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The aqueous geochemistry of the Berkeley Pit, Butte, Montana, U.S.A.

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Abstract—Water levels in the Berkeley Pit, Butte, Montana are currently rising approximately 22m per year following the cessation of pumping in 1982. Projections suggest that the pit may be filled to capacity at the 5520-ft (1682-m) elevation by the year 2009 if remedial action is not implemented. In addition, as the water level in the pit continues to rise, there is the potential for encroachment of contaminated water into the alluvial aquifer and subsequent transport of metals downgradient to Silver Bow Creek. Geochemical measurements and aqueous samples collected during October 1987 indicate that water in the Berkeley Pit is moderately oxidizing (Eh +460 mV below 30 m), acidic (pH 3.0) Ca–Fe sulfate solution. The principal ions are Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Na, SO_4 and Zn, which typically increase in concentration from the surface to the bottom of the pit. Arsenic occurs mainly as As (V) in total metal concentrations up to 1 mg/l, Fe as Fe(III) in the top 3 m, and as Fe(II) below this depth in concentrations up to 1000 mg/l. Sulfate was measured in concentrations up to 6780 mg/l from the deepest (130 m) sample. Copper and Zn were found in total metal concentrations of 202 and 512 mg/l, respectively, at the 130 m sampling depth. To verify the field Eh measurements, MINTEQ was used to calculate a theoretical Eh based on the Fe(II)/Fe(III) couples. The results suggest that the ratio Fe(II) : Fe(III) is representative of the system Eh when both species occur in measurable quantities (>0.25 mg/l) and when the minor species constitutes at least 5% of the total concentration. Data from this study were used in the geochemical computer code PHREEQE to evaluate potential remediation of the water body through the addition of alkaline tailings fluid produced at the current milling operation on site. Five cases were evaluated, two representative of conditions under ice cover (PCO_2 not fixed), and three open system simulations ($PCO_2 = 10^{-3.5}$). Mineral controls included $Fe(OH)_3$, gypsum ($CaSO_4.2H_2O$), jurbanite ($AlOHSO_4$) and jarosite [$KFe_3(SO_4)_2(OH)_6$]. The addition of three volumes of alkaline slurry to the existing volume of acidic fluid would raise the pH to 5.0. This option would take approximately 7 a at the current rate of production (11.6 million gallons per day; 43.9 Ml/d). At this time the fluid level would be approximately 20 m above the alluvial/bedrock contact.

INTRODUCTION

THE BERKELEY pit in the Butte Mining District encompasses approximately 2.5 km^2 of the upper Silver Bow Creek drainage area, southwestern Montana (Fig. 1). During excavation it reached a maximum depth of 542 m with a lateral extent of approximately 1.8 km by 1.4 km across at the rim. In the U.S.A. it is exceeded in size only by the Bingham pit, Salt Lake City, Utah. Flooding of the pit commenced in late 1983, one year following cessation of dewatering pumpage in the adjacent Kelley shaft in April 1982. In October 1987, the static water level in the pit was approximately 200 m below the rim of the pit, and was rising at a rate of 22 m per year.

The hydrological components controlling the present Berkeley Pit water balance are net evaporation, surface water inflows and ground water inflows. Since 1984 the total average inflow rate to the Berkeley Pit has been estimated from water levels in the hydraulically connected Kelley Shaft to be 7.6 million gallons per day (28.7 Ml/d). Ground water flow into the pit includes seepage from the Yankee Doodle tailings pond, the leach pads, and the West Camp mines. The major sources of surface water runoff into the pit are the gland seal bleed, acidic water seeping from the leach pads, and a discharge from the alluvial aquifer intercepted by the pit which combine and spill over the eastern rim (Fig. 1). Net evaporation has been estimated to be 0.08 million gallons per day (0.3 Ml/d; CAMP DRESSER and MCKEE, 1988).

In order to estimate the date of inundation, a relation between void space filled and time was developed using water level data from the Kelley shaft. Extrapolating this linear relation indicates that the pit will overtop (at elevation 5520 ft; 1682 m) during the year 2009, plus or minus one year, and that the interface between the bedrock and the alluvial aquifer (at elevation 5320 ft; 1622m) would be inundated by 1996.

The objectives of this study were to characterize the aqueous solution in the pit, to define processes which may control metal concentrations and distribution, and to model the feasibility of neutralizing the pit fluid using an alkaline tailings solution produced at the Weed concentrator, adjacent to the Berkeley Pit.

Currently, the pit contains an acidic metal sulfate

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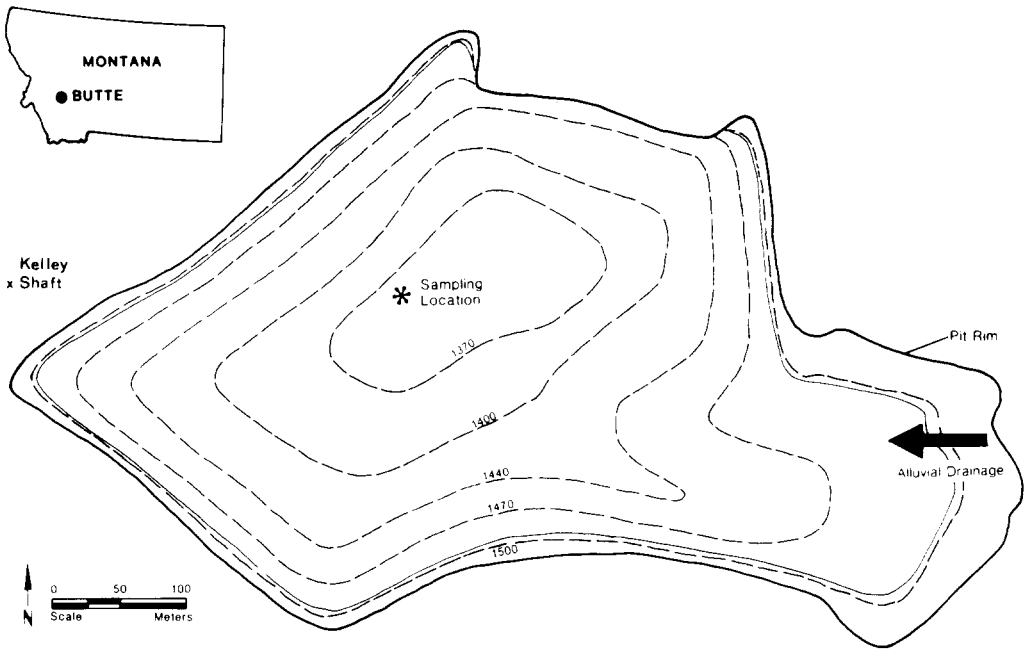


FIG. 1. Topography of the Berkeley Pit (Anaconda datum) showing the location of the Kelley Shaft and the surface water inflow.

solution. Two important constituents are Fe and As. Iron is important because of the capacity of amorphous ferric hydroxide to scavenge metal ions from solution (FAIR *et al.*, 1968). Creating conditions conducive to amorphous ferric hydroxide precipitation may therefore aid in remediating solutions containing elevated metal concentrations. An understanding of As chemistry in the pit is necessary to determine impacts on the alluvial aquifer which may act as a conduit to Silver Bow Creek downgradient from the pit. Arsenic(III) is of special concern because of its toxicity (PENROSE, 1974), its mobility compared to As(V) (DEUEL and SWOBODA, 1972), and because As may not be significantly retarded under the more alkaline conditions which will be created if the acidic pit water interacts with the calcareous alluvial aquifer.

Both the Fe(II)/Fe(III) and As(III)/As(V) couples may be linked with the system pH and Eh; thus accurate Eh measurements are critical in predicting the fate of these metals, either during remedial activities or to estimate contaminant transport in the alluvial aquifer.

Although dilute ground water systems have been shown not to have a "system" Eh (LINDBERG and RUNNELLS, 1984), the same is not true for high ionic strength solutions containing elevated concentrations of Fe. BALL and NORDSTROM (1985) have shown that the ratio of Fe(II) : Fe(III) activities is representative of measured Eh values in surface waters impacted by acid mine drainage in California. DAVIS *et al.* (1988) showed that in an acid mine drainage environment in Colorado, the field Eh could be calculated accurately using the relative activities of the Fe^{2+}/Fe^{3+} couple at low pH (<3.0), and by the $Fe^{2+}/Fe(OH)_3$ reaction at >pH 3.0. In addition, they proposed that at least 1 mg/l of Fe was necessary to poise redox equilibrium in the system. Finally, the oxidation of Fe(II) to Fe (III) appears to be kinetically feasible based upon the work of LANGMUIR and MAHONEY (1985) who established a half rate of 8.6 min for the reaction:

$$4\ Fe^{2+} + O_2 + 2H_2O = 4FeOH^{2+} \qquad (1)$$

between pH 2.2 and 3.5 in a bacterially mediated environment. These data suggest that the Fe couple reaches equilibrium rapidly in response to changes in solution potential. By analogy, Eh measurements should be representative of the system Eh in solutions containing both Fe(II) and Fe(III).

Another factor controlling dissolved metal concentrations is the tendency of the analytes to form insoluble compounds. The potential for *in situ* mineral precipitation under ambient conditions in the pit, during remedial activities, or through rock/water interactions, may be predicted using the saturation index (SI). The SI is based on the relation between analyte activities (the ion activity product; IAP) and the thermodynamic calculation for the solubility product (K_{sp}). The SI of a mineral may be determined by geochemical computer codes, using the equation:

$$SI = \log_{10} \frac{[IAP]}{[K_{sp}]}. \qquad (2)$$

If the SI is greater than zero, the solid is theoretically oversaturated with respect to the solution, and may precipitate in the water column. If the SI is less than zero, the solid is undersaturated with respect to

the solution, and, if present in the system, will dissolve into the solution. At SI = 0, the solid and solution are in equilibrium.

The SI is based on equilibrium thermodynamics; therefore only minerals or solid phases for which precipitation of dissolution are kinetically favorable may reasonably be considered in the Berkeley Pit system. These solids are generally amorphous (ferric hydroxide) and dissolve or precipitate rapidly (calcium carbonate, gypsum). Over a longer time span (months/years), minerals which are known to form authigenic precipitates (e.g. quartz overgrowths, secondary microcline, anhydrite) may be considered for inclusion in simulations which consider the interaction between the pit solution and the alluvial aquifer. Throughout the ensuing discussion, precipitation of solids is included as a potential control on metal solubility.

FIELD PROCEDURES

Because of the difficulty of gaining access to the water surface of the pit, investigators and a fiberglass boat were transported by helicopter from the rim to a bench at the 1500 m level on 16 October 1987. Personnel in the boat were guided to the location that was expected to provide the deepest profile based on the topographic maps, and a depth sounding made using a Hydrolab Surveyor II Sonde assembly. The maximum recorded water column depth was measured at 134 m. Replicate measurements determined that the pit bottom was consistently at about 130 m, compared to a mapped depth of 168 m. This suggested that sloughing of the pit walls had filled in at least 38 m at the base of the cone, and that the bottom was essentially flat.

In situ measurement of physical parameters using the pre-calibrated sonde proceeded from the bottom of the pit to the surface. Profile data were evaluated for the presence of a thermocline (based on the temperature) or a chemocline (based on the pH or Eh). These data provided information on depths at which there were large fluctuations in water chemistry over a short vertical distance, aiding selection of sampling points during sonde ascent. To ensure that samples were collected contemporaneously with measurements of the physico-chemical parameters, water samples were pumped from depth through vinyl tubing strapped to the sonde housing and conductor cable. It must be stressed that the profile in this study represents only one point in time and space in the pit, and that the distribution of metals, solids, and the physico-chemical measurements themselves may vary both temporally and spatially.

Temperature, pH, Eh and specific conductivity measurements were also made at the surface: (1) to ensure that an adequate water volume had been purged through the tubing to provide a representative sample from the depth of interest, and (2) to check that there were no significant changes in the physico-chemical parameters, and therefore fluid chemistry, as water was raised from that depth. At the surface, the pH was measured using a Haake Buchter pH stick, specific conductivity and ambient water temperature by a YSI Model 33 probe, and the Eh of the solution determined using an Orion meter and probe.

After an adequate purge period, water from each depth was passed through a pre-weighed, qualitative Fisher No. 44 filter in tandem with a 0.45 μm Nuclepore filter. The volume of water filtered (3.2 l/depth) was estimated based on the size and number of sample bottles collected. Following sample collection at each depth, the filter assembly was dismantled, the equipment thoroughly rinsed with deionized water, and the filters placed in a plastic bag for further analysis.

Samples from each depth (surface, 1, 3, 15, 31, 66, 100 and 130 m) were collected for total metals (unfiltered, acidified to 0.5% HNO_3), dissolved metals (filtered, acidified to 0.5% HNO_3), anions (filtered, unacidified), and species of As and Fe (filtered and acidified to 0.5% HCl). Hydrochloric acid was used rather than HNO_3 in order to prevent possible oxidation of Fe(II) to Fe(III) and of As(III) to As(V).

Upon return to the laboratory, samples were stored in a refrigerator and shipped on ice to the analytical laboratory the next day. Samples for Fe and As speciation were analyzed within 24 h after sample collection. The filters were air-dried overnight at room temperature and re-weighed to determine the mass of particulate material (>0.45 μm) filtered from solution at each depth, after which they were submitted for total metals and sulfate analysis.

ANALYTICAL METHODS

Aqueous metal concentrations were determined using inductively coupled plasma spectrometry, and major anions measured spectrophotometrically by VERSAR Inc., Springfield, VA, following procedures established by the Contract Laboratory Program (CLP, USEPA, 1986). In addition to the samples collected from each of the eight depths, a travel blank, an equipment blank, and adequate sample for one duplicate analysis were submitted to the laboratory. None of the data were qualified by either duplicate or spike limitations.

In addition to the CLP analyses, As was measured by the arsine hydride method (Shaikh and Tallman, 1978) by the Montana Bureau of Mines and Geology (MBMG). Following reduction of the sample using KI, total As was determined using a Perkin Elmer model flame spectrometer. Arsenic(III) was measured on the untreated sample and As(V) obtained by difference. Use of this method to determine total As is less subject to broad spectrum interference than is the CLP procedure. However, the As (III) analysis is subject to interference by elevated concentrations of Cu and Fe (Crock and Lichte, 1982), as evidenced by the poor spike recoveries (53%) for this method.

Iron was analyzed using the bipyridine technique (USGS, 1979). Iron(II) and total Fe were determined colorimetrically at the MBMG, and Fe(III) obtained by difference. Table 1 compares CLP total Fe analyses with the spectrophotometric total Fe determination. With the exception

Table 1. Concentrations of Fe^{2+}, Fe^{3+}, and total Fe in Berkeley Pit samples as a function of depth, pH and Eh

Depth (m)	pH	Field Eh(v)	Predicted* Eh(v)	Fe^{2+}† (mg/l)	Fe^{3+}‡ (mg/l)	Fe (total)† (mg/l)	Fe (total)§ (mg/l)‡	RPD‖ (total)
0	2.76	0.82	0.88	0.25	196	196	185	6
1	2.72	0.72	0.73	60	142	202	202	0
3	2.84	0.64	0.62	262	14	276	386	33
15	2.95	0.57	0.62	622	28	650	688	6
31	3.08	0.50	0.58	900	10	910	916	1
66	3.15	0.46	¶	938	¶	854	1010	17
100	3.15	0.47	0.59	944	14	958	1020	6
130	3.14	0.46	0.60	962	24	986	1060	7

* Eh calculated by MINTEQ using the Fe(II)/Fe(III) couple.
† Analysis performed at Montana Bureau of Mines and Geology.
‡ By difference.
§ CLP analysis.
‖ Relative percent difference is computed by:

$$\text{RPD} = \frac{\text{CLP Fe} - \text{on-site Fe}}{0.5\ (\text{CLP Fe} + \text{on-site Fe})} * 100.$$

¶ Fe(III) and Eh cannot be determined because the measured ferrous Fe concentration was greater than the total Fe concentration.

of the sample from the 3 m depth, the relative percent differences are all <10%, indicating that the CLP data are comparable with those from MBMG. The charge imbalances for this study were calculated for the speciated solutions using MINTEQ (Felmy *et al.*, 1983). All were ≤ to 15%, indicating that these data are suitable for further analysis.

RESULTS

The thermal profile (Fig. 2) appears to be a result of mixing of surface runoff with the body of water in the pit, upon which was superimposed a seasonal diel cooling in the surficial 2–3 m. The deeper stratum of water (below 30 m) is probably perennially stagnant. Based on the temperature and specific conductivity measurements, water in the pit may be classified as meromictic, characterized by incomplete mixing through the water column accompanied by a salinity gradient (Wetzel, 1975).

The specific conductance (corrected to 25°C) of the water increased with depth from 4100 μmhos/cm at the surface to an average of 7100 μmhos/cm near the pit bottom.

The pH increased from 2.7 at the surface to 3.17 at

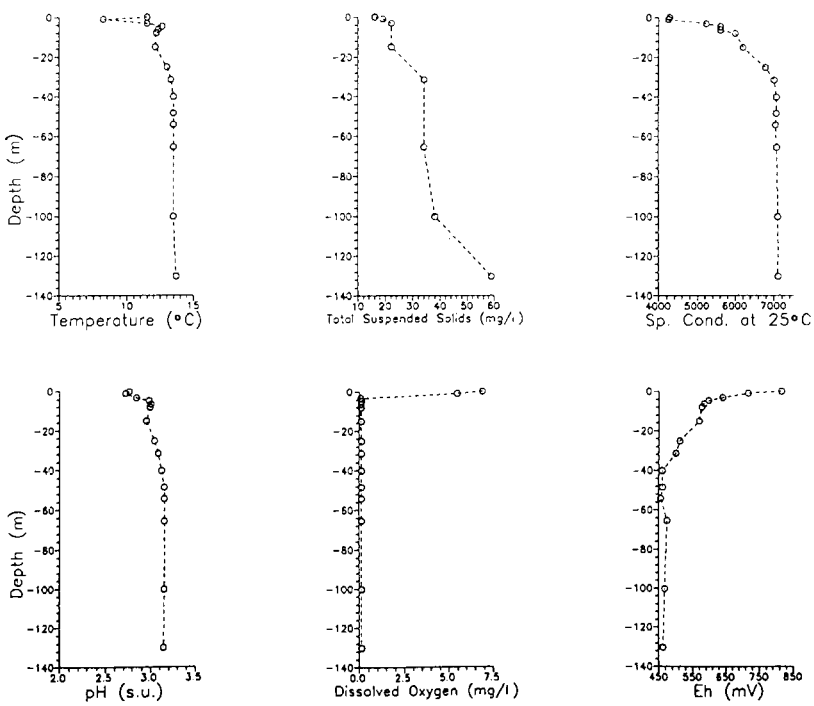


Fig. 2. Temperature, specific conductivity, suspended solids, pH, dissolved oxygen and Eh profiles

the bottom. The acidic nature of the pit water is probably due to bacterially mediated oxidation of pyrite and other metallic sulfides in the mine shafts and workings which transport water into the pit. The slightly lower surface pH may be a result of mixing with the more acidic surface water runoff from the leach pads, in conjunction with the precipitation of amorphous ferric hydroxide by the reaction:

$$Fe^{2+} + 3H_2O = Fe(OH)_3(s) + 3H^+ + e^- \quad (3)$$

which results in a consequent depression of the pH as Fe^{2+} is oxidized and precipitates to form amorphous ferric hydroxide.

The dissolved oxygen (DO) profile in the Berkeley Pit is dominated by diffusion across the air/water interface, the concentration decreasing exponentially from the surface (6.9 mg/l) to 3 m (0.1 mg/l). Below this depth the system is essentially anoxic.

