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Spatial and temporal relationships among watershed mining, water quality, and freshwater mussel status in an eastern USA river

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HIGHLIGHTS

- Surface coal mining has been conducted in the Powell River headwaters for >35 years.
- Mining-influenced water constituents in the Powell River exhibit increasing trends.
- The river's downstream areas serve as habitat for freshwater mussels.
- Freshwater mussels have declined in density over the period of mining influence.
- Linkages between water constituents and mussel status are poorly understood.

GRAPHICAL ABSTRACT

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ABSTRACT

The Powell River of southwestern Virginia and northeastern Tennessee, USA, drains a watershed with extensive coal surface mining, and it hosts exceptional biological richness, including at-risk species of freshwater mussels, downstream of mining-disturbed watershed areas. We investigated spatial and temporal patterns of watershed mining disturbance; their relationship to water quality change in the section of the river that connects mining areas to mussel habitat; and relationships of mining-related water constituents to measures of recent and past mussel status. Freshwater mussels in the Powell River have experienced significant declines over the past 3.5 decades. Over that same period, surface coal mining has influenced the watershed. Water-monitoring data collected by state and federal agencies demonstrate that dissolved solids and associated constituents that are commonly influenced by Appalachian mining (specific conductance, pH, hardness and sulfates) have experienced increasing temporal trends from the 1960s through ~2008; but, of those constituents, only dissolved solids concentrations are available widely within the Powell River since ~2008. Dissolved solids concentrations have stabilized in recent years. Dissolved solids, specific conductance, pH, and sulfates also exhibited spatial patterns that are consistent with dilution of mining influence with increasing distance from mined areas. Freshwater mussel status

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Specific conductance
Total dissolved solids

indicators are correlated negatively with dissolved solids concentrations, spatially and temporally, but the direct causal mechanisms responsible for mussel declines remain unknown.

1. Introduction

Impacts by mining to water resources occur worldwide (Younger and Wolkersdorfer, 2004). Surface mining disturbs geologic strata and soils, exposing disturbed materials to atmospheric oxygen and rainfall; and, as a consequence, often enables accelerated chemical weathering that releases soluble constituents that enter surface waters. Historically and globally, acids and acid-soluble metals released by oxidation of pyritic minerals have been primary mining-related water pollution concerns (Younger et al., 2002; Jacobs et al., 2014). However, even when acids are controlled, mining disturbances can release other constituents of environmental concern such as major ions and trace elements. Mining has been recognized as a source of elevated major ions and associated constituents in non-acidic surface waters of Australia (Hancock et al., 2005), Germany (Schreck, 1995; Bäthe (1997); Bäthe and Coring, 2011; Braukmann and Böhme, 2011), Spain (García-Criado et al., 1999; Cañedo-Argüelles et al., 2013), South Africa (Goetsch and Palmer, 1997), and eastern USA (Griffith et al., 2012).

Concerns for water resource impacts by mining are acute in eastern USA due to extensive surface coal mining in the Appalachian coalfield. Rivers draining Appalachian mined areas include the Powell River of southwestern Virginia and northeastern Tennessee, which hosts exceptional biological richness and a high diversity of at-risk species that include multiple freshwater mussels (Johnson et al., 2012; Ahlstedt et al., 2005). Freshwater mussels (Unionidae) occur worldwide but achieve their greatest diversity in North America, especially in southeastern USA (Lydeard et al., 2004). Freshwater mussels have experienced high rates of imperilment globally (Williams et al., 1993; Lydeard et al., 2004; Strayer et al., 2004; IUCN, 2015). Mussel declines have occurred in several North American rivers affected by watershed mining (Warren and Haag, 2005; Angelo et al., 2007; Johnson et al., 2014) as well as in the Powell River (Ahlstedt et al., 2015). There is interest in the region to identify specific toxicants that are responsible for the mussel declines that have been observed in streams draining the Appalachian coalfield (Warren and Haag, 2005; Jones et al., 2014) and to determine if such toxicants originate from mining.

Due to legal protections (Zipper, 2000), the acidic waters that characterize coal mining drainages in other world regions are no longer a major concern throughout much of the Appalachian coalfield. Yet, a number of studies have documented stressed biotic resources in the region's mining-influenced rivers and streams. Water salinity, measured as specific conductance (SC) and/or total dissolved solids (TDS), is often elevated in such streams (Bryant et al., 2002; Hartman et al., 2005; Merricks et al., 2007; Pond et al., 2008; Wood and Williams, 2013; Gangloff et al., 2015; Pond et al., 2014; Timpano et al., 2015), and recent research has linked elevated salinity with biotic impacts. Depressed richness of benthic macroinvertebrate communities often occurs in mining-influenced low-order streams with elevated SC (Green et al., 2000; Hartman et al., 2005; Pond et al., 2008; Cormier et al., 2013a, 2013b; Pond et al., 2014; Timpano et al., 2015). Recent studies have also found fish assemblage structure (Hitt and Chambers, 2014), salamander abundance (Wood and Williams, 2013) and richness (Muncy et al., 2014), and microbial community composition (Bier et al., 2015) to be altered in salinized mining-influenced streams; and freshwater mussel richness and densities to be depressed in salinized river segments (Johnson et al., 2014). Water borne trace elements often occur at elevated concentrations in association with elevated salinity in such waters (Pond et al., 2008; Lindberg et al., 2011; Pond et al., 2014) and are also of concern due to potential biotic impacts (Palmer et al., 2010; Johnson et al., 2014). Depressed aquatic communities have also been observed in salinized freshwater bodies of other world regions (Cañedo-Argüelles et al., 2013).

Freshwater mussels are long-lived mollusks that are sensitive to water- and bed-sediment quality. Juvenile mussels burrow into sediments, and are sensitive to sediment and interstitial water quality (Yeager et al., 1994; Cope et al., 2008). Mature mussels are filter-feeding organisms that process large volumes of water to extract suspended organic particles for sustenance. Laboratory studies have documented freshwater mussels' sensitivity to water and sediment contaminants that include major ions (Keller et al., 2007, Gillis, 2011; Kunz et al., 2013) and dissolved metals (Havlik and Marking, 1987; Jacobson et al., 1993, 1997; Naimo, 1995; Keller et al., 2007; Cope et al., 2008; Wang et al., 2010) such as those occurring in Appalachian coal mine drainages; but mussel-specific toxic effect levels for most of these constituents are not known. Mussels are also sensitive to other constituents that occur in the Powell River, including ammonia and chlorine from sewage effluents (Goudreau et al., 1993; Augspurger et al., 2003; Mummert et al., 2003; Wang et al., 2007) and polycyclic aromatic hydrocarbons (Wang et al., 2013).

With understanding of that background, we investigated relationships among surface coal mining land disturbance, water quality, and mussel status in the Powell River. Our research objectives were to determine spatial and temporal patterns of water quality change; determine correspondence of those changes with known spatial and temporal patterns of watershed disturbance by mining; and determine relationships of mining disturbance and corresponding water quality change to changes of freshwater mussel status in the Powell River, Virginia and Tennessee.

2. Materials and methods

The research focus was spatiotemporal change. Factors of primary interest were watershed disturbance by mining, water quality in the Powell River, and status of the river's mussel assemblages. The spatial dimension of interest was the Powell River's linear extent as it connects headwater mining with monitored mussel populations located >100 km downstream. Both watershed mining and mussel declines have occurred over multi-decadal time periods.

The Powell River is a largely free-flowing tributary of the upper Tennessee River which drains to the Mississippi River and the Gulf of Mexico. The Powell River originates in the Appalachian Plateaus ecoregion (US EPA, 2015) that is heavily mined for coal and flows into the Ridge and Valley ecoregion where its watershed is primarily forested and agricultural (Fig. 1).

2.1. Mining

Mining disturbance within the Powell River watershed was assessed by accessing data generated by Li et al. (2015a, 2015b). These authors analyzed 24 Landsat satellite, each covering ~90% of the watershed's coal-bearing areas, to identify surface mined areas by location and by year of most recent disturbance for the 1984–2011 period. New mining disturbances could not be assessed for the years 1991, 1996, 2006, and 2009; but they interpreted new disturbances for the years following as representing the two years of mining. They also reported that the 1984 image detected more "new" mining disturbance than any other year, which they interpreted as representing mining disturbances over multiple prior years.

