Measuring edge-of-field water quality: Where we have been and the path forward

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Abstract: Heightened pressure to demonstrate the resource benefits of conservation practices and continued high-profile water quality impairments and concerns are increasing the need to quantify edge-of-field (EOF) water quality. With this in mind, this manuscript summarizes previous developments in EOF water quality sampling and presents current research and glimpses into the future. This manuscript focuses on constituent sampling at the field-scale or at the "edge-of-field;" however, many of the findings are also applicable for small stream or small watershed sampling. With development of programmable automated samplers and initiation of numerous automated sampling projects, it became readily apparent that neither equipment manufacturers nor researchers could provide guidance on design components (e.g., sample initiation, timing/intervals, and type). This was problematic as available monitoring resources are too limited and data needs too great for such projects to be designed solely based on field experience and without a scientific basis or with complete disregard for potential data quality implications. Thus practical, science-based guidance for EOF sampling was developed and fundamental understanding of the inherent uncertainty was established to assist researchers, municipalities, consulting firms, and regulatory agencies improve data quality and monitoring resource efficiency. Looking to the future, further improvements are needed related to lower cost systems, practical improvements, and enhanced in situ sampling, along with enhanced understanding and consideration of data uncertainty in modeling and decision making.

Key words: decision making—monitoring—nonpoint source pollution—water quality

Water quality research and mitigation efforts are often constrained by the lack of adequate data on nonpoint source pollution, specifically constituent flux under differing soil, hydro-climatic, and land use and management conditions. The need for additional data is particularly important for watershed modeling, which often guides regulatory, programmatic, and management decision making (Sharpley et al. 2002; White et al. 2012, 2014; Black et al. 2014). Although watershed models, regional relationships, or professional judgment can provide useful information, measured field-scale data are needed to confirm and/or improve these estimates. The need for field-scale or "edge-of-field" (EOF) data appears to be increasing (figure 1), likely due to increased pressure to demonstrate the water quality benefits of conservation expenditures, evaluate long-standing and innovative practices, and address high-profile water quality

impairments and concerns (e.g., City of Des Moines, Iowa, Water Works [Henderson 2015]; Lake Erie [Borchardt 2015]).

With this increasing need in mind, this manuscript presents background information, which sets the stage for recent developments and summarizes how those developments advanced the science of EOF water quality sampling. In addition, current research and a glimpse into the future are presented. This article focuses on constituent sampling at the field scale or at the "edge-of-field" (~0.01 to 250 ha); however, many of the findings are also applicable at the small stream or watershed scale at which well-mixed conditions can be reasonably assumed such that water quality is adequately captured at a single intake point. Water quality sampling at this scale necessitates quantifying flux in surface runoff produced by precipitation excess and snowmelt, which can also be referred to as "wet weather" or stormwater sampling.

Background—Where We Have Been

Historical View of Edge-of-Field Sampling. To evaluate sampling equipment and collection methods used in EOF water quality sampling, the 67 field-scale studies of nitrogen (N) and phosphorus (P) runoff from agricultural land uses published from 1968 through 2014 were analyzed (MANAGE database; Harmel et al. 2016b). Manual sample collection and collection of samples by mechanical automated samplers were relied upon in the 1970s and 1980s (figure 1). Beginning in the 1990s, use of electronic (programmable) automated samplers (e.g., ISCO [Lincoln, Nebraska] and Sigma) increased substantially; however, mechanical automated samplers were still used, presumably in remote areas without power and/or as a low cost alternative (Parker and Busch 2013).

Need for Automated Sampling Guidance. Around the year 2000, researchers, consultants, and others tasked with water quality monitoring recognized the lack of and need for practical guidance on "wet weather" or stormwater sampling to assess nonpoint source contributions (McFarland and Hauck 2001; Harmel et al. 2003; Behrens et al. 2004). Extensive guidance on field techniques and quality control for manual sampling was available at that time for stream and river sampling (Wells et al. 1990); however, little guidance was available for the relatively new technology—electronic (programmable) automated water quality samplers.

