OXIC LIMESTONE DRAINS FOR TREATMENT OF DILUTE, ACIDIC MINE DRAINAGE[a]

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Abstract

Limestone treatment systems can be effective for remediation of acidic mine drainage (AMD) that contains moderate concentrations of dissolved O_2, Fe $^{3+}$, or $A1^{3+}$ (1-5 mg-L^{-1}). Samples of water and limestone were collected periodically for 1 year at inflow, outflow, and intermediate points within underground, oxic limestone drains (OLDs) in Pennsylvania to evaluate the transport of dissolved metals and the effect of pH and Fe- and Al-hydrolysis products on the rate of limestone dissolution. The influent was acidic and relatively dilute (pH <4; acidity < 90 mg-L^{-1}) but contained 1-4 mg-L^{-1} Of O_2, Fe $^{3+}$, $A1^{3+}$, and Mn^{2+}. The total retention time in the OLDs ranged from 1.0 to 3.1 hours. Effluent remained oxic (02 >1 mg-L^{-1}) but was near neutral (pH = 6.2-7.0); Fe and Al decreased to less than 5% of influent concentrations. As pH increased near the inflow, hydrous Fe and Al oxides precipitated in the OLDs. The hydrous oxides, nominally Fe(OH)3 and Al(OH)3, were visible as loosely bound, orange-yellow coatings on limestone near the inflow. As time elapsed, Fe(OH)3 and Al(OH)3 particles were transported downflow. During the first 6 months of the experiment, Mn 2+ was transported conservatively through the OLDs; however, during the second 6 months, concentrations of Mn in effluent decreased by about 50% relative to influent. The accumulation of hydrous oxides and elevated pH (>5) in the downflow part of the OLDs promoted sorption and coprecipitation of Mn as indicated by its enrichment relative to Fe in hydrous-oxide particles and coatings on limestone. Despite thick (~1 mm) hydrous-oxide coatings on limestone near the inflow, $CaCO_3$ dissolution was more rapid near the inflow than at downflow points within the OLD where the limestone was not coated. The rate of limestone dissolution decreased with increased residence time, pH, and concentrations of Ca $^{2+}$ and HCO_3- and decreased P_{CO2}. The following overall reaction shows alkalinity as an ultimate product of the iron hydrolysis reaction in an OLD:

$$Fe^{2+} + 0.25\,O_2 + 2\,CaCO_3 + 2.5\,H_2O \rightarrow Fe(OH)_3 + 2\,Ca^{2+} + 2\,HCO_3^-$$

where 2 moles of $CaCO_3$ dissolve for each mole of $Fe(OH)_3$ produced. Hence, in an OLD, rapidly dissolving limestone surfaces are not stable substrates for $Fe(OH)_3$ attachment and

armoring. Because overall efficiency is increased by combining neutralization and hydrolysis reactions, an OLD followed by a settling pond requires less land area than needed for a two-stage treatment system consisting of an anoxic limestone drain an oxidation-settling pond or wetland. To facilitate removal of hydrous-oxide sludge, a perforated-pipe subdrain can be installed within an OLD.

Introduction

Acidic mine drainage (AMD) typically contains elevated concentrations of dissolved and particulate iron (Fe) and dissolved sulfate ($SO_4{}^{2-}$) produced by the oxidation of pyrite (FeS_2):

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4{}^{2-} + 2\ H^+$$

$$Fe^{2+} + 0.25\ O_2 + H^+ \rightarrow Fe^{3+} + 0.5\ H_2O \qquad (2)$$

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3\ (s) + 3\ H^+ \qquad (3)$$

Despite the stoichiometry indicated by reaction 1, the molar ratio of dissolved sulfate to iron $[SO_4{}^{2-}]/([Fe^{2+}]+[Fe^{3+}])$ in AMD containing oxygen (O_2) commonly exceeds 2 because of the relatively high solubility of $SO_4{}^{2-}$ and low solubility of ferric ions (Fe^{3+}), which tend to precipitate as $Fe(OH)_3$ and related solids in moderately acidic to neutral solutions ($3.5 \leq pH \leq 7$) (Bigharn et *aL*, 1996; Nordstrom and Alpers, 1998). Concentrations of manganese (Mn^{2+}), aluminum ($A1^{3+}$), and other solutes in AMD commonly are elevated due to aggressive dissolution of carbonate, oxide, and aluminosilicate minerals by acidic water along flow paths downflow from oxidizing pyrite (Cravotta, 1994).

AMD commonly develops where the carbonate minerals, calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), are absent or deficient relative to pyrite in coal overburden (Brady et *aL*, 1994). Dissolution of calcite, which is the principal component of limestone, can neutralize acidity and increase pH and concentrations of alkalinity (HCO_3- + OH-) and calcium (Ca^{2+}) in mine water by the following reactions:

$$CaCO_3\ (s) + 2H^+ \leftrightarrow Ca^{2+} + H_2CO_3{}^* \qquad (4)$$

$$CaCO_3\ (s) + H_2CO_3{}^* \leftrightarrow Ca^{2+} + 2\ HCO_3{}^- \qquad (5)$$

$$CaCO_3\ (s) + H_2O \leftrightarrow Ca^{2+} + HCO_3{}^- + OH^- \qquad (6)$$

where $[H_2CO_3{}^*] = [CO_2\ (aq)] + [H_2CO_3{}^0]$ (Plummer et *al*, 1979; Stumm and Morgan, 1996). The overall rate of calcite dissolution depends on the partial pressure of carbon dioxide (P_{CO2}) and the activities of H^+, H_2O, Ca^{2+}, and HCO_3- near the calcite surface (Plummer et *al*, 1979; Arakaki and Mucci, 1995). Generally, the overall rate of calcite dissolution will decrease as the pH and activities of Ca^{2+} and HCO_3- increase and the P_{CO2} decreases.

Use of limestone for neutralization of AMD in surficial environments has been limited because of its low solubility and slow dissolution rate relative to other alkaline reagents and decreased efficiency of neutralization associated with its "armoring" (strong adhesion and complete pacification by encrustation) with Fe^{3+} and $A1^{3+}$ compounds (Hill and Wilmoth, 1971; Lovell, 1972). Recently, treatment systems including anoxic limestone drains (Turner and McCoy, 1990; Brodie et *al,* 1991; Hedin and Watzlaf, 1994; Hedin et *al,* 1994a,b), open limestone channels (Ziemkiewicz et *al,* 1996, 1997), and limestone diversion wells (Arnold, 1991; Cram, 1996) have been demonstrated to neutralize AMD and downstream water in mined watersheds in the eastern U.S.A. Each of these systems has limitations in effectiveness and applicability.

Anoxic limestone drains (ALDs), which have been designed to avoid armoring, are particularly effective for generation of alkalinity (Hedin et *al.*, 1994b). In its simplest form, an ALD is a buried, limestone-filled trench that intercepts AMD before its exposure to atmospheric O_2. Retaining CO_2 within an enclosed ALD can enhance calcite dissolution and alkalinity production by reaction 5. By this mechanism, a greater quantity of alkalinity can be generated in an ALD, which is enclosed to minimize gas flux, compared to systems such as limestone channels or diversion wells that are open to the atmosphere. After treatment by an ALD, effluent is exposed to the atmosphere, and solid $Fe(OH)_3$ is produced by the oxidation of ferrous ions (Fe^{2+}) to Fe^{3+} by reaction 2 and the consequent hydrolysis of Fe^{3+} by reaction 3 or by

$$Fe^{3+} + 3\ HCO_3^- \rightarrow Fe(OH)_3\ (s) + 3\ CO_2. \tag{7}$$

Excluding O_2 from contact with the mine water in an ALD minimizes the potential for in situ precipitation of $Fe(OH)_3$. The precipitation of $Fe(OH)_3$ and various other hydroxide and/or sulfate compounds of Fe^{3+}, $A1^{3+}$, and possibly Ca^{2+}, within an ALD can armor the limestone surface, decreasing the rate and extent of limestone dissolution and alkalinity production (Watzlaf *et al,* 1992; Hedin and Watzlaf, 1994; Aschenbach, 1995; Robbins *et al,* 1997). Furthermore, the accumulation of precipitated compounds can decrease the porosity and permeability within an ALD (Watzlaf *et al,* 1994; Robbins *et al,* 1996). Hence, design criteria for ALDs as proposed by Hedin *et al (1* 994a) and Hedin and Watzlaf (1994) generally are conservative with respect to influent chemistry (requirement of <1 $mg\text{-}L^{-1}$ of dissolved O_2, Fe^{3+}, or $A1^{3+}$) and sizing (prolonged residence time) to ensure "maximum" alkalinity production over the life of an ALD.

Stringent requirements for low concentrations of O_2, Fe^{3+}, and $A1^{3+}$ in AMD make ALDs inappropriate for treatment of oxic or highly mineralized water, which commonly occurs in mined areas (Wood, 1996; Rose and Cravotta, in press). Thus, variations on the basic ALD design have been proposed. One alternative uses pretreatment by a compost layer to decrease concentrations of dissolved O_2, Fe^{3+}, and $A1^{3+}$ in the mine water to acceptable levels before routing the water through a limestone layer (Kepler and McCleary, 1994). Nevertheless, short-term laboratory studies (1 -2 years) indicate that limestone alone can be as effective as this layered system for neutralization of oxic mine water containing moderate concentrations of Fe^{3+} and $A1^{3+}$ (10-20 $mg\text{-}L^{-1}$) (Watzlaf, 1997). This variation on the ALD design is essentially an oxic limestone drain (OLD). In an enclosed OLD, oxidation and hydrolysis reactions will not be prevented (reactions 2, 3, and 7). If sufficiently rapid flow rates can be attained, the solid hydrolysis products can be transported through the OLD. Despite potential for armoring and clogging, the hydrous oxides can be effective for the sorption of dissolved Mn $^{2+}$ and trace metals (Anderson and Rubin, 1981; Coston *et al,* 1995; Smith *et al,* 1998). Additionally, the in situ production and retention of H^+ and CO_2 in an OLD may promote limestone dissolution (reactions 4 and 5). However, the processes and function of OLDs under field conditions have not been evaluated to date.

To investigate hydrogeochemical processes within limestone drains under oxic conditions, the U.S. Geological Survey (USGS) constructed three experimental OLDs in 1995 to treat acidic drainage from an abandoned coal mine. The flow rate and initial dissolved O_2 concentration of the influent to one or more of the OLDs were varied to determine any effects on the rates of dissolution and precipitation reactions and the transport of reaction products through the OLDs. Monitoring was conducted for 1 year during 1995-96. Water and rock samples were collected and analyzed to explain changes in water chemistry within the OLDs as a result of oxygenation, dissolution, precipitation, and sorption reactions. This report evaluates effects of pH, dissolved O_2, solute concentrations, hydrolysis of Fe $^{3+}$ and A1^{3+}, and flow rates (residence time) on limestone dissolution and metals transport within these experimental OLDs. The present report summarizes the content of the more detailed report of Cravotta and Trahan (in press).

