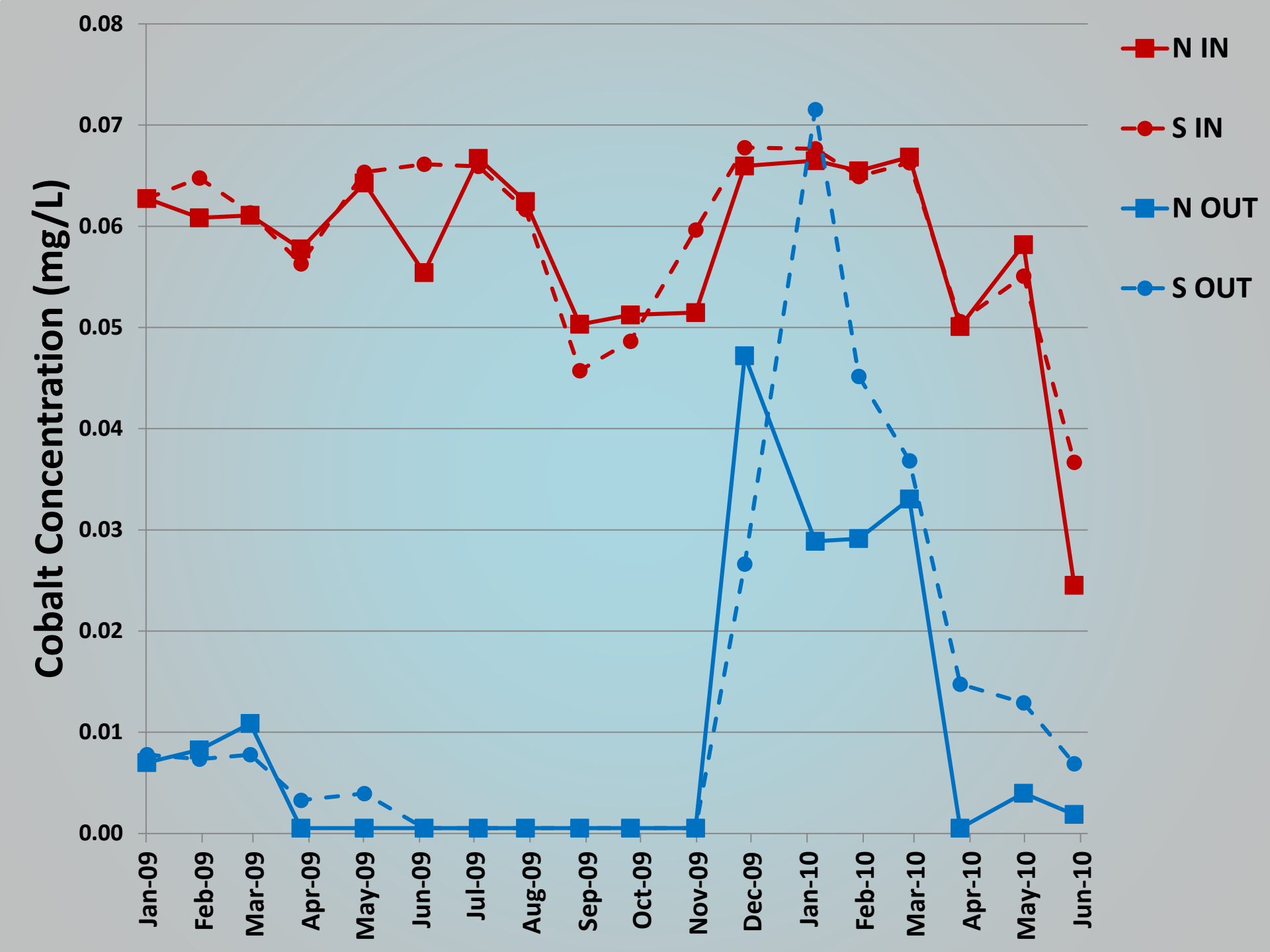
CONCLUSIONS

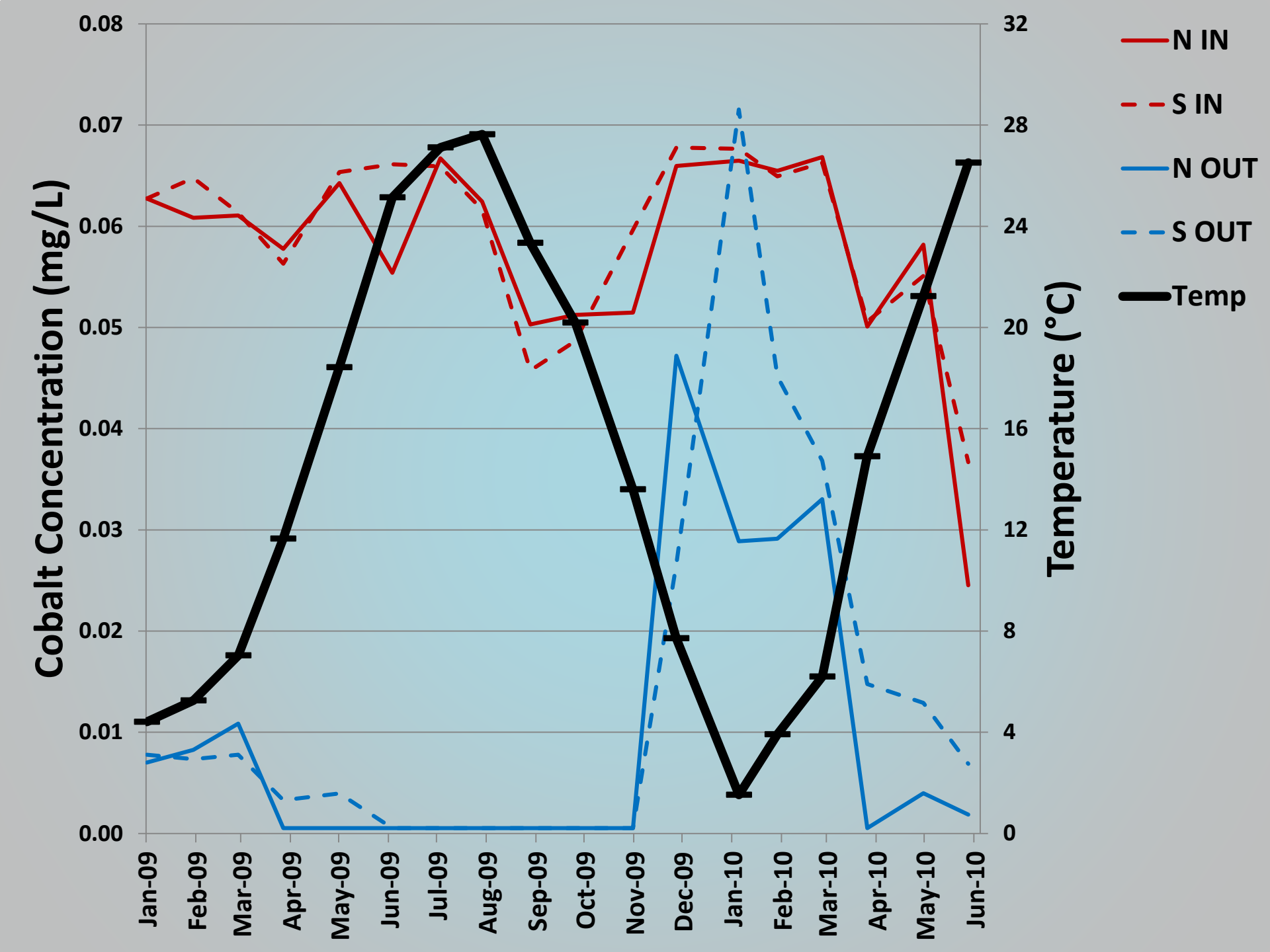
RESULTS – Water Quality

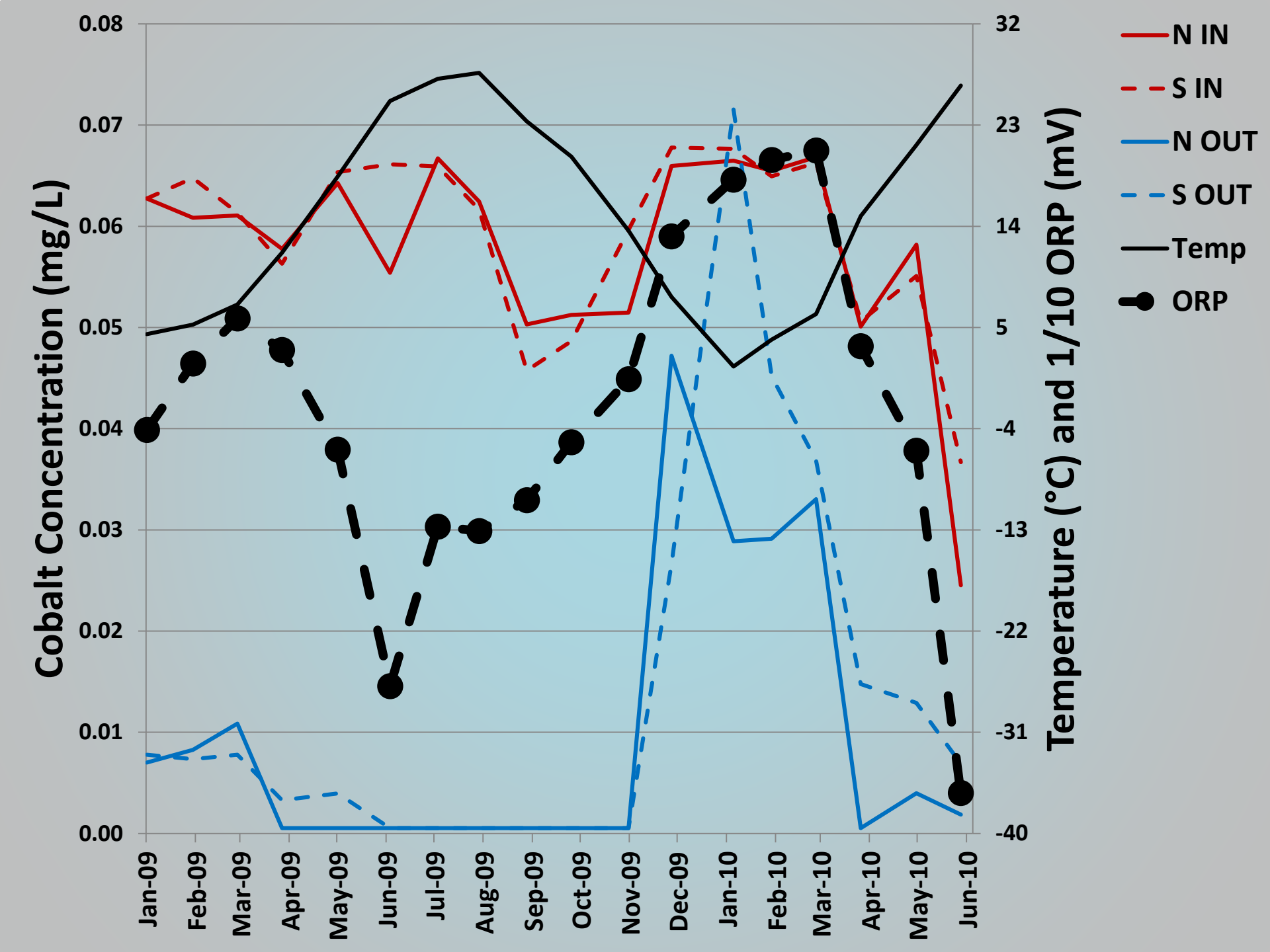
- Near 100% removal of trace metals in summer months
  - Not as efficient under low temperature conditions