The need for automated sampling guidance became clearly apparent as a rapidly growing number of studies began to deploy automated samplers (figure 1) to collect stormwater samples at the EOF and small watershed scale. Automated sampling

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Figure 1

Methods of sample collection for published field-scale water quality studies (Harmel et al. 2016b).
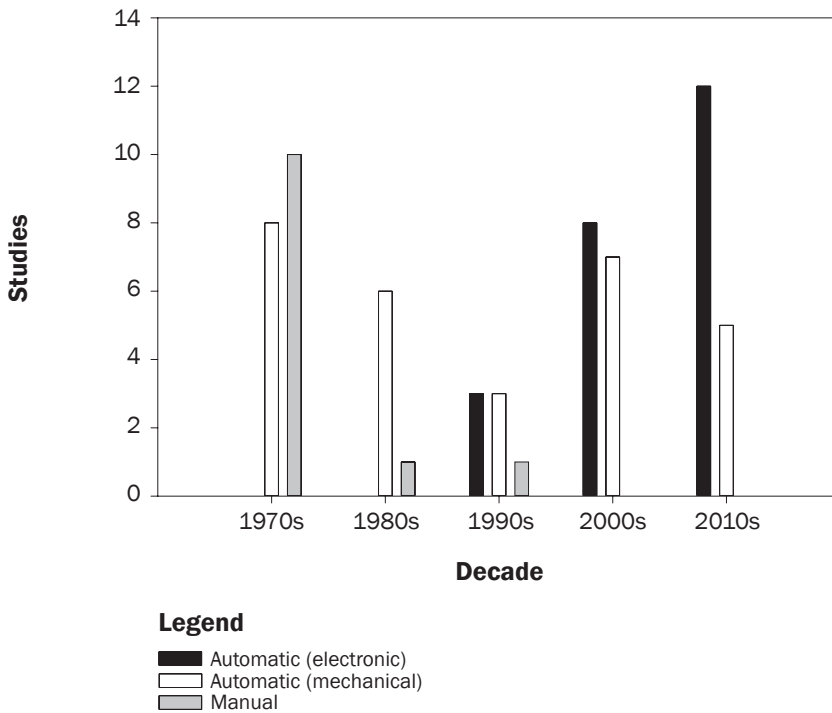
became the preferred alternative because manual storm sampling is very difficult for many reasons, including short runoff durations, remote site locations, inclement weather conditions, and expensive personnel requirements. Deploying automated samplers necessitated that researchers and technical staff examine published methods for collecting runoff water samples; however, researchers such as King et al. (2001) found that design components needed for programming these samplers had not been studied. Additionally, neither equipment manufacturers nor researchers could provide guidance on setting storm thresholds (when to initiate sampling), choosing the sample type (composite or discrete), or determining the sampling frequency (based on time or flow intervals). Since science-based guidance on technical components of automated sampling was not available, previous monitoring projects were ideally designed based on field experience, but too commonly with no regard for data quality and cost implications.

Whereas guidance documents (USDA 1996; USEPA 1997) provided valuable information on equipment types, monitoring plans, study design, and data analysis for EOF and small watershed sampling,

they did not address these technical design components. Although mechanical automated samplers had been developed years before to sample at these smaller scales (Geib 1933; Parsons 1954, 1955; Allen et al. 1976; Claridge 1975; Edwards et al. 1976; Sheridan et al. 1996; Bonta 1999), previous research focused on installation and operation of the mechanical samplers.

Automated Samplers (Mechanical). Mechanical automated samplers have been utilized for decades for numerous applications at the EOF and small watershed scale. Chickasha samplers collect time-weighted samples when activated by a float water level switch (Allen et al. 1976). In contrast, rotating slot samplers and multislot divisor samplers collect flow-weighted samples and estimate flow volume, event mean concentrations (EMCs), and constituent loads. The Coshocton wheel sampler is a rotating slot sampler that was designed and developed by W.H. Pomerene (Parsons 1954, 1955) and has been used in many sampling projects. It does not require electric power or extensive maintenance (Edwards et al. 1976). Bonta (1999, 2002) modified the original Coshocton sampler to accommodate flow with high sediment concentrations

