Deterministic and probabilistic approaches to the development of pH total maximum daily loads: a comparative analysis

A. Elshorbagy, K. Parasuraman, G. Putz and L. Ormsbee

ABSTRACT

The most commonly used deterministic approach to the development of total maximum daily loads (TMDLs) fails to explicitly address issues related to a margin of safety and inherent variability of streamflows in the process of TMDL development. In this paper, the deterministic approach to pH TMDL development for Beech Creek watershed, Muhlenberg County, Kentucky, proposed by Ormsbee, Elshorbagy and Zechman is discussed. The shortcomings and the limitations of the assumptions associated with the deterministic approach are highlighted. An alternative probabilistic approach, to cope with the percentile-based water quality standards based on Monte Carlo simulation, is presented and compared to the deterministic approach. The proposed probabilistic approach provides a deeper insight into the issue of uncertainty and emphasizes the importance of handling the water quality standards and TMDLs in terms of magnitude and frequency rather than a single-valued approach. Expected exceedances and the confidence of compliance with percentile-based standards are estimated. Accordingly, an objective method of estimating the margin of safety for pH TMDLs is proposed.

Key words | acid mine drainage, nonpoint source pollution, pH, probabilistic analysis, TMDL, uncertainty

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INTRODUCTION

The Total Maximum Daily Load (TMDL) program, although initiated in the 1972 Clean Water Act in the United States, has only recently emerged as the fundamental approach to meet water quality standards in water bodies. The TMDL process usually refers to the plan to develop and implement the TMDL of a quantifiable pollutant that achieves compliance with a surface water quality standard (NRC 2001). Section 303(d) of the Clean Water Act and the United States Environmental Protection Agency (US EPA) Water Quality Planning and Management Regulations (40 CFR Part 130) require states to develop TMDLs for water bodies that are not meeting designated beneficial uses under technology-based controls for pollution. Development of TMDLs for different pollutants at the watershed scale enables managers to enforce constraints on the allowable level of pollutant input; therefore the TMDL approach comes under the *protection* category of Best Management Practices (BMPs). If the level of pollutant input or a water quality parameter in a water body violates the recommended value from the TMDL study, a pollutant load reduction in the watershed could be proposed, which also makes the TMDL approach a candidate for the *rehabilitation* practices category of BMPs (Elshorbagy *et al.* 2005).

Acid mine drainage (AMD) is a significant problem in western Kentucky due to coal mining operations. AMD leads to an increase of the acidity levels in streams and lowers measured pH. pH values of less than 6.0 (Kentucky

doi: 10.2166/hydro.2007.024

Division of Water (KYDOW) 1981) render the streams incapable of meeting their designated use for aquatic life and primary recreational contact (Ormsbee *et al.* 2004). For primary contact and warm water aquatic habitat, the pH level should be maintained between 6.0 and 9.0 (KYDOW 1981). Ormsbee *et al.* (2004) have proposed a methodology for pH TMDL development. Their basic idea is to convert the pH standard unit into a quantifiable hydrogen ion load, and therefore recommend load reduction to ensure the pH level in the stream does not fall below 6.0. The protocol developed by Ormsbee *et al.* (2004) relies on a regression relationship between streamflow (ft^3/s) and hydrogen ion load (g/d) based on measured pH. The recommended load reduction is based on meeting the standards at a chosen single value of flow; the critical flow (Q_c). The purpose of this paper is to discuss the validity of the assumptions made by Ormsbee *et al.* (2004), and to provide a probabilistic perspective of pH TMDL development. A comparative analysis between both deterministic and probabilistic approaches is provided to highlight possible shortcomings due to the adoption of the deterministic approach of Ormsbee *et al.* (2004).

ACID MINE DRAINAGE

In the process of coal mining, iron sulfide (FeS_2) is uncovered and exposed to the oxidizing action of atmospheric oxygen (O_2), water and sulfur-oxidizing bacteria. As described by Ormsbee *et al.* (2004), the end products of this oxidation reaction are ferrous (Fe^{2+}) iron as ferrous sulfate ($FeSO_4$) and sulfuric acid (H_2SO_4). The $FeSO_4$ is subsequently slowly oxidized to ferric (Fe^{3+}) iron as ferric sulfate [$Fe_2(SO_4)_3$]. The ferric solution is diluted and neutralized in a receiving stream and the pH rises. As the ferric iron hydrolyses, brownish yellow ferric hydroxide ($Fe(OH)_3$) precipitates and may remain suspended in the stream. The sulfuric acid that is produced causes low pH. The overall balanced reaction shown in Equation (1) indicates that a net of four moles of H^+ is liberated as H_2SO_4 for each mole of FeS_2 oxidized, causing it to be an extremely effective strong acid-producing reaction (Ormsbee *et al.* 2004):

$$4FeS_2 + 15O_2 + 14H_2O \leftrightarrow 8H_2SO_4 + 4Fe(OH)_3. \tag{1}$$

The TMDL describes the maximum amount of pollutant a stream can assimilate on a daily basis without violating water quality standards. The units of the load measurement are mass per unit time (e.g. mg/h). pH is typically measured in standard pH units with no directly associated mass unit. In this paper, the approach proposed by Ormsbee *et al.* (2004) and approved by the US EPA is adopted. The total load is expressed in terms of an equivalent hydrogen ion load since the hydrogen ion load in a water column can be related to measured pH. The relationship between hydrogen ion activity and pH can be expressed as follows:

