

Estimating storm discharge and water quality data uncertainty: A software tool for monitoring and modeling applications

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ABSTRACT

Uncertainty estimates corresponding to measured hydrologic and water quality data can contribute to improved monitoring design, decision-making, model application, and regulatory formulation. With these benefits in mind, the Data Uncertainty Estimation Tool for Hydrology and Water Quality (DUET-H/WQ) was developed from an existing uncertainty estimation framework for small watershed discharge, sediment, and N and P data. Both the software and its framework-basis utilize the root mean square error propagation methodology to provide uncertainty estimates instead of more rigorous approaches requiring detailed statistical information, which is rarely available. DUET-H/WQ lists published uncertainty information for data collection procedures to assist the user in assigning appropriate data-specific uncertainty estimates and then calculates the uncertainty for individual discharge, concentration, and load values. Results of DUET-H/WQ application in several studies indicated that substantial uncertainty can be contributed by each procedural category (discharge measurement, sample collection, sample preservation/storage, laboratory analysis, and data processing and management). For storm loads, the uncertainty was typically least for discharge (± 7 – 23%), greater for sediment (± 16 – 27%) and dissolved N and P (± 14 – 31%) loads, and greater yet for total N and P (± 18 – 36%). When these uncertainty estimates for individual values were aggregated within study periods (i.e. total discharge, average concentration, and total load), uncertainties followed the same pattern ($Q < \text{TSS} < \text{dissolved N and P} < \text{total N and P}$). This rigorous demonstration of uncertainty in discharge and water quality data illustrates the importance of uncertainty analysis and the need for appropriate tools. It is our hope that DUET-H/WQ contributes to making uncertainty estimation a routine data collection and reporting procedure and thus enhances environmental monitoring, modeling, and decision-making. Hydrologic and water quality data are too important for scientists to continue to ignore the inherent uncertainty.

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Software/data availability

A Beta version of DUET-H/WQ was used in all analyses presented. Bill Komar, programmer with AgriLife Research part of the Texas A&M University System, completed the development in December 2007. This and future revisions are available at no cost online in an open source format at <ftp://ftp.brc.tamus.edu/pub/outgoing/bkomar/programs/>. The software with the interface is

also available from Daren Harmel, 808 E. Blackland Rd., Temple, TX 76502, USA. Tel.: +1 254 770 6521, daren.harmel@ars.usda.gov. DUET-H/WQ is written in Visual Basic and is distributed as an installable Windows file that requires the Microsoft.NET 2.0 Framework with Service Pack 1.

1. Introduction

In spite of advanced modeling capabilities, water resource decision-making still relies strongly on measured hydrologic and water quality data (Silberstein, 2006), and understanding the inherent data uncertainty is vital for appropriate assessment, management, and modeling (Brown et al., 2005; Brouwer and De Blois, 2008). First, optimal water quality monitoring can only be achieved if measurement uncertainty and alternatives to reduce uncertainty are understood and considered in project design and

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implementation (Beven, 2006a; Harmel et al., 2006b; Rode and Suhr, 2007). Second, enhanced decision-making and stakeholder understanding can only be fully realized if measurement uncertainty is estimated and adequately communicated to other scientists, modelers, public interest groups, regulators, and elected officials (Collins et al., 2000; Bonta and Cleland, 2003; Reckhow, 2003; Nature, 2005; Beven, 2006a; Pappenberger and Beven, 2006). Similarly, analysis of uncertainty in measured data, which drive model calibration and validation, improves model application and enhances decisions based on modeling results (Reckhow, 1994; Kavetski et al., 2002; Pappenberger and Beven, 2006; Beven, 2006b; Shirmohammadi et al., 2006; Harmel and Smith, 2007).

The typical data collection procedures (monitoring methods) for discharge, sediment, and nutrient water quality data have been classified into four categories: discharge measurement, sample collection, sample preservation/storage, and laboratory analysis (Harmel et al., 2006a). Typically, it is by procedures in these categories that uncertainty is introduced into discharge and water quality data. Brief descriptions of uncertainty related to these procedural categories related to small watersheds appear subsequently in this manuscript; for detailed descriptions see Harmel et al. (2006a). These categories and descriptions are not meant to be exhaustive (e.g. in situ water quality sensors are not included) but to address common methods used in small watershed monitoring projects. Alternatives to reduce uncertainty for each procedural category were not presented but appear in Pelletier (1988), Kotlash and Chessman (1998), USGS (1999), Jarvie et al. (2002), Meyer (2002), Harmel et al. (2006a,b), and Rode and Suhr (2007). Rode and Suhr (2007) also provide an excellent summary of uncertainty in basin-scale water quality data. Throughout this manuscript, “error” and “uncertainty” are used synonymously and are defined as random variation affected by the appropriate use of accepted procedures (Haan, 2002).

1.1. Uncertainty in discharge measurement

Many researchers have analyzed uncertainty associated with discharge (flow) measurement, but uncertainty estimates are rarely made and reported to data users. One exception is the US Geological Survey (USGS) that does publish uncertainty estimates corresponding to instantaneous discharge measurements and annual station discharge records (Novak, 1985). For small watersheds, discharge is commonly measured with a hydraulic control structure (weir or flume), and thus uncertainty is introduced mainly by stage (depth) measurement (Hersch, 1995). The velocity–area method is also commonly used for instantaneous measurement or to establish a stage–discharge relationship. With the velocity–area method, uncertainty is introduced by stage and velocity measurements typically conducted in vertical cross-section segments (Young, 1950; Carter and Anderson, 1963; Rantz et al., 1982; Pelletier, 1988; Hipolito and Loureiro, 1988; Sauer and Meyer, 1992). Continuous discharge data are typically estimated from stage measurements based on their relationship with discharge (Buchanan and Somers, 1976; Brakensiek et al., 1979; Kennedy, 1984; Carter and Davidian, 1989; Slade, 2004). The uncertainty in continuous stage measurement is mainly determined by stage sensor accuracy, presence/absence of a stilling well, and channel bed conditions (Pelletier, 1988; Sauer and Meyer, 1992). Uncertainty introduced by translating continuous stage measurements into discharge is determined to a large extent by the presence/absence of a hydraulic control structure, the stability of the channel, and the range of measured flows used to develop the relationship (Dickinson, 1967; Pelletier, 1988; Sauer and Meyer, 1992; Hersch, 1995; Schmidt, 2002). In-stream velocity meters are also commonly used to provide continuous discharge data based on measured velocities

and the cross-sectional flow area. The uncertainty of in-stream discharge sensor data largely depends on equipment accuracy relative to the entire cross-sectional flow area, depth-area based on stage measurements, stability of the channel morphology, and variability of water chemical and physical characteristics (McIntyre and Marshall, 2008).