The Eh profile indicates that the solution is moderately oxidizing (Baas Becking *et al.*, 1960) with a minimum Eh of +450 mV (pE 7.6) and a maximum at the surface of +817 mV (pE 13.8). To test the validity of the Eh measurements, MINTEQ was used to calculate the theoretical Eh based on the measured concentration of the Fe(II) and Fe(III) species at each depth (Table 1).

Comparison between the measured and predicted Eh values shows good agreement (<20 mV) for the samples from 1 and 3 m, but larger discrepancies (>50 mV) at the surface and with increasing depth (Table 1). The success at 1 and 3 m is probably due to the presence of both Fe(II) and Fe(III) at concentrations well above the method detection limit (0.25 ppm) with the minor of the two species representing at least 5% of the total concentration. At other depths the minor species were at, or close to, the method detection limit, coinciding with deviations between the measured and calculated Eh values. This suggests that the concentrations reported for Fe(II) at the surface, and for Fe(III) at 15 m and deeper represent inaccuracy inherent in the technique at low concentrations, and the partial oxidation of Fe II, respectively.

Similar calculations to determine the theoretical Eh for the As species were not possible, due either to poor agreement between CLP and MBMG As analyses or to an inadequate percent spike recovery for As(III).

PIT WATER CHEMISTRY

Major ions

Concentrations of Ca, K and Mg increased with depth while Na remained at approximately 70 mg/l throughout the profile (Fig. 3). All the major cations occurred primarily in the dissolved form, although up to 30% of K, and 50% of Ca were associated with colloidal material. The occurrence of Ca in the particulate fraction suggests precipitation of a solid phase (e.g. gypsum) in the water column. This hypothesis is supported by a parallel increase in SO_4 concentrations with depth, by the large concentrations of SO_4 measured on the filters, and by the theoretical oversaturation of gypsum throughout the water column (Fig. 4). Chloride concentrations increased sharply from the 15 m to the 30 m depth with a smaller percentage increase between the 100 and 130 m depth (Fig. 4).

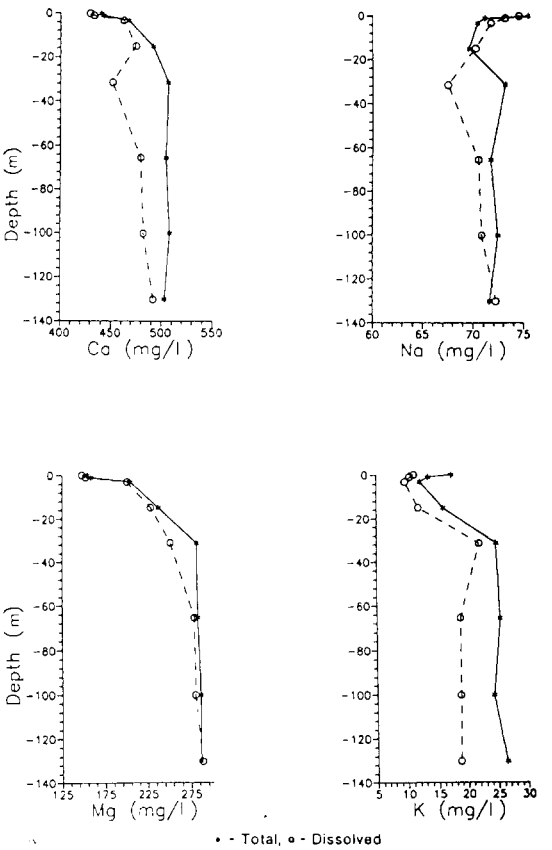


FIG. 3. Calcium, Na, Mg and K profiles.

Aluminum

Elevated concentrations of Al are probably a result of the acid-enhanced dissolution of Al-silicate minerals. Aluminum exists principally in the dissolved form (Fig. 5). The remainder is either sorbed to particulate material or occurs as a solid phase. Nordstrom (1982) suggested that an aluminum sulfate solid may control Al solubility in some acidic sulfate-rich waters (Fig. 6). Of the possible mineral phases, alunite $[KAl_3(SO_4)_2(OH)_6]$, "microcrystalline" gibbsite, K-alum, basaluminite and kaolinite are all undersaturated by many orders of magnitude based on MINTEQ calculations, but jurbanite ($AlOHSO_4$) is oversaturated with respect to the solution. Jurbanite was selected as a solubility control

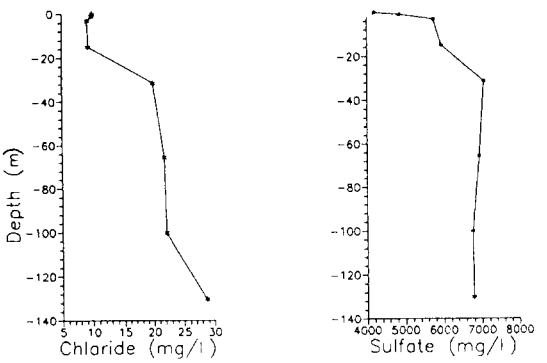


FIG. 5. Aluminum profile and SI profile of $AlOHSO_4$.

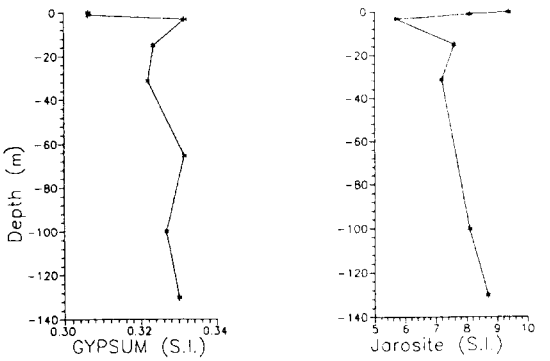


FIG. 4. Chloride and sulfate profiles, and SI profiles of gypsum and K-Jarosite.

because superposition of Berkeley Pit data on a plot of pAl + 3pOH vs 2pH + pSO_4 (VAN BREEMEN, 1973) falls on the line represented by $AlOHSO_4$. In addition, alunite, the only other solid possibly represented by pit Al chemistry, is stable only over the pH range 3.3–5.7 for the activity of SO_4 reported in the Berkeley Pit (NORDSTROM, 1982).

Iron

Iron in the Berkeley Pit fluid is an important constituent because of its ability to flocculate and scavenge trace metals (FAIR *et al.*, 1968; LECKIE *et al.*, 1980). Therefore, the Fe concentration and the redox state are important pieces of information when considering cleanup alternatives. Field observations indicate that following ice-out in the spring, the surface water of the pit is a blue-green color. By midsummer it has turned brown, suggesting that the water color is directly related to Fe chemistry in the pit. We hypothesize that during the winter, amorphous ferric hydroxide present in the water column dissolves, with concomitant reduction of Fe(III) to Fe(II) under the ice cover as conditions become anoxic. The cause of the blue–green color evident immediately after ice-out is probably due to the ferrous sulfate complex, $FeSO_4^0$. During the summer months, oxygen diffuses through the top 4 m and oxidizes Fe(II) to amorphous ferric hydroxide, producing a brown, cloudy solution. This is a surficial phenomenon only; below 4 m in October the water color was blue–green and Fe was in the ferrous state (Fig. 7).

Chemical analysis indicates that the majority of Fe was in the dissolved form, therefore, even at the surface, amorphous ferric hydroxide is of minor significance in terms of its ability to scavenge other metals. This conclusion is supported by the preponderance of trace metals occurring in the dissolved fraction compared to the total metal fraction, and by the work of SCHULTZ *et al.*, (1987) who found that ferrihydrite loaded with trace metals at a pH of 9.5 desorbed all metals as the pH decreased to 4.5. Extrapolating their data to this study suggests that although amorphous ferric hydroxide may precipitate, it is not capable of scavenging metals in significant quantities under the acidic conditions prevalent in the Berkeley Pit.

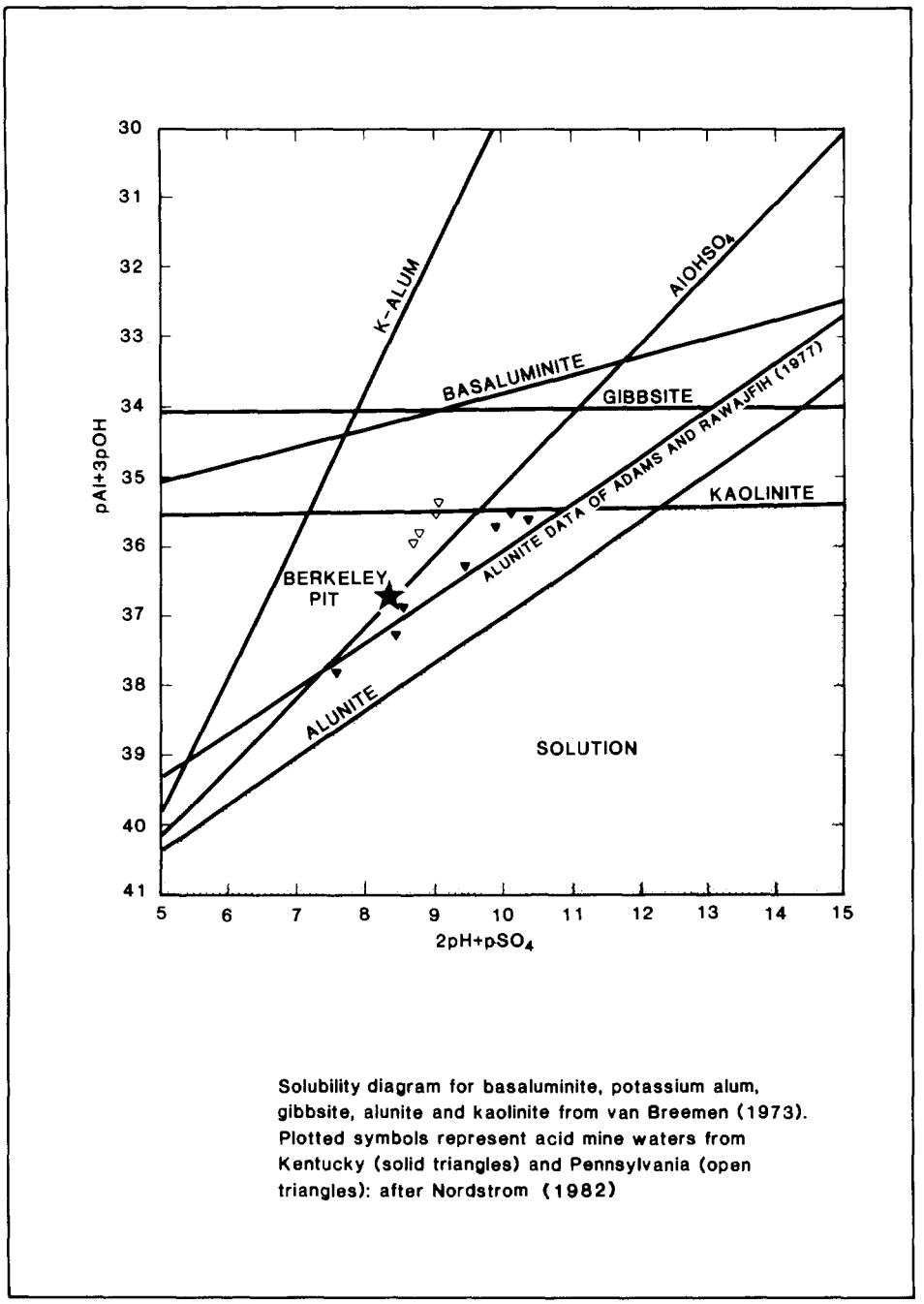
The presence of amorphous ferric hydroxide in the top 4 m and its visual absence below this depth suggest that it is oversaturated at depths above 4 m and undersaturated below this depth. Based on PHREEQE (pH Redox Equilibrium Equations, PARKHURST *et al.*, 1985) calculations, a pK_{sp} of −15.7 for amorphous ferric hydroxide was found to satisfy the saturation index conditions in the Berkeley Pit. This value is equivalent to a pK_{sp} of 38.4 for the reaction:

$$Fe(OH)_3 = Fe^{3+} + 3OH^- \qquad (4)$$

which is in close agreement with the value of 37.5 determined for the fresh material by the laboratory experiments of LANGMUIR and WHITTEMORE (1970).

Arsenic

The possible sources of As are from the dissolution of arsenopyrite and from leaching of mine timbers which were treated with arsenic-bearing solutions for preservation purposes. However, the latter source appears to be insignificant because surficial As concentrations in the upper 30 m of the pit were lower



Solubility diagram for basaluminite, potassium alum, gibbsite, alunite and kaolinite from van Breemen (1973). Plotted symbols represent acid mine waters from Kentucky (solid triangles) and Pennsylvania (open triangles): after Nordstrom (1982)

FIG. 6. Activity diagram showing candidate solids controlling Al solubility.

than at depth, despite the presence of a large number of mine timbers floating on the surface.

The majority of dissolved As occurs as As(V) (Fig. 8). This is consistent with the redox state of the fluid and with the distribution of As species under the pH–Eh regime predominant at depth in the Berkeley Pit. The phases, and therefore the mechanism controlling As solubility, may be investigated by constructing an Eh–pH diagram using the data in Table 2 in conjunction with the As, Fe and SO_4 activities calculated using PHREEQE. Figure 9 depicts the predominant species under surface conditions. In this diagram, Berkeley Pit surface water plots in the $FeSO_4^+$ field. It is noteworthy that the only solid phase found in an oxic environment, scorodite ($FeAsO_4.2H_2O$), controls As solubility only between pH 4 and 5. The other phases are included for completeness and to indicate the probable solubility controls on As, Fe and S if neutralization of the acidic water was to be selected as a remedial treatment (represented by the "reaction path" on Fig. 9). Figure 10 shows the same system with the addition of K-jaro-

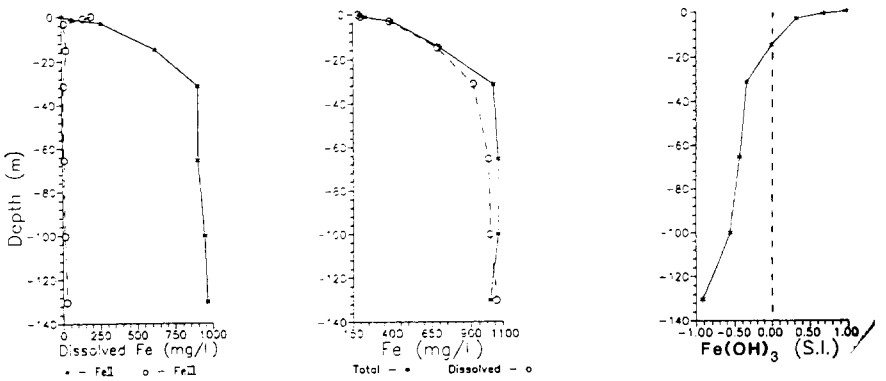


FIG. 7. Fe(II), Fe(III) and total Fe profiles and SI profile of $Fe(OH)_3$.

site, ubiquitous in acid mine drainage environments (CHAPMAN *et al.*, 1983; FILLPEK *et al.*, 1988). Evidence for the occurrence of jarosite in the water column is provided by the filter analyses which exhibited significant concentrations of K, Fe and SO_4, and by the differences between dissolved and total K and Fe concentrations in solution (Figs 3 and 7).

The jarosite field encompasses the pH–Eh domain of Berkeley Pit surface water and may potentially control the solubility of K, Fe and S over a wide range of pH and Eh, depending on the kinetics of precipitation and dissolution of the mineral. The extensive area of predominance in acidic to neutral, oxidizing pH–Eh space explains why it is such a common alteration product in pyritiferous mine waste.

Trace metals

Trace metals (especially Cu and Zn) in the Berkeley Pit solution occur at concentrations high enough that economic recovery through such techniques as electrowinning or reverse osmosis may be a tractable alternative to remediate the acidic pit water. For comparison purposes and to highlight the potential impact of intrusion of the pit water into the alluvial aquifer, the Federal primary drinking water standards (USEPA, 1985) are compared with trace metal concentrations in the pit solution.

Lead occurs in low concentrations (<1 mg/l) in the Berkeley Pit (Fig. 11), probably because mining operations did not significantly intrude into the Pb–Ag zone of the porphyry cupola, resulting in limited dissolution of galena. Cadmium concentrations (from the dissolution of sphalerite, where it occurs in solid solution with Zn) reach a maximum of 1.9 mg/l at the 100 m depth (the drinking water standard is 10 μg/l). Copper (from chalcopyrite dissolution) has a maximum concentration of 214 mg/l at 200 m, compared to a secondary drinking water standard of 1 mg/l. Manganese, a metal ubiquitous to many mineral deposits, occurs at a maximum concentration of 165 mg/l, while Zn occurs at a maximum concentration of 500 mg/l, compared to Federal secondary drinking water standards of 50 mg/l and 5 mg/l, respectively. Obviously, if the pit water ever intruded into the alluvial aquifer there would be multiple violations of Federal water standards. This problem may be mitigated to some extent by retardation of these metals in the calcareous alluvium/colluvium. Any caliche present in the aquifer will neutralize the acidic pit water resulting in the precipitation of metal carbonates and hydroxides, and the sorption of cations to negatively charged clay minerals and metal oxyhydroxides.

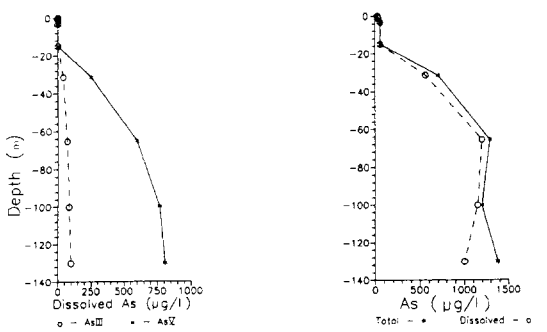


FIG. 8. As(III), As(V) and total As profiles.

METAL RATIOS IN SURFACE AND DEEP WATER

Inspection of the metal profiles in the pit indicates that there is an increase in analyte concentrations from the surface down to approximately 30 m, below which the water body appears to be chemically homogeneous. This stratification appears to be the result of past and present surficial dilution by the surface water inflow which enters the pit over the east wall (Fig. 1). This more dilute solution (Table 3) has apparently mixed with the more concentrated water from the mine workings to produce a solution of intermediate concentration in a zone which extends through the top 30 m. This hypothesis is further supported by the temperature and conductivity profiles (Fig. 2) which increase steadily to 30 m, below which a constant value was recorded.

Table 2. Thermodynamic data used to construct the Eh–pH diagrams shown in Figs 9 and 10

Species	Free energy (kJ/mole)
Aqueous	
K^+	−274.930
H_2CO_3	−623.165
HCO_3^-	−586.848
CO_3^{-2}	−527.895
SO_4^{-2}	−741.991
HSO_4^-	−756.010
H_2S	−27.865
HS^-	12.040
H_3AsO_3	−639.820
$H_2AsO_3^-$	−587.140
$HAsO_3^{-2}$	−509.230
AsO_3^{-3}	−430.740
AsO^+	−163.800
H_3AsO_4	−766.010
$H_2AsO_4^-$	−753.160
$HAsO_4^{-2}$	−714.590
AsO_4^{-3}	−648.390
Fe^{+2}	−78.910
Fe^{+3}	−16.990
$Fe(OH)^{+2}$	−229.410
$Fe(OH)_2^+$	−436.140
$FeSO_4^+$	−785.379
$FeSO_4$	−848.222
$Fe(OH)_4^{-2}$	−796.680
$Fe(OH)_4^-$	−830.106
$Fe_2(OH)_2^{+4}$	−467.350
$Fe_3(OH)_4^{+5}$	−926.590
$Fe(OH)^+$	−277.400
$Fe(OH)_2$	−463.180
$Fe(OH)_3^-$	−614.880
$Fe(OH)_3$	−667.640
$FeH_2AsO_4^{+2}$	−793.700
$FeHAsO_4$	−814.210
$FeH_2AsO_4^+$	−847.680
$FeAsO_4$	−767.760
$FeHAsO_4^+$	−788.680
$FeH_2AsO_3^{+2}$	−619.610
$Fe(H_2As_2O_3)_2^+$	−1213.030
$FeH_2AsO_3^+$	−670.280
Solids	
$Fe(OH)_3$	−687.850
$FeCO_3$	−666.720
$FeAs_2$	−52.090
FeAsS	−125.70
$Fe(OH)_2$	−479.900
$FeHAsO_4$	−846.420
$Fe_3(AsO_4)_2$	−1753.100
$Fe(AsO_2)_2$	−689.060
FeS_2	−160.240
FeS	−101.336
$KFe_3(SO_4)_2(OH)_6$	−3299.500
$FeAsO_4.2H_2O$	−1267.100

The figures were calculated at 298.15°K because free enthalpies of formation are not available for the majority of the species. However, the effect on the location of the equilibrium lines is negligible between 281°K and 298°K and for hydrostatic pressures of 30 atm compared to 1 atm. Thermodynamic data for the Fe–As species were made available by Professor Bob Robins of the University of New South Wales, Australia.

A comparison between the sample collected from 30 m in the pit with a sample of the surface water inflow by MBMG in 1984 shows that all elements are more concentrated in the 30 m sample, with the exception of Cl, Cd and Na. Sodium is concentrated by a factor of only 1.1. The presence of a conservative tracer (Na) found in similar concentrations in both fluids provides additional evidence that the influent water has diluted the upper 30 m of water in the pit. Another method of evaluating the data is to predict the results of the mixing, which should be most apparent in the surficial water. The surface (0 and 1 m) analyses are not considered because of precipitation and sorption reactions which will remove metals from solution. However, below the chemocline (~3 m), the analyte concentrations should fall between those at 100 m and in the water from the leach pad. This is the case for Al, As, Ca, Fe, K, Mg, Mn, SO_4 and Zn (Table 3). In conclusion, it appears that metal concentrations in the top 30 m of the pit solution are the result of an extremely complex set of variables, including mineral precipitation at the surface, a seasonally fluctuating chemocline, and mixing of two chemically distinct waters.

Table 3. Comparison of 3 m, 100 m, and surface water runoff chemistry

Analyte (mg/l)	Leach water	3 m	100 m
Ca	453	462	506
Mg	194	201	272
Na	66	72	73
K	4	10	25
Cl	12	9	20
SO_4	3850	5740	7060
As	0.03	0.05	0.7
Al	126	152	206
Cd	1.3	1.3	1.9
Cu	69	156	218
Fe	250	386	1040
Mn	79	95	162
Zn	184	280	496
pH	2.86	2.80	3.08

Analysis of filters

Analysis of suspended solids in the water column aids in understanding metal solubility controls on pit fluid chemistry. Total suspended solids at each depth were determined gravimetrically (Table 4). The concentrations of total suspended solids are typical of any freshwater body, ranging up to 59 mg/l at the 130 m depth. It is possible that there are two processes driving their concentrations in the pit. The first may be the surficial precipitation of amorphous $Fe(OH)_3$, followed by dissolution as the solid descends through the water column. The other may be introduction of particulate material into the water body through sloughing of talus from the pit walls.

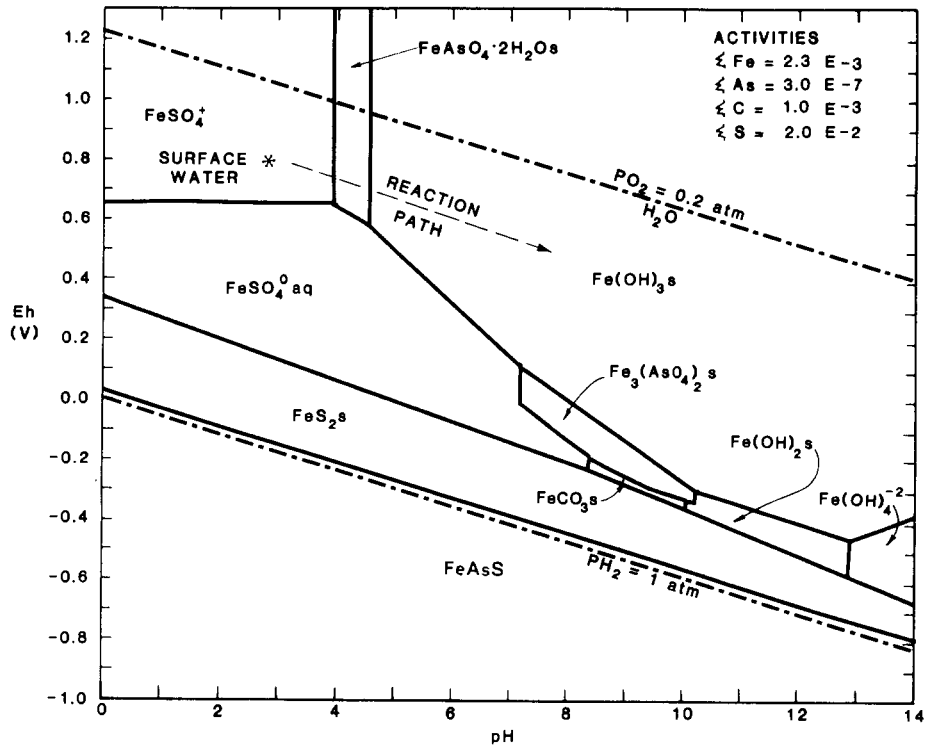


FIG. 9. Eh–pH diagram of the As–Fe–S system at the surface.

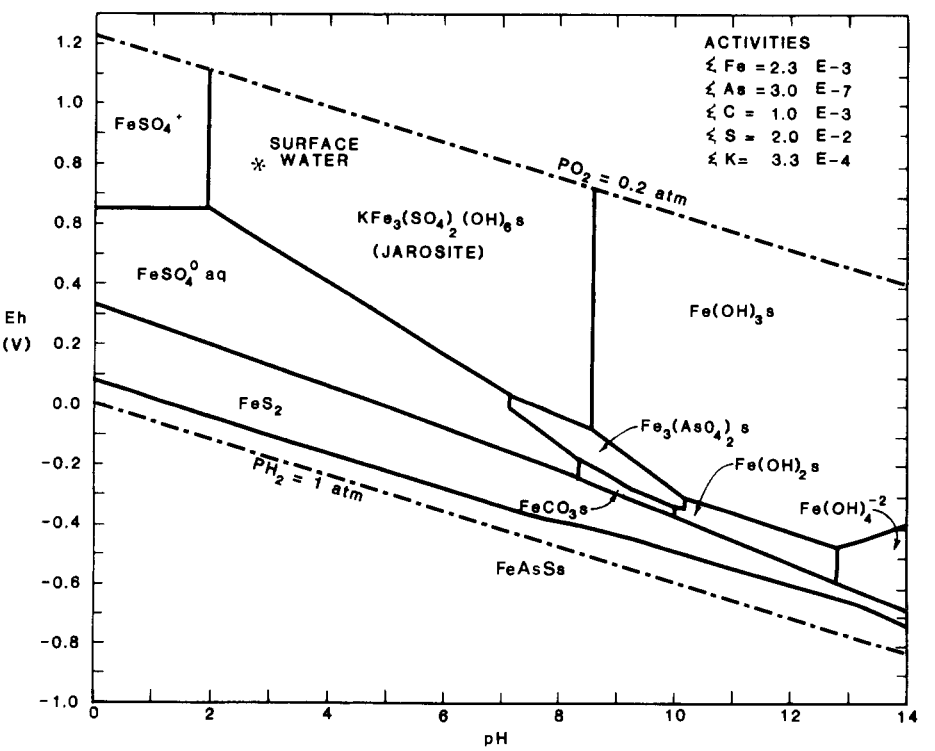


FIG. 10. Eh–pH diagram of the AS–Fe–S system at the surface, including jarosite.

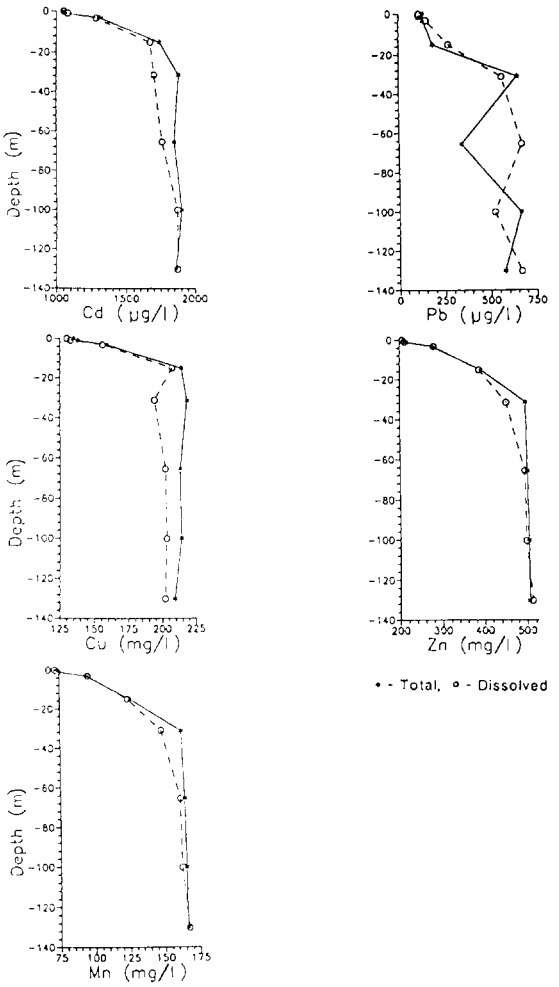


FIG. 11. Cadmium, Cu, Mn, Pb and Zn profiles.

After gravimetric analysis, the filters were subjected to chemical analysis. The particulate matter consists principally of Al, Ca, Fe, K, SO_4 and Zn. Based on geochemical computer modeling of these aqueous analyses, visual observations and work at other acid mine sites (NORDSTROM, 1982, CHAPMAN *et al.*, 1983) realistic candidate minerals include jurbanite ($AlOHSO_4$), jarosite [$KFe_3(SO_4)_2(OH)_6$)], gypsum ($CaSO_4.2H_2O$) and amorphous ferric hydroxide.

This mineral assemblage may be tested by comparing the molar ratios in each solid with those recovered in the filter. For example, at 0 m, the combined Al and Ca accounts for all the SO_4, suggesting that gypsum and jurbanite control Al, Ca, and SO_4 solubility at this depth, with amorphous ferric hydroxide controlling Fe solubility. However, SO_4 could also occur in the form of jarosite (150 μmoles) leaving 21 μmoles to be distributed between Al and Ca. In addition, the ratio Fe : K is 2.4, close to the theoretical 3 : 1 stoichiometry of jarosite. This suite of solids is incorporated into the ensuing modeling effort.

GEOCHEMICAL SIMULATIONS

One option that has been suggested to raise the pH of the pit water is to neutralize the acid pit water with alkaline fluid from the current mineral processing activities. In theory, this should result in an elevation of the system pH, subsequent metal oxyhydroxide precipitation, and concurrent trace metal co-precipitation or sorption. However, the oxidized zone only extends to a maximum depth of 4 m under fall conditions. Below this depth amorphous ferric hydroxide has been shown to dissolve, releasing Fe and any bound metals back into solution under ambient pH conditions.

There are two major classes of alternatives to neutralize the pit water. The acid solution may either be pumped or treated in batch mode, or the alkaline tailings could be pumped directly into the pit. Both alternatives are likely to generate large quantities of sludge. The latter option has the additional problem that ice cover during the winter months will prevent gas exchange across the air/water interface. An additional assumption is that the alkaline tailings slurry (Table 5) will interact predominantly with water at the surface of the pit.

Five conditions were modeled. The first two cases simulated reactions in a closed system (no exchange of CO_2 with the atmosphere), representative of the aqueous environment under ice cover. Case 1 allowed no mineral precipitation or dissolution, while Case 2 incorporated gypsum and amorphous ferric hydroxide in the titration reaction. Cases 3 through 5 simulated conditions in an open system ($PCO_2\ 10^{-3.5}$) while sequentially introducing additional minerals into the model, e.g. Case 3: gypsum and amorphous $Fe(OH)_3$; Case 4: gypsum, amorphous ferric hydroxide and jurbanite; and Case 5: gypsum, amorphous ferric hydroxide, jurbanite and jarosite. The fate of As is not an issue here because, although the acidic pit solution will pass through the scorodite ($FeAsO_4.2H_2O$) domain in Eh–pH space as it is neutralized (Fig. 9), the concentrations of As in both the pit surface water and the alkaline tailings fluid were below the method detection limit.

To ensure that the reaction was modeled correctly, it is important that the thermodynamic data used in the simulations are both accurate and internally consistent. The data base used in PHREEQE was the same as that developed for WATEQ2 by BALL *et al.*, (1979, 1980). This compilation has been critically reviewed by NORONHA and PEARSON (1983) and undergone comparison with WATEQF (PLUMMER *et al.*, 1976). The values of pK_{sp} for solids utilized in these simulations, together with the reactions from which they were calculated, are presented in Table 6.

The results of the simulations show that neutralization of the pit fluid approximates a titration curve. The most rapid increase occurred between pH 3.5 and 5.5, followed by a slow but consistent pH increase in Cases 1 and 2, and stabilization at pH 8.0 in Case 3,

Table 4. Concentration (μg/g) and mass (μmoles) of analytes on filters

Depth (m)	Analyte concentration Al	As*	Ca	Cu	Fe	K	Mn	Zn	SO_4	Mass of solids on filter (g)	Filter weight (g)
0	1280	1 u	2130	394	3280	1610	261	2360	9,640	0.05	1.70
1	1050	1 u	1930	419	3280	1670	233	2370	17,400	0.06	1.68
3	1820	1 u	2850	665	3070	2280	400	3600	10,200	0.07	1.70
15	1560	1 u	2140	590	2280	1990	349	3290	18,300	0.07	1.72
31	1590	7	2200	641	3190	1940	473	3540	29,600	0.11	1.75
66	1490	10	2210	690	3530	1680	527	3330	35,400	0.11	1.76
100	2060	21	2710	790	4240	2600	569	4480	17,700	0.12	1.71
130	2990	82	3450	1330	8280	2890	849	5070	18,000	0.19	1.80
					Micromoles on filter†						
0	81	<0.02	91	11	100	41	8	63	171		
1	65	<0.02	81	11	98	42	7	63	305		
3	115	<0.02	121	18	93	58	12	96	181		
15	99	<0.02	92	16	70	50	11	89	328		
31	103	0.16	96	18	100	49	15	98	540		
66	97	0.23	97	19	111	43	17	92	649		
100	130	0.48	116	21	129	66	18	121	315		
130	199	2.0	155	38	266	73	28	144	338		

*The designator "u" indicates a metal concentration below the reported detected limit.
†Micromoles on filter calculated from:

$$\mu\text{moles} = \frac{\mu\text{g}}{\text{g}} \times \frac{\text{filter wt(g)}}{\text{molecular weight (g/mole)}}.$$

at pH 7.0 in Case 4, and at pH 5.6 in Case 5. The results are expressed in terms of "equivalent pit volumes", where one "equivalent pit volume" represents the volume of fluid in the pit (3.6×10^7 m^3) as of October 1987.

Case 1 showed the most rapid initial rise in pH (Fig. 12). Subsequent simulations which incorporated mineral control generally resulted in a depression in the pH of the mixed solution, presumably due to the release of protons as a result of $AlOHSO_4$, amorphous $Fe(OH)_3$ and jarosite precipitation during the simulation (Table 6).

The solids selected for Cases 2 through 5 were those most likely to be oversaturated, based on the filter paper analyses, field observations and the SI calculations described earlier. Incorporation of gyp-

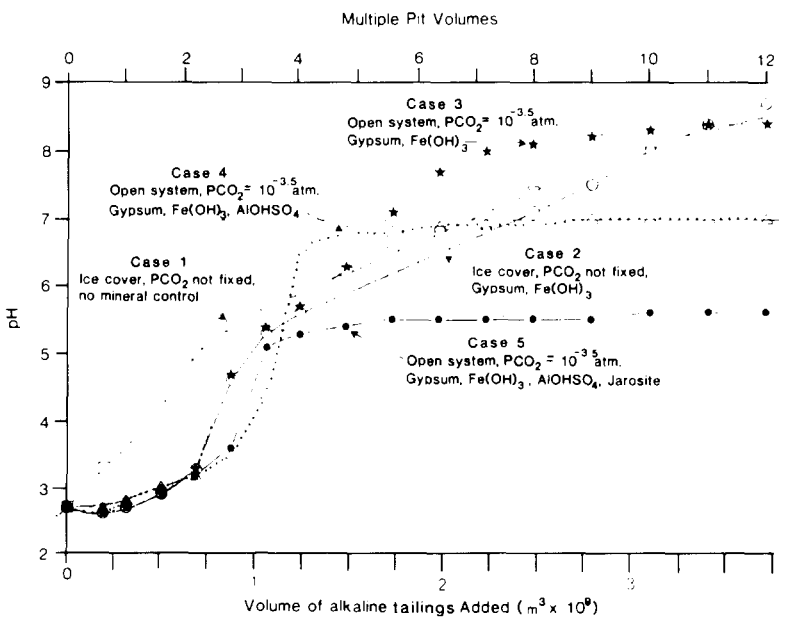


FIG. 12. pH of solution as the acidic pit fluid is titrated with an alkaline tailings fluid.

Table 5. Chemical analysis of the weed concentrator waste stream August 1981 (CH_2M HILL, 1981). Selected values (mg/l) represent the median concentrations

pH	11.3
Total alkalinity ($CaCO_3$)	271
SO_4	1860
As(III)	0.01
Fe(Total)	0.13
Cu	0.04
Zn	0.05
Mn	0.02
Ca	817
Mg	0.3
Pb	<0.01
Cd	<0.01
Hg	0.28

sum, (predicted to be oversaturated in the pit) and amorphous ferric hydroxide (visually observed in the surface water) in the closed simulation resulted in a retardation of inflection in the pH response. Allowing free exchange of CO_2 between fluid and the atmosphere (Case 3) resulted in the same lag as in Case 2, but with an equilibrium pH value of 8.0. Evidently, the simulation pH is affected by the carbonate system. In the closed environment the PCO_2 reached $10^{-1.7}$ atm resulting in a lower pH in the mixed solution.

The addition of jurbanite to the system (Case 4) results in a reaction similar to Case 3 except for attenuation of the initial neutralization, a steeper pH inflection, and an equilibrium condition at a pH of 7.0. The incorporation of jarosite into the model (Case 5) produces a result similar to Case 4, except that the final pH is approximately 5.6. The last three cases demonstrate the effect that the incorporation of additional proton producing reactions (Table 6) into the simulation has on the system pH.

Of particular interest is the volume of alkaline tailings required to elevate the solution pH, maximize As insolubility, increase amorphous ferric hydroxide precipitation and enhance sorption of metals to the precipitate. A pH of 5.0 will optimize As insolubility (Fig. 9), result in increased yield of amorphous ferric hydroxide, and result in partial sequestering of trace metals by the sludge (Leckie *et al.*, 1980). If Case 3 is selected as representative of the reaction, approximately 3 volumes of alkaline fluid are required to achieve a pH of 5.0 in the pit fluid. This would take 7 a at the current rate of production (11.6 million gallons per day; 43.9 Ml/d). The total fluid volume in the pit would be 1.4×10^8 m^3 (elevation 1609 m; 5280 feet) approximately 20 m above the contact between the alluvial aquifer and the subjacent bedrock, assuming that all inflow to the pit, except alluvial and bedrock ground water contributions, could be controlled. This suggests that addition of the alkaline slurry could be a tractable solution to mitigate the impact of the acid mine drainage in the pit; however, the fate and direction of flow in the alluvial aquifer would be prerequisite information prior to implementation of this option.

CONCLUSIONS

The chemical profile of the water body in the Berkeley Pit has been investigated and found to be controlled by mixing of the pit water with surface water runoff, and by both short term and seasonal chemical reactions. Based on realistic geochemical constraints, gypsum, amorphous ferric hydroxide, jarosite and jurbanite have been identified as solids which may control metal solubility in the pit solution.

These solids were incorporated in PHREEQE simulations to predict the neutralizing capacity of an alkaline slurry on the acidic fluid in the pit. The results of this modeling effort suggest that titrating the pit solution with the basic tailings should be considered as an alternative to reduce the concentration of metals and raise the pH in the pit solution.

Based on the results of this initial survey and data interpretation, it is evident that bench scale testing of the neutralization reaction and a determination of the efficacy of precipitating solid phases are necessary. In addition, the effect of ice-cover on the chemocline and hence on redox processes should be investigated. Finally, in order to evaluate the effect of the acid fluid on the alluvial aquifer, a field test is necessary to measure the hydrological characteristics of the aquifer and the interaction between the pit solution and the alluvial material.

Table 6. Thermodynamic data (pK_{sp}) and associated reactions utilized in PHREEQE for solids of interest in the Berkeley Pit simulations at reference temperature 298°K

Solid	Dissociation reaction	pK_{sp}
Amorphous ferric hydroxide*	$Fe(OH)_3 + 3H^+ + e^- = Fe^{2+} + 3H_2O$	−15.70
Gypsum	$CaSO_4.2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O$	4.85
Jurbanite	$AlOHSO_4 + H^+ = Al^{3+} + SO_4^{2-} + H_2O$	3.23
Jarosite	$KFe_3(SO_4)_2(OH)_6 + 6H^+ = K^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O$	−24.3

*The reaction is written in terms of ferrous Fe to meet the data entry requirements of PHREEQE. Mass transfer calculations operate on the solution only after distribution of the valence species based on the measured Eh (assumed for this simulation to be close to that of the mixed solution).

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Chemistry of Snow Meltwater: Changes in Concentration During Melting

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Over much of Norway a large portion of the yearly precipitation falls as snow, and the pollutants contained in precipitation accumulate in the snowpack to be released during a short period in spring. Atmospheric fallout of sulfur compounds has been estimated to be about 30% of the total deposition in Norway, but fallout on the snow cover is probably considerably smaller. During winters with little or no snowmelt before spring, most of the pollutant load is retained in the snowpack. Laboratory and field lysimeter experiments indicate that 50–80% of the pollutant load is released with the first 30% of the meltwater. The average concentration of pollutants in this fraction is 2–2.5 times the concentration in the snowpack itself. The very first fractions may contain more than 5 times the snowpack concentrations. These high concentrations may be due to a freeze-concentration process during snow recrystallization and melting in which contaminants accumulate preferentially at the surfaces of ice particles. The resulting increase in the acid concentration of low-buffered water courses occasionally leads to severe physiological stress to fish and other aquatic organisms and even to massive fish kills. This process occurs at a time which is critical to the hatching stage of salmonid fish species.

INTRODUCTION

Acidic precipitation containing high concentrations of H^+, SO_4, NO_3, NH_4, and several heavy metals falls over large areas of southern Scandinavia [*Dovland et al.*, 1976]. In Norway, where much of the annual precipitation comes as snow, these pollutants accumulate in the snowpack and are released during snowmelt in the spring or during occasional warm periods in midwinter. Regional surveys of the snowpack in late winter show that the acid pollutant load in the snowpack prior to melting is highest in southeastern Norway and adjacent Sweden but that areas of northernmost Norway and adjacent Finland are also affected (R. F. Wright and H. Dovland, unpublished manuscript, 1977).

S. Odén and J. Bergholm (unpublished data, 1972), of the Swedish Agricultural College in Uppsala, describe an experiment in which snow was melted in a tubelike plastic bag kept slightly above 0°C. They collected successive fractions of the meltwater and found higher concentrations of dissolved ions in the first fractions than in the bulk snow.

This fractionation of the pollutants in the snow cover appears to be the main cause of sharp drops in the *p*H of surface waters during the spring melt period [*Gjessing et al.*, 1976; *Haapala et al.*, 1975; *Henriksen and Wright*, 1977]. The short-term increase in acid concentration during spring may cause severe physiological stress to fish and other aquatic organisms and has led to massive fish kills [*Leivestad and Muniz*, 1976; *Leivestad et al.*, 1976]. The physiochemical processes occurring during the snowmelt may thus be critical to the freshwater ecosystem.

As part of the Norwegian project 'Acid Precipitation—Effects on Forest and Fish' (SNSF project) we have studied the release of chemical components from snow samples with different pollutant loads under controlled melting conditions in the laboratory and under natural conditions by means of field lysimeters. The main objective of these studies is to ascertain if and to what degree the concentration process suggested by Odén and Bergholm occurs in nature. Preliminary results are reported by *Johannessen et al.* [1975].

METHODS

Samples of newly fallen snow were collected in January 1974 at three sites in southern Norway (Figure 1). The chemical composition of the samples is given in Table 1.

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The laboratory lysimeters consisted of a 56-cm length of 13-cm-diameter plastic tube equipped with a permeable disc at the lower end and a thermostated jacket kept at a temperature at 2.5°–3.0°C (Figure 2). The tube was filled with roughly homogenized snow. A 1.1-atm pressure of N_2 was applied to the top of the lysimeter, and the meltwater was collected in 25-ml aliquots by a fraction collector. The aliquots were analyzed for *p*H, specific conductance, Na, K, Ca, Mg, NH_4, NO_3, SO_4, Cl, SiO_2, PO_4-P, and the heavy metals Cu, Zn, Pb, Cd, and Mn by using procedures described by *Wright and Henriksen* [1978] and *Henriksen and Balmér* [1977].

The field lysimeter consisted of a polyethylene cylinder (30 cm high and 53.5 cm in diameter) which was buried in the ground prior to winter such that the top extended 3 cm above the ground surface and was covered by a perforated polyethylene sheet. During the winter the snowpack accumulated naturally on the top of the sheet. During periods of snowmelt the meltwater ran through the cylinder and was collected in a polyethylene bottle.

RESULTS

Laboratory Experiments

The concentrations of all components were 3–5 times higher in the first fractions of meltwater than in the bulk snow but were much lower in the last fractions than in the bulk snow (Figure 2). Melting of all samples followed this typical pattern in spite of tenfold differences in the concentrations in the bulk snow samples (Figure 3). The first 30% of the meltwater contained 41–80% of the total amounts of all 16 chemical components examined (Table 2).

No systematic differences in the behavior of monovalent and divalent ions were observed, indicating that differences in size and charge of ions are not important factors in the fractionation process.

Field Experiments

To confirm these laboratory results, we conducted several experiments with field lysimeters. A successful field lysimeter experiment requires that it be installed before the snow starts to fall, that the snow accumulate through the winter months without any severe mild spells, and that the snowmelt proceed slowly during a period without any precipitation. Nature seldom behaves like this. Nevertheless, two experiments proceeded under acceptable conditions.

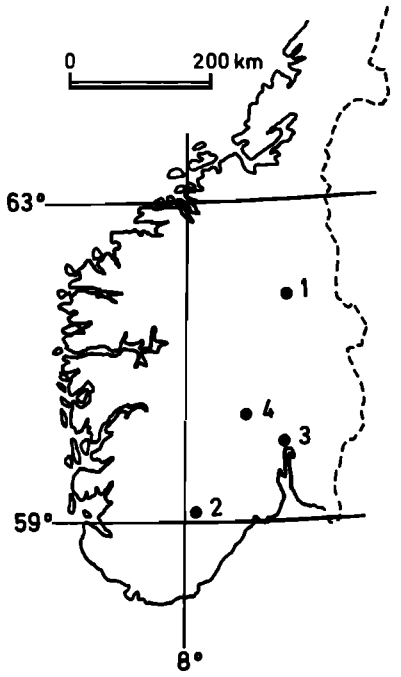

Fig. 1. Map of southern Norway showing snow-sampling locations: 1, Storefjell; 2, Fyresdal and Valebjørg; 3, Blindern; and 4, Gulsvik and Langtjern.

A field lysimeter was installed at Gulsvik (Figure 1), 120 km northwest of Oslo on January 3, 1974, just before the permanent snow accumulation started. Figure 4*a* shows the cumulative incoming precipitation during the winter. A short warm spell occurred in the last part of February which resulted in a release of water and pollutants from the snowpack (Figures 4*b* and 4*c*) amounting to about 15% of the water equivalent of the snowpack and about 40% of the H^+ load. This meltwater was thus highly enriched with pollutants. The main spring melt, however, took place during the last part of March and early April, a period of no precipitation (Figure 4*a*). The concentrations of H^+, SO_4, and Pb in successive meltwater fractions exhibited a pattern similar to that obtained in the

TABLE 1. Chemical Composition of Snow Samples Used for Lysimeter Experiments

Component	Sample 1	Sample 2	Sample 3
*p*H	4.91	4.57	3.98
Specific conductance, μS/cm		17	67
Na, mg/l	0.77	1.40	1.32
K, mg/l		0.14	0.87
Ca, mg/l	0.30	0.47	0.87
Mg, mg/l	0.03	0.14	0.15
NH_4, μg N/l		300	700
NO_3, μg N/l	280	370	970
SO_4, mg/l	0.6	2.3	6.5
Cl, mg/l		1.6	2.8
SiO_2, mg/l			0.2
PO_4-P, μg P/l	6	3	2
Cu, μg/l			13
Zn, μg/l	20		105
Pb, μg/l	4		56
Cd, μg/l	2.8		4
Mn, μg/l			17

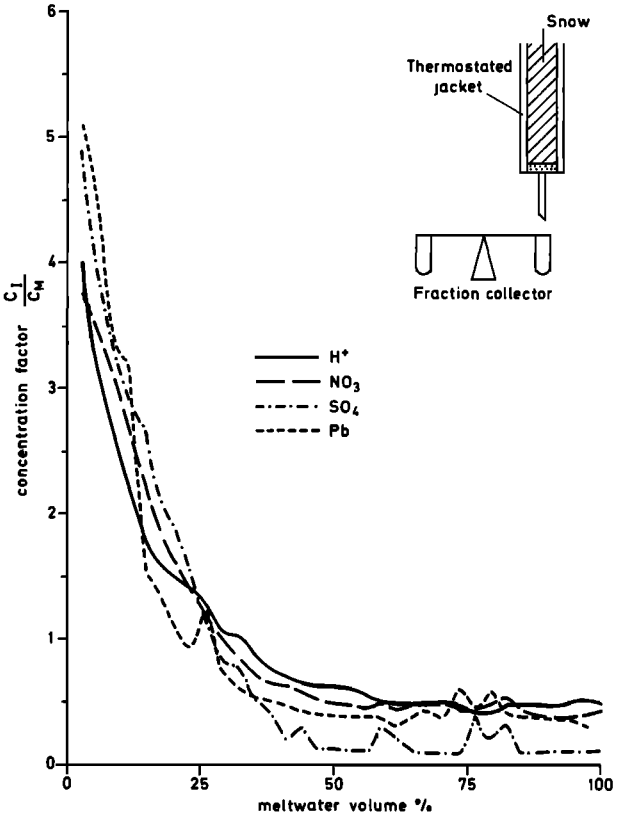

Fig. 2. Concentration factors for H^+ (calculated from *p*H), SO_4, NO_3, and Pb in fractions of meltwater from snow sample 1. C_I is the concentration in the *I*th fraction, and C_M the concentration in the bulk snow. Inset is a schematic diagram of the laboratory lysimeter.

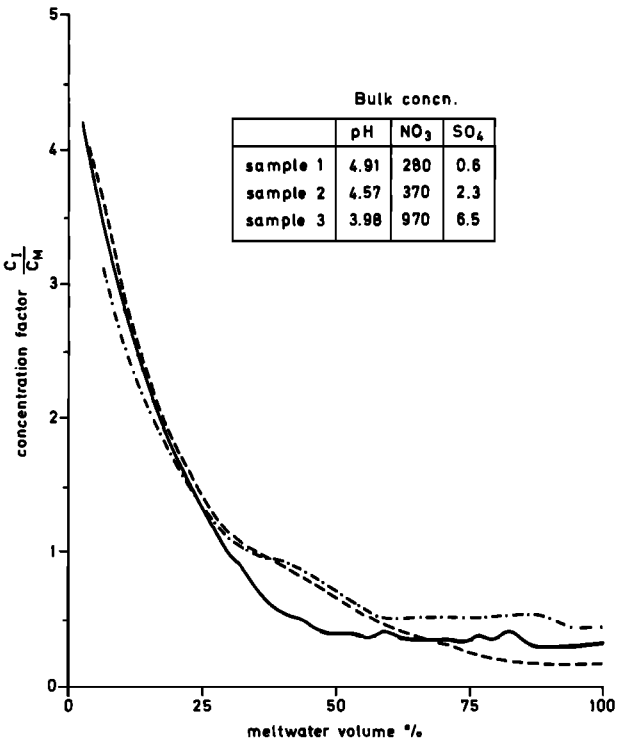

Fig. 3. Mean of concentration factors for H^+ (calculated from *p*H), NO_3, and SO_4 in fractions of meltwater from the three snow samples. Solid line, sample 1; dotted-dashed line, sample 2; and dashed line, sample 3. Inset shows concentrations in the bulk snow (NO_3, μg N/l; SO_4, mg/l).

TABLE 2. Percent of Total Amount of Components in Snow Released With the First 30% of Meltwater for Three Snow Samples Used in the Laboratory Experiments

	H^+	SO_4	NO_3	NH_4	PO_4-P	SiO_2	Cl	Ca	Mg	Na	K	Zn	Pb	Cu	Cd	Mn
Sample 1	61	74	66					61	71	63		68	67			
Sample 2	70	57	58	58			57	73	56	48		69	50	53	41	70
Sample 3	68	71	68	57	61	61	56	78	73	54	50	73	68	70	55	80

Percents were calculated from the mean concentrations in the fractions.

laboratory (Figure 5), having concentrations as high as 6.5 times the concentration in the bulk snow. Most of the pollutant load was released from the snowpack during melting of only 35% of the snow.

Results from a similar field experiment conducted in Fyresdal (Figure 1) in 1975 again followed the same pattern (Figure 6). The 35-cm-deep snowpack melted during 1 week in March. The experiment was stopped before the snow had melted completely, because of heavy rainfall. The results again indicate the same concentration pattern, 3–6 times higher concentrations in the first phase of the snowmelt than in the bulk snow.

The first 30% of the meltwater contained 44–76% of the total amount of all 14 chemical components examined in these two field lysimeter experiments (Table 3). The field experiments thus confirm the results from the laboratory experiments, but the concentration effect in nature appears to be even greater.

Storage of Pollutants in the Snowpack During Winter

In conjunction with the field lysimeter experiment at Gulsvik in 1974 we studied the stability of the chemical composition of the snow pack at Langtjern, 8 km east of Gulsvik. Because Langtjern is at 516-m elevation, the melt episode in mid-February observed at Gulsvik (Figure 4) did not occur to the same extent at Langtjern [*Henriksen and Wright*, 1977]. The total snowpack was sampled quantitatively weekly or biweekly during winter 1974. There was apparently no significant loss of water or of the pollutant ions H^+, SO_4, NO_3, NH_4, and Pb during the winter of 1974 (Figure 7). They were not released before the spring melt started in April. By April 11, 60–90% of the ions had been washed out (Figure 7); the water equivalent of the snowpack, however, had only decreased by about 35%. This is in complete agreement with the results from the laboratory and field experiments.

DISCUSSION

Concentration Mechanisms

The experiments described in this paper demonstrate that a concentration of the pollutants occurs during the snowmelt process in spring. The pollutants released during the first phases of the snowmelt cause sudden changes in the water quality of streams and lakes.

Knowledge of the distribution of pollutants within the snow crystals would be valuable for understanding the concentration effect. Although it is known that small amounts of some materials may be included in solid solution in ice crystals [*Fletcher*, 1970], there are reasons to believe that most of the pollutants are found on the surface of the snow crystals. Odén and Bergholm postulated that snow crystals are formed in relatively clean air masses and that the pollutants are adsorbed to the surface as the snow passes through polluted air. The meltwater from the polluted surfaces would then give rise to the first meltwater.

A further concentration of pollutants may be the result of alternating melting and freezing during winter. The first meltwater presumably forms near the snow surface and may later freeze, either because of a change in air temperature or because of contact with colder snow as the water percolates through the snowpack. This process may lead to the formation of essentially pure ice and more concentrated meltwater solutions, which eventually run off to the water course.

We can only speculate as to which of these or other physiochemical processes are causing the concentration effect reported. A study of variables such as diurnal temperature fluctuations within the snowpack during melting, direction of heat transfer, pollutant load, and pollutant gradients would give us more information about the conditions necessary for the concentration effect.

Deposition of sulfur compounds by atmospheric fallout has been estimated to be about 30% of the total deposition in Norway [*OECD*, 1977]. Deposition by fallout on the snow cover during winter is probably considerably smaller [*Dovland*

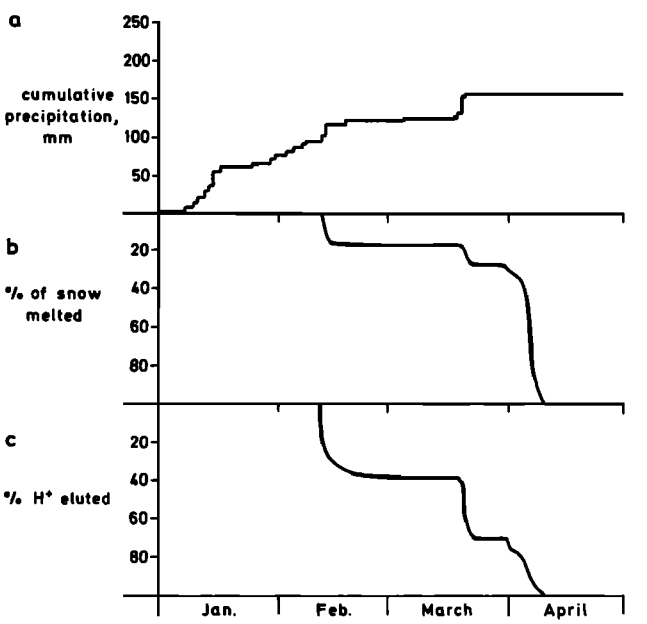

Fig. 4. Field lysimeter experiment. Accumulation and melting of the snowpack at Gulsvik. (*a*) Cumulative incoming precipitation during the period January–April 1974. (*b*) Percent of snowpack (water volume) melted and collected in the field lysimeter. (*c*) Percent of total amount of H^+ eluted from the snowpack and collected in the field lysimeter.

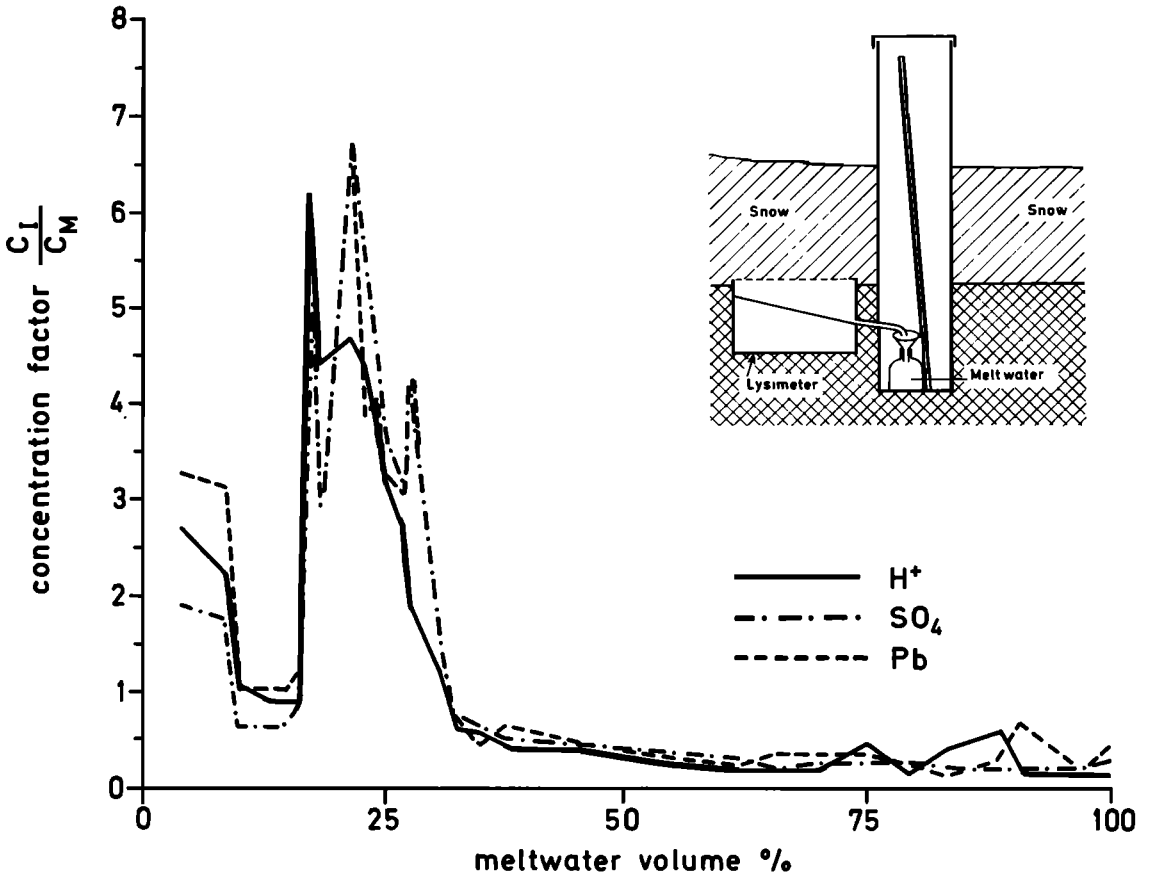

Fig. 5. Concentration factors for H^+ (calculated from pH), SO_4, and Pb in meltwater from the field lysimeter at Gulsvik in 1974. Inset is a schematic diagram of the field lysimeter.

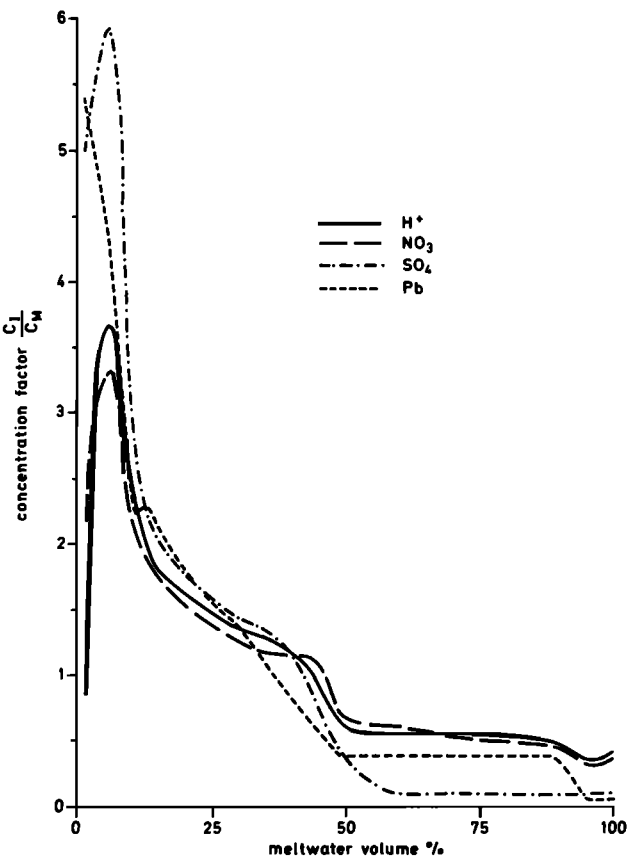

Fig. 6. Concentration factors for H^+ (calculated from pH), NO_3, SO_4, and Pb in meltwater from the field lysimeter at Fyresdal in 1975.

and Eliassen, 1976]. Regional snow surveys of the snowpack in Norway during the winters of 1973–1976 also indicate small amounts of fallout (R. F. Wright and H. Dovland, unpublished data, 1977). Atmospheric fallout on the snow cover therefore contributes to only a small part of the total pollutant load in the snowpack.

pH Drops in Stream Waters During Snowmelt

The sudden release of the pollutants stored in the snowpack during the first phase of the snowmelt in spring causes rapid changes in the chemical composition of streams and lakes. The impacts of these changes are largely unknown but most likely have an effect upon the plankton and littoral communities. The effect on fish is best understood, and the changes may lead to severe physiological stress and occasionally massive fish kills [*Leivestad and Muniz,* 1976; *Leivestad et al.,* 1976]. The spring melt occurs at a time which is critical to the hatching stage of salmonid fish species.

Under natural conditions when the soil is frozen, snowmelt occurs because of heat transfer to the upper surface. The field experiments were performed under such conditions. During the laboratory experiments, however, the snow receives heat mostly laterally. Some of the meltwater will therefore pass by the snow column close to the cylinder walls and may dilute the more concentrated solution formed by percolation through the snow column. This might explain why the field experiments tend to show higher concentration factors in the first phase of the snowmelt.

The laboratory experiments could be refined by redesigning the container in such a way that the meltwater is collected from a snow column within a larger snow mass, the heat being

TABLE 3. Percent of Total Amount of Components in Snow Released With the First 30% of Meltwater From Two Field Lysimeter Experiments

Location	Year	H^+	SO_4	NO_3	NH_4	Total P	Cl	Ca	Mg	Na	K	Zn	Pb	Cu	Cd
Gulsvik	1974	75	76	52	60	62	61	51	54	53	50	73	82	44	55
Fyresdal	1975	51	76	51	57	56	52	58	63	53	63	72	69	46	97

Percents were calculated from the weighed-mean concentrations in the collected meltwater.

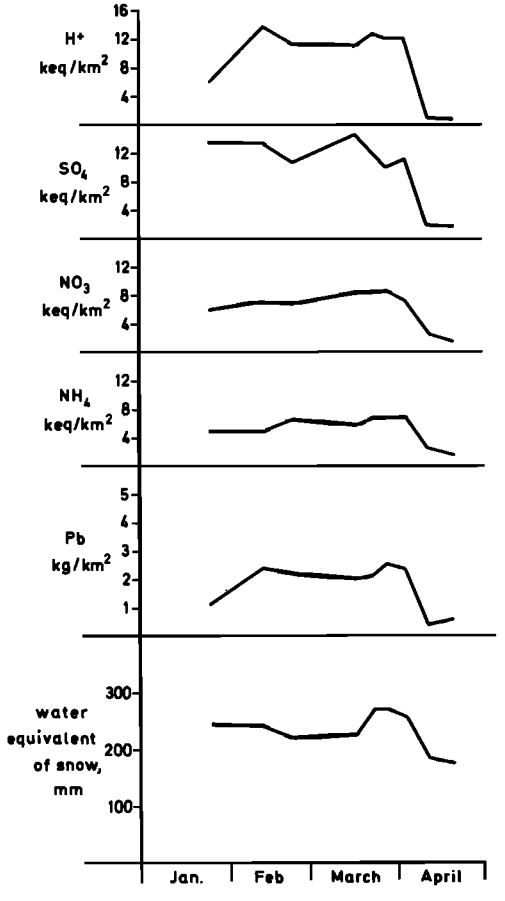

Fig. 7. Load of H^+ (calculated from *p*H), SO_4, NH_4, NO_3, and Pb and water volume in the snowpack at Langtjern during the winter of 1974.

delivered from above. The concentration factors would then probably be closer to those observed in field experiments.

These experiments indicate that the first 30% of the meltwater contains 2–2.5 times higher concentrations of pollutants than bulk snow (Table 4). Although the first 0–10% probably has still higher concentrations, it is not likely that the snowmelt would occur uniformly throughout even small catchment areas. Therefore for streams draining areas larger than 0.1 km^2 the first meltwater reaching the streams in quantities sufficient to increase discharge above winter base flow levels will contain at most 2–2.5 times the concentrations in the bulk snow. For example, a snowpack with a bulk *p*H of 4.4 might give rise to an initial meltwater 'wave' of *p*H 4.1. In the stream water a higher *p*H would be expected, because the more neutral base flow would tend both to dilute and to buffer part of the acid.

TABLE 4. Weighed-Mean Concentration Factors for the First 30% of the Meltwater for Both Laboratory and Field Experiments

	H^+	SO_4	NO_3
	Laboratory Experiments		
Sample 1	2.4	2.0	2.1
Sample 2	2.0	1.9	2.0
Sample 3	1.9	2.5	2.3
	Field Lysimeter		
Gulsvik	2.4	2.4	2.5
Fyresdal	2.2	2.5	1.9

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An Approach for Assessing Cumulative Effects in a Model River, the Athabasca River Basin

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ABSTRACT

Novel approaches addressing aquatic cumulative effects over broad temporal and spatial scales are required to track changes and assist with sustainable watershed management. Cumulative effects assessment (CEA) requires the assessment of changes due to multiple stressors both spatially and temporally. The province of Alberta, Canada, is currently experiencing significant economic growth as well as increasing awareness of water dependencies. There has been an increasing level of industrial, urban, and other land-use related development (pulp and paper mills, oil sands developments, agriculture, and urban development) within the Athabasca River basin. Much of the historical water quantity and quality data for this basin have not been integrated or analyzed from headwaters to mouth, which affects development of a holistic, watershed-scale CEA. The main objectives of this study were 1) to quantify spatial and temporal changes in water quantity and quality over the entire Athabasca River mainstem across historical (1966–1976) and current day (1996–2006) time periods and 2) to evaluate the significance of any changes relative to existing benchmarks (e.g., water quality guidelines). Data were collected from several federal, provincial, and nongovernment sources. A 14% to 30% decrease in discharge was observed during the low flow period in the second time period in the lower 3 river reaches with the greatest decrease occurring at the mouth of the river. Dissolved Na, sulfate, chloride, and total P concentrations in the second time period were greater than, and in some cases double, the 90th percentiles calculated from the first time period in the lower part of the river. Our results show that significant changes have occurred in both water quantity and quality between the historical and current day Athabasca River basin. It is known that, in addition to climatic changes, rivers which undergo increased agricultural, urban, and industrial development can experience significant changes in water quantity and quality due to increased water use, discharge of effluents, and surface run-off. Using the results from this study, we can begin to quantify dominant natural and man-made stressors affecting the Athabasca River basin as well as place the magnitude of any local changes into an appropriate context relative to trends in temporal and spatial variability. Integr Environ Assess Manag 2010;6:119–134. © 2009 SETAC

Keywords: Water quality Water quantity Benchmarks Athabasca River basin Cumulative effects

Original Research

INTRODUCTION

Cumulative effects assessment (CEA) is the process of systematically assessing impacts resulting from incremental, accumulating, and interacting stressors and is regulated under the Canadian Environmental Assessment Act (Reid 1993; Dubé et al. 2004; Duinker and Greig 2006). The original context of CEA methods was causal or stressor-based focused and is specific to a proposed new development project (Spaling and Smit 1995). It has been recognized that there is a need to shift from these local, project-scale CEAs to broader, landscape, or regional scale assessments to accurately assess cumulative effects across an entire river ecosystem (Duinker and Greig 2006). However, there is not presently a mechanism for this to occur under the current regulatory process.

Effects-based methods for Canadian CEA have developed largely through watershed studies conducted by university and government researchers and focus first on measuring changes in the aquatic environment (i.e., determining the existing environmental state) over a broader spatial scale and second on determining the cause or stressor of the effect if effects are measured (Dubé 2003). This approach is founded on the premise that, if the ''performance'' or ''health'' of the environment is affected by the cumulative insults of man-made activities, then mitigation is required, and any new project proposals must ensure development activities do not affect the environment further. Examples of effects-based CEAs include the Moose River Basin study (Munkittrick et al. 2000), and studies under the Northern Rivers Basin Study (Culp et al. 2000), and the Northern Rivers Ecosystem Initiative (Dubé et al. 2006). Although effects-based approaches are conducted at the appropriate scale for CEA and are effective for determining the ''health'' of a system, development of predictive models to understand how the system may respond to future development pressures has not occurred.

Much of the confusion in assessing cumulative effects on aquatic ecosystems is due to poorly defining the resources of concern and the spatial and temporal scales of the analysis (MacDonald 2000). Limited temporal and spatial dimensions generally narrow impact analysis to inclusion of immediate

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effects of a specific environmental attribute at an individual site (Spaling and Smit 1995). To minimize bias, the spatial scale of the assessment should be defined by the spatial scale of the processes (i.e., the industry, land uses) that affect the resources of concern (i.e., the catchment or watershed) (MacDonald 2000). Impacts attributed to these processes should also be considered over multiple scales such as reach, catchment, and regional landscape (Schindler 1998). In addition, the river continuum concept is a fundamental ecological concept that characterizes how a river naturally changes along its length from headwaters to mouth (Vannote et al. 1980). These accumulated changes in biophysical attributes of a river along its length must also be accounted for in a CEA framework.

A common practice in CEA is to use the state of the current environment as the baseline. This cannot be considered the most appropriate way to assess multiple impacts because this assumes no changes have occurred to date and amalgamates the effects of past and present actions of individual contributors into an accumulated baseline (McCold and Saulsbury 1996). Instead, it can be argued that a more appropriate baseline for considering the significance of cumulative impacts is that time in the past when the valued environmental attribute (or resource) was most abundant or less affected. Assessing changes in a river over a significant period of time provides an improved baseline from which to evaluate if changes have occurred. It also provides the opportunity to relate changes in biophysical indicators such as water quality parameters, sediment quality parameters, and indicators of biological populations or communities to the occurrence of man-made stressors. On this basis then, a CEA method for rivers should include impacts accumulating along the river continuum as measured over history to the present day.

In addition to the appropriate boundaries and indicators, CEA requires that changes in indicators be measured and the magnitude of the change evaluated relative to some threshold value. Thresholds represent a degree of change in an indicator that is linked to a decision-making process. In this context, if a threshold is approached or exceeded, decision makers know the action they will take (i.e., adaptive management). Due to the complexity of biological systems, thresholds for rivers do not exist. However, many benchmarks do exist that can be the first starting point to quantify the level of change in a river over space and time (Dubé 2003; Kennett 2006; YESAB 2006; Kilgour et al. 2007).

Cumulative effects should not be assumed to be defined exclusively as the combined effects of several parameters. A cumulative effect can also occur for a single parameter along a large spatial extent or long temporal scale influenced by multiple stressors affecting a common response. This is especially true when looking at concentrations of specific water quality parameters along a river continuum. The inputs of multiple sources can contribute significant loadings of certain water quality parameters along the river mainstem (nutrients, organic carbon, salinity), resulting in substantially higher concentrations than otherwise would occur in the mouth of these systems.

One way of quantifying these inputs is to calculate the Total Maximum Daily Loads (TMDLs) (USEPA 2009a). TMDLs are specific to 1 pollutant in a single waterbody and are able to account for seasonality and both point and nonpoint sources. The main purpose of TMDLs is to be able to calculate the maximum load of a specific parameter in a waterbody so that point source contributions can be better managed. One of the main modeling systems frequently used to calculate TMDLs is the Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) program (USEPA 2009b). BASINS is an interactive, freely available GIS-based software that by integrating data and applying existing assessment and planning tools and water quality modeling software, attempts to quantify the inputs of water parameters in a river system. The main purpose of BASINS is to assist in watershed management and TMDL development by 1) characterizing water quality data, 2) identifying pollution sources, and 3) allocating loadings (USEPA 2009b). BASINS is specialized software that focuses on water quantity and quality data needed to calculate TMDLs and does not calculate other types of guidelines or benchmarks that may be required in a watershed-based CEA.

Despite the global acknowledgement that cumulative effects are an expanding issue that must be addressed (Schindler 1998; Duinker and Greig 2006), there is currently not a single conceptual approach or even several general principles that are widely accepted by scientists and managers. Therefore, methods that can assess these multiple types of effects over a broad spatial and time scale must be developed. The main objectives of this study are 1) to quantify spatial and temporal changes in water quantity and quality over space (along the river continuum) and time (historical and present day) in our model river and 2) to evaluate the significance of any changes relative to existing benchmarks (e.g., water quality guidelines).

The Athabasca River in Alberta, Canada, serves as a good model to develop a methodology for aquatic CEA because it has experienced an increasing level of land-use development over the past decades including forestry/pulp and paper, coal mining, oil and natural gas, agriculture, tourism, wildlife trapping, hunting, and oil sands mining (Wrona et al. 2000; Culp et al. 2005). The basin holds significant cultural and economic importance supporting more than 9 First Nation groups, and providing water to hundreds of industries, including the multibillion-dollar oil sands mining industry.

METHODS

Athabasca River Basin as a model river

The Athabasca River basin covers 157 000 km^2, accounting for approximately 22% of the landmass of Alberta (Gummer et al. 2000) (Figure 1). It originates at the Columbia Ice Fields, the largest ice field in the North American Rocky Mountains, located in Jasper National Park and flows northeast across Alberta until it reaches Lake Athabasca. Running more than 1538 km, the Athabasca is the longest river wholly contained within Alberta and the longest unregulated river in the prairies.

To date, there have been 3 CEAs for parts of the Athabasca River basin including the Northern River Basins Study, the Northern River Ecosystem Initiative, and the Regional Aquatic Monitoring Program. The Northern River Basins Study and the Northern River Ecosystem Initiative were a series of research studies examining various aspects of water and biota quality over a total of 10 y. CEAs were conducted at the end of the program and consisted of a qualitative synthesis of conclusions from various researchers (Culp et al. 2000;

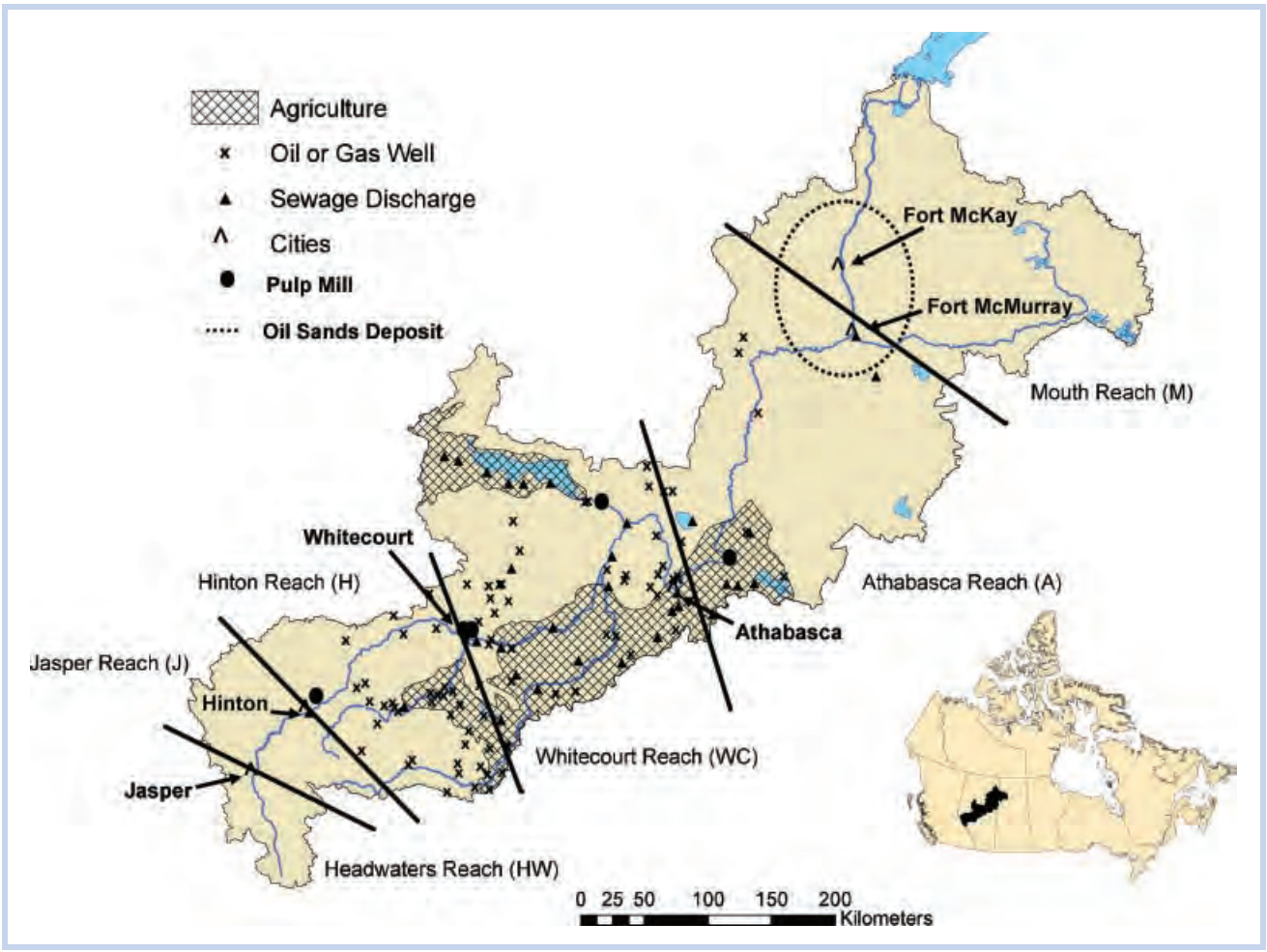

Figure 1. Map of the Athabasca River Basin showing locations of the current major industries and urban centers.

Dubé et al. 2006). The Regional Aquatic Monitoring Program is specific to the oil sands industry and operates over that development region for the longer term. These CEAs focus on specific portions of the Athabasca River basin, but as of yet, no attempt has been made to assess cumulative effects from headwaters to mouth (Lawe et al. 2005).

The major land-use changes between time period 1 and time period 2 are outlined in Table 1. Point source sewage discharges to the Athabasca River occur on a continuous basis from 5 larger communities (all with a population >5000), including the Town of Hinton, which has a contract to have its sewage treated and discharged along with the Weldwood of Canada Ltd. pulp mill (Scrimgeour and Chambers 2000). All of these facilities currently use a minimum of secondary effluent treatment with 1 of 5 practicing tertiary treatment for nutrient removal. In 1993, sewage discharge to the

Table 1. Land-use changes between the historical (1966–1976) and current (1996–2006) time points for the Athabasca River basin

Land-use	1966–1976	1996–2006
Nr of pulp mills discharging into basin	1	5
Population	126 345[a] (1981)	151 750[a] (2001)
Total farm area (Acres)	47 218 170[a] (1981)	52 058 898[a] (2001)
Water withdrawals (m^3/y)	12 069 340[b]	595 580 497[b]
Nr of operating oil sands leases	2	3,360[c]
Fertilizer use (nr of acres)	Not available	957 651[a] (2000)

[a]Statistics Canada (2007).
[b]Available through Alberta Environment.
[c]Available through Alberta Energy Oil Sands Development Division.

Athabasca River from these facilities (excluding Hinton) totaled 25 046 m^3 (Chambers et al. 2000).

There are 2 bleached kraft pulp mills and 3 chemithermomechanical pulp mills that currently discharge into the Athabasca River and its tributaries (Figure 1). The first pulp mill, opened in 1957, discharges into the town of Hinton near the headwaters of the river, and is currently operated by Weldwood of Canada Ltd. The next longest operating mill (Miller Western Pulp) opened in 1988, with the remaining 3 (Alberta Newsprint Co., Slave Lake Pulp and Alberta Pacific Forest Industries) opening in the early 1990s. The combined discharge of these pulp mills in 1993 (including the combined discharge of Weldwood and the town of Hinton) to the Athabasca River basin was 206 658 m^3 (Chambers et al. 2000).

One of the major industries in the lower Athabasca River is the oil sands operations located north of the town of Fort McMurray (Table 1; Figure 1). The 2 largest surface mining companies are Syncrude Canada Ltd. and Suncor Energy Inc., and they have been extracting oil sands from this region since 1978 and 1967, respectively. Current mining processes require 2 to 4.5 barrels of water to produce 1 barrel of oil (Schindler et al. 2007). The oil sands operations must follow a zero discharge policy with regard to their tailings effluent, and consequently these must be stored on site in massive tailings ponds that currently cover over 50 km^2. However, there is a recorded discharge of treated utility water from Suncor Energy Inc. of approximately 35 020 m^3/d, amounting to 0.05% of local annual stream flow (Scrimgeour and Chambers 2000). Existing oil sands mining operations (including the newest Albian Sands operation) are licensed to divert 349 million m^3 of water per year from the Athabasca River with less than 10% of this being returned.

In addition to these major industries, there is an abundance of agricultural and urban development occurring throughout the basin (Wrona et al. 2000). Agriculture consists primarily of forage crops, located in the central portion of the basin. There are more than 200 populated centers with greater than 2000 people. The total population of the basin is currently 151 750 or 0.96/km^2 when population is divided by the total area of the watershed.

Available data. Cumulative effects assessment requires a significant amount of data with coverage over broad spatial and temporal scales. These are not the type of data available from a single researcher. Consequently, water quality data for this study were collected from several sources, including both the provincial (Alberta Environment) and federal (Environment Canada) governments and industrial (Regional Aquatic Monitoring Program for the oil sands) sources. Data from 3 primary water quality databases covering a 50-y period were examined including over 1800 variables and 4.5 million sample values. Examination and integration of this multisource data were facilitated using The Healthy River Ecosystem Assessment System (THREATS) software (Dr. M. Dubé, University of Saskatchewan, Saskatoon, SK, Canada).

All water quality data used in this study were checked for errors and omissions both by the organizations providing the data (Environment Canada and Alberta Environment), and by the authors. Data obtained from Environment Canada are reviewed according to internal protocols and released to the public only after this process is complete. Alberta Environment data are reviewed and validated following Alberta Environment's surface water data validation process involving review by field staff, the project limnologist, and finally the data management staff, who play an audit role.

Based on the examination of available data at several water quantity and quality stations along the Athabasca River and the locations of several urban, agricultural, and industrial inputs, the basin was divided into 6 reaches (Figure 1). For each reach, water quantity and water quality parameters were graphed over 2 time periods, historical (1966–1976) and current (1996–2006), to assess the differences in trends between periods. The rationale for choosing these 2 periods is based on both the availability of data and on the start up dates of several major industrial operations including both pulp mill and oil sands developments. Despite the examination of almost 5 million data points, the number of water quality variables available for examination over our selected temporal and spatial boundaries was limited due to the frequency of collection and the changes in analytical methods of analyses over time. There existed many gaps of years in which data were collected infrequently or not at all from many of the stations. Despite choosing those stations with the best coverage of data across all years, in some instances there were few data points available for analyses. The data used are described in more detail in Table 2. Water quality parameters selected for further analyses were total organic carbon (TOC), dissolved nitrogen (DN), turbidity, total phosphorous (TP), conductivity, dissolved chloride (Cl), dissolved sodium (Na), and dissolved sulfate (SO_4). These parameters were selected because data coverage met the spatial and temporal boundaries selected for the cumulative effects assessment in the basin. In addition, the parameters were potentially influenced by industry (Na, SO_4, and Cl) and were hypothesized to change naturally along the river continuum (conductivity, turbidity, TOC, DN, and TP).

Discharge (flow) data were obtained from Canada's national archive for water quantity data (HYDAT), managed by the Water Survey of Canada. A total of 7 HYDAT stations monitor flow in the Athabasca River basin; five of these provide real-time current data. We selected 1 station at the most downstream point of each reach to represent the flow for that entire reach. These data were analyzed on a monthly time step for each reach over each time period.

Mean weighted averages and standard errors were calculated for each parameter (water quality variables and flow) across each time period. These were weighted based on sample size to remove bias due to unequal contributions of larger sized samples to annual averages (Bland and Kerry 1998). To assess the presence of a trend in water quality across the 6 reaches for each time period, the nonparametric Mann-Kendall trend test was performed. This trend test was performed separately for each parameter on the weighted averages across all reaches for each time period (2 trend tests per parameter). This test does not require data to be normally distributed, or to have equal variances (Helsel and Hirsch 2002). To test for a significant difference between the 2 time periods, the nonparametric Kruskal-Wallis unpaired *t* test was performed for each parameter (including flow) at each reach for a total of 54 tests.

Average total annual flow could not be calculated due to a lack of data for each time period across all reaches. Cumulative average loadings (kg/d) were calculated for each water quality parameter, with the exception of turbidity and conductivity, by multiplying the weighted average concen-

Table 2. Numbers of samples (high flow/low flow) used to calculate a weighted average for each reach in water quantity (Figure 3) and quality (Figure 7) analyses for both the historical (1966–1976) and current (1996–2006) time periods for the Athabasca River basin

Reach	Time period	Monthly Range	TOC	Dissolved chloride	Dissolved nitrogen	Total phosphorous	Conductivity	Dissolved sulfate	Dissolved sodium	Turbidity
Headwaters	1966–1976	Jan–Dec	60/103	59/104	91/117	81/112	—	62/103	59/103	104/121
Jasper	1966–1976	Jan–Dec	44/90	68/163	119/185	95/143	163/195	68/162	69/152	136/189
Hinton	1966–1976	Jan–Dec	4/5	26/54	23/54	7/12	26/31	21/29	26/46	24/54
Whitecourt	1966–1976	Jan–Aug	1/2	1/2	1/2	1/2	3/4	1/2	1/2	1/2
Athabasca	1966–1976	Jan–Dec	9/16	35/76	32/70	8/19	45/81	35/76	36/75	36/76
Mouth	1966–1976	Jan–Dec	14/13	33/50	29/44	12/11	36/56	33/49	33/49	33/50
Headwaters	1996–2006	Jan–Dec	51/93	39/76	51/93	50/95	76/152	39/76	39/76	88/169
Jasper	1996–2006	Jan–Dec	7/6	96/189	98/206	113/242	228/462	96/189	55/114	269/574
Hinton	1996–2006	Feb–Oct	0/2	24/34	4/12	38/71	74/83	26/32	26/32	26/49
Whitecourt	1996–2006	Jan–Oct	0/2	14/14	0/2	20/43	32/59	14/14	14/14	14/21
Athabasca	1996–2006	Jan–Oct	0/2	6/9	5/11	13/20	31/30	6/9	6/9	13/21
Mouth	1996–2006	Jan–Dec	26/35	26/35	75/96	100/154	150/186	102/146	72/108	138/200

tration (across the time period) of each water quality parameter by the average discharge (across the time period) at its corresponding HYDAT station for each reach and a conversion factor to account for unit differences. Statistics were not calculated for cumulative loadings due to the spatial dependence of sampling across reaches.

Climate data were obtained from the National Climate Data and Information Archive, operated and maintained by Environment Canada. Average total precipitation (snow plus rain) and average annual temperature were calculated and graphed for each time period as well as for the entire record of data across all reaches. To test for significant differences in temperature and precipitation between the 2 time periods, a parametric paired *t* test was performed by pooling data from all reaches to generate a test statistic for the entire time period.

Due to the lack of developed guidelines for the purpose of protecting aquatic life for many of the parameters in this study, the 10th and 90th percentiles were calculated for the first time period. This was done because this time period is considered to represent a reference-type condition due to the absence of many of the land-use related stressors which are present in the second, more developed time period (Table 1). These percentiles can offer some measure of acceptability when compared with the concentrations of these parameters in the second time period. For example, concentrations in the second time period that exceed the 90th percentile can be considered above a threshold of acceptability compared with the first time period.

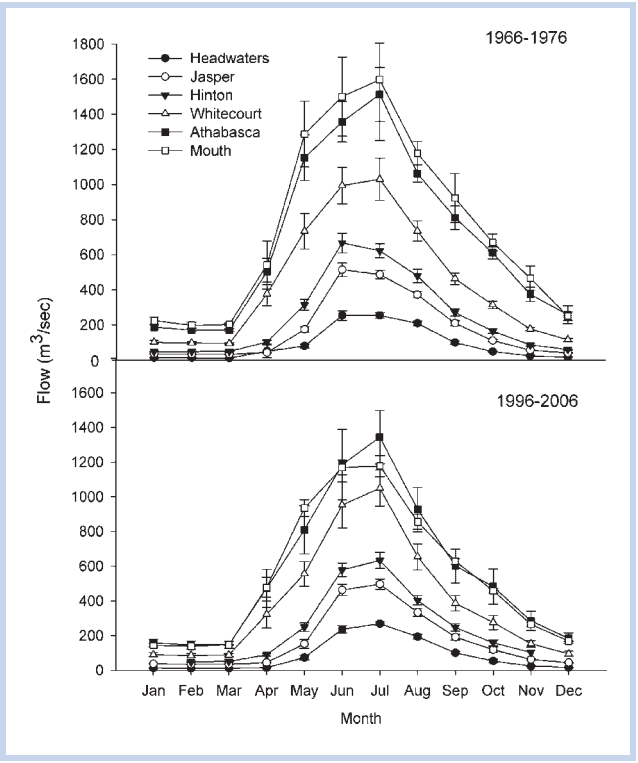

Figure 2. Mean monthly (± SE) discharge at HYDAT stations (1 per reach) along the Athabasca River continuum in 2 time periods; historical (1966–1976) and current day (1996–2006).

RESULTS

Water quantity

Reach mean discharge for each month during time period 1 (historical) and time period 2 (current day) are shown in Figure 2. The Headwaters, Jasper, and Hinton peak discharge occurred 1 month earlier than the Whitecourt, Athabasca, and Mouth discharges in time period 1 but not time period 2, suggesting a delayed freshet in the upper reaches during time period 2. The Mouth reach had the highest mean discharge of all the reaches in time period 1, whereas there were only 2 months (May, September) when discharge at the Mouth reach was higher than the Athabasca reach in time period 2. The discharge in the mouth reach in time period 2 was 16% lower on average than in time period 1.

When the high flows (May to August) were averaged at each reach for both time periods, we observe a decrease of 6 to 356 m^3/s across all reaches from Headwaters to Mouth between time period 1 and time period 2 (Table 3). In the Athabasca and Mouth reaches, this translates to a statistically significant decrease of 16% and 26% in high flow, respectively ($p < 0.05$). When the low flows (September to April) were averaged at each reach for both time periods, we observe a significant decrease ($p < 0.05$) of 14% to 30% in the lower 3 reaches (Table 4).

Table 3. Differences in average high flows (May–August) for 6 reaches in the Athabasca River basin across 2 time periods (1966–1976 and 1996–2006)

Reach	HYDAT station	High flow (m^3/s) 1966–1976	High flow (m^3/s) 1996–2006	Difference (m^3/s)	Percent difference (%)
Headwaters	07AA002	198	192	−6	−3.1
Jasper	07AD002	386	361	−25	−6.6
Hinton	07AE001	520	465	−54	−10.5
Whitecourt	07BE001	872	803	−69	−8.0
Athabasca	07DA001	1271	1066	−205	−16.1[a]
Mouth	–[b]	1390	1034	−356	−25.6[a]

[a]Significant at $p < 0.05$.
[b]Data are provided by HYDAT (07DD001) for time period 1 and the Regional Aquatic Monitoring Program (S24) for time period 2.

Table 4. Differences in average low flows (September–April) for 6 reaches in the Athabasca River basin across 2 time periods (1966–1976 and 1996–2006)

Reach	HYDAT station	Low flow (m^3/s) 1966–1976	Low flow (m^3/s) 1996–2006	Difference (m^3/s)	Percent difference (%)
Headwaters	07AA002	34	31	−3	−10
Jasper	07AD002	70	71	1	1
Hinton	07AE001	104	116	12	12
Whitecourt	07BE001	217	187	−30	−14[a]
Athabasca	07DA001	386	310	−76	−20[a]
Mouth	–[b]	434	303	−131	−30[a]

[a]Significant at $p < 0.05$.
[b]Data are provided by HYDAT (07DD001) for time period 2 and the Regional Aquatic Monitoring Program (S24) for time period 2.

Weighted average flow showed a significant increasing trend along the river continuum in both time periods ($p = 0.005$ and 0.015 in time period 1 and time period 2, respectively). The flow was significantly higher in time period 1 compared with time period 2 for the Headwaters ($p = 0.012$), Athabasca ($p = 0.018$), and Mouth ($p < 0.001$) reaches (Figure 3).

Climate. Average temperature and total precipitation followed a similar pattern from headwaters to mouth, peaking in the Hinton reach during both time periods as well as over the entire record of data (Figure 4). Temperature in time period 2 was consistently warmer than that in time period 1 across all reaches. The average temperature for the entire period of record across all reaches was higher than the average time period 1 temperature, but cooler than the average time period 2 temperature. Total precipitation showed the reverse trend where time period 1 was wetter across all reaches, except the Jasper reach. The average total precipitation for the entire record of data across all reaches was comparable to the trend and amounts seen in time period 1. The peak difference in average temperature was +1.4 °C and the difference in peak total precipitation was approximately −81.8 mm between time periods 1 and 2 among all reaches (Figure 4).

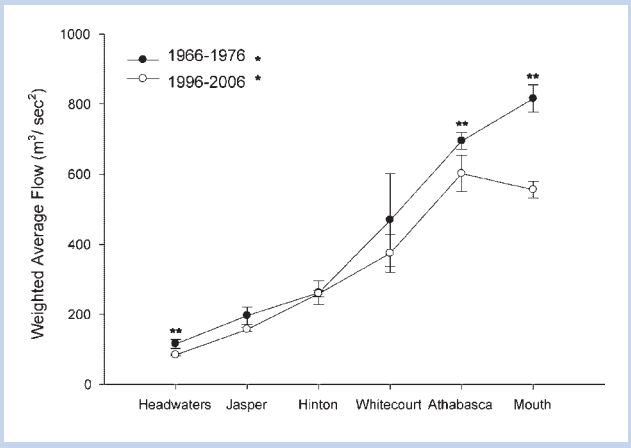

Figure 3. Average flow for reaches along the Athabasca River continuum across 2 time periods: historical (1966–1976) and current day (1996–2006) calculated from data in Table 2. * in the legend indicates a significant trend across reaches ($p < 0.05$) for that time period; ** for a reach denotes a significant difference in flow between time periods at that reach ($p < 0.05$).

Water allocations in the Athabasca River Basin

The amount of water allocated to be removed and the actual consumptive use of this licensed water in the Athabasca River over both time periods was obtained from Alberta Environment and is shown in Figure 5. There was an

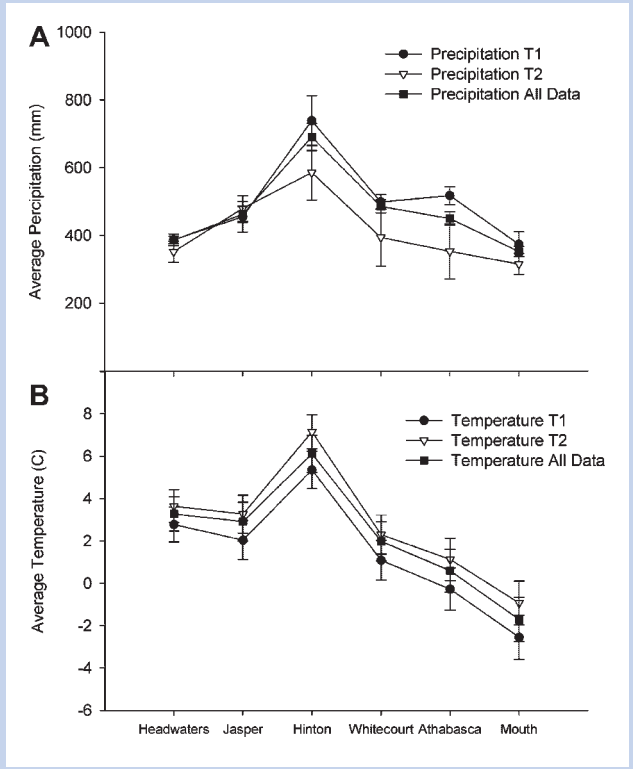

Figure 4. Total and average annual precipitation (A) and air temperature (B) at stations along the Athabasca River continuum historical or time period 1 (1966–1976), current day or time period 2 (1996–2006) and for all available data (1966–2006). There is a significant difference in both average annual temperature (+1.4°C) and total precipitation (−81.8 mm) ($p < 0.05$) between the 2 time periods.

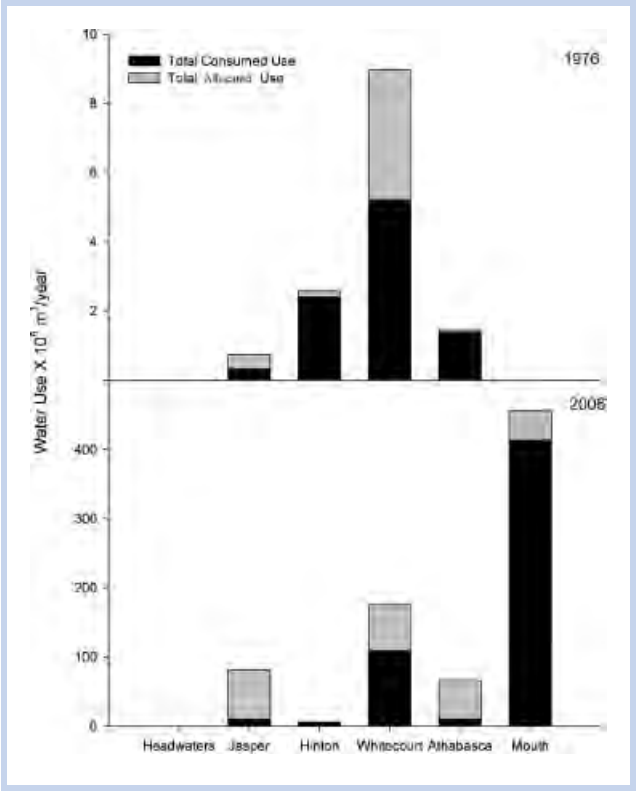

Figure 5. The total actual consumption and total allowable allocated consumption of surface water (m^3/y) along the Athabasca River continuum historical (1976) and current day (2006).

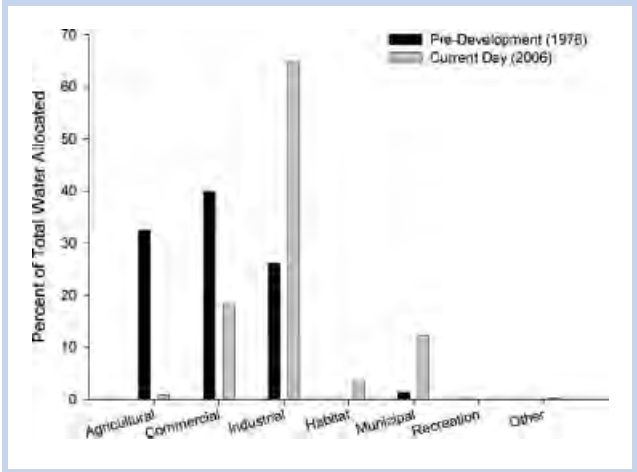

Figure 6. Percentage of surface water allocated to each sector along the Athabasca River continuum historical (1976) and current day (2006).

increase of between 3 482 472 and 455 573 728 m^3/y in the amount of water allocated to be used in the Athabasca River across reaches between the 2 time periods (Figure 5). The greatest increases in licensed allocations have been in the lower 3 reaches (Whitecourt, Athabasca, and Mouth). These trends are mirrored in the actual consumptive use of the allocated water in each reach (Figure 5). However, in all reaches the actual consumptive use of water was less than the allowable allocated water amounts. Overall, there was an increase of between 3 178 487 and 413 750 193 m^3/y in the amount of consumptive water use in the Athabasca River across reaches between the 2 time periods with the greatest increase in the Mouth reach (Figure 5). The greatest increases were seen in the industrial, habitat management, and municipal sectors where water allocations more than doubled (Figure 6).

Water quality

Mean concentrations. The weighted average and cumulative loading of the analyzed water quality parameters are shown in Figure 7. A significant increasing trend in total phosphorous was observed across all reaches in the second time period ($p = 0.005$). A peak in total phosphorous concentration in time period 1 was noted at the Hinton reach, but was not observed during time period 2. Total phosphorous concentrations were significantly higher in time period 1 in the Jasper ($p = 0.003$) and Mouth reaches ($p = 0.008$); however, the reverse was observed for the Athabasca reach ($p = 0.001$). Dissolved nitrogen concentrations peaked in time period 1 at the headwaters followed by a decrease in the Whitecourt reach before rising again to be similar to time period 2 at the mouth reach. Concentrations of dissolved nitrogen were significantly higher ($p = 0.034$) in time period 2 at the Athabasca reach.

In time period 1, average dissolved chloride concentrations peaked at the Hinton reach. In time period 2, this peak was not observed, however, concentrations of dissolved chloride were significantly higher ($p < 0.001$) then time period 1 in the Mouth reach. Dissolved chloride did show a significant increasing trend from headwaters to mouth in time period 2 ($p = 0.015$). In time period 1, dissolved sulfate concentrations peaked at the Jasper reach. In time period 2, dissolved sulfate concentrations were significantly higher than in time period 1 for both the Hinton ($p < 0.001$) and Athabasca ($p = 0.017$) reaches. However, even though sulfate concentrations were higher overall in time period 2, they were not significantly different from time period 1 at the Mouth reach.

Average total organic carbon exhibited significant increasing trends across all reaches in time periods 1 and 2 ($p = 0.005$ and 0.015), but the concentrations were significantly lower in time period 2 in the Headwaters ($p < 0.001$), Jasper ($p < 0.001$), Athabasca ($p = 0.047$), and Mouth ($p > 0.001$) reaches. Turbidity showed the same pattern across all reaches in both time periods. Conductivity showed a significant increasing trend across the Athabasca River during the second time period. Conductivity values were significantly higher in the Hinton reach in time period 1 ($p = 0.022$) and significantly higher in time period 2 in the Mouth reach ($p = 0.002$). Sodium concentrations showed a significant increasing trend in both time periods 1 and 2 ($p = 0.005$ and 0.005) along the river continuum. These concentrations were significantly higher during time period 2 in the Hinton ($p < 0.001$), Athabasca ($p = 0.003$), and Mouth ($p < 0.001$) reaches than time period 1.

Cumulative loadings. The total cumulative loading of sodium was approximately 20 kg/d higher in time period 2. Cumulative total organic carbon and dissolved nitrogen were 13 386 kg/d and 767 kg/d lower across the river basin in time period 2 compared with time period 1, respectively.

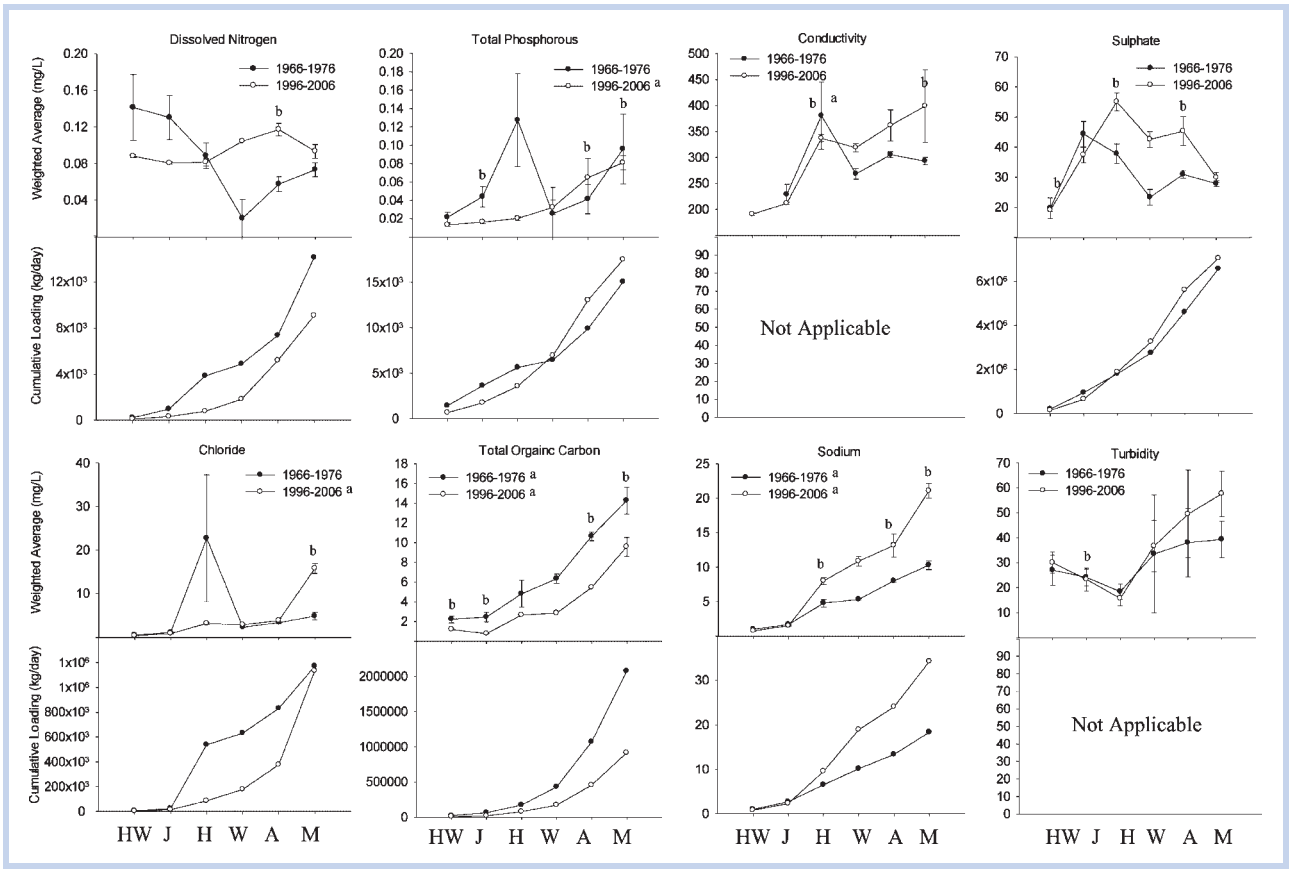

Figure 7. Weighted average (± SE) and cumulative loadings for selected water quality parameters at stations along the Athabasca River continuum across 2 time periods historical (1966–1976) and current day (1996–2006) calculated from data in Table 2. Reach names are abbreviated as: HW, Headwaters; J, Jasper; H, Hinton; W, Whitecourt; A, Athabasca; M, Mouth. For each weighted average parameter, [a] in each legend indicates a significant trend across reaches ($p < 0.05$); [b] for a reach denotes a significant difference between time periods in that parameter at that reach ($p < 0.05$). [1] Units are weighted average (μS/cm) and cumulative (μS/cm). [2] Units are weighted average (NTU) and cumulative (NTU).

Cumulative loadings of chloride were 453 038 kg/d higher at the Hinton reach in time period 1 than time period 2. This increase was no longer observed in time period 2; however, cumulative dissolved chloride did increase by 757 688 kg/d between the Athabasca and Mouth reaches in time period 2 allowing the levels of chloride to reach a similar cumulative total concentration in the Mouth reach in both time periods.

Cumulative total phosphorous loadings were lower in the Headwater, Jasper and Hinton reaches in time period 2 compared with time period 1. However, this trend reversed in the lower half of the basin where the concentrations in the Whitecourt, Athabasca, and Mouth reaches were higher in time period 2 compared with time period 1. Cumulative sulfate loadings showed a similar trend to total phosphorous loadings.

Comparison to benchmarks. A summary of the current water quality guidelines at the Canadian federal level as well as for selected provinces are listed in Table 5. Few guidelines for the protection of aquatic life exist for these parameters. However, several guidelines for these variables do exist for agricultural and irrigation waters as well as drinking water for human consumption. Only turbidity and total phosphorous exceeded any of the guidelines listed in Table 5 in the time periods considered in this study. Turbidity exceeded both national and provincial guidelines across all reaches in both time periods. Total phosphorous exceeded chronic levels in the Alberta provincial guidelines for the Hinton and Mouth reaches in time period 1 and in the Athabasca and Mouth reaches of time period 2.

Percentiles were calculated for each reach using time period 1 as a reference baseline for water quantity (average flow) and water quality (total organic carbon, dissolved nitrogen, dissolved sodium, turbidity, total phosphorous, conductivity, dissolved chloride, dissolved sulfate) parameters in this study (Table 5). Average flow in time period 2 fell between the 90th and 10th percentiles from time period 1 in all reaches. Concentrations of total organic carbon were below the 10th percentile in the Whitecourt, Athabasca, and Mouth reaches in time period 2. The Whitecourt reach showed concentrations in time period 2 that exceeded the 90th percentile for dissolved sodium, conductivity, dissolved chloride, and sulfate. Concentrations of dissolved sodium in the second time period also exceeded the 90th percentiles in the Athabasca and Mouth reaches and are consistent with the significant increases in weighted average concentrations between the 2 time periods. Concentrations of dissolved chloride in the Mouth reach also exceeded the calculated 90th percentile in the second time period.

Table 5. Benchmarks for evaluation of changes in selected water quantity and quality parameters, including Canadian federal and provincial guidelines for the protection of aquatic life and objectives calculated for each reach based on the 10th and 90th percentiles of time period 1 (1966–1976)

Parameter	Canadian (National and Provincial)	Percentile	Headwater reach	Jasper reach	Hinton reach	Whitecourt reach	Athabasca reach	Mouth reach
Average flow (m^3/sec)		10th	12.34	33.20	48.36	186.5	170.5	202.2
		90th	254.0	498.0	667.2	734.0	1357.2	1500.6
Total organic carbon (mg/L)	± 20% of median	10th	0.50	0.50	1.65	6.00	6.00	9.60
		90th	5.00	6.00	7.80	6.80	19.90	22.40
Dissolved nitrogen (mg/L)		10th	0.04	0.04	0.003	0.002	0.003	0.01
		90th	0.22	0.233	0.13	0.04	0.13	0.18
Dissolved sodium (mg/L)	0–30[a]	10th	0.40	0.60	1.90	4.14	4.00	5.11
		90th	1.40	2.50	9.80	6.46	12.49	17.82
Turbidity (NTU)	2–8[b]	10th	0.60	1.60	2.00	10.52	1.49	3.52
		90th	70.00	68.40	37.00	59.00	70.60	89.80
Total phosphorous (mg/L)	0.05 (chronic) and 0.1–0.3[c]	10th	0.002	0.003	0.007	0.004	0.004	0.02
		90th	0.07	0.10	0.38	0.05	0.09	0.08
Conductivity (μS/cm)		10th	No data	131	204	247	216	211
		90th		393	439	300	418	415
Dissolved chloride (mg/L)	100–700[a]	10th	0.20	0.20	0.53	1.76	1.00	1.20
		90th	0.80	1.96	9.43	2.80	6.52	7.50
Dissolved sulfate (mg/L)	100–1000[d]	10th	8.00	13.33	19.48	18.20	16.48	17.11
		90th	42.20	90.76	58.82	27.00	50.58	43.04

[a]For agricultural irrigation water (Alberta, British Columbia).
[b]Dependent upon background levels of turbidity (Federal, British Columbia).
[c]This is an interim guideline (Alberta, British Columbia, and Ontario).
[d]For agricultural livestock water (Federal, Alberta, and British Columbia).

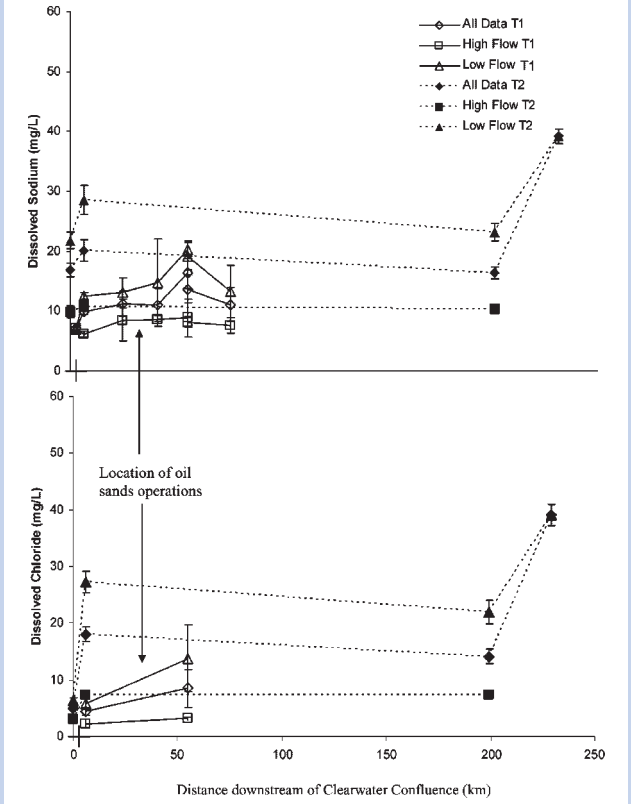

Figure 8. Concentrations of dissolved sodium and chloride (mg/L) in the Athabasca River measured downstream of the Clearwater River confluence in the mouth reach of the Athabasca River Basin.