$$\{H^+\} = 10^{-pH} \tag{2}$$

where pH is the negative log of the H^+ ion activity in mol/L. The actual molar concentration $[H^+]$ is related to the measured activity $\{H^+\}$ as follows:

$$\lfloor H^+ \rfloor = \{H^+\}/\gamma \tag{3}$$

where γ is an activity coefficient that is dependent on the ionic strength μ of the source water (Snoeyink & Jenkins 1980). Formally, μ has units of moles per litre. However, it is often reported without stating the units explicitly. The ionic strength of a given source water can be approximated using the total dissolved solids (TDS) in mg/L or specific conductance (SC) in μ ohms/cm (Snoeyink & Jenkins 1980) as follows:

$$\mu = (2.5 \times 10^{-5}) \times TDS \tag{4}$$

$$\mu = (1.6 \times 10^{-5}) \times SC. \tag{5}$$

The atomic weight of hydrogen is 1 gram per mole so the concentration of hydrogen ions in mol/L and g/L is the same. For a given day, the multiplication of average flow rate by the mole concentration of H^+ ions results in the ion load for that day in g/L. Therefore, based on a minimum pH value of 6.0 and the flow rate, the TMDL of hydrogen ions can be calculated. Additionally, the TMDL should include both load and waste load allocation, and an allowance for a margin of safety:

$$TMDL = sum(WLAs) + sum(LAs) + MOS \tag{6}$$

where WLAs is the waste load allocations for point sources, LAs is the load allocations for both nonpoint sources and natural background levels and MOS is the margin of safety. The TMDL can be obtained as a function of the flow rate and an envelope of MOS incorporated by considering observed and conservative values of the activity coefficient γ. For more details see Ormsbee *et al.* (2004). The H^+ TMDL that results in at least a pH level of 6.0 is determined based on the following Equation (Ormsbee *et al.* 2004):

$$\mathrm{TMDL} = 2.45 \times Q \tag{7}$$

where TMDL is in g/d and Q is the streamflow in ft^3/s.

METHODS

Deterministic load reduction requirement

The methodology proposed by Ormsbee *et al.* (2004) for determining the required load reduction relies mainly on the following simplifying assumptions: (i) the acidity draining from a specific watershed can be quantified in terms of an associated hydrogen ion (H^+) load, (ii) the H^+ load can be linked to the streamflow using a simple regression relationship without error between streamflow and H^+ load, (iii) a designated critical flow (Q_c) can be set *a priori* and used to estimate the corresponding H^+ load using the regression equation and (iv) a load reduction can be recommended based on the difference between the estimated TMDL and predicted load.

Although the methodology is mainly based on a regression model between Q and H^+ load, which is parametric, it is called a deterministic approach for the following reasons: (1) predicted loads are estimated using the regression model as single values, ignoring possible prediction errors that are represented by the model residuals and (2) both the estimated TMDL and the predicted load are evaluated at a single value of streamflow (e.g. Q_c), ignoring the effect of natural variability of streamflows.

Validity of simplifying assumptions

While assumption (i) of those mentioned above is not questioned in this paper, the other three assumptions are revisited to investigate their effects on the recommended load reduction. First, the assumption of linking the pollutant load to the streamflow using a regression equation could be problematic because the H^+ loads are estimated using the flow values. This may lead to a circular dependence. A better practice is to develop a regression model between streamflow and concentration of H^+. Second, the importance of the selection of Q_c on the TMDL analysis cannot be overemphasized. Basing the predicted H^+ load and TMDL on a single value of an inherently random flow variable may result in an unreasonable and unidentified level of uncertainty. For example, when the actual streamflow is lower than Q_c, the actual TMDL of a certain stream will be less than that calculated based on Equation (7). The subsequent recommended load reduction could be more or less than the actual required reduction. Third, the load reduction that is recommended based on the TMDL and predicted load relies, implicitly, on the MOS included in the TMDL.

The MOS accounts for the uncertainty in the relation between pollutant loads and the quality of the receiving water bodies (NRC 2001; Ormsbee *et al.* 2004). The MOS should also account for uncertainties in the data used for water quality assessment and for the variability of background water quality contributions. According to NRC (2001), it should also reflect the reliability of the models used for estimating load capacity. Ormsbee *et al.* (2004) accounted for the MOS by assuming an activity coefficient γ of 1.0 (worse case scenario) for the calculation of TMDL, while using γ of 0.83 (based on SC measurements) for calculating the predicted load. In light of this discussion, one can easily perceive that the deterministic approach proposed in Ormsbee *et al.* (2004) is oversimplified and incapable of evaluating the adequacy of the MOS (less than 20% in Ormsbee *et al.* (2004)). A probabilistic approach is adopted in this paper to address some of the above-mentioned uncertainties.

Probabilistic load reduction requirement

Any TMDL program has to be designed in the face of several types of uncertainty (Eheart & Ng 2004). The difficulties of water quality modeling and analysis are aggravated by uncertainties inherent in many steps throughout the modeling exercise. First, the water quality measurements are usually insufficient for reliable calibration and validation of models. The regression models used for the case study under consideration are no exception. Second, the impairment, evaluated based on concentrations that exceed a certain threshold, is dependent on flow. Flow is a random variable and those days when sampling occurred may not represent the hydrologic conditions over a long period of time. Third, violations and compliance evaluated by a model are subject to uncertainties due to parameters and/or structure of the model.