1.2. Uncertainty in sample collection

Until recently, relatively little information had been available on uncertainty related to sample collection for the determination of constituent concentrations. In small watersheds (roughly described as <10,000 ha), manual grab samples and/or automated samples can be used to characterize water quality. Uncertainty related to baseflow water quality sampling is determined by the frequency of collection, type of constituent, and choice of collection method, whether manually integrated, manual grab, or automated (Martin et al., 1992; Ging, 1999; USGS, 1999). Similarly, the uncertainty introduced by manual and automated storm water sampling is determined by constituent type, collection methodology, and sampling frequency (Martin et al., 1992; Ging, 1999; USGS, 1999; Robertson and Roerish, 1999; King and Harmel, 2003; Harmel et al., 2003; Harmel and King, 2005; Miller et al., 2007; Rode and Suhr, 2007). In addition, the definition of storm occurrence as it relates to the determination of sample collection timing also introduces uncertainty in storm water data (Harmel et al., 2002).

1.3. Uncertainty in sample preservation/storage

Considerable research has established that nutrient forms and concentrations can be altered during the interval between sample collection and analysis and that water chemical and biochemical characteristics affect the magnitude and rate of alteration (Fitzgerald and Faust, 1967; Johnson et al., 1975; Lambert et al., 1992; Robards et al., 1994; Haygarth et al., 1995; Jarvie et al., 2002). The increased use of automated samplers since the 1990s has magnified the potential for substantial alterations because of the time delay between sample collection and retrieval (Kotlash and Chessman, 1998). Therefore, quality assurance often focuses on sample preservation and storage procedures to minimize physical, chemical, and biological transformation and thus reduces uncertainty. Preservation and storage procedures typically utilize cold, dark storage environments and/or chemical preservatives; however, container characteristics and filtration methodology can also influence post-collection nutrient transformations (Henriksen, 1969; Ryden et al., 1972; Latterell et al., 1974; Skjemstad and Reeve, 1978; Fishman et al., 1986; Maher and Woo, 1998; Kotlash and Chessman, 1998; Haygarth and Edwards, 2000; Jarvie et al., 2002).

1.4. Uncertainty in laboratory analysis

The uncertainty introduced in water quality data by various analytical procedures to determine constituent concentrations also receives considerable quality assurance focus to reduce uncertainty (Ramsey, 1998). Recent efforts such as the North American Proficiency Testing program have contributed valuable data and insight into analytical uncertainty by quantifying differences in results across laboratory techniques and locations. The main sources of laboratory uncertainty are associated with sample handling, chemical preparation, analytical method and equipment, and calibration standards and reference materials (Robards et al., 1994; Gordon et al., 2000; Ludtke et al., 2000; Mercurio et al., 2002; Jarvie et al., 2002; CAEAL, 2003). The relative uncertainty associated with sediment concentrations is typically low because only basic filtration and/or mass determination are necessary. The uncertainty

introduced by nutrient analysis is typically greater than for sediments because of added steps and increased analytical complexity. Relative uncertainties, which are typically inversely related to ambient concentrations, are generally least for sediment, more for total N, total P, and $\text{NO}_3\text{-N}$, and greatest for $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$ (Horwitz et al., 1980; Meyer, 2002; Harmel et al., 2006a).

1.5. Development and initial application of the uncertainty estimation framework

According to Beven (2006a), the first step in advancing hydrologic and water quality science related to data uncertainty is determining realistic methods of representing that uncertainty. The value of uncertainty information, as well as the scientific integrity of communicating that information, prompted Harmel et al. (2006a) to make this initial step by developing a framework for quantifying the uncertainty in measured discharge and sediment, N, and P load and concentration data collected at the field and small watershed scale.

The framework foundation consists of: 1) establishment of categories within which to classify monitoring procedures (discussed previously) and 2) presentation of an accepted method for estimating cumulative uncertainty in individual (single) measured values resulting from component uncertainties within procedural categories (Harmel et al., 2006a). The framework utilizes the root mean square error (RMSE) method to propagate uncertainty from each component to estimate the cumulative uncertainty in individual discharge, concentration, and load values.

The framework was initially applied to estimate the cumulative uncertainty for a variety of arbitrary “data quality” scenarios (Harmel et al., 2006a). While several researchers (e.g. Gentry et al., 2007; Keener et al., 2007; McCarthy et al., 2008; Quansah et al., 2008) have accepted and applied this framework, it can be cumbersome to apply repeatedly by hand to data sets with multiple values for multiple parameters. Therefore, the objective of this manuscript was to demonstrate the application of the Data Uncertainty Estimation Tool for Hydrology and Water Quality (DUET-H/WQ), which was based on this established framework. The utility and limitations of DUET-H/WQ were explored by its application in several case studies with real-world monitoring data.

2. Method and software description

2.1. DUET-H/WQ development

DUET-H/WQ was designed to be a user-friendly application of the uncertainty estimation framework developed by Harmel et al. (2006a). Both DUET-H/WQ and its framework-basis were developed to estimate uncertainty in individual discharge, concentration, and load values, which are typically collected periodically (e.g. weekly), continually (e.g. hourly), or as storm event totals. It should be noted that load values are not measured directly but are calculated as the product of incremental discharge volumes and corresponding concentrations. Both DUET-H/WQ and its framework-basis focus on measured discharge, sediment, and N and P (dissolved and particulate) data collected at the small watershed scale.

2.1.1. Data processing and management procedural category

The first step in developing DUET-H/WQ was adding a procedural category “data processing and management” to the Harmel et al. (2006a) framework. The original procedural categories focused on sampling uncertainty resulting from random variation from the actual value and assumed appropriate use of accepted procedures; therefore, uncertainty contributed by equipment malfunction or personnel mistakes was not included. The potential

importance of uncertainty due to missing or incorrect values later became apparent, and the data processing and management procedural category was added. This allowed quantitative estimates for uncertainty contributed by missing and/or incorrect data to be included in cumulative uncertainty estimates.

2.1.2. RMSE propagation method

The foundational mathematical component of the software is the RMSE propagation method (Topping, 1972). The RMSE method was selected based on its simplicity, which was important to broad-scale application, and on its acceptance and previous application as a valid error propagation methodology in hydrologic and water quality science. The RMSE method, which formed the mathematical basis of the uncertainty estimation framework of Harmel et al. (2006a), is used by USGS for uncertainty estimation in individual discharge measurements (Sauer and Meyer, 1992) and has been applied in hydrologic and water quality uncertainty analyses by Cuadros-Rodriguez et al. (2002), Cooper (2002), and Allmendinger et al. (2007).