Methods

Design of Experimental Limestone Drains

In February 1995, three identical OLDs were constructed in parallel to treat AMD seeping from the entrance to the Orchard Mine in the Southern Anthracite Coalfield in the northern part of Swatara Creek Watershed of east-central Pennsylvania. The three OLDs were installed side by side in a horizontal, 4-m wide by 30-m long trench. Each OLD was constructed using 0.79-m inside-diameter (ID) corrugated steel culvert pipe that was split lengthwise to form a semicircular trough that was 24.4 m long, with a cross-sectional area of 0.244 m ^{2} (Fig. 1). After lining each trough with layers of polyethylene and vinyl sheeting, a total of 12,700 kg of tabular, 3-cm minimum width by 1 0-cm maximum length, limestone fragments (97% $CaCO_3$) was placed in each OLD and the vinyl liner was wrapped over the top of the limestone before backfilling with 1-2 m of excavated soil to the original land-surface grade. Water was first routed through the system on March 15, 1995.

At the inflow to the OLDs, plumbing valves and a static mixer, consisting of a 30-cm ID standpipe filled with polyethylene trickling media, enabled aeration (pure O_2), deaeration (N_2 sparging), or no pretreatment of the inflow to all three or to only one of the OLDs (Fig. 1). For pretreatment, raw mine water and compressed N_2 or O_2 gas were introduced at the bottom of the static mixer (about 1 m below ground level) and flowed upward 2.1 m through the trickling media to promote gas exchange before the water was diverted into the OLD(s). A one-way valve at the top of the static mixer allowed excess gas to escape. The outflow pipe from each OLD consisted of a U-shaped trap and riser that extended about 0.2 m above the top of the limestone to ensure continuous inundation of the limestone and to minimize airflow into the OLDs.

For water and rock sampling, capped, 5-cm ID PVC pipes were installed within the OLDs at ports 1.5, 3, 6.1, 12.2, and 18.3 m downflow from the inflow (Fig. 1). Sampling access ports also were installed at the inflows to the static mixer and to each OLD. Flexible vinyl tubing, which was clamped shut where accessible at the surface, was extended down through a hole in each cap to the outside of the pipe mid-depth within each OLD, 0.2 m from the bottom of the OLDs. To prevent clogging by large particles, polyester filter fabric was wrapped around the sampling tube ending within the drain.

Sampling and Analytical Methods

Water samples were routinely collected at 3- to 4-week intervals during March 1995 - March 1996, except when access was blocked by deep snow cover during December and January. Field measurements and water samples from each OLD were collected sequentially upflow at sampling ports (Fig. 1) while maintaining a constant flow rate through each OLD. Samples of untreated AMD were collected at the inflow to the OLDs and also at an adjacent ditch, which bypassed the OLDs (untreated control). The volumetric flow rate was measured by repeatedly measuring the time to collect a known volume of water at the drain outflow and ditch sampling points.

Temperature, dissolved O_2 (DO), specific conductance (SC), redox potential (Eh), and pH of water samples were measured electrometrically in the field by diverting unprocessed water through a glass flow cell according to methods of Wood (1976). Before conducting sample measurements, all meters were calibrated in the field with appropriate electrodes and standards that had been thermally equilibrated to sample temperatures. Eh was measured with a combination Pt and Ag/AgCl electrode, checked with Zobell's solution, and corrected to $25^{O}C$ according to methods of Wood (1976) and Nordstrom (1977). Alkalinity and acidity for unfiltered samples usually were titrated in the field at ambient temperature with sulfuric acid (1.6 and 0.16 N H_2SO_4) and sodium hydroxide (0.1 N NaOH) to pH 4.5 and 8.3 endpoints, respectively, using methods of Fishman and Friedman (1989) and Ott (1986). However, on some occasions, generally within 24 hours after sample collection, the alkalinity and/or acidity titrations were completed in the USGS Laboratory in Lemoyne, Pa. The polyethylene bottles for alkalinity and acidity samples were filled completely, tightly capped, and refrigerated until analyzed. Field and laboratory alkalinity or acidity on split samples were indistinguishable.

Water samples were analyzed for concentrations of sulfate (SO_4), silica (SiO_2), calcium (Ca), magnesium (Mg), sodium (Na), iron (Fe), manganese (Mn), aluminum (Al), and selected trace metals (Cravotta and Trahan, in press) using methods of Fishman and Friedman (1989). Water samples were split into filtered and unfiltered subsamples and stored in sample-rinsed polyethylene bottles, on ice, until laboratory analysis. Two unfiltered subsamples for analysis of (1) acidity and alkalinity and (2) anions were capped leaving no head space. A third subsample for analysis of "dissolved" cations and silica was filtered under pressure through a 0.45-mm pore-size nitrocellulose capsule filter, transferred to an acid-rinsed bottle, and preserved with nitric acid to pH <2. The fourth subsample for analysis of "total" metals was not filtered and was preserved with nitric acid to pH <2. Because sampling tubes within the OLDs were covered by a filter fabric, the whole-water sample for total metals was collected only at the inflow, outflow, and overflow.

Partial pressures Of CO_2 (P_{CO2}), activities of aqueous species, and mineral saturation indices were calculated using the WATEQ4F computer program (Ball and Nordstrom, 1991). The saturation index (SI) provides a basis for evaluating the potential for dissolution or precipitation of a solid phase by the water (Stumm and Morgan, 1996). Values of SI that are negative (<-0.1), approximately zero (±0.1), or positive (>0.1) indicate the water is undersaturated, saturated, or supersaturated, respectively, with the solid phase. If undersaturated, the water can dissolve the solid phase. If supersaturated, the water cannot dissolve the solid phase but can potentially precipitate it.

In March 1995, sawed pieces of limestone (1 -2 cm thick by 3-4 cm width "slabs") were initially measured for weight, porosity, and geometric surface dimensions (thickness, width, length) and then were suspended with braided nylon chord to be immersed within the OLDs. In August 1995 and March 1996, the immersed limestone slabs were retrieved and remeasured to determine the rate of limestone dissolution and the chemistry and mineralogy of the encrustation. Encrustations on the limestone samples were detached by gently rinsing the samples with deionized water. The detached material was dried at 180 ^{0}C, weighed, and dissolved in a 50% solution of 1:1 hydrochloric and nitric acid for analysis of "total" metals. Then, the limestone was oven dried and weighed to determine the extent of dissolution on the basis of weight loss over the time. The dissolution rate was normalized with respect to the measured surface area of the sample so that the field results could be compared with rate estimates from published laboratory experiments. Additionally, hydrous oxides collected from the OLDs in 1997 were analyzed for mineralogy by X-ray diffractometry (XRD).

Determination of Residence Time

Data for the porosity and flow rate were used to compute the residence time for water at each point sampled and over the range of flow rates evaluated. On the basis of the known drain volume and measured velocities for specific flow rates, Cravotta and Trahan (in press) estimated porosity to be 0. 14 for the OLDs. According to Darcy's equation (Freeze and Cherry, 1979), the velocity of flow through a porous medium is

$$v = Q / (A \cdot n), \qquad (8)$$

where Q is the volumetric flow rate, A is the cross-sectional area perpendicular to flow, and n is the porosity. By substituting $v = L/t_R$, where L is the distance along the flow path, and rearranging, residence time at any distance from the inflow was determined for a given Q (Fig. 2), assuming constant values for the cross-sectional area, $A = 0.244\ m^2$, and the porosity, n = 0. 14:

$$t_R = (L \cdot A \cdot n) / Q \qquad (9)$$

Note that the t_R is proportional to downflow distance, and the numerator of equation 9 is the void volume at that distance.

Results and Discussion

Hydrochemical Trends

During March 1995 - March 1996, the untreated AMD influent had ranges of pH = 3.2-3.8, SC = 410-710 mS cm^{-1}, and concentrations of DO = 1.3-3.4 mg-L^{-1}, acidity = 31-85 mg-L^{-1}, SO_4 = 130-300 mg-L^{-1}, and Al, Fe, and Mn, in order of increasing abundance, of 0.6-4 mg-L^{-1} (Table 1). Schwertmannite and goethite were present in the untreated AMD and intake pipes to the OLDs (J.M. Bigham, 1997, written commun.). The untreated AMD also hosted numerous microorganisms, including rod-shaped bacteria, fungi, and protozoans in suspension and in association with the hydrous iron oxides that formed in the intake pipes and on limestone, calcite, gypsum, and glass immersed at the inflow to the OLDs (Robbins et al, 1997).

The OLD treatment increased pH and concentrations of Ca and alkalinity of effluent relative to influent (Fig. 3, Table 1). On the basis of solute transport, effluent from each of the OLDs was statistically indistinguishable from one another, but was significantly different from the untreated AMD. Despite variations in the flow rate and chemistry of the influent, the effluent from the OLDs had pH >6 (pH 6.2-7.0) and was net alkaline. In contrast, AMD that bypassed the treatment and flowed about 35 m through an open ditch adjacent to the OLDs exhibited little change in chemistry relative to the upflow source; the only notable changes in the untreated surface flow were increased concentrations of DO and Fe^{3+} and decreased total Fe and Fe^{2+} (Table 1) due to oxidation and hydrolysis of Fe (reactions 2 and 3).

As water flowed through the OLDs, concentrations Of SO_4 and Mg did not change, pH and concentrations of alkalinity and Ca increased, and concentrations of acidity, Fe, and Al decreased (Table 2, Fig. 3). Despite increased pH, alkalinity, and Ca through the OLDs, limestone could dissolve throughout and neither Ca nor SO_4 could precipitate as gypsum ($CaSO_4$ $2H_2O$) because the water was undersaturated with respect to calcite and gypsum (Table 2, Figs. 4a and 4b). The pH and solute concentrations generally changed most rapidly near the inflow, after only a few minutes of contact with the limestone and mixing with water in the OLDs (Figs. 3 and 5). As pH increased, Fe^{3+} and $A1^{3+}$ concentrations decreased primarily due to in situ precipitation of hydrous oxides, such as amorphous $Fe(OH)_3$, ferrihydrite, schwertmannite, or goethite and amorphous $Al(OH)_3$ or poorly crystalline gibbsite (Table 2, Figs. 4c and 4d). Consequently, acidity was removed from the effluent (Fig. 6a). We hypothesized that the hydrous oxides would not inhibit limestone dissolution but would be transported as suspended particles as water flowed rapidly (v $\geq$0.4 m/min) through the OLDs.