and large sediment particles. Malone et al. (2003) modified the rotating slot sampler to collect flow-weighted samples from various flow conditions from tile drains, springs, or lysimeters (i.e., slow drips to continuous flows). Variations of the Geib (1933) multislot sampler have also been used for various flow and topographic conditions (Sheridan et al. 1996; Franklin et al. 2001; Pinson et al. 2003). Another type called siphon samplers or single-stage samplers were developed by the Inter-Agency Committee on Water Resources, Subcommittee on Sedimentation (ICWR-SS 1961) to collect a sample of near-surface water during the hydrograph rising limb. Siphon samplers are simple, inexpensive alternatives, but have several limitations as described by Edwards and Glysson (1988) and Graczyk et al. (2000).

Development of Guidance for Automated Sampling. In the 1990s and 2000s, substantial research focused on the impact of various sampling strategies and load estimation techniques on perennial streams and rivers (Cohn et al. 1989; Rekolainen et al. 1991; Preston et al. 1992; Robertson and Roerish 1999; Stone et al. 2000; Haggard et al. 2003; Robertson 2003), but a few others (Agouridis and Edwards 2003; Toor et al. 2008) conducted similar research at smaller scales. Previous research comparing time and flow-weighted composite sampling (Shih et al. 1994; Izuno et al. 1998) and evaluating the effects of sample timing and frequency (Tate et al. 1999; Wang et al. 2003) set the stage for research on design components for automated sampling.

The growing awareness of the need for research and practical knowledge around the year 2000 prompted experienced professionals (McFarland and Hauck 2001; Behrens et al. 2004) to begin sharing practical recommendations related to automated sampling at these smaller scales. This influenced researchers to launch concerted research programs to provide the scientific basis to complement practical knowledge, which produced a substantial body of literature on EOF and small watershed sampling (King and Harmel 2003, 2004; King et al. 2005; Miller et al. 2007; Stuntebeck et al. 2008; Harmel et al. 2002, 2003). This work was compiled and used to establish sampling protocols (Harmel et al. 2006a) for the USDA Conservation Effects Assessment Project (CEAP) (Mausbach and Dedrick 2004).

Automated Samplers (Electronic). The science-based and practical guidance on automated sampling at the EOF and small watershed scale is summarized subsequently. The storm sampling threshold is an important design component because sample collection begins and typically continues throughout the duration of flow above this threshold or until flow stops. Thus, the sampling threshold plays an important role in the number of samples collected and the proportion of the runoff that is sampled. Harmel et al. (2002) suggested that increasing the storm sampling threshold introduces substantial uncertainty; therefore, thresholds should be set low enough to sample the vast majority of the storm event. In general, if runoff produces water deep enough to sample, then sampling should commence.

The sample collection intake should be firmly fixed in well-mixed flow in the channel center in a run/riffle, not a pool, or upstream of the local hydraulic control. To prevent pump malfunction, locate the sampler intake such that it is completely submerged when flow reaches the storm sampling threshold. At EOF sites, it is safe to assume a single intake adequately captures constituent concentrations because of well-mixed and shallow flow conditions (McCarthy et al. 2008, 2009). However, potential concentration gradients should be considered, especially for constituents commonly associated with larger particulates (Taylor et al. 2005; Harmel et al. 2003, 2006a). Although it is likely unnecessary at EOF sites, a vertical intake with multiple entry points or a depth-integrated sampling arm could be employed to better capture vertical concentration gradients (Gettel et al. 2011; Selbig et al. 2012). Where this is not feasible, the relationship between concentrations at the intake and in the total cross-section can be established for the range of expected discharges (Ging 1999). Then, intake concentrations can be corrected to represent the actual cross-sectional concentration; however, these relations can change over time, requiring subsequent adjustment (R. Slade, personal communication, 2005).