We characterized 2011 landcover for four nested Powell River watersheds, each defined water monitoring location: Virginia DEQ's

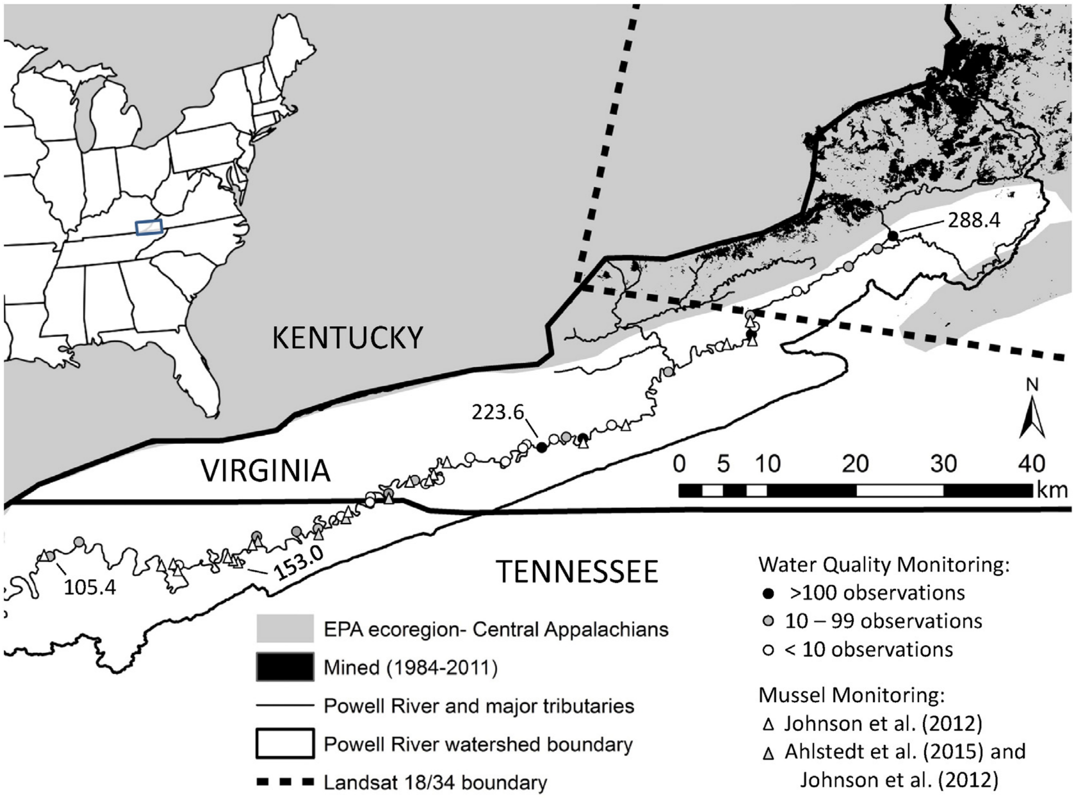

Fig. 1. Map of the Powell River and its watershed, with locations of monitoring points yielding data that are the focus for the article. Surface mined area designations (1984–2011) are from Li et al. (2015a, 2015b); some areas outside of the Landsat 18/34 boundary, and outside the time period studied by Li et al. (2015b) have been surface mined. Numbers on the map designate river km of selected monitoring locations (Table 2). The box on the inset shows map location. Additional geographic details are available as supplemental data.

(VDEQ) 6BPOW179.20 at river kilometer (RKM) 288.4, where the river drains most of the watershed's area in Wise County but none from neighboring Lee County; VDEQ's 6BPOW138.91 at RKM 223.6, which receives drainage from all watershed coal mining; a former Tennessee Valley Authority (TVA) monitoring point (475097) at RKM 153.0, within the study reach where mussels occur; and Tennessee Department of Environment and Conservation's (TDEC) POWEL065.5CL at RKM 105.4, the furthest downstream point with available water quality data. Mining disturbance maps (Li et al., 2015b) were overlaid on the National Land Cover Data 2011 (MRLC, 2015) to estimate land cover.

Annual surface coal production was estimated for the RKM 288.4 watershed and the entire Powell River watershed upstream from RKM 105.4. These estimates were prepared by obtaining coal production data for Wise and Lee Counties from US EIA (2015a, 2015b), and predecessor publications. For each year, a fraction of Wise County surface coal production was allocated to the Powell River watershed in direct proportion to the Wise County mined area locations for that year. All of Lee County's surface coal production occurs within and was allocated to the RKM 223.6 and downstream watersheds. For missing years of the mined-area sequence, the following year's mined area was used for allocation; area distributions for 1984 were used to allocate 1980–1983 production; and the 2011 area distribution was used to allocate 2012–2014 coal production. Ratios of estimated coal production to disturbed area were calculated for the RKM 288.4 watershed for annual and 5-year time periods.

Coal production data were used to estimate watershed geologic disturbance by mining by assuming a constant ratio of disturbed rock to produced coal tonnage. Conversations with industry personnel indicate typical mining ratios over the study period have been in the range of 9 to 21 bank cubic meters per coal tonne. To produce geologic disturbance estimates, we used a 12.8:1 ratio of in-ground rock (m^3) disturbed to tonnes of coal produced and 20% (on average) volumetric expansion due to fracturing.

Cumulative geologic disturbance for the RKM 288.4 and RKM 223.6 watersheds was calculated on a temporal decay-weighted basis considering known processes governing TDS release by mining-disturbed rocks in the Appalachian coalfield. Both laboratory (Orndorff et al., 2015) and field studies (Sena et al., 2014; Ross, 2015) demonstrate that TDS release by Appalachian mine spoils occurs most rapidly during the initial water exposures and declines with subsequent exposures until reaching a relatively constant concentration described as "stabilized" (Orndorff et al., 2015). Peak and stabilized concentrations vary widely among spoil types (Orndorff et al., 2015). Evans et al. (2014) analyzed SC over time for water outflows from 137 Virginia valley fills. The average peak concentration (1706 μS/cm), times required to reach that peak (9 years) and for decline to ~500 μS/cm (~20 years), and an assumed 500 μS/cm stabilization level (Orndorff et al., 2015) were used to construct a temporal decay model for use in assessing water-quality impacts by mining-disturbed geologic materials (Fig. 2).

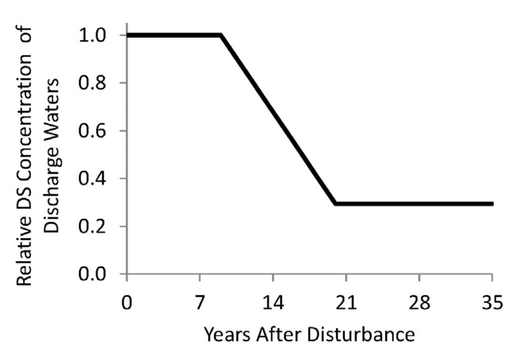

Fig. 2. Temporal decay function used to translate geologic disturbance estimates into decay-weighted geologic disturbance, considering mine spoils' dissolved solids' release potentials.

2.2. Water quality

2.2.1. Data sources

Water quality data were obtained in 2010 from Virginia Department of Environmental Quality (VDEQ) and Tennessee Department of Environment and Conservation (TDEC); and updated in August 2014 (VDEQ) and March 2015 (TDEC). Data from Tennessee Valley Authority (TVA), 1964 to 1993, were obtained from the Legacy STORET database (US EPA, 2010). Variables from different data sources recorded as or computed as proxies for identical STORET codes were combined for analysis (Table 1).

Primary factors governing variable selection were data availability and study goals. Mining-related variables recorded with sufficient frequency to enable analysis (pH, SC, and TDS) were emphasized. Sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), calcium (Ca^{2+}), and magnesium (Mg^{2+}) are generally recognized as the predominant ions in non-acidic waters draining Appalachian surface mines (Pond et al., 2008; Pond et al., 2014; Orndorff et al., 2015; Timpano et al., 2015); hence, SO_4^{2-}, hardness and alkalinity were also included. Two additional variables (total nitrogen, total N; and chloride, Cl^-) that represent anthropogenic impacts more generally were also obtained and analyzed.

