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WATER CHEMISTRY-BASED CLASSIFICATION OF STREAMS AND IMPLICATIONS FOR RESTORING MINED APPALACHIAN WATERSHEDS

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Abstract—We analyzed seasonal water samples from the Cheat and Tygart Valley river basins, West Virginia, USA, in an attempt to classify streams based on water chemistry in this coal-mining region. We also examined temporal variability among water samples. Principal component analysis identified two important dimensions of variation in water chemistry. This variation was determined largely by mining-related factors (elevated metals, sulfates, and conductivity) and an alkalinity-hardness gradient. Cluster analysis grouped water samples into six types that we described as reference, soft, hard, transitional, moderate acid mine drainage, and severe acid mine drainage. These types were statistically distinguishable in multidimensional space. Classification tree analysis confirmed that chemical constituents related to acid mine drainage and acid rain distinguished these six groups. Hard, soft, and severe acid mine drainage type streams were temporally constant compared to streams identified as reference, transitional, and moderate acid mine drainage type, which had a greater tendency to shift to a different water type between seasons. Our research is the first to establish a statistically supported stream classification system in mined watersheds. The results suggest that human-related stressors superimposed on geology are responsible for producing distinct water quality types in this region as opposed to more continuous variation in chemistry that would be expected in an unimpacted setting. These findings provide a basis for simplifying stream monitoring efforts, developing generalized remediation strategies, and identifying specific remediation priorities in mined Appalachian watersheds.

Keywords—Acid mine drainage Acid precipitation Aquatic geochemistry Stream classification Watershed restoration

INTRODUCTION

Coal has been extensively mined in the central Appalachian Mountains for almost 200 years, and impacts to water quality from acid mine drainage have been a persistent environmental problem in this region. Acid mine drainage (AMD) forms when pyritic minerals in coal and overburden materials are exposed to water and oxygen [1,2]. The result is highly acidic, sulfate-rich stream water with high concentrations of total dissolved solids [2]. Acid precipitation has been another significant environmental problem in this region since the mid-1900s [3–5]. Burning fossil fuels releases sulfur dioxide and nitrogen oxides, which react with water, oxygen, and other chemicals in the atmosphere to form various acidic compounds. As a result, precipitation is a solution of dilute sulfuric and nitric acid, which leaches cations (e.g., Ca^{2+} and Mg^{2+}) and metals from the surrounding soils and causes reduced productivity and biodiversity in surface waters [3]. Acid rain and AMD are such extensive problems in the central Appalachians that more than 25% of streams are negatively affected in West Virginia, USA, alone [6–8].

Given the extent of the acidification problem, integrated watershed restoration programs are needed in this region [7]. However, restoration efforts in the central Appalachians are hindered by the fact that so many streams are impaired. Remediation of AMD is technically difficult and extremely expensive [2]. The overwhelming expense of acid stream restoration stems from the need to access numerous remote locations and the need for continued remediation over time [7]. Consequently, for restoration programs to be successful, we need procedures that can be used to identify restoration priorities and effective remediation actions.

Stream classification based on water chemistry may provide an important step toward simplifying water quality management in mined watersheds. Streams with similar water quality would be expected to have similar ecological conditions and require similar remediation prescriptions. Instead of designing a remediation plan for each individual stream, remediation plans could be designed for groups of streams of the same water quality type. Stream classification systems based on size [9] and channel morphology [10,11] have proven to be quite powerful. In addition, Dodds et al. [12] produced an initial classification based on nutrients and chlorophyll to assess trophic status of streams. However, to our knowledge, no attempts have been made to categorize streams in mined watersheds on the basis of water chemistry.

The constituents that define water quality of surface waters are highly variable both spatially and temporally [13–15]. Because of this variation, one would expect that stream water quality would also vary continuously. However, Stiles et al. [16] found several discrete water quality types draining from completely and partially flooded underground mines in the Pittsburgh coal basin. This finding suggests that a water quality–based classification of streams draining mined watersheds of this region may be possible.

Given the value of a stream classification system and the lack of such efforts in the central Appalachians, we conducted a watershed-scale survey of water chemistry in streams of the Cheat and Tygart Valley river basins, two intensively mined basins in northeastern West Virginia. Our specific objectives

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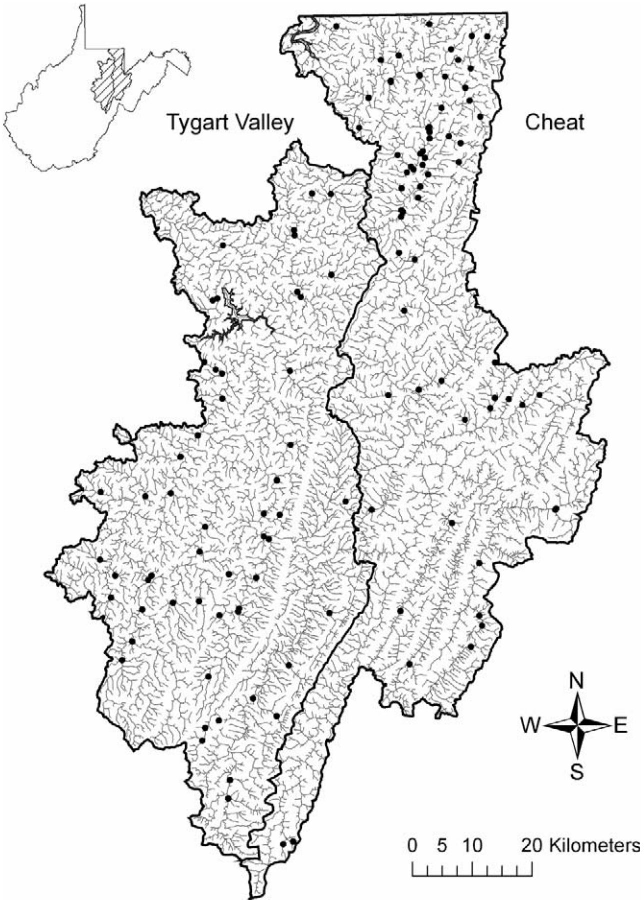

Fig. 1. Locations of water samples taken within the Tygart Valley and Cheat river basins, West Virginia, USA. Geographic Information System data layers from Natural Resource Analysis Center, West Virginia University [18].

were to use cluster analysis to group water samples from stream reaches into discrete categories based on water chemistry, determine if the water chemistry clusters were statistically distinguishable by describing the chemical characteristics of clusters, and finally quantify seasonal variability in cluster assignment of water samples from the same location.