Sample tubing should be installed such that a continuous negative gradient (downhill slope) occurs to facilitate drainage of residual water after sample collection to minimize the build-up of sediment and other constituents (Boyer and Kuczynska 2003; Hathaway et al. 2010, 2014). It is also important to ensure the sample tube is securely attached, covered from direct sunlight, and does not block flow. Raising the intake slightly off the channel bottom will mitigate this, while not impacting the representativeness of subsequent samples (although this may increase the storm sampling threshold). Pre- and post-collection tube rinsing and purging (one to two cycles) is also recommended to clean the sample tube between samples and between events (Solo-Gabriele et al. 2000; Hach 2008). Alternatively, the sample tube can be cleaned (be careful to remove residual soap or disinfectants) or replaced regularly, but these options are costly and labor intensive.

The timing and frequency of sample collection are also important design components, as automated samplers can be programmed to take samples on time or flow volume intervals. With time-weighted sampling, samples are taken on time increments, such as every 30 minutes. Time intervals are easy to measure accurately and clock failures are rare; however, with short time intervals, frequent sampling can quickly exceed sampler capacity, causing much of the runoff event to be missed. Although time-weighted sampling does not rely on discharge measurement to determine sampling intervals, discharge data are needed to calculate constituent loads. With flow-weighted sampling, samples are collected based on flow volume (e.g., 5,000 m³). Establishing flow-weighted sampling intervals in terms of volumetric depth (e.g., 2 mm runoff depth based on watershed area) facilitates consistent sampling frequency for different sized watersheds. Flow-weighted sampling does require continuous flow measurement but readily produces the commonly reported EMC. The constituent load for a particular event can be readily determined as the product of the EMC and the total flow volume.

Several studies have shown that small/short sampling intervals should be used to better characterize water quality (Richards and Holloway 1987; Shih et al. 1994; Miller et al. 2000; Leecaster et al. 2002; King and Harmel 2003, 2004; Harmel and King 2005); however, the intervals must also consider the importance of sampling throughout long duration/large volume events. King and Harmel (2003) and Harmel et al. (2003) provide guidance on selecting time and volume intervals for automated sampling on small catchments, and King et al. (2005) developed a procedure to determine sampling intervals based on catchment and constituent characteristics. Although Harmel and King (2005) concluded that volumetric depth intervals up to 6 mm may be appropriate in certain conditions, smaller intervals (1 to 2.54 mm) are more widely applicable. These smaller volumetric depth intervals allow smaller storm events to be sampled and moderate to large storm events to be sampled more intensively with little to no increase in uncertainty, especially if composite sampling is utilized.

The choice between discrete versus composite sampling is another important design component. Automated samplers typically can collect discrete samples (one per bottle) or composite samples (two or more subsamples per bottle). Discrete sampling best captures temporal concentration variability within events to better understand system dynamics, but it increases uncertainty in long duration/large volume events if sampler capacity is exceeded prior to the end of the event. In contrast, composite sampling allows longer duration/larger volume events to be sampled throughout (McFarland and Hauck 2001). Because these sampling methods produce either individual (discrete) or aggregated (composite) data, the choice between the two will depend on study goals and data quality needs.

Composite automated sampling increases sampler capacity by placing two or more subsamples in each bottle, making it a valuable, cost-saving alternative. Composite sampling introduces less error than increasing minimum flow thresholds or increasing sampling intervals, especially for volume-proportional sampling (Miller et al. 2000; Harmel et al. 2002; King and Harmel 2003; Harmel and King 2005). Composite strategies are valuable for projects designed to quantify average concentrations or total loads. Composite flow-weighted sampling with a single-bottle is an effective strategy for reducing analytical costs while intensively sampling entire events (Shih et al. 1994; Harmel et al. 2003, 2006a). With this strategy, many 100 to 200 mL subsamples can be composited into a single sample to produce the EMC. For composite sampling, subsample volumes of at least 100 to 200 mL are recommended because smaller volumes are difficult to accurately pump (Harmel et al. 2006a). Alternatively, unnecessarily large sample aliquots should be avoided because pumping large volumes can take two to seven minutes per sample (depending on

the pumping rate, head, and tubing length), which can result in missed samples.