The US EPA guidelines for state water quality assessments can be considered percentile-based standards. They recommend listing a water body as impaired if more than 10% of the samples from that water body violate the water quality standards (US EPA Office of Water 1997). An effective way of developing a percentile-based TMDL has been proposed by Borsuk *et al.* (2002) and adopted in this study. The residuals of the regression models are fitted by a Normal distribution, and then a longer set of residuals (e.g. 1000 values) is generated using Monte Carlo simulation. A predicted concentration value, identified using the regression model at a certain flow value (e.g. Q_c), can be replaced by a corresponding set of 1000 instances according to Equation (8):

$$C_i = \overline{C} \pm R_i \tag{8}$$

where C_i is one of the possible concentration values, $\overline{C}$ is the mean concentration assessed using the regression model and R_i is one of the residual values. Based on the generated set of concentrations C_i, the percentage of values violating the standards (e.g. 20% of the values are higher than the permissible concentration) can be calculated.

The percentage estimated based on the above-outlined methodology is a single prediction of the frequency of standard violations at a specified flow. More generally, the overall frequency of violations across all flows can be estimated using historical flow values or generated flow by a second set of Monte Carlo simulations. The above-mentioned methodology is repeated using a set of 3650 values of flow (equivalent to 10 years of daily values) instead of a single-valued flow (Q_c). This set of values allows for computing the overall expected exceedance frequency. Information about the uncertainty in that prediction of exceedance frequency is highly useful because it provides a realistic expectation of the chances of compliance with the percentile-based standards (Borsuk *et al.* 2002). This can be computed with the EPA's 10% standard, the 90% confidence interval (*CI*) and the confidence of compliance (*CC*) (Borsuk *et al.* 2002). The *CC* is the probability that the violation (i.e. the exceedance frequency) does not exceed a pre-specified percentile, such as the 10% indicated by the US EPA guidelines. These measures of uncertainties are quantitative indices that represent the probability distribution of the frequency of violations (exceedances). Such a distribution can be obtained by perturbing the values of the regression model parameters (slope; m and intercept; b). A set of m and b can be generated based on the mean value and the standard error of the parameters; maintaining the correlation between them. Monte Carlo simulation was used to propagate this type of uncertainty.

Other investigators have used first-order error analysis (FOEA) to address issues related to uncertainties (Zhang & Yu 2004), whereas Monte Carlo simulation is the basis of the method adopted in this paper.

CASE STUDY: BEECH CREEK WATERSHED

The Beech Creek watershed in Western Kentucky (the watershed used as a case study by Ormsbee *et al.* (2004)) is used in this paper. The 1998 303(d) list of waters for Kentucky (KYDOW 1998) indicates 3.4 miles of Beech Creek, from the headwaters to the confluence with Pond Creek in Muhlenberg County, does not meet its designated uses for both contact recreation (swimming) and aquatic life. The Beech Creek watershed is entirely contained within Muhlenberg County, in southwestern Kentucky (Figure 1). Muhlenberg County is bounded on the northeast by the Green River, on the east by Indian Camp Creek and on the west by the Pond River. The Beech Creek watershed provides a classic example of impairment caused by AMD. Bituminous coal mine drainage found in the Beech Creek watershed contains very concentrated sulfuric acid and high concentrations of metals, especially iron, manganese and aluminum. Beech Creek's mainstem is approximately 5.47 km (3.4 miles) long and drains an area of 10.55 km^2 (4.12 mi^2). The average gradient is 12.8 feet per mile. Elevations along Beech Creek range from 152 m (500 ft) above mean sea level (msl) in the headwaters to 137 m (450 ft) above msl at the mouth. Like most of the smaller watersheds, many of the tributary streams are intermittent.

Coal, oil and natural gas are among the natural resources of Muhlenberg County. Coal is the county's most important revenue-producing natural resource and at one time Muhlenberg County was the largest coal-producing county in the United States. In 1973, this county produced over 19 million tons of coal from strip mines and over 5 million tons from underground mines (Ormsbee *et al.* 2004). The Beech Creek watershed contains three main land uses: resource extraction (mining and disturbed land area), forest and agriculture. Several nonpoint loading sources were identified in the Beech Creek watershed. In order to provide a more recent characterization of the pH levels in the watershed, the University of Kentucky (as part of the study contract with the KYDOW) subcontracted with Murray