Water-column metals, although recorded less frequently, were also analyzed due to mussels' known sensitivities to certain metals (Naimo, 1995). Those with highest collection frequencies were analyzed. Non-metallic trace elements available with comparable frequencies (arsenic, As; and selenium, Se) also were selected.

2.2.2. Initial screening

Data observations considered erroneous were identified and deleted (Zipper et al., 2002; Price et al., 2014). If >1 observations of a variable were recorded on the same day at the same location, those values were averaged.

Observations recorded as below a detection limit (censored observations) were inspected and, in some cases adjusted. For variables with a single detection limit at a level also representing uncensored observations, censored observations were set equal to ½ the detection limit. For variables with multiple detection limits, the highest common detection limit was defined and all observations recorded at lower values were handled identically to those recorded at that detection limit. If observations also were recorded as an uncommon detection limit that was greater in magnitude than the highest common detection limit, observations censored at the uncommon detection limit were excluded from analysis. Water pH values prior to 1985, when VDEQ was using colorimetric methods, were excluded.

2.2.3. Constructing total N from component variables

Total N was sometimes measured directly as STORET 00600; otherwise, it was calculated when possible by adding total Kjeldahl N (TKN, 00625) to total nitrate and nitrite N (00630) if available, or to nitrate N (00620) and nitrite N (00615) otherwise if both were available. Concentrations reported as less than the highest commonly occurring detection limits (0.1 and 0.05 mg/L, respectively, for TKN and nitrate N) were set to one-half of those detection limits. For nitrite N, all observations censored at <0.01 mg/L were set at 0.01 mg/L. We estimated nitrite N as 0.01 mg/L when necessary to calculate total N. If TKN was not available but organic N (00605) and ammonia-N (00610) were available, TKN was calculated as their sum.

2.2.4. Estimating dissolved solids (DS) when not directly measured

Total filterable residue at 180 °C (70300) was used to represent DS when available; otherwise total filterable residue at 105 °C (00515) was used when available; otherwise, a composite measure (TR-NFR) was calculated if possible by subtracting non-filterable residue (00530) from total residue (00500). For observations with multiple DS proxy variables, close correspondence among measured values was observed.

2.2.5. Specific conductance

A prior analysis of VDEQ data (Zipper and Berenzweig, 2007) found that SC was unreliable as a water-quality indicator prior to 3/2000. Therefore, only SC values from 3/2000 and later were used.

2.2.6. Metals and trace elements (dissolved)

To evaluate potential toxicity by trace elements, we compared measured concentrations with continuous criterion concentrations (CCC) recommended for the protection of freshwater aquatic life (US EPA, 2014); CCC for aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni) and zinc (Zn) were calculated using hardness values of 100 mg/L $CaCO_3$ (Price et al., 2014). For Cu, we used the VDEQ (2011) CCC. For manganese (Mn), we used a CCC proposed by the state of Illinois (Timpano et al., 2015). We used CCCs for this analysis because generally recognized protective levels for freshwater mussels are not available.

2.3. Biology: mussels

Freshwater mussel sampling data from Johnson et al. (2012) and Ahlstedt et al. (2005) were accessed to describe variation among the river's mussel assemblages over space and time.

Johnson et al. (2012) characterized mussel assemblages at 21 locations in the Powell River, extending from RKM 269.4 to 104.8, in 2008 and 2009. They recorded mussel densities, species observed, and catch-per-unit-effort (CPUE). These data were used to describe spatial variation.

Ahlstedt et al. (2005) initiated quantitative mussel surveys in 1979. They sampled four locations, extending from RKM 159.7 to 188.9, just north of the Virginia–Tennessee border, on six occasions through 2004, and Johnson et al. (2012) re-sampled these four sites in 2008–2009. Data from these four locations were averaged by year of sampling to describe mussel temporal variation.

Table 1
List of water quality variables analyzed within the study reach, with STORET codes, numbers of observations, and dates of coverage.

Parameter	STORET code	n	Dates available	
			Minimum	Maximum
Field pH	FDT_Field_pH	769	1/1985	8/2014
Field SC	FDT_Specific_Conductance	370	3/2000	8/2014
Residue, total filterable	70300, 00515 (00500–00530)[a,b]	1179	5/1964	6/2014
Nitrogen, total (mg/L as N)	00600[a]	1172	6/1964	6/2014
Hardness, total (mg/L as $CaCO_3$)	00900	580	9/1967	11/2013
Alkalinity, Total (mg/L as $CaCO_3$)	00410	577	5/1964	6/2014
Chloride, total in water (mg/L)	00940	401	5/1964	6/2009
Sulfate, total (mg/L as SO_4)	00945	476	5/1964	9/2013

[a] Numbers of observations include values calculated from data recorded under other STORET codes, as described in text.
[b] The term dissolved solids (DS) is used to represent total filterable residue and calculated proxy values.

2.4. Statistical analyses

Primary water quality variables (pH, SC, DS, total N, alkalinity, hardness, and SO_4^{2-}) from monitoring locations extending from RKM 288.6 to RKM 105.4 were analyzed using mixed effects models in SAS statistical software (version 9.3, SAS Institute, Cary NC) to determine effects of spatial location (expressed as RKM), sampling time, and season on the continuous water quality variables using restricted maximum likelihood. Season was defined as categorical variables at two-month intervals. Sampling location also was defined categorically and modeled as a random effect. Station-to-station variability is expressed as a variance component in this mixed model. Repeated measures modeling was used to account for autocorrelation across time. An exponential covariance structure was assumed across time to account for temporal autocorrelation among measurements at individual stations. Modeling with the above data structures converged for all but one dependent variable, sulfate. Hence, the model was re-run for sulfate with the temporal autocorrelation structure removed. These analyses were conducted for all 8 primary variables assuming linear models. In order to investigate temporal trends within individual river sections independently, that modeling procedure was also applied separately for three river sections. We also analyzed DS concentrations at two monitoring locations (RKM 223.6 and RKM 288.4) using piecewise regression (Toms and Lesperance, 2003) assuming linear segments joined at an unknown point.

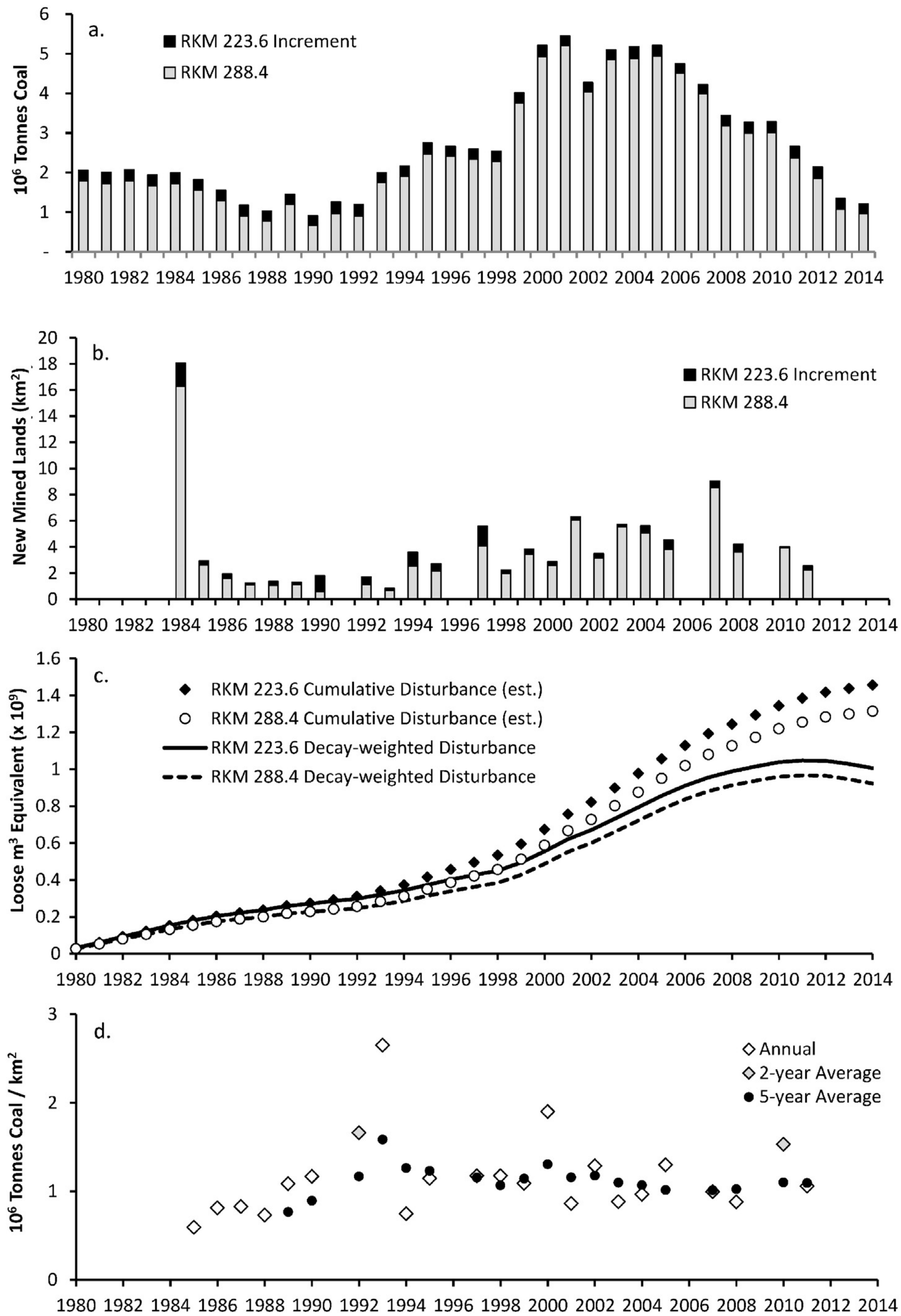

Fig. 3. Estimates of (a) annual coal production, (b) land surface disturbance, by year of detection, and (c) cumulative and geologic disturbance (actual and decay weighted) for the watersheds defined by the RKM 223.6 and 288.4 monitoring points; and (d) annual, 2-year, and 5-year ratios of coal production to land-surface disturbance for the RKM 288.4 watershed, calculated from data in (a) and (b) above, with 2- and 5-year periods terminating with the designated year.

Table 2
Land use within watersheds defined by water monitoring points at the downstream end, near the midpoint, and at the upper end of the study reach; as of 2011.

Land use	RKM 288.4	RKM 223.6	RKM 153.0	RKM 105.4
% of area				
Surface coal mining (1984–2011)[a]	29%	12%	7%	5%
Other disturbance within mine permits[a,b]	4%	2%	1%	1%
Other barren lands, shrub/scrub	3%	2%	2%	2%
High- and medium-intensity developed	<1%	<1%	<1%	<1%
Low-intensity and open-space developed	4%	7%	7%	7%
Agriculture, herbaceous[c]	4%	13%	25%	27%
Forest	56%	64%	59%	58%
Open water, wetlands	<1%	<1%	<1%	<1%
km^2				
Total area	290	839	1429	1772

[a] Mining land use within Landsat 18/34 from Li et al. (2015a, 2015b); other data from NLCD (2011).
[b] A large fraction of these lands appear to have been mined prior to 1984.
[c] Review of aerial photography indicates that some areas in agricultural land uses (hay production, livestock pasture) have been classified by NLCD (2011) as “herbaceous” land cover.

A linear model also was used to evaluate spatial and temporal variation of dissolved trace elements; because of small numbers of recent observations downstream from RKM 288.4, observations at RKM 296.4 were included and a seasonal coefficient was not. In addition to recent (2000–2011) VDEQ data, TVA measurements of dissolved Mn were available for 1967–1981 over the RKM 153.0–230.3 river segment. These data were analyzed separately from the VDEQ data for dissolved Mn.

We used a generalized linear model (GLM) to test for significance of trends in mussel mean densities over time from 1979 to 2009 using a Poisson distribution and log link function (R Development Core Team, 2006).

Relationships of mussel spatial and temporal variation to upper-watershed landscape disturbance and water quality were analyzed using Spearman correlation. Temporal correlations were conducted using annual time steps. Mining-disturbance variables were expressed on a cumulative basis. Dissolved solids were used to represent water quality considering it to be representative of mining impacts generally.

Correlations also were conducted to evaluate spatial relationships with the mussel-status indicators measured by Johnson et al. (2012). Because water quality data are not available for most sampling sites and because the strong spatial effects revealed by the regression models, RKM was also included to represent relative mining-related water-quality differences among sampling sites.

Except where otherwise reported, statistical analyses were conducted using JMP software (v. 11, SAS Institute, Cary NC) and interpreted for significance at $\alpha = 0.05$.

3. Results

The upper Powell River watershed was mined throughout the study period (Fig. 3a). In the watershed area defined by RKM 288.6, at least 29%, and perhaps as much as 33% (including observed disturbances within mine permits) of land surface was detected as mined by Li et al. (2015b) (Table 2). Although the RKM 223.6 watershed has a greater area of mining disturbance than the RKM 288.6 watershed, the proportionate disturbance is less (Table 2); yet, at least 11.6%, and perhaps as much as 13% of land area was detected as disturbed by mining. The RKM 223.6 watershed's surface disturbance is underestimated, however, since southwestern section of Lee County's coalfield was not visible in the Li et al. (2015b) Landsat images. The RKM 153.0 and 105.4 watersheds were less impacted, proportionally, by mining; have similar forest areas, and greater agricultural areas then the RKM 223.6 and 288.4 watersheds (Table 2). Primary non-mining land uses throughout the study area are forestry and agriculture. Aside from the mining, little non-agricultural development is evident as high- and medium-intensity developed land uses constituted less than 1% of total area at all watershed levels.

Coal production and related land and geologic disturbance progressed over the study period, with coal production peaking in 2000–2005 (Fig. 3a–c). The ratio of coal produced to land-surface disturbance in the RKM 288.4 watershed changed over the study period. Approximately 0.74 million tonnes of coal were produced for each km^2 of land disturbed over the 1985–1989 period but this ratio increased to >1 million tonnes per km^2 in 1990 and remained at those levels for most following years (Fig. 3d). Toward the end of the study period, decay-weighted geologic disturbance exhibits increased divergence from actual geologic disturbance (estimated) as peak coal production (2000–2005) becomes increasingly distant in past time.

Mining-influenced water-quality constituents exhibited significant spatial and temporal patterns (Table 3). Four mining-related water-quality measures (pH, SC, DS, and sulfate concentrations) all demonstrated positive spatial trends, indicating that inputs of these constituents are exerting maximum influence near the headwaters and are diluted moving downstream, and positive temporal trends indicating increasing levels over time. Alkalinity exhibited an increasing temporal

Table 3
Numbers of observations and mean values for primary water constituents, and for dissolved solids within river sections of interest; with results of linear models intended to test for effects of time (modeled as year), river km (to represent inverse distance from mining influence), and season (6 per year) on those constituents.[a]

Constituent & river segment	n	Mean (±std. err.)[a]	Year		River km		Season
			Direction[b]	p-Value	Direction[b]	p-Value	p-Value
RKM 105.4–288.4							
pH	769	8.0 (±0.01)	pos	0.0006	pos	0.03	0.0025
Specific conductance (μS/cm)	370	553 (±10)	pos	<0.0001	pos	<0.0001	<0.0001
Dissolved solids (mg/L)	1179	271 (±4)	pos	<0.0001	pos	<0.0001	<0.0001
Total N (mg/L)	1172	0.8 (±0.01)	pos	<0.0001	ns		0.0091
Hardness (mg/L)	580	162 (±2)	pos	<0.0001	ns		<0.0001
Alkalinity (mg/L)	577	112 (±2)	pos	<0.0001	neg	0.03	<0.0001
Chloride (mg/L)	401	6 (±0.1)	pos	<0.0001	ns		<0.0001
Sulfate (mg/L)	476	99 (±3)	pos	<0.0001	pos	<0.0001	<0.0001
Dissolved solids within river sections							
RKM 105.4–194.2	168	210 (±5)	pos[c]	<0.0001	ns[d]		<0.0001
RKM 223.6–231.0	385	242 (±4)	pos	<0.0001	na		<0.0001
RKM 288.4	325	358 (±9)	pos	<0.0001	na		<0.0001

[a] All constituents except pH (standard units) expressed as mg/L; alkalinity and hardness are mg/L as $CaCO_3$.
[b] pos = positive; neg = negative; ns = not significant ($p < 0.05$); na = not applicable.
[c] The temporal autocorrelation model failed to converge with river km included as a term; so river km was removed from the model to determine temporal effects for this section.
[d] The temporal autocorrelation model failed to converge; so the temporal autocorrelation structure was removed to determine river km effects for this section.

trend but a negative spatial trend. Like the mining-related constituents, total N and Cl^{-} exhibited positive temporal trends, but these constituents' relationships with river km were not statistically significant. The river-section analyses revealed increasing temporal trends for DS in the upstream, middle, and downstream sections of the study reach (Table 3, Fig. 4). The breakpoint regression analyses revealed increasing trends extending to for RKM 223.6 and to June 2010 for RKM 288.4; and that temporal trends beyond those dates were not statistically significant.

Among trace elements, dissolved Mn, Ni, and Se exhibit positive spatial trends that reflect higher concentrations near the headwaters and mining areas; and dissolved As exhibited a declining temporal trend (Table 4). All recorded observations of dissolved trace elements are well below CCC (Table 4).

Long-term trends in mussel density at the four locations sampled repeatedly by Ahlstedt et al. (2005) and then by Johnson et al. (2012) exhibit a long-term declining trend (Fig. 5). Mean mussel densities at these locations are negatively correlated temporally with watershed coal production and with upstream water quality; while upstream water quality is highly and positively correlated with both coal production and with geologic disturbance (Fig. 6). All three of the mussel community metrics recorded by Johnson et al. (2012) in 2009 (density, richness, and catch per unit effort, CPUE) are highly and positive correlated with one another and negatively correlated with river km (Fig. 7).

4. Discussion

4.1. Mining disturbance

The upper Powell River watershed has been strongly affected by surface coal mining. It appears that as much as 1/3 of the watershed area was disturbed by mining detectable by Landsat over the 1984–2011

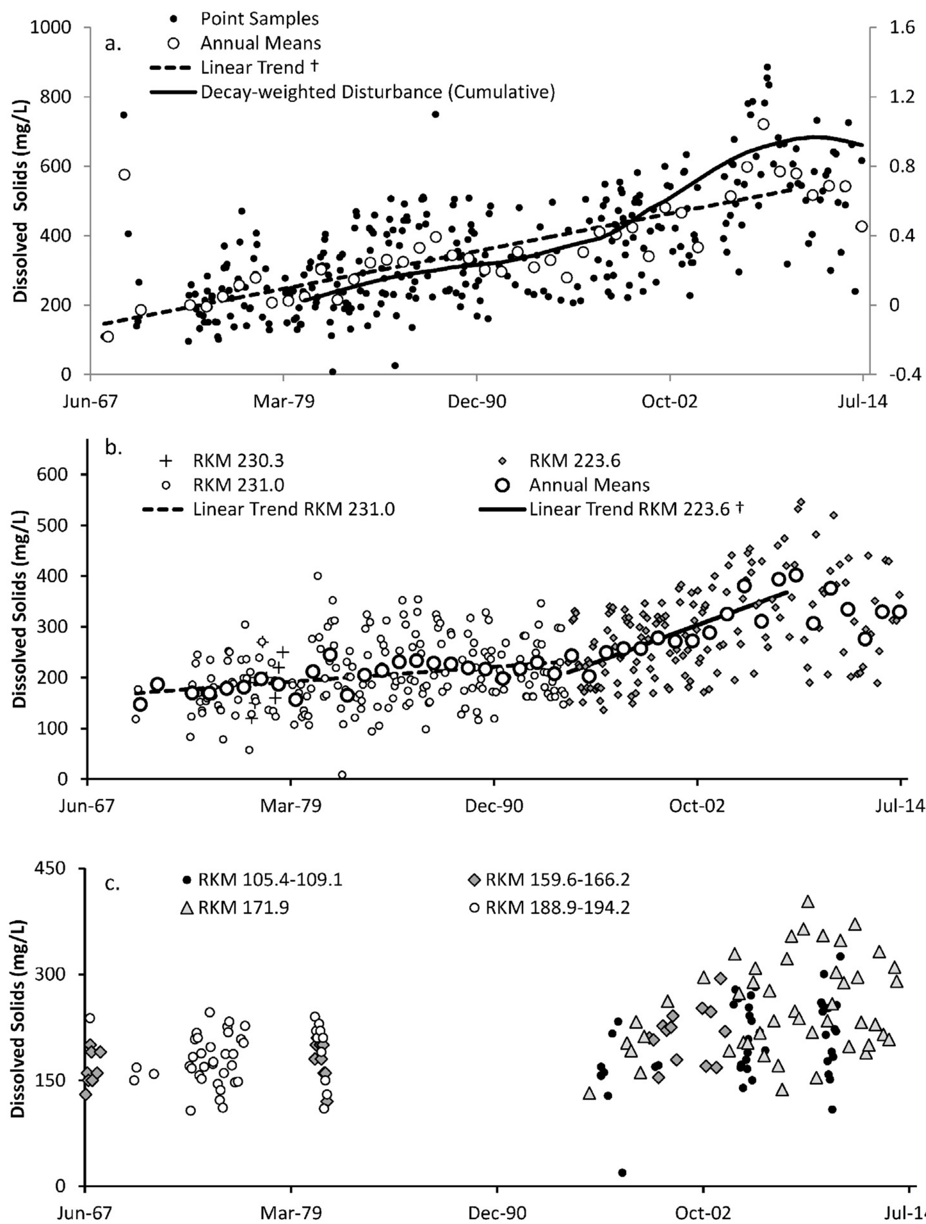

Fig. 4. Dissolved solids vs. time for (a) river km 288.4 (b) the river km 223.6–231.0 segment, and (c) the river km 105.4–194.2 segment, with annual means for (a) and (b). All available monitoring data from locations with >1 observation are included. For (a), decay-weighted geologic disturbance, plotted on right axis, is superimposed over the water quality data. For (b), linear trends for RKM 223.6, and for 231.0 through 8/13/2008 (the highest value reported), calculated without including a seasonal variable, are also represented; both are increasing and significant ($p < 0.0001$); but the post-8/13/2008 linear trend for RKM 231.0 is not significant. †Linear trends are shown only to change points designated by the breakpoint regression procedure (Jan-08 for RKM 223.6; Jun-2010 for RKM 288.4).

period. Actual disturbance likely exceeds that level, given that surface mining occurred in the watershed prior to 1980 (Haering et al., 2004) and extended past 2011. Common reported thresholds for aquatic faunal impacts by watershed impervious cover are often in the range of 10%, but impacts on certain fauna have been reported to occur when watershed impervious cover exceeds 2% of land area (Wang et al., 2001; Wenger et al., 2008), although mining creates a different set of impacts than watershed development with impervious cover. Working in West Virginia, Bernhardt et al. (2012) estimated 5.4% of watershed area disturbed by mining as a biotic impairment threshold for benthic macroinvertebrates in headwater streams. The upper Powell River watershed's mining disturbance far exceeds these thresholds estimated by other studies for other areas. Mining is the predominant non-forested land use in the upper Powell River watershed (Table 2).

The ratio of coal produced to land-surface disturbance in the RKM 288.4 watershed increased in the early part of the study period. We interpret this increase as a response to expanded size of equipment and operations, as large equipment enables more cost-efficient spoil movement, greater depths of excavation, and increased coal recovery. Rolling 5-year averages were calculated as > 1.00 to < 1.31 million tonnes km^{-2} for all but one period since 1992. These levels are similar to those calculated by Lutz et al. (2013) for West Virginia and Kentucky coal surface mining: 1.15 tonnes per km^2 over the 1985–2005 period, a correspondence that we interpret as validating our study methods.

4.2. Water quality

For the entire study reach, water pH, SC, DS, and sulfate concentrations all demonstrated positive spatial trends that are consistent with a hypothesis that inputs of mining-related constituents are exerting maximum influence near the headwaters and are diluted moving downstream. Numerous studies have demonstrated that the pH, SC, and DS and sulfate concentrations of mining-influenced waters in Appalachia has increased in surface coal mining areas, relative to areas that have not been substantially disturbed by mining (Hartman et al., 2005; Pond et al., 2008; Pond et al., 2014; Timpano et al., 2015). Studies of these effects typically take place in headwater streams, close to mining areas. Given the spatial extent of surface mining in the upper Powell watershed, it is not surprising that these constituents also are elevated in the Powell River itself. Lindberg et al. (2011) also found elevated concentrations of mining-origin constituents in a non-headwater stream influenced by mining, as did Johnson et al. (2014) in the Clinch River of southwestern Virginia and eastern Tennessee. Johnson et al. (2014) also observed diminishing concentrations of mining-influenced constituents and SC moving downstream from mining influence in the Clinch River of Virginia and Tennessee, which they attributed to dilution caused by influxes of waters from non-mined tributaries.

The positive temporal trends for mining-related constituents (water pH, SC, DS, sulfate, and alkalinity) are consistent with the hypothesis that effects by Appalachian coal surface mining on water resources are cumulative, e.g. the total mass of mining-disturbed materials exposed to environmental waters is influential. Price et al. (2014) also noted increasing temporal trends for DS in the Clinch River, which is similarly influenced by Appalachian surface coal mining that has occurred continuously and progressively over a multi-decade study period.

The increasing temporal trends exhibited by water pH, SC, DS, and sulfate concentrations over the full study period are as expected given the progressive increases of mining disturbance in Powell River headwaters (Fig. 3). Closer inspection of the DS data for individual river sections (Fig. 4) revealed that the linear model did not conform to observed patterns in the latter portion of the study period (Fig. 4). Water quality at RKM 288.4 is strongly influenced by mining; visual inspection reveals an apparent correspondence with the decay-weighted geologic disturbance indicator during the latter portion of the study period (Fig. 4). Both the steepening slope of DS temporal increases over time during the 1990s and early 2000s, and the cessation of increasing trends near the end of the study period are reflected by the decay-weighted geologic disturbance indicator (Fig. 4). Although we see the decay-weighting function used for this study (Fig. 2) as a crude approximation of what likely occurs in nature, we interpret this correspondence as a reflection of fundamental geochemical processes governing major ion release from freshly exposed and non-pyritic mine spoils. Typically, peak releases occur in response to initial water exposures, and release concentrations decline with continued leaching (Sena et al., 2014; Orndorff et al., 2015). The greatest divergence of in-stream DS concentrations from the decay-weighted indicator's temporal pattern occurs early in the study period, when the decay-weighted indicator does not reflect pre-1980 mining.

We are not aware of other studies that have demonstrated similar changes in mining-related water quality influences due to progressive geologic disturbance over multi-decade time periods at the large watershed scale, nor are we aware of other studies that have demonstrated temporal-decay of water-quality influence by mining-disturbed geologic materials at similar spatial and temporal scales. Evans et al. (2014) demonstrated temporal decay of geologic influence on individual mine discharges, a finding that influenced our approach here. Bäthe and Coring (2011) and Coring and Bäthe (2011) reported declining mining-origin salinity over a 17-year period in Germany's River

Table 4
Dissolved trace metals and other trace elements in the Powell River, 2000–2011, as concentrations and relative to CCC (estimated at 100 mg/L hardness); with statistically significant results of linear model testing for spatial (vs. river km) and temporal (vs. time) effects on the elements.

Element	n	CCC (μg/L)	Concentrations (μg/L)		Relative CCC (%)		Model effects[a]	
			Median	Range	Median	Range	Temporal	Spatial
Al	11	87	17.5	(4.2–31)	20.1	(4.8–35.6)	ns	ns
As	11	150	0.2	(0.17–0.34)	0.1	(0.1–0.2)	neg[*]	ns
Cd	11	0.25		[b]				
Cr	11	85	0.4	(0.1–1.17)	0.5	(0.1–1.4)	ns	ns
Cu	11	9	0.6	(0.47–1.24)	6.7	(5.2–13.8)	ns	ns
Fe	11	n/a		[c]				
Pb	11	2.5		[b]				
Mn	11	1862	11.4	(3.7–36.9)	0.6	(0.2–2.0)	ns	pos[**]
Mn	47[d]	1862	30	(6–300)	1.6	(0.3–16)	ns	pos[**]
Ni	11	52	1.3	(0.53–2.9)	2.5	(1.0–5.6)	ns	pos[**]
Se	11	5	0.86	(0.5–2.33)	17.2	(10.0–46.6)	ns	pos[*]
Zn	11	120	1.7	(1–3.59)	1.4	(0.8–3.0)	ns	ns

[a] pos = positive; neg = negative; ns = not significant ($p < 0.05$).
[b] All values recorded at less than detection limit (<0.1 μg/L).
[c] All values recorded at less than detection limits (< 100 μg/L, most <50 μg/L).
[d] Data from TVA (1967–1981), analyzed separately; all other data from VDEQ (2000–2011).
[*] $0.01 < p < 0.05$.
[**] $p < 0.01$.

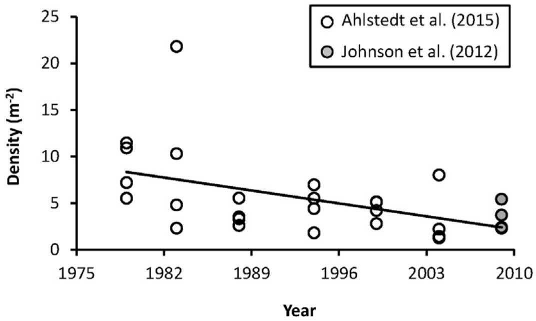

Fig. 5. Mussel density vs. time at four locations extending from RKM 159.6 through RKM 188.8, with data from Ahlstedt et al. (2005) and Johnson et al. (2012). The regression line is significant statistically ($p < 0.01$).

Werra, and Petruck and Stöffler (2011) reported similar salinity decline in Germany's River Lippe over a century; but these declines occurred due to cessation of active mining-effluent discharge, a mechanism differing from that we believe to be at work here.

We consider alkalinity also to be a mining-influenced constituent given that HCO_3^- is often a predominant constituent of high-TDS Appalachian mine drainage (Pond et al., 2008, 2014; Orndorff et al., 2015; Timpano et al., 2015). Natural waters from undisturbed watersheds within the Appalachian coalfields are typically dilute and low in bicarbonate alkalinity (Pond et al., 2008; Pond et al., 2014; Timpano et al., 2015). Hence, the increasing temporal trend for alkalinity is likely caused by mining influence. The lack of alkalinity dilution moving downstream may reflect the Powell River's geologic gradient. The river flows from the Appalachian coalfield just below RKM 288.4 and enters the Ridge and Valley physiographic province where predominant geologic materials are carbonates and, hence, sources of bicarbonate alkalinity.

Both total N and Cl^- are often elevated in mining-influenced streams, relative to levels in undisturbed watersheds (Pond et al., 2008, 2014). Chloride is released from Appalachian mine spoils but in far lower concentrations than the elements of primary concern (Orndorff et al., 2015). Nitrogen is also often elevated in mining-influenced streams (Northington et al., 2011; Krenz, 2015). Although some mineral-origin N is present in mine spoils (Li and Daniels, 1994), primary sources appear to be post-mining fertilization and explosives. We are not aware of studies that demonstrate the persistence (or lack thereof) for these effects. However, a variety of non-mining anthropogenic sources release Cl^- including road salt applications, agricultural land uses, and sewage effluents (Kaushal et al., 2005; Mullaney et al., 2009; Anning and Flynn, 2014; Corsi et al., 2015). Similarly, numerous anthropogenic activities release N, including sewage effluents, agriculture, fossil fuel combustion emissions that enter watersheds as atmospheric deposition (Gruber and Galloway, 2008; US EPA-SAB, 2011). We do not see mining as a primary source of these elements for the Powell River. This expectation is supported by the data, as the apparent dilution effects caused by downstream flows (i.e., the statistically significant and positive relationship with river km) that are evident for the mining-origin constituents are not present for Cl^- and total N.