During the 12-month monitoring period, the treated effluent appeared clear and contained less than 5% of the influent concentrations of dissolved Fe and Al; however, suspended particles of hydrous Fe-Al oxides and associated metals constituted a substantial proportion of the metals transport through the OLDs (Figs. 6b and 7). Initially, rusty floc was visible only in water samples 1.5 m from the inflow (pH $\leq$5), and dissolved Mn was transported relatively conservatively through the 24.4-m long drains (Figs. 3b, 6b, and 7). After 6 months, however, the rusty floc was visible in all samples $\leq$6.1 m from the inflow (pH <5.5), and concentrations of Mn in effluent declined to about 50% of influent concentrations (Figs. 3d, 6b, and 7). After 9 months, the iron floc was present in all samples within 18.3 m of the inflow (pH $\leq$7). When monitoring ceased at 12 months, the floc had not appeared in the effluent. The trends were the same for all three OLDs, despite periodic O_2 pretreatment of drain 1, only.

Attenuation of Dissolved Metals

Concentrations of Fe and Al decreased downflow through the OLDs due to the increased pH and the consequent precipitation of hydrous Fe-Al oxides (Figs. 3, 4, 6, 7, and 8). The hydrous oxides were visible as loosely bound, orange coatings on limestone samples near the inflow and as a gelatinous rusty "floc" in water samples retrieved from the OLDs. After 2 years of operation, numerous black flakes also were visible mixed with the rusty floc. On the basis of chemistry and XRD (J.M. Bigham, 1997, written commun.; G.L. Nord Jr., 1998, written commun.), the solids were identified as mixtures of amorphous to crystalline Fe, Mn, and Al oxides. Schwertmannite and goethite were dominant. However, despite significant concentrations of Mn and Al in mixed solids (Fe>Al>S=Si>Mn) and Mn-enrichment in the black flakes (Mn>Fe=Ca>Al), the identities of crystalline Mn and Al phases could not be determined by XRD of the samples. Amorphous to poorly crystalline phases of Fe, Mn, and Al likely were present (e.g. Figs. 4c and 4d).

During the second 6 months of treatment (October 1995 - March 1996), concentrations of Mn^{2+} declined precipitously at pH ≥ 5 (Figs. 3d and 8b). Chemical analysis of the hydrous-oxide precipitate that coated limestone samples revealed concentrations of Mn increased relative to Fe in the coatings with increased distance downflow, hence with increased pH (Table 3; August 23, 1995). However, for the entire monitoring period, ratios of Mn to Fe in the coatings no longer showed a consistent trend with respect to pH (Table 3; March 26, 1996). The change in trace-metal content of the coatings through time probably resulted from a change in the character of the hydrous oxides at different points through the OLDs due to the variations in the accumulation of Mn with the hydrous Fe-Al oxides. Ratios of Mn/Fe and Mn/Al increased by 2 orders of magnitude during the second 6-month monitoring interval relative to the first 6 months (Table 3). Watzlaf (1997) and Brandt and Ziemkiewicz (1997) also reported substantial Mn removal from AMD by limestone that had been coated by hydrous oxides after a time lag.

The removal of Mn^{2+} from solution (Figs. 4, 7, and 8) and its enrichment relative to Fe in particles and coatings on limestone (Table 3) resulted from sorption and coprecipitation reactions with the hydrous oxides of Fe(III), Mn(II-IV), and to a lesser extent Al as described by previous investigators (Hem, 1963, 1964,1977, 1978; McKenzie, 1980; Benjamin and Leckie, 1981; Kooner, 1993; Coston *et al,* 1995; Smith *et al,* 1998). Uncoated limestone (calcite) generally is not an effective sorbent of the trace metals at pH <7 (Zachara *et al,* 1991). At the effective pH, adsorption of Mn^{2+} and trace metals on hydrous Fe and Mn oxides is very fast, on the order of minutes, and tends to be much faster than the Fe^{2+} and Mn^{2+} oxidation rates (Benjamin and Leckie, 1981; Davies and Morgan, 1989). Similar trends have been reported for dissolved Mn^{2+} and trace metals to adsorb to hydrous Fe, Al, and Mn oxides, except that the Mn oxides are generally more effective sorbents at lower pH than Fe or Al oxides (Loganathan and Burau, 1973; McKenzie, 1980), and Zn^{2+} tends to be associated more strongly with Al oxides (Coston *et al,* 1995). Hence, as the Mn content of the oxides in the OLDs increased, trace-metal removal generally would be more effective at lower pH and with lower concentrations of sorbent.

Computed saturation indices indicate pure solid phases of Mn were undersaturated throughout the OLDs (Table 2). Despite Mn-oxide undersaturation, Hem (1963) showed that when $Fe(OH)_3$ was precipitated from an aerobic, sterile solution of Mn^{2+} and Fe^{2+} the concentration of Fe^{2+} quickly decreased, and that of Mn^{2+} also decreased although at a slower rate, so long as pH was >6.5. The "autocatalytic" sorption and coprecipitation reaction

$$2\ Fe(OH)_3\ (s) + Mn^{2+} + 2\ H^+ \rightarrow MnO_2\ (s) + 4\ H_2O + 2\ Fe^{2+} \qquad (10)$$

which was proposed by Hem (1964) to explain this trend, can explain the removal of Mn^{2+} and dissolved trace metals within the OLDs (Cravotta and Trahan, in press). According to Hem (1964), reaction 10 generally would be expected to go to the left; however, at near-neutral pH, when the activity of Fe^{2+} is very low and that of Mn^{2+} is relatively high (as found downflow within the OLDs), the reaction will go to the right and some replacement of $Fe(OH)_3$ by MnO_2 Will occur. Formation of Mn oxides within the OLDs may have been favored by near-neutral pH adjacent to limestone surfaces. At pH _>5, negatively charged surfaces of the $Fe(OH)_3$ and Mn oxides tend to attract cations, including Fe^{2+} and Mn^{2+} which can be rapidly reoxidized in an aerobic system (Tamura et al, 1976; Hem, 1977, 1978). Additionally, microorganisms can promote the oxidation and precipitation of Mn oxides (Ehrlich, 1990; Robbins et al, 1992). Robbins et al (1997) reported black Mn oxides in association with fungus and holdfasts of the "iron bacteria," *Leptothrix discophora,* that grew on calcite suspended within the OLDs at 12.2 m (midflow).

Rates of Limestone Dissolution

Limestone would tend to dissolve throughout the OLDs under the conditions evaluated because the water was undersaturated with respect to calcite (Figs. 4a, 5a, and 8a). However, the rate of limestone dissolution is expected to decline as dissolution proceeds and conditions within the OLD approach calcite saturation. The calcite saturation index generally increased with increased residence time (Fig. 5a) and increased pH (Fig. 8a). After 1 hour residence time, the water had pH >6 and was net alkaline; however, by tripling residence time from 1 to 3 hours, pH increased by about 0.5 (Fig. 5a), and alkalinity and Ca concentrations of effluent only doubled from about 60 to 120 mg-L^{-1} and 90 to 180 mg-L^{-1}, respectively (Fig. 5b). Note that because alkalinity can not be measured for pH <4.5, the concentration of dissolved Ca generally is a better indicator of limestone dissolution.

Limestone samples, which were suspended at the inflow and at downflow points within the OLDs, showed effects of both precipitation and dissolution, particularly near the inflow. After rinsing off the hydrous oxide crusts, initially dark gray, smooth-surfaced limestone slabs appeared powdery white and grainy. Although accumulations of the hydrous oxides on limestone were relatively thick (-1 mm) at the inflow to the OLDs, $CaCO_3$ dissolution rates remained greater at the inflow than at downflow points within the drain where such accumulations were thin to nonexistent (Table 4). The calculated $CaCO_3$ dissolution rates decreased with increased pH and activities of Ca^{2+} and HCO_3- and decreased P_{CO2}. During the initial 6 months, the limestone dissolution rate was $10^{-6.9}$ mmol cm^{-2} s^{-1} at the inflow (pH = 3.5-4) and $10^{-7.6}$ mmol cm^{-2} S^{-1} at the midflow (pH = 6-6.5) (Table 4). These trends are consistent with rate laws established by laboratory experiments which used hydrochloric acid (HCl) to maintain constant pH as rotating calcite discs dissolved (Plummer et al, 1979; Arakaki and Mucci, 1995). However, the field rates for $CaCO_3$ reaction with AMD (Table 4) are about an order of magnitude less than the reported laboratory rates at comparable pH. In a recent evaluation, Aschenbach (1995) demonstrated that calcite dissolved more rapidly in HCl solutions than in synthetic AMD (sulfuric acid solutions) for a given pH and that calcite remained undersaturated in the synthetic AMD at near-neutral pH.

Although the concentrations of Ca and alkalinity added to effluent were greatest for slowest flow rates or longest residence time (Fig. 5b), the overall limestone dissolution rate and amount of limestone dissolved, as indicated by the net transport of Ca and alkalinity, were independent of flow rate and did not change significantly during the study period (Cravotta and Trahan, in press). The cumulative limestone dissolution rate for the three OLDs combined was 4.4 kg d^{-1} on the basis of net Ca transport. This dissolution rate of 4.4 kg d^{-1} ($Q = 29.9$ m^3 d^{-1}; t_R =2 hr) is equivalent to a dissolution rate of $10^{-7.9}$ mmol cm^{-2} . S^{-1} computed for limestone samples immersed for 1 year at the 12.2-m midpoint of the drain 1 (Table 4) and is intermediate to rates of 17.9 and 2.7 kg d^{-1} for the Howe Bridge ($Q = 138$ m^3 d^{-1}; $t_R = 23$ hr) and Morrison ($Q = 9.8$ m^3 d^{-1}; $t_R = 51$ hr) ALDs, respectively (Hedin et al., 1994b). On the basis of the limestone dissolution rate of 4.4 kg d^{-1} and the total of 38,200 kg of limestone, linear extrapolation indicates that the limestone used to build the OLDs could theoretically last 24 years. Before the limestone is exhausted, however, failure of the OLDs could result from various factors that affect flow paths and reaction rates or extent in the drains.