METHODOLOGY

Study area

The Cheat and Tygart Valley rivers (Fig. 1) are major tributaries to the Monongahela River. Both rivers flow northward from their headwaters located in the mountains of Pocahontas County, West Virginia, USA. The Central Appalachian and Ridge and Valley physiographic provinces dominate each basin. Both basins consist of highly variable terrain, soil, and hydrogeology. The entire area is characterized by rounded, parallel upland ridges that are dissected by numerous valleys, with the relief being greatest in the southern portions [17]. Land cover in both basins is over 70% diverse mesophytic and mountain hardwood forest, of which oak forests dominate. Pasturelands and grasslands, which constitute nearly all the agricultural land use, make up about 18% of the basins. Urban land use activities affect less than 1% of these watersheds ([18]; http://www.nrac.wvu.edu/).

Geology of the basins consists of Pennsylvanian, Mississippian, and Devonian aged sedimentary rocks, mostly sandstones and shales with thin, nutrient-poor, slightly acidic soil layers above ([19]; http://pubs.usgs.gov/circ/circ1202/; [20]). Coal deposits are found only in Pennsylvanian strata. Kittanning and Freeport coals within the Allegheny formation and Bakerstown coal within the Conemaugh formation are widespread throughout the Cheat and Tygart Valley river basins. Pittsburgh and Waynesburg coals within the Monongahela formation make up only a small portion of coal deposits [18]. Most coal in the region has been mined from the Allegheny formation, which contains little capacity to neutralize acidity produced from the moderate to high sulfur materials [8].

Sample collection

Water quality samples were collected at 123 sites distributed throughout the Cheat and Tygart Valley river basins (Fig. 1). Study sites were distributed across a range of stream sizes, elevations, bedrock geology (e.g., sandstone, shale, or limestone), coal geology (e.g., Freeport, Kittanning, or Pittsburgh seams), and relative mining intensity (from unmined to intensively mined). Sites were spread across the two basins as much as possible to minimize interdependency among sites and to capture a wide range of water quality conditions. We know from other studies in this region that water chemistry is influenced predominantly by acidic precipitation and acid mine drainage from abandoned mine lands [6,7,21].

Following suggestions of Petty and Barker [6], three seasonal water samples were obtained at each location, two during early spring (April 2004 and 2005) and another in early autumn (October 2004). Water samples in spring were timed to capture relatively high base flow conditions, whereas the autumn sample was conducted during low base flow conditions. Water samples and direct field measurements were collected in accordance with standard operating procedures of the West Virginia Department of Environmental Protection, with duplicate samples taken at 2.5% of all sampling locations. Temperature (°C), pH, specific conductivity (μs/cm), dissolved oxygen (mg/L), and total dissolved solids (g/L) were measured in the field with a multiparameter YSI 650 unit fitted with a 600XL sonde (Yellow Springs Instruments, Yellow Springs, OH, USA). The YSI probe was calibrated before each use. Average current velocity was measured with a digital Marsh–McBirney flow meter, and discharge (m^3/s) was calculated using area-velocity techniques.

Two water samples were collected at each site during each of the three site visits. First, a filtered 250-ml sample was collected with a prerinsed Nalgene polysulfone filter holder and receiver fitted with mixed cellulose ester membrane discs (0.45-μm pore size). Filtered samples were immediately treated with 5 ml 1:1 nitric acid to maintain dissolved metals in solution. Filtered samples were analyzed within six months for the following dissolved parameters. Aluminum, barium, cobalt, copper, iron, manganese, nickel, cadmium, chromium, calcium, magnesium, sodium, and zinc were analyzed using inductively coupled plasma/atomic emission spectrometry, and chloride was analyzed with ion chromatography. Second, an unfiltered 500-ml sample was collected and kept at 4°C. These samples were analyzed for alkalinity and acidity within 14 d of collection using an automatic titrator. Sulfate was determined within 28 d using flow injection analysis. Method detection limits and sources of analytical methods are listed in Table 1. One-half of the value of a method's detection limit for a particular chemical constituent was substituted into the data set whenever concentrations were less than detection limits. All samples were analyzed at the National Research Center for Coal and Energy at West Virginia University. Quality con-

Table 1. Method detection limits (MDLs) of analytical methods used to determined concentrations of water chemistry parameters in water samples. ICP = inductively coupled plasma/atomic emission spectrometry; IC = ion chromatography. The U.S. Environmental Protection Agency (U.S. EPA) method source is also given

Parameter	Analytical method	MDLs (mg/L)	U.S. EPA method [38]
Al	ICP	0.021	200.7
Ba	ICP	0.0024	200.7
Ca	ICP	0.1	200.7
Cd	ICP	0.0028	200.7
Cl	IC	0.11	325.2
Co	ICP	0.003	200.7
Cr	ICP	0.0024	200.7
Cu	ICP	0.003	200.7
Fe	ICP	0.0026	200.7
Mn	ICP	0.0034	200.7
Mg	ICP	0.1	200.7
Na	ICP	0.1	200.7
Ni	ICP	0.0038	200.7
Zn	ICP	0.0032	200.7
Sulfates	Flow injection analysis	0.117	375.1
Acidity	Automatic titrator	—	310.1
Alkalinity	Automatic titrator	—	305.1

trol and assurance procedures were followed in accordance with standard methods [22].

Identification of water quality types

We used a combination of principal components analysis (PCA) and cluster analysis (CA) to examine the possibility of discrete water quality types within the water chemistry data. Principal components analysis reduces the dimensionality of a large multivariate data set to a smaller number of newly derived orthogonal variables called principal components (PCs). Principal components are ordered by proportion of variance explained by each [23]. Prior to analysis, all variables except pH were normalized with the natural logarithm function because PCA assumes that variables have a normal distribution. Alkalinity was normalized after adding 1 mg/L $CaCO_3$ equivalents to its value because alkalinity can have valid zero values. Total acidity was not included in the analysis because of its strong dependence on other included constituents.

The SAS (SAS Institute, Cary, NC, USA) procedure Factor was used with the Principal method option to perform PCA, and the procedure Score was employed to calculate factor scores for each sample [24]. The constituents included in PCA were pH, specific conductivity, total alkalinity, aluminum, barium, calcium, chloride, cadmium, cobalt, chromium, copper, iron, magnesium, manganese, sodium, nickel, zinc, and sulfate. Principal components with eigenvalues >1.5 were considered significant. Water chemistry parameters were considered significant components of a PC if their factor loadings had an absolute value >0.5 [23].

Cluster analysis was performed with the SAS procedure Cluster to identify particular water types in the data set based on water chemistry parameters that were significant components in PCA [24]. Ward's minimum-variance method was employed with the square of the Euclidean distance measure to define clusters. Because the normalized data set did not possess any outliers, no trimming algorithms were employed with the Ward method. This analysis was performed on all water samples. However, because Ba, Cd, and Cr did not contribute significantly to any of the PCs defined by PCA, these constituents were removed from CA.

Verification and chemical description of water quality clusters

Our second objective was to determine if the water quality types identified by CA were statistically distinguishable from one another or if sample-to-sample variation in water chemistry was best described continuously. To meet this objective, we used a combination of analysis of variance (ANOVA) and classification and regression tree (CART) analysis. The chemical characteristics of the water types were examined with basic statistics on the water quality constituents of the samples within each type. Basic statistics calculated for each raw water quality constituent and PC score included maximum, minimum, median, mean, and standard deviation. We used ANOVA with post hoc Tukey tests to test for statistical differences in mean PC 1 and 2 scores among the water types. An a priori alpha level was set at 0.05 for this test. Our underlying null hypothesis was that there were no differences in water chemistry as described by the PCs among water types identified by CA.

We used CART analysis to examine the relationship between water quality variables and water quality types derived from CA and to quantify the relative classification strength of the types. Classification and regression tree analysis partitions variation in a categorical or continuous response variable by recursively splitting the response variable into groups defined by combinations of explanatory variables that minimize within-group variation [25]. Classification and regression tree analysis is a nonparametric statistical technique, and therefore its strength is its ability to find relationships within complex data sets containing multiple variables that may each have different patterns of variance (lack multivariate normality) [26]. Results of CART are contained in decision trees showing splitting levels of explanatory variables that partition groups. Tree nodes represent splitting levels of explanatory variables that define groups, and tree leaves represent terminal groups, which can be described with summary statistics [25].

Interpretation of CART results is simple and achieved by following the splitting decisions down to terminal leaves. When the response variable is categorical (classification), the strength of the CART (classification tree) model can be evaluated by how many observations were misclassified [25]. We implemented the CART algorithm with the R language and environment for statistical commuting version 2.2.0 [27; http://www.r-project.org/], which follows Breiman et al. [28]. Group membership defined by CA on water chemistry data (water type) was the response variable, and the untransformed water chemistry parameters were the explanatory variables. This analysis allowed us to identify the most important water chemistry predictors of cluster membership and to examine the repeatability of water quality cluster assignment.

Temporal variation in water quality clusters and impairment criteria

Our final objective was to quantify the extent to which water quality types varied at a given site from season to season. To measure this tendency, we simply tallied the number of times the water type of all sites shifted to another type or stayed the same from sample to subsequent sample. The initial cluster type for a site was that observed in spring 2004, when the first water samples were taken. Subsequent water types for a site were those observed during subsequent sampling dates (fall 2004, then spring 2005).

Finally, water samples were considered in need of treatment (were impaired) if at least one of pH, aluminum, iron, or

Table 2. Means (and standard deviations) of water quality constituents and principal component (PC) 1 and PC 2 scores for each water quality type (number in parenthesis is number of samples classifying into that type). For PC 1 and PC 2, means with different letters are statistically different from one another ($p < 0.05$; analysis of variance, Tukey posttest). Means are reported in mg/L except where indicated. Conductivity (Cond) is reported in μs/cm, and alkalinity (Alk) is reported in mg/L $CaCO_3$ equivalents. AMD = acid mine drainage