The RMSE method estimates the “most probable value” of the cumulative or combined error by propagating the error from each procedure (Topping, 1972). The resulting cumulative probable error, hereby called uncertainty, is defined as the square root of the sum of the squares of the maximum values of the separate errors. This probable error estimate is often reported with, or instead of, the maximum error, which is the simple sum of the maximum values of component errors. Thus in DUET-H/WQ, the maximum errors for each step (or source of uncertainty) within each procedural category (Table 1) are propagated to estimate the cumulated probable uncertainty in each measured discharge, concentration, or load value (Eq. (1)). Whereas errors were assumed to represent the 0.68 significance level (1 standard deviation for the normal distribution) by Sauer and Meyer (1992), the 0.9999 significance level (3.9 standard deviations) was assumed in the present research based on Harmel and Smith (2007).

The RMSE calculation, when applied to estimate the uncertainty of individual measured values, assumes that uncertainty introduced by each procedure is symmetrical about the measured value and thus bi-directional with equal likelihood of over- and under-estimation (Topping, 1972). Although little relevant information is available to support or refute this assumption, it is a reasonable expectation for most discharge and water quality data. A noteworthy exception is sediment concentration measured from a single location in the cross-section, since these data tend to be biased due to vertical stratification.

Table 1

Data collection procedures (sources of uncertainty) in typical monitoring projects.

Discharge measurement (Q)	Sample preservation/storage (PS)
Individual discharge measurement	Duration from sample collection until retrieval
Continuous discharge measurement	Sample preservation/storage prior to retrieval
Continuous stage measurement	Duration from sample retrieval until analysis
Effect of streambed condition	Sample preservation/storage prior to analysis
Sample collection (C)	Laboratory analysis (A)
Sample collection method	Quality of standards
Sampling frequency (interval)	Pre-analytical processing
Discrete or composites sampling	Standard relationship to determine concentration
Minimum storm threshold (storm sampling only)	Accuracy of analytical procedure/equipment
Data processing and management (DPM)	
Missing data	
Incorrect values	

$$EP = \sqrt{\sum (E_Q^2 + E_C^2 + E_{PS}^2 + E_A^2 + E_{DPM}^2)} \quad (1)$$

where EP is the cumulative probable error or uncertainty for individual measured values ($\pm \%$), E_Q = uncertainty in discharge measurement ($\pm \%$), E_C = uncertainty in sample collection ($\pm \%$), E_{PS} = uncertainty in sample preservation/storage ($\pm \%$), E_A = uncertainty in laboratory analysis ($\pm \%$), and E_{DPM} = uncertainty in data processing and management ($\pm \%$).

The Topping (1972) method also assumes that the uncertainties for various procedures are independent (not that measured values are uncorrelated, as discharge and concentration values are often correlated especially in large rivers). Literature on this subject is notably absent; however, several publications present or imply relevant information. Sauer and Meyer (1992) provide an in-depth discussion of procedures necessary to make individual discharge measurements and imply that procedural uncertainties are uncorrelated. Cuadros-Rodriguez et al. (2002) also imply lack of correlation between procedural steps in pesticide analytical procedures. Kotlash and Chessman (1998) confirm that uncertainties in nutrient analysis procedures are related to sample concentrations, but the authors do not state or imply any correlation between procedural uncertainties. Thus, in lieu of relevant published correlation data, uncertainties for flow and concentration measurement procedures are assumed to be uncorrelated in the present application. It should be noted, however, that additional research is needed to enhance scientific understanding and provide relevant information on hydrologic and water quality measurement uncertainty.

The RMSE method is certainly not the only viable alternative to estimate cumulative uncertainty for individual values. More complex statistical methods could also be applied, but their application requires information related to the selection of appropriate uncertainty distributions and corresponding distributional parameters for each procedure. Thus, since relevant distributional information is limited, unsubstantiated assumptions would be necessary for more complex uncertainty propagation. While it is important for the software to be simple and user-friendly in its initial application (especially in the current environment where uncertainty analyses are rarely conducted and relevant information is limited), future versions can include more complex statistical methods and thus better represent potential serial correlation, asymmetrical distributions, and value-uncertainty correlation.

2.2. DUET-H/WQ application

The first step in applying DUET-H/WQ to estimate the uncertainty for individual discharge, concentration, and load values is to select the procedures utilized to determine that value. To accomplish this, the user selects the appropriate procedures used and/or monitoring conditions encountered from the appropriate DUET-H/WQ look-up tables for the discharge measurement, sample collection, sample preservation/storage, and laboratory analysis procedural categories (Fig. 1a–d). For each procedural category, a DUET-H/WQ look-up table lists the common procedures utilized and monitoring conditions encountered along with published uncertainty estimates. These tables are based on Harmel et al. (2006a), which provides a detailed description of data collection procedures and associated uncertainties within each procedural category. Then, the user selects an uncertainty estimate based on published data displayed by the software (Fig. 1a–d). The user can adjust these uncertainty estimates based on project-specific information and/or professional experience. DUET-H/WQ then calculates the uncertainty introduced by each procedural category and allows the user to input the uncertainty contributed by project-specific data processing and management

issues (Fig. 1e). Finally, DUET-H/WQ calculates the cumulative probable uncertainty for individual discharge, concentration, or load values (Eq. (1)). The user can choose to apply that same uncertainty estimate to other data collected with the same procedure and under similar conditions or to repeat the procedure for other measured values to account for relationships between data characteristics (such as magnitude) and measurement uncertainty. In situations where little/no information is available on the procedures used and conditions encountered, the software also gives the user the choice of using default uncertainty estimates based on Harmel et al. (2006a).

2.2.1. Issues related to DUET-H/WQ application

In applying DUET-H/WQ, several important issues (e.g. user-subjectivity and temporal/spatial variability) should be kept in mind. The process by which users determine a reasonable uncertainty estimate for each procedure is quite subjective because of the considerable variability of published uncertainty information as affected by study design, collection methods, and monitoring conditions. In the face of this subjectivity, users should strive to make the most accurate uncertainty estimate possible for each data collection procedure. The benefits of uncertainty estimates corresponding to measured data cannot be fully achieved if uncertainty is purposefully under-estimated in an attempt to make data appear to be “better” or less uncertain. As the subsequent results show, even data collected with concerted quality assurance can have appreciable uncertainty.

DUET-H/WQ does not include all sources of uncertainty (e.g. uncertainty contributed by spatial and temporal variability). Such uncertainty sources were excluded to maintain a focus on uncertainty estimation for individual measured values. DUET-H/WQ does, however, provide necessary inputs, specifically measurement uncertainty, for comprehensive uncertainty analyses conducted with watershed models or other geospatial-statistical tools.

3. Description of case studies

3.1. Measured data sets

The uncertainty estimation framework was initially applied to arbitrary best case, worst case, and typical scenarios in Harmel et al. (2006a). While those uncertainty estimates are reasonable in the absence of project-specific information, it was also important to apply the software to real-world monitoring data to demonstrate its ability to quantify project-specific data uncertainty. Thus, DUET-H/WQ was applied to measured data from small watersheds in Texas (Riesel, Hamilton, and Austin), Indiana (Waterloo), and Ohio (Centerburg). Studies with a wide range of monitoring conditions (e.g. hydrologic setting, land use, and watershed size, as described in Table 2) and field and laboratory techniques were selected to demonstrate the software’s broad applicability.