Design Considerations for Limestone Drains

The residence time for water in limestone drains is a critical factor affecting their performance because of kinetic controls on dissolution, precipitation, and sorption reactions that control pH and dissolved ion concentrations. Thus, Hedin and Watzlaf (1994) evaluated construction characteristics, residence times, and chemistry of influent and effluent of more than 20 limestone drains to determine the optimum size for maximum alkalinity production. They derived the following sizing technique, which was incorporated into guidelines of Hedin et *al* (1994a):

$$M_S = Q \cdot ((t_L \cdot C / x) + (t_R \cdot \rho_b / n)) \qquad (11)$$

Equation 11 computes the mass of limestone, MS, needed for treatment of AMD of a given flow rate, Q. Variables in the first term include the desired longevity of treatment (k), desired alkalinity concentration for the effluent (C), and the purity of limestone expressed as $CaCO_3$ mole fraction (x). Additional variables for residence time (t_R), bulk density (Pb), and porosity (n) in the second term assure a specified retention time to achieve the maximum alkalinity. In this study, where tabular mixed-size limestone fragments were used, measured values were $t_R \leq 3.1$ hr; Pb = 2,140 kg m^{-3}; and n = 0.14. Thus, values assumed by Hedin and coworkers for $t_R = 15$ hr; Pb = 1,600 kg m^{-3}; and n = 0.5 could be poor estimates for the second term, particularly for drains that used tabular limestone fragments. Nevertheless, errors in the second term specifying retention time cancel due to the interdependence Of t_R, Pb, and n. For example, computed mass of limestone required for a given flow rate is the same using consistent data from Hedin and coworkers or this study, where (t_R Pb / n) = (15 1600 / 0.5) = (3.1 2140 / 0.14), respectively. However, the dimensions of the area or trench for installation would be affected by the assumed value for bulk density, because the same mass of limestone would occupy one-third larger volume for Pb = 1,600 kg m^{-3} than for Pb = 2,140 kg m^{-3}. Furthermore, rate-dependent reactions and potential for abrasion and transport of hydrous oxides from the drains can be misunderstood if residence time and velocity of flow are poorly characterized.

Hedin et *al (1* 994a) advised against the use of horizontally oriented limestone drains for treatment of AMD containing >1 mg-L^{-1} Of O_2, Fe^{3+} or $A1^{3+}$ due to potential for armoring and clogging of the drains. This study evaluated OLDs for treatment of relatively dilute AMD containing <90 mg-L^{-1} of acidity and <5 mg-L^{-1} of Fe, Mn, and Al. However, results of this study combined with recent results of Watzlaf (1997), Sterner and others (in press), and Brant and Ziemkiewicz (1997) suggest that limestone treatment systems can effectively increase pH and remove dissolved metals, including Mn^{2+} , from AMD containing moderate concentrations of O_2, Fe^{3+} , or $A1^{3+}$ (1-5 mg-L^{-1}).

In an OLD, oxidation and hydrolysis reactions will proceed and the solid and dissolved products will accumulate to some extent within the treatment system. The following overall reaction, which combines reactions 2, 3, 4, 5, and 7, shows alkalinity as an ultimate product of the iron hydrolysis reaction in an OLD:

$$Fe^{2+} + 0.25\ O_2 + 2\ CaCO_3 + 2.5\ H_2O \rightarrow Fe(OH)_3 + 2\ Ca^{2+} + 2\ HCO_3^- \qquad (12)$$

where 2 moles of $CaCO_3$ dissolve for each mole of $Fe(OH)_3$ produced. Hence, in an OLD, rapidly dissolving limestone surfaces are not stable substrates for $Fe(OH)_3$ attachment and armoring. Because overall efficiency can be increased by combining neutralization and hydrolysis reactions, an OLD may require less land area than needed to construct an ALD and subsequent oxidation pond. Limestone near the inflow to the OLDs that was loosely coated by $Fe(OH)_3$ dissolved more rapidly than uncoated limestone that was downflow. The measured flow velocities of 0.1 to 0.4 m-min^{-1} associated with residence times of $\leq$3.1 hr were adequate to transport a fraction of the solid hydrolysis products ($Fe(OH)_3$, $Al(OH)_3$, MnO_2) through the OLDs as suspended particles. As demonstrated by this study, dissolved metals can be removed from solution by sorption and coprecipitation with the hydrous Fe, Mn, and Al oxides within the OLDs. Additionally, the in situ production and retention of H^+ and CO_2, which are dissolved hydrolysis products (reactions 3 and 7), may enhance limestone dissolution (reactions 4 and 5). However, insufficient time elapsed during the study to evaluate the potential for steady-state formation and transport of hydrolysis products whereby total concentrations of metals (dissolved + suspended solids) in influent and effluent are equal. Furthermore, because the redox state of Fe could not be effectively controlled in the field experiment as conducted, rates of dissolution, precipitation, and sorption reactions over a range of redox conditions at constant pH could not be evaluated. Comparable data on limestone dissolution rates and metal attenuation rates have not been reported for other limestone drains or for more mineralized AMD.

An elongate structure, such as that used for the subject experimental OLDs or possibly using baffling to produce meanders within a broad area, could provide sufficient residence times and high flow velocities necessary to achieve neutralization of AMD and transport of hydrolysis products. If the water contains Fe^{2+} and Mn^{2+}, hydrolysis reactions can be promoted by introducing O_2. To enhance trace-metal attenuation by hydrous oxide particles within the OLDs, the cross-section of the drain could be enlarged near the outflow to decrease flow velocities and increase residence time where pH is expected to be highest. To insure against clogging from an excessive accumulation of hydrous oxides, perforated piping could be installed as subdrains for periodic flushing of excess sludge. Some of these conceptual designs have recently been constructed but have not been evaluated (C.A. Cravotta, 1997, unpublished data; G.R. Watzlaf, 1997, oral commun.). Additional studies are needed to evaluate such designs and to determine optimum criteria for utilization and construction of limestone drains for AMD remediation. In general, additional information is needed to understand potential for, and effects of, the dissolution of limestone and the formation, accumulation, and transport of secondary solids in AMD treatment systems. Because of the wide range of water-chemistry and hydrologic conditions at coal and metal mines (Rose and Cravotta, in press; Nordstrom and Alpers, 1998), simple to complex remedial alternatives could be appropriate depending on site characteristics.

Conclusions

This study showed that enclosed limestone drains can be effective for neutralizing oxic, relatively dilute AMD (O_2 >1 m L^{-1}; acidity <80 mg L^{-1}) and decreasing concentrations of dissolved $A1^{3+}$, Fe^{3+}, Fe^{2+}, Mn^{2+}, and trace metals (<5 mg L^{-1}). In less than 3 hours residence time, limestone dissolution within the OLDs increased pH from 3.5 to $\geq$6.2, producing net alkaline effluent. The effluent was undersaturated with respect to calcite. With increased distance downflow through the OLDs, and accordingly with increased residence time for a given flow rate, pH and concentrations of alkalinity and Ca increased; acidity, Fe, and Al decreased, ultimately to <5% of influent concentrations; and O_2, SO_4, and Mg did not change. After flowing a short distance through the OLDs, the water became saturated with hydrous Fe and Al oxides which formed loosely bound, orange-yellow coatings on limestone near the inflow and suspended particles at sampling points downflow. Low concentrations of dissolved O_2 throughout the OLDs exceeded that needed (<0.3 mg L^{-1}) for the oxidation of all Fe^{2+} (<2 mg L^{-1}) in the influent; however, nearly complete removal of dissolved Fe greatly exceeded the expected rate of removal by coupled Fe^{2+} oxidation and Fe^{3+} hydrolysis, indicating that sorption and coprecipitation of Fe^{2+}, Fe^{3+}, and other cations could be important.

The accumulated hydrous oxides and elevated pH (>5) within the OLDs promoted sorption and coprecipitation of Fe^{2+} and Mn^{2+} with the hydrous oxides. Although undersaturated with Mn compounds, concentrations of dissolved Mn^{2+} in the effluent decreased by $\geq$50% relative to the influent after hydrous oxides had accumulated in downflow parts of the OLDs. With increased distance downflow, hence with increased pH, concentrations of Mn in the water decreased while those in the corresponding hydrous oxides increased relative to Fe. The removal of dissolved Mn $^{2+}$, by the autocatalytic reaction of Mn $^{2+}$ with $Fe(OH)_3$, also produced Mn oxides. The hydrous Fe, Mn, and Al oxides are effective sorbents and catalysts for oxidation of Fe $^{2+}$ and Mn^{2+} at near-neutral pH. Consequently, at pH >5 within the OLDs, negatively charged surfaces of the oxides could attract and attenuate Fe $^{2+}$, Mn $^{2+}$, and trace metals. Extensive oxidation of Fe^{2+} and Mn^{2+} was possible due to attenuation and catalysis by the oxides.

The rate of limestone dissolution was minimally affected by the accumulation of hydrous Fe-Mn-Al oxides as loosely bound coatings. Despite the ~1 -mm thick accumulation of hydrous oxides on limestone surfaces, pH increased most rapidly near the inflow as a result aggressive dissolution of limestone by the influent AMD. The rate of limestone dissolution decreased with increased distance from the inflow, which corresponded with increased residence time, pH, and concentrations of Ca $^{2+}$ and HCO_3- and decreased P_{CO2}. Under the "closed system" conditions in which hydrolysis products including H^+ and CO_2 could not escape the drains and were retained as reactants, limestone surfaces rapidly dissolved, and true armoring was avoided, despite oxygenated conditions. However, the computed dissolution rates for the field experiment were about an order of magnitude less than reported laboratory rates at comparable pH. The reason for slower rates of $CaCO_3$ dissolution by AMD (field) than by HCl (laboratory) was not determined but could involve variations in ion pairing, surface charge, and potential for various minerals to precipitate on the surface. Additional studies are needed to determine the hydrochemical conditions and role of microorganisms in mineral precipitation reactions that promote or inhibit limestone dissolution and ultimately can cause failure of limestone treatment systems.

Although only a small fraction of the solid hydrolysis products was transported through the OLDs during the study, the progressive accumulation of hydrous oxides at increased distances downflow indicated eventual breakthrough of particle-rich effluent was probable. In fact, samples collected in 1997 verify the breakthrough of suspended particles, which cause the effluent to be turbid. Monitoring generally would be needed for extended periods to evaluate potential for the steady-state formation and transport of hydrolysis products and the ultimate longevity of treatment systems. Different conceptual designs may be considered for promoting the transport of hydrous oxides and optimizing the long-term neutralization of AMD and removal of dissolved metals. Before criteria can be refined for the construction of OLDs to neutralize AMD, however, various innovative conceptual designs need to be tested, and available data for existing systems need to be evaluated. Accurate information on variations in the water chemistry, residence time, rates of limestone dissolution, and effects of hydrolysis products on limestone dissolution, sorption of trace metals, and hydraulic properties in OLDs and ALDs is needed to optimize designs and minimize costs for effective implementation of these passive-treatment systems.

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Fig. 1

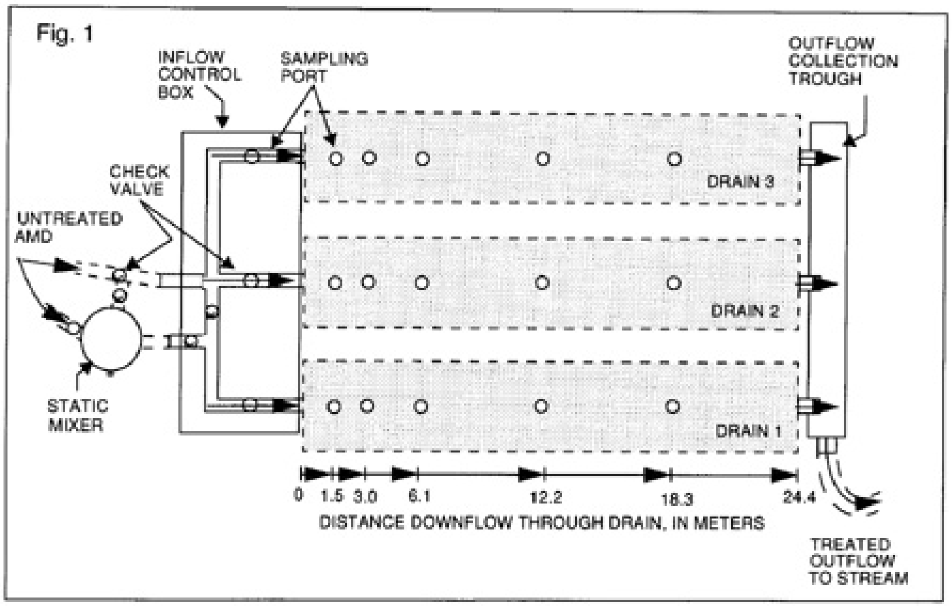

Fig. 1: Schematic design of the oxic limestone drains (OLDs) at the Orchard Overflow in the upper part of the Swatara Creek watershed, east-central Pennsylvania.

Fig. 2

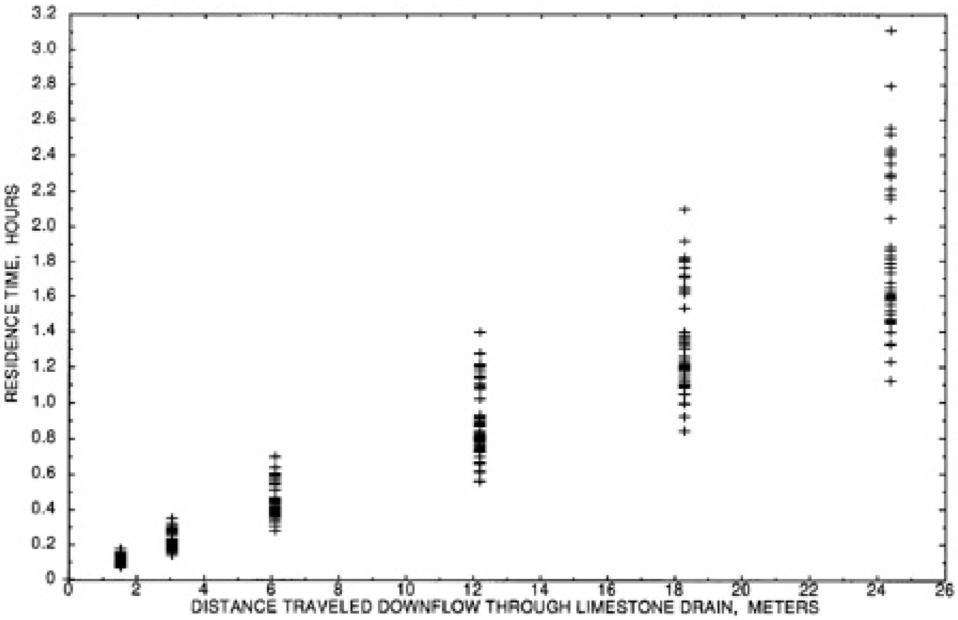

Fig. 2: Relation between calculated residence time and distance traveled through OLDs (drains 1, 2, and 3) for the range of flow rates evaluated. Residence time computed as distance times cross-sectional area (0.244 m^2) times porosity (0.14) divided by volumetric flow rate (m^3-hr^{-1}).

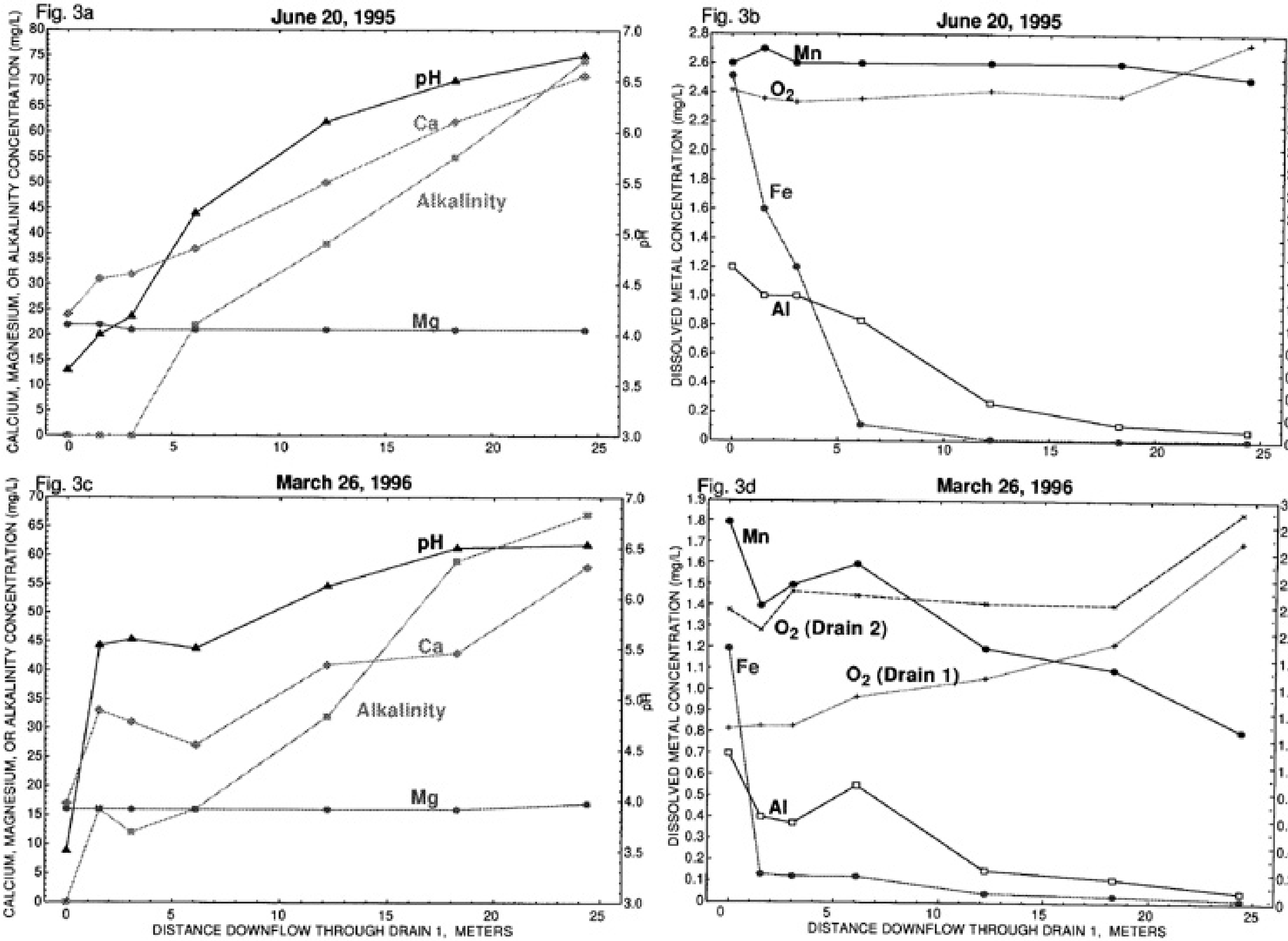

Fig. 3: Sequential changes in water chemistry within limestone drain 1. Data for June 20, 1995: (a) pH, and concentrations of alkalinity and dissolved calcium and magnesium; (b) Concentrations of dissolved oxygen, iron, aluminum, and manganese. Data for March 26, 1996: (c) pH, and concentrations of alkalinity and dissolved calcium and magnesium; and (d) Concentrations of dissolved oxygen, iron, aluminum, and manganesl. Samples filtered through 0.45 μm. For (d), dissolved oxygen in drain 2 (no pretreatment) is shown for comparison with drain 1 (N_2 sparging). Samples were collected sequentially upflow; samples at 24.4 and 0 m were collected 2 and 6 hours, respectively, after starting N_2 sparging. Dissolved O_2 concentrations in effluent samples were elevated relative to upflow samples from the drains because of oxygenation within the open-ended outflow pipes; however, water-filled traps connecting the drains to the outlet pipes prevented the influx of air into the drains.