DISCUSSION

Water quantity

In aquatic ecosystems, variability in flow is needed to maintain natural habitat dynamics and support the maintenance and persistence of biota (Baron et al. 2002). Disruption in the natural magnitude, frequency, duration, timing, and rate of change of flow in aquatic systems can lead to the elimination of some aquatic environments (Poff et al. 1997). In the Athabasca River, flows in the Mouth reach have decreased by more than 260 m^3/s in time period 2 compared with time period 1 (Figure 3). This is equal to more than the total flows in the headwaters in time period 1 (115 m^3/s) and time period 2 (85 m^3/s). The ecological significance and acceptability of this level of water loss is not known in the absence of target in-stream flow needs for the Athabasca River (Schindler et al. 2007). What is known is that a loss of 260 m^3/s at the mouth of the river over the past 30 y will only increase in the years to come given the increasing developmental pressures, especially in the lower part of the basin (Woynillowicz et al. 2005). Given the development projections, consequences to public health (drinking water), the economy (transportation routes, energy production), and water policy on both provincial and national levels require more serious consideration.

Peak flows and flooding events of the Athabasca River basin are associated with snowmelt, and approximately 70% of the moisture input into the basin originates from precipitation (Culp et al. 2005). Decreases in the average and cumulative flows could be attributed to both natural and anthropogenic sources including human water withdrawals, increased warming causing increased evapotranspiration, and decreased winter snowpack (Schindler and Donahue 2006). Therefore, it is important to examine the potential causes for decreasing flows in the Athabasca River, one of the largest unregulated and diversely used freshwater sources in the province of Alberta.

It is widely acknowledged that increasing global temperatures are causing significant decreases in our glacier volumes. Glaciers from the headwaters of the Athabasca River basin and, consequently, decreases in their size will impact the quantity of water along the entire river. The average temperature in time period 2 was 1.4°C higher than the average temperature in time period 1 across all reaches (Figure 4). This trend is further corroborated with the work of Schindler and Donahue (2006) who showed that, since 1970, the Athabasca River has seen an overall increase in air temperature of 2°C. These authors also show that, due to this increase in air temperature, most large glaciers in the headwaters of the nearby Bow and Saskatchewan Rivers, along with the Athabasca River have shrunk by approximately 25% in the past century. Further glacier decline is expected move the downstream hydrograph toward a snowmelt dominated regime (Comeau 2008).

In addition to glacial melt, another significant source of water to the Athabasca River is the snow pack. In recent years, climate change has been connected to significant changes in the maximum depths and melting rates of snow packs in the northern region of the province of Alberta (Schindler and Donahue 2006; Romolo et al. 2006a, 2006b). In the Peace River Basin, north of the Athabasca River, Romolo et al. (2006b) showed that the date of spring snowmelt in this river basin has occurred progressively earlier during 1963–1996. These trends are similar to the Athabasca River Basin where we showed that spring melt has been occurring 1 month earlier in the lower half of the basin in time period 2 (1996–2006) compared with time period 1 (1966–1976). This earlier spring melt can be mostly attributed to the increasing air temperatures between these 2 time periods, which triggers the earlier melt of the snow pack (Schindler and Donahue 2006; Romolo et al. 2006b).

In the Athabasca River basin, time period 2 saw a lower total precipitation (81 mm) than time period 1 averaged across all reaches (Figure 4). These changes, coupled with warming air temperatures and decreasing glacial size at the headwaters will not only cause spring melt to peak sooner in the year, but it will also decrease the amount of spring runoff and thereby affect the overall level and flow rates across the entire basin (Lapp et al. 2005; Schindler and Donahue 2006). These effects are already taking place, as we have observed with the significantly lower average high and low flows during the second time period in the lower half of the Athabasca River Basin (Tables 3 and 4).

Differences in peak and cumulative discharges could also be a result of greater instream flow requirements in this basin during the second time period (more industry, agriculture, urban, population growth, etc.). Allocations for surface water withdrawal along the entire Athabasca River represent 8% of all allocated surface water use in Alberta (Schindler et al. 2007). There is an increasing amount of both industrial and urban land uses in the second time period (Table 1). These

include 4 more pulp mills, an increase in the population in the province of Alberta by 40%, and an increase in the amount of farm area in Alberta by almost 5 000 000 acres (Statistics Canada 2007). In response to these increased developments, water allocations have increased dramatically in several reaches (Whitecourt, Athabasca, and Mouth) in the second time period (Figure 5), coinciding with the observed decrease in flow in the lower half of the river (Figure 3). This trend has also been discussed by Schindler et al. (2007) where they argue that in addition to increased water allocation and consumption, the amount of runoff downstream of Hinton has been steadily decreasing over the past 30 y, contributing to our observed trend of decreasing cumulative flow.

Development of the Athabasca oil sands deposit near Fort McMurray, Alberta (Figure 1) is expanding at a tremendous pace. This expanded development requires a greater draw of water from the Athabasca River in the Mouth reach to accommodate oil sands processing. Currently, 76% of allocated water in the Athabasca River is for oil sands extraction (Schindler et al. 2007). To counteract this increased demand, many of the companies currently extracting bitumen from the Athabasca oil sands deposits are making an effort to reduce the amount of water required per barrel of oil. Formerly, 4 barrels of water were required to produce 1 barrel of oil, currently through the recycling of process water, this number has been reduced to 2 barrels of fresh water for every barrel of oil (Schindler et al. 2007).

Water quality

Specific conductance (conductivity) is highly correlated with the amount of total dissolved solids in the water and, as such, is a representation of the salinity and a measure of the ability of water to conduct an electrical current (Said et al. 2004). An increase in conductivity, as is seen in the second time period, could be an indication that the Athabasca River is becoming more concentrated with salts. This could be a result of the reduced flows also observed in the second time period, or it could be attributed to the increase in industrial and urban development along the river basin.

Turbidity can affect the toxicity of other contaminants by affecting processes such as photoactivation and by binding to, and, therefore, altering the bioavailability of contaminants (Ireland et al. 1996). High levels of turbidity can also affect the health of aquatic ecosystems by damaging habitats for fish and other aquatic organisms (Said et al. 2004). One aspect of turbidity that has been studied is its affects on the ability of fish to detect prey or mates, thereby affecting the growth and reproduction of fish (De Robertis et al. 2003; Engström-Öst et al. 2006). These can all be future issues of concern if the turbidity in the lower reaches of the river become too great.

The impact of agriculture on water quality can become more evident in areas where agriculture is the most dominant form of land use and the effects of numerous small sources can accumulate to produce a more serious ecological effect (Schroder et al. 2004). While the total area of crop land farmed in the Athabasca River basin specifically was unavailable, in the province of Alberta it has increased by only 1.9% over the past 10 y. Applications of herbicides and insecticides have increased by 9.5 and 14.5%, respectively (Statistics Canada 2007). This provides an indication of the increase in intensity of agriculture practices, providing more opportunities for the leaching of nutrients and organic chemicals into the surrounding surface waters. In addition, both nutrients and dissolved organic carbon can be higher during spring runoff due to the flushing of natural organic matter from the soil and shallow groundwater systems (Schroder et al. 2004; Barber et al. 2006). Total phosphorous and total nitrogen have been shown to be strongly linked to particulate matter in the headwaters of the Athabasca River, providing a possible reason for these similar trends we observed between nutrients and dissolved organic matter (Glozier et al. 2004).

Cumulative total organic carbon was lower across the river basin in time period 2 compared with time period 1. Decreased stream flows, due to climate change, allow for increased residence time in the water column and can be a major contributing cause to decreases in dissolved organic carbon. However, drier soils and lower water tables can decrease allochthonous dissolved carbon inputs along the river continuum, which can provide the mechanism for settling of organic matter along the river continuum over time (Schindler 2001).

During periods of low and high flow, concentrations of certain parameters (total phosphorous, TOC, and turbidity) can fluctuate. In times of low flow these parameters can become more concentrated, thereby exhibiting a greater biological effect. Table 2 outlines the number of samples available during high flow (May to August) and low flow (September to April) periods. Although we believe that we have an adequate representation of the yearly variations in concentrations of the most seasonally affected parameters, we did not have enough data to calculate the average annual high flow and low flow concentrations in time period 1 across all reaches. A greater dispersion of data is necessary to adequately assess the effects of seasonal changes in flow on the concentrations of these parameters.

Glozier et al. (2004) examined nutrient concentrations downstream of the town of Jasper across the years 1973–2002. They found the median total phosphorous levels to be 0.010 mg/L, the median total organic carbon to be 1.17 mg/L and the median dissolved nitrogen to be 0.11 mg/L. Another study conducted as part of the Northern Rivers Ecosystem Initiative, looked at nutrient levels across the lower portion of the Athabasca River from 1985 to 2000. They found the median concentrations of total phosphorous to be >0.08 mg/L, and dissolved inorganic and total nitrogen to be >0.2 mg/L and >0.7 mg/L, respectively, across this time period (Chambers et al. 2006). Both of these studies report levels that are similar to, or higher than those in this study. The values stated by Glozier et al. (2004) fall between the first and second time periods of this study (Figure 7). The dissolved inorganic and total nitrogen values reported by Chambers et al. (2006) are higher than the dissolved nitrogen values in this study, and their total phosphorous values are higher than the total phosphorous in both time periods with the exception of the Hinton and Mouth reaches of time period 1. The differences in concentrations reported in these 2 studies and our study could be due to the different time periods and sources of data used for calculations. Both of these variations can skew results, providing us with a different value which may or may not be of concern. These differences highlight the importance of continuous and consistent water quality monitoring programs to monitor long-term changes in this region.

Sources of dissolved nitrogen in surface waters are from both natural and anthropogenic sources. Most of the nitrogen in the cycle is unavailable to the majority of organisms (N_2 gas); therefore, the greatest impact humans can have on this cycle is to liberate this fixed nitrogen into more bioavailable forms (Vitousek et al. 1997). Anthropogenic sources can include agricultural fertilizers, municipal effluent discharge, atmospheric transport, and bacterial breakdown of in-stream organic matter (Glozier et al. 2004). Previous studies conducted as part of the larger Northern Rivers Ecosystem Initiative study showed nutrient concentrations can increase by 2 times downstream from secondary treated pulp mill and sewage effluent discharges (Chambers et al. 2006).

The concentrations of dissolved nitrogen in time period 1 were higher than concentrations in time period 2 in the upper half of the basin. This trend in dissolved nitrogen could be due to the better treatment for sewage and pulp and paper mill effluent. The addition of secondary and in some cases tertiary treatment systems can decrease the amount of nutrients and particulate matter that are released directly into the river system (Chambers et al. 2000, 2006). After the Whitecourt reach, however, cumulative dissolved nitrogen is higher in time period 2. Increased intensity of agriculture in time period 2, along with the addition of a pulp mill between time periods 1 and 2 in the Athabasca reach could be contributing factors toward this trend.

Sulfate loadings increased across the river continuum in both time periods, however, they decreased substantially after the Whitecourt reach in time period 2, and were markedly lower in time period 2 at the mouth reach. Two major causes of increased sulfate in surface waters are oxidation of sulfide within the sediment, more specifically peat, and the suppression of sulfide reducing activity deeper into the sediment profile through increased oxidation of sediments (Bottrell et al. 2004). In the Athabasca oil sands, the most economical way to remove the bitumen from the ground is through strip mining. This involves the removal of a peat and natural soils overburden layer, usually less than 75 meters in thickness before the bitumen can be removed for processing (Hein and Cotterill 2006). It is possible, therefore, that this initial step of strip mining the peat and natural soil overburden in the oil sands region is decreasing the inputs of sulfur into the overlying waters during the second time period through the removal of the sulfur-containing peat, and the suppression of the sulfur reducing bacteria through the oxidation of the removed layer of natural sediment.

Sodium had higher cumulative loadings in time period 2 downstream from the Jasper reach compared with time period 1. The oil sands area has been shown to have a higher distribution of salinity and there is some evidence to support the idea of the oil sands deposit near Fort McMurray, Alberta, to be of marine origin (Conly et al. 2002; Adams et al. 2004; Headley et al. 2005). This provides a natural source of sodium and chloride to this area, and once disturbed through surface mining, these ions may leach into the surrounding surface waters. The MacKay River, which is a major tributary near the mouth of the Athabasca River, has shown trends of increasing chloride and sodium concentrations from its headwaters to mouth (Headley et al. 2005).

Chloride can come from anthropogenic sources such as road de-icers and marine sediments (Barber et al. 2006). Chronic concentrations of chloride of 250 mg/L have been recognized as harmful to freshwater life and not potable for human consumption (Kaushal et al. 2005). While concentrations of chloride in this study did not reach these levels, concentrations in the Whitecourt and Mouth reaches during time period 2 did exceed the 90th percentiles from time period 1 and, therefore, shows the potential to be of greater concern in future years.

Cumulative concentrations of chloride in this study showed a marked increase at the Hinton reach in time period 1 and in the Mouth reach in time period 2. This could be attributed to the use and, therefore, release of elemental chlorine as the bleaching agent in the Hinton pulp mill during this earlier time period. This spike was no longer observed in time period 2, and this may be primarily due to the elimination of chlorine dioxide as the primary bleaching agent in June 1993 (Chambers et al. 2000). However, chloride concentrations reached a similar cumulative total concentration in the Mouth reach in both time periods because of a marked increase occurring between the Athabasca and Mouth reaches in time period 2.

There are several large tributaries that enter the mainstem of the Athabasca River. These include the Clearwater, Lesser Slave, Pembina, and McLeod Rivers. The discharges from these tributaries could either increase or dilute the concentrations of certain water quality parameters in the mainstem. However, the extent of these tributary contributions is unknown. It is, therefore, important to consider the impact of these sources when examining water quality trends along the mainstem.

The greatest changes in water quality and quantity between time periods 1 and 2 have occurred in the mouth reach of the Athabasca River. Both dissolved chloride and dissolved sodium increased significantly between time period 1 and 2 in the mouth reach (Figure 7). The major tributary contributing to this reach is the Clearwater River, which enters toward the beginning of this reach. To further explore the contribution of this tributary, we plotted the concentrations of dissolved sodium and chloride in each time period and by high and low flows as a function of distance from the Clearwater River confluence (Figure 8). In time periods 1 and 2, both sodium and chloride concentrations increase downstream of the confluence, especially during low flow. However, these parameters increase even further downstream of the oil sands operations in time period 2. This increase was not observed in time period 1, which occurred before the development of any major oil sands operations. Because we lack the spatial resolution of data between the Clearwater tributary and the oil sands operations, we cannot determine if concentrations increase at the oil sands beyond the tributary influences. However, we can conclude based on the data resolution that we have and through examination of the differences between time periods 1 and 2 that the oil sands operations has had an effect over and above the tributary influences. Further consideration should be taken in future work to determine the exact influence of major tributaries on these water quality parameters considering flow and land use.

Comparison to benchmarks

Phosphorous concentrations exceeded the chronic interim provincial guideline (0.05 mg/L) for Alberta in the Athabasca (0.06 mg/L) and Mouth (0.08 mg/L) reaches in time period 2 (Table 5). Excessive phosphorus is a major cause of eutrophic conditions in lakes and other water ways (Chambers et al.

2001). Eutrophication can cause a major decrease in the dissolved oxygen levels and increases in the temperature of water, resulting in deaths of fish and other organism populations (Said et al. 2004).

The absence of guidelines for other parameters considered here prevented assessment of the significance of any changes measured between time periods 1 and 2. There is a need to develop site-specific objectives for 2 reasons: 1) to fill in gaps for parameters where guidelines do not exist, and 2) to account for naturally high levels of some parameters in some areas. Several methods have been proposed to calculate benchmarks for water quality comparisons including reference condition approaches and percentiles or standard deviates from reference conditions in space or time (Bailey et al. 1998; Kilgour et al. 2007). The reference condition approach for example is largely reserved for biological assessments with greater emphasis placed on benthic macroinvertebrate community structure. It requires the comparison between a system that has undergone stress to a series of reference sites unexposed to this stress (Bailey et al. 1998). To apply this method, the biological condition of several reference sites must be sampled and their variation represents the acceptable range of a reference condition. If the exposed site falls outside of this reference condition, typically in multidimensional multivariate space, it is deemed to be impacted. This method is both labor and data intensive and requires many sites with adequate biological data.

It is possible that, depending upon the natural habitat of a location, pristine waters unaffected by human development can exceed national or provincial guidelines set for certain water quality parameters (e.g., waters that run through an area of high natural metals, such as the oil sands region). In an effort to improve the development of guidelines to assess changes in waters, other more site-specific methods are being considered, such as summarizing background concentrations of parameters at pristine and undeveloped sites in a region and using the 90th percentile as a site-specific benchmark (Glozier et al. 2004; de Rosemond et al. 2009). This method has the potential to be applied across many indicators (biological and physical), providing the opportunity to make comparisons to a reference condition across different indicators.

Our results showed that Whitecourt reached concentrations in the second time period which exceeded the 90th percentile objective from time period 1 for dissolved sodium, conductivity, dissolved chloride, and sulfate (Table 5). However, this may be due to the smaller sample sizes available to calculate the 90th percentile in this reach, rather than any stressor-related causes (Table 2). Concentrations of dissolved sodium in the second time period exceed the 90th percentile objective from time period 1 in the Athabasca and Mouth reaches. Concentrations of dissolved chloride in the mouth reach also exceeded the calculated 90th percentile in the second time period. These results corroborated the significant differences seen with weighted average concentrations between the 2 time points. The significance of increased sodium and chloride in the water of the lower Athabasca River is beyond the scope of this study. What can be said, however, is that sodium and chloride concentrations have significantly increased over 30 y with increases in the present day in the top 10% of levels observed 30 y ago.

The data used to calculate these percentiles was the total amount of data over a 10-y time period (1966–1976) (Table 2). When considering the biological significance of these percentiles, we must look at the effects of seasonal changes in flow on the concentrations of these parameters. In times of low flow, concentrations may increase in the river, making their effects more pronounced when compared with high flow periods. A greater distribution of data to provide better seasonal resolution is required to determine if these exceedances are seasonally dependent and if this percentile approach is applicable over a broad time scale.

Average flow in time period 2 was compared and was found to be within the calculated 10th and 90th percentiles from time period 1. Although we were able to assess significant changes when comparing the average, peak, and cumulative flow between the 2 time periods, this confirmed when compared with the calculated benchmarks. This could be a result of how these percentiles were calculated. It may be more useful to focus on producing benchmarks for comparing the low and peak flows only, instead of over an entire year or time period. This way, changes in flow during these more ecologically sensitive flow periods can be assessed and managed.

CONCLUSIONS

Because it is not yet understood how much water is needed to maintain the ecological integrity of the Athabasca River basin, no clear decisions have been made regarding the sustainability of this resource under the high demands of industrial growth. However, we do know that the natural flow dynamic of the Athabasca River must be preserved to maintain the ecological integrity of this important river basin. River flow regimes are determined by several factors such as size, climate, geology, and vegetative cover. This is a significant unregulated river in Alberta and based on our data, the intensity, timing, and volume of flow have changed over the past 30 y. The significance and acceptability of this change requires attention, especially considering development intensity will only increase with time.

Despite there being both federal and provincially managed water quality monitoring programs, there was a limited amount of consistent and reliable data available for use in this study. Our objectives were to measure change in water quality and water quantity at a watershed scale. Considering the increasing emphasis of regional assessments and watershed management, our study shows that data simply do not exist to optimally assess change at this scale. Thus, it is critical to improve our monitoring programs so that data are collected in a continuous and consistent way to facilitate continued broad scale assessments to protect one of our most important natural resources.

Despite it being widely recognized that there is a need to shift from local, project scale CEAs to broader, landscape, or regional scale assessments to accurately assess cumulative effects across an entire river ecosystem, no study previous to this has attempted to quantitatively isolate the important water quantity and quality variables that can potentially affect the health and condition of an entire river basin over a period of 40 y. This study provides the base for further evaluation of indicators (water quality parameters, sediment quality parameters, indicators of biological populations of communities) along the river continuum. Over time, this can reveal indicators that have changed and the magnitude of this change and its potential impact on the Athabasca River basin.

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