Composite samples can also be produced in the lab from discrete field samples (McCarthy et al. 2008). To manually composite samples from discrete flow-weighted samples, withdraw and combine equal-volume subsamples. For discrete time-weighted samples, withdraw and combine subsample volumes proportional to the flow during the time interval. Manual compositing requires considerable postprocessing time and effort but does allow considerable flexibility. For example, each discrete sample can be analyzed for one constituent, while the composite sample can be analyzed for others. Similarly, manual compositing can minimize errors associated with sampler failure during an event (i.e., missing one sample in a volume-proportional, composite strategy will increase uncertainty as the volume sampled is no longer accurate; while manual compositing can compensate for missed samples).

Other practical guidance has emerged concurrently with the science-based recommendations regarding technical sampling components, and both are critical for successful EOF and small watershed sampling. The practical recommendations begin with a sincere acknowledgment that EOF runoff sampling is difficult, time consuming, and expensive (Agouridis and Edwards 2003; Harmel et al. 2006a). Additionally, gathering all available site-specific information and previous data and determining the type and amount of data to collect and equipment required is essential to estimate personnel and budget requirements. Although automated electronic samplers can sample consistently at multiple sites and take multiple samples throughout storm events, they are much more expensive than mechanical samplers. In addition, they are far from trouble-free, thus proactive maintenance and prompt repair is necessary to limit equipment malfunction and data loss (USDA 1996; USEPA 1997; Harmel et al. 2006a). Maintenance should be performed weekly or biweekly, whether for remote or readily accessible sampling sites. Routine maintenance should include inspection of the power source, pump tube, sample intake, and desiccant; calibration of the stage recorder to ensure flow measurement accuracy; and data retrieval to avoid data loss in potential power failures or equipment malfunctions.

EOF sampling sites are best established at the field boundary, preferably within the natural drainage way (USDA 1996); however, construction of small earthen berms/barriers may be necessary to direct runoff to a single outlet. Precalibrated hydraulic control structures (established stage-discharge relationship) are highly recommended (Holtan et al. 1962; Harmel et al. 2006a). Proper installation and maintenance are critical for accurate discharge measurement (Stuntebeck et al. 2008; Komiskey et al. 2013). Shelters should be built to house and protect sampling equipment from natural threats, vandalism, and theft, and they should be accessible during wet weather (Haan et al. 1994; USEPA 1997). The shelter location should be as close to the sample intake as possible to reduce pumping distances (Stuntebeck et al. 2008). Livestock, rodents, and insect access to equipment shelters, electric lines, communication cables, and sample tubes should be controlled to avoid equipment damage and sample contamination.

Successful EOF water quality sampling relies on committed, on-call field staff trained in quality assurance/quality control (QA/QC) methods, equipment operation and maintenance, hydrology, and safety (USEPA 1997). In addition to routine maintenance, personnel should go to sampling sites as soon as feasible after events based on QA/QC guidelines to collect data, retrieve samples, maintain equipment, and conduct necessary repairs.

Uncertainty of Edge-of-Field Data. Much of the research and practical guidance on EOF and small watershed sampling presents a similar conclusion, specifically that project success is determined by achieving a proper balance between monitoring resources and the quality of resulting data (Shih et al. 1994; Tate et al. 1999; Agouridis and Edwards 2003; Abtew and Powell 2004; King et al. 2005; Harmel and King 2005; Harmel et al. 2006b; Miller et al. 2007). This common conclusion highlighted the need for methods to estimate the quality of data collected (measurement uncertainty) and the importance of understanding that uncertainty. Also, some contend that uncertainty estimation should be required in field and modeling studies (Beven 2006; Pappenberger and Beven 2006).

Thus, building on work by Montgomery and Sanders (1986), uncertainty estimation methods were developed specifically for estimating runoff, sediment, and nutrient data

uncertainty at the EOF and small watershed scales (Harmel et al. 2006b, 2009, 2016a; McCarthy et al. 2008). Combined with scientific and practical knowledge, measurement uncertainty can now be considered to better allocate project resources and accurately characterize water quality. This knowledge formed the basis of USDA Natural Resources Conservation Service (NRCS) Interim Conservation Practice Standard Monitoring and Evaluation Code #799, which was later updated to Conservation Activities #201 and #202 for Edge-of-Field Water Quality Monitoring (USDA NRCS 2012a, 2012b). These standards were developed by university and USDA Agricultural Research Service (ARS) researchers to address programmatic, financial, operational, and technical issues including uncertainty and data quality for EOF sampling projects.

