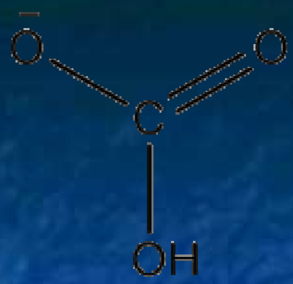
Montana Department of ENVIRONMENTAL QUALITY

Sodium Bicarbonate and Coal Bed Methane Production: Standards Development

Bicarbonate interaction with competitive or associative displacement ions and their combined effects on metals toxicity



Carbonic acid = H_2CO_3

Bicarbonate = HCO_3^{-}

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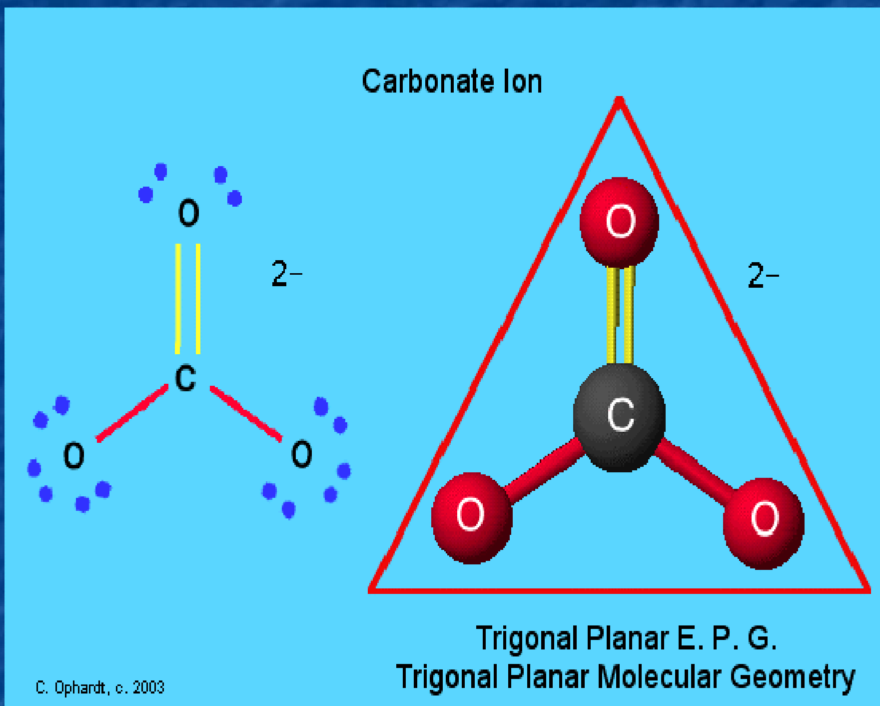
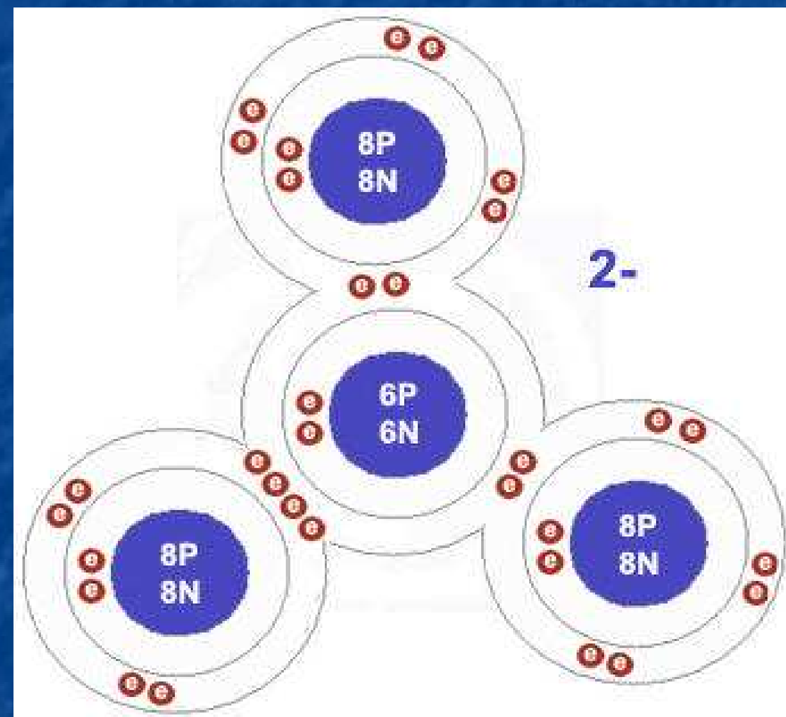
Carbonate = CO_3^{2-}

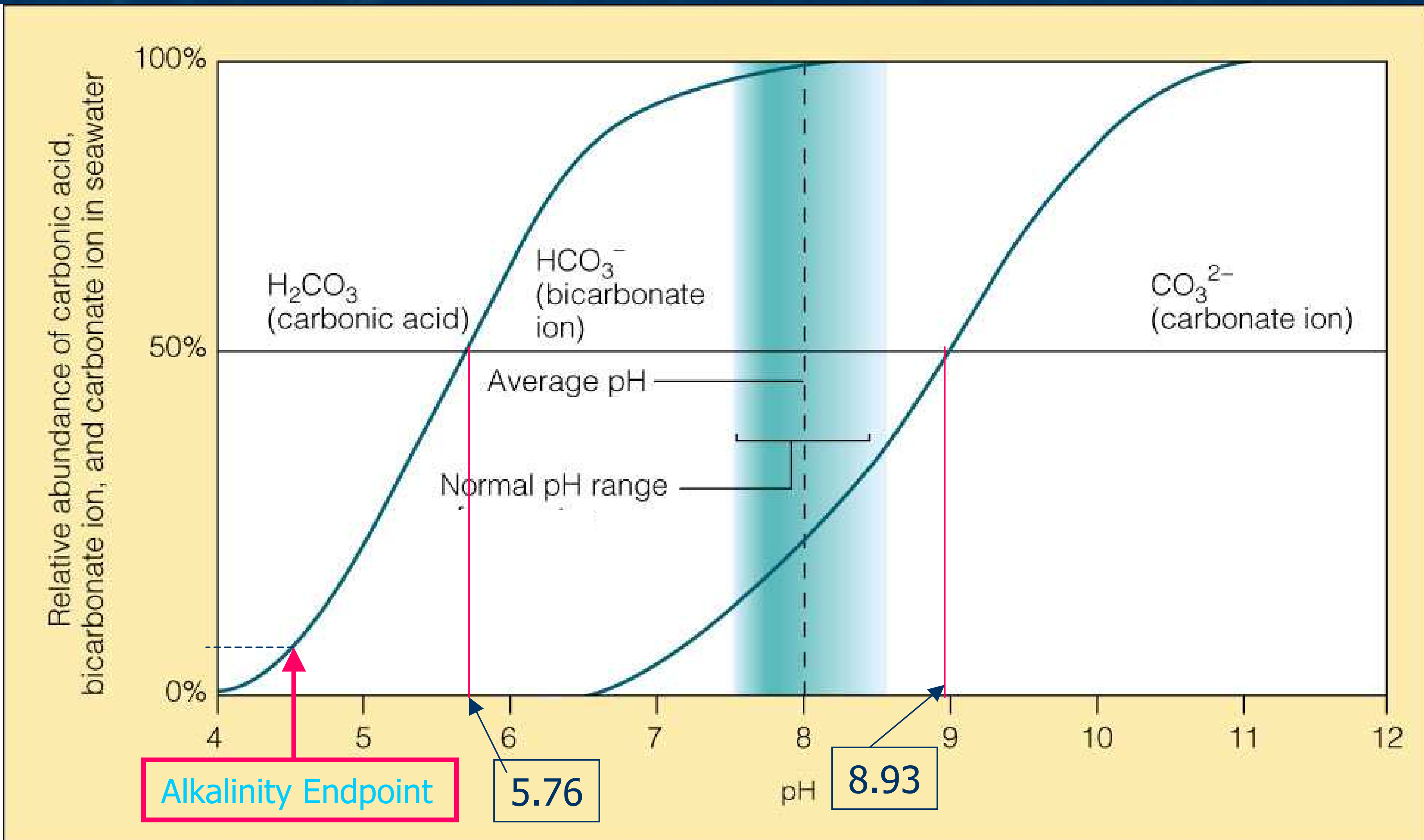
$$H_2CO_3 + 2\,H_2O \leftrightharpoons HCO_3^{-} + H_3O^{+} + H_2O$$





Bicarbonates are critical as the buffer system/pH control of all aquatic organisms, with the exception of the chemolithotrophs

Relative Proportions of Carbonate Ions are Related to pH

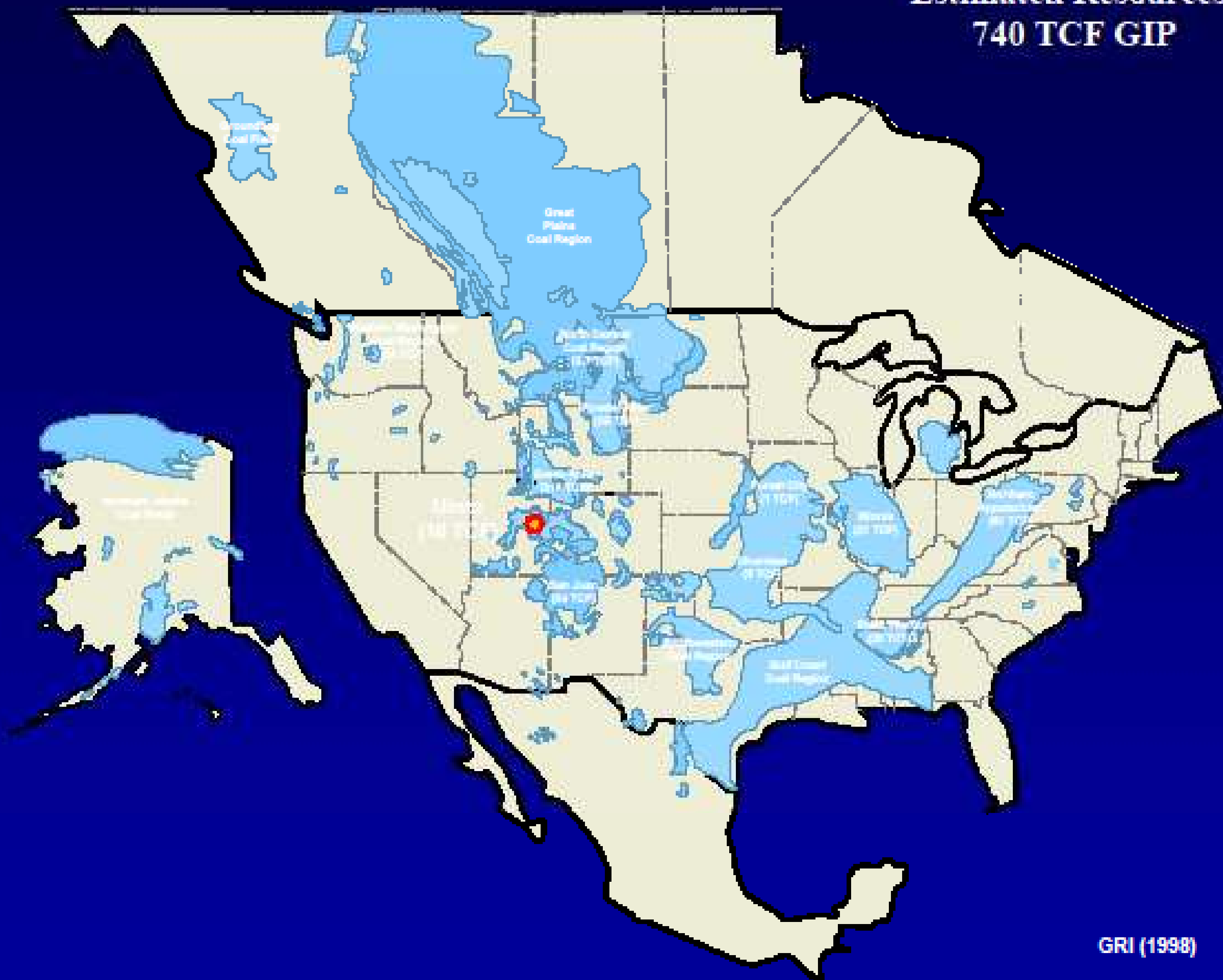


Where does bicarbonate originate from?

- Geochemical dissolution from sedimentary deposits
- Biochemical photosynthetic daily production from all plants
- BICARBONATE IS IMPORTANT IN MONTANA TODAY, DUE TO THE LARGE LEVELS OF SODIUM BICARBONATE DISCHARGED WITH COAL BED NATURAL GAS INDUSTRY DEVELOPMENT

North American Coalbed Methane Potential

Estimated Resources:
740 TCF GIP



GRI (1998)

Coal Bed Methane (CBM or CBNG) development is occurring in Tongue, Powder & Rosebud watersheds in SE Montana

Comparison of Water Chemistries

USGS report 2007-5146, mg/L

Water body	Tongue	Powder	CBNG
Ca^{+2}	56 (44%)	125	54 (5.5%)
Mg^{+2}	37	58	32 (3.3%)
K^{+}	2.8	7.5	8.6 (1%)
Na^{+}	32	225 (54%)	880 (90%)
Cl^{-}	4.2	94	54 (2.4%)
F^{-}	0.28	0.45	NA
$SO_4^{=}$	130	690 (77%)	12.4 (0.6%)
HCO_3^{-}	210 (61%)	190	2186 (97%)
TDS	470	1350	3277

Trace metal comparisons between drainages and CBNG inputs, ug/L

	Tongue River	Tongue CBM	Powder River	Powder CBM
Zn	3.8	54.0	73	80.0
Al	1.32	181.7	120	18.5
Cr	4.1	8.3	14	9.0
Pb	0.14	0.2	17	0.2
Cu	22.4	110.0	19	208.0
As	0.5	0.2	5	0.2
Ni	1.84	21.4	21	35.0
Ba	64	27.1	156	141.3
B	44	108.7	54.6	390.0

Scale of the Water load related to CBNG

- Average well produces 4.5 GPM, 365 days a year or 2.36 million gallons/year/well
- There are 27,280+ wells in Wyoming and almost 1500 in Montana
- = approx. 59 trillion gallons/year
- What are the effects of this discharge and its inorganic contents on drinking water supplies, crops, aquatic life and livestock in the area?

Scale of the Chemistry load from CBNG

- Potential to add 168,000 tons of bicarbonate per year to the surface and ground waters of an arid region (10-14 inches of rain/year) only 107x130 miles in size. This represents a 38% increase in TDS to the drainages and a potential 240% increase in annual bicarbonate loading.
- The sodium counter-ion to the bicarbonate can shift sodicity (decreasing soil permeability) and induce direct toxic effects in aquatic life.
- Above about 400+ mg/L, sodium bicarbonate has direct chronic toxic effects of its own.

Interrelationship between bicarbonate concentration and pH

- At any pH between 5.76 and 8.93, bicarbonate is partially disassociated, placing at least half of its counter ion in solution. This can be any electropositive ionic species with a valency state of one or two. The disassociation series is as follows: (Li, Na, K, Be, Mg, Ca, Sr, Ba).
- The concentration of all anions in solution affects alkalinity (includes bicarbonates, carbonates, sulfates, borates, hydroxides, silicates and phosphates)

Carbonate Water Chemistry = Dissolved Ions

- Anions
  - CO_3^{-2} and HCO_3^- (21-61%
  - SO_4^{-2} (38-69%) dominant in the Powder River
  - Cl^- (1.2-10.2%)
- Cations
  - Ca^{+2} (30-44%)
  - Mg^{+2} (14-29%)
  - Ba^{+2} (0.5-2%)
  - Na^+ (25-54%)
  - K^+ (1.8-2.2%)
- Alkalinity
  - $[CO_3^{-2}] + [HCO_3^-] + [SiO_3^{-2}] + [PO_4^{-2}] + [OH^-] + [BO_3^{-2}] + [SO_4^{-2}]$
  - Acid buffering capacity for all electronegative anionic species
- TDS
  - $[CO_3^{-2}] + [SO_4^{-2}] + [HCO_3^-]\ [Ca^{+2}] + [Mg^{+2}] + [Na^+] + [K^+] + [X^+] + [X^{+2}] + [A^-] + [A^{-2}]$
  - The sum weight of all non-volatile species in a known volume of solution
- Hardness
  - $[Ca^{+2}] + [Mg^{+2}]$
  - Used in metals (Zn, Pb, Cd, Cu, Cr, Ni, Ag) relative concentration corrections

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USGS report 2007-5146

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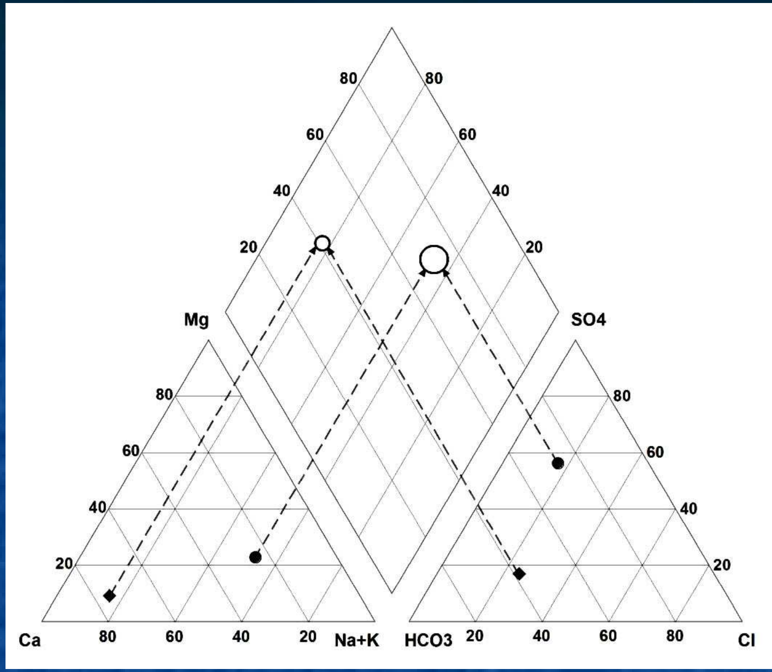
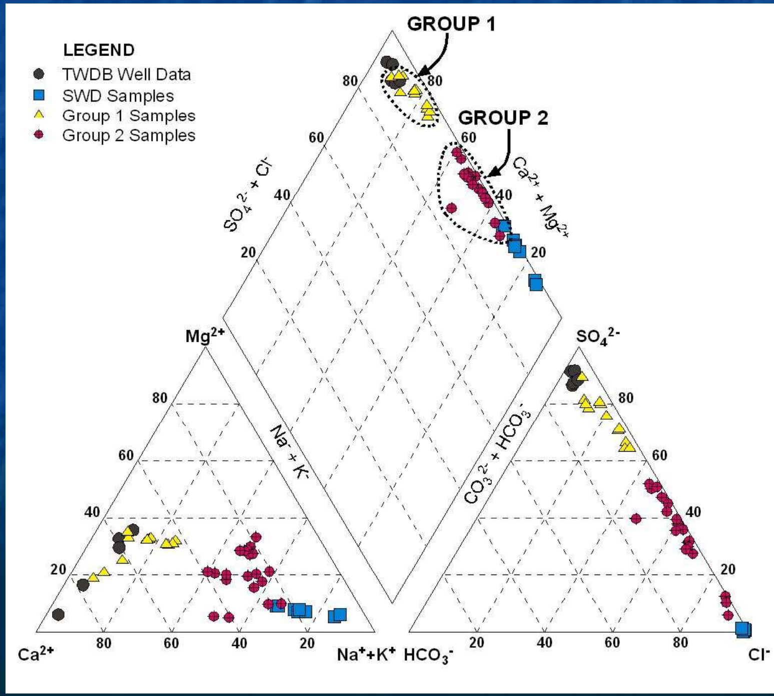
Piper Diagrams

- Two ternary diagrams with a central field
- Used for grouping the chemistry of water samples based on relative concentrations of ions
- Groups are called <u>hydrochemical facies</u>





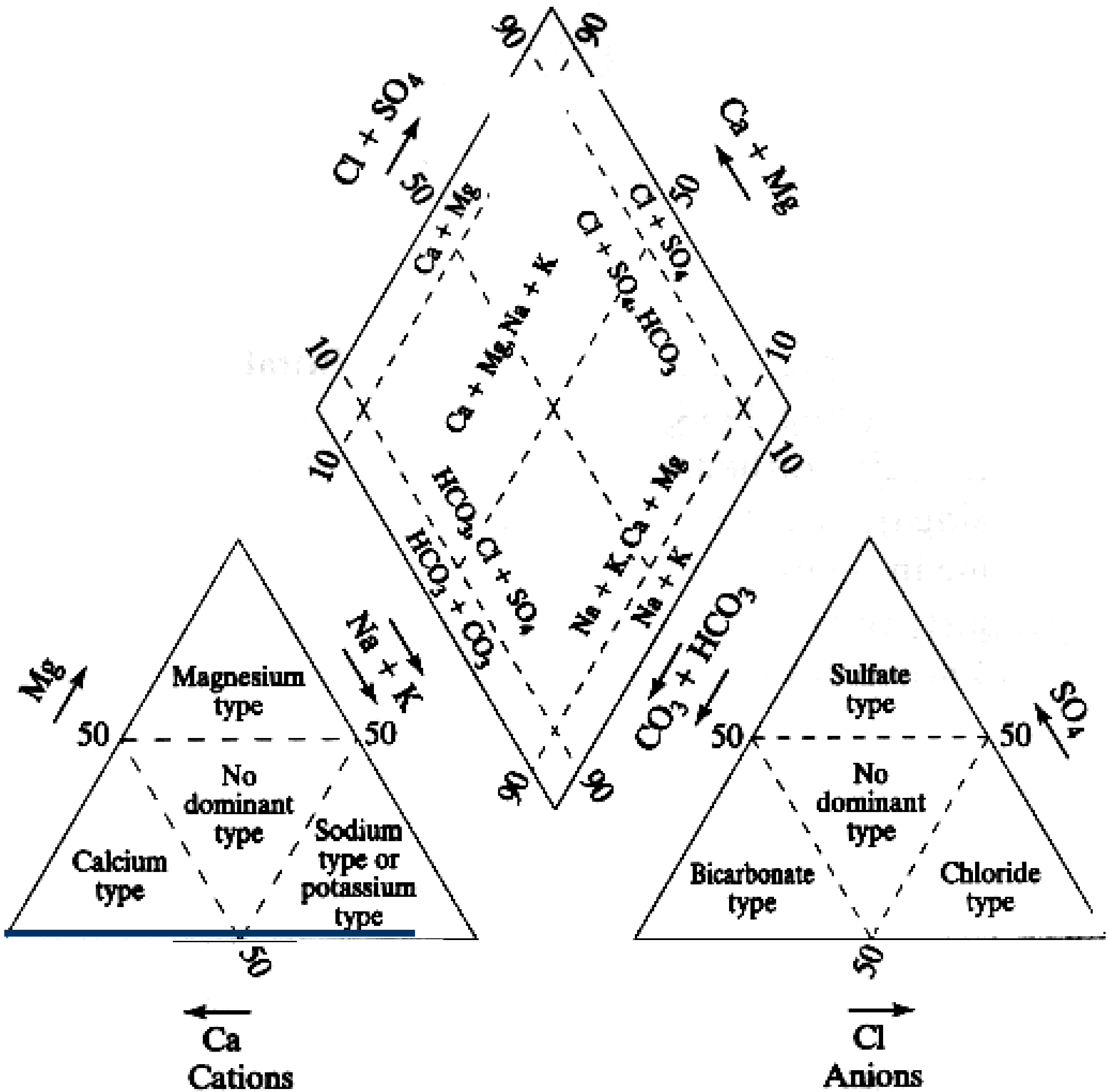
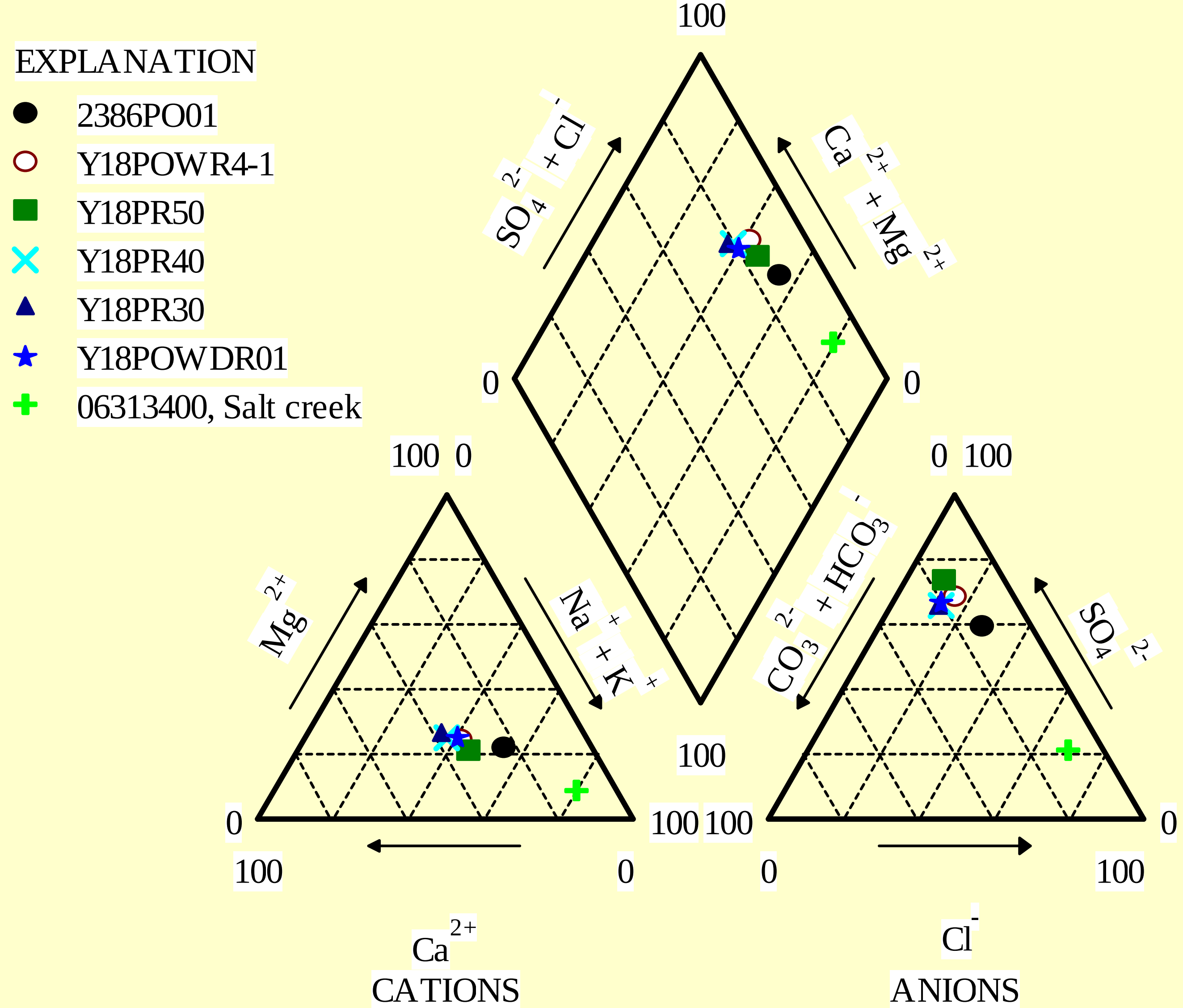
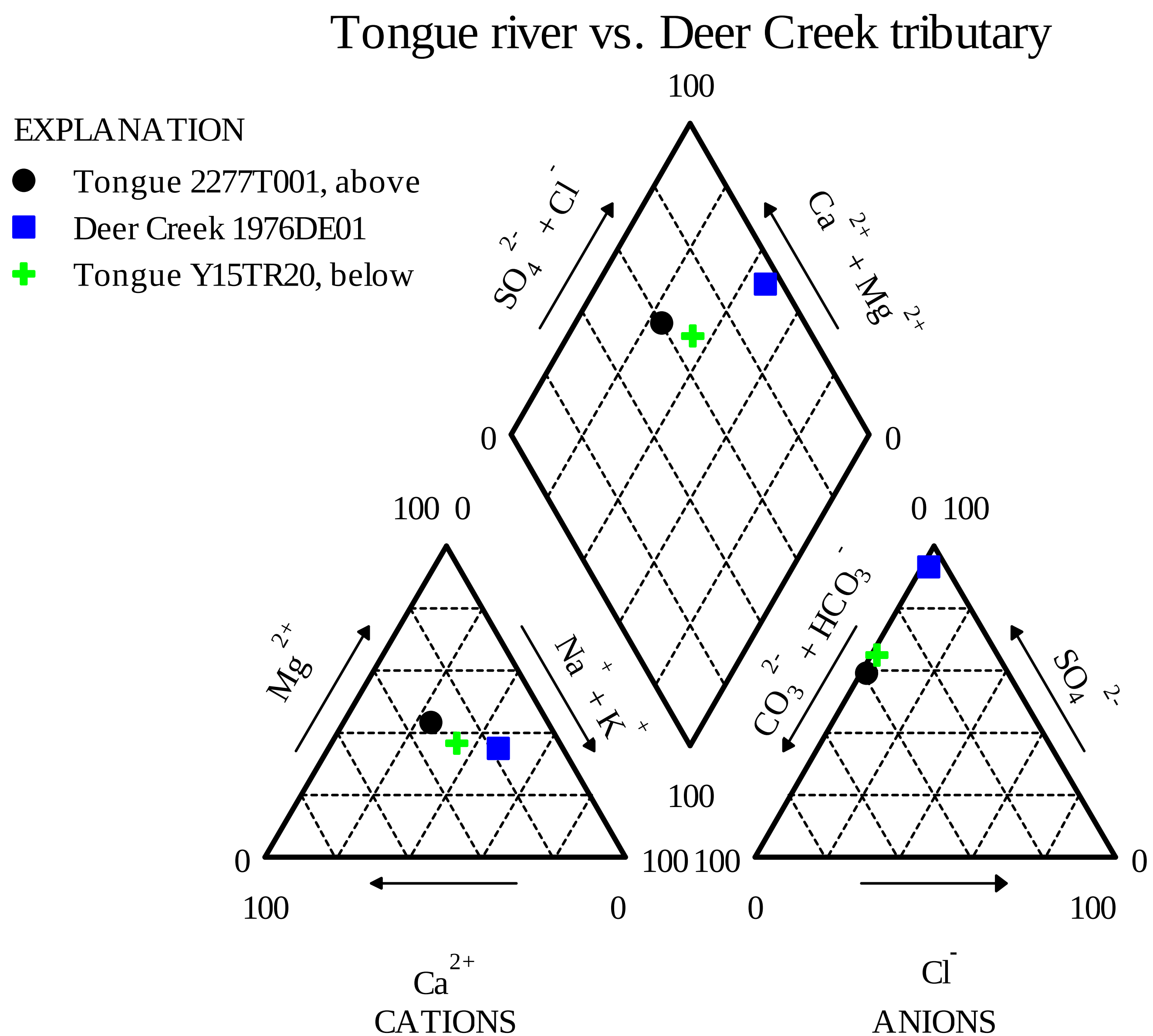


Figure 1-7 from Kehew (2001). Classification of hydrochemical facies using the Piper plot.

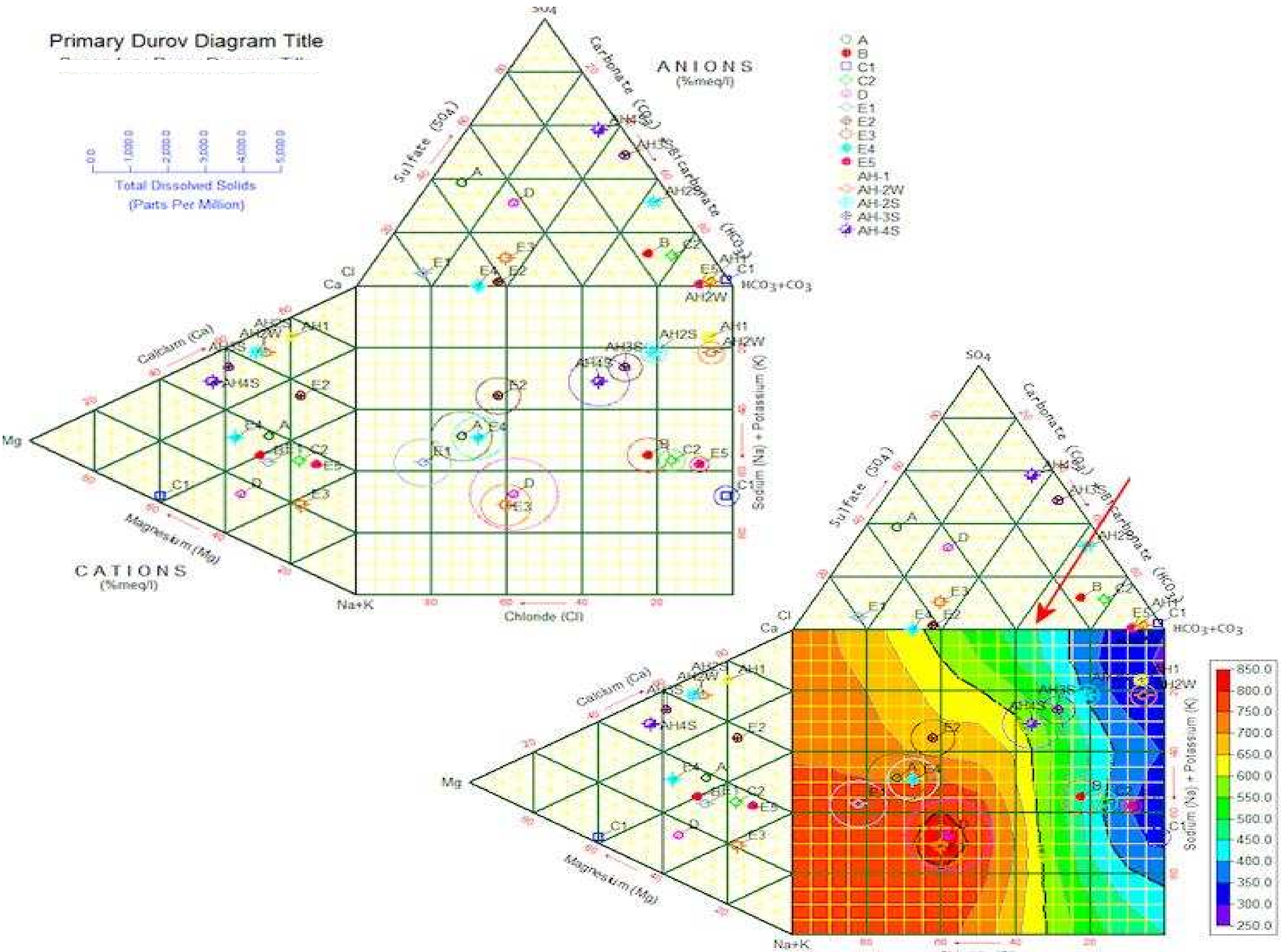
Powder River vs Salt creek tributary




Tongue river vs. Deer Creek tributary
EXPLANATION
Tongue 2277T001, above
Deer Creek 1976DE01
Tongue Y15TR20, below
$SO_4^{2-} + Cl^-$
$Ca^{2+} + Mg^{2+}$
Mg^{2+}
$Na^+ + K^+$
$CO_3^{2-} + HCO_3^-$
SO_4^{2-}
Ca^{2+}
CATIONS
Cl^-
ANIONS
100
0

Dramatic Short term, Local effects

- The higher calcium or sulfate content of tributaries causes sodium disassociation from sodium bicarbonate, forming calcite precipitates (calcium carbonate). This causes the dissolved bicarbonate concentrations to drop by 20% over a distance of less than 400 meters in the Tongue River mainstem, during spring snowmelt.
- The river turns white for 1/2 mile downstream. What are the mechanical toxicity effects of these fine particulates on gill function?
- Precipitation events are principally calcium carbonate (calcite) or calcium sulphate (gypsum)


Primary Durov Diagram Title
ANIONS
(%meq/l)
CATIONS
(%meq/l)
Total Dissolved Solids
(Parts Per Million)
0.0
1,000.0
2,000.0
3,000.0
4,000.0
5,000.0
SO4
Sulfate (SO4)
Carbonate (CO3)
Bicarbonate (HCO3)
Cl
Ca
HCO3+CO3
Calcium (Ca)
Mg
Magnesium (Mg)
Na+K
Chloride (Cl)
Sodium (Na) + Potassium (K)
A
B
C1
C2
D
E1
E2
E3
E4
E5
AH-1
AH-2W
AH-2S
AH-3S
AH-4S
850.0
800.0
750.0
700.0
650.0
600.0
550.0
500.0
450.0
400.0
350.0
300.0
250.0

Biological Processes affecting Bicarbonate/alkalinity Concentrations on a Diel basis

- Photosynthesis

$106CO_2+16NO_3+HPO_4+122H_2O+18H^+ \longrightarrow (C_{106}H_{263}O_{110}N_{16}P_1) +138O_2$

Nitrification and Denitrification

$NH_4^++20_2 \rightarrow NO3^- + H_2O + 2H^+$ $\quad 5CH_2O+4NO_3^-+4H^+ \rightarrow 5CO_2+2N_2+7H_2O$

Sulfate reduction

$SO_4^{-2} + 2CH_20 + H^+ \rightarrow 2CO_2 + HS^- +H_2O$

Sulfide oxidation

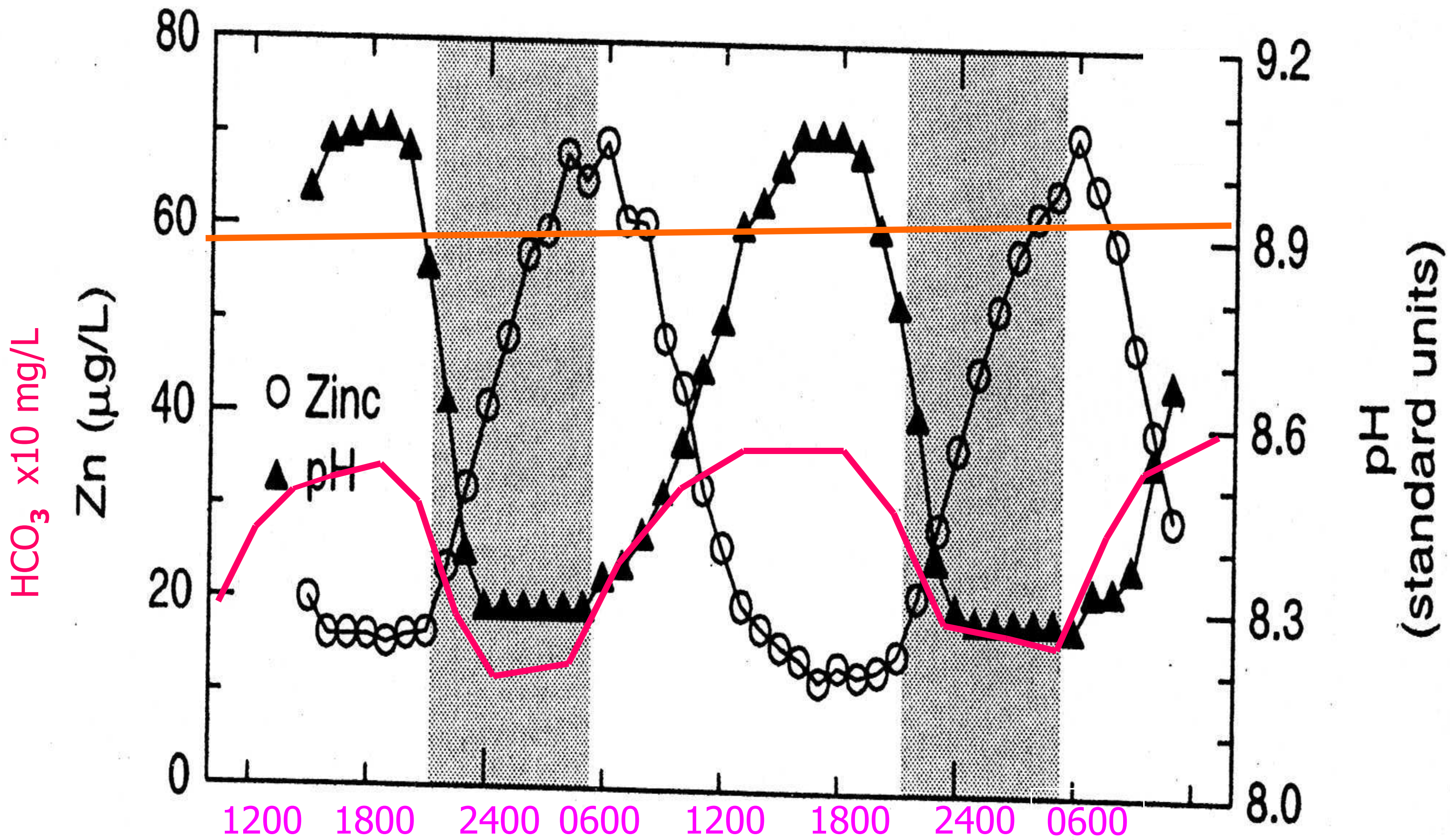
$HS^- +2O_2 \rightarrow SO_4^{-2} +H^+$ $\quad FeS(s)+4O_2+3.5H_2O \rightarrow Fe(OH)_3(s)+4H^++2SO_4^{-2}$

$CaCO_3$ dissolution from sedimentary rock formations

$CaCO_3 + CO_2 +H_2O \longrightarrow Ca^{2+} + 2HCO_3^-$

Net result can be a 2 fold shift in $HCO_3^=$ concentrations on a daily basis, producing a pH shift of >1.0 log unit. Photosynthesis can create undetected chronic toxicity effects unless the timing of sampling is standardized or corrections are made for photosynthetic activity

From Nimick (7) describing relationship between bicarbonate, pH and diel Zn concentrations



Inorganic's who's toxicity is influenced by bicarbonate concentrations (DIC), pH, hardness and DOC. Orange indicates that the element is typically found in CBNG water

- Cadmium
- Chromium +3
- Copper
- Lead
- Nickel
- Silver
- Zinc
- Selenium
- Vanadium
- Boron

Hardness dependent metals criteria may be calculated from the following formula:

CMC (dissolved) = $\exp\{m_A [ln(\text{hardness})] + b_A\}$ (CF)

CCC (dissolved) = $\exp\{m_C [ln(\text{hardness})] + b_C\}$ (CF)

National Recommended Water Quality Criteria

Appendix B—Parameters for Calculating Freshwater Dissolved Metals Criteria That Are Hardness-Dependent

Chemical	mA	bA	mC	bC	Freshwater Conversion Factors (CF)	
					CMC	CCC
Cadmium	1.0166	-3.924	0.7409	-4.719	1.136672-[(lnhardness)(0.041838)]	1.101672-[(lnhardness)(0.041838)]
Chromium III	0.819	3.7256	0.819	0.6848	0.316	0.86
Copper	0.9422	-1.7	0.8545	-1.702	0.96	0.96
Lead	1.273	-1.46	1.273	-4.705	1.46203-[(lnhardness)(0.145712)]	1.46203-[(lnhardness)(0.145712)]
Nickel	0.846	2.255	0.846	0.0584	0.998	0.997
Silver	1.72	-6.59	—	—	0.85	—
Zinc	0.8473	0.884	0.8473	0.884	0.978	0.986

Consideration of the BLM model in bicarbonate standards development

- The conventional Biotic Ligand Model (BLM) utilizes corrections for pH, DOC, major competitive or associative displacement ions (Ca^{2+}, Mg^{2+}, Na^{+}, $SO_4^{=}$, K^{+}, Cl^{-}) and <u>either alkalinity</u> or dissolved inorganic carbon (used by the BLM to estimate bicarbonate cationic complexation)
- Since bicarbonate ions can bind or release numerous metal ions as pH shifts, and light input will alter bicarbonate concentrations, how do we compensate for these simultaneous effect in developing a bicarbonate standard?

Photosynthesis and bicarbonate generation.

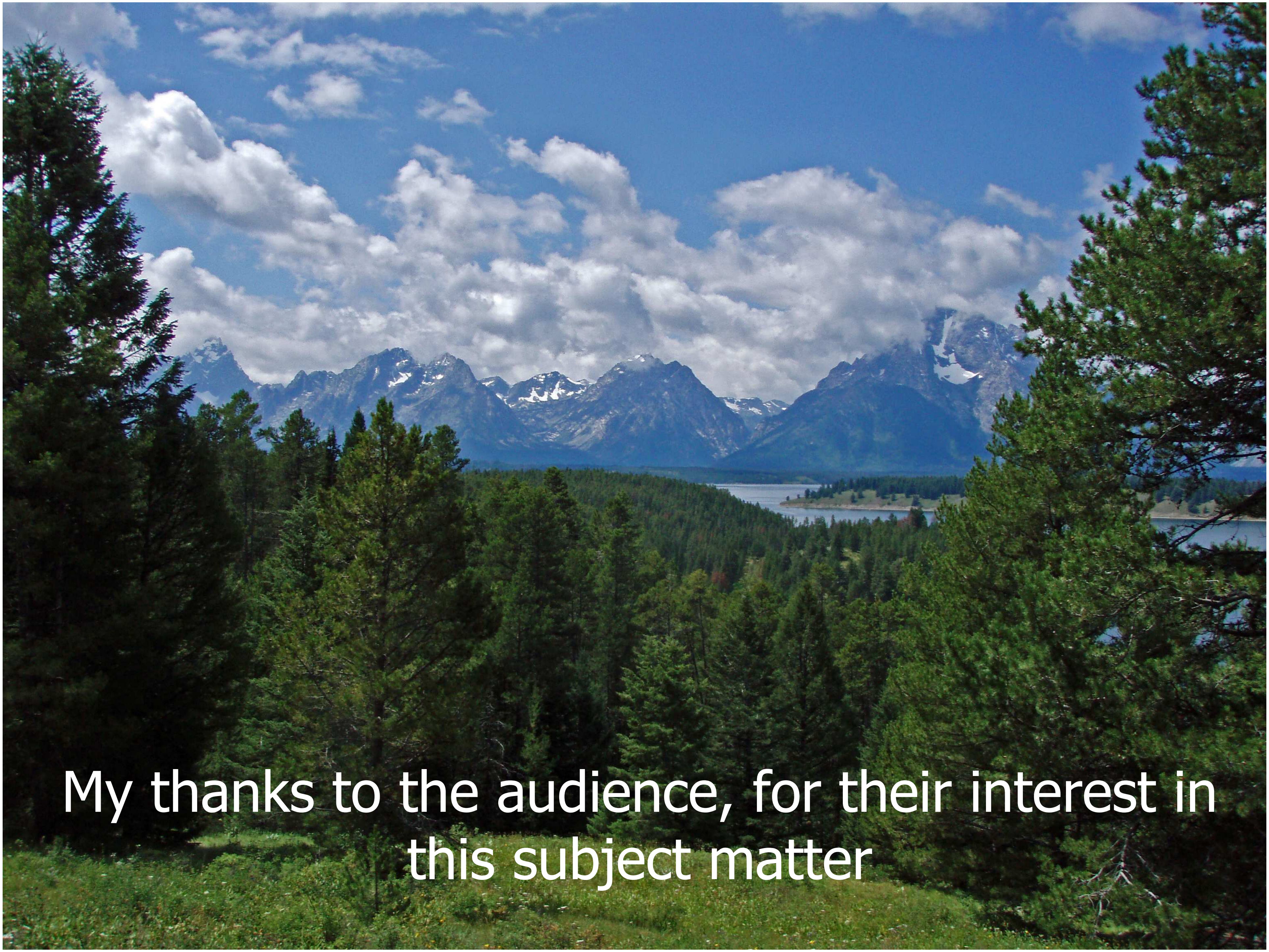
- Since bicarbonate increases buffer capacity and biological system stability between a pH of 5.76 and 8.93, the addition of CBM bicarbonate will increase pH and potentially reduce photosynthesis. Excess bicarbonate acts as a feedback control mechanism on the Calvin Cycle, reducing oxygen output. Dependent on chlorophyll and pH levels, as much as 200 mg/L of bicarbonate can be contributed by photosynthesis to add to the CBM waters. A numeric standard will have to take this into account.

Observations

- The use of Piper and Durov diagrams will allow prediction of precipitation events, to determine the likely makeup of the resultant waters and the toxicity of the resultant bicarbonate concentrations and related toxic metals effects.
- Photosynthetic activity will have to be considered in conjunction with baseline bicarbonate values to set numeric standards.
- Diel photosynthetic cycling of bicarbonate concentration and resultant pH shifts will affect the toxicity of numerous metals (Cr, Cd, Pb, Cu, Ag, Zn and Ni, at a minimum) and set the times that are appropriate for sampling.

References

- Stumm, W. and J. Morgan (1981) *Aquatic Chemistry*
- Broecker, W.S. and T.-H. Peng (1982) *Tracers in the Sea*
- Butler, J.N. (1982) *Carbon Dioxide Equilibria and Their Applications*
- Morel, F.M. and Hering, J.G. (1993) *Principles and Applications of Aquatic Chemistry*
- Langmuir, Donald (1997) Aqueous Environmental Geochemistry
- Zeebe, R.E. and D. Wolf-Gladrow (2001) CO2 in *Seawater: Equilibrium, Kinetics, Isotopes*
- Nimick, David, et al., *Diel Cycles in dissolved metal concentrations in streams: Occurence and possible causes,* Water Resources Research, Vol 39-9, pp1247-1264


My thanks to the audience, for their interest in this subject matter