3.1.1. Riesel, Texas

The Riesel, Texas, sites are field-scale (Y8) and farm-scale (Y2) watersheds characterized by ephemeral to intermittent well-mixed flow conditions. In 2004–2006, flow and storm water quality data were collected with an ISCO 6700 automated sampler and 730 bubbler module (Teledyne ISCO, Inc., Lincoln, Nebraska). Storm water samples were collected with a single-bottle, composite, flow-interval (1.32 mm) sampling strategy. Each of these sites utilizes a combination of Columbus shallow notch weir and Parshall flume structure with well-established, stable stage–discharge relationship. Collected samples were not preserved but were retrieved from the field within 24 h of storm completion. Total suspended solid (TSS) concentrations were determined by mass after drying for 24 h at 110 °C. NO₃-N and PO₄-P concentrations were determined with

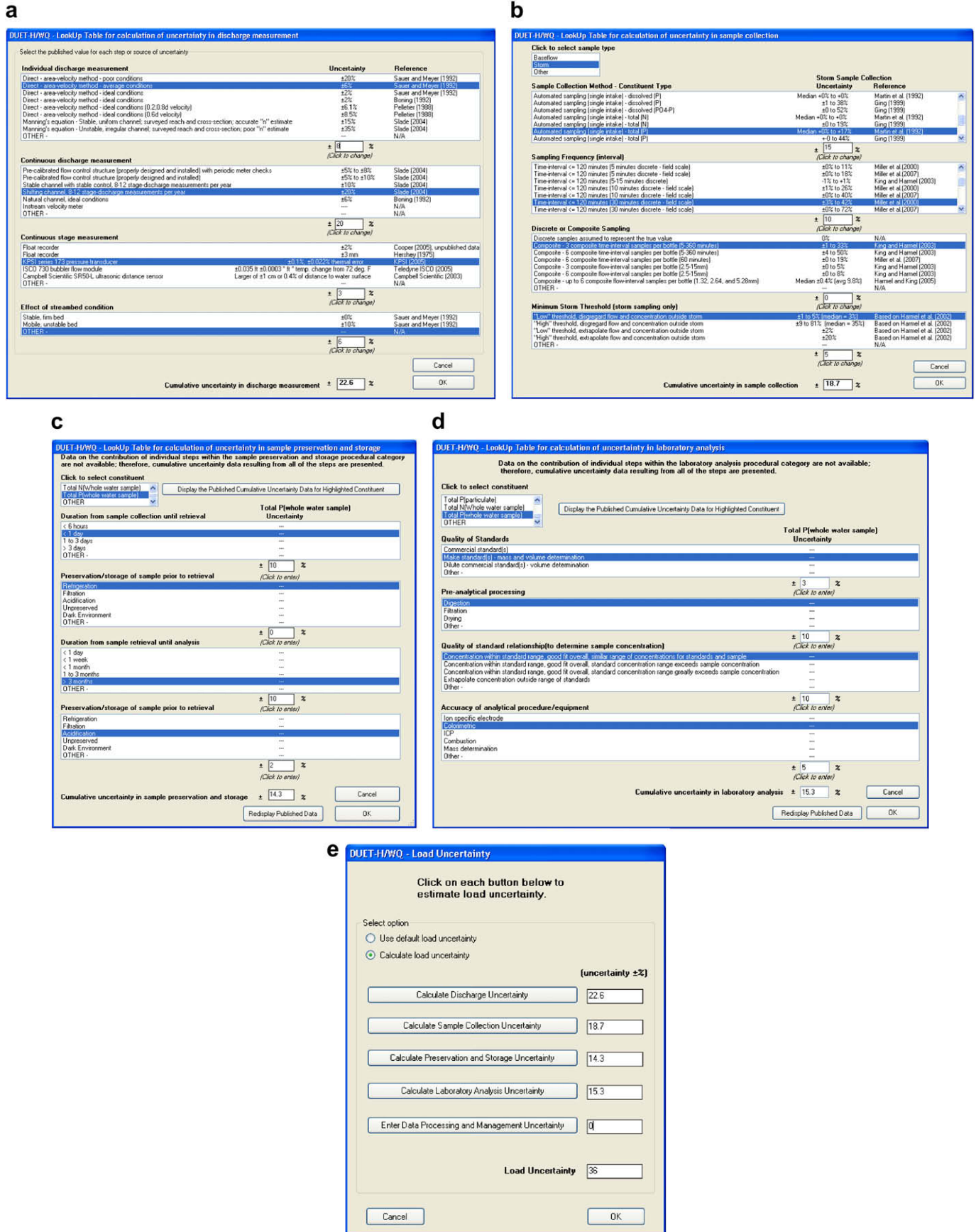


Fig. 1. Application of DUET-H/WQ to the measured total P load for site ALG in the May 9, 2004 storm event; a) discharge measurement uncertainty, b) sample collection uncertainty, c) sample preservation/storage uncertainty, d) laboratory analysis uncertainty, and e) cumulative uncertainty in the measured load.

Table 2

Watershed conditions and measured storm discharge with cumulative probable uncertainty estimates for discharge totals within study periods.

Site name (location)	Area (ha)	Land use	Monitoring period (s)	Measured discharge	Storm events (n)
Y8 (Riesel, Texas)	8.4	Agricultural (corn)	Aug 2004–Jul 2005	163 mm ($\pm 8\%$)	6
			Aug 2005–Jul 2006	124 mm ($\pm 10\%$)	4
Y2 (Riesel, Texas)	53.4	Mixed agricultural	Aug 2004–Jul 2005	225 mm ($\pm 7\%$)	9
Mustang Creek (Hamilton, Texas)	5506	Mixed agricultural	Jan 2005–Dec 2005	95 mm ($\pm 14\%$)	6
AS1 (Waterloo, Indiana)	2.2	Agricultural (corn – tile drained)	Apr 2004–Nov 2004	30 mm ($\pm 5\%$)	13
CME (Waterloo, Indiana)	373	Mixed agricultural (tile drained), forest	Apr 2005–Nov 2005	3 mm ($\pm 19\%$)	5
			Apr 2006–Nov 2006	104 mm ($\pm 5\%$)	16
ALG (Waterloo, Indiana)	2228	Mixed agricultural (tile drained), forest	Apr 2004–Nov 2004	107 mm ($\pm 7\%$)	14
S2 (Austin, Texas)	66.5	Mixed urban (golf course, airport, residential)	Jan 2000–Dec 2000	291 mm ($\pm 5\%$)	26
D1 (Centerburg, Ohio)	428	Mixed agricultural, forest	Jan 2006–Dec 2006	396 mm ($\pm 2\%$)	32

a 2003 OI Analytical, Flow IV, rapid flow colorimetric analyzer (OI Analytical, College Station, Texas). The N and P content of sediment was determined by a semimicro-Kjeldahl digestion procedure.

3.1.2. Hamilton, Texas

The Mustang Creek site near Hamilton, Texas, is located at the outlet of a small rural watershed and is characterized by intermittent flow conditions. The site has a low water dam (~ 10 m wide), which served as a hydraulic control. In 2005, storm water samples were collected with an ISCO 6700 automated sampler (Teledyne ISCO, Inc., Lincoln, Nebraska) and a 24-bottle, discrete, flow-interval (2.54 mm) sampling strategy. Continuous stage measurements were made with a 730 bubbler module and translated into flow measurements with a stage–discharge relationship established from a series of flow and stage measurements. Collected samples were not preserved in the field but were retrieved from the field within 24 h of storm completion. TSS concentrations were determined by mass after drying for 18–24 h at 116 °C. $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations were determined with a 2003 OI Analytical, Flow IV, rapid flow colorimetric analyzer (OI Analytical, College Station, Texas). The N and P content of sediment was determined by a semimicro-Kjeldahl digestion procedure.

3.1.3. Austin, Texas

The Austin, Texas, site (S2) is located on a small urban watershed with perennial flow contributed by irrigation return flow. In 2000, storm water samples and corresponding discharge data were collected with an ISCO 6700 automated sampler and 730 bubbler module (Teledyne ISCO, Inc., Lincoln, Nebraska) with a 24-bottle, composite, variable time-interval (5–60 min) sampling strategy. Collected samples were not preserved but were iced and acidified upon retrieval within 24 h of storm completion. The samples were analyzed for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations with a Technicon Autoanalyzer and methods published by Technicon Industrial Systems (1973, 1976).

3.1.4. Waterloo, Indiana

Flow and storm water quality data were collected from 2004 to 2006 for three sites near Waterloo, Indiana. At the ephemeral field-scale site (AS1), a drop-box weir (~ 2.5 m) hydraulic control was installed, and the associated stage–discharge relationship was used to estimate flow. At the larger-scale, perennial flow sites (CME, ALG) in drainage canals (~ 2 m wide), flow was estimated with an established stage–discharge relationship prior to 2006 and with an ISCO 2150 area–velocity meter (Teledyne ISCO, Inc., Lincoln, Nebraska) in 2006. Aquatic vegetation growth and die-off did contribute to uncertainty in measured discharge at sites CME and ALG. At each site, storm water samples were collected with an ISCO 6700 automated sampler (Teledyne ISCO, Inc., Lincoln, Nebraska) and a 24-bottle, time-interval (30 min) sampling strategy with three samples composited in each bottle. Storm samples were retrieved within 24 h. At all sites, samples were stored in automatic chillers

prior to retrieval. Samples were split for dissolved or total nutrient analysis and frozen prior to analysis. For AS1, TSS concentrations were determined by mass after drying for 24 h at 110 °C. For all sites, filtered samples were analyzed for dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations with USEPA methods 353.1 and 365.2 (USEPA, 1983). Digested samples (including water and sediment) were analyzed for Total Kjeldahl N and P by USEPA methods 351.2 and 365.4 (USEPA, 1983) after mercuric sulfate digestion of the unfiltered samples. All analyses were conducted colorimetrically with a KoneLab Aqua-Chem20 (EST Analytical, Medina, Ohio).

3.1.5. Centerburg, Ohio

In 2006, flow along with storm and baseflow water quality data were collected at site D1 on the headwaters of Sugar Creek near Centerburg, Ohio. A Parshall flume (2.44 m) control structure was installed to improve flow measurement on this perennial flow site. Water samples were collected continuously with an ISCO 6712 automated sampler programmed with a flow-interval (1.0 mm) sampling strategy. Samples were composited four per bottle by the sampler and composited weekly in the lab. Continuous stage measurements were made with an ISCO 4230 Bubbler Flow Meter. In addition, an ISCO 2150 Area–Velocity sensor (Teledyne ISCO, Inc., Lincoln, Nebraska) was used to collect measure velocity and provide a secondary stage measurement. Samples were refrigerated in the field until retrieval. Following collection, all samples were handled according to USEPA methods 353.3 and 365.1 for N and P analysis, respectively (USEPA, 1983). Samples were stored below 4 °C and analyzed within 28 days. Samples were vacuum filtered through a 0.45 μm pore diameter membrane filter for analysis of dissolved nutrients. Concentrations of $\text{NO}_3 + \text{NO}_2\text{-N}$ and $\text{PO}_4\text{-P}$ were determined colorimetrically by flow injection analysis using a Lachat Instruments QuikChem 8000 FIA Automated Ion Analyzer (Hach Company, Loveland, Colorado). $\text{NO}_3 + \text{NO}_2\text{-N}$ was determined by application of the copperized-cadmium reduction, and $\text{PO}_4\text{-P}$ was determined by the ascorbic acid reduction method (Parsons et al., 1984). Total N and total P analyses were performed in combination on unfiltered samples following alkaline persulfate oxidation (Koroleff, 1983) with subsequent determination of $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$.

3.2. Uncertainty estimation for individual storm values

For each of ten case study data sets, DUET-H/WQ was used to estimate the uncertainty for each component in each procedural category and to estimate the cumulative uncertainty for individual measured storm event values. To compare procedural categories, the uncertainty introduced by each category was determined for individual discharge ($n = 131$) and concentration ($n = 510$) values measured in 131 storm events. To compare constituent types, the cumulative uncertainty for individual TSS, $\text{NO}_3\text{-N}$, $\text{PO}_4\text{-P}$, total N, and total P concentrations and loads were determined for each event. Because of the large number of measurements and corresponding

uncertainty estimates ($n > 1150$), results for the total P load measured from site ALG near Waterloo, Indiana, for the May 9, 2004 storm event were presented as an example (Fig. 1a–e).

3.3. Uncertainty estimation for aggregated data

Since aggregated data (e.g. weekly, monthly, annual, or study period) are typically reported instead of individual values, it was also important to estimate the uncertainty in aggregated data.