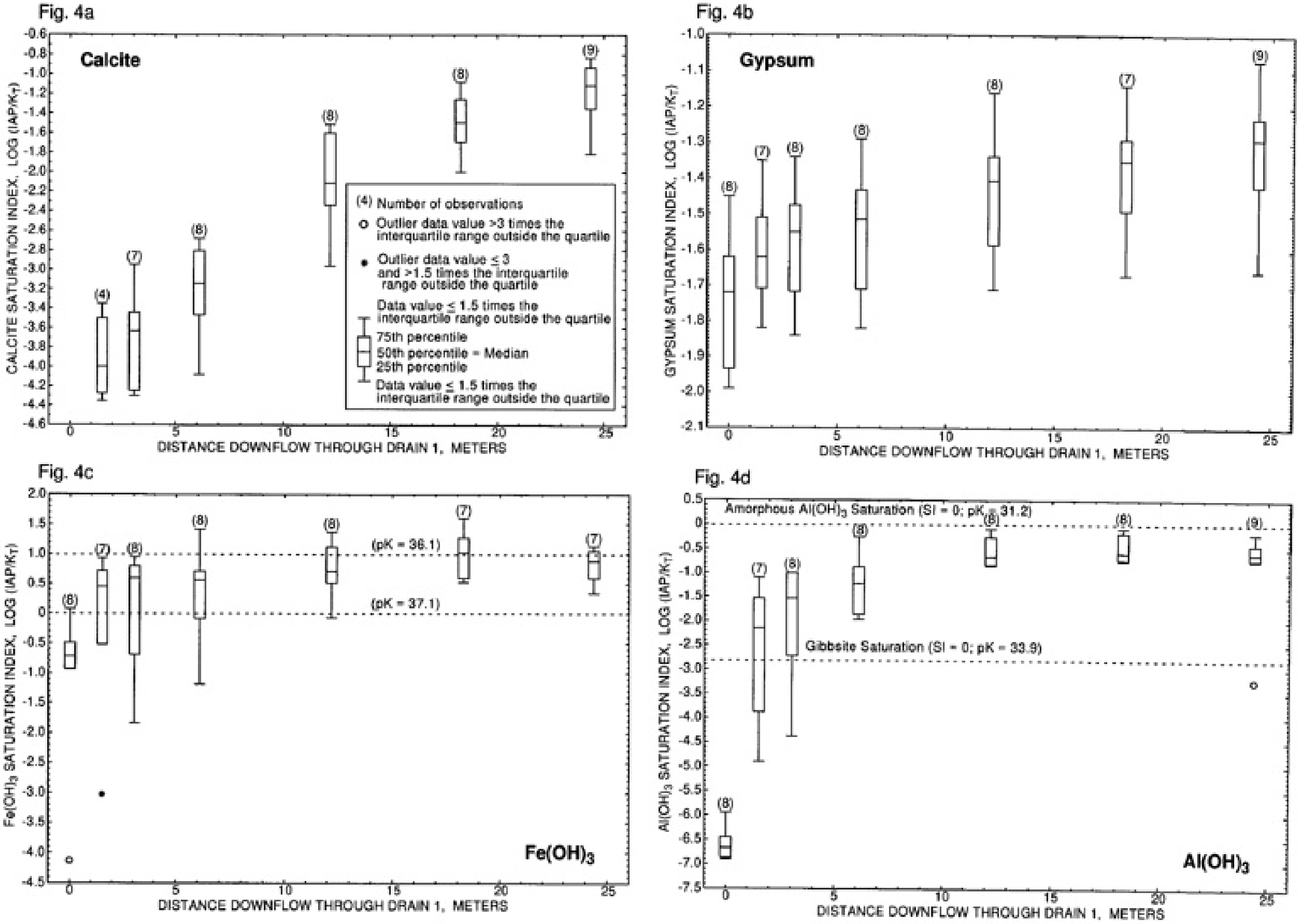

Fig. 4: Sequential changes in saturation with respect to various minerals that could dissolve or precipitate within limestone drain 1: (a) Calcite; (b) Gypsum; (c) Ferrihydrite; and (d) Amorphous aluminum hydroxide.Saturation index calculated using the WATEQ4F computer program (Ball and Nordstrom, 1991); see notes on table 2. Data for samples collected March 1995 - March, 1996.

Fig. 5a

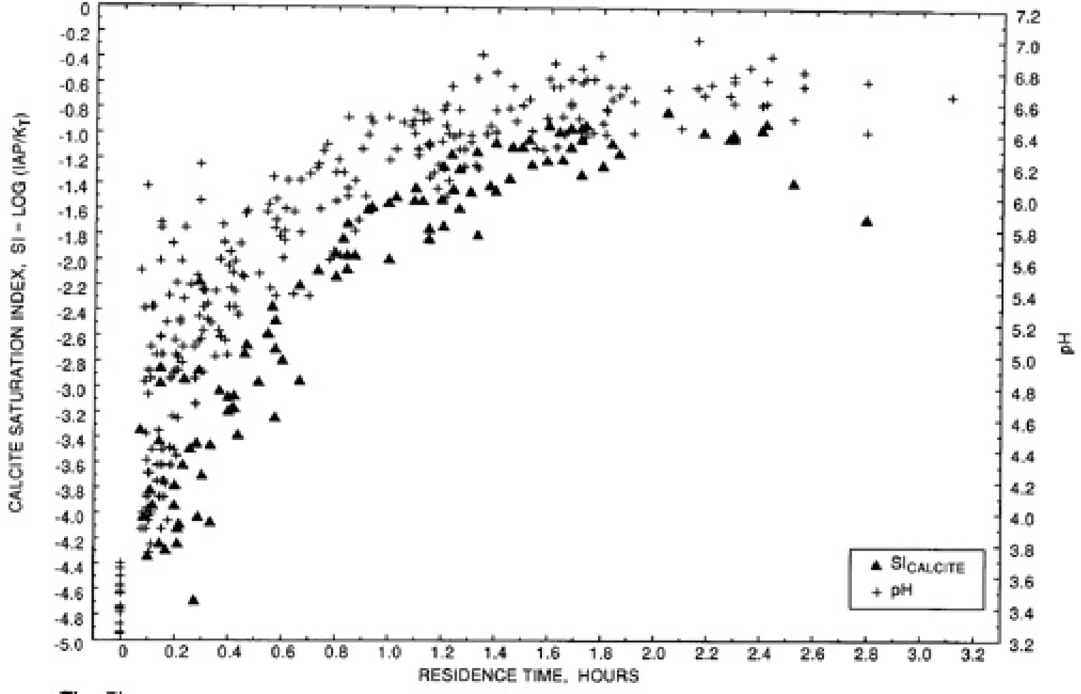

Fig. 5b

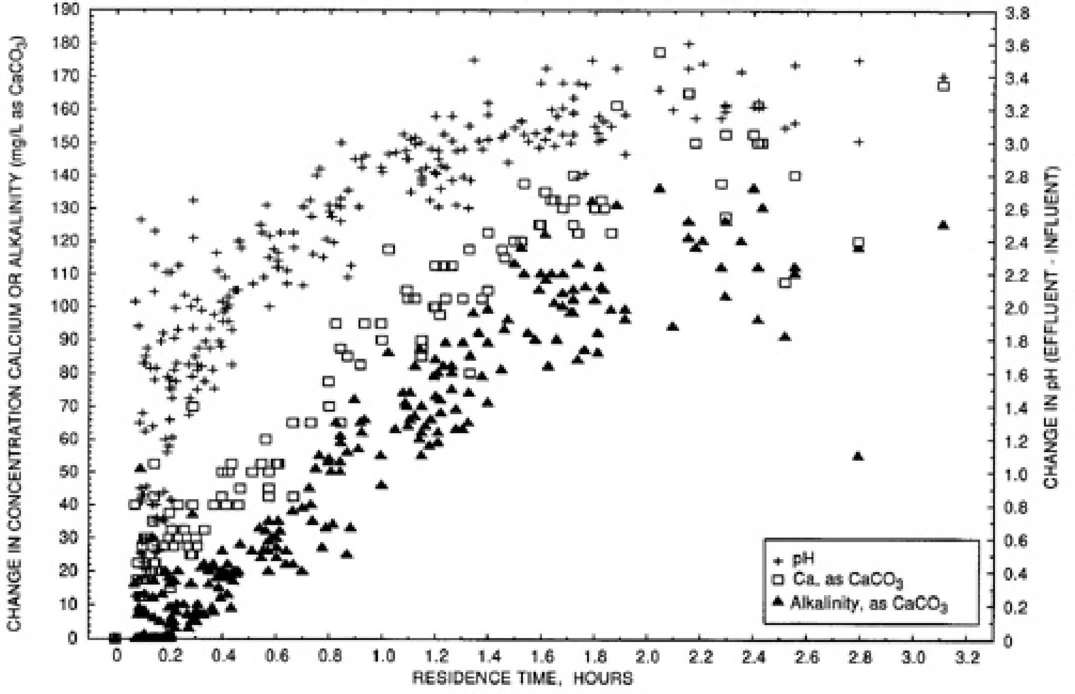

Fig. 5: Composition of water at inflow, outflow, and points within limestone drains as a function of residence time: (a) pH and calcite saturation index; and (b) Net increases in pH and concentrations of alkalinity and calcium, relative to influent composition. Data for samples collected March 1995 - March, 1996 from drains 1, 2, and 3.

Fig. 6a

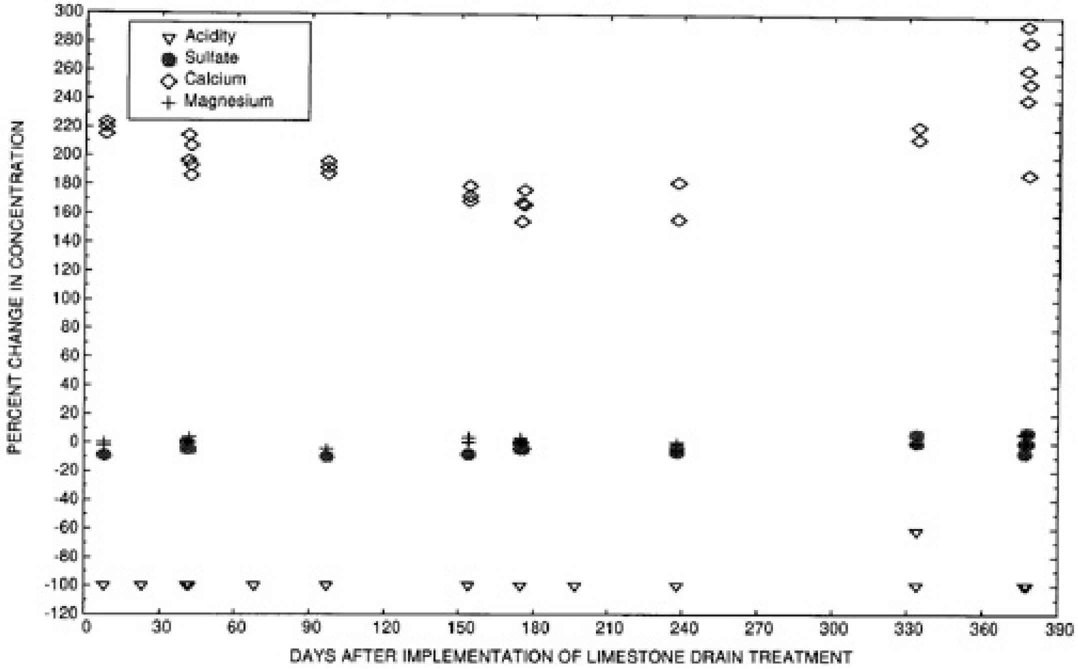

Fig. 6b

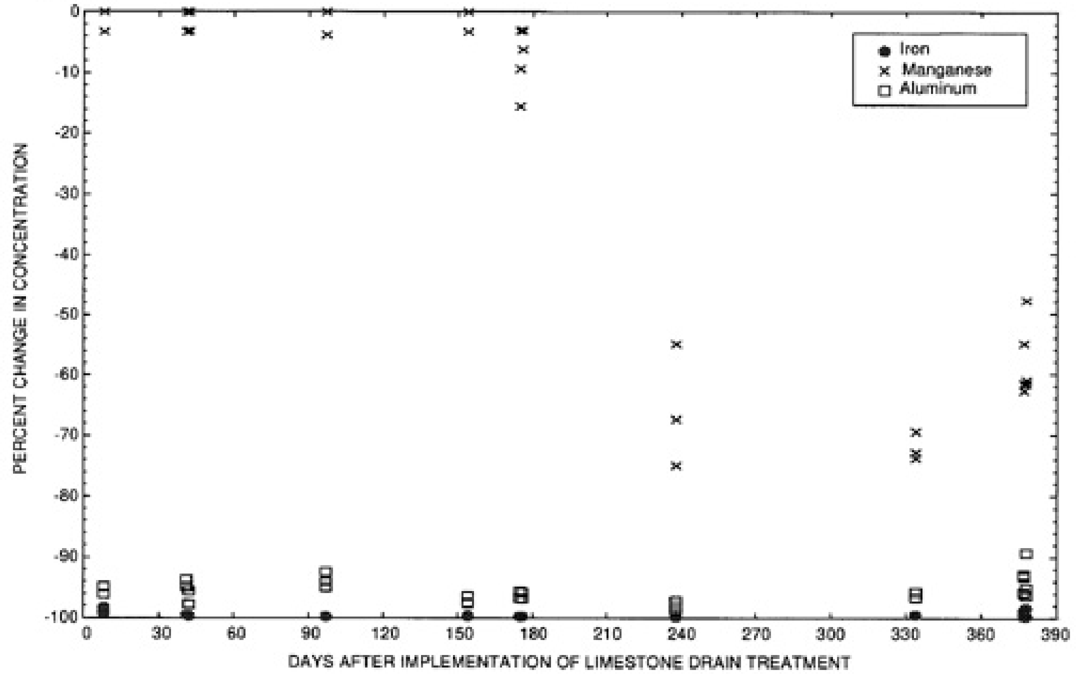

Fig. 6: Temporal changes in composition of effluent relative to influent: (a) Acidity, sulfate, calcium, and magnesium; and (b) Aluminum, iron, and manganese. Data for samples collected March 1995 - March, 1996 from drains 1, 2, and 3. Samples filtered through 0.45 μm.

