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RESEARCH ARTICLE

Assessing landscape and contaminant point-sources as spatial determinants of water quality in the Vermilion River System, Ontario, Canada

Carrie Strangway[1] · Michelle F. Bowman[1,2] · Andrea E. Kirkwood[1]

Abstract The Vermilion River and major tributaries (VRMT) are located in the Vermilion watershed (4272 km^2) in north-central Ontario, Canada. This watershed not only is dominated by natural land-cover but also has a legacy of mining and other development activities. The VRMT receive various point (e.g., sewage effluent) and non-point (e.g., mining activity runoff) inputs, in addition to flow regulation features. Further development in the Vermilion watershed has been proposed, raising concerns about cumulative impacts to ecosystem health in the VRMT. Due to the lack of historical assessments on riverine-health in the VRMT, a comprehensive suite of water quality parameters was collected monthly at 28 sites during the ice-free period of 2013 and 2014. Canadian water quality guidelines and objectives were not met by an assortment of water quality parameters, including nutrients and metals. This demonstrates that the VRMT is an impacted system with several pollution hotspots, particularly downstream of wastewater treatment facilities. Water quality throughout the river system appeared to be influenced by three distinct land-cover categories: forest, barren, and agriculture. Three spatial pathway models (geographical, topographical, and river network) were employed to assess the complex interactions between spatial pathways, stressors, and water quality condition. Topographical landscape analyses were performed at five different scales, where the strongest relationships between water quality and land-use occurred at the catchment scale. Sites on the main stem of Junction Creek, a tributary impacted by industrial and urban development, had above average concentrations for the majority of water quality parameters measured, including metals and nitrogen. The river network pathway (i.e., asymmetric eigenvector map (AEM)) and topographical feature (i.e., catchment land-use) models explained most of the variation in water quality (62.2%), indicating that they may be useful tools in assessing the spatial determinants of water quality decline.

Keywords Spatial pathways · Emissions · Effluent · Catchments · River networks · Water quality · Land-use

Introduction

Inputs from the surrounding landscape, including point and non-point sources of pollution, can significantly influence the water quality of aquatic systems, which in turn can affect ecosystem structure and function. Inputs from point sources are relatively easy to monitor and regulate compared to non-point sources since they originate from a single source (e.g., smelters, wastewater treatment facilities (WWTFs)). Emissions or effluents are typically only monitored as they exit facilities and are not regularly monitored downstream for their impacts to receiving ecosystems (Ontario Ministry of the Environment and Climate Change (MOECC) 2016). Conversely, inputs from non-point sources are difficult to monitor and regulate compared to point sources, since they do not originate from a single source (e.g., runoff from the properties of mining industries, roadways, development, agriculture).

Due to the vast amount of point and non-point sources acting within numerous spatial pathways, monitoring the water quality of aquatic systems has become a challenging task.

✉ Andrea E. Kirkwood
andrea.kirkwood@uoit.ca

1 Faculty of Science, University of Ontario Institute of Technology, 2000 Simcoe St.N., Oshawa, ON L1H 7K4, Canada

2 Forensecology, 70 Swift Crescent, Guelph, ON NIE 7J1, Canada

For example, contaminants can travel overland by aerial transport (i.e., geographic pathway) (Steinnes et al. 2011), be transported across the landscape via elevation gradients and the movement of water (i.e., topographical pathway) (Chang 2008; Pratt and Chang 2012; Grabowski et al. 2016), and flow within aquatic systems in an upstream-downstream direction (i.e., river network pathway) (Blanchet et al. 2011). Traditionally, these pathways have been considered individually; however, from a management perspective, it is important to understand all spatial pathways and the significance they play in governing water quality.

In the Vermilion River and its major tributaries (VRMT) located in north-central Ontario, Canada, there are notable impacts to water quality ranging from WWTF discharges to runoff from mining and urbanization activities near the City of Sudbury. Although these point and non-point sources from the surrounding landscape, plus in-stream stressors (e.g., modified flow regimes and sediment contamination from legacy mining activities), are known, system-wide water quality conditions in the VRMT remain largely unknown.

Development of the Sudbury region began in the late nineteenth century when nickel- and copper-ore deposits were discovered. Since then, the Vermilion watershed has experienced changes in land-cover due to urban expansion and natural resource development. Although this watershed continues to be dominated by natural land-cover, a considerable extent has been converted to either urban, industrial, or agricultural land-use. These landscape changes have likely increased the mobilization of contaminants, causing them to enter aquatic waterways more easily by erosion or surface runoff (Seilheimer et al. 2007; Ballantine et al. 2009). Currently, about 160,000 people reside in Greater Sudbury with the majority of residents residing in population centers and 13.4% living in rural areas (Statistics Canada 2012). In 2013–2014, approximately 131,000 residents relied on municipal WWTFs and sewage lagoons to treat their domestic waste, whereas the remainder of the residents rely on septic-tank systems (Greater Sudbury 2014; Greater Sudbury 2015). Municipal WWTFs, including sewage lagoons, can be significant sources of nutrients (primarily phosphorus and nitrogen) and other contaminants (e.g., metals) in aquatic systems (Chambers et al. 1997). However, the quantity and quality of effluent are largely dependent on the population served by these facilities, their level of treatment, and the frequency of bypass events that release under- or non-treated effluent. Similarly, the quantity and quality of effluent exiting industrial WWTF is largely dependent on the type and size of the industrial facility and their effluent-treatment processes. For instance, the effluent exiting the Copper Cliff Creek industrial WWTFs to the VRMT has been shown to have elevated concentrations of many contaminants (e.g., various forms of nitrogen and metals) (Rozon-Ramilo et al. 2011). Although advances in wastewater technologies have increased contaminant removal from treated

effluent, the effluent exiting these municipal and industrial facilities remains a primary point source of contaminants to the VRMT.

In addition to inputs from the surrounding landscape, numerous flow regulation features (i.e., a run-of-river hydroelectric dam and several control dams) have modified the natural flow regime of the VRMT. The concern with flow regulation in any aquatic system is that it can modify the natural flow regime via hydropeaking and reductions in water renewal-rate, thus changing the physical and chemical properties of water (Ellis and Jones 2013). However, with respect to the run-of-river dams that dominate the VRMT, the impacts are believed to be less severe than hydroelectric impoundments, since they maintain more regular flow rates throughout the year.

Overall, the VRMT are believed to have been affected by the cumulative impacts of changing land-use, WWTF discharges, and legacy mining contamination along their continua. Additionally, the VRMT watershed has experienced decades of emissions from mining and smelting industries. These atmospheric emissions, which were mainly composed of sulfur dioxide and various metals (e.g., Co, Cu, Fe, and Ni), acidified the landscape and increased the proportion of barren land-cover in Greater Sudbury (Nriagu et al. 1998). Contaminants from emissions also impaired and degraded terrestrial and aquatic systems in the region (Gunn et al. 1995; Havas et al. 1995). With industrial upgrades and site decommissioning over the last 30 years, many terrestrial and aquatic ecosystems have recovered both chemically and biologically (Gunn et al. 1995; Havas et al. 1995), but large river networks such as the VRMT continue to show signs of degradation such as excessive algae and aquatic plant growth at several locations and the persistence of water quality exceedances at long-term provincial monitoring stations.

Further development in the Vermilion watershed has been proposed, including hydroelectric dams and the expansion of mining activities. Thus, it is necessary to document and assess current (baseline) water quality conditions in the VRMT to understand the influence that the surrounding landscape (i.e., point and non-point sources), flow regulation, and legacy smelting activities have on water quality and ecosystem health. Due to the complex interactions between main stressors and water quality conditions, various spatial pathways along the VRMT flow network must be considered. As such, the objectives for this study were to (1) characterize the watershed landscape of the VRMT (i.e., point and non-point sources, flow regulation features, and legacy mining structures), (2) evaluate the state of VRMT water quality and identify sites where water quality is deteriorated, and (3) determine the relationship between spatial configurations (i.e., geographical, topographical, and river network pathways) and water quality in the VRMT. A conceptual layout of our assessment approach is presented in Fig. 1.
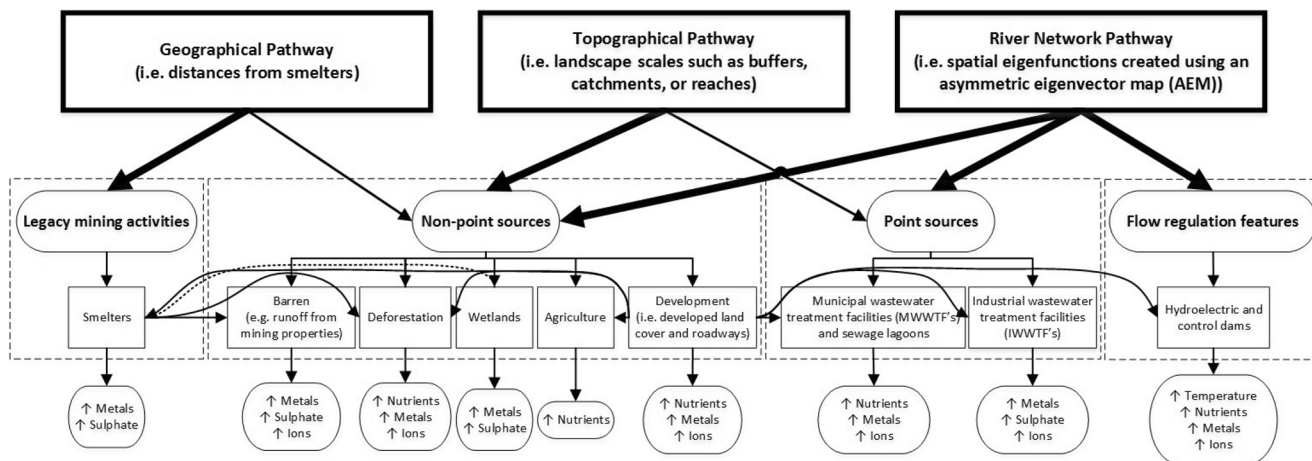
Fig. 1 Conceptual spatial configurations and their predicted association with main VRMT stressors, along with the predicted influence these stressors have on the water quality

Methods

Study area

The VRMT are located in the Vermilion watershed (4272 km^2), a large watershed in north-central Ontario (Fig. 2) (Natural Resources Canada 2010a, 2010b, 2011, 2013a, 2013b; QGIS Development Team 2016). The VRMT receive inputs from various point (e.g., WWTFs and sewage lagoons) and non-point sources (e.g., runoff from mining-industry properties, roadways, urban development, and agricultural activities) and have modified flow regimes due to several flow regulation features (i.e., a run-of-river hydroelectric impoundment and several control dams). The Copper Cliff smelter is located in the Vermilion watershed, and two other smelters (Coniston smelter and Falconbridge smelter) are located in an adjacent watershed (Fig. 2). In addition, tailings ponds and abandoned roast beds can also be found within the Vermilion watershed as well as three industrial WWTFs that discharge effluent into Copper Cliff Creek, Nolin Creek, and Garson Creek. Besides industrial sources, municipal sources that discharge effluent directly or indirectly into the VRMT include eight municipal WWTFs and one sewage lagoon; these facilities and their locations are listed in Table 1 along with the population they serve and the annual loadings of total phosphorus and nitrogen (Greater Sudbury 2014; Greater Sudbury 2015). The VRMT also has a run-of-river hydroelectric dam located on the Vermilion River (i.e., Wabagishik (Lorne) Falls Dam) and several control dams either on or directly upstream/downstream of the VRMT (e.g., Stobie Dam, Ramsey Lake Dam, Kelly Lake Dam) which have modified the natural flow regime (Fig. 2).

Twenty-eight sites were monitored in total, where seven are MOECC Provincial Water Quality Monitoring Network (PWQMN) sites (ONP-3, WIT-7, WIT-8, LEV-9, VER-10, LIL-11, JUN-13), and the remaining 21 sites are Vermilion River Stewardship (VRS) sites selected for this study. The Vermilion River is the main stem river in the VRMT with 14 sites, including several lakes that occur along the river reach: VER-1, VER-2, VER-5, VER-6, VER-10, MC-19, KUS-21, VER-22, GRA-23, ELA-24, ELA-25, WAB-26, WAB-27, and VER-28. Five major tributaries that flow in to the Vermilion River were also included in this study: Onaping tributary (ONP-3 and ONP-4), Whitson tributary (WIT-7 and WIT-8), Levey tributary (LEV-9), Fairbank tributary (FB-20), and Junction tributary (LIL-11, CC-12, JUN-13, MB-14, MUD-15, SIM-16, MC-17, and MC-18). It is also important to note that LIL-11 and MB-14 are not on the main stem of the Junction tributary but flow into it. Point and non-point sources, flow regulation features, and legacy mining structures for the VRMT study area are also shown in Fig. 2.

Water quality sampling

Sites were monitored monthly (6 months per year) over a period of 2 years (2013–2014), from May to October in 2013 and from June to November in 2014. Samples were collected, transported, processed, and shipped by Conservation Sudbury. Nutrient samples were collected as non-volume-weighted, tube-composite samples through the euphotic zone determined by Secchi Disc estimates. VRS samples were sent to the certified analytical lab Maxxam in Mississauga, Ontario. PWQMN samples were also sent to Maxxam for chlorophyll-a and *Escherichia coli*; however, the majority of analyses were carried out by were sent to the Ontario Ministry of Environment Laboratory Services Branch in Etobicoke, Ontario as part of the long-term monitoring program. There were some differences in the suite of chemicals analyzed between VRS and PWQMN sites, but the large majority of parameters were covered in each group of analyses (Table 2).

Fig. 2 Location of the 28 sites that were monitored during 2013–2014 and point sources (i.e., municipal WWTFs, sewage lagoons, and industrial WWTFs), non-point sources (i.e., land-cover and roadways), flow regulation features (i.e., dams), and legacy mining structures (i.e., smelters) of the VRMT study area. VRS sites are outlined in black and PWQMN sites are outlined in white
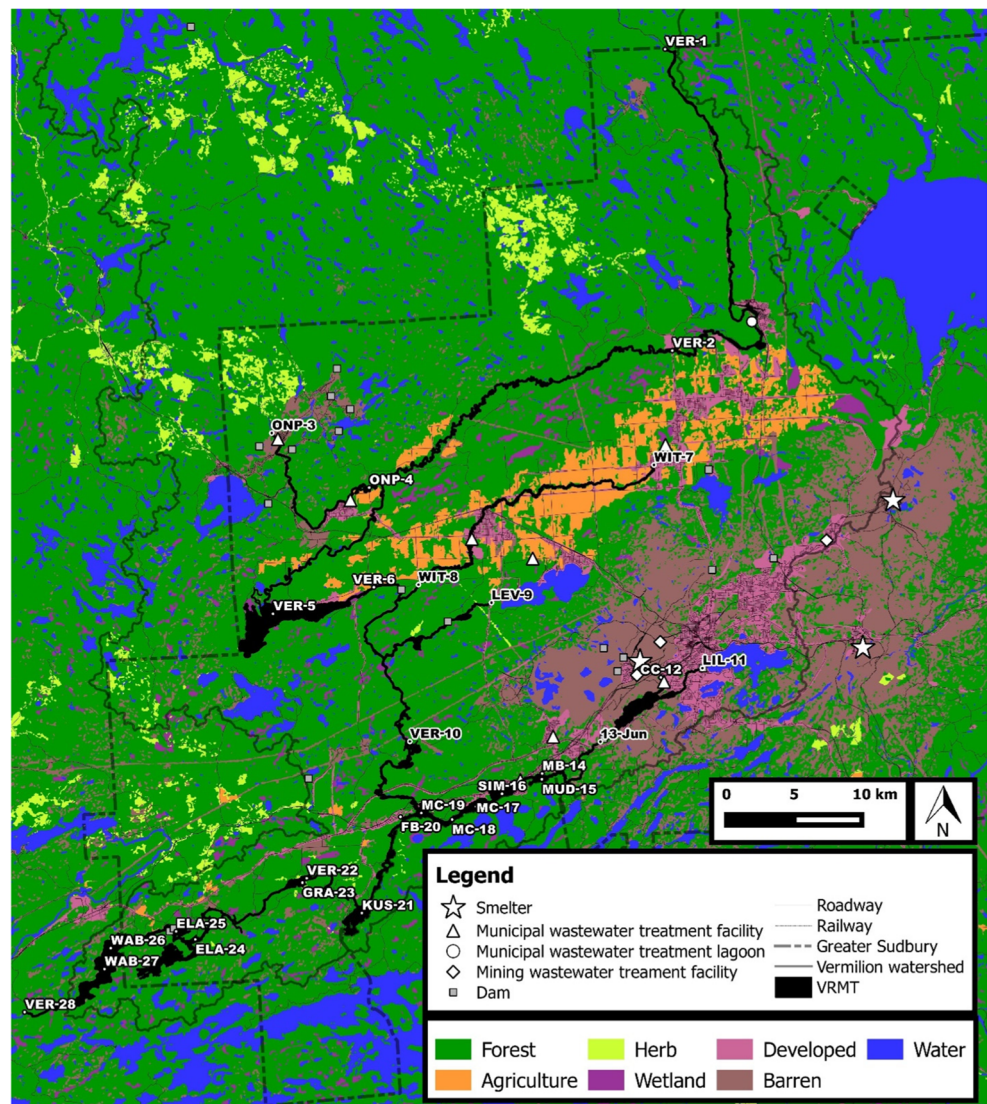
Land-use source data

Similar land-cover types were amalgamated to make the following categories: forest (i.e., coniferous, broadleaf, mixed-wood), agriculture (i.e., annual crops, perennial crops and pasture), herb, wetland (i.e., treed, shrub), developed barren (i.e., rock/rubble, exposed land), and water. Data was extracted from land-cover and national road network shapefiles using the constructed landscape scales (Natural Resources Canada 2010b, 2013b). Land-cover percent and road density were calculated by dividing the land-cover area or road length by the appropriate landscape-scale area.

Data analyses

Ordination techniques were used to extract the main trends, as they perform particularly well when analyzing large, complex environmental datasets. Principal component analysis (PCA)

is one of the most common methods to visualize differences between numerous sites. This unconstrained ordination technique utilizes one dataset to ordinate sites on the basis of quantitative variables (e.g., land-use or water quality variables). Redundancy analysis (RDA) is also very common; however, it associates two or more datasets. Thus, it can be used to explore the relationships between a response dataset (e.g., water quality) and an explanatory dataset (e.g., land-use). Sometimes the number of explanatory variables must be reduced for an RDA; thus, forward selection is often applied. If two or more explanatory datasets (e.g., geographical, topographical, and river network pathways) are used to explore a response dataset (e.g., water quality), variation partitioning can be used to quantify the variation explained uniquely and jointly by these explanatory datasets.

All descriptive and statistical data analyses were performed using the statistical platform R (R Core Team 2016). Stacked bar graphs were constructed to visualize site and landscape-

Table 1   Location of municipal WWTFs and sewage lagoon that discharge directly or indirectly into the VRMT

	Latitude	Longitude	Population Served	TP Loading (kg/year)		TN Loading (kg/year)	
				2013	2014	2013	2014
Azilda WWTP	46.551575	− 81.154410	4105	216	225	12,263	9627
Chelmsford WWTP	46.566757	− 81.212044	7147	310	382	23,583	19,228
Dowling WWTP	46.596648	− 81.327452	1857	341	397	6229	4883
Levack WWTP	46.639544	− 81.394546	2320	97	94	5276	4089
Lively WWTP	46.432195	− 81.143448	2761	384	250	9991	7543[a]
Sudbury WWTP	46.465132	− 81.034216	84,609	10,037	16,138	321,485	400,368
Valley East WWTP	46.622771	− 81.020748	17,365	1083	1309	54,668	51,607
Walden WWTP	46.404282	− 81.177050	3313	285	397	17,837	16,281
Capreol Lagoon	46.702029	− 80.931058	3408	1300	1700	N/A	N/A

Population served and annual loadings of total phosphorus (TP) and nitrogen (TN) are provided for 2013 and 2014

N/A total nitrogen loadings from Capreol Lagoon could not be calculated because nitrate and nitrite values were not present within the 2013 and 2014 annual reports

[a] Nitrogen values were absent for the month of October in the 2014 annual report; thus, total nitrogen loadings presented above may be slightly lower than the actual amount discharged

scale differences for road density and land-cover percent using the ggplot command (Wickham 2009). A PCA was used to detect land-use correlations and to distinguish sites, tributaries, and landscape scales which had above average values for land-cover types and road density. This PCA was performed on centered-scaled $\log(x + 1)$ transformed land-cover percent and road density using the rda command which can also carry out a PCA (Oksanen et al. 2016). The water landcover type was omitted from this PCA analysis. The ordination scores were extracted using the scores command and plotted using the ggplot command (Wickham 2009; Oksanen et al. 2016). To decide how many axes were needed for adequate representation, the Kaiser-Guttman criterion procedure (i.e., axis eigenvalue > mean of eigenvalues for all axes) was used.

A PCA was used to detect if VRMT water quality was influenced spatially or temporally. This PCA was performed on centered-scaled $\log(x + 1)$ transformed raw water quality data using the rda command in R (Oksanen et al. 2016). Only parameters monitored at all sites were used for this PCA, excluding biological parameters (Chl-a and *E. coli*) and Zn, which had missing values. Values below Reported Detection Limit (RDL) for VRS sites and negative values for PWQMN sites were set to zero for this analysis. The ordination scores were extracted using the scores command and plotted using the ggplot command (Wickham 2009; Oksanen et al. 2016). To decide how many axes were worth representing and displaying, the Kaiser-Guttman criterion procedure was used. If PCA loadings had strong positive (> 0.70) or negative (< − 0.70) correlations with PCA1 or PCA2 scores, they were noted.

Boxplots were created using the ggplot command to display all of the water quality parameters which

exceeded the Canadian recreational water quality guideline (CRWQG), long-term Canadian water quality guideline for the protection of aquatic life (CWQG), and/or provincial water quality objective (PWQO) at one or more sites during the 2013–2014 sampling period (Ontario 1994; Health Canada 2012). Lines representing guidelines were omitted for certain water quality parameters (i.e., Cd, Cu, Pb, and Ni) when water quality guidelines were dependent on hardness. To accurately represent the distribution of the data, values below RDLs were set to zero, boxplots were produced, and all lines below the RDLs were removed (Helsel and Hirsch 2002).

Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI) values were determined using the software application CCME WQI 1.2 (CCME 2001, 2001). To reflect current water quality guidelines, this index was manually updated and modified to take into account the CRWQG for *E. coli* (400 CFU/100 mL) and other CWQGs such as NO_2 (0.06 mg/L) and U (15 μg/L) (Health Canada 2012). Thus, 16 parameters were tested for all sites. A boxplot was created using the ggplot command to display the variation in CCME WQI values for each site.

Means and standard deviations for 2013–2014 were calculated. If one or more values fell below the RDL (i.e., censored values) for a parameter, a robust method was employed to determine the mean and standard deviation (Helsel and Hirsch 2002; Lee, 2012). This method was only used for VRS sites as there were no censored values for PWQMN sites. PWQMN sites did however have negative values which were set to zero.

A detrended correspondence analysis (DCA) was performed on the 2013–2014 water quality means using the

Table 2 A list of water quality parameters analyzed, differences between VRS and PWQMN datasets, and the analytical methods used by Maxxam and the Ontario Ministry of Environment

	VRS	PWQMN	Maxxam	Ontario Ministry of Environment
Chlorophyll-a (Chl-a)	X	X	SM-10200 H	
Escherichia coli (E. coli)	X	X	MOE LSB E3371	
Total phosphorus (TP)	X	X	SM 4500 P, B, F	E3367A or E3516
Orthophosphate (OP)	X	X	EPA 365.1	E3364A
Total Kjeldahl nitrogen (TKN)	X	X	EPA 351.2 Rev. 2	E3367A or E3516
Nitrate and nitrite ($NO_3 + NO_2$) and nitrite (NO_2)	X	X	SM 4500 NO3I/NO2B	E3364A
Dissolved organic carbon (DOC)	X	X	SM 5310 B	E3370A
pH	X	X	SM 4500H+ B	E3218A
Hardness (Hard)	X	X	SM 2340 B	E3497
Conductivity (Cond)	X	X	SM 2510	E3218A
Dissolved chloride (Cl)	X	X	SM 4110B	E3016A
Total aluminum (Al), total barium (Ba), total beryllium (Be), total bismuth (Bi), total cadmium (Cd), total calcium (Ca), total chromium (Cr), total cobalt (Co), total copper (Cu), total iron (Fe), total lead (Pb), total lithium (Li), total magnesium (Mg), total manganese (Mn), total molybdenum (Mo), total nickel (Ni), total potassium (K), total silver (Ag), total sodium (Na), total strontium (Sr), total tin (Sn), total titanium (Ti), total uranium (U), total vanadium (V), total zinc (Zn), and total zirconium (Zr)	X	X	EPA 6020	E3497
Nitrate (NO_3)	X		SM 4500 NO3I/NO2B	
Dissolved oxygen (DO)	X		APHA 4500 OG	
Dissolved bromide (Br)	X		SM 4110B	
Dissolved calcium (D-Ca)	X		SW-846 6010C	
Dissolved magnesium (D-Mg)	X		SW-846 6010C	
Dissolved sulfate (SO_4)	X		SM 4110B	
Fluoride (F)	X		APHA 4500FC	
Mercury (Hg)	X		SW-846 7470A	
Total antimony (Sb), total arsenic (As), total boron (B), total selenium (Se), total silicon (Si), total tellurium (Te), total thallium (Tl), and total tungsten (W)	X		EPA 6020	

decorana command (Oksanen et al. 2016). Since the length of the first DCA axis was 1.67 S.D. units, linear ordination methods (i.e., RDAs rather than CCAs) were performed using the rda command to explore the relationship between the 2013–2014 centered-scaled water quality means and land-use (excluding water land-cover) at differing landscape scales (i.e., 5-km buffer, catchment, 1-km, 2-km, and 3-km reaches) (Oksanen et al. 2016). Global tests were performed using the anova.cca command set at 1000 permutations (Blanchet et al. 2008b, Oksanen et al. 2016). All of the RDAs passed global tests so linear dependencies were explored by computing the variables' variance inflation factors (VIFs) using the vif.cca function (Blanchet et al. 2008b; Oksanen et al. 2016). Some RDA analyses had VIF values greater than 10 (i.e., 5-km buffer, catchment, and 3-km reach); therefore, explanatory variables were removed from those RDAs. The adjusted R^2 values for the global models were determined using the RsquareAdj function (Blanchet et al. 2008b; Oksanen et al.

2016). Using the ordiR2step function, forward selection was used to select the explanatory variables for the 5-km buffer, catchment, and 3-km reach RDAs, but terminated if the adjusted variation explained by the selected explanatory variables reached the adjusted R^2 value of its respective global model (Blanchet et al. 2008b, Oksanen et al. 2016). Thus, barren was selected for the 5-km buffer RDA; barren, developed, and agriculture were selected for the catchment RDA; and barren and developed was selected for the 3-km reach RDA. The adjusted R^2 values for the new models were also determined using the RsquareAdj function (Oksanen et al. 2016). The catchment scale had the strongest relationship with water quality, so it was used as the topographical pathway in the following analysis.

To assess the complex interactions between spatial pathways and water quality, variation partitioning was performed on the geographical, topographical, and river network models using centered-scaled water-quality means for both study

years. Using methods outlined above, one explanatory variable was selected from the geographical model reflecting distance from the Copper Cliff smelter (i.e., DFS-CC), three land-use explanatory variables were selected for the topographical pathway (i.e., barren, developed, and agriculture), and six explanatory variables were selected from the river network model (i.e., AEM7, AEM14, AEM15, AEM16, AEM17, and AEM19) using forward selection. Variation partitioning was performed on the forward selected geographical, topographical, and river network models for 2013–2014 water quality means. Variation explained uniquely and jointly, and the unexplained fractions were shown numerically (total variation = 1). The significance of each testable fraction was also shown. A RDA was performed on the 2013–2014 centered-scaled water quality means and the selected explanatory variables using the rda command; then, ordination scores were extracted using the scores command and plotted using the ggplot command.
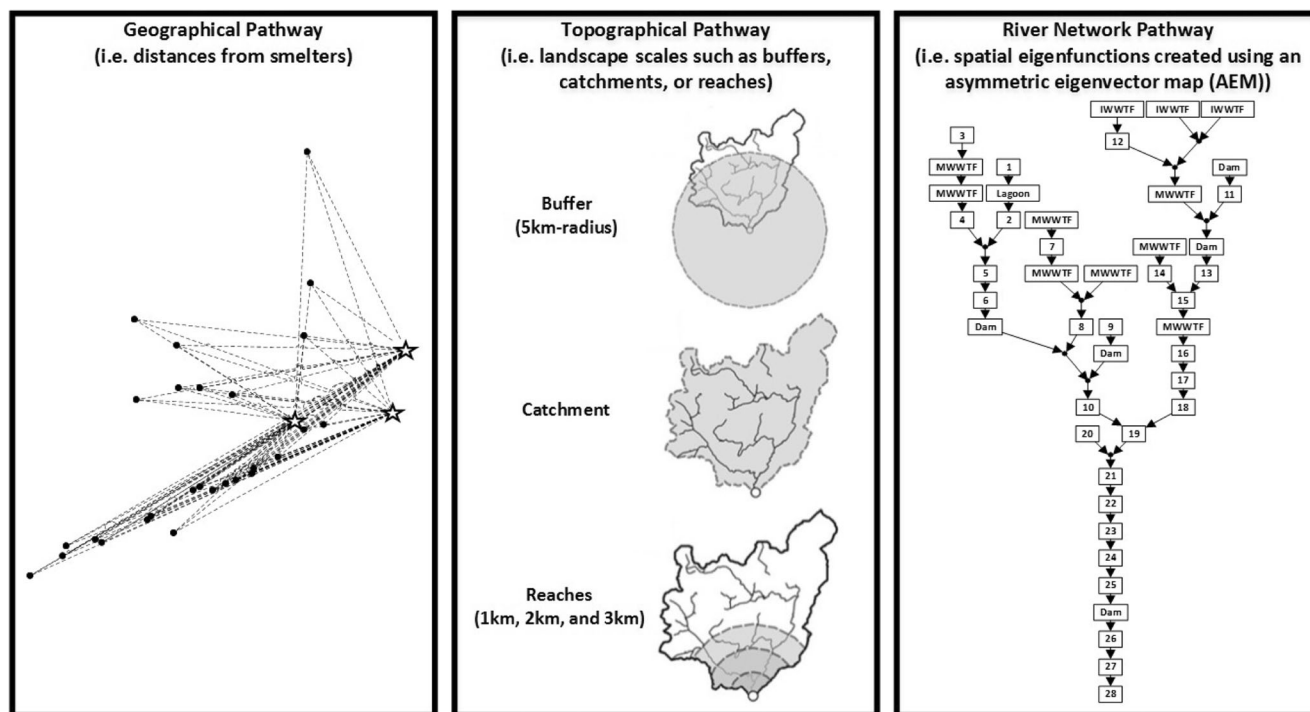
Construction of spatial pathways

The conceptual spatial-configuration pathways are presented in Fig. 1, including geographical, topographical, and river network models (Fig. 3).

Geographical pathway The geographical pathway represents the influence of legacy mining emissions from three smelting point source locations near Sudbury, Ontario (Fig. 2). Through this hypothetical pathway, sites should display a gradient of deterioration (e.g., gradient in metal concentrations and acid pH) based on the overland dispersal of past and current smelter emissions. The geographical pathway was formed using the distances between each site and each smelter.

Topographical pathway The topographical pathway primarily represents the influence of non-point sources on water quality. However, point sources associated with non-point sources (e.g., point source smelter emissions becoming non-point runoff on the landscape) are likely detected through this pathway as well. Through this hypothetical pathway, the water quality at a site is influenced by the land-use within a specific boundary. Boundaries, such as buffers, catchments, and reaches, are advantageous for studying the water quality of aquatic systems because lakes and rivers are not well-bounded, and transport of nutrients, metals, etc. are influenced by differing landscape scales (Post et al. 2007). The landscape scales used for this study include: buffer (5-km radius), catchment, and reaches (1, 2, and 3 km radius). The landscape scales were constructed in QGIS 2.8 using 1:50,000 digital elevation models, national hydro network shapefiles, and site coordinates (Natural Resources Canada 2006, 2011; QGIS Development Team 2016). A 5-km-radius buffer surrounding each site was made using the QGIS buffer tool. A catchment

Fig. 3 Three hypothetical spatial pathways that influence water quality in the VRMT. The geographical pathway was constructed by calculating distances between each site and each smelter; the topographic pathways were constructed by creating a buffer (5 km radius), delineating a catchment, and creating reaches (1, 2, and 3 km) for each site; the river network pathway was constructed by creating a asymmetric eigenvector map (AEM) and calculating spatial eigenfunctions

for each site was delineated using the GRASS plugin (GRASS Development Team 2016). Finally, 1-, 2-, and 3-km-radius reaches were made using the QGIS buffer tool on each site catchment. Thus, topographical pathways were formed by extracting land-use data (i.e., land-cover percent and road density) for each site at each landscape-scale (i.e., 5-km buffer, catchment, 1-km, 2-km, and 3-km reaches).

River network pathway The river network pathway represents the cumulative impacts from multiple sources. Through this hypothetical pathway, sites should display a gradient of deterioration based on the quantity and quality of effluent released from municipal and industrial WWTFs (i.e., point sources), in conjunction with land-use in the surrounding landscape (i.e., non-point sources) and flow regulation features (i.e., dams). An asymmetric eigenvector map (AEM) was constructed for the VRMT by methods outlined in Blanchet et al. (2008a). Afterward, a binary-coded sites-by-edges table was assembled, weightings were added based on distance between sites, and this table was transformed into spatial eigenfunctions by singular value decomposition using the svd function in the R statistical platform (Core Team, 2016). The river network pathway was formed from the spatial eigenfunctions.

Results

Characterizing the surrounding landscape

The Vermilion watershed is dominated by natural land-cover, including 73.9% forest, 10.6% water, 5.9% barren, 3.2% developed, 2.6% agriculture, 2.4% herb, and 1.4% wetland (Figs. 2 and 4). The sampling sites represent a broad range of road density and land-cover types at all landscape scales (Fig. 4). By examining the eigenvalues using the Kaiser-Guttman criterion, it was determined that the first two axes could be displayed for the PCA performed on land-cover and road density for sites at all landscape scales (Fig. 5). The proportion of variation accounted for by the first two axes was 60.0%. Clusters of sites and tributaries were evident, for example, sites on the upper main stem of the Junction tributary (e.g., LIL-11, CC-12, JUN-13, MB-14) had above average values for barren land-cover, and a site (LIL-11) located within the Junction tributary (but not on the main stem) had above average values for road density and developed land-cover for 1 and 2 km reach landscape scales. Additionally, some sites located on the Vermilion River, Onaping tributary, and Whitson tributary (e.g., ONP-4, VER-6, WIT-7, WIT-8) had above average values for agriculture land-cover.

Evaluating water quality trends and hotspots

Boxplots display all of the water quality parameters that exceeded the CRWQG, CWQG, and/or PWQO at one or more sites during the 2013–2014 sampling period (Fig. 6). Water quality parameters that exceeded guidelines were as follows: *E. coli*, TP, NO_2, pH, Cl, F, Al, Cd, Co, Cu, Fe, Pb, Ni, Se, Ag, Tl, U, and Zn. Based on the CCME WQI 1.2 results, seven sites were ranked as marginal, five sites were ranked fair, 15 sites were ranked good, and one site was ranked excellent (Fig. 7).

By examining the eigenvalues using the Kaiser-Guttman criterion, it was determined that the first seven axes could be displayed for the PCA performed on water quality data to view spatial and temporal patterns; however, only the first two were displayed (Fig. 8). The proportion of variance accounted for by the first two axes was 51.9%. Many water quality parameters exhibited strong positive correlations ($r > 0.70$) with PCA1 scores (i.e., $NO_3 + NO_2$, Hard, Cond, Cl, Ba, Ca, Co, K, Li, Mg, Na, Ni, Sr). No obvious clusters were observed for sampling period or year; however, clusters of sites and tributaries were evident. For example, sites on the upper main stem of the Junction tributary (i.e., CC-12, JUN-13, MUD-15, SIM-16, MC-17, MC-18) had above average values for the majority of water quality parameters.

Determining the relationships between various spatial pathways and water quality

After multiplying the adjusted R^2 values with their respective accumulated constrained eigenvalue percentages, it was determined that the first and second RDA axes cumulatively explained 18.95, 38.10, 19.95, 26.21, and 29.09% of the total variance for the 5 km buffer, catchment, 1 km, 2 km, and 3 km reaches, respectively. Thus, the catchment landscape-scale with forward selected variables (i.e., barren, developed, and agriculture land-cover) was the best at modeling the relationship between the 2013–2014 water quality means and the land-use.

Based on the variation explained by the forward selected models, the river network had a unique contribution of 20%, the topographical pathway had a unique contribution of 4.2%, and the geographical pathway had no unique contribution (Fig. 9). A RDA was performed on the 2013–2014 centered-scaled water quality means and the selected explanatory variables from each spatial model (Fig. 10). After multiplying the adjusted R^2 values and accumulated constrained eigenvalue percentages, it was determined that the proportion of variance accounted for by the first two axes was 44.7%, thus the interpretation of RDA1 and RDA2 extracts' most relevant information from the data (Fig. 10a). Clustering of sites within the same tributary was evident (Fig. 10b, c). Sites on the main
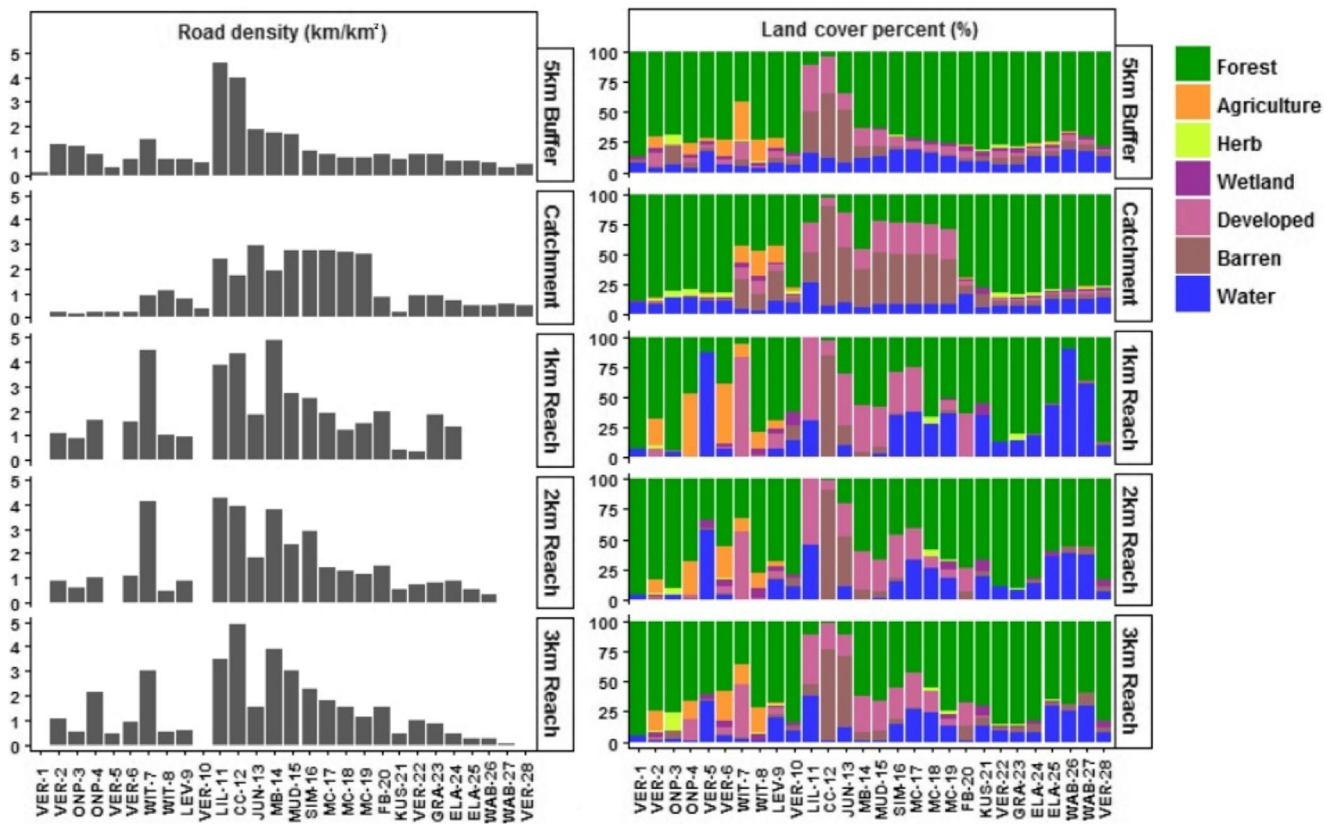
Fig. 4 Road density and land-cover percent of 5 km buffers, catchments, 1 km, 2 km, and 3 km reaches

stem of the Junction tributary (e.g., MUD-15, SIM-16, MC-17, MC-18) clustered together and sites on the Whitson tributary (i.e., WIT-7, WIT-8) clustered together. Sites CC-12 and JUN-13 were the most dissimilar from all other sampling locations. These sites both had higher proportions of developed and barren land-cover as well as above average values for many water quality parameters (Fig. 10d).

Discussion

Although the Vermilion watershed is dominated by forest land-cover, our results show that it also has notable land-use impacts from decades of mining and smelter activities, urban expansion, industrial development, and agriculture (Figs. 2 and 4). The water quality monitoring sites in this study
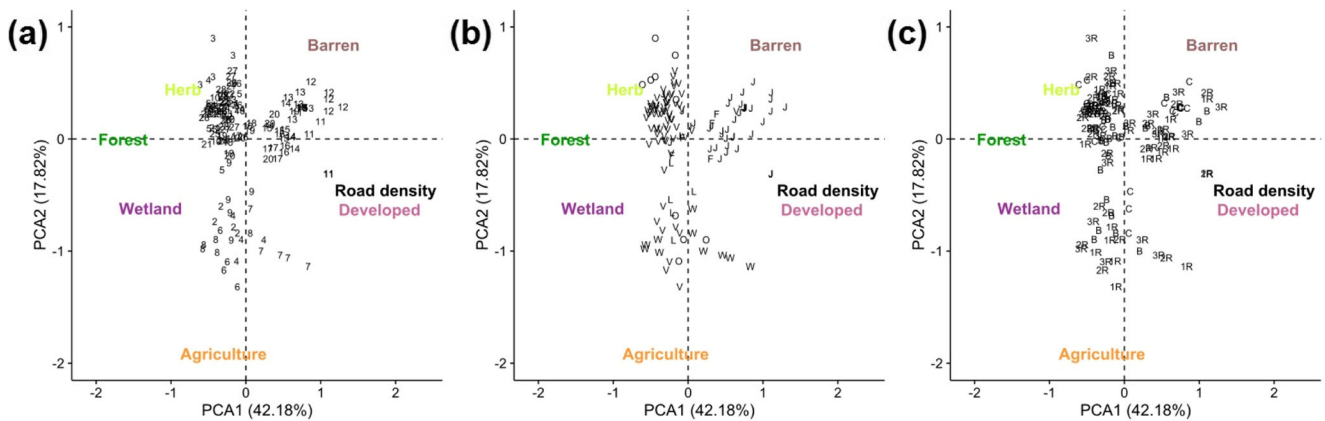
Fig. 5 Principal components analysis (PCA) performed on centered-scaled log(x + 1) transformed percent land-cover (excluding water) and road density for sites at all landscape scales (scaling 2). **a** Symbols represent site numbers. **b** Symbols represent reach location, including the main stem river system (V), Onaping tributary (O), Whitson tributary (W), Levey tributary (L), Junction tributary (J), or Fairbank tributary (F). **c** Symbols represent spatial-scales, including land-use with 5 km buffers (B), catchments (C), or 1 km (1R), 2 km (2R), or 3 km (3R) reaches. The first and second PCA axes explain 60.0% of the total variation. Developed land-cover and road density were strongly positively correlated with each other (r = 0.85)
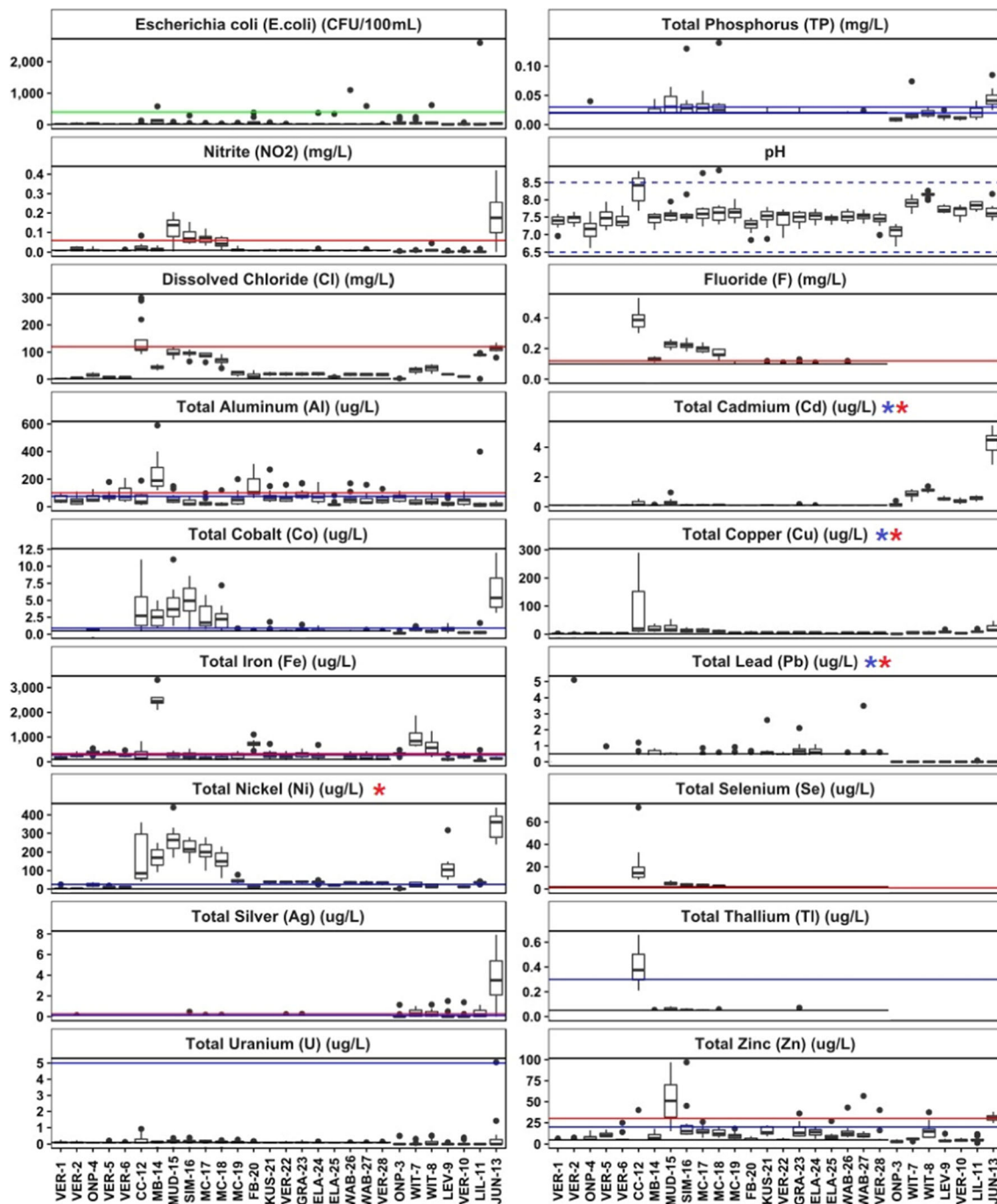
Fig. 6 Water quality parameters that exceeded the CRWQG, CWQG, and/or PWQO at one or more sites during the 2013–2014 sampling period. Due to the different suites of analyses performed for VRS and PWQMN sites, some variables are absent at PWQMN sites. Boxplots were constructed using pooled data and represent the median, first and third quartiles, and 95% confidence interval of median. The RCWQG for *E. coli* is indicated with a green line. The CWQGs for NO$_2$, Cl, F, Al, Fe,

Se, Ag, and Zn are indicated with red lines. The PWQOs for TP (0.020 mg/L for lakes and 0.030 mg/L for rivers and streams), pH, Al, Co, Fe, Ni, Ag, Tl, U, and Zn are indicated with blue lines. Asterisks indicate CWQG (red) or PWQO (blue) parameters that are dependent on hardness and thus omitted. Black lines represent RDL values for VRS sites as they were typically higher than PWQMN sites

represent receiving water locations from a broad range of land-cover/land-use types at all landscape scales. These broad landscape gradients permitted a robust assessment of the relative contribution of different land-cover and land-use types

on water quality, in addition to assessing the relative importance of point source impacts to water quality in the VRMT (Fig. 5). Though some of the barren land-cover reflects natural exposed bedrock, the majority of barren land-cover in the