Another common error propagation method for determining uncertainty in a sum of values (Topping, 1972) was utilized to estimate the uncertainty in total flow and load data within study periods (Eq. (2)). The same equation is also valid for determination of uncertainty in an average; therefore, it was used to estimate the uncertainty in the average concentration values for each study period. The uncertainties for aggregated values were estimated by hand not with DUET-H/WQ because of its focus on individual values; however, future versions might include uncertainty estimation methods for both individual and aggregated values.

$$EP_{total} = \frac{100}{\sum_{i=1}^n x_i} \sqrt{\sum_{i=1}^n \left(x_i \times \frac{EP_i}{100} \right)^2} \quad (2)$$

where EP_{total} = cumulative probable error (\pm %) for the aggregated (sum or average) of n measured values, n = number of measured values with corresponding uncertainty estimates, x_i = i th measured value, and EP_i = cumulative probable error (\pm %) for i th measured value.

4. Results and discussion

4.1. Uncertainty estimation for individual values using DUET-H/WQ

4.1.1. Comparison of procedural categories

To compare procedural categories, the uncertainties introduced by each category were determined for individual storm discharge and concentration values. Fig. 2 presents these results grouped across all sites and by constituent type with dissolved N and P and total N and P further grouped, since little difference occurred between dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ or between total N and P. The uncertainties in discharge measurements for storm events ranged from 7 to 27% with a median of 14% (Fig. 2), which were similar to estimates of 6% by Keener et al. (2007) and 11–27% by Cooper

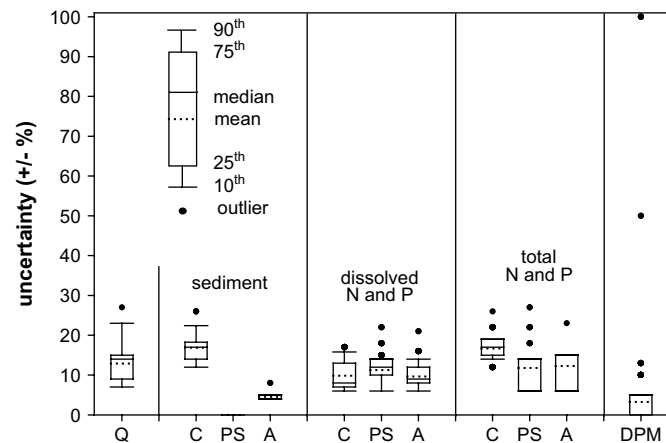


Fig. 2. Uncertainty introduced into storm event discharge and constituent concentration data by the five procedural categories (Q – discharge measurement; C – sample collection; PS – sample preservation/storage; A – laboratory analysis; DPM – data processing and management).

(2002). Since discharge measurement can contribute considerable uncertainty, accurate measurements are important to correctly quantify this fundamental driver of constituent flux.

Although the uncertainty in sample collection is often ignored, it can be the dominant source in environmental investigations (Ramsey, 1998). This was certainly the case for sediment and total N and P sample collection in the present study (Fig. 2). Collection of representative sediment and total N and P samples is quite difficult because streams can have substantial cross-sectional and vertical gradients in particulate-associated concentrations. In contrast, collection of dissolved N and P samples is quite easy since these constituents are typically uniformly distributed within the channel (Martin et al., 1992; Ging, 1999; Rode and Suhr, 2007). This difference was exemplified by greater sample collection uncertainties for sediment and total N and P concentrations, which ranged from 12 to 26%, than for dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations, which ranged from 6 to 17% (Fig. 2).

The uncertainty contributed by sample preservation/storage regularly receives considerable attention in quality assurance efforts to reduce uncertainty in water quality data (Lambert et al., 1992; Kotlash and Chessman, 1998; Jarvie et al., 2002). Results of the present study justify this attention in storm water sampling. For sediment concentration determination, sample preservation and storage are irrelevant because little post-collection transformation is possible. In contrast, uncertainties contributed by sample preservation/storage ranged from 6 to 22% for dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations and from 6 to 27% for total N and P concentrations (Fig. 2).

Similar to sample preservation/storage, laboratory analysis can be an important contributor to uncertainty in measured N and P concentrations (Jarvie et al., 2002; Meyer, 2002). For storm events, laboratory analysis introduced little uncertainty ($<8\%$) in sediment concentrations due to relatively simple analytical procedures but often introduced considerable uncertainty in N and P concentrations (Fig. 2). Whereas little difference occurred between the uncertainty contributed by sample collection and sample preservation/storage in dissolved and total N and P concentrations, an important difference occurred for laboratory analysis. Although laboratory analysis uncertainty was typically similar for dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations (range = 6–21%) and for total N and P (range = 6–15%), uncertainty increased to 23% for one event with very low total P concentrations (<0.05 mg/l). Kotlash and Chessman (1998) noted this influence on reference stream data with very low nutrient concentrations, which are sensitive to small absolute errors and result in high relative errors.

The data processing and management procedural category, which accounts for processing mistakes and missing values, was quite variable in these case studies (Fig. 2). The data processing and management activities that introduced uncertainty in measured data included sampler failure during portions of storm events, misplaced split subsamples, inadequate sample volume, inadequate sediment sample mass to determine associated nutrients, and separation of storm events and baseflow; all of which are common problems in monitoring projects. Data processing and management typically introduced $<5\%$ uncertainty, but missing and incorrect data did introduce 10–100% uncertainty in several cases (Fig. 2). The potential for high uncertainty in these cases emphasizes the importance of frequent preventative maintenance and operator training to minimize mistakes and missing values.

4.1.2. Comparison of constituent types

To compare constituent types, the cumulative uncertainties in concentrations and loads were determined for individual storms. Figs. 3 and 4 present these results grouped across all sites. For individual TSS values, the uncertainties in measured storm

concentrations ranged from 12 to 26% with a median of 18% (Fig. 3). Sediment load uncertainties ranged from 15 to 35% with a median of 20% (Fig. 4), which are similar to the 35% uncertainty estimated for sediment volume by Allmendinger et al. (2007) and the average load uncertainty of 18% reported by Harmel et al. (2006a). No sampler malfunction occurred during the study period for sites with TSS data, but uncertainty would have increased substantially for a few values (i.e. ~100% for other constituents as shown in Figs. 3 and 4) if samples had been missed. The uncertainties in TSS data were typically less than in other constituents because of limited post-collection transformation, simpler analytical procedures, and relatively high concentration values. It should be kept in mind, however, that only half of the measured data sets contained TSS data.

As stated in the previous discussion of procedural categories, little difference in uncertainty was evident between dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ (Figs. 3 and 4). The uncertainties in $\text{NO}_3\text{-N}$ concentrations ranged from 13 to 102% (median = 17%) and in $\text{PO}_4\text{-P}$ concentrations ranged from 13 to 103% (median = 19%). Load uncertainties ranged from 14 to 103% (median = 22%) for $\text{NO}_3\text{-N}$ and from 14 to 104% (median = 23%) for $\text{PO}_4\text{-P}$. Using the uncertainty estimation framework (RMSE method), Keener et al. (2007) estimated uncertainty to be 27% for $\text{PO}_4\text{-P}$ concentrations and 28% for $\text{PO}_4\text{-P}$ loads, and Gentry et al. (2007) estimated uncertainty to be <10% for P loads. Similarly, Harmel et al. (2006a) estimated load uncertainties to average 17% for $\text{NO}_3\text{-N}$ loads and 23% for dissolved P loads. The occasional high uncertainty estimates (~100%) in the present study resulted from extreme high flows and/or missing samples. The uncertainties in dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ data were typically greater than in TSS data in spite of uniform concentration distributions because of post-collection transformation potential, more complex analytical procedures, and lower concentration values.

Similar to dissolved $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$, little difference in uncertainty occurred between total N and total P (Figs. 3 and 4). Concentration uncertainties ranged from 14 to 104% (median = 23%) for total N and from 16 to 104% (median = 24%) for total P. Load uncertainties ranged from 15 to 105% (median = 25%) for total N and from 17 to 105% (median = 27%) for total P. The occasional high uncertainties again resulted from extreme high flows and/or missing samples. The uncertainties in total N and P data were typically greater than in TSS data because of more complex analytical procedures. Total N and P uncertainties were also greater than for dissolved N and P because of increased difficulty in collecting representative particulate samples and added

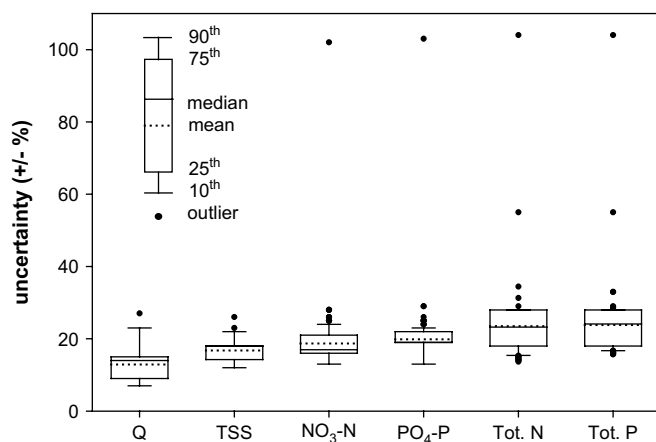


Fig. 3. Uncertainty in individual storm concentrations plotted with storm discharge uncertainty.

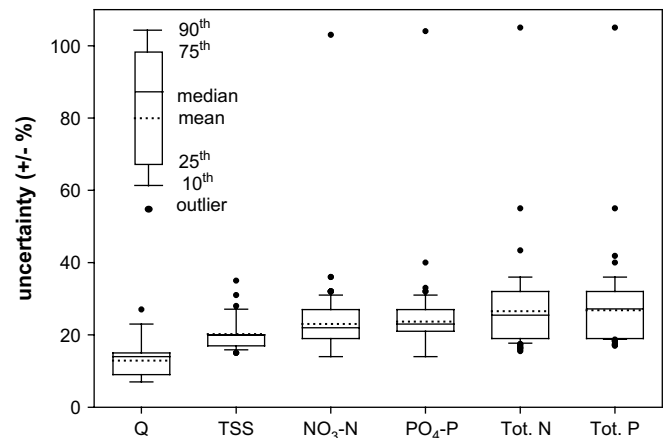


Fig. 4. Uncertainty in individual storm loads plotted with storm event discharge uncertainty.

analytical steps when total N and P were determined by summing dissolved and particulate fractions.

While the typical pattern of uncertainty across constituents ($Q < \text{TSS} < \text{dissolved N and P} < \text{total N and P}$) is important, the consistency of uncertainties across widely varying watershed conditions is equally noteworthy. Across all watersheds, the 10th and 90th percentiles for uncertainty in measured storm discharge were 7–23%; in concentrations were 12–22% for TSS, 13–24% for dissolved N and P, and 16–28% for total N and P; and in loads were 16–27% for TSS, 14–31% for dissolved N and P, and 18–36% for total N and P. Since no complete error propagation results have been previously published for real-world data, these results provide initial uncertainty estimates for field staff, modelers, stakeholders, and regulators to use in data analysis and decision-making.

It is important to note that the uncertainty of loads was always greater than or equal to the uncertainty in corresponding concentrations. Compared to concentration uncertainties, which are not affected by discharge uncertainty, load uncertainties averaged 21% more for TSS, 23% more for dissolved N, 19% more for dissolved P, 13% more for total N, and 12% more for total P. This increase occurs when loads are calculated as the product of discharge and concentration (as in the present study), since both discharge and concentration determinations contribute uncertainty. It would not be the case when load and flow data are reported without concentration data, and thus concentration would have to be estimated by dividing the load by the flow.

4.2. Uncertainty estimation for aggregated data

In addition to uncertainties for individual values, the uncertainties in total discharges, total loads, and average concentrations aggregated within study periods were also estimated and presented in Tables 2–4. The uncertainties in aggregated totals ranged from 2 to 19% for discharge, 10–27% for TSS loads, 5–30% for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$ loads, and 6–32% for total N and total P loads. The uncertainties in average concentrations ranged from 5 to 11% for TSS, from 3 to 13% for $\text{NO}_3\text{-N}$ and $\text{PO}_4\text{-P}$, and from 4 to 13% for total N and total P. This same pattern of increasing uncertainty ($Q < \text{TSS} < \text{dissolved N and P} < \text{total N and P}$) was observed in individually measured values. Note that when using equation (2) to estimate relative uncertainties for aggregated values (i.e. $\pm\%$ for sums and averages in the present application), uncertainties are smaller than for individual values. The opposite would have been true (aggregated > individual) if the absolute uncertainties ($\pm\text{mg/l}$ or $\pm\text{kg/ha}$) had been considered.

Table 3
Constituent loads with cumulative probable uncertainty estimates for load totals within study periods.

Site (time period)	TSS	NO ₃ -N	PO ₄ -P	Total N ^a	Total P ^a
Y8 (Aug 2004–Jul 2005)	1385 kg/ha (±10%)	13.6 kg/ha (±13%)	1.6 kg/ha (±16%)	16.4 kg/ha (±11%)	2.6 kg/ha (±11%)
Y8 (Aug 2005–Jul 2006)	1436 kg/ha (±21%)	10.2 kg/ha (±14%)	0.2 kg/ha (±13%)	12.8 kg/ha (±12%)	0.8 kg/ha (±17%)
Y2 (Aug 2004–Jul 2005)	627 kg/ha (±10%)	6.1 kg/ha (±12%)	0.8 kg/ha (±14%)	7.5 kg/ha (±10%)	1.1 kg/ha (±10%)
Mustang Creek (Jan 2005–Dec 2005)	550 kg/ha (±27%)	0.3 kg/ha (±13%)	0.1 kg/ha (±14%)	2.4 kg/ha (±27%)	0.2 kg/ha (±21%)
AS1 (Apr 2004–Nov 2004)	716 kg/ha (±11%)	2.7 kg/ha (±12%)	0.1 kg/ha (±12%)	0.7 kg/ha (±15%)	0.5 kg/ha (±15%)
CME (Apr 2005–Nov 2005)	na	<0.05 kg/ha (±30%)	<0.05 kg/ha (±27%)	0.1 kg/ha (±32%)	<0.05 kg/ha (±31%)
CME (Apr 2006–Nov 2006)	na	4.4 kg/ha (±12%)	0.1 kg/ha (±12%)	1.9 kg/ha (±11%)	0.3 kg/ha (±11%)
ALG (Apr 2004–Nov 2004)	na	9.0 kg/ha (±10%)	0.1 kg/ha (±10%)	2.2 kg/ha (±11%)	0.5 kg/ha (±12%)
S2 (Jan 2000–Dec 2000)	na	0.7 kg/ha (±8%)	0.5 kg/ha (±10%)	na	na
D1 (Jan 2006–Dec 2006)	na	14.3 kg/ha (±5%)	0.5 kg/ha (±6%)	18.8 kg/ha (±6%)	0.8 kg/ha (±6%)

^a Total N and P loads in storm events were determined from total N and P concentrations from total sample (including water and sediment) digests at the Indiana sites (AS1, CME, and ALG) and Ohio site (D1). At the Texas sites (Y8, Y2, and Mustang Creek), total N and P loads were determined as the sum of dissolved (NO₃-N, NH₄-N, and PO₄-P) and particulate loads.

Table 4
Constituent concentrations with cumulative probable uncertainty estimates for average concentrations within study periods.

Site (time period)	TSS	NO ₃ -N	PO ₄ -P	Total N ^a	Total P ^a
Y8 (Aug 2004–Jul 2005)	1075 mg/l (±5%)	7.1 mg/l (±12%)	0.7 mg/l (±9%)	9.3 mg/l (±9%)	1.6 mg/l (±8%)
Y8 (Aug 2005–Jul 2006)	1046 mg/l (±9%)	10.0 mg/l (±12%)	0.3 mg/l (±13%)	11.8 mg/l (±11%)	0.8 mg/l (±10%)
Y2 (Aug 2004–Jul 2005)	261 mg/l (±6%)	2.1 mg/l (±9%)	0.3 mg/l (±7%)	2.7 mg/l (±7%)	0.4 mg/l (±6%)
Mustang Creek (Jan 2005–Dec 2005)	518 mg/l (±11%)	0.4 mg/l (±11%)	0.1 mg/l (±12%)	2.3 mg/l (±13%)	0.3 mg/l (±12%)
AS1 (Apr 2004–Nov 2004)	2024 mg/l (±7%)	12.0 mg/l (±11%)	0.3 mg/l (±7%)	2.0 mg/l (±9%)	1.2 mg/l (±10%)
CME (Apr 2005–Nov 2005)	na	0.7 mg/l (±12%)	0.1 mg/l (±12%)	1.4 mg/l (±12%)	0.2 mg/l (±12%)
CME (Apr 2006–Nov 2006)	na	2.5 mg/l (±7%)	0.1 mg/l (±7%)	1.7 mg/l (±8%)	0.3 mg/l (±8%)
ALG (Apr 2004–Nov 2004)	na	7.9 mg/l (±6%)	0.1 mg/l (±6%)	1.9 mg/l (±8%)	0.4 mg/l (±9%)
S2 (Jan 2000–Dec 2000)	na	0.1 mg/l (±4%)	<0.05 mg/l (±6%)	na	na
D1 (Jan 2006–Dec 2006)	na	3.2 mg/l (±3%)	0.1 mg/l (±4%)	4.6 mg/l (±4%)	0.2 mg/l (±5%)

^a Total N and P concentrations in storm events were determined by total sample (including water and sediment) digests at the Indiana sites (AS1, CME, and ALG) and Ohio site (D1). At the Texas sites (Y8, Y2, and Mustang Creek), total N and P concentrations were determined as the sum of dissolved (NO₃-N, NH₄-N, and PO₄-P) and particulate concentrations.

5. Conclusions

Although most water monitoring agencies utilize quality assurance protocols to reduce uncertainty, few spend the time and effort to estimate and report data uncertainty. A simple, straightforward procedure to facilitate uncertainty estimation would produce multiple benefits associated with uncertainty information (e.g. enhanced monitoring design, decision-making, model application, and regulatory formulation). The Data Uncertainty Estimation Tool for Hydrology and Water Quality (DUET-H/WQ) was developed with these benefits in mind to be a user-friendly tool to assist data collectors and data users in estimating measurement uncertainty. It is our hope that DUET-H/WQ contributes to making uncertainty estimation a routine procedure in data collection and reporting. Hydrologic and water quality data are too important for scientists to continue to ignore the inherent uncertainty.

Both DUET-H/WQ and its framework-basis utilize the RMSE uncertainty propagation methodology. For its initial applications, the relatively simple RMSE method was preferred instead of more rigorous approaches requiring detailed statistical information, which is often unavailable for discharge and water quality data. Although the RMSE method does not provide the most rigorous uncertainty estimates, it is a widely accepted and should encourage broader practical application than statistical alternatives with unsubstantiated assumptions.

While all uncertainty analyses involve some degree of subjectivity, Pappenberger and Beven (2006) concluded that user-subjectivity should not preclude uncertainty analyses in hydrologic modeling. The same conclusion applies for uncertainty estimation in measured data. Reporting data uncertainty should be applauded, even in face of considerable uncertainty, as long as the estimation method is explicit and data have been collected using appropriate

procedures and quality assurance protocols as far as practicable. It is unrealistic to expect all monitoring programs to be conducted under ideal conditions with ample resources. As the present results have shown, data collected with concerted quality assurance can have appreciable uncertainty.

In the present research, the broad applicability of DUET-H/WQ was established by its application in case studies with diverse watershed conditions, which was important because its framework-basis had been applied to arbitrary “data quality” scenarios not real-world data. Results of the present application indicated that each procedural category (discharge measurement, sample collection, sample preservation/storage, laboratory analysis, and data processing and management) can contribute substantial uncertainty. Results also indicated that uncertainty is related to constituent type ($Q < \text{TSS} < \text{dissolved N and P} < \text{total N and P}$) for both individual storms and overall study periods. The uncertainty estimates presented for measured TSS, NO₃-N, PO₄-P, total N, and total P loads and concentrations provide fundamental information related to discharge and water quality data. Thus, a scientific basis is now available to answer such questions as: What is the typical uncertainty for measured storm NO₃-N loads? “14–31%.” What about TSS storm concentrations? “12–22%.” This information has immediate value in decision-making and scientific endeavor, especially since project-specific data are rarely available.

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