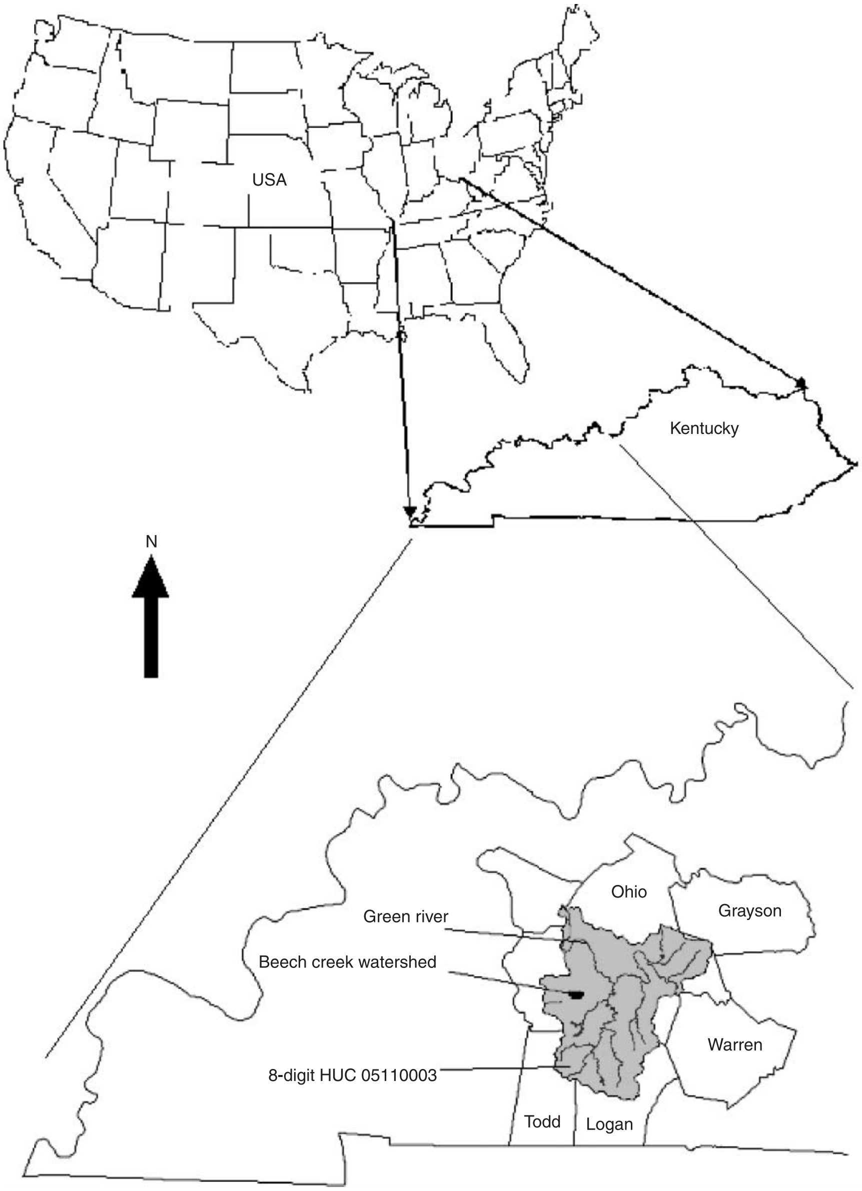

Figure 1 | Location of Beech Creek watershed in Western Kentucky.

State University to collect additional data from the watershed at the sites indicated in Figure 2. A summary of the results obtained from these sites is shown in Table 1.

Table 1 | Flow and pH monitoring results in the Beech Creek watershed

	Site P1		**Site P2**	
Date	**Flow in cfs (m^3/s)**	**pH**	**Flow in cfs (m^3/s)**	**pH**
10/24/2000	0.01 (0.0003)	2.74	0.03 (0.0009)	2.60
11/7/2000	0.06 (0.0017)	3.12	0.18 (0.005)	2.89
11/9/2000	0.44 (0.013)	3.49	1.90 (0.054)	3.06
3/27/2000	0.46 (0.013)	3.15	0.94 (0.027)	3.31
4/20/2001	0.02 (0.0006)	3.30	0.53 (0.015)	3.19
8/13/2001	0.01 (0.0003)	2.94	0.13 (0.0037)	2.85
8/22/2001	0.00	–	0.10 (0.003)	2.93
1/9/2002	0.15 (0.004)	3.58	0.51 (0.015)	4.50

RESULTS AND ANALYSIS

Results and analysis of the deterministic approach

The use of the deterministic approach to TMDL development, as briefly explained above and detailed by Ormsbee *et al.* (2004), results in a TMDL of 0.014 lb/d (6.36 g/d) of hydrogen ions at critical flow at the mouth of the watershed (Table 2). The critical flow is the lowest ten-year mean annual discharge as proposed by the Kentucky Division of Water (KYDOW). The TMDLs for each individual subbasin were obtained using a simple mass balance technique. For a mass balance to be obtained, the load at the watershed outlet must equal the summation of the incremental load from each subbasin (Figure 2). Therefore, the outlet load is distributed throughout the watershed based on subbasin area. This process gives the larger subbasins a larger incremental load; likewise, it gives the smaller subbasins a smaller incremental load.

Specific conductance values in Beech Creek range from 1650–1900 μΩ/cm (Ormsbee *et al.* 2004), which yield ionic strength values between 0.026–0.030, respectively (Equation (5)). In Beech Creek, this yields activity coefficients of 0.88–0.89 (Ormsbee *et al.* 2004). For Beech Creek, an activity coefficient of 0.83 (based upon regional maximum measurements of SC) was used for calculation of the observed load. A conservative activity coefficient of 1.0 was used in Equation (7) to determine the TMDL, thus providing for an implicit margin of safety in the pH TMDL.