Uncertainty Estimation Framework. Montgomery and Sanders (1986) developed the first known conceptualization of uncertainty associated with water quality data. Later, Harmel et al. (2006b) produced the first cumulative uncertainty estimates for runoff and sediment and nutrient flux (figure 2) using an uncertainty estimation framework, which categorized the sources of uncertainty into the following procedural categories:

- Discharge measurement: The uncertainty in flow measurement has been understood for decades (Buchanan and Somers 1976, 1982; Brakensiek et al. 1979; Rantz et al. 1982; Kennedy 1984; Chow et al. 1988; Pelletier 1988; Carter and Davidian 1989; Sauer and Meyer 1992).

- Sample collection: The uncertainty introduced by manual and automated stormwater sampling is a function of constituent type and the sample collection method and frequency (Martin et al. 1992; Ging 1999; USGS 1999; Robertson and Roerish 1999; King and Harmel 2003; Harmel et al. 2003, 2006a, 2010a; Harmel and King 2005; Miller et al. 2007; Rode and Suhr 2007).

- Sample preservation/storage: Physical and biochemical processes occurring between sample collection and analysis can affect nutrient and microorganism concentrations, thus contributing uncertainty in the resulting data (Lambert et al. 1992; Kotlash and Chessman 1998; Jarvie et al. 2002; McCarthy et al. 2008, 2009).

- Laboratory analysis: Sample analysis contributes measurement uncertainty in

EOF data (Ludtke et al. 2000; Jarvie et al. 2002; McCarthy et al. 2008, 2009).

From the 2006 framework, Harmel et al. (2009) developed the Data Uncertainty Estimation Tool for Hydrology and Water Quality (DUET-H/WQ). Both utilize the root mean square error propagation methodology to estimate cumulative probable uncertainty, assuming that under- and over-estimation are equally likely. DUET-H/WQ helps users assign appropriate uncertainty estimates by providing published uncertainty information for data collection procedures. Application of DUET-H/WQ to several real-world data sets (Harmel et al. 2009) indicated that, typically, uncertainty was lower for flow (±7% to 23%) than for sediment (±16% to 27%), dissolved N and P loads (±14% to 31%), and total N and P loads (±18% to 36%).

McMillan et al. (2012) highlighted the DUET-H/WQ tool and Data Uncertainty Engine (Brown and Heuvelink 2007) as starting points for data uncertainty analysis, lending transparency and repeatability to uncertainty quantification along with emphasizing the importance of utilizing quantitative, site-specific information when available. McMillan et al. (2012) close their review with the call for an improved "culture of engagement" for working with data uncertainty.

Recent studies have continued and extended the uncertainty line of research (Birgand et al. 2010, 2011, 2013; Moatar et al. 2012; Williams et al. 2015). Much of this research has focused on furthering scientific understanding of flow measurement uncertainty and the uncertainty in nutrient flux related to sampling frequency and load estimation technique. McCarthy et al. (2008) extended the uncertainty research to address *E. coli* flux in stormwater. Their analysis produced a mean uncertainty of ±33% and a range of ±15% to 67% due to storage and analytical uncertainty in discrete *E. coli* concentrations. Building on McCarthy et al. (2008), Harmel et al. (2016a) conducted a comprehensive uncertainty analysis for *E. coli* that included random bi-directional uncertainty as in the previous work, as well as systematic uncertainty to account for directional bias (e.g., die off). The resulting random measurement uncertainty for *E. coli* concentrations were ±34%, ±70%, and ±106% for the good, average, and poor "data quality" scenarios (figure 2).

Figure 2

Total random uncertainty for flow and sediment, nitrogen (N), phosphorus (P), and *E. coli* concentrations (whiskers represent the maximum and minimum for the typical data quality scenario, and black dot represents the average). For *E. coli* