PHYSICAL LIMNOLOGY AND GEOCHEMISTRY OF TWO CIRCUM-NEUTRAL pH MINE PIT LAKES IN NE WASHINGTON[1]

Rodney T. Lentz[2]

Abstract:. Limnologic and water chemistry data from Echo Bay Mineral's Key West and Equinox Resources' Van Stone mines were collected between August, 2000 and September, 2001. Pit lake elevations, areas and depths are 1,318 and 1,050 m; 1.1 and 1.9 ha; and 28 and 31 m, respectively. Depth profiles of temperature, pH, specific conductivity, oxidation-reduction potential (ORP), and dissolved oxygen were collected on a monthly basis during this period. Results indicate that both water bodies are oligotrophic and dimictic, experiencing complete mixing during the spring and fall. Seasonal water temperatures range between near 0° and 22° C and ice covers the lakes approximately 5 months per year. Thermal stratification becomes well developed in both water columns during late summer. The dissolved oxygen profile at Key West is clinograde, ranging from 8-10 mg/l at the surface to 1-2 mg/l at total depth, except during turnover. Van Stone displays an orthograde oxygen profile with relatively high concentrations (>6 mg/l) at lake bottom through out the year. Values for pH tend to fall with depth in both lakes. Waters in Key West and Van Stone pits are slightly alkaline (7-8.5), calcium-sulfate types. TDS concentrations average 628 mg/l at Key West and 386 mg/l at Van Stone; likewise sulfate currently averages about 336 mg/l and 138 mg/l, respectively. Metal concentrations are low in both waters. Contrary to expectation, sulfate concentrations in Key West lake waters have decreased over time, despite abundant sulfide minerals in the pit wall. Also unanticipated, were diminished concentrations of dissolved zinc, arsenic, molybdenum, antimony and selenium concentrations in the oxygen deficient hypolimnion at Key West.

The observations and empirical data from Key West and Van Stone pit lakes are useful for, and should be considered, when developing, calibrating, and validating water quality models for circum-neutral mine pit lakes in temperate climates.

Additional Key Words: dimictic, oligotrophic, sulfate.

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[2] Rodney T. Lentz is an Area Mining Geologist, USDA Forest Service, 1240 2nd Ave. South, Okanogan, WA 98840-9723.

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Introduction

Successful pit lake water quality modeling requires the input of reasonable physical-chemical parameters. The concentrations of minor metals in particular, are not easily predicted using theoretical solubilities (Eary, 1999). Where empirical data is unavailable, assumptions must be substituted, resulting in ambiguities and uncertainties that can have serious consequences. A recent example is the Crown Jewel Project, an open-pit gold mine proposed in north central Washington. Uncertainties concerning the water quality of the resultant pit lake were an important factor in the appeal and cancellation of the proponent's Clean Water Act permits.

Published limnologic data for mine pit lakes is scarce (Doyle and Runnells, 1997), particularly for circum-neutral pH waters in mid-latitudes. Limited data are summarized by Doyle and Runnells (1997) for eight pit lakes in California, Nevada, Montana, and northwestern Saskatchewan. Stevens and Lawrence (1998) reports stability and stratification in a large pit lake at the Brenda Mine, British Columbia. Pit lake water chemistry has received more consideration in the literature. Water quality of 18 hard rock mine pit lakes in Nevada and 6 others from USA and Canada are evaluated by Eary (1999).

This paper describes the physical limnologic characteristics and chemistry of two lakes developed in hard rock mine pits in northeastern Washington: Key West, developed by Echo Bay Minerals Company; and Van Stone, most recently activated by Equinox Resources, Ltd. Emphasis is placed on subsurface profiling of temperature, pH, electrical conductivity, oxidation-reduction potential (ORP), and dissolved oxygen (DO) and their relationship to water quality.

Figure 1. Location map

Site Descriptions and Setting

The subject mines are located in mountainous terrain of the Okanogan Highlands geomorphic province, northeastern Washington (Figure 1). Both are side hill pits which daylight well below the maximum bench elevation. Regional climate is temperate; characterized by cold, wet/snowy winters and warm, moderately dry summers. Average annual precipitation ranges from 47 cm (18.5 in) at Key West to approximately 60 cm (25 in) at Van Stone. Table 1 compares geographic and morphological features of the Key West and Van Stone pit lakes. The lakes are relatively small at 1.2 and 1.9 ha (3 and 4.7 ac), respectively. Relative depths (the maximum depth taken as a percentage of the mean lake diameter; Wetzel, 2001) of the lakes are 9 and 10 percent. By comparison, most natural lakes have a relative depth of less than 2 percent and undergo complete seasonal mixing. Natural meromictic—incompletely mixed--lakes studied in North America generally have a relative depth greater than 5 percent. Relative depths of pit lakes reported in the literature vary between 9 and 40 percent (Doyle and Runnels, 1998).

Table 1. Geography and morphology of the pit lakes

	Key West	**Van Stone**
Latitude	48^{o} 42' 40"	48^{o} 45' 37"
Longitude	118^{o} 33'37"	117^{o} 45' 30"
Elevation m	1,318	1,050
Pit configuration	Side hill, day lights E	Side hill, day lights W
Slope Aspect	NE	W
Area m^2	11,260	19,150
Volume m^3	128,550	311,500
Max. Depth	28	31
Mean Depth (Vol./Area)	11	16
Relative Depth (Wetzel, 2001)	9%	10%

Key West. This mine develops a gold deposit in (1) massive oxide-sulfide and (2) sheeted pyrrhotite and quartz-sulfide veinlets that replace and invade Permian carbonate, clastic and volcanic rocks (Rasmussen and Hunt, 1990). Final configuration of the pit was attained in September 1993 and infilling by precipitation/surface and ground water began (Figure 2). Meanwhile, a decline, opened June 1994 some 15 m (50 ft) above the bottom of the pit, was driven eastward to access a small underground ore body. This working was partially backfilled and sealed before the rising pit lake submerged it.

Consultants initially predicted that the pit would fill slowly, reaching overflow elevation after 20 years (HydroGeo, 1996). However, a revised water balance suggests that pit overflow will occur within 10 years after the end of mining at an average rate of 38 liter min^{-1} (10 gpm) (HydroGeo, 2001). The maximum depth of the lake is currently about 28 m.

Pit wall rock is composed as follows: 42 percent fine-grained limestone; 26 percent low grade ore (magnetite, disseminated and massive sulfide, quartz-sulfide veins in altered sandstone and conglomerate); 21 percent clastics (mudstone, siltite, sandstone); and 11 percent hornblende porphyry (Hydro-Geo, 1996 [estimated from Figure 3]). Sulfide content ranges from a trace to as much as 90 percent of the rock locally. Species present include pyrrhotite, pyrite, chalcopyrite, arsenopyrite, sphalerite and galena, in decreasing order of abundance. While as much as 15 percent of the waste rock removed from the Key West and near-by Key East pits was predicted to be potentially acid producing, it also exhibited excess neutralization capacity provided by limestone. Where ground water seepage coincides with high-sulfide concentrations, iron staining and sulfurous odors are evidence of locally intense oxidation reactions. In waters that contain sufficient buffering capacity to maintain near neutral pH, pyrite oxidation is represented by:

Figure 2. Aerial and oblique (inset) photographs of Key West (a) and Van Stone pit lakes.

$$FeS_2(s) + 15/4O_2 + 7/2H_2O + 4CO_3^{2-} \rightarrow Fe(OH)_{3(solid)} + 2SO_4^{2-} + 4HCO_3^{-} \qquad (1)$$

Early pit lake water quality monitoring revealed water of neutral pH with an increasing trend in alkalinity and sulfate concentrations. Hydro-Geo (1996) predicted, on this basis, that pit lake water would remain near neutral or slightly alkaline and that sulfate and calcium, controlled by precipitation of gypsum, would increase to 1,018 and 353 mg l^{-1} respectively. Such concentrations were never attained, however, and the current sulfate and TDS trends are downward (Hydro-Geo, 2001). Pit lake water is moderately buffered calcium-sulfate water with near neutral to alkaline pH and moderately elevated concentrations of TDS. Metals are typically at or below detection limits (Table 2).

Several dozen rainbow trout fingerlings were released into the pit lake some time in 1999. Fresh water shrimp were also reported to have been introduced. Owing to the lack of natural occurring food sources, the fish were fed periodically, first by hand and later using an automatic feeder. Feeding was suspended in September 2001.

Van Stone. Zinc and lead ore was extracted from the Van Stone mine intermittently between 1930 and 1992. The deposit, hosted by fine- to medium-grained dolomite of Cambrian age, is composed of disseminated grains, pods and stringers of sphalerite, galena, and minor amounts of pyrite, chalcopyrite and pyrrhotite. Irregular zones of jasperoid-tremolite alteration in the dolomite host appear unrelated to the sulfide mineralization. (Mills, 1977; Neitzel, 1972) Water balance information is not available for the lake. The water level is relatively stable however; controlled, for much of the year, by evaporation and outflow seepage through compacted waste rock at the pit mouth and the bedrock walls. An estimated 76 liters min^{-1} (20 gpm) was observed flowing from the mouth of the pit during one visit in May, 2001. A perennial surface flow into the lake from the upper pit is estimated at 20-40 liters sec^{-1} (5-10 gpm).

Potential for acid generation from the Van Stone pit wall and waste rock is minimal due to the lack of iron sulfides and abundant carbonate in the host. Water quality data for Van Stone is limited (Table 2). Pit lake water is moderately buffered calcium-sulfate water with near neutral to alkaline pH and moderately elevated concentrations of TDS. Metals are typically at or below detection limits.

Experimental

Surface and subsurface observations were recorded above the deepest region of the pit lakes, as determined from as-built mine maps and limited depth soundings. The maximum depth at Key West (28 m) occurred within a small area and was difficult to locate consistently. Consequently, most samples bottomed on the main pit floor (25 m). Data was collected approximately monthly between August 2000 and September 2001. A StowAWay thermistor logger was used to obtain temperature profiles. Subsurface samples were collected for water analysis with a WaterMark horizontal sample bottle constructed of PVC. Electrical Conductivity (Cond), pH, oxidation-reduction potential (ORP), and dissolved oxygen (DO) measurements were made in the field using Hanna Instrument water test meters. Early DO values (August-November, 2000) were estimated using a CHEMmetrics Vacu-

Table 2. Average pit lake chemistry

Parameter		**Unit**	**Key West**[1]	**Van Stone**[2]
pH		S.U.	8.1	8.56*
Total Alkalinity		mg CaCO3/l	76	
hardness		mg CaCO3/l	345	
Specific Conductance		umhos/cm	690	615
TDS		mg/l	521	460*
TSS		mg/l	3	14
Calcium	Dissolved	mg/l	98	
	Total	mg/l	98	76*
Chloride		mg/l	0.8	1*
Fluoride		mg/l	0.1	
Potassium	Dissolved	mg/l	1.8	
	Total	mg/l	1.9	
Sodium	Dissolved	mg/l	12.9	
	Total	mg/l	13	4*
Sulfate		mg/l	289	170*
Nitrate		mg N/l	3.16	
Nitrite		mg N/l	0.08	
Nitrite + Nitrate		mg N/l	3.3**	1.3*
Ortho-Phosphate		mg PO4/l	0.01	
Aluminum	Dissolved	mg/l	0.018	
	Total	mg/l	0.036	
Antimony	Dissolved	mg/l	0.012	
	Total	mg/l	0.009	<.02*
Arsenic	Dissolved	mg/l	0.003	
	Total	mg/l	0.003	0.003*
Barium	Dissolved	mg/l	0.022	
	Total	mg/l	0.021	
Beryllium	Dissolved	mg/l	0.001	
	Total	mg/l	0.001	
Cadmium	Dissolved	mg/l	0.001	
	Total	mg/l	0.001	0.00019*
Chromium	Dissolved	mg/l	0.004	
	Total	mg/l	0.004	
Copper	Dissolved	mg/l	0.005	
	Total	mg/l	0.005	<.002
Iron	Dissolved	mg/l	0.01	
	Total	mg/l	0.065	0.03*
Lead	Dissolved	mg/l	0.001	
	Total	mg/l	0.001	0.005
Magnesium	Dissolved	mg/l	25.8	
	Total	mg/l	25.5	41*
Manganese	Dissolved	mg/l	0.008	
	Total	mg/l	0.012	0.002*
Mercury	Dissolved	mg/l	<0.0001	
	Total	mg/l	<0.0001	<.0002
Molybdenum	Dissolved	mg/l	0.087	
	Total	mg/l	0.088	
Nickel	Dissolved	mg/l	0.009	0.01*
	Total	mg/l	0.01	
Selenium	Dissolved	mg/l	0.004	
	Total	mg/l	0.004	
Silver	Dissolved	mg/l	0.003	
	Total	mg/l	0.003	<.01*
Thallium	Dissolved	mg/l	0.001	
	Total	mg/l	0.001	
Zinc	Dissolved	mg/l	0.036	
	Total		0.039	0.11

[1] 26-29 samples, 1993-2000 (HydroGeo 2001)

[2] 1-5 samples, 1994-1997

*Calculated from 2 or fewer samples

**Skewed by early samples, currently <.05

vials test Kit (1 mg l^{-1} resolution). Equipment failure prevented subsurface sampling for the November 1 & 2 dates. Secchi disc transparencies were recorded using a 20 cm disk generally between 1000 and 1400 hours, PDT. Before and after fall turnover a limited number of water samples were collected at depth to evaluate vertical changes in dissolved constituents. A Washington state certified lab conducted laboratory analyses of multiple chemical parameters and provided pre-sterilized and pre-preserved containers for sample storage and transport.

Results

General Observations

Ice covers the pit lakes for approximately 5 months of the year. By November 21, 2000, thin ice had formed on Key West and was just coalescing on Van Stone. A maximum ice thickness of 45 cm was measured at both lakes during the winter. April 12, 2001 found a shrinking ice cover on Van Stone with about a meter of open water around the shoreline. By April 23, 2001, a band of open water 3-m wide surrounded the ice "island" at Key West. All ice and snow had vanished from both sites by mid-May 2001. Wind is a significant energy source at the mines, particularly during spring and fall seasons. A light breeze (est. <10 km hr^{-1}) was common on most visits, requiring anchoring of the boat to prevent drifting. Occasionally stronger winds of 10-20 km hr^{-1} caused some drift despite the anchor. Wind was more often present and its velocity greater at the higher-elevation Key West location.

Secchi disk transparencies vary from 5-11 m at Key West and 6.5-16 m at Van Stone (Table 3). Light transmissivity is greatest in late summer and fall and poorest in spring. Lake appearance varies distinctively at Van Stone. The water takes on the milky, pale bluish green color of some natural glacial lakes after spring runoff (Figure 2b, inset), but darkens as summer progresses. Fine particles eroding from adjacent glacial deposits during spring runoff are the likely cause of this discoloration. Key West lacks any obvious annual color change. Despite the apparent cloudiness of the Van Stone water, its springtime Secchi disk transparencies are similar to those of Key West during the same period. Overall, pit water at Van Stone demonstrated greater optical transmissivity.

Table 3. Secchi disk transparencies

Key West			**Van Stone**		
Date	Time	Depth	Date	Time	Depth
8/11/00	1500	7.3	8/11/00	1100	8.5
9/25/00	1400	11	9/28/00	1030	10
6/21/01	1400	6.5	6/21/01	1130	6.5
7/20/01	1200	6.7	7/26/01	1000	9.5
8/23/01	1600	5	8/24/01	1100	16
9/20/01	1300	7.5	9/19/01	1400	14.5

While biota was not the emphasis of this study, the following observations deserve note. The pit lakes are markedly different in their physical and biological substrates. Coarse gravel dominates the substrate at all levels of the Key Stone lakebed. Plant life is sparse, even in the littoral zone, and consists of a few upland grass individuals and small, scattered algal colonies. The resident trout appeared healthy, vigorous, and always hungry. A small amphibian larva population occupied the shallows in mid-summer, with one adult, tentatively identified as a spade-footed toad, seen in September, 2001. Tiny dark-colored arthropods (~0.5 mm) were also noted moving in the upper levels during the September, 2000 visit; approximately 12 individuals per 100 ml. The substrate at Van Stone, by contrast, consists of coarse gravel overlain by silty and clayey sediment of variable thickness. Plant life is abundant, if not diverse. *Veronica anagallis-aquatica,* a leafy aquatic plant, dominates the littoral zone (Ahlenslager, personal communication, 2001), forming a open mat in the shallows and thinning into the sublittoral. Horsetails, rushes, cattails and unidentified grasses are also present. The substrate is organic rich and fetid in the few shallow, gently-sloping littoral areas (haul road entry). *Veronica* is ubiquitous around the entire shoreline , even occupying steep, rocky slopes of the lakebed. Fish have not been planted, nor were observed in the lake. I found two resident adult amphibian species in June 2001, along with juveniles and a diverse invertebrate group. Water blooms of bluegreens (Cyanobacteria) were not noted at either lake during my monthly visits.

Profile Data

Field Measurements. Figure 3 displays temperature, electrical conductivity, pH, ORP, and DO values with depth. Temperature profiles for the Key West and Van Stone pit lakes are strikingly similar. Both show periods of relatively uniform temperature with depth between mid-November and April. Incipient stratification developing by May progresses through a multiple-layer stage, to a single thermocline with well developed epilimnion and hypolimnion by August. Measured surface water temperatures varied from near zero below winter ice to 22° C in late summer. Temperatures at maximum depths remained within a narrow range: 3.7-6.4° C. Field pH readings for surface water in the lakes ranged between 7.3 and 8.7. Key West averaged slightly lower surface pH, 8.1, compared to Van Stone's 8.3: otherwise, the data are analogous. The pH decreases several tenths of a unit or more with increasing depth in most months. Notable exceptions are one late under-ice month at each lake (April and March, respectively), where the reverse was true; and during spring and fall when pH is essentially uniform. Electrical conductivities measured in the field generally vary less than 10 percent between the surface and maximum depth. The data show both decreasing and increasing increments with depth, but no annual pattern is evident at either lake. Surface and maximum-depth conductivities averaged 618 and 668 µS, respectively at Key West and 494 and 508 µS at Van Stone.

The vertical distribution of DO is an obvious character of distinction between the two lakes. Oxygen content is typically greater in the Van Stone waters at any depth. Mean DO levels in surface water, for example, average 9.5 mg l^{-1} at Van Stone opposite Key Stone's 8.5. Except during spring and fall DO in Key West water decreases to <2 mg l^{-1} at maximum depth, while at Van Stone oxygen content averages 7.8 mg l^{-1} on the lake bottom year around. The ORP of both lake waters generally falls between +100 and +200 mV, indicating oxidizing conditions throughout the water columns. ORP decreases to a minimum as DO approaches zero (Figure 3a). An ORP of –20 mV was recorded September 20, 2001 from a Key West lake-bottom sample. DO was 1 mg l^{-1} and a strong hydrogen sulfide odor was also detected from the sample. Dark, porous sediment particles were found in bottom samples from both lakes.

Laboratory Analyses. Figure 4 displays Key West and Van Stone pit lake water chemistry as a function of depth, before and after fall overturn. Profiles showing water temperature and the other field parameters are repeated in this figure for convenient comparison. Immediately evident is the homogeneity of surface and bottom waters in both lakes after fall mixing. The analyses detect no appreciable differences of major and minor ion content or pH in the water column at that time.

Analyses of samples from the epilimnion, metalimnion and hypolimnion at near-peak thermal stability reveal noticeable differences (Figure 4, outlined data). The data indicate that pH steadily decreases and electrical conductivity increases slightly with depth in both lakes. Incremental enhancement of alkalinity and TDS also accompanies increasing calcium ion concentrations with depth. By contrast, zinc is reduced in the hypolimnion by 15 and >50 percent. The magnitude of these differences is, in each case, greater at Key West. Near-bottom manganese concentrations, on the other hand, jump from <5 µg l^{-1} in the epilimnion and metalimnion to 27 and 120 µg l^{-1}, with the greater change apparent at Van Stone. Barium also increased with depth an Van Stone but remained unchanged at Key West. The data show that the oxyanions--arsenic, antimony, selenium, and molybdenum--are reduced by up to 50 percent in the hypolimnion of the Key West pit lake. This effect is less conspicuous at Van Stone, where reduction in arsenic alone was detected.

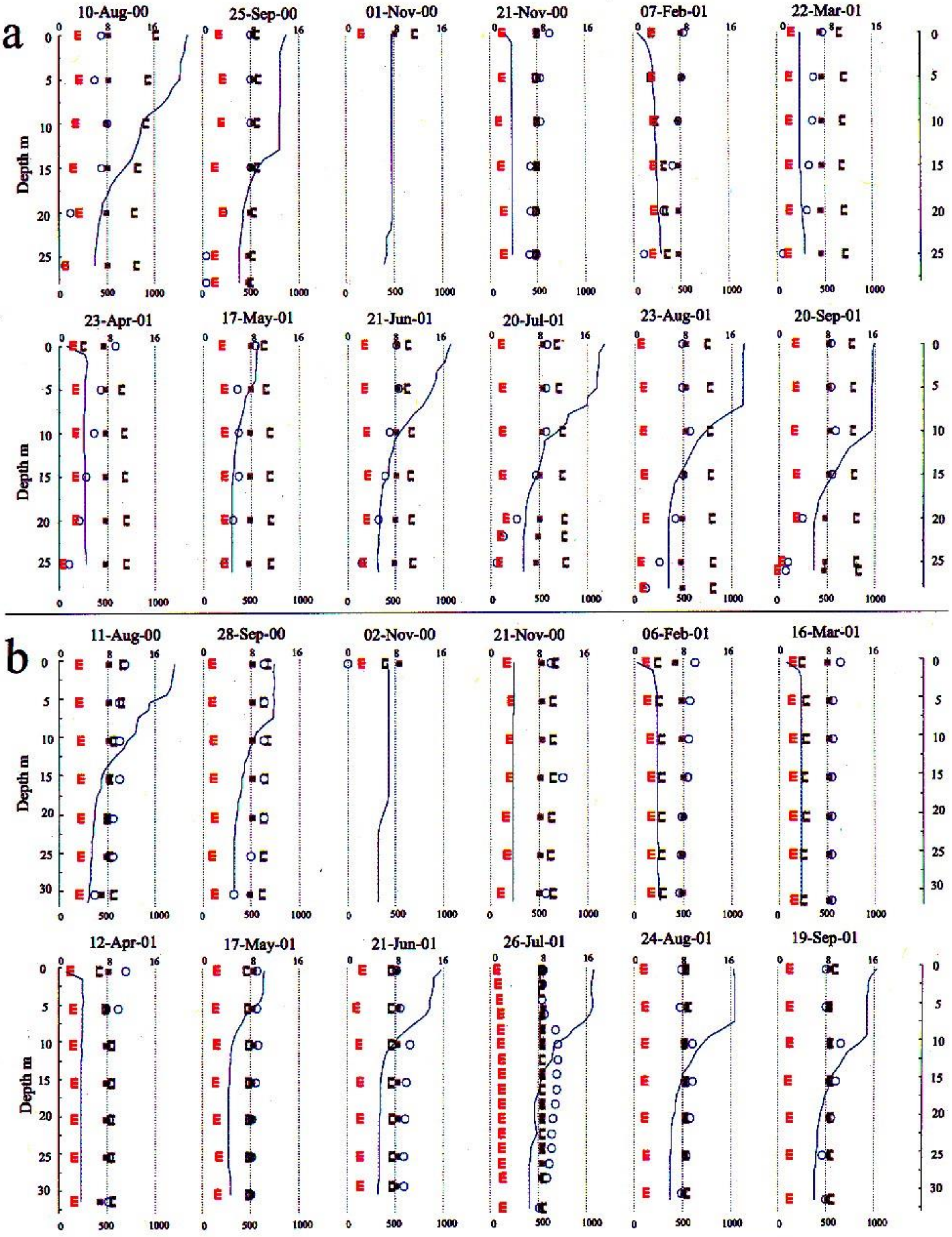


Figure 3. Depth profile data for Key West (a) and Van Stone (b) mine pit lakes. Temperature in °C (continuous line), pH (■), and DO in mg l^{-1} (○) are read on the upper scales. Electrical conductivity in uS (ᑕ), and ORP in mV (E) are read on the lower scales.

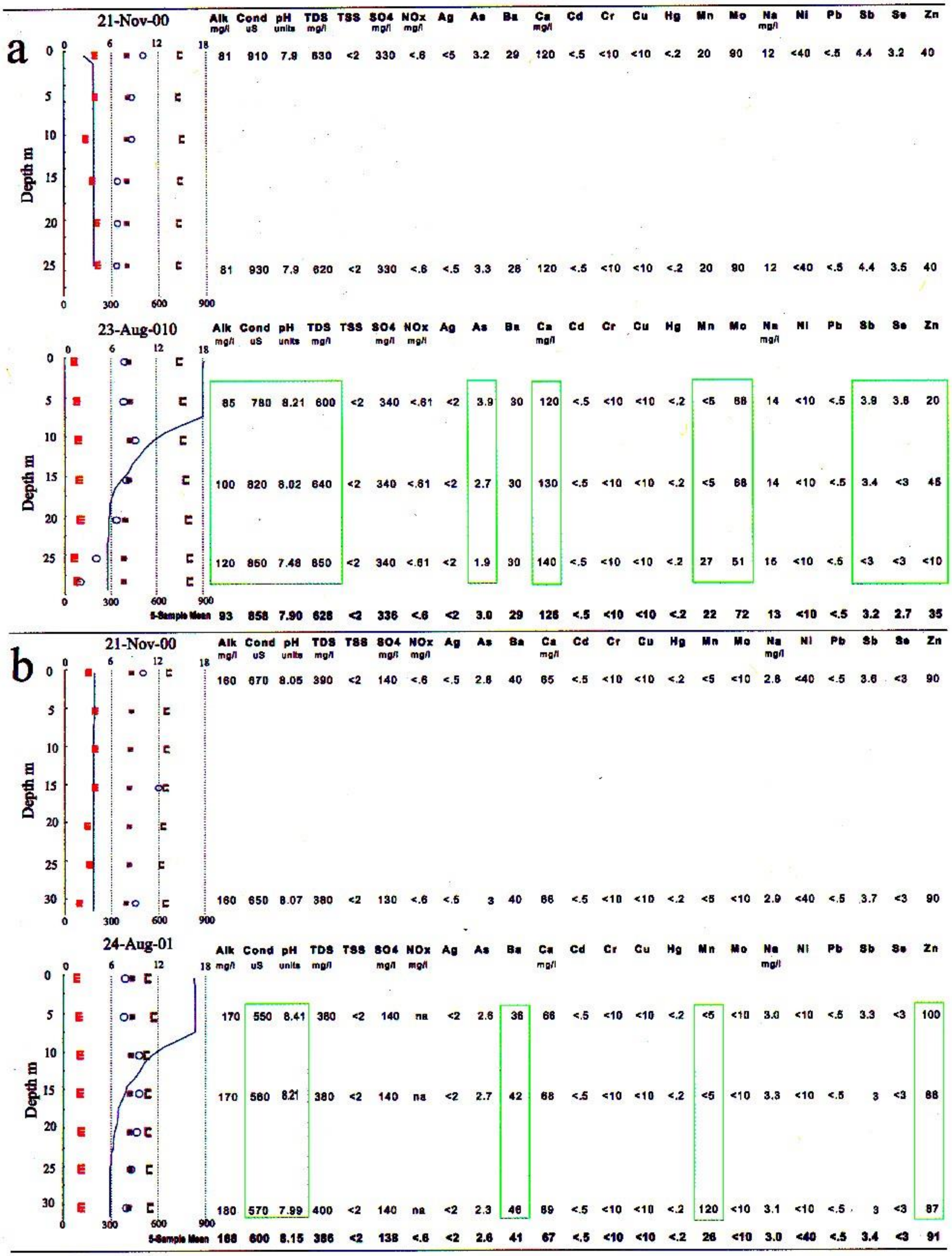
Discussion and Conclusions

Typology

Based upon features listed by Cole (1994) Key West and Van Stone pit lakes are classified as oligotrophic based on morphology (shape, bed slope, depth); blue-green water color and transparency; and apparent lack of nutrients, biological production and organic-rich sediments. Van Stone also exhibits the characteristic orthograde oxygen profile and Key West, the sterile littoral zone, of oligotrophic lakes. Two features more commonly associated with eutrophy are also present: Abundant littoral macrophyte population at Van Stone and the clinograde (decreasing) oxygen profile at Key West. Clinograde oxygen profiles are normally attributed to the decomposition of trophic zone organic detritus in the hypolimnion (Wetzel, 2001). But, biological productivity at Key West is low. While a small fish population is present, when compared with phytoplankton and littoral flora, limnologists believe that fish and other larger animals are only a small contributor of organic detritus in lakes (Wetzel, 2001). A better explanation for oxygen loss may be continued, slow oxidation of sulfide-rich zones in the submerged pit floor and walls.