Fig. 7

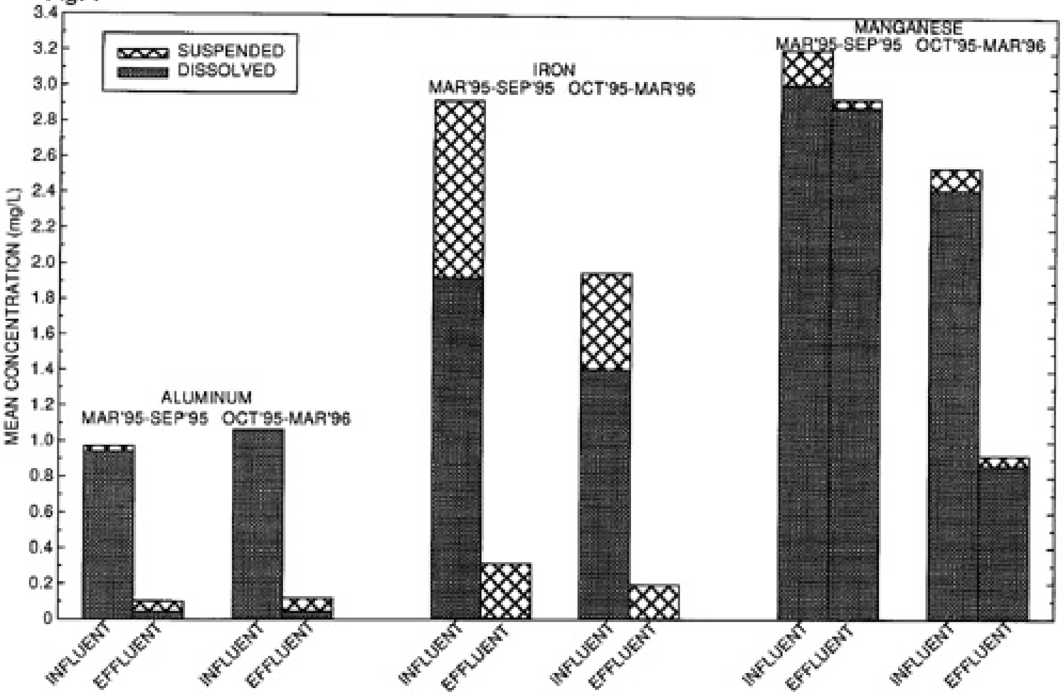

Fig. 7: Semiannual mean concentrations of suspended and dissolved aluminum, iron, and manganese in untreated influent and treated effluent from limestone drains. Means for samples collected March 1995 - September 1995 and October 1995 - March 1996. Samples filtered through 0.45 μm.

Fig. 8a

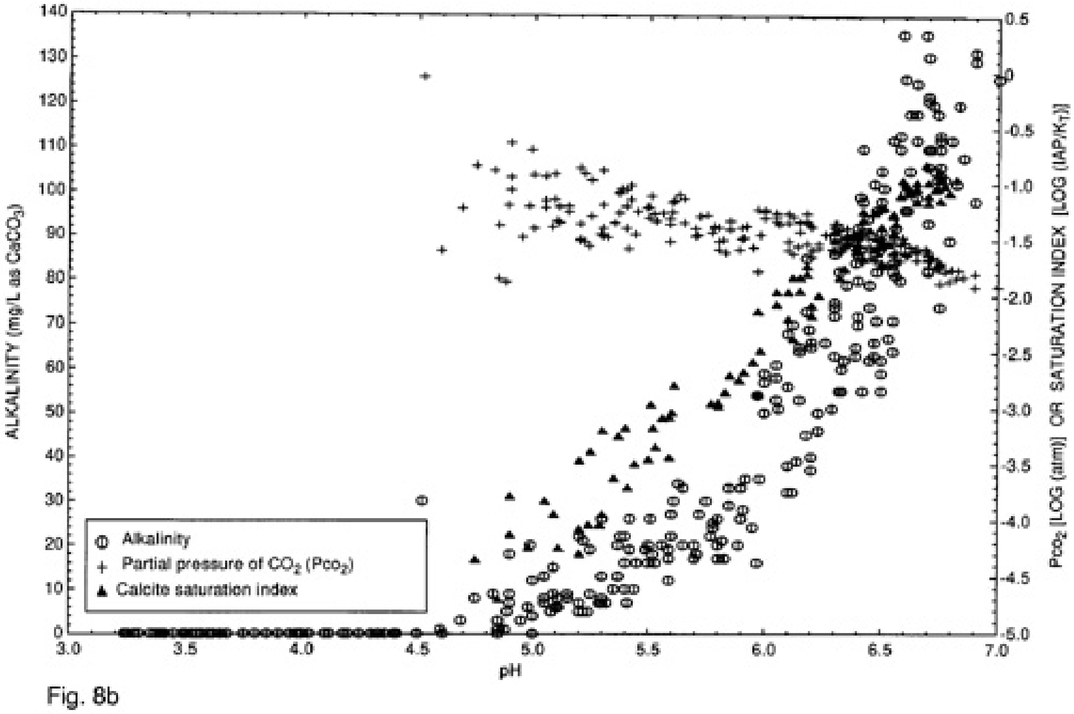

Fig. 8b

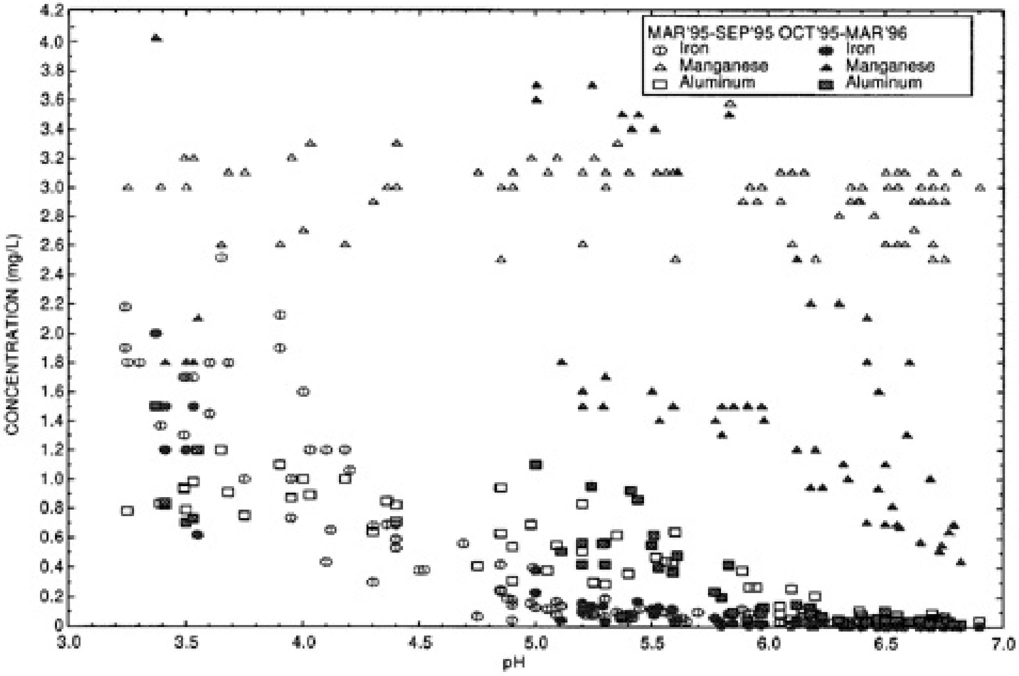

Fig. 8: Composition of water at inflow, outflow, and points within limestone drains as a function of pH: (a) Alkalinity, calcite saturation index, and partial pressure of carbon dioxide (P_{CO_2}); and (b) Iron, manganese, and aluminum. Data for samples collected March 1995 - March, 1996 from drains 1, 2, and 3. Samples filtered through 0.45 µm.

Table 1: Summary of measured compositions of water at inflow, bypassed flow, and outflow of the three oxic limestone drains at Orchard Overflow, Pennsylvania, March 1995 - March 1996
[constituents dissolved (0.45-µm filter) and units milligrams per liter, except as noted; <, less than]

Parameter or Constituent	Untreated Inflow			Untreated Bypassed Flow[a]			Outflow from Limestone Drains[a]		
	N	Median	Minimum / Maximum	N	Median	Minimum / Maximum	N	Median	Minimum / Maximum
Discharge, m^3/d	16	29.9	(23.4 / 44.8)	9	57.7	(16.4 / 150.9)	48	29.9	(23.4 / 44.8)
Temperature,°C	17	10.7	(8.3 / 12.6)	16	12.9	(5.7 / 15.0)	49	10.7	(7.5 / 12.4)
Eh, volts	17	.70	(.49 / .77)	16	.67	(.33 / .73)	49	.40	(.31 / .52)
Spec. Cond., µS/cm	17	550	(410 / 710)	16	550	(410 / 590)	49	610	(390 / 790)
Dissolved O_2	17	2.2	(1.3 / 3.4)	14	9.7	(1.8 / 17.8)	49	2.9	(1.8 / 19.5)
pH, units	17	3.5	(3.2 / 3.8)	16	3.5	(3.3 / 5.0)	49	6.6	(6.2 / 7.0)
Alkalinity as $CaCO_3$	17	0	(0 / 0)	15	0	(0 / 0)	48	108	(55 / 136)
Acidity as $CaCO_3$	14	63	(31 / 85)	12	34	(23 / 51)	27	0	(0 / 26)
Net alkalinity as $CaCO_3$	14	-63	(-85 / -31)	11	-33	(-41 / -23)	27	113	(67 / 136)
Ca	10	29.0	(16.0 / 39.0)	5	29.0	(17.0 / 49.0)	33	79.0	(49.0 / 110.0)
Mg	10	26.0	(16.0 / 35.0)	5	27.0	(16.0 / 35.0)	33	26.0	(16.0 / 35.0)
Na	10	.8	(.8 / .9)	5	.9	(.8 / .9)	33	.8	(.7 / 1.0)
SO_4	10	215	(130 / 300)	5	220	(140 / 290)	33	200	(130 / 290)
SiO_2	10	9.6	(9.2 / 10.0)	5	10.0	(9.3 / 10.0)	33	9.4	(7.7 / 10.0)
Al	10	.93	(.73 / 1.50)	5	1.10	(.90 / 1.30)	33	.04	(.02 / .09)
Al, total	10	.89	(.70 / 1.30)	5	1.20	(.82 / 1.30)	32	.08	(< .01 / .40)
Fe^{2+}, computed [b]	13	1.07	(.18 / 2.00)	5	.27	(.24 / .81)	33	.003	(.001 / .031)
Fe	13	1.80	(.62 / 2.80)	5	.83	(.24 / 1.70)	33	.003	(< .003 / .031)
Fe, total	10	2.70	(1.40 / 3.70)	5	1.20	(.39 / 3.00)	33	.18	(< .01 / .85)
Mn	10	3.00	(1.80 / 4.00)	5	3.00	(1.90 / 3.70)	33	2.70	(.55 / 3.10)
Mn, total	10	3.05	(1.70 / 4.40)	5	2.90	(1.70 / 3.70)	33	2.70	(.57 / 3.10)