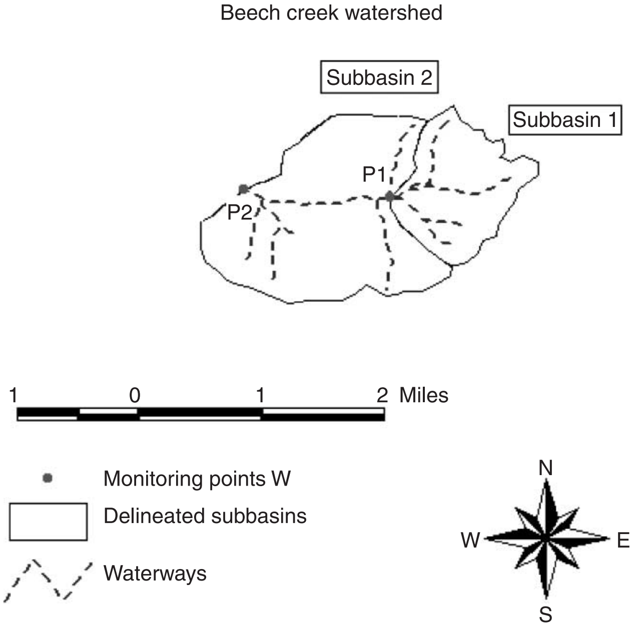

Figure 2 | Beech Creek watershed sampling sites.

There are no known permitted point sources in this watershed. As a result, the waste load allocations for the Beech Creek watershed are assumed to be zero. Thus the remaining load allocations are equal to the associated TMDL. Hence, the load allocations for each subbasin are simply equivalent to the associated incremental TMDLs shown in Table 2.

Table 2 | Lowest ten-year mean annual flows and corresponding TMDLs (after Ormsbee *et al.* 2004)

Subbasin	**Area in mi² (km²)**	***Q* in cfs (m^3/s)**	**TMDL in lb/d (g/d)**
Total	4.12 (10.55)	2.56 (0.073)	0.014 (6.36)
1	1.25 (3.2)	0.78 (0.022)	0.004 (1.82)
2	2.87 (7.35)	1.78 (0.051)	0.010 (4.54)

Based on a physical inspection of the watershed, it is hypothesized that the decrease in pH in the stream is directly related to oxidation of pyrites that occurs as runoff flows over the spoil areas associated with previous mining activities in the basin. Using the most recent monitoring data, inductive (regression) models were developed for each monitoring site. Ormsbee *et al.* (2004) developed these inductive models by regressing flow vs. hydrogen ion load. As indicated earlier, a better practice would be to relate flow and ion concentration through regression equations. The models developed for subbasins 1 (site P1) and 2 (site P2) are shown in Figure 3. One observation was excluded from the regression model for P2 (1/9/2002) as it appeared to be an outlier compared to the rest of the observations. A natural log transformation was applied to both flow and concentration values to obtain linear relationships. The developed relationships may be used to predict ion concentrations in the stream on the basis of streamflow. As can be seen from Figure 3, there is an inverse relationship between flow and hydrogen ion concentration, indicating a dilution effect at higher flows. It can be reasonably concluded that nonpoint sources are important because the dilution at higher flows is not as significant as it would be if a constant source was the only source of acidity, in which case the regression model would have a slope of -1.0. Both sites yield similar slopes but different intercepts, suggesting that the nonpoint source mass inputs (that increase with increasing runoff) are similar, but the point source mass inputs (that do not increase with runoff) could be different.

It can be seen from Figure 3 that the lower pH limit of 6.0 (corresponding to an ion concentration of 0.001 g/m^3 or -6.9 on the log scale) is violated at all reasonable flows, including the critical flow. Corresponding predicted hydrogen ion loads could be calculated by multiplying flows and concentrations. Application of this approach yields the predicted loads at critical flow for each site, as shown in Table 3. Note that, for an independent tributary the incremental load is equal to the cumulative load for that tributary. In contrast, a subbasin that has flows entering from adjacent or upstream subbasins requires a mass balance application to find the incremental load. For example, the incremental load for subbasin 2 is determined by subtracting the load for subbasin 1 from the cumulative load for subbasin 2.

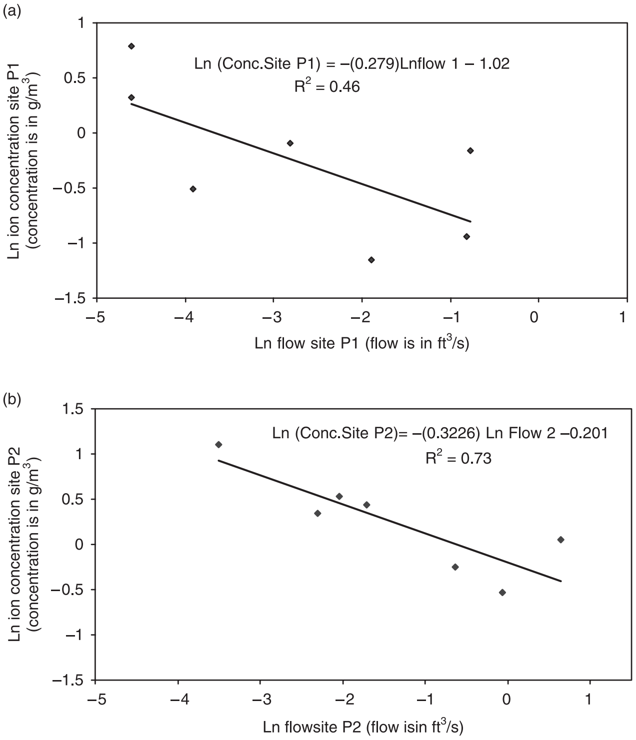

Figure 3 | Flow vs H^+ concentrations at: (a) site P1, (b) site P2.