Stratification and Mixing

Thermal stratification patterns at Key West and Van Stone pit lakes are dimictic. Fall water column instability, overturn and mixing at both lakes is demonstrated by the destruction of thermal stratification and homogeneous water chemistry in mid-November. Except for inverse thermal stratification directly under the ice cover, this thermal profile persists through the winter months (Figure 3). As the lake opens in spring, the water column is unstable and susceptible to complete mixing, even by small amounts of wind energy (Wetzel, 2001). The vertical uniformity of EC, pH, ORP, and DO in Key West and Van Stone lakes during the May 2001 observations, is evidence of such mixing. Based upon the condition of the ice-cover in April and comparing April and May thermal profiles, spring turnover likely occurred shortly after ice loss in mid to late April, respectively.



a

21-Nov-00

	Alk mg/l	Cond uS	pH units	TDS mg/l	TSS	SO4 mg/l	NOx mg/l	Ag	As	Ba	Ca mg/l	Cd	Cr	Cu	Hg	Mn	Mo	Na mg/l	Ni	Pb	Sb	Se	Zn
	81	910	7.9	630	<2	330	<.6	<5	3.2	29	120	<.5	<10	<10	<.2	20	90	12	<40	<.5	4.4	3.2	40
	81	930	7.9	620	<2	330	<.6	<.5	3.3	28	120	<.5	<10	<10	<.2	20	90	12	<40	<.5	4.4	3.5	40

23-Aug-010

	Alk mg/l	Cond uS	pH units	TDS mg/l	TSS	SO4 mg/l	NOx mg/l	Ag	As	Ba	Ca mg/l	Cd	Cr	Cu	Hg	Mn	Mo	Na mg/l	Ni	Pb	Sb	Se	Zn
	85	780	8.21	600	<2	340	<.61	<2	3.9	30	120	<.5	<10	<10	<.2	<5	88	14	<10	<.5	3.9	3.8	20
	100	820	8.02	640	<2	340	<.61	<2	2.7	30	130	<.5	<10	<10	<.2	<5	88	14	<10	<.5	3.4	<3	45
	120	860	7.48	650	<2	340	<.61	<2	1.9	30	140	<.5	<10	<10	<.2	27	51	15	<10	<.5	<3	<3	<10
5-Sample Mean	93	858	7.90	628	<2	336	<.6	<2	3.0	29	126	<.5	<10	<10	<.2	22	72	13	<10	<.5	3.2	2.7	35

b

21-Nov-00

	Alk mg/l	Cond uS	pH units	TDS mg/l	TSS	SO4 mg/l	NOx mg/l	Ag	As	Ba	Ca mg/l	Cd	Cr	Cu	Hg	Mn	Mo	Na mg/l	Ni	Pb	Sb	Se	Zn
	160	670	8.05	390	<2	140	<.6	<.5	2.8	40	65	<.5	<10	<10	<.2	<5	<10	2.8	<40	<.5	3.6	<3	90
	160	650	8.07	380	<2	130	<.6	<.5	3	40	66	<.5	<10	<10	<.2	<5	<10	2.9	<40	<.5	3.7	<3	90

24-Aug-01

	Alk mg/l	Cond uS	pH units	TDS mg/l	TSS	SO4 mg/l	NOx mg/l	Ag	As	Ba	Ca mg/l	Cd	Cr	Cu	Hg	Mn	Mo	Na mg/l	Ni	Pb	Sb	Se	Zn
	170	550	8.41	380	<2	140	na	<2	2.6	36	66	<.5	<10	<10	<.2	<5	<10	3.0	<10	<.5	3.3	<3	100
	170	560	8.21	380	<2	140	na	<2	2.7	42	68	<.5	<10	<10	<.2	<5	<10	3.3	<10	<.5	3	<3	88
	180	570	7.99	400	<2	140	na	<2	2.3	46	69	<.5	<10	<10	<.2	120	<10	3.1	<10	<.5	3	<3	87
5-Sample Mean	168	600	8.15	386	<2	138	<.6	<2	2.6	41	67	<.5	<10	<10	<.2	26	<10	3.0	<40	<.5	3.4	<3	91

Figure 4. Comparison of water chemistry, depth, and lake stability; Key West (a) and Van Stone (b) mine pit lakes. Total dissolved constituents are shown in ug l^{-1} unless otherwise specified. Alkalinity= Alk, electrical conductivity =Cond, sulfate=SO4, and nitrate+nitrite=NOx. See Figure 4 for an explaination of the depth profile graphs.

Water Chemistry. Modification of water column chemistry during periods of stratification is of particular interest in this study. The relationship among various forms of CO_2, photosynthesis, and pH are well known in natural waters (Wetzel, 2001; Cole, 1994) and is defined by the following equilibrium equation:

$$Ca(HCO_3)_2 \rightleftarrows CaCO_{3(Solid)} + H_2O + CO_{2(Asimilated)} \qquad (2)$$

Photosynthetic consumption of carbon dioxide in the surface trophic zone results in the precipitation of calcium carbonate and the accompanying reduction of calcium ions and electrical conductivity and an increase in pH. This reaction occurs, though is less pronounced in oligotrophic lakes, and is the likely cause of increasing calcium and TDS and decreasing pH with depth in Key West and Van Stone pit lakes.