Fig. 7 Spatial variation of CCME WQI values in 2013–2014. Boxplots were constructed using pooled CCME WQI values for 2013–2014 and represent the median, first and third quartiles, and 95% confidence interval of median. CCME WQI categories range from poor (0–44), marginal (45–64), fair (65–79), good (80–94), and excellent (95–100). Sixteen variables were tested for all sites
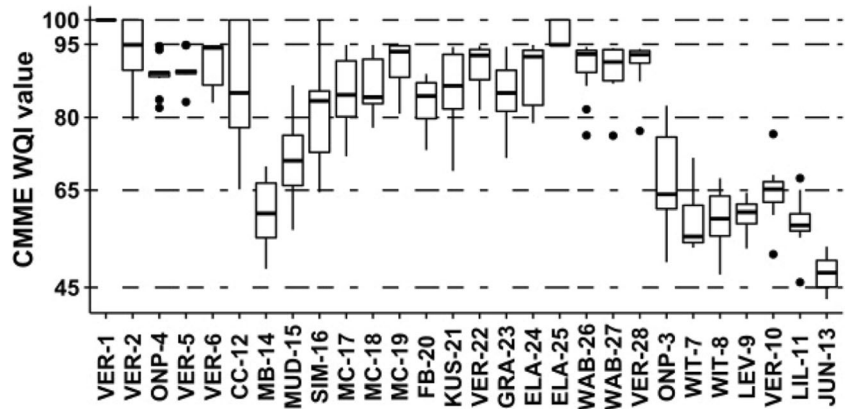
Fig. 8 PCA performed on select centered-scaled log(x + 1) transformed water quality data to view spatial and temporal patterns (scaling 2). **a** Biplot arrows for water quality parameters. **b** Symbols represent site numbers. **c** Symbols represent reach location, including the main stem river system (V), Onaping tributary (O), Whitson tributary (W), Levey tributary (L), Junction tributary (J), or Fairbank tributary (F). **d** Symbols represent sampling period: May 2013 (1), June 2013 (2), July 2013 (3), August 2013 (4), September 2013 (5), October 2013 (6), June 2014 (7), July 2014 (8), August 2014 (9), September 2014 (10), October 2014 (11), or November 2014 (12). **e** Symbols represent year: 2013 (13) or 2014 (14). The first and second PCA axes explain 51.90% of the total variation

## Geographical Pathway   River Nework Pathway
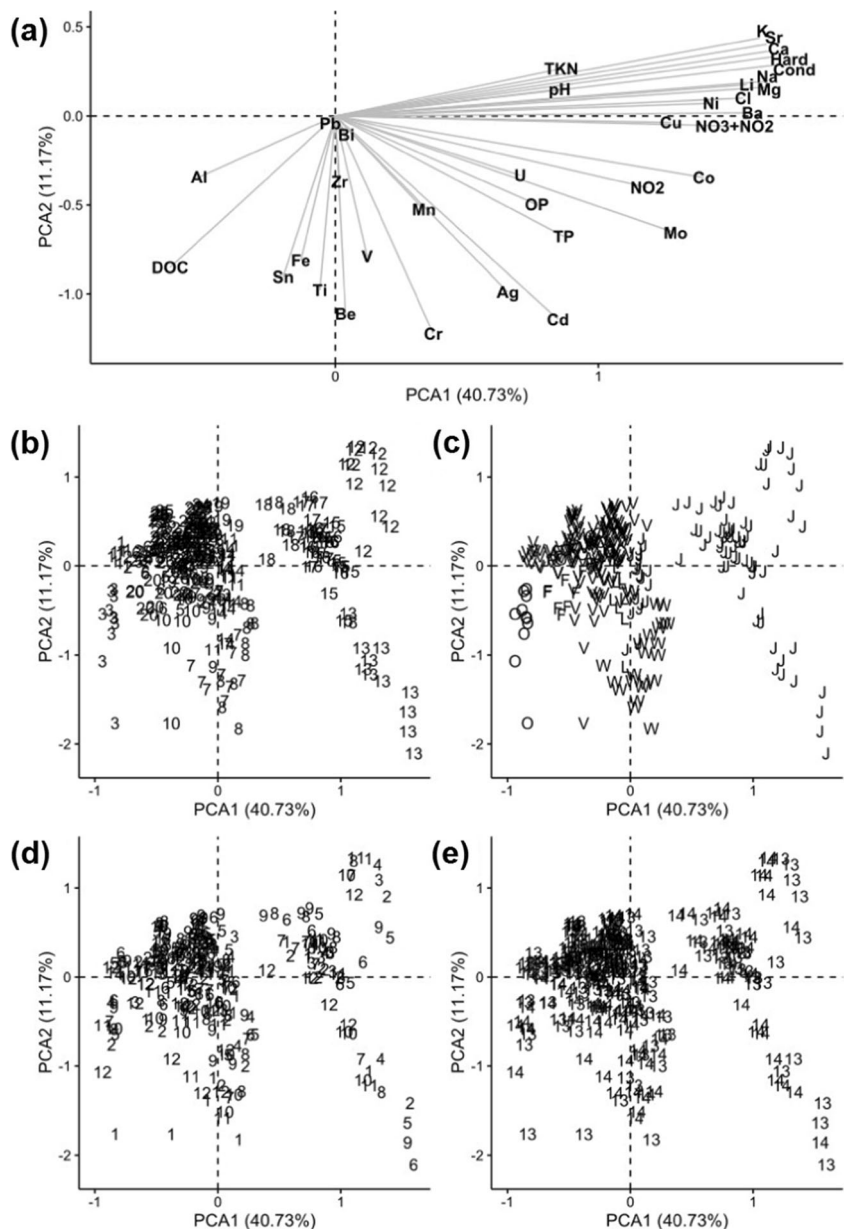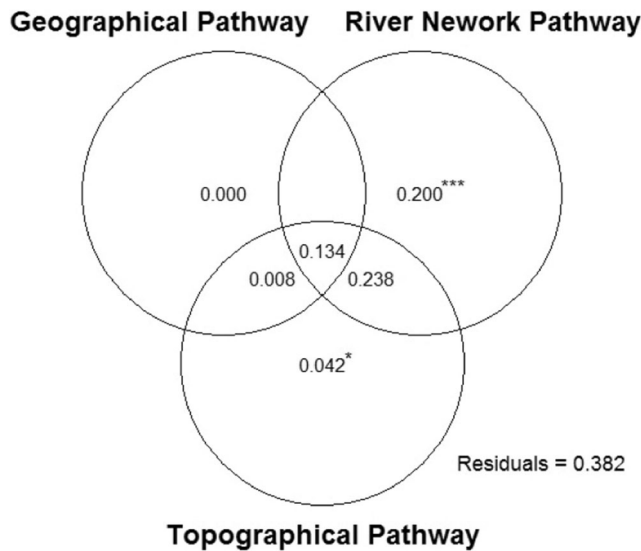
Fig. 9 Venn diagrams showing the results of variation partitioning performed on the geographical, topographical, and river network models for 2013–2014 water quality means. Variation was explained uniquely and jointly, and the unexplained fractions were shown numerically (total variation = 1). The significance of each testable fraction was shown as *$p < 0.05$, **$p < 0.01$, or ***$p < 0.001$

watershed is due to historical impacts of acid rain and metal contamination from local smelter emissions (Nriagu et al. 1998). As such, the legacy of this anthropogenic land-use type appears to be driving water quality for a significant fraction of sampling sites. Another interesting finding is that even though

the percent land-cover of agriculture in the watershed is low (Fig. 4), the relative influence on water quality appears to be high (Fig. 5). Water quality in about one third of sites in the VRMT appear to be driven by agricultural land-use. This is an important finding because it infers that agriculture can have a disproportionate impact on surface water quality in regions dominated by natural land-cover and shallow, granitic soils (Thornton and Dise 1998).

Canadian water quality guidelines and objectives (i.e., RCWQG, CWQG, and PWQO) were not met by an assortment of water quality parameters (Fig. 6). This demonstrates that the VRMT is an impacted system with several pollution hotspots along its continua, particularly sites downstream of WWTFs. Additionally, the PCA of water quality data clearly shows that sites located on the main stem of the Junction tributary are above average for the majority of parameters measured. While the CCME WQI is useful for detecting water quality hotspots and providing a rating based on the index values, it does not accurately represent water quality deterioration (De Rosemond et al. 2009; Hurley et al. 2012). This is because the WQI relies on a small subset of water quality variables and does not take into account the magnitude in which index parameters were surpassed. Thus, the raw water-quality PCA (Fig. 8) proved more useful for detecting sites where water quality was deteriorated, since it takes into account all variables measured and their magnitude of impact.