The required load reduction for a watershed is the amount the actual in-stream load must be reduced in order to meet the TMDL. This is calculated by subtracting the incremental TMDLs (Table 2) from the incremental predicted loads for each subbasin (Table 3). This approach allocates the total load reduction for Beech Creek (site P2) between each of the contributing sites in the watershed, so that the entire watershed is rehabilitated and the pH is improved throughout the stream network. Application of this approach yields the values of required load reductions in Table 4.

RESULTS AND ANALYSIS OF THE PROBABILISTIC APPROACH

The probabilistic analysis outlined earlier is first performed to estimate the frequency of standard violations at the critical flow and the uncertainty in this frequency. Then a target set of flow values is used to estimate the

Table 3 | Predicted H^+ loads (after Ormsbee *et al.* 2004)

Subbasin	Cumulative *Q* in cfs (m^3/s)	Cumulative load in lb/d (g/d)	Incremental load in lb/d (g/d)
1	0.78 (0.022)	2.44 (1,107)	2.44 (1,107)
2	2.56 (0.073)	11.82 (5,37)	9.38 (4,265)

Table 4 | TMDL summary for Beech Creek

	Required load reduction in lb/d (g/d)
Total	11.81 (5,366)
Subbasin 1	2.43 (1,105)
Subbasin 2	9.38 (4,261)

overall frequency of violations and the associated uncertainty. A set of 3650 values of flow was used in this analysis to represent a possible range of flows. Such a record is not available for the watershed under consideration. Therefore, the daily flows of the last ten years at the nearest available USGS station (site number 03320500: Pond River near Apex, Muhlenberg County, KY) were used. Flows for the Beech Creek watershed were estimated using a percentage of the Pond River flows, based on the relative area of Beech Creek watershed to total drainage area contributing flows to site number 03320500. An alternative approach of generating flows that have the same mean and standard deviation of the sampled (measured) flow values using lognormal distribution (Novotny 2004) could be used. The results indicate that there will be 100% violation of standards (i.e. pH $<$ 6.0) within the entire range of ten-year flows because concentrations are far exceeding the permissible level.

Load (nonpoint source mass input) reduction scenarios can be perceived as different slopes in the regression-based model; keeping the intercept (i.e. the concentration at flow where $\ln Q \approx 0$) constant. It should be noted that the concentration of a point source pollution in a stream decreases linearly with increasing flow, i.e. doubling the flow causes the concentration due to the same load to decrease to half (i.e. slope of -1 of the regression line). Different levels of point source pollution are expected to generate similar regression lines (slope of -1) with different values of regression intercept. Based on the same logic, varying the levels of nonpoint source pollution means varying the slope of the regression line; while keeping the intercept constant. Knowing that the H^+ value of -6.9 (-6.72 when $\gamma = 0.83$) secures compliance with the standard, load reduction scenario 1 based on the deterministic approach at Q_c can be represented as a new line passing through pH $= 6.0$ at Q_c (Figure 4). The probabilistic analysis based on distribution of residuals is performed with the new line representing the load reduction scenario 1. It is found that, at Q_c there is 50% chance of violating the standards (i.e. pH $<$ 6.0) in subbasins 1 and 2, due to the remaining variability. Apparently, this happens when a positive residual (i.e. residuals falling on the upper side of the regression line) causes the concentration to be higher than the deterministic value. The uncertainty about this estimate can be assessed by performing Monte Carlo simulation on the parameter uncertainty. A set of 1000 values of model parameters are generated using Normal distribution for the slope (m). The value of m is used as the mean value while the standard error (0.135 for site P1 and 0.09 for site P2) of the slope of the original regression Equation (Figure 3) is used as the standard deviation. Further, the overall exceedance frequency can be estimated using the 3650 range of flows. The expected exceedance is found to be 68% and the confidence of compliance is around 24% at site P1 (Table 5). This is a nontrivial outcome of the probabilistic analysis that suggests that enforcing the single-valued TMDL based on the deterministic analysis (Ormsbee *et al.* 2004) means that the pH level in the stream could be violated 68% of the time. This is not surprising since the critical flow is chosen to be the mean annual flow. Only 34% of the daily flows in the last ten years exceed the critical flow Q_c, thus creating critical conditions (violation of standards) during 66% of the time. Apparently, the confidence that pH could meet the standards (*CC*) is low (24%). The important point in this discussion is that, even with the MOS considered in Ormsbee *et al.* (2004), the risk of violation is considerably high. The same analysis is repeated at site P2 and the results are provided in Table 5 as “scenario-1”.