[a] Water sampled at outflow from limestone drains (treated) and at adjacent ditch an equivalent distance downstream from inflow that collected bypassed mine drainage (untreated).

[b] Concentration of Fe^{2+} computed using data for Fe, Eh, and temperature-corrected equilibrium constant for the half-reaction: $Fe^{2+} = Fe^{3+} + e^-$ (as included in WATEQ4F; Ball and Nordstrom, 1991).

Table 2: Measured compositions of water and calculated saturation indices at inflow and downflow within oxic limestone drain 1, August 16, 1995
[constituents dissolved (0.45-µm filter) and units milligrams per liter, except as noted; <, less than; n.d., no data]

Parameter or constituent	Distance, meters						
	0	1.5	3.0	6.1	12.2	18.3	24.4
Residence time, hours[a]	0	.10	.20	.40	.80	1.20	1.59
Specific conductance, µS/cm	430	370	380	390	420	460	620
Oxygen	2.0	1.9	1.9	1.9	1.9	1.9	2.6
Eh, volts	.71	.55	.50	.43	.41	.42	.4
pH, units	3.4	4.8	4.9	5.3	6.0	6.6	6.8
Acidity, as $CaCO_3$	56	11	18	23	21	<20	<20
Alkalinity, as $CaCO_3$	0	8	18	26	54	84	110
SO_4	240	220	220	220	220	220	220
SiO_2	9.7	9.8	9.7	9.8	9.6	10	9.7
Ca	29	40	44	49	57	74	79
Mg	27	28	27	28	27	28	28
Na	.9	.9	.9	.9	.9	.9	.9
Al	.83	.41	.31	.29	.12	.05	.03
Fe	1.37	.069	.042	.034	.013	.005	.003
Mn	3.0	3.1	3.0	3.1	3.0	3.0	2.9
Saturation index, unitless[b]							
Calcite ($CaCO_3$)	n.d.	-4.4	-3.8	-3.2	-2.1	-1.3	-.9
Gypsum ($CaSO_4 \cdot 2H_2O$)	-1.6	-1.5	-1.5	-1.4	-1.4	-1.3	-1.3
Siderite ($FeCO_3$ ppt)	n.d.	-5.4	-5.0	-4.5	-4.0	-4.5	-4.5
Ferrihydrite [$Fe(OH)_3$]	-.9	-.5	-1.1	-1.2	-.1	.6	.6
Goethite (FeOOH)[c]	2.6	3.0	2.4	2.3	3.4	4.1	4.1
Schwertmannite [$Fe_8O_8(OH)_6SO_4$][c]	4.2	4.6	-0.3	-1.9	5.7	9.9	9.3
$Al(OH)_3$, amorphous	-6.9	-3.2	-2.9	-1.8	-.8	-.4	-.6
Gibbsite [$Al(OH)_3$]	-4.1	-.4	-.1	1.0	2.0	2.4	2.2
Allophane [$Al(OH)_3]_{(1-x)}(SiO_2)_x$]	-1.7	-.7	-.6	.0	.8	1.3	1.3
Jurbanite [$Al(SO_4)(OH) \cdot 5H_2O$]	-1.7	-.7	-.8	-.5	-.8	-1.6	-2.1
Basaluminite [$Al_4(SO_4)(OH)_{10} \cdot 5H_2O$]	-13.2	-1.3	-.5	3.0	5.6	6.0	5.2
Hausmannite (Mn_3O_4)	-25.8	-20.2	-20.7	-20.0	-15.3	-10.4	-9.8
Manganite (MnOOH)	-7.2	-5.9	-6.3	-6.3	-4.7	-2.8	-2.6
Birnessite (MnO_2)	-9.6	-9.7	-10.9	-11.7	-9.8	-7.4	-7.0
Log (Pco_2, atm)[b]	n.d.	-.8	-.6	-.9	-1.2	-1.6	-1.7

[a] Residence time computed as distance times cross-sectional area (0.244 m^2) times porosity (0.14) divided by volumetric flow rate. The flow rate was 0.51 m^3/hr (12.2 m^3/day) on August 16, 1995.

[b] Saturation index [SI = log (IAP/K_T)] and log Pco_2 calculated with WATEQ4F (Ball and Nordstrom, 1991); Fe and Al assumed to be at detection limit, if not detected. Temperature of samples was 11.5 to 13.3 °C.

[c] SI values for goethite and schwertmannite computed using activities of species calculated with WATEQ4F (Ball and Nordstrom, 1991) and solubilities reported by Bigham and others (1996), where log $K_{GOETHITE}$ = 1.4 (instead of -1.0 in WATEQ4F data base) and log $IAP_{SCHWERTMANNITE}$ = 18.

Table 3: Concentrations and ratios of metals encrusting limestone slabs retrieved after 5 months or 12 months immersed at inflow or within oxic limestone drains

[mg, milligram; µg, microgram; mmol, millimole; mol, mole; <, less than; n.d., not determined]

Sample location[a]	Weight, mg	Concentration, µg/mg				Molar ratio, mmol/mol		
		Ca	Fe	Al	Mn	Al/Fe	Mn/Fe	Mn/Al
Samples collected August 23, 1995								
Inflow	800.3	30	356	25	0.69	145	2.0	13.5
1-06	518.3	82	222	54	.39	503	1.8	3.5
1-12	74.1	34	38	8.8	.54	480	14.5	30.2
2-06	311.8	120	84	32	.23	795	2.7	3.4
2-12	84.1	208	95	58	.48	1265	5.1	4.0
Samples collected March 26, 1996								
Inflow	361.4	n.d.	692	4	.98	13	1.4	112.6
1-06	76.0	190	79	16	4.1	413	53.4	129.1
1-12	78.2	256	27	10	.96	787	36.3	46.1
2-06	139.5	154	100	31	12.9	642	130.6	203.5
2-12	174.4	247	401	22	2.1	1137	53.0	46.6

[a] Sample location indicates drain 1 or 2 and distance, in meters, downgradient from inflow (at 0 m). For example, 1-06 is drain 1 at 6 m from inflow.

Table 4: Rates of limestone dissolution computed on the basis of limestone samples retrieved after 5 months or 12 months immersed at inflow or within oxic limestone drains [cm, centimeter; g, gram; %, percent; mmol, millimole; s, second; yr, year]

Sample Location[a]	Surface Area, cm^2	Initial Weight, g	Final Weight, g	Weight Loss, %	Dissolution Rate[b]	
					g/g/yr	log(mmol/cm^2/s)
Limestone slabs immersed within OLD for 5 months (March 23, 1995 - August 23, 1995)						
Inflow	42.12	43.3788	34.0796	21.43	0.5114	-6.78
Inflow	44.10	49.9887	40.9369	18.10	.4319	-6.81
Inflow	35.52	31.5680	26.9189	14.72	.3513	-7.00
Avg. 0-m						-6.86
1-06	41.80	46.0653	43.8176	4.879	.1164	-7.39
1-06	42.30	47.6974	45.1482	5.344	.1275	-7.34
1-06	20.06	17.4558	16.0444	8.085	.1928	-7.27
2-06	34.98	30.3221	28.5925	5.704	.1360	-7.43
2-06	28.18	27.0120	25.6713	4.963	.1184	-7.44
2-06	35.92	33.7302	31.9752	5.203	.1241	-7.43
Avg. 6-m						-7.39
1-12	39.08	34.9815	33.6858	3.703	.0883	-7.60
1-12	43.34	49.6653	48.0459	3.260	.0777	-7.55
1-12	39.42	46.3258	44.4346	4.082	.0973	-7.44
2-12	35.52	32.2868	31.4310	2.650	.0632	-7.74
2-12	35.02	32.2045	31.1104	3.397	.0810	-7.63
2-12	33.32	32.8591	31.8046	3.209	.0765	-7.62
Avg. 12-m						-7.60
Limestone slabs immersed within OLD for 12 months (March 23, 1995 - March 26, 1996)						
1-06	38.56	40.0301	37.2362	6.979	.0692	-7.64
1-06	35.50	37.2105	35.5586	4.439	.0440	-7.83
1-06	36.94	35.0955	33.2948	5.130	.0508	-7.81
2-06	39.68	30.8110	27.8474	9.618	.0954	-7.63
2-06	34.4	30.9177	28.7229	7.098	.0704	-7.70
2-06	30.16	36.9740	35.5580	3.829	.0379	-7.83
Avg. 6-m						-7.74
1-12	41.16	36.9858	35.2625	4.659	.0462	-7.88
1-12	33.06	32.9569	31.8929	3.228	.0320	-7.99
1-12	20.46	23.1696	22.3484	3.544	.0351	-7.90
2-12	26.72	22.4805	20.8161	7.403	.0734	-7.71
2-12	27.02	25.4095	24.2530	4.551	.0451	-7.87
2-12	32.44	29.0688	28.0004	3.675	.0364	-7.99
Avg. 12-m						-7.89

[a] Samples had been immersed continuously at fixed locations at inflow or within a specific limestone drain. Sample location indicates drain 1 or 2 and distance, in meters, downgradient from inflow (at 0 m). For example, 1-06 is drain 1 at 6 m from inflow.

[b] Dissolution rate computed using initial mass and surface area of samples; no adjustment made for expected decreases in these parameters through time. Rates normalized using specific surface area (A_{SP}); mean A_{SP} = 1.004 cm^2/g for 75 limestone slabs.