- Reducing conditions present May – October
  - Highest temperatures
  - Lowest effluent concentrations
- No significant differences between north and south
  - Influent and effluent

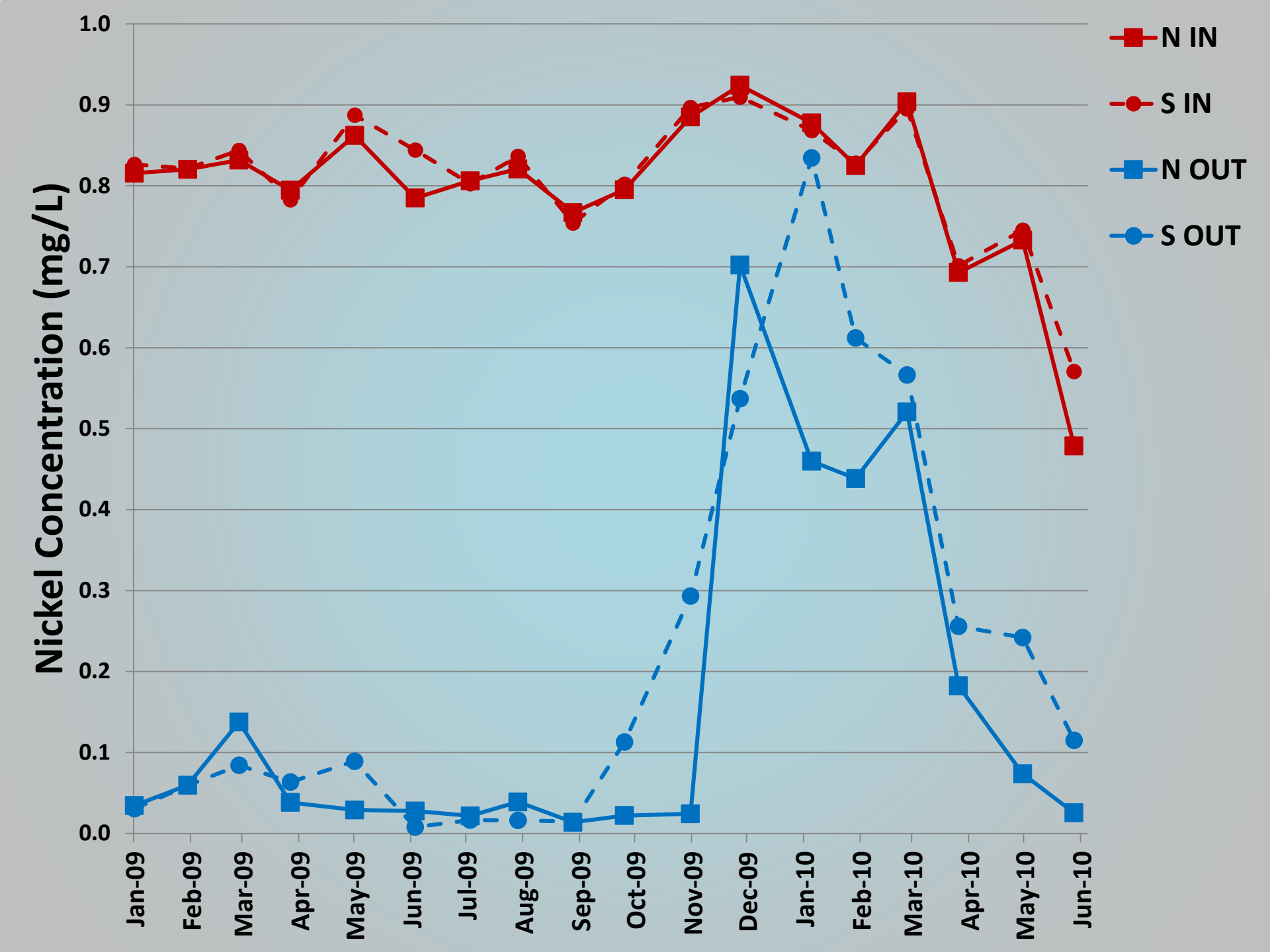
Mean Influent and Effluent Water Quality

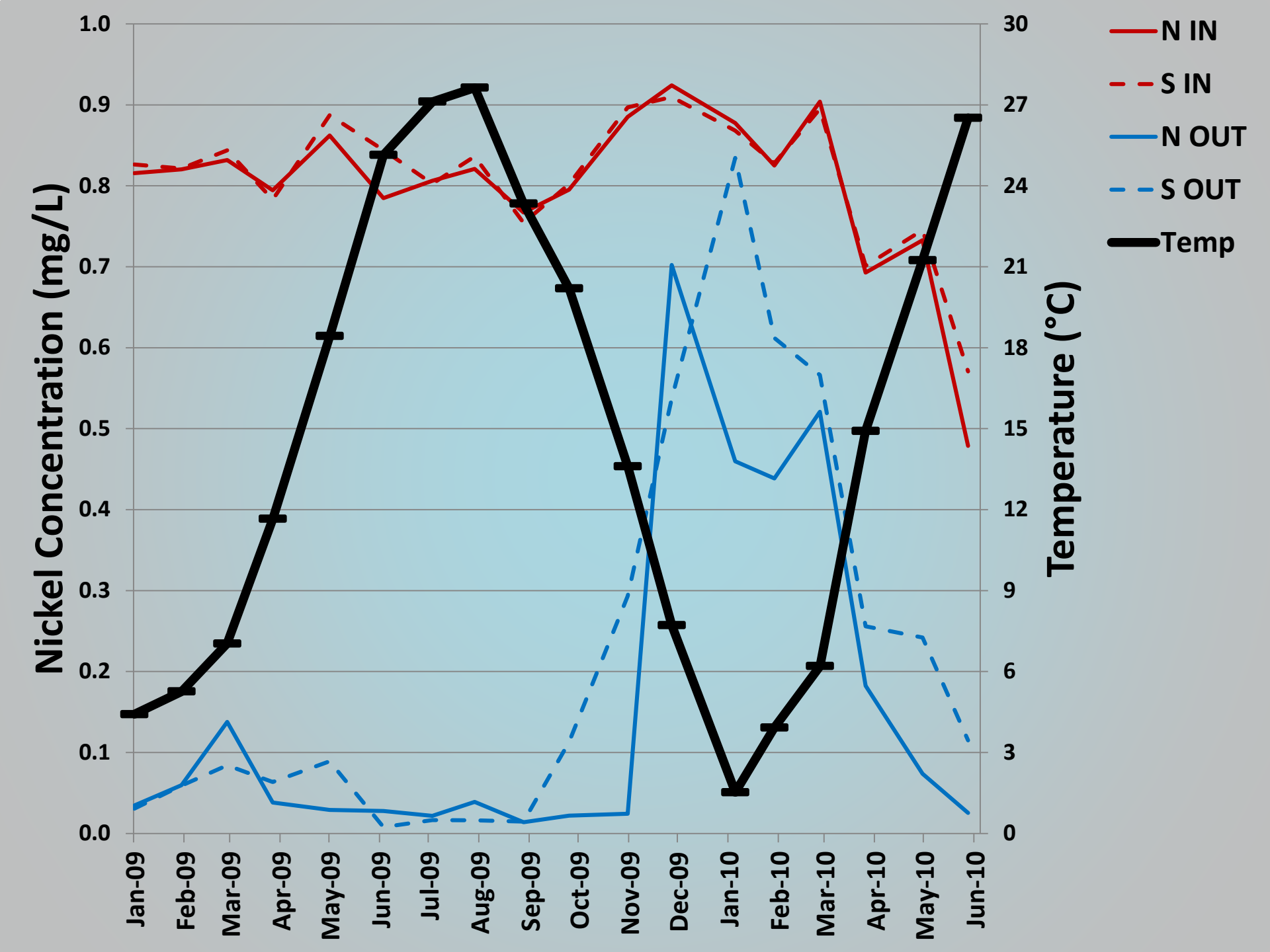
		N IN	S IN	N OUT	S OUT	n
pH	**(s.u.)**	6.55	6.54	6.84	6.81	18
DO	**(mg/L)**	8.43	8.08	0.74	0.94	18
Alkalinity	**(mg/L as $CaCO_3$)**	148	151	259	242	18
Fe	**(mg/L)**	8.36	8.83	1.66	2.10	18
Zn	**(mg/L)**	5.69	5.86	0.84	1.30	18
Co	**(mg/L)**	0.06	0.06	0.01	0.01	9-18
Ni	**(mg/L)**	0.81	0.81	0.16	0.22	18
Mn	**(mg/L)**	1.44	1.52	1.17	1.30	18
Cd	**(mg/L)**	0.003	0.002	0.001	0.002	3-9
Pb	**(mg/L)**	0.025	0.030	-	-	1-2
SO_4^{2-}	**(mg/L)**	2267	2394	2405	2284	18

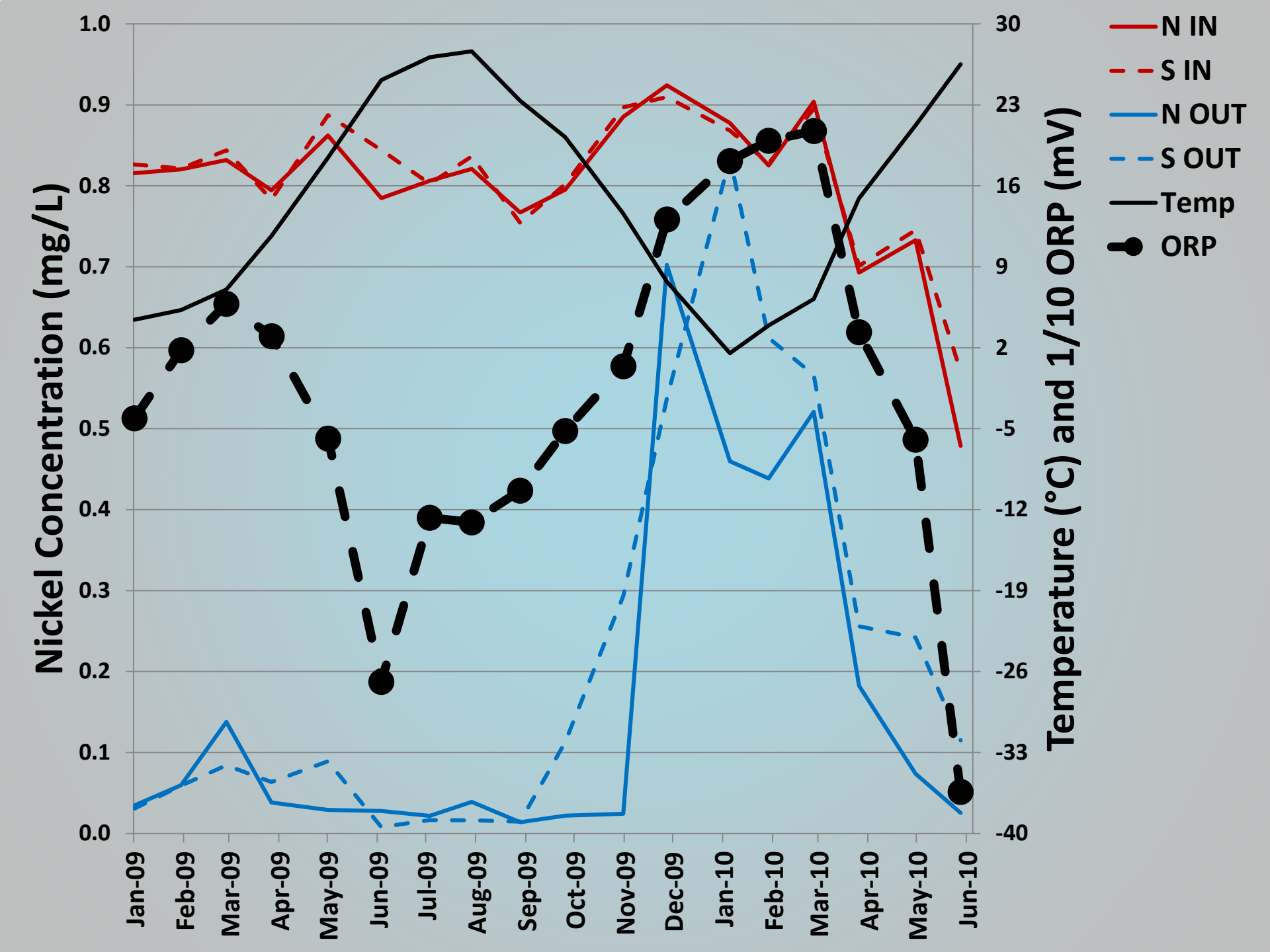

Cobalt Concentration (mg/L)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT

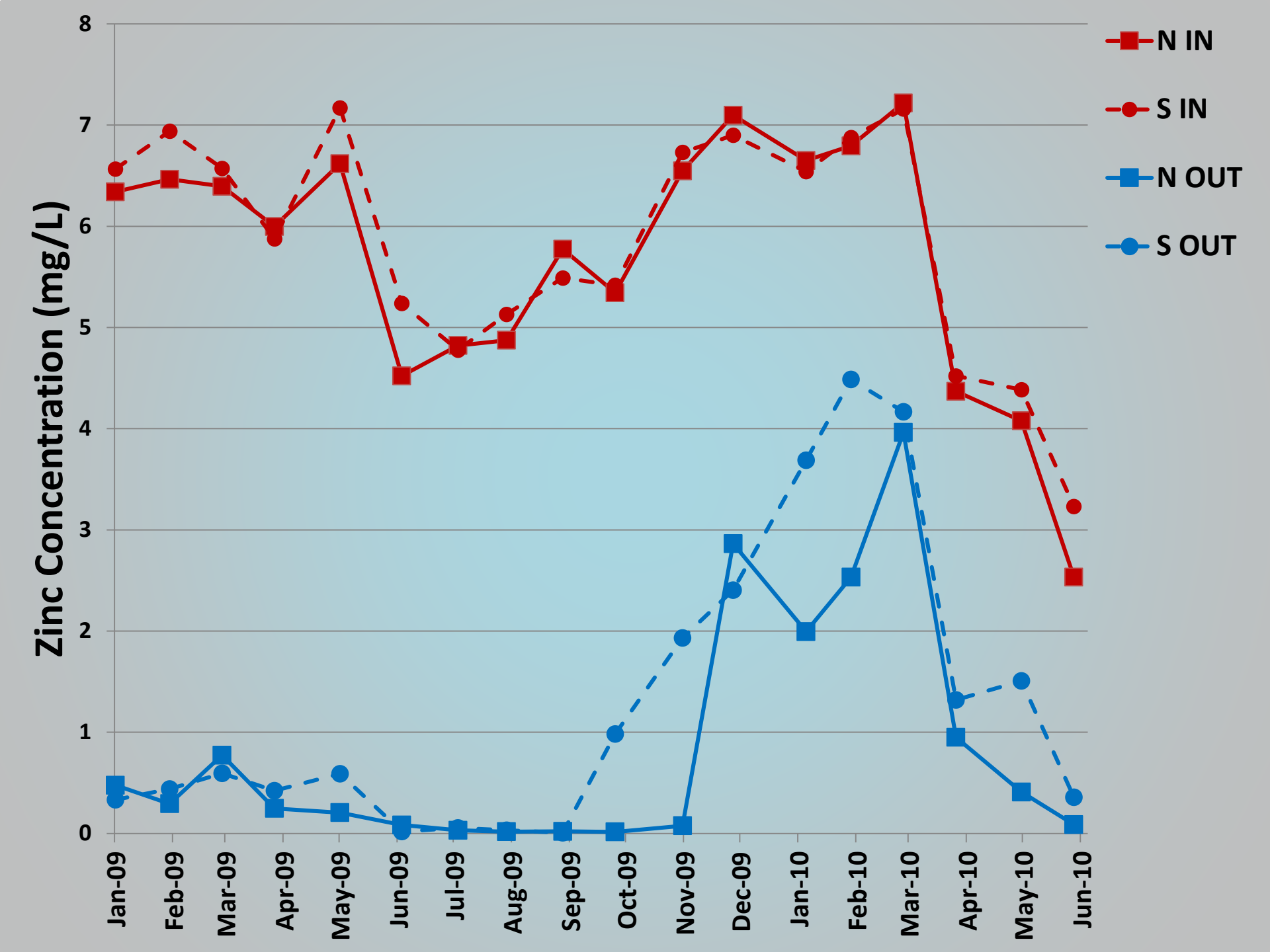

Cobalt Concentration (mg/L)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Temperature (°C)
32
28
24
20
16
12
8
4
0
N IN
S IN
N OUT
S OUT
Temp
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10

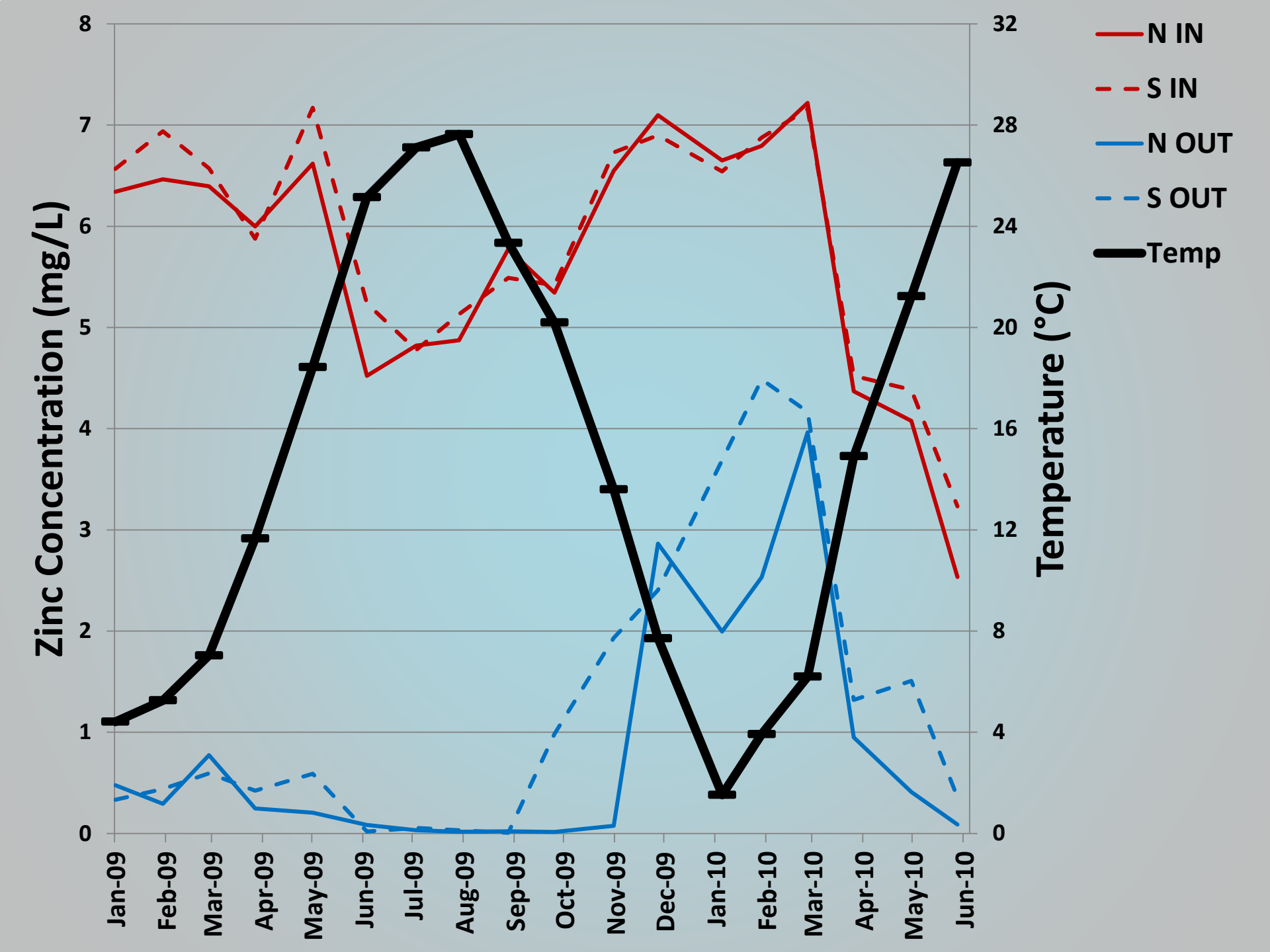

Cobalt Concentration (mg/L)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
Temperature (°C) and 1/10 ORP (mV)
32
23
14
5
-4
-13
-22
-31
-40
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT
Temp
ORP

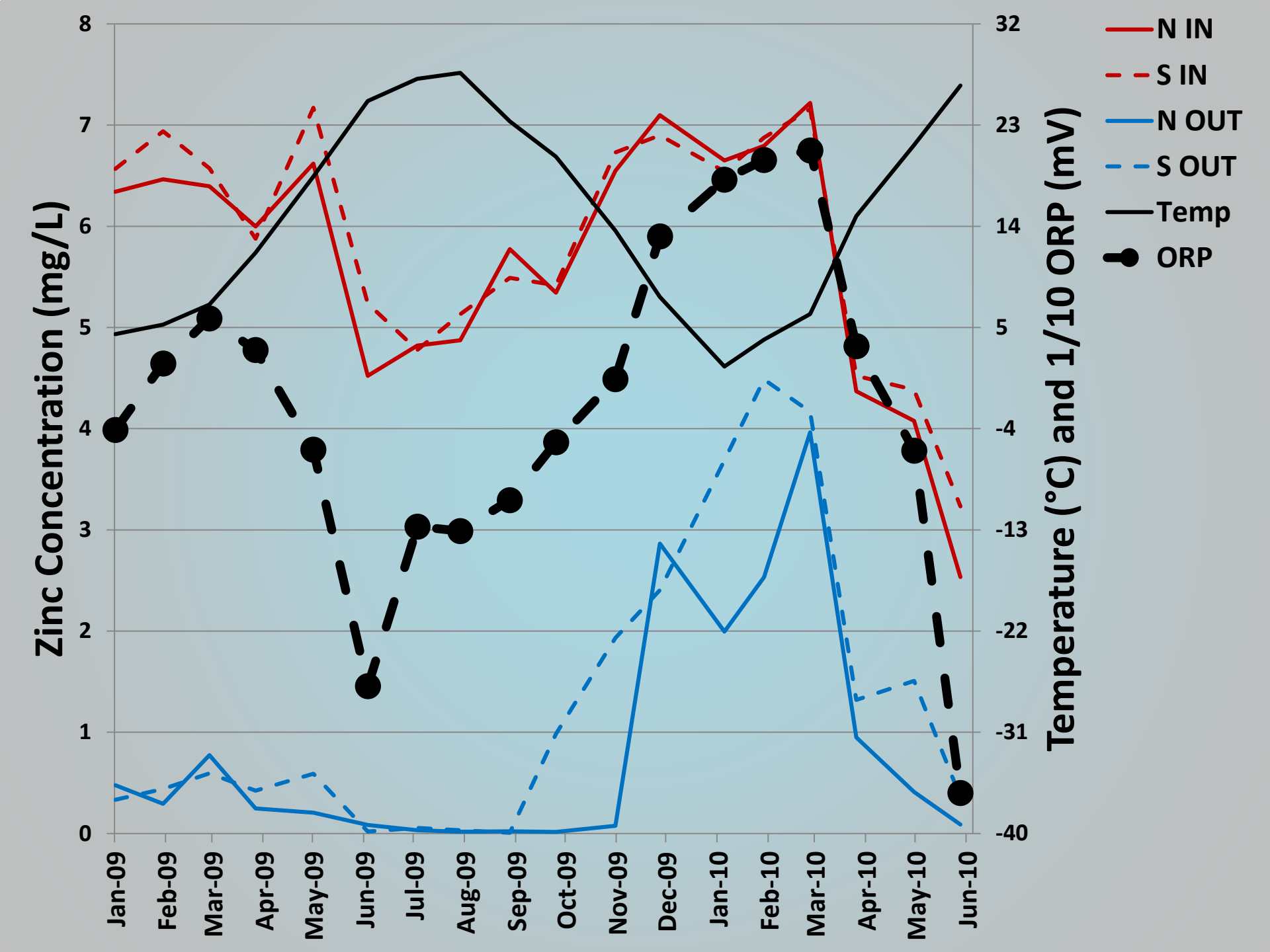

Nickel Concentration (mg/L)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT


Nickel Concentration (mg/L)
Temperature (°C)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
30
27
24
21
18
15
12
9
6
3
0
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT
Temp


Nickel Concentration (mg/L)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Temperature (°C) and 1/10 ORP (mV)
30
23
16
9
2
-5
-12
-19
-26
-33
-40
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT
Temp
ORP

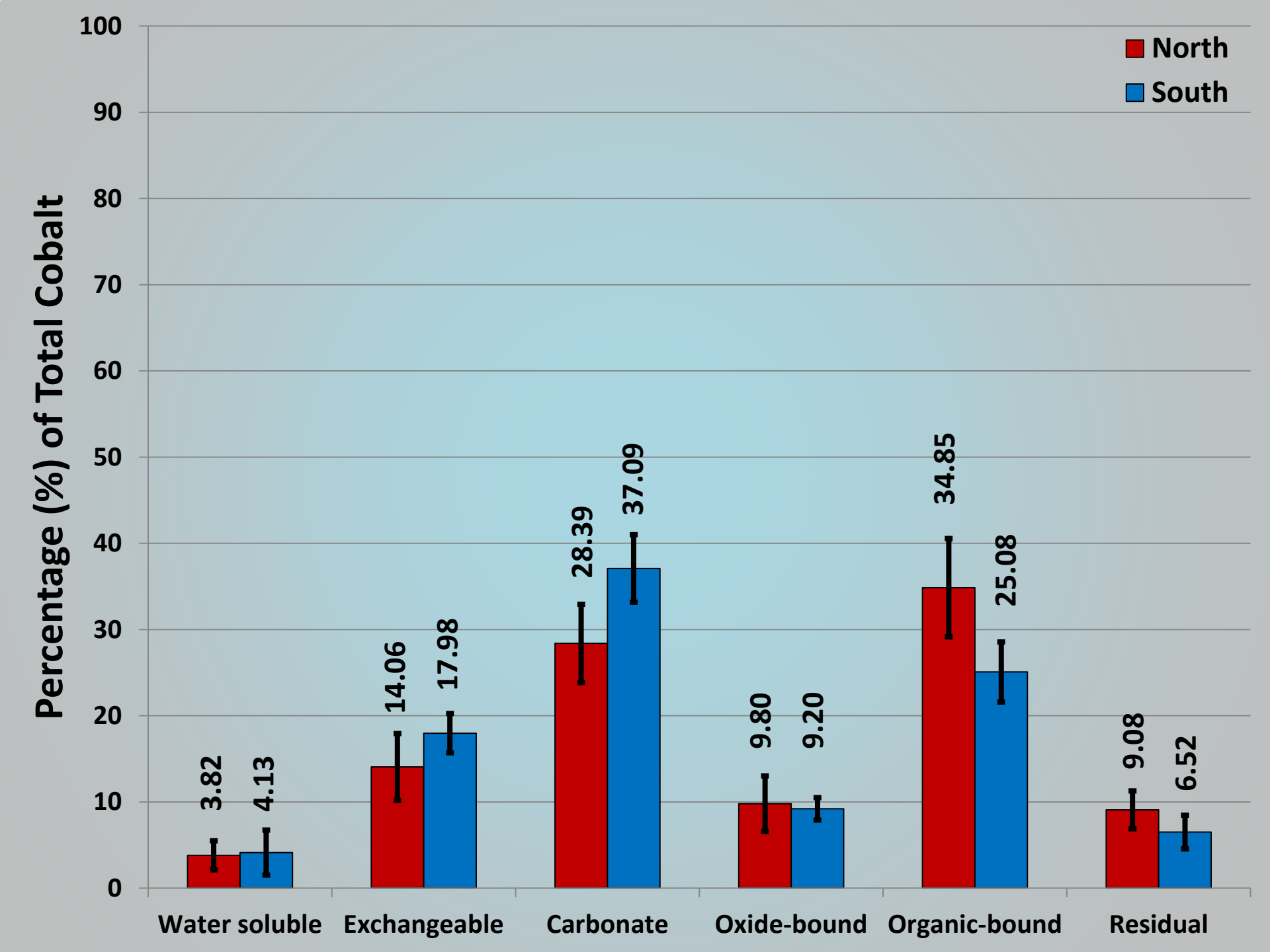

Zinc Concentration (mg/L)
8
7
6
5
4
3
2
1
0
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT

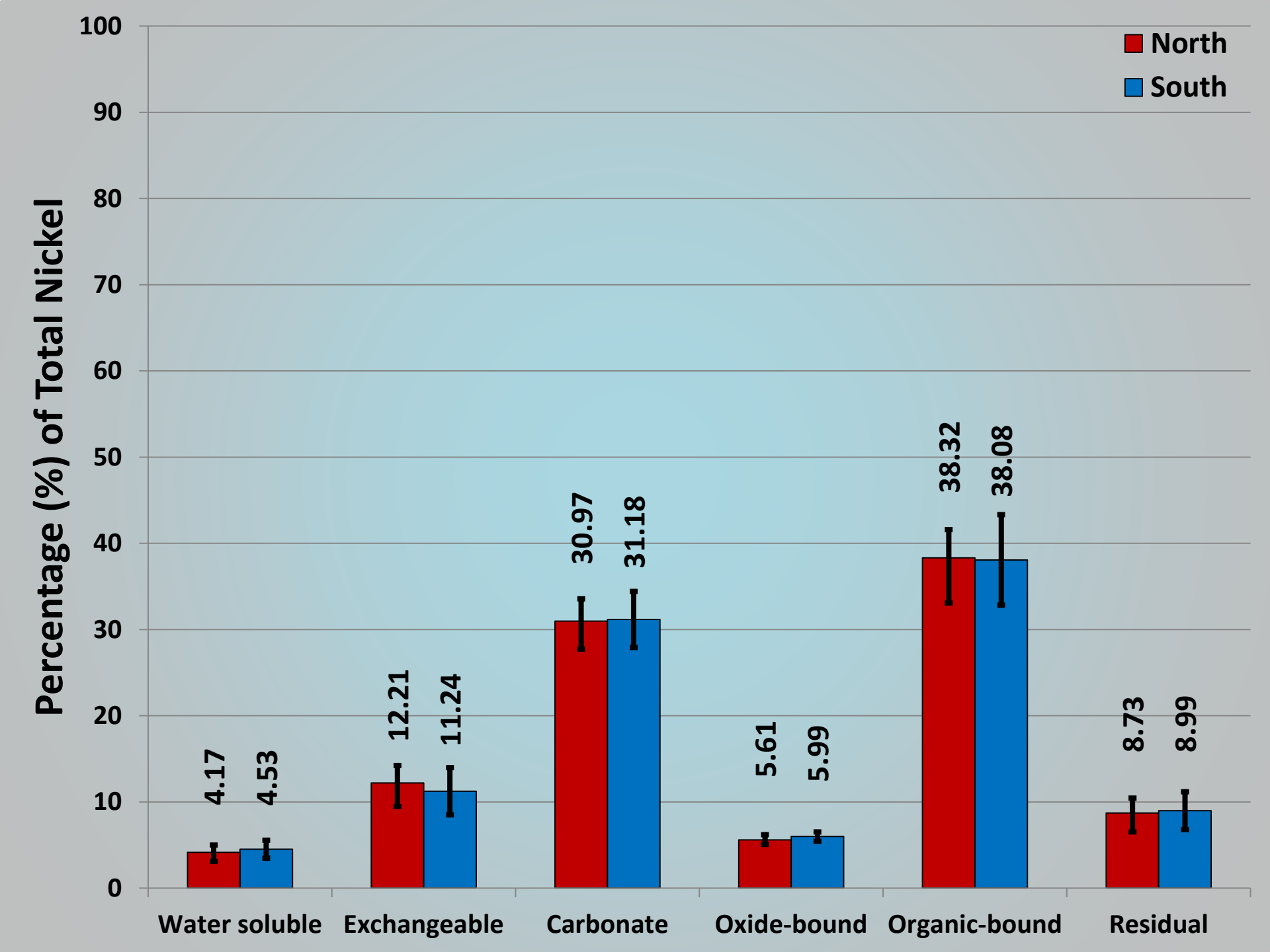

Zinc Concentration (mg/L)
Temperature (°C)
N IN
S IN
N OUT
S OUT
Temp
0
1
2
3
4
5
6
7
8
0
4
8
12
16
20
24
28
32
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10

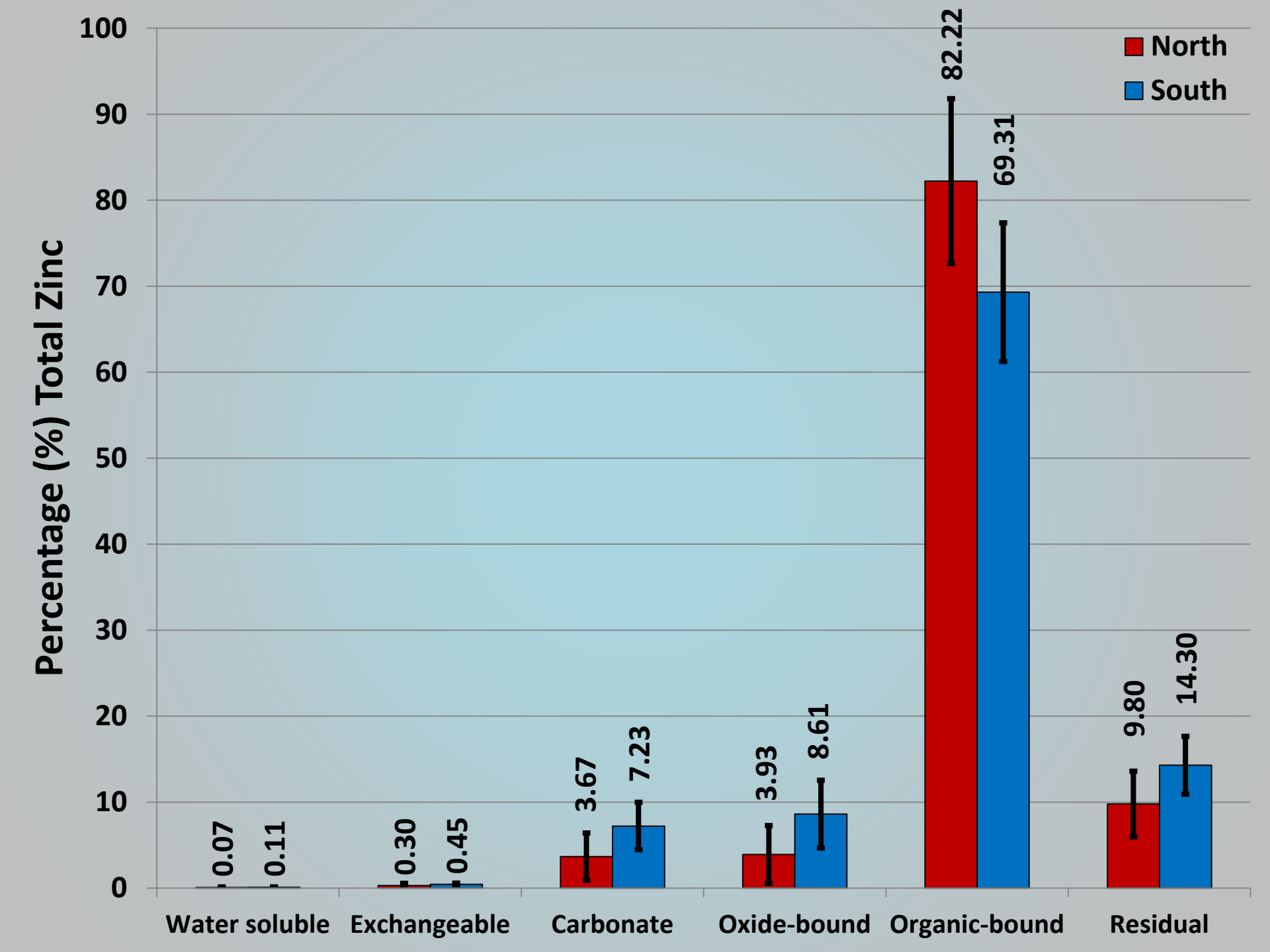

Zinc Concentration (mg/L)
Temperature (°C) and 1/10 ORP (mV)
8
7
6
5
4
3
2
1
0
32
23
14
5
-4
-13
-22
-31
-40
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT
Temp
ORP

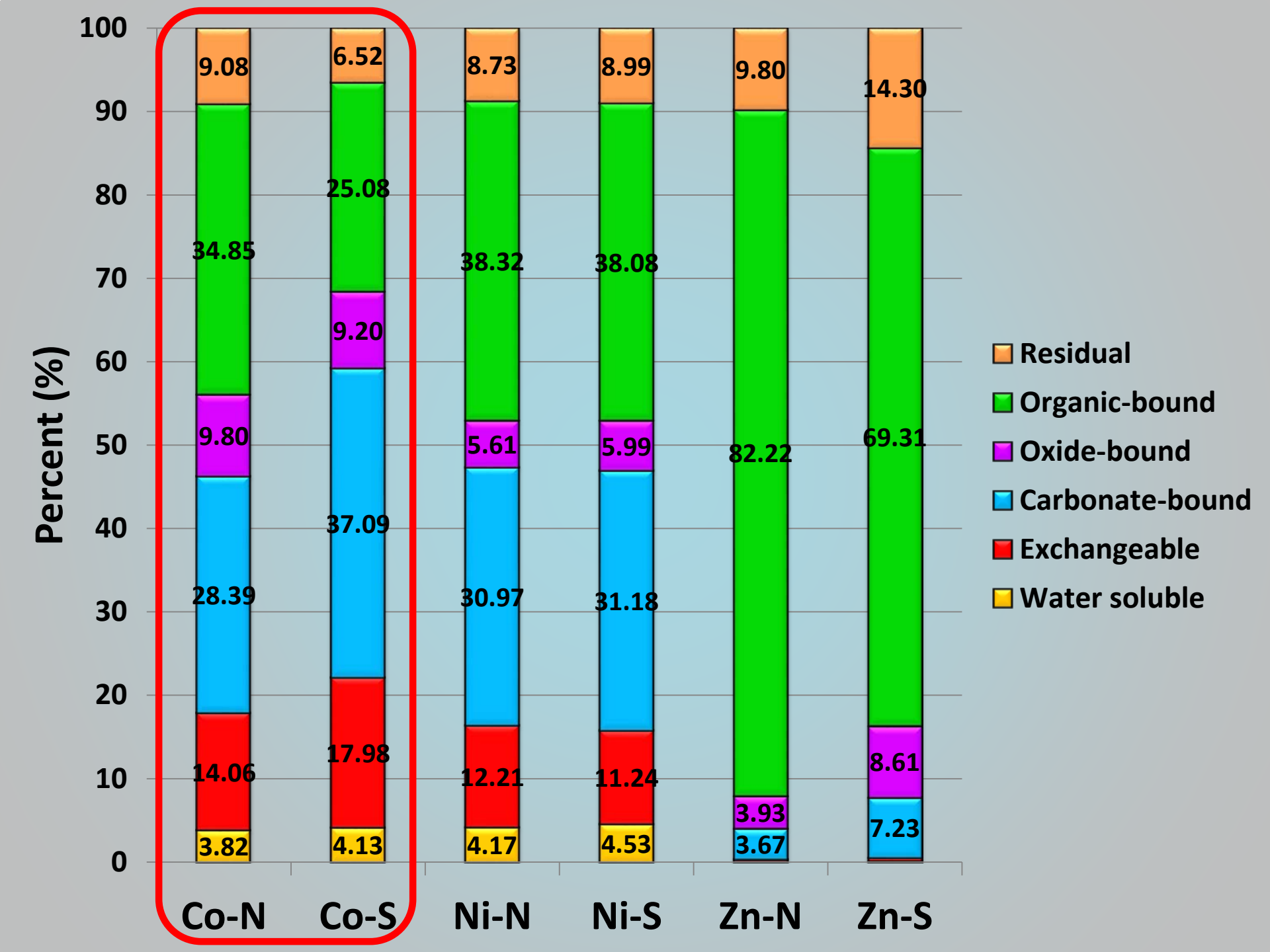
RESULTS – Sequential Extractions

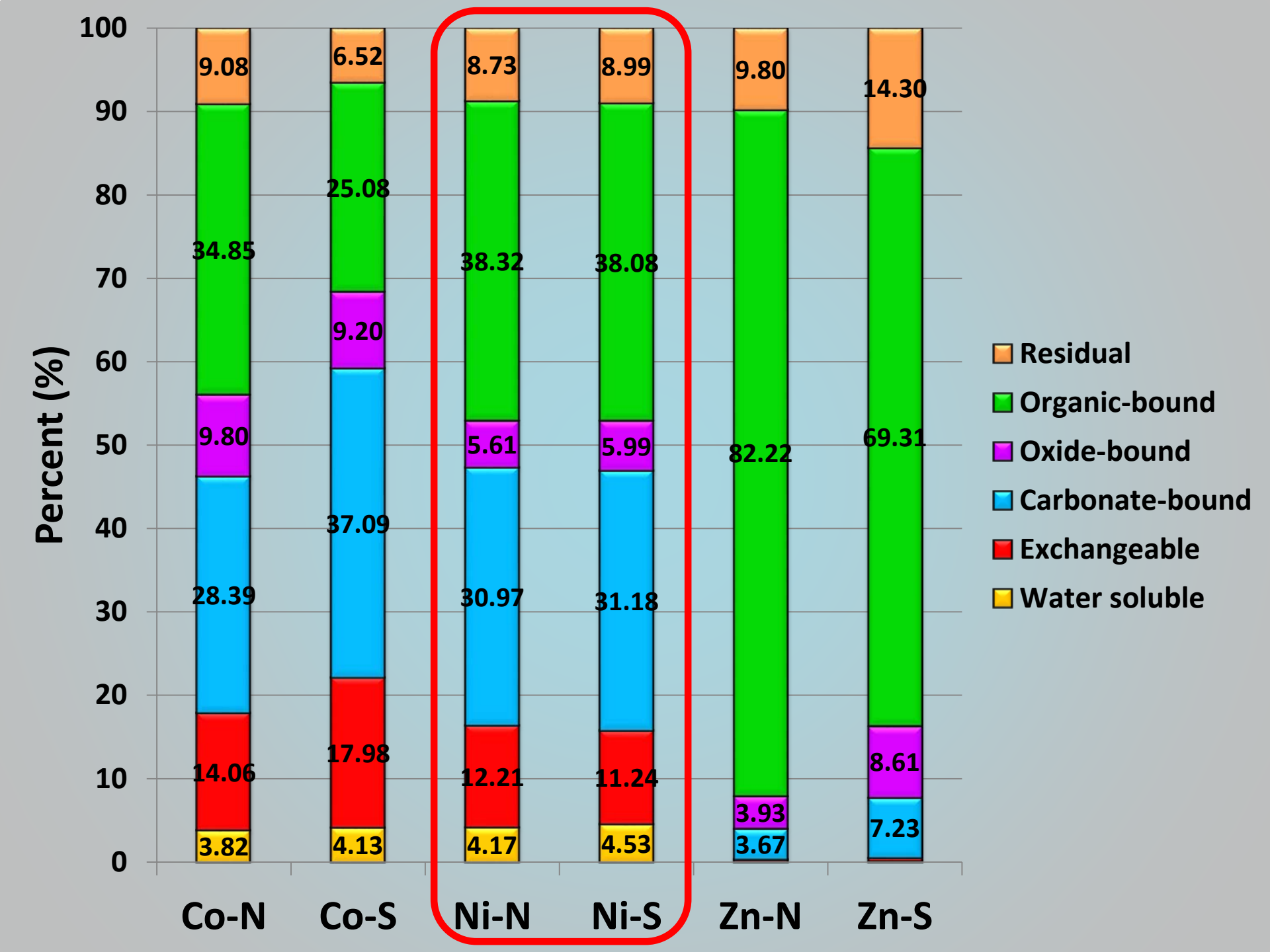
- Net increase: Cd, Co, Fe, Mn, Ni, Pb, Zn
- Net decrease: K, Na
- No significant change: Al, As, Ca, Cr, Cu, Mg
- Significant differences between north and south
  - Co – exchangeable, carbonate, organic, residual
  - Zn – carbonate, oxide, organic, residual


Percentage (%) of Total Cobalt
100
90
80
70
60
50
40
30
20
10
0
North
South
3.82
4.13
14.06
17.98
28.39
37.09
9.80
9.20
34.85
25.08
9.08
6.52
Water soluble
Exchangeable
Carbonate
Oxide-bound
Organic-bound
Residual


Percentage (%) of Total Nickel
100
90
80
70
60
50
40
30
20
10
0
North
South
4.17
4.53
12.21
11.24
30.97
31.18
5.61
5.99
38.32
38.08
8.73
8.99
Water soluble
Exchangeable
Carbonate
Oxide-bound
Organic-bound
Residual


Percentage (%) Total Zinc
100
90
80
70
60
50
40
30
20
10
0
North
South
0.07
0.11
0.30
0.45
3.67
7.23
3.93
8.61
82.22
69.31
9.80
14.30
Water soluble
Exchangeable
Carbonate
Oxide-bound
Organic-bound
Residual


Percent (%)
100
90
80
70
60
50
40
30
20
10
0
Co-N
Co-S
Ni-N
Ni-S
Zn-N
Zn-S
9.08
34.85
9.80
28.39
14.06
3.82
6.52
25.08
9.20
37.09
17.98
4.13
8.73
38.32
5.61
30.97
12.21
4.17
8.99
38.08
5.99
31.18
11.24
4.53
9.80
82.22
3.93
3.67
14.30
69.31
8.61
7.23
Residual
Organic-bound
Oxide-bound
Carbonate-bound
Exchangeable
Water soluble


Percent (%)
100
90
80
70
60
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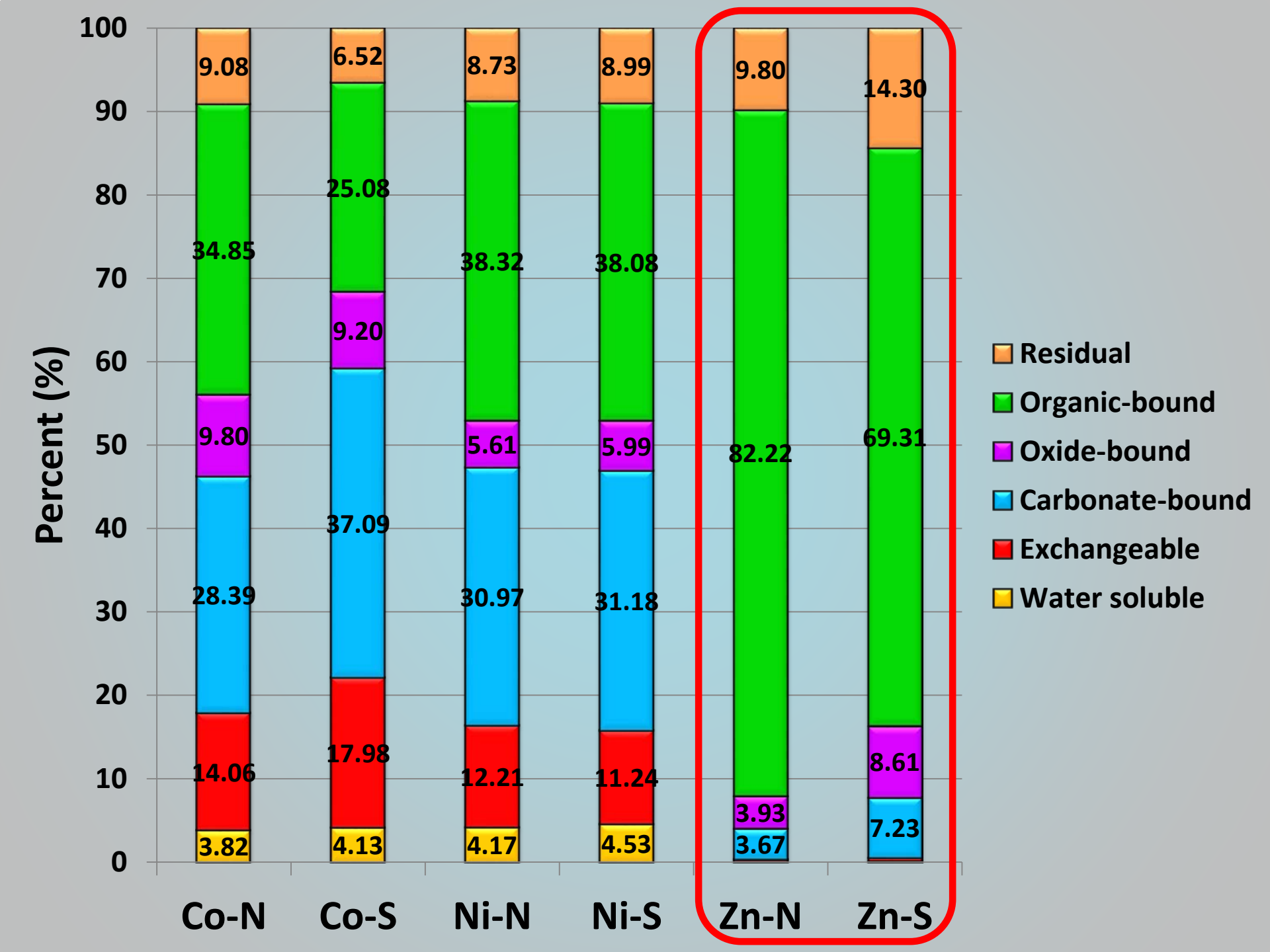
40
30
20
10
0
9.08
34.85
9.80
28.39
14.06
3.82
6.52
25.08
9.20
37.09
17.98
4.13
8.73
38.32
5.61
30.97
12.21
4.17
8.99
38.08
5.99
31.18
11.24
4.53
9.80
82.22
3.93
3.67
14.30
69.31
8.61
7.23
Co-N
Co-S
Ni-N
Ni-S
Zn-N
Zn-S
Residual
Organic-bound
Oxide-bound
Carbonate-bound
Exchangeable
Water soluble


Percent (%)
100
90
80
70
60
50
40
30
20
10
0
9.08
34.85
9.80
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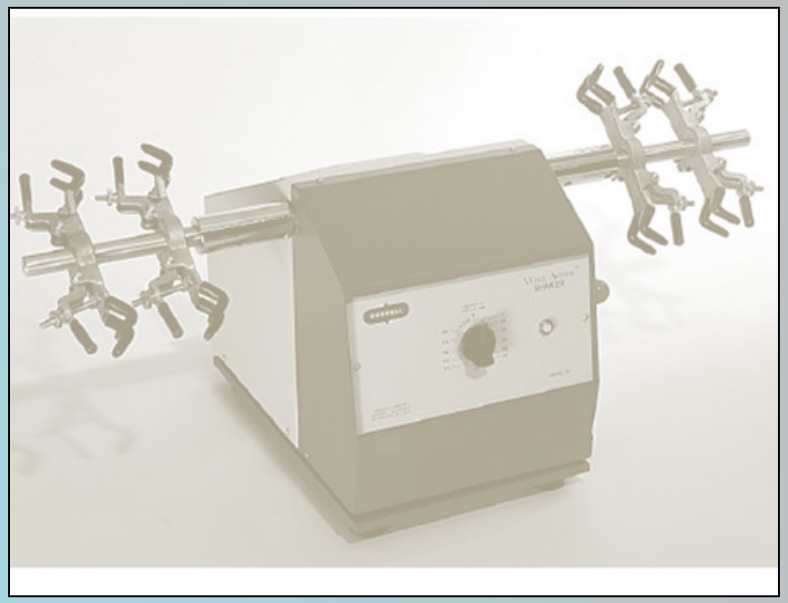
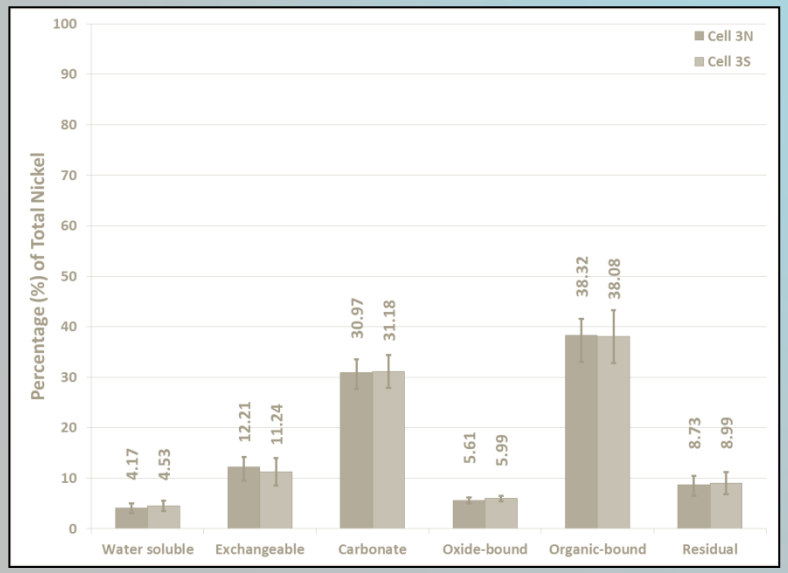
14.06
3.82
6.52
25.08
9.20
37.09
17.98
4.13
8.73
38.32
5.61
30.97
12.21
4.17
8.99
38.08
5.99
31.18
11.24
4.53
9.80
82.22
3.93
3.67
14.30
69.31
8.61
7.23
Co-N
Co-S
Ni-N
Ni-S
Zn-N
Zn-S
Residual
Organic-bound
Oxide-bound
Carbonate-bound
Exchangeable
Water soluble

INTRODUCTION

METHODS



RESULTS



CONCLUSIONS

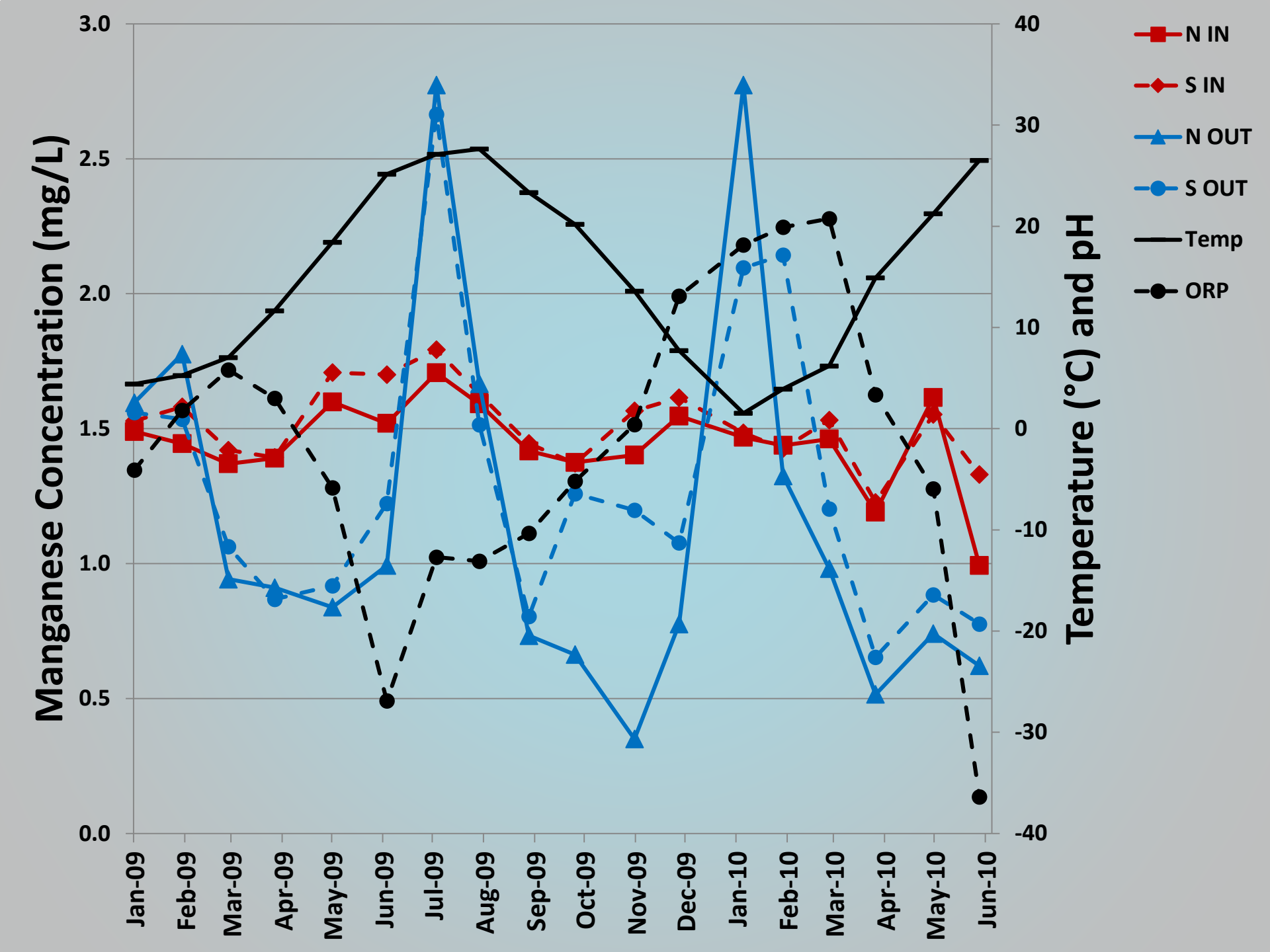
CONCLUSIONS

- Trace metals are being effectively removed
  - Seasonality indicated
- Large amounts of trace metals retained in organic-bound fraction
  - Co and Ni also high in carbonate fraction
  - Residual fraction not as large as anticipated
- Explore extraction options that include greater specificity, particularly for sulfides
- Potential mineralogical analyses
  - SEM/TEM show promise and are available

ACKNOWLEDGEMENTS

- USEPA Agreements FY04 104(b)(3) X7-97682001-0 and R-829423-01-0
- Private Landowners
- US Dept. of Education GAANN Program
- ASMR PhD Research Grant 2011
- ASMR Memorial Scholarship, PhD Level 2012

QUESTIONS?


Manganese Concentration (mg/L)
Temperature (°C) and pH
3.0
2.5
2.0
1.5
1.0
0.5
0.0
40
30
20
10
0
-10
-20
-30
-40
Jan-09
Feb-09
Mar-09
Apr-09
May-09
Jun-09
Jul-09
Aug-09
Sep-09
Oct-09
Nov-09
Dec-09
Jan-10
Feb-10
Mar-10
Apr-10
May-10
Jun-10
N IN
S IN
N OUT
S OUT
Temp
ORP