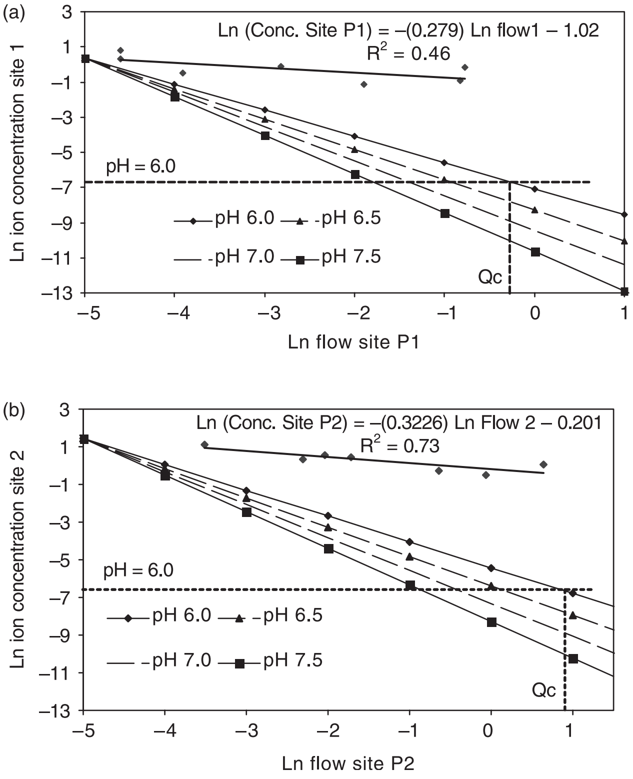

Figure 4 | Four load reduction scenarios: (a) subbasin 1, (b) subbabsin 2.

Table 5 | The effect of load reduction scenarios on the frequency of violation of the pH standard

Load reduction scenario	pH at Q_c	Expected exceedances (%)	90% confidence interval	Confidence of compliance
Site P1				
Base case	3.5	100		0.0
Scenario 1	6.0	68	67–69	24
Scenario 2	6.5	55	54–56	38
Scenario 3	7.0	47	46–48	48
Scenario 4	7.5	41	40–43	55
Site P2				
Base case	3.3	100		0.0
Scenario 1	6.0	68	67–69	27
Scenario 2	6.5	54	53–55	42
Scenario 3	7.0	45	43–46	53
Scenario 4	7.5	38	37–40	59

DOES THE PROBABILISTIC APPROACH AFFECT THE LOAD REDUCTION STRATEGY?

A Monte Carlo simulation technique is used in this study to sample from 1000 values of residuals of ion concentration and 1000 values of parameter sets (coefficients of the regression model). Therefore, various combinations of parameters and model residuals are considered by sampling randomly from the probability distributions of both variables. The 1105 g/d and 4261 g/d values of load reduction (Table 4) for subbasins 1 and 2, respectively, recommended based on the deterministic approach (Table 4), have been tested within the context of the probabilistic approach. The expected frequencies of violation (expected exceedances) discussed in the previous section, and presented as scenario 1 in Table 5, point out the need for considering other load reduction scenarios. Three more scenarios of additional load reduction are considered by changing the slope of the flow–concentration relationships (Figure 4). The scenarios are designed so that the pH level is increased to 6.5, 7.0 and 7.5 at the critical flows for scenario 2, 3 and 4, respectively. These values correspond to ln (ion concentrations) of −7.88, −8.97 and −10.13 on the vertical scale of Figure 4.

The Monte Carlo simulation performed with regard to scenario 1 was repeated with the other three scenarios for sites P1 and P2. The results of the analysis are summarized in Table 5. For example, the expected exceedances at site P2 can be reduced from 68% (scenario 1) to 38% (scenario 4) by raising the pH level at the critical flow from 6.0 to 7.5. At this point the confidence of compliance increases from 27% to 59%. US EPA guidelines allow up to 10% violation, therefore 10% can be interpreted as the recommended value of the expected exceedance. Either the confidence of compliance or the expected exceedance can be used as a criterion to quantify the MOS and decide on the required load reduction scenario. Once the confidence of compliance or the expected exceedance is set in advance, the load reduction requirement can be quantified. The probabilistic analysis summarized in Table 5 provides a deeper insight and more comprehensive perspective than that offered by the deterministic approach for the pH TMDL development.

DISCUSSION

The wide range of the flow-dependent assimilating capacity (TMDL) of a stream makes it extremely difficult for a single-valued TMDL to prevent violation conditions. This natural variability has been addressed in this paper through evaluating the pollutant concentration at many values of streamflow. In this paper 3650 (equivalent of 10 years of daily flows) values are estimated and used. The variability in the concentrations that is not explained by a deterministic model has also been quantified using a probability distribution of model residuals to predict the frequency of standard violations. The probabilistic approach helps provide a better perception of the stream health over a range of flows. If decisions are to be made based on the critical flow only, it means that uncertainty due to the natural variability of flow is ignored. In this case, only the uncertainty due to prediction error is considered. The frequencies of violation at Q_c are estimated to be 50%, 5%, 0.0% and 0.0% for scenarios 1, 2, 3 and 4, respectively, at site P1. Similarly, the frequencies of violation are 50%, 3%, 0.0% and 0.0% for scenarios 1, 2, 3 and 4, respectively, at site P2 (Table 6).