	Reference (98)	Soft (32)	Hard (42)	Moderate AMD (32)	Transitional (134)	Severe AMD (37)
pH	6.9 (0.5)	5.0 (0.8)	7.1 (0.5)	6.0 (1.0)	6.8 (0.7)	3.5 (0.7)
Cond	94 (80)	74 (96)	591 (543)	171 (103)	125 (130)	703 (455)
Alk	21.3 (18.8)	2.3 (2.9)	82.4 (102.7)	25.4 (55.9)	22.9 (21.3)	0.5 (1.6)
Al	0.01 (0.01)	0.21 (0.14)	0.04 (0.05)	0.43 (0.97)	0.06 (0.08)	9.72 (9.37)
Ba	0.03 (0.01)	0.03 (0.01)	0.04 (0.01)	0.04 (0.03)	0.04 (0.01)	0.03 (0.01)
Ca	9.8 (9.4)	1.9 (1.3)	58.3 (33.9)	16.9 (12.1)	11.0 (7.6)	51.0 (45.3)
Cd[a]	3.0 (0.3)	3.0 (0.0)	3.2 (8.9)	4.0 (2.2)	3.9 (1.8)	3.5 (1.5)
Cl	1.7 (1.5)	1.5 (2.2)	48.5 (252.3)	3.8 (4.4)	6.4 (7.6)	3.9 (3.1)
Co[a]	1.5 (1.1)	1.9 (1.3)	2.6 (2.2)	19.7 (95.9)	1.6 (3.5)	57.4 (47.8)
Cr[a]	2.2 (1.4)	1.9 (1.1)	2.3 (1.3)	2.2 (1.1)	2.2 (1.2)	4.9 (3.0)
Cu[a]	1.6 (1.5)	2.0 (3.1)	2.2 (3.2)	2.0 (3.1)	1.7 (2.4)	15.9 (13.4)
Fe	0.03 (0.03)	0.09 (0.1)	0.13 (0.33)	0.17 (0.13)	0.14 (0.11)	12.23 (19.91)
Mg	1.7 (1.6)	0.6 (0.4)	15.7 (11.0)	4.7 (3.6)	2.2 (1.2)	18.7 (21.6)
Mn	0.01 (0.01)	0.07 (0.05)	0.35 (0.31)	0.38 (0.37)	0.10 (0.16)	1.85 (2.50)
Na	1.6 (1.7)	0.7 (1.4)	43.6 (124.4)	2.9 (3.4)	4.8 (5.5)	3.9 (2.9)
Ni[a]	2.4 (1.9)	3.1 (1.6)	5.3 (4.8)	18.5 (13.2)	2.4 (1.4)	87.9 (62.9)
Zn[a]	2.9 (3.4)	17.5 (50.2)	5.2 (5.6)	23.3 (27.3)	2.3 (2.0)	173.6 (121.8)
SO_4	9.6 (11.4)	7.7 (3.4)	198.9 (201.2)	44.5 (47.2)	14.6 (8.0)	266.2 (210.1)
PC 1	−0.87A (0.30)	−0.66A (0.45)	0.40B (0.29)	−0.18C (0.43)	0.94D (0.34)	2.25E (0.60)
PC 2	−0.00A (0.56)	−1.68B (0.51)	1.56C (0.78)	0.25A (0.64)	−0.37D (0.71)	−0.90E (0.39)

[a] Units = μg/L.

manganese did not meet water quality standards. These impairment criteria are in U.S. Environmental Protection Agency ([29]; http://www.epa.gov/reg3wapd/tmdl/wv_tmdl/CheatRiver/#Final%20bCheat%20TMDL%20(March%202001).pdf) and are established for aquatic life and human health use categories. The impairment criterion for iron was considered at chronic doses for trout water use designation (>0.5 mg/L). Impairment due to aluminum was considered at acute doses for trout waters (>0.75 mg/L). Manganese and pH impairment were defined by standards of the human health use category (>1.0 and <6.0 mg/L, respectively).

RESULTS

Identification and verification of water quality types

We observed high levels of variability in water chemistry among samples distributed across the Cheat and Tygart Valley river basins (Table 2). Principal components analysis reduced this variation to four important components with eigenvalues >1.0, but only PC 1 and PC 2 were interpreted (eigenvalue >1.5) (Table 3). Combined, PC 1 and PC 2 explained 63% of the total variance in the water chemistry data set. Principal component 1 represented a gradient of AMD chemistry where large positive values indicated streams with decreasing pH, high conductivity, and high concentrations of sulfate and dissolved metals (Table 3). In contrast, PC 2 represented a hardness–salinity gradient. High positive values on PC 2 were characterized by increasing pH, alkalinity, hardness, sodium, and chloride (Table 3).

Cluster analysis identified six water chemistry clusters within three hierarchical levels (Fig. 2). At the first level, cluster 6 was highly differentiated from the remaining five clusters. At the second level, cluster 1 was differentiated from the remaining four clusters. Finally, clusters 2 and 3 were differentiated from clusters 4 and 5 (Fig. 2). A bivariate plot of sites from each cluster in PC 1 and PC 2 space illustrates the general differences in water chemistry among the types identified (Fig. 3). This plot suggested that water quality types identified by CA could be labeled as reference (type 1), soft (type 2), transitional (type 3), hard (type 4), moderate AMD (type 5), and severe AMD (type 6). Figure 3 reflects this labeling convention, as do categories in subsequent tables and figures. Differentiation among type 1, types 2 to 4 as a group, and types 5 and 6 was influenced predominantly by AMD chemistry as described by PC 1. In contrast, differentiation among types 2 to 4 was influenced predominantly by alkalinity, water hardness, and salinity as described by PC 2 (Fig. 3).

Analysis of variance on mean PC 1 and PC 2 scores indicated a significant level of differentiation among the water quality types identified by CA (Table 2). Analysis of variance detected statistical differences among water quality types on both PC 1 ($F = 393$; degrees of freedom (df) = 5,369; $p <$

Table 3. The factor pattern (loadings) and eigenvalue magnitude for the first four principal components (PC) identified by principal components analysis

	PC 1	PC 2	PC 3	PC 4
Eigenvalue	7.8857	3.4849	1.3221	1.0718
pH	−0.6741	0.5910	0.0542	−0.0945
Conductivity	0.7933	0.4607	−0.1712	−0.0162
Alkalinity	−0.3611	0.8273	0.0293	−0.1193
Al	0.7794	−0.3956	−0.1038	0.0471
Ba	0.1041	0.3214	0.4917	−0.1877
Ca	0.6596	0.6362	−0.1286	−0.1714
Cl	0.3861	0.5709	0.1134	0.4861
Co	0.8558	−0.2039	0.2014	−0.1519
Cr	0.3978	−0.0726	0.3746	0.6163
Cu	0.6710	−0.2622	−0.1324	0.2159
Cd	0.2008	0.1130	0.8091	−0.0826
Fe	0.7540	−0.2495	−0.1446	0.2178
Mg	0.7761	0.5142	−0.1336	−0.1649
Mn	0.8109	−0.0410	−0.0713	−0.1038
Na	0.4131	0.7419	−0.0781	0.2775
Ni	0.8639	−0.1585	0.2525	−0.2005
Zn	0.7774	−0.3585	0.1118	−0.2565
SO_4	0.8592	0.2965	−0.1671	−0.1435