Of the dissolved trace elements exhibiting positive spatial trends indicative of mining release and downstream dilution, Mn and Se are

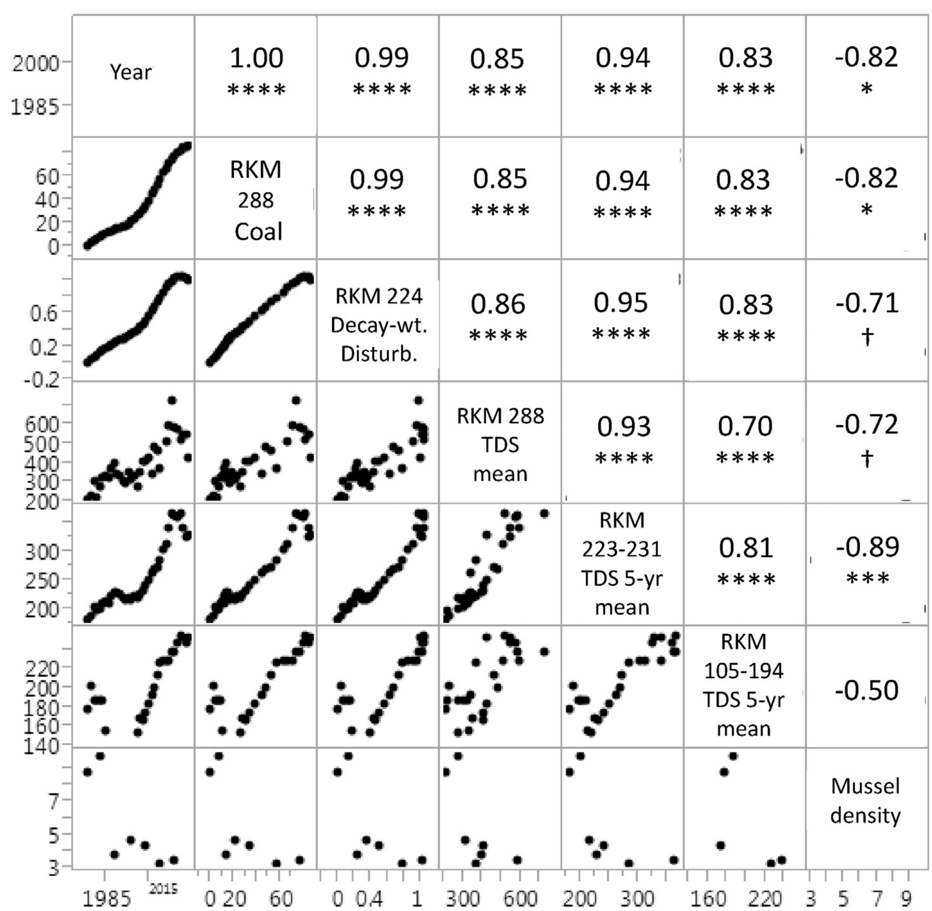

Fig. 6. Scatterplots (left) and coefficients (right) of spearman correlations among selected temporal variables: Year; estimated coal production within the RKM 288.4 watershed; estimated decay-weighted geologic disturbance within the RKM 233.6 watershed; annual mean dissolved solids concentrations at RKM 288.4; mean 5-year dissolved solids concentrations for RKM 223.6–231.0 monitoring data, with 5-year periods terminated at the year represented; and mean mussel densities at four locations extending from RKM 159.7 through 188.9 as reported by Ahlstedt et al. (2005) and supplemented with data collected by Johnson et al. (2012). ****$p < 0.0001$; ***$0.0001 < p < 0.001$; *$0.01 < p < 0.05$; †$0.05 < p < 0.10$. All correlations are pairwise.

strongly associated with Appalachian coal mining. Selenium is especially problematic as a mining-origin element (Pond et al., 2008; Lindberg et al., 2011; Presser, 2013). Manganese is strongly associated with Appalachian mining (Larsen and Mann, 2005; Griffith et al., 2012) and is a regulated water constituent in mining operation discharges in the USA (US EPA, 2013). Although less well known as a common mining-influenced water constituent, Ni also is commonly found at elevated concentrations in Appalachian mining water discharges, perhaps due to its association with pyritic mineral forms that occur in association with coal (Griffith et al., 2012). Because of the low numbers of observations, it is difficult to draw strong conclusions from these results although they are consistent with the findings of mining effects on Powell River water quality that are especially strong near the headwaters. It is not clear if the declining temporal trends for As are of significance relative to our study goals. Arsenic does occur in coal, generally as components of pyritic mineral forms (Kolker et al., 1996), but our data reveal no evidence of a spatial gradient for As.

4.3. Relationships among mining, water quality, and mussel declines

The decline of mussel fauna in the mid-reaches of the Powell River (RKM 159.7–188.9, Fig. 5) has occurred in association with expansion of geologic disturbance by coal mining in the headwaters. Our data demonstrate that water quality trends in Powell River segments upstream from the zone of mussel decline have occurred in association with expansion of watershed coal mining over the study period (Fig. 6), but water quality within the zone of mussel decline has not been well documented. Given our findings, however, we expect that DS concentrations within RKM 159.7–188.9 were strongly and positively correlated with time and with upstream concentrations; and, hence, were also correlated with the mussel decline that has been documented within this river reach. Mussel density and other metrics measured by Johnson et al. (2012) also are correlated negatively with river km and, hence, positively with distance from mining influence (Fig. 7). We interpret river km as an indicator of DS concentrations given results of our regression models (Table 3), and DS concentrations as an indicator of mining influence. These correlations are clear and lead to essential questions concerning causation: Has the mining-related water-quality change over the study period been a primary cause of mussel decline? If so, which constituents are responsible?

Our findings for the Powell River are similar to what has been observed in the lower Clinch River, where mussel declines correspond temporally with increasing trends for DS, likely of mining origin, and where mussel status improves with distance from a primary mining-origin DS source: water influx to the Clinch by the Guest River (Johnson et al., 2014; Jones et al., 2014; Price et al., 2014; Zipper et al., 2014). This correspondence of observations for the two rivers adds urgency to the essential questions.

In our view, it is clear that mining disturbances of geologic materials in the Powell River watershed are influencing water quality in the river, i.e. that the relationship between watershed mining and mining-origin water constituents is causative. We see the strong and positive temporal correlations of SC, pH, DS, alkalinity, hardness, and sulfate with the progression of mining in the Powell River watershed as evidence that supports this conclusion. We also see the composition of DS in the Powell River as supporting evidence (Table 5). Studies conducted in the laboratory (Orndorff et al., 2015), in experimental settings located outdoors (Agouridis et al., 2012; Sena et al., 2014; Ross, 2015), and in the field (Pond et al., 2008, Timpano et al., 2015) demonstrate clearly that exposure of unweathered sedimentary rocks from the Appalachian coalfield releases DS, generally with SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+} as predominant constituents. The Powell River watershed also is high in Na, which sometimes occurs in mining-influenced headwater streams (Timpano et al., 2015) as a result of factors such as leaching from Na-rich rock spoils (W.L. Daniels, Virginia Tech, unpublished data), leachates from coal refuse (Ross, 2015), and treatment of acidic drainage using NaOH (Skousen et al., 2000).

Elevated dissolved solids have been identified as a potential cause for mussel declines observed in the Clinch River (Johnson et al., 2014) and can be considered as such in the Powell River as well. Supporting evidence include the altered benthic macroinvertebrate and fish communities in Appalachian coalfield streams with significant mining influence that includes elevated SC and mining-origin major ions (Pond et al., 2008, Hopkins and Roush, 2013; Hitt and Chambers, 2014; Daniel et al., 2014; Pond et al., 2014; and other studies). Although benthic community relationships with SC are correlational, they have been documented with sufficient consistency to suggest that major ions may be causative. It is well known, however, that dissolved solids' toxicity to laboratory test organisms varies with the ion composition (Mount et al., 1997) and we expect that to be the case for mussels as well.