In this paper, only uncertainties due to prediction errors and the natural variability are addressed. However, uncertainties due to other parameters (e.g. γ) can be addressed as well. Another factor that could be influential and needs to be revisited by the KYDOW is the critical flow (Q_c). The selected Q_c is high because it is greater than 66% of daily flows in any given year. This leads to an overestimated TMDL, and therefore increasing the chances of violation. Decreasing Q_c could result in a lower value of TMDL and higher values of load reduction, which in turn could reduce the expected exceedances. The probabilistic approach presented in this paper borrows and lends support to the statement: "*States should consider a statistical modeling approach to assessing the condition of waters. This approach would combine monitoring data with estimates of water quality based on statistical models*" (NRC 2001). The results and analysis presented in the previous section indicate the importance of setting water quality standards in the form of allowable frequencies of violation rather than deterministic values (NRC 2001).

A limitation of this study is the number of flow and concentration values (Table 1) used to construct the regression model is limited. Additional observations are necessary to provide better estimates of the model parameters, and thus a higher confidence in the probability distribution of the model parameters and the results obtained based on the probabilistic approach.

In the probabilistic analysis presented earlier, reduction in nonpoint source load has been mathematically interpreted as changing the slope of the regression model that relates streamflows and ion concentrations. Further and effective reduction scenarios could also be generated by lowering the intercept, which could be interpreted as reducing the point source pollution. This approach was

Table 6 | A comparison between expected exceedances at critical flow (Q_c) and over a range of 3650 flow values

Load reduction scenario	pH at Q_c	Expected exceedances (%) based on 3650 flow values	 Critical flow (Q_c)
Site P1			
Base case	3.5	100	100
Scenario 1	6.0	68	50
Scenario 2	6.5	55	5
Scenario 3	7.0	47	0.0
Scenario 4	7.5	41	0.0
Site P2			
Base case	3.3	100	100
Scenario 1	6.0	68	50
Scenario 2	6.5	54	3
Scenario 3	7.0	45	0.0
Scenario 4	7.5	38	0.0

not taken in this research since there is no point source pollution on record in the watershed under consideration. However, the entire probabilistic analysis could be easily replicated with other scenarios.

CONCLUSIONS

This paper questions the assumptions used to develop the pH Total Maximum Daily Load by Ormsbee *et al.* (2004). An alternative percentile-based pH TMDL has been developed for the Beech Creek watershed. Some uncertainty about the frequency of standard violations has been assessed by addressing both natural variability and prediction error using a probabilistic analysis. The probabilistic approach provides a deeper insight into the possible ranges of standard violation as well as the confidence of compliance. Regulators can quantify the margin of safety and the required level of load reductions by choosing an appropriate level of confidence of compliance. The efficacy of the single-valued TMDL and load reductions recommended based on the deterministic approach can be better evaluated based on the outcome of the probabilistic approach. The proposed probabilistic approach highlights the importance of assessing stream health and setting water quality standards in probabilistic terms to accommodate the inherent randomness of hydrologic parameters and other uncertainties related to water quality analysis.

ACKNOWLEDGEMENTS

The first author acknowledges the financial support of the Natural Sciences and Engineering Research Council (NSERC) of Canada through its Discovery Grant Program.

REFERENCES

Borsuk, M. E., Stow, C. A. & Reckhow, K. H. 2002 Predicting the frequency of water quality standard violations: a probabilistic approach for TMDL development. *Environ. Sci. Tech.* **36** (10), 2109–2115.

Eheart, J. W. & Ng, T. L. 2004 Role of effluent permit trading in total maximum daily load programs: overview and uncertainty and reliability implications. *J. Environ. Engng., ASCE* **130** (6), 615–621.

Elshorbagy, A., Teegavarapu, R. & Ormsbee, L. 2005 Total maximum daily load (TMDL) approach to surface water quality management: concepts, issues and applications. *Can. J. Civil Engng.* **32** (2), 442–448.

Kentucky Division of Water (KYDOW) 1981 *The Effects of Coal Mining Activities on the Water Quality of Streams in the Western and Eastern Coalfields of Kentucky*. Department for Environmental Protection, Kentucky Natural Resources and Environmental Protection Cabinet.

Kentucky Division of Water (KYDOW) 1998 *303(d) List of Waters for Kentucky*. Department for Environmental Protection, Kentucky Natural Resources and Environmental Protection Cabinet.

National Research Council (NRC) 2001 *Assessing the TMDL Approach to Water Quality Management*. National Academy Press, Washington, DC.

Novotny, V. 2004 Simplified databased total maximum daily loads, or the world is log-normal. *J. Environ. Engng., ASCE* **130** (6), 674–683.

Ormsbee, L., Elshorbagy, A. & Zechman, E. 2004 A methodology for pH TMDLs: application to Beech Creek watershed. *J. Environ. Engng., ASCE* **130** (2), 167–174.

Snoeyink, V. L. & Jenkins, D. 1980 *Water Chemistry*, pp. 77–78. Wiley, New York.

US EPA Office of Water 1997 *Guidelines for Preparation of the Comprehensive State Water Quality Assessments. EPA-841-B-97-002*. US Environmental Protection Agency, Washington, DC.

Zhang, H. X. & Yu, S. L. 2004 Applying the first-order error analysis in determining the margin of safety for total maximum daily load computations. *J. Environ. Engng., ASCE* **130** (6), 664–673.