The distribution and cycling of iron and manganese in natural lakes is also well documented (Wetzel, 2001; Cole, 1994). Like iron, manganese solubility is sensitive to ORP conditions. These elements precipitate as hydroxides and carbonates under oxidizing conditions and neutral pH. Thus, dissolved concentrations of iron and manganese are typically low. The metals become more soluble as reducing conditions are approached, especially adjacent the sediment-water interface. This is a creditable explanation for manganese concentrations at the base of the Key West hypolimnion, but does not readily fit those at Van Stone where ORP and DO change little with depth.

Trace metals and perhaps metalloids are adsorbed by and coprecipitated with and iron and manganese hydroxides (Wetzel, 2001; Smith and Mudder, 1991; Dzombak and Morel, 1990). Some modelers (Schafer and Associates, 1995) have assumed therefore, that oxygen deficient waters of the hypolimnion will dissolve these hydroxides and remobilize trace metals. However, the diminution of dissolved zinc, arsenic, molybdenum, antimony and selenium concentrations in the deep hypolimnion waters at Key West appears to counter that supposition and suggests that other chemical processes, reactions, or interactions are active.

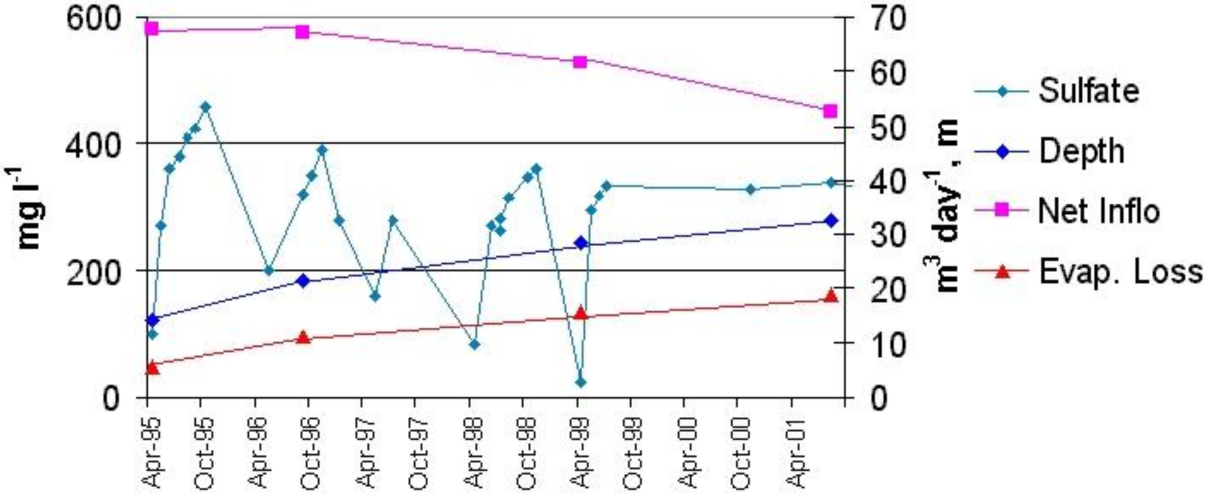


Figure 5. Comparison of sulfate concentrations (mg l^{-1}), water depth (m), evaporative loss (m^3 day^1), and net inflow (m^3 day^{-1}), over time; Key West Pit Lake (Data from Geo-Hydro, 2001).

Figure 5 compares sulfate concentrations in the Key West pit lake to net inflow, evaporative loss and depth over time. Decreasing sulfate concentrations in the lake water were unexpected. Early modeling predicted an accumulation of sulfate caused by progressive oxidation of sulfide minerals in the pit walls (Hydro-Geo, 1996). Modelers assumed that precipitation of gypsum would eventually limit sulfate at an equilibrium level of 1,018 mg l^{-1}. However, peak sulfate concentrations declined steadily from 440 mg l^{-1} in 1995, to 340 mg l^{-1} in 2001. Dilution accompanying pit filling does not explain this decline as net inflow has decreased and evaporative losses increased with the rising lake level; both of which, should increase sulfate concentrations—assuming constant sulfate influx. Instead, either sulfate loading has diminished significantly or the anion is being removed from the system. Reduced sulfate loading could be expected when sulfides exposed to weathering become fully oxidized, are isolated by oxide coatings (Blanchard, 1968) or are submerged by rising waters (Steffen et al., 1992). Considering the evidence for anaerobic bottom waters at Key West, sulfate could be removed by sulfate reducing bacteria at the sediment-water interface (Wetzel, 2001; Cole, 1994), or possibly by other chemical processes. The development of true anoxic conditions at Key West appears to be limited and intermittent, however, and I believe that reduced loading is the most likely explanation for falling sulfate concentrations in this lake. If true, oxidation and potential acid generation processes at Key West have been relatively short lived, despite significant exposure of pyrrhotite, pyrite and other sulfides in the pit walls.

The observations and empirical data from the Key West and Van Stone pit lakes are useful for, and should be considered, when developing, calibrating, and validating water quality models for circum-neutral mine pit lakes in temperate climates.

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