Of the eight municipal WWTFs and one sewage lagoon that discharge effluent into the VRMT, the Sudbury WWTF
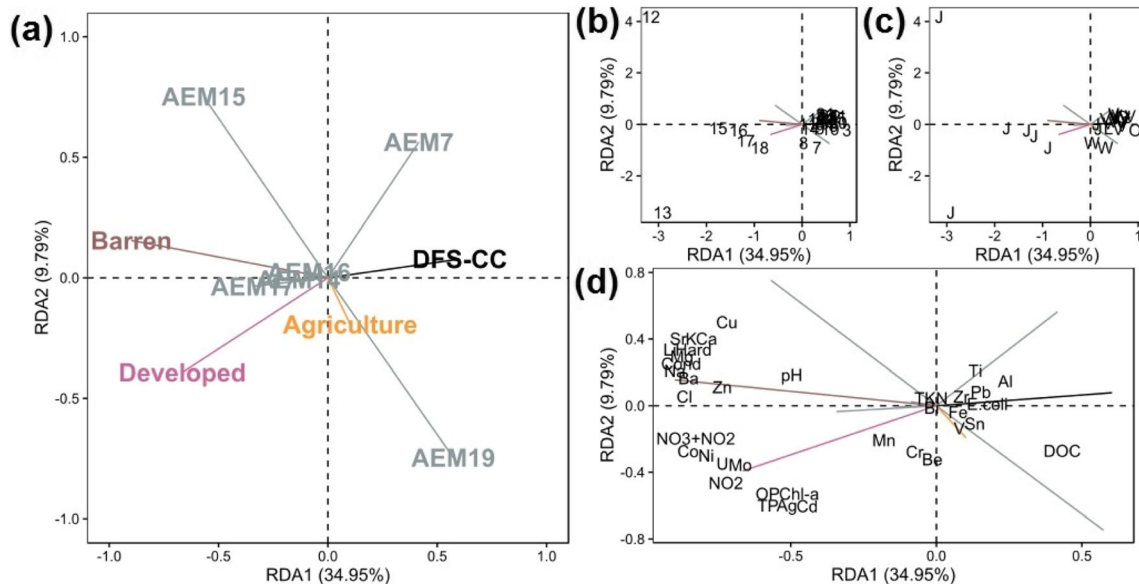
Fig. 10 Redundancy analysis (RDA) of selected explanatory variables: geographical, topographical, and river network models for 2013–2014 water quality means (scaling 2). Explanatory variables were removed if they were collinear (redundant) using forward selection. **a** Biplot arrows for selected geographical (DFS-CC), topographical (Barren, Developed, and Agriculture), and river network (AEM7, AEM14, AEM15, AEM16,

AEM17, and AEM19) explanatory variables. **b** Symbols represent site numbers. **c** Symbols represent reach location, including the main stem river system (V), Onaping tributary (O), Whitson tributary (W), Levey tributary (L), Junction tributary (J), or Fairbank tributary (F). **d** Symbols represent water quality parameters. The first and second RDA axes explain 44.74% of the total variation

served the largest population (84,609 residents) in the watershed and was by far the largest contributor of nutrients to the VRMT in both 2013 and 2014 (approximately 70–80% of the TP and TN loadings) and likely other contaminants associated with sewage including metals and organics. Similarly, of the three industrial WWTFs that discharge effluent into the VRMT, the Copper Cliff Creek WWTF is likely the greatest contributor of contaminants (Rozon-Ramilo et al. 2011). Since the study site CC-12 is downstream of this WWTF, and JUN-13 is also downstream of this WWTF (plus the Sudbury WWTF), it was anticipated that CC-12 and JUN-13 would be the most impacted sites. As anticipated, these sites had consistently above average values for the majority of water quality variables measured, yet they differed based on their water quality profiles. The subsequent RDA confirmed this finding by revealing that the majority of water quality parameters were elevated at both sites, but their main water quality constituents differed. These analyses not only flag these sites as water quality hotspots but also revealed that their different water quality profiles may require contrasting abatement strategies.

Of the three spatial-configuration pathways (geographical, topographical, and river network), the geographical pathway was expected to have a minimal influence on water quality considering that the VRMT has a relatively high flow-through rate. Thus, environmental signals (e.g., sulfates, metal contamination) from legacy mining/smelting activities may no longer be detectable in the VRMT due to the inherently low residence time. However, considering the detected influence of barren land-cover on the water quality of a significant fraction of VRMT sites, the geographic pathway was still worthwhile pursuing, and was shown to explain 14.2% of the variation in water quality, although its unique contribution explained 0% (Fig. 9). It is important to note that this finding does not refute the water quality impacts from legacy mining activities, but rather supports the notion that they likely act via other spatial pathways (i.e., topographical and river network pathways). Although others have reported on the decline of smelting-emission impacts in the Sudbury Region (Gunn et al. 1995), for the first time, we have shown that a geographic pathway for contamination is likely not important in the VRMT.

The topographical pathway primarily represents the influence of non-point sources on water quality; however, point sources are likely detected through this pathway as well (Fig. 1). For instance, WWTFs and sewage lagoons discharging directly into aquatic systems are likely detected from developed land-cover, causing an interaction between pathways (i.e., river network pathway and topographical pathway). Of the three landscape scales considered, it was expected that catchments and reaches would have the most influence on water quality as these boundaries are delineated based on topographical features (e.g., elevation, slope); thus, water

within those boundaries would eventually drain into a specific sampling point. Through preliminary RDA analyses, the catchment landscape-scale proved to be the best at modeling the relationship between the 2013–2014 water quality means and the land-use; thus, it was used for variation partitioning. A similar result was observed in a study by Sliva and Williams (2001) where they determined that the catchment scale was better at modeling relationships between land-cover and water quality than a 0.1-km reach scale. Of the three pathways, this pathway was expected to have a significant influence on water quality as numerous studies have shown that land-use (e.g., deforestation, development, agriculture, roadways) is an important driver for water quality compared to other landscape features (e.g., surficial geology) (Osborne and Wiley, 1988; Sliva and Williams 2001; Foley et al. 2005). This pathway was able to explain 42.2% of the variation in water quality, but its unique contribution, although statistically significant ($p = 0.029$), only explained 4.2%.

The river network pathway represents the cumulative impact from multiple sources. For instance, water that flows off of the landscape into a specific point will then travel through the river network, causing a joint interaction between topographical and river network pathways. Of the three pathways, this pathway was expected to have the greatest influence on water quality as it reflects the cumulative impacts from upstream inputs (i.e., point sources, flow regulation features), in conjunction with land-use in surrounding landscape (i.e., non-point sources), and is a commonly used approach in other studies (e.g., Chang 2008). This pathway was able to explain 57.2% of the variation in water quality, and its unique contribution was significant ($p = 0.001$) explaining 20% of total variation (Fig. 9). When applying the three spatial pathway models to redundancy analysis, the river network pathway and topographical features explained most of the variation in water quality (62.2%); however, a large portion of this explained variation was shared between these two pathways (37.2%). The RDA ordination revealed that many water quality variables were elevated at sites on the main stem of the Junction tributary, which is the tributary that is receiving the most pressure from urbanization and industry.

In conclusion, our study was the first to perform a comprehensive assessment of water quality trends and spatial hotspots of environmental degradation in the VRMT. The spatial determinants of water quality were successfully delineated to uncover the relative contributions of land-use type and point source inputs using a multi-model approach. Clearly, advances in smelting technologies over several decades have ameliorated their environmental impacts in the Sudbury region (Crawford 1995; Gunn et al. 1995), and our results confirm this. In contrast, our results highlight the significant influence that municipal and industrial wastewater discharges continue to have on water quality in the VRMT. This is an important finding with respect to water quality

management in the Sudbury region because it supports a shift away from smelting impacts, which were historically important, to point source WWTF impacts along the river network. Additionally, the topographic and river network (AEM) models in combination have shown that wastewater discharge and land-use have an apparent cumulative impact on water quality. These findings infer that future development in the Vermilion watershed will likely contribute to further declines in water quality.

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