We are aware of two studies characterizing mussel responses to solutions with ion composition characteristic of mining influence in the Appalachian coalfield. A study characterizing response of juvenile *Lampsilis siliquoidea* in 28-day exposures to two simulated surface-water solutions with SO_4^{2-}, HCO_3^-, Ca^{2+}, and Mg^{2+} as predominant major ions relative to more dilute controls, at 504 and 565 μS/cm (Kunz et al., 2013). Mean SC levels in the RKM 104.5–194.2 reach that is inhabited by mussels as high 690 μS/cm have been recorded; and the data indicate that SC levels similar to the Kunz et al. (2013) effect levels occur frequently (75th percentile of recorded values is 494 μS/cm). However, the Kunz et al. (2013) ion suites were intended to simulate relatively small streams receiving discharges from Appalachian coal surface mines and differ in some respects from major ion composition of DS in the Powell River. Also, *L. siliquoidea* is not native to the Powell River.

Ciparis et al. (2015) tested response by juvenile *Villosa iris*, a Powell River native mussel, to elevated DS (>900 mg/L) with an ion composition intended to simulate the upper Powell River; no significant effects on growth or survival were found over a 55 day study period. Test concentrations were based on the highest recorded concentrations of major

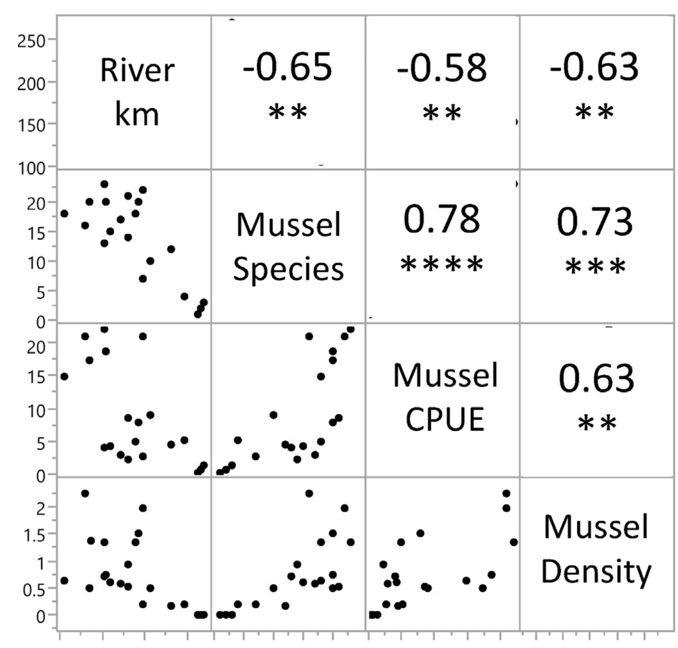

Fig. 7. Scatterplots (left) and coefficients (right) of spearman correlation among selected spatial variables: River km; and mussel species richness, mussel catch per unit effort (CPUE) during sampling, and mussel density (m^{-2}) at locations designated by river km, as reported by Johnson et al. (2012). Water quality data are not available for the mussel sampling locations, but mining-related constituents vary positively as a function of river km (see Table 3). ****p < 0.0001; ***0.0001 < p < 0.001; **0.001 < p < 0.01. All correlations are pairwise.

Table 5
Major ion concentrations in the Powell River at two locations, as measured by Virginia DEQ.[a]

Constituent	STORET	RKM 288.4 (2006)		RKM 266.8 (2008)	
		n	Mean (±std. err.)	n	Mean (±std. err.)
HCO_3^-	[b]	12	186 (±11.3)	12	178 (±10.6)
Chloride, total in water (mg/L)	00940	12	6 (±0.5)	12	9 (±0.5)
Chloride, dissolved in water (mg/L)	00941	5	5 (±0.2)	12	9 (±0.5)
Sulfate, total (mg/L as SO4)	00945	12	231 (±20.1)	12	231 (±16.6)
Sulfate, dissolved (mg/L as SO4)	00946	5	276 (±12.1)	11	222 (±15.5)
Calcium, dissolved (mg/L as Ca)	00915	12	58 (±3.3)	12	60 (±3.7)
Magnesium, dissolved (mg/L as Mg)	00925	12	30 (±2.0)	12	29 (±2.6)
Sodium, dissolved (mg/L as Na)	00930	12	63 (±11.2)	12	54 (±7.1)
Potassium, dissolved (mg/L as K)	00935	12	4 (±0.2)	12	4 (±0.3)

[a] These are the only times and locations where the full suite of major ions measurements is available on multiple dates.
[b] Calculated from STORET 00410, alkalinity, total (mg/L as Ca CO3), as 1.22× measured value.

ions at RKM 288.4 and thus were substantially higher than mussels are likely to be experiencing within RKM 159.7–188.9 zone of documented decline. These authors concluded that major ion concentrations may not be the primary cause for mussel declines in the Clinch and Powell Rivers but recommend that similar studies be conducted on all critical mussel life stages and for longer time periods.

Although numerous studies have documented biotic declines in rivers and streams affected by mining (e.g. Hughes, 1985; García-Criado et al., 1999; Daniel et al., 2014), most have focused in influence acid mine drainage and related constituents, which are not influential in the Powell River sections where long-term mussel declines have been noted (Fig. 5); and few such studies have focused on freshwater mussels. Angelo et al. (2005) surveyed mussel fauna above and below mining areas in midwestern USA; and found significant reductions of mussel density and richness downstream of mining influence relative to upstream areas; and that mussel metrics demonstrated strong negative association with a metric based on concentrations of Zn, Cd, and Pb in stream sediments. Wang et al. (2013) tested toxicity of sediments collected from eastern USA rivers that receive effluent from coal mining and from natural gas extraction activities, including three samples from the Powell River, to freshwater mussels of two species. They found that sediments obtained from river sections where mussel declines or extirpations had occurred were toxic in their laboratory test; and that sediment-recoverable metals, PAHs, and major ions demonstrated apparent correspondences with laboratory-determined toxicities. Johnson et al. (2014) assessed associations of water and sediment quality in the Clinch River of eastern USA with mussel status indicators, and found negative associations with water-column trace metals and major ions.

5. Summary and conclusions

Surface coal mining has caused dramatic landscape changes in the Powell River watershed's headwater areas. Mining has affected water quality in the river mainstem, and those effects are evident for >150 km downstream and in river sections that host mussel assemblages that remain at high diversity relative to many other eastern US rivers and include at-risk species. Concentrations of DS and related constituents have exhibited increasing temporal trends throughout much of the river's extent from the late 1960s through the early 2000s but DS concentrations appear to have stabilized or declined recently. Mussel densities in the lower Powell River, ~100 km downstream from the most intensive mining influence, declined over the 1979–2009 period of generally rising DS, while density and richness vary positively with distance from mining influence. Thus, a main finding of our study is that associations of mussel status indicators with mining-related water constituents are negative and statistically significant, although the potential causal linkages between measured water constituents that are influenced by mining and depressed mussel status remain poorly understood. Hence, research is needed to improve understanding of potential influences by major ion and trace metal concentrations that are present in the Powell River sections inhabited by freshwater mussels on their survival, growth, and reproduction.

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Supplementary data

Supplemental data (actual data have been provided as a .kmz file. Below is the description of those data).

Map of Powell River watershed show spatial relationships of mining activity, water monitoring, and mussel sampling and monitoring locations. The blue line is the outline of the Powell River watershed upstream of RKM 105.4 (the study area). White lines are county boundaries. The rectangular black box is the boundary of the Landsat images analyzed by Li et al. (2015a, 2015b) to identify Virginia surface coal mining areas. Red areas are surface coal mines identified by Li et al. (2015a, 2015b) within the study area. Blue circles, orange rectangles, and yellow triangles are water monitoring points, mussel sampling points (2008–2009), and mussel monitoring points (1979–2009), respectively. Additional information concerning each sampling and monitoring point can be obtained by clicking on the symbols. Supplementary data associated with this article can be found in the online version, at doi:http://dx.doi.org/10.1016/j.scitotenv.2015.09.104. These data include Google maps of the most important areas described in this article.

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