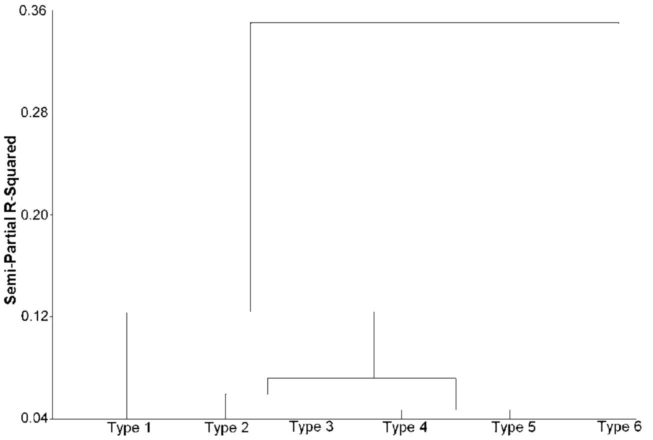

Fig. 2. Upper part of the dendrogram from cluster analysis. The portion of the dendrogram with a semipartial $r^2 < 0.4$ was not displayed. Labels at the bottom identify discrete water quality clusters (types 1–6) identified by cluster analysis.

0.0001) and PC 2 ($F = 126$; $df = 5{,}369$; $p < 0.0001$) (Table 2). Along PC 1, all water quality clusters, except the soft water type (i.e., Type 2), differed significantly from the reference type (Table 2 and Fig. 3). Only the moderate AMD type (type 5) was statistically equivalent to the reference type along PC 2 (Table 2 and Fig. 3).

Classification tree analysis further supported a high level of differentiation among the six water quality types identified by CA (Fig. 4). Overall, CART analysis produced a classification tree with a 12% misclassification rate, meaning that CART correctly classified 88% of the water samples into the water quality type to which they were previously assigned by CA. Manganese, sulfate, aluminum, calcium, and zinc concentrations and alkalinity were all useful variables in distinguishing among the six clusters (Fig. 4). Consistent with the results of CA and ANOVA, CART analysis indicated that the reference cluster and the severe AMD cluster were the most highly differentiated groups, with an overall misclassification rate of 3% for reference and 5% for severe AMD. Although higher, the misclassification rates of the remaining clusters also were quite low. Soft water type samples were misclassified as transitional types 11% of the time (Fig. 4). Hard water types were misclassified either as transitional or moderate AMD types 10% of the time. Transitional samples were misclassified at a rate of 17% and were most often misclassified as reference samples (13 of 26 total misclassifications). The highest rate of misclassification was observed in the moderate AMD type (18%), which was most often misclassified as a transitional type (Fig. 4). The overall low rates of misclassification suggest that the six water chemistry clusters identified by CA may be appropriately considered discrete water quality types.

Chemical description of water quality types

In combination, our analyses enabled us to describe specific chemical characteristics of the six water quality types identified by CA and verified by ANOVA and CART analysis (Table 2 and Figs. 3 and 4).

The reference cluster represented water samples characterized by circumneutral pH; low conductivity; low calcium, chloride, cobalt, magnesium, sodium, nickel, zinc, and sulfate concentrations; and very low aluminum, iron, and manganese concentrations (Table 2 and Figs. 3 and 4). Streams of this

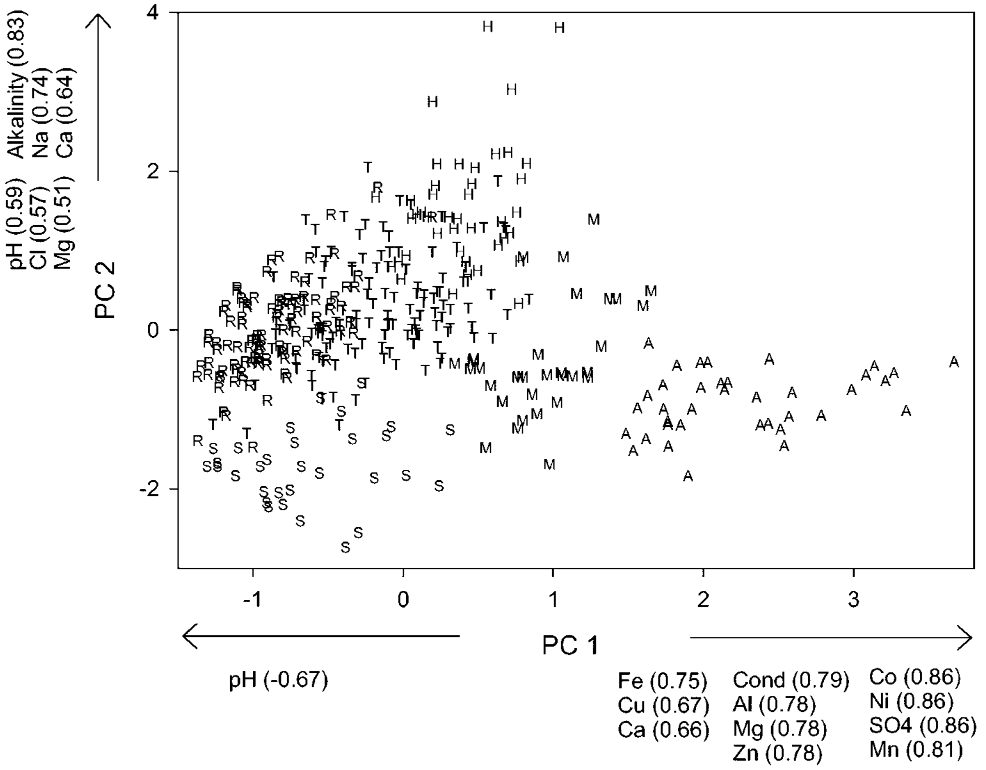

Fig. 3. Bivariate scatter plot of principal component (PC) 1 and 2 scores for each water chemistry sample. Samples are identified by cluster type assigned by cluster analysis and are descriptively labeled as A = severe acid mine drainage (AMD); M = moderate AMD; S = soft; H = hard; T = transitional; and R = reference water quality types. Chemical variables with high (>|0.5|) factor loadings on each PC are shown on the corresponding axis. SO_4 = sulfate; Cond = conductivity.

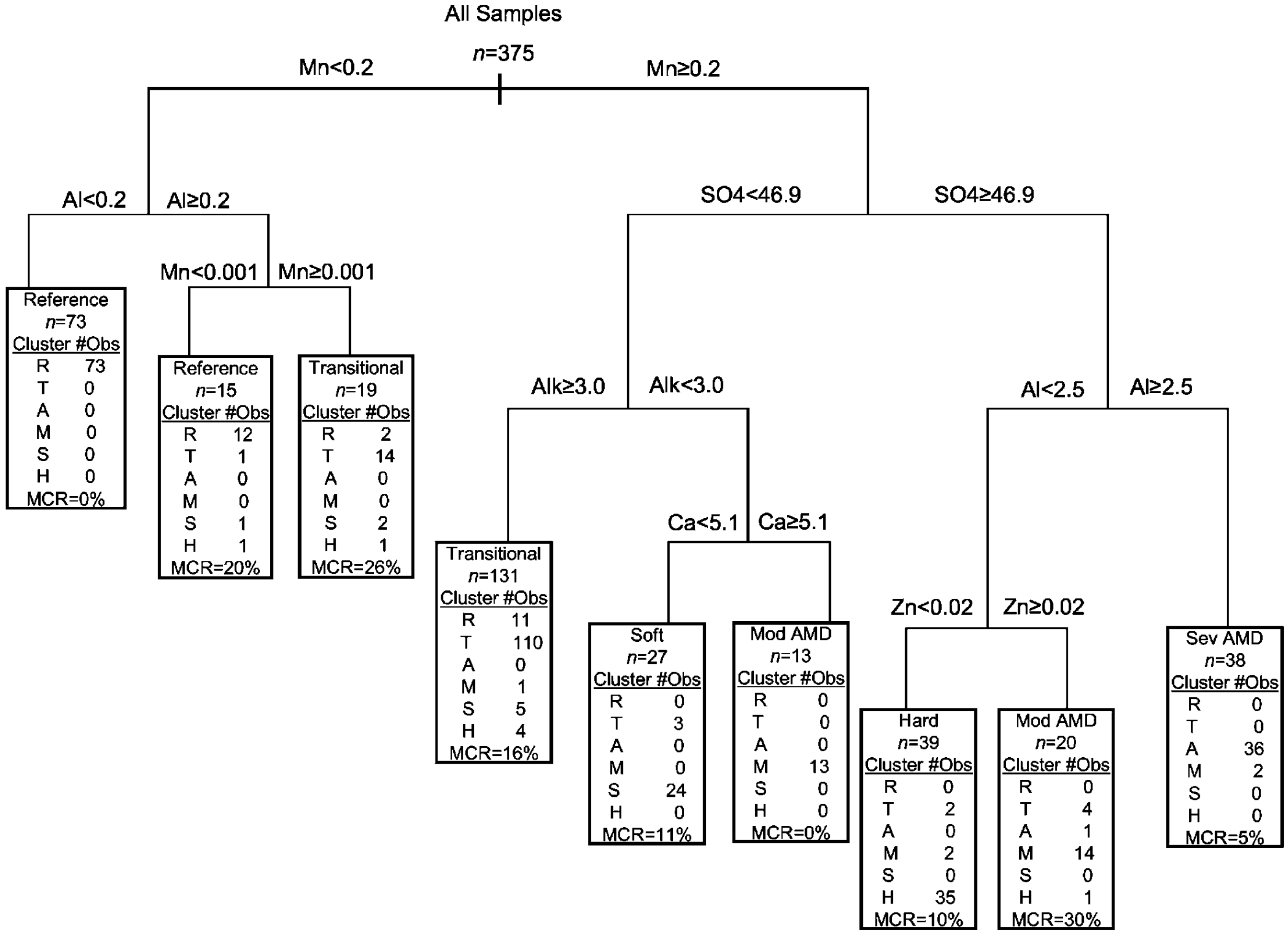

Fig. 4. Classification tree on water types derived from cluster analysis. The top of each leaf in the tree is labeled with its a priori assigned cluster type (Sev AMD = severe acid mine drainage and Mod AMD = moderate AMD). Also listed is the number of samples per leaf (*n*) and the predicted distribution of the samples (#OBS) among the available cluster types where A = severe AMD; M = moderate AMD; S = soft; H = hard; T = transitional; and R = reference water quality types. For example, leaf type Sev AMD had *n* = 38 water samples assigned to it by classification and regression tree (CART) analysis. Only two of the 38 samples actually belonged to another cluster (M, in this case). MCR is the misclassification rate for a terminal leaf. The misclassification rate for the full tree model was 12%, compared to 64% for the null model (majority rule). SO_4 = sulfate.

type probably drain unmined watersheds that contain geological attributes that buffer receiving streams from acid precipitation (e.g., higher proportions of shale and limestone).

The soft water cluster possessed highly reduced pH, alkalinity, calcium, and magnesium; low conductivity; and low concentrations of sulfate and manganese (Table 2 and Figs. 3 and 4). This chemical signature probably is typical of streams draining unmined watersheds influenced by high acid precipitation rates and low buffering capacity in surrounding soils.

The hard water cluster was characterized by circumneutral pH and significantly elevated levels of conductivity, alkalinity, calcium, chloride, magnesium, manganese, sodium, and sulfate (Table 2 and Figs. 3 and 4). However, concentrations of aluminum, iron, and other metals (e.g., nickel and zinc) remained low. This chemical profile is representative of saline mine drainage characteristic of streams draining mined watersheds where AMD is being actively treated or the surrounding overburden possesses naturally high buffering capacity.

The transitional water cluster possessed highly variable chemistry (Table 2 and Fig. 3) and consequently is difficult to describe in a general sense. This cluster is best described as a transitional type between the reference and moderate AMD type. The presence of slightly elevated manganese and aluminum concentrations relative to reference samples suggests that this type is characteristic of highly dilute AMD chemistry (Table 2 and Figs. 3 and 4).

The moderate AMD cluster was characterized by low to moderate pH and significantly elevated concentrations of aluminum, iron, manganese, nickel, zinc, and sulfate. Streams of this type probably drain watersheds that have been mined at a moderate level of intensity. In addition, AMD inputs probably are not being actively treated, nor are there natural sources of alkalinity in the surrounding overburden.

The severe AMD cluster possessed extremely low pH, extremely high conductivity, and extremely high concentrations of dissolved metals and sulfate. Streams classifying into this type probably drain intensively mined watersheds abundant in acid-producing minerals with little chemical treatment or geological potential for acid neutralization.

Temporal variation in water quality types

The general trend in water chemistry over our sampling period was for water types to remain constant from season to season (Table 4). Constancy ranged from 63 to 95% depending

Table 4. Temporal patterns in water chemistry type. Values along the diagonal represent the number (%) of sites that maintained a constant water quality type from season to season. Off diagonals represent the tendency for the initial water quality type (first season type) to change type in subsequent samples (subseason type). For example, 82% of the severe acid mine drainage (AMD) samples remained severe AMD type in subsequent samples, whereas 14% shifted from severe AMD to moderate AMD type in subsequent samples

	First season type					
Subseason type	Reference	Soft	Hard	Transitional	Moderate AMD	Severe AMD
Reference	47 (69)	1 (4)		16 (18)		
Soft		19 (79)		1 (1)		
Hard			21 (95)	10 (12)		
Transitional	21 (31)	4 (17)	1 (5)	55 (63)	7 (35)	1 (4)
Moderate AMD				5 (6)	13 (65)	4 (14)
Severe AMD						23 (82)
Total observations	68	24	22	87	20	28

on water quality type. Water samples classifying as hard were most stable (95% constancy) followed by the severe AMD type (82% constancy) and the soft water type (79% constancy). In contrast, transitional, moderate AMD, and reference types were more likely to shift from one type to another over time (63, 65, and 69% constancy, respectively) (Table 4). Several important patterns of shift from initial water type emerged from our analysis. The reference type always varied in the direction of transitional type, and this occurred 31% of the time over our sampling period (Table 4). Likewise, the transitional type usually varied in the direction of reference type, and this occurred 18% of the time (Table 4). The transitional type also had some tendency to move to the hard water type (12% of the time) and the moderate AMD type (6% of the time) over the sampling period (Table 4). Finally, soft water and moderate AMD types tended to vary toward the transitional type 17 and 35% of the time, respectively (Table 4).

Water quality types and impairment

The percentage of samples within a given cluster that possessed legally impaired water quality varied from a low of 8% in the reference cluster to a high of 100% in the severe AMD cluster (Table 5). The soft water cluster experienced an impairment rate of 81%, all resulting from low pH (Table 5). The moderate AMD cluster had a similar impairment rate of 84%. However, impairment of this water quality type was a combination of depressed pH and elevated dissolved metals (Table 5). Transitional and hard water types experienced low to moderate rates of impairment (19 and 14%, respectively) but for very different reasons. The transitional type tended to experience depressed pH, whereas the hard water type was most often impaired by elevated iron and manganese (Table 5).

DISCUSSION

Although stream chemistry was highly variable across sites, the results of our analyses support the existence of discrete water chemistry types within the Cheat and Tygart Valley river basins. The six stream types that we identified by cluster analysis were significantly different from one another and chemically interpretable in multivariate space. Furthermore, CART produced a classification tree model with a low error rate that was consistent with the patterns extracted from PCA. Interpretation of our combined analyses identified water quality in streams of the Cheat and Tygart Valley river basins as reference, soft, hard, transitional, moderate AMD, and severe AMD types.

Other studies that have attempted to identify and classify water chemistry types have had mixed success. For example, Abollino et al. [13] attempted to classify waters from Antarctic lakes and found that samples did not group neatly in multidimensional space constructed from a suite of selected elements. However, samples from the same lakes tended to group together. Papatheodorou et al. [15] examined 10 years of water chemistry data from a shallow, eutrophic Greek lake to determine the dominant factors related to temporal sources of variation in water quality and to classify water samples. They found six principal factors describing variation in the data but did not find distinct water type clusters.

In contrast, there have been numerous successful attempts to classify water types in highly impacted water bodies [5,14,30–33]. For example, Kowalkowski et al. [30] identified four natural cluster types of water chemistry and were able to distinguish and characterize polluted samples of water from clean samples taken along the Brda River in Poland. McNeil

Table 5. Number of samples (and %) within cluster types exceeding specific water quality criteria applicable to West Virginia, USA ($\mathrm{pH} < 6.0$; $\mathrm{Fe} > 0.5$ mg/L, $\mathrm{Al} > 0.75$ mg/L, and $\mathrm{Mn} > 1.0$ mg/L).[a] The number of water samples classified into each water cluster type is also given

Cluster type	No. of samples per cluster type	No. of samples (%) requiring treatment	No. of samples requiring treatment			
			pH	Al	Fe	Mn
Reference	98	8 (8)	8 (8)	0 (0)	0 (0)	0 (0)
Soft	32	26 (81)	26 (81)	0 (0)	0 (0)	0 (0)
Hard	42	6 (14)	1 (2)	0 (0)	2 (5)	3 (7)
Transitional	134	25 (19)	23 (17)	0 (0)	1 (1)	1 (1)
Moderate AMD	32	27 (84)	26 (81)	17 (53)	2 (6)	4 (13)
Severe AMD	37	37 (100)	37 (100)	37 (100)	33 (89)	22 (59)

[a] Mn criterion is public water supply standard. The Fe criterion is designated specifically for trout waters in West Virginia and is evaluated at chronic standards; Al is also designated specifically for trout waters and aquatic life use in general but is evaluated at acute standards [29].

et al. [14] used a similar approach to classify a large, broad-scale water chemistry data set from Queensland, Australia. Their analysis found nine water types that subsequently allowed for the designation of provinces characterized by similar water chemistry. Likewise, Lent et al. [31] found good support that a large basin used for drinking water supply in central Massachusetts, USA, could be classified into three subbasins based on water chemistry data.

Given findings from studies in other regions where chemical pollution is prevalent, we were not surprised to find discrete water quality types in the Cheat and Tygart Valley basins. However, the occurrence of discrete types does not mean that water chemistry was not highly variable or that it did not vary continuously across samples. In fact, the water quality types we identified varied continuously across the two dominant gradients extracted by PCA (Fig. 3). The water type we identified as transitional was notoriously variable. We believe this variability warrants class designation because this type would not exist in the absence of acid inputs from human activity. Other studies using similar analytical approaches as ours have also found highly and continuously variable water chemistry across sites [5,13–15,31,32]. Continuous variation in surface water chemistry is common feature of aquatic ecosystems probably because the host of underlying processes also vary continuously [32].

Many natural processes determine surface water chemistry, potential water types, and the accompanying spatial and temporal variability. Especially important factors are basin and aquifer geology, climate, and topography [32]. In our study region, the preponderance of sandstone and shale geology favors stream water that is naturally circumneutral to slightly acidic with low total dissolved solid concentrations and conductivity. Surface waters influenced by limestone occur but are uncommon. Given the natural geochemistry of this region, we would expect unimpacted watersheds to possess a relatively low degree of variability in water chemistry among streams and little if any evidence for discrete water types.

However, our results indicate that acid precipitation and AMD punctuate the range of expected variation in water chemistry and produce discrete water types. This occurs via two mechanisms. First, acidic precipitation produces streams with extremely low conductivity, low buffering capacity, and low pH, as acidic rain and snowfall strip buffering capacity from soils in the surrounding landscape [34]. The soft water type that results is distinct from reference streams where buffering capacity remains intact. Second, mining produces streams with varying degrees of AMD, which, along with surrounding geology, results in four additional water types. If the surrounding geology does not possess significant buffering capacity and AMD is dilute, then the transitional type is produced. The moderate and severe AMD types are the result of increasing levels of AMD production from increasingly intensive mining. Finally, the hard water type results when AMD from mining is either treated with calcium and sodium hydroxide or interacts with high-buffering-capacity geology.

Although we chose sites to minimize their interdependence, variation in our water chemistry data may have resulted at least in part from spatial autocorrelation even at scales larger than watershed boundaries [35]. Any similarity in chemical composition of sites resulting simply from their location, however, is still variation that warrants inclusion into a classification algorithm for categorization. Overall, our analyses found that definable water types exist in this region, where severe anthropocentric stressors (acid precipitation and AMD) are common. These stressors interacting with geologic mechanisms and site location appear to produce distinct water quality types in contrast to more continuous variation in chemistry that would be expected in an unimpacted setting.

Temporal variability in water quality types observed at a given sample location also was an important component in our water chemistry data. Overall, reference, transitional, and moderate AMD types tended to be the most variable streams. This result is consistent with the findings of Petty and Barker [6], who found a high degree of temporal variability in water chemistry of moderately impaired streams. In contrast, the severe AMD, hard, and soft water types were extremely stable. This suggests that increasing pollutant levels tend to produce extreme but relatively stable chemical conditions.

The modeling and classification success we had in defining water types in this region is valuable because it potentially simplifies decisions needed to restore and protect water quality in mined watersheds. First, our results indicate that a relatively short list of chemical constituents is needed to classify a given water body (stream or river) into a particular water quality type. These constituents included alkalinity and manganese, aluminum, sulfate, calcium, and zinc concentrations (Fig. 4). We also found that a given stream could be consistently classified with two or three samples collected each year across a range of base flow conditions. Consequently, this study makes clear how to efficiently characterize the chemical conditions of streams in mined watersheds.

Second, the existence of meaningful water types translates into groups of streams that could be efficiently restored using similar remediation technologies. For example, streams classifying into transitional or soft water types could be targeted for limestone sand addition, whereas full remediation of the severe AMD streams would require a combination of alkaline injection to increase pH and precipitate metals and anaerobic wetland systems to reduce sulfate concentrations.

Finally, identification of discrete water types along with their relative rates of impairment (Table 5) provides a basis for setting objective restoration priorities in these intensively mined watersheds. For example, our analysis identified soft water types that are highly vulnerable to acidification from acid precipitation. These types of streams should receive the highest priority in a stream restoration program because this type of impairment is so common and because this type is relatively easy to reclaim with processed limestone amendments [36]. This approach would also effectively restore many transitional and moderate AMD streams and quickly recover ecological productivity to many stream miles. In contrast, severe AMD and hard water type streams would receive lower restoration priorities because reduction of dissolved metal and sulfate concentrations is a very difficult and complex process [2,8]. However, these streams should receive long term attention and effort in an ecologically based framework to identify which streams, if restored, would translate into the greatest chemical and ecological benefit to the watershed as a whole [7].

Several important questions extend from this study. It is uncertain whether the water quality types that we identified in the Cheat and Tygart Valley basins can be consistently reproduced in other mining regions of Appalachia. If the classification system is reproducible, then it would be possible to develop regionwide rather than watershed-specific remediation strategies. We also would be interested to know whether the water quality types that we identified can be predicted from mapped watershed characteristics (e.g., elevation, geology, drainage area, and land cover). If so, then it would be possible to generate continuous maps of expected water quality conditions without having to obtain water chemistry samples from all streams in a watershed. Finally, it is unclear whether biological communities respond in a predictable manner to the water quality types. Our hypothesis is that such discrete water types should produce discrete community types by punctuating gradual change in community composition [37]. If such relationships exist, then it would be possible to predict community response to remediation actions designed to improve water quality, and this would greatly improve our ability to set meaningful restoration priorities.

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