Evaluation of Denitrification as a Natural Attenuation Mechanism in a Nitrate-Contaminated Aquifer

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Outline

- Background information
- Investigation methodology and site characterization results
- Assessment of nutrient impact to groundwater and potential for denitrification

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Background information

- Turkey farming operation – area of interest for environmental investigation was solid manure storage area
- Animal manure is a potential source of nutrients (N, P, K), salts, and bacteria to groundwater
- Nitrate is a common contaminant in agricultural areas – human health risk in drinking water

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Background information

- Farm is located approx. 5 km NW of Devon, Alberta (25 km SW of Edmonton)

- Area is dominated by bedrock low, which is associated with a network of buried valleys

- Up to 50 m of drift underlies site
  * dune sand and occasional peat near surface
  * more silt and sandy silt with depth
  * coarse sand associated with buried valleys

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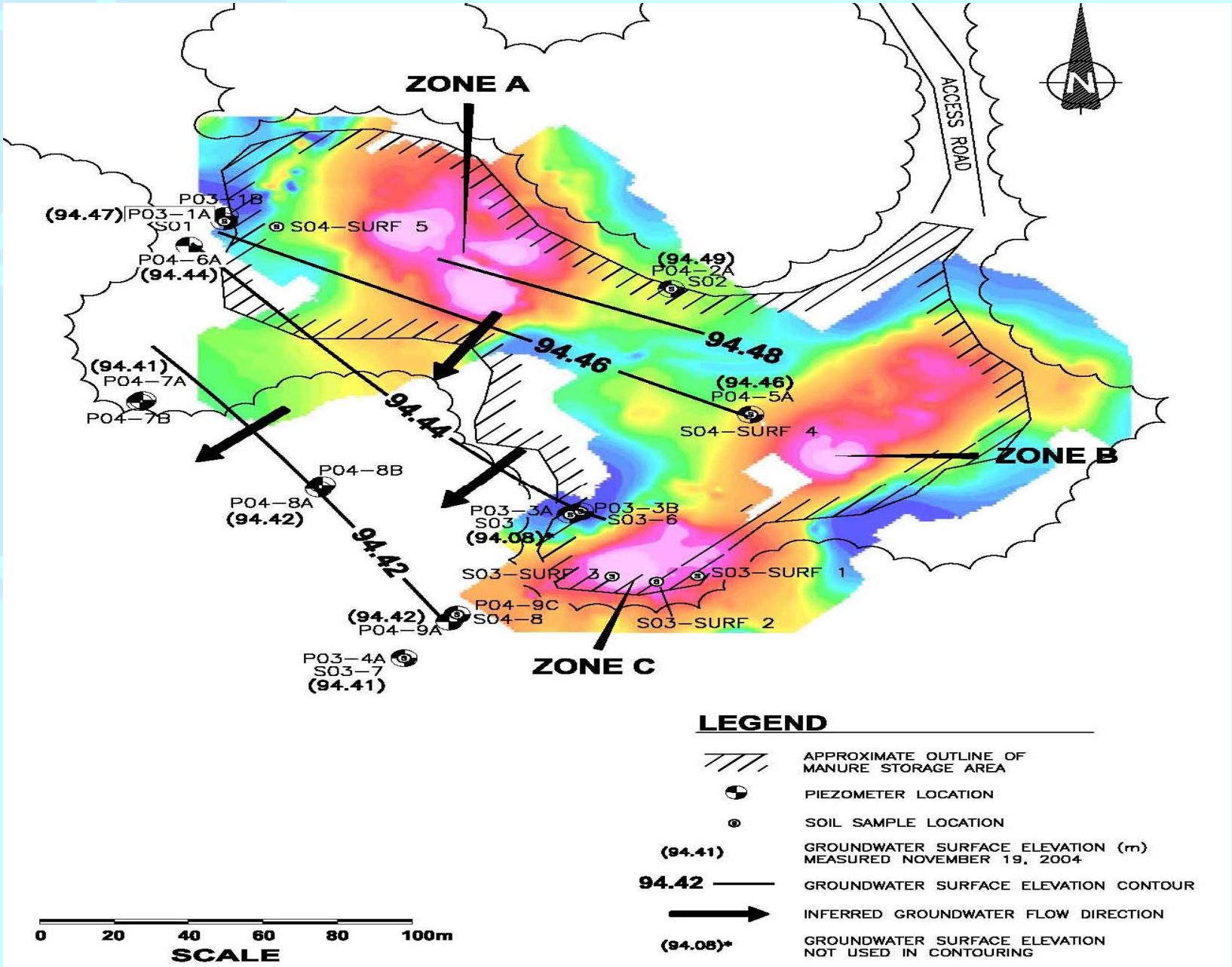
ZONE A
ACCESS ROAD
N
P03–1B
(94.47) P03–1A
S01
S04–SURF 5
P04–6A
(94.44)
(94.49)
P04–2A
S02
94.48
94.46
94.44
(94.41)
P04–7A
P04–7B
(94.46)
P04–5A
S04–SURF 4
ZONE B
P04–8B
P04–8A
(94.42)
P03–3A
P03–3B
S03
S03–6
(94.08)*
94.42
S03–SURF 3
S03–SURF 1
P04–9C
(94.42)
S04–8
P04–9A
S03–SURF 2
P03–4A
S03–7
(94.41)
ZONE C
LEGEND
APPROXIMATE OUTLINE OF MANURE STORAGE AREA
PIEZOMETER LOCATION
SOIL SAMPLE LOCATION
(94.41) GROUNDWATER SURFACE ELEVATION (m) MEASURED NOVEMBER 19, 2004
94.42 GROUNDWATER SURFACE ELEVATION CONTOUR
INFERRED GROUNDWATER FLOW DIRECTION
(94.08)* GROUNDWATER SURFACE ELEVATION NOT USED IN CONTOURING
0 20 40 60 80 100m
SCALE

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Potential receptors

- Approximately 70 water wells identified within a 2-km radius of the site
- About 20% of these are completed at a depth of 15 m bgs or less
- Regional hydrogeological study identified area of site as being at “very high risk” to groundwater contamination

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Soil characterization results

- Surficial soils (<1 m bgs) generally characterized with elevated EC, salt (Na,Cl), and select available nutrient concentrations
  - * NO_3, K, SO_4, sometimes P

- Composite samples from the ground surface had even higher concentrations and significant NH_4

- Vertical profile at one location (S03-6) showed that nutrient concentrations and salinity parameters decreased with depth in the surficial sand

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Groundwater characterization results

- Stratigraphic profile
  - Sand from ground surface to 6 to 15 m bgs
  - Silty clay/clay confining unit to 20 m bgs
  - Coarse sand and gravel in buried valley to max depth (27 m bgs)

- Groundwater flow up to 20 m/year, vertical gradients indicate downward components of groundwater flow

- Initial results showed that nitrate-impacted shallow groundwater appeared to be limited to directly beneath manure storage area

- Geochemical conditions may be favourable for denitrification

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Assessment of nutrient impact to groundwater

- Elevated concentrations of indicator parameters known to be present in manure, beneath and extending away from source areas
  - K, Cl, NH_4, NO_3, DKN, DOC

- Indirect indicators: elevated EC, TDS, select major ions (*e.g.*, sulphate) altered from natural conditions

- Of indicators, Cl and NO_3 are most soluble and mobile in groundwater – use their distributions to delineate the nutrient impact to groundwater

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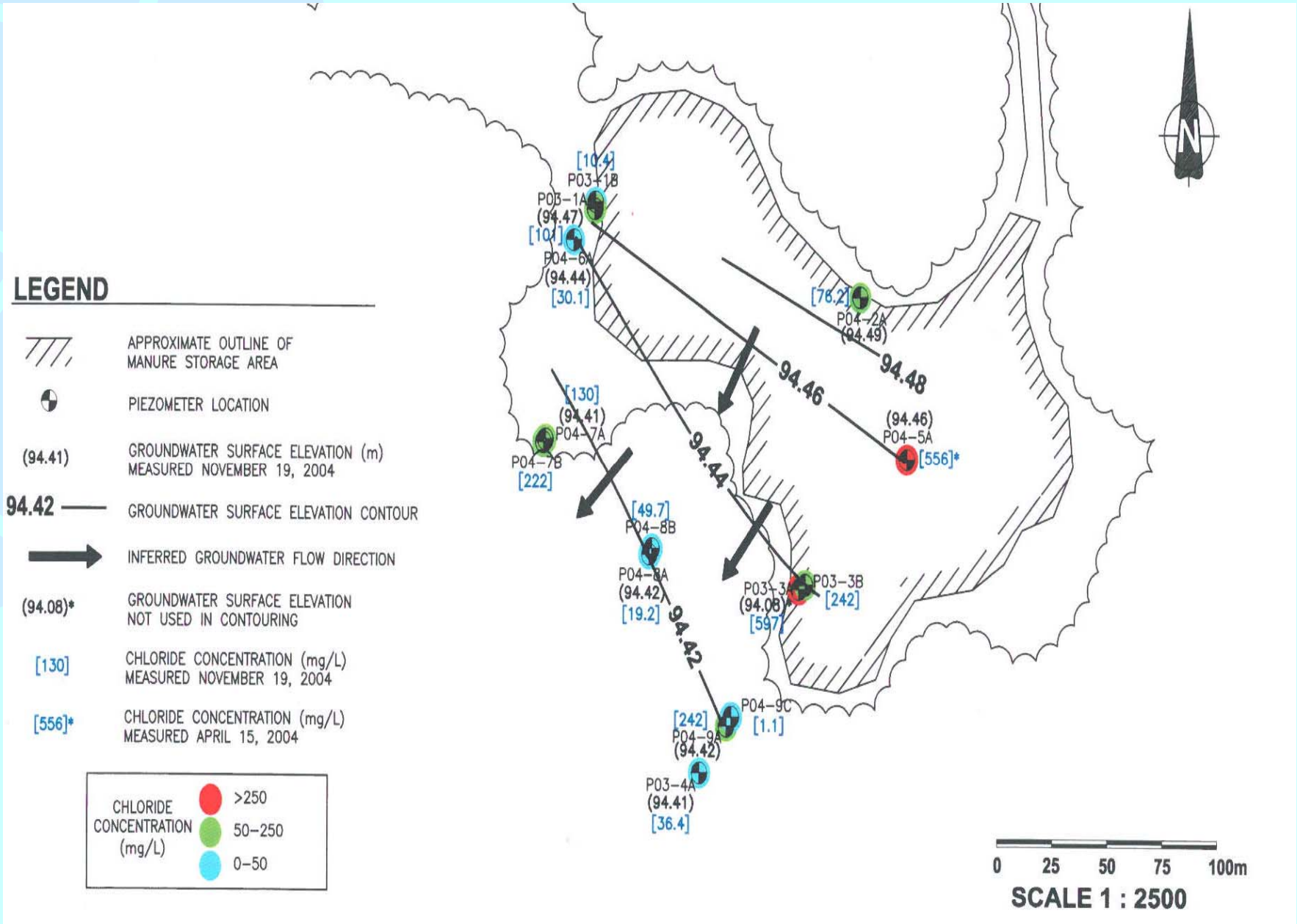
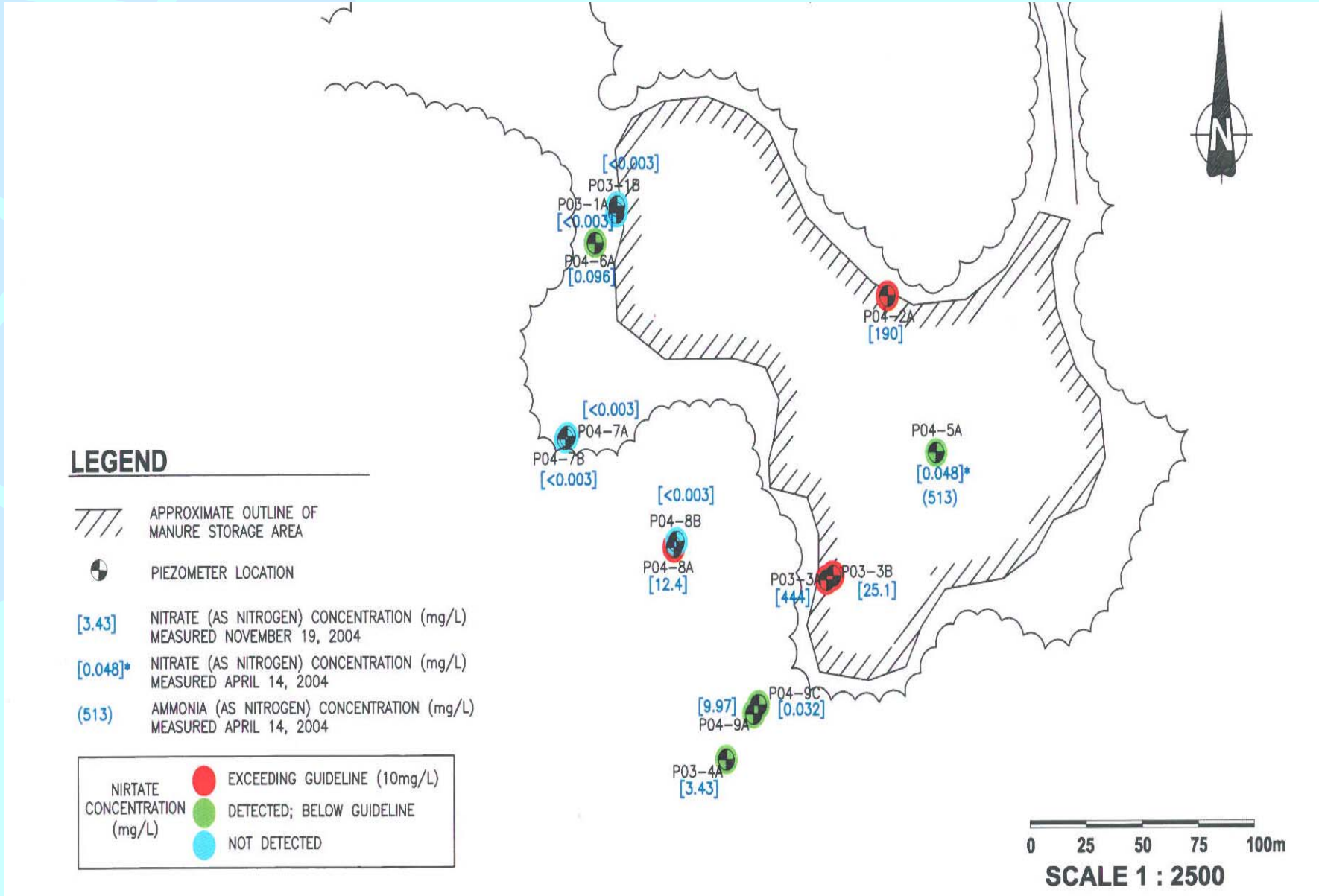

LEGEND
APPROXIMATE OUTLINE OF MANURE STORAGE AREA
PIEZOMETER LOCATION
(94.41) GROUNDWATER SURFACE ELEVATION (m) MEASURED NOVEMBER 19, 2004
94.42 GROUNDWATER SURFACE ELEVATION CONTOUR
INFERRED GROUNDWATER FLOW DIRECTION
(94.08)* GROUNDWATER SURFACE ELEVATION NOT USED IN CONTOURING
[130] CHLORIDE CONCENTRATION (mg/L) MEASURED NOVEMBER 19, 2004
[556]* CHLORIDE CONCENTRATION (mg/L) MEASURED APRIL 15, 2004
CHLORIDE CONCENTRATION (mg/L)
>250
50–250
0–50
[10.4]
P03-1B
P03-1A
(94.47)
[10.1]
P04-6A
(94.44)
[30.1]
[76.2]
P04-2A
(94.49)
94.48
94.46
(94.46)
P04-5A
[556]*
[130]
(94.41)
P04-7A
P04-7B
[222]
94.44
[49.7]
P04-8B
P04-8A
(94.42)
[19.2]
P03-3A
(94.08)*
[597]
P03-3B
[242]
94.42
[242]
P04-9A
(94.42)
P04-9C
[1.1]
P03-4A
(94.41)
[36.4]
N
0 25 50 75 100m
SCALE 1 : 2500

KOMEX


[<0.003]
P03-1B
P03-1A
[<0.003]
P04-6A
[0.096]
P04-2A
[190]
[<0.003]
P04-7A
P04-7B
[<0.003]
P04-5A
[0.048]*
(513)
[<0.003]
P04-8B
P04-8A
[12.4]
P03-3A
[444]
P03-3B
[25.1]
[9.97]
P04-9A
P04-9C
[0.032]
P03-4A
[3.43]
N
LEGEND
APPROXIMATE OUTLINE OF MANURE STORAGE AREA
PIEZOMETER LOCATION
[3.43] NITRATE (AS NITROGEN) CONCENTRATION (mg/L) MEASURED NOVEMBER 19, 2004
[0.048]* NITRATE (AS NITROGEN) CONCENTRATION (mg/L) MEASURED APRIL 14, 2004
(513) AMMONIA (AS NITROGEN) CONCENTRATION (mg/L) MEASURED APRIL 14, 2004
NIRTATE CONCENTRATION (mg/L)
EXCEEDING GUIDELINE (10mg/L)
DETECTED; BELOW GUIDELINE
NOT DETECTED
0 25 50 75 100m
SCALE 1 : 2500

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Potential for denitrification

- Overall goal of program is to monitor reduction of nitrate concentrations with distance from source areas
  - * Biodegradation, dilution, dispersion, abiotic transformations could all contribute to decreasing nitrate concentrations

- Denitrification = natural attenuation!

$$5CH_2O + 4NO_3^- \rightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^-$$

converts nitrate to an innocuous product and removes nitrogen from the system, improving water quality

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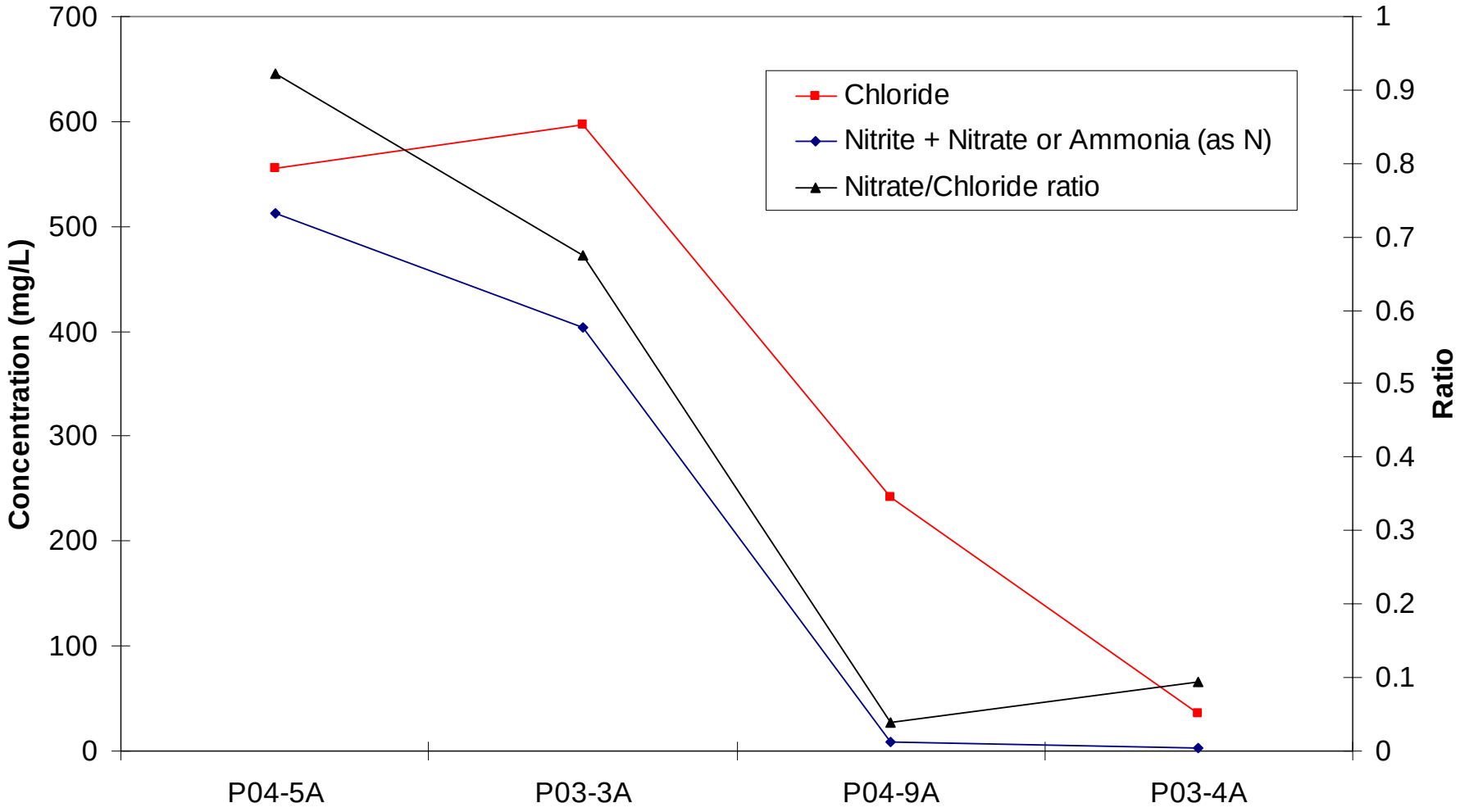
700
600
500
400
300
200
100
0
Concentration (mg/L)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Ratio
Chloride
Nitrite + Nitrate or Ammonia (as N)
Nitrate/Chloride ratio
P04-5A
P03-3A
P04-9A
P03-4A

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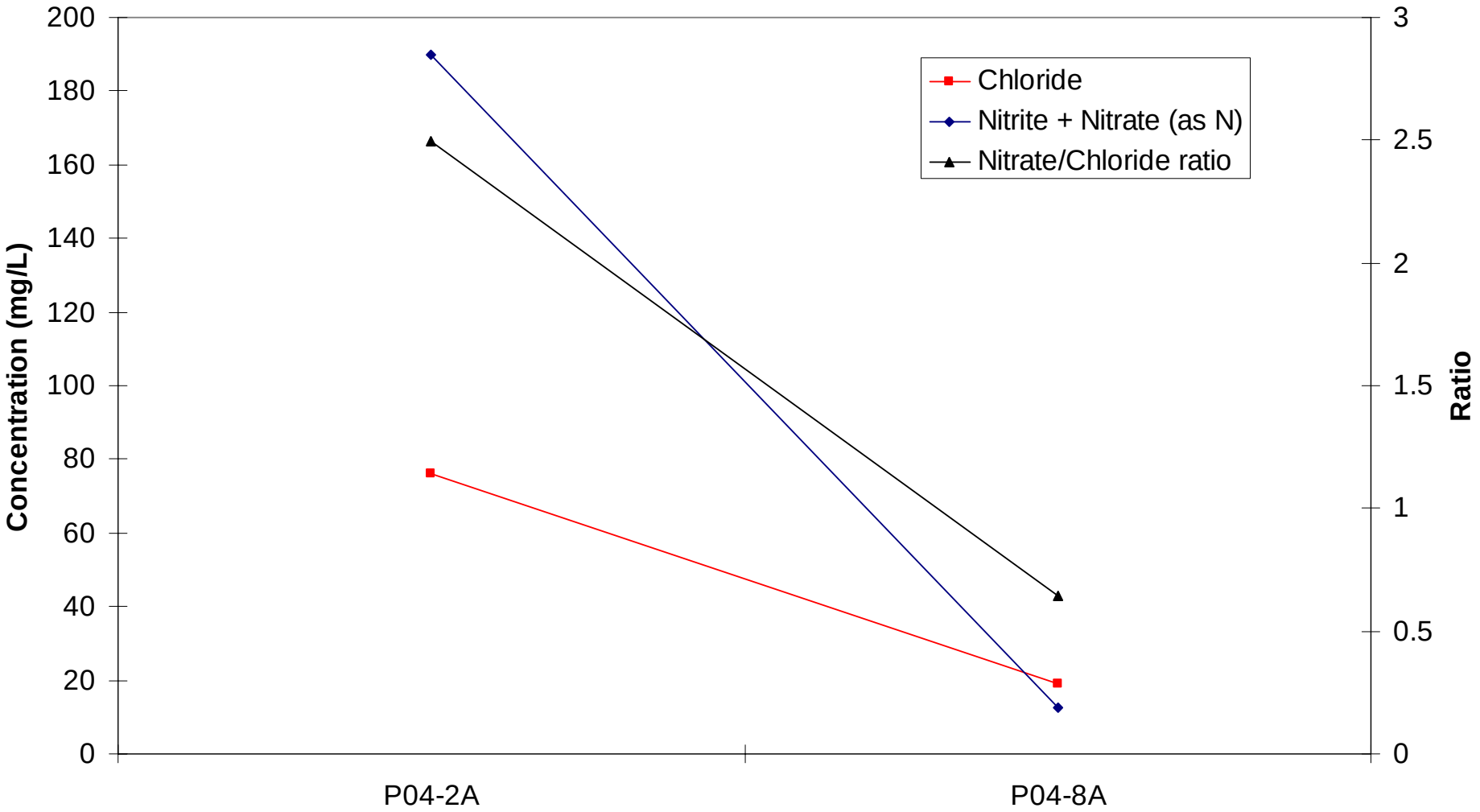
Concentration (mg/L)
Ratio
200
180
160
140
120
100
80
60
40
20
0
3
2.5
2
1.5
1
0.5
0
P04-2A
P04-8A
Chloride
Nitrite + Nitrate (as N)
Nitrate/Chloride ratio

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Conditions necessary for denitrification

1. A source of nitrate
2. Denitrifying bacteria
3. A source of labile organic carbon
4. Anaerobic, reducing conditions in the aquifer

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Unsaturated zone processes

Nitrification of "effluent" NH_4^+

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

Consumption of "effluent" DOC

$$CH_2O + O_2 \rightarrow CO_2 + H_2O$$

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+$$

Results: production of nitrate, consumption of oxygen, acidification, production of bicarbonate

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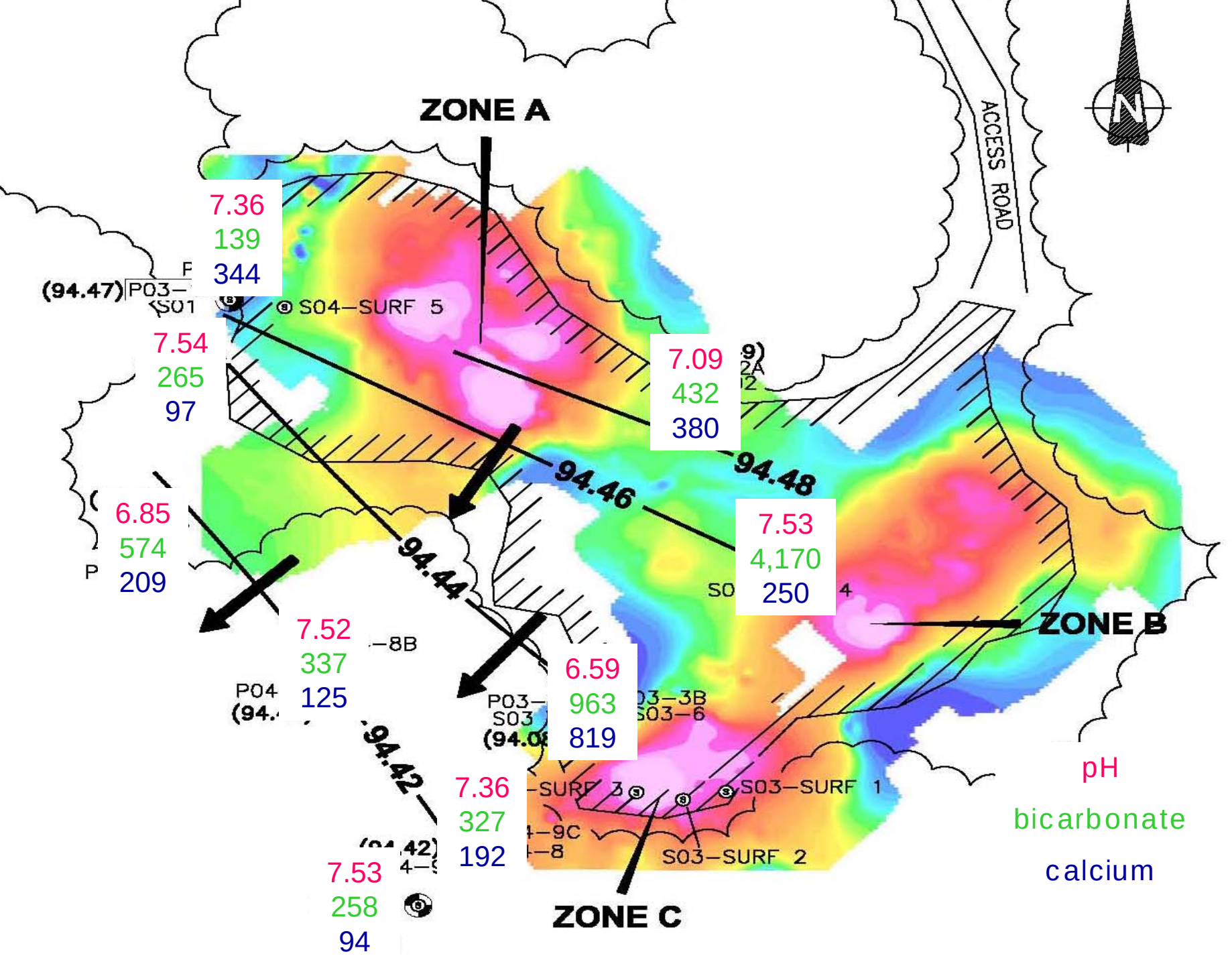
ZONE A
ACCESS ROAD
N
7.36
139
344
7.54
265
97
7.09
432
380
94.46
94.48
6.85
574
209
7.53
4,170
250
94.44
ZONE B
7.52
337
125
6.59
963
819
94.42
7.36
327
192
7.53
258
94
ZONE C
pH
bicarbonate
calcium

Labile organic carbon

- Dissolved organic carbon (DOC) concentrations range from approximately 10 to 830 mg/L

- Turkey manure typically has a low TOC:TN ratio
  * Organic carbon readily breaks down, rapid rate of mineralization = labile
  * Litter/bedding may also be source, but typically has a higher TOC:TN ratio

- Aquifer is also likely a source of DOC
  * TOC was 0.2 to 2.5 wt.% of solid phase samples obtained

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Anaerobic, reducing conditions

- Well defined sequence of redox reactions in organic-matter containing aqueous systems
- We have seen that bacterial respiration of organic matter removes oxygen from the system, therefore lowering the redox potential
- Do field-based measurements of DO and redox potential corroborate other evidence for denitrification?

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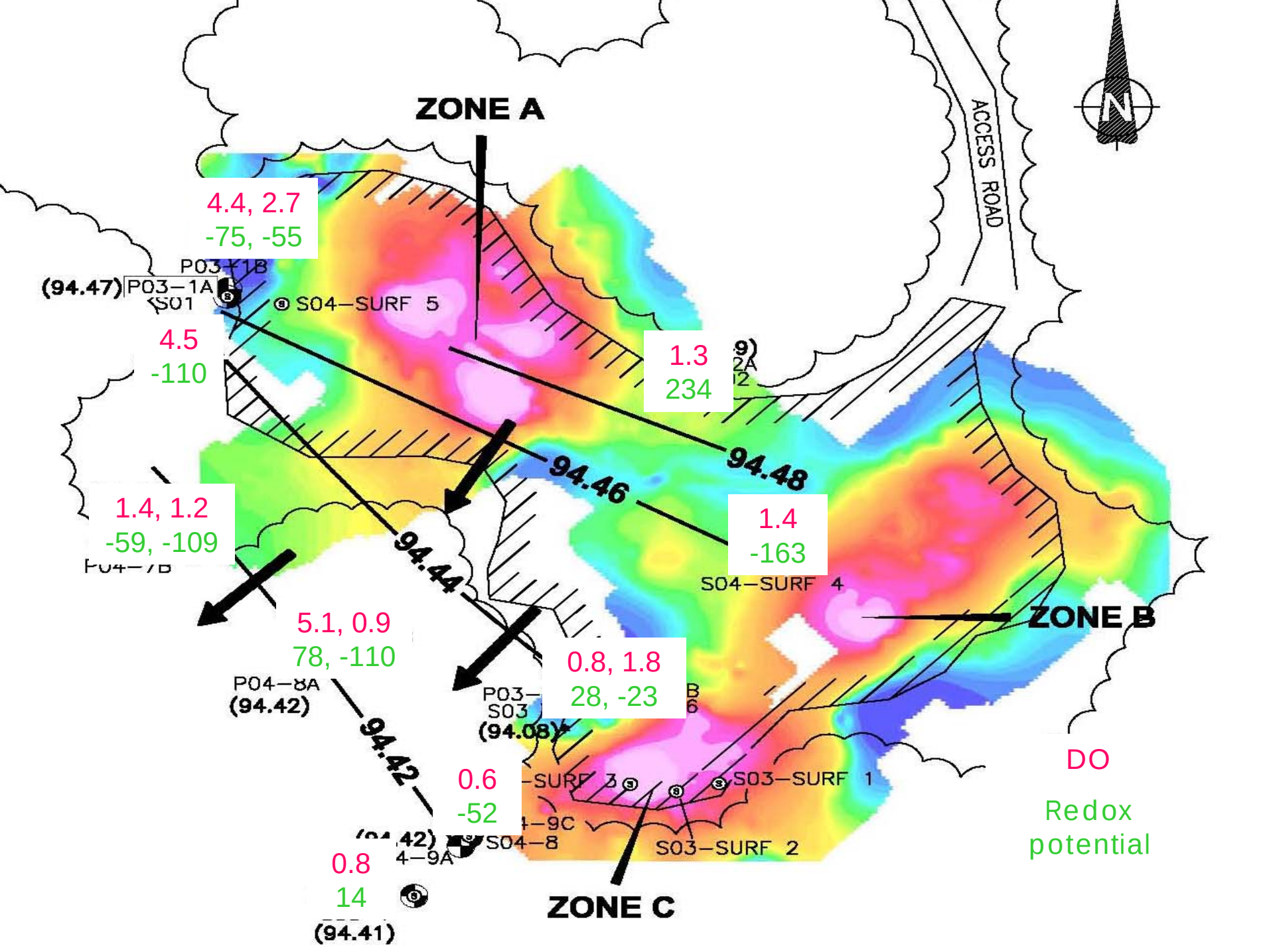
ZONE A
ACCESS ROAD
N
4.4, 2.7
-75, -55
(94.47)
P03–1A
S01
S04–SURF 5
4.5
-110
1.3
234
94.46
94.48
1.4, 1.2
-59, -109
94.44
1.4
-163
S04–SURF 4
ZONE B
5.1, 0.9
78, -110
P04–8A
(94.42)
0.8, 1.8
28, -23
P03–
S03
(94.08)
94.42
0.6
-52
S03–SURF 1
S03–SURF 2
S04–8
0.8
14
(94.41)
ZONE C
DO
Redox
potential

Summary

- Denitrification is occurring at the site
  * High source area nitrate concentrations decrease in downgradient direction, not conservative relative to chloride
  * No apparent stratigraphic barrier to vertical nutrient migration in upper sand → geochemical conditions responsible for nitrate reduction with depth
  * Geochemical conditions necessary for denitrification were demonstrated at the site
    - Source of nitrate, labile organic carbon, anaerobic, reducing conditions

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Summary

- Surficial soil samples taken after source removal indicated that remaining soils continue to be a source of elevated nutrient concentrations

- Continue to monitor and assess potential for denitrification as an effective remedial option, ensure that above guideline nitrate concentrations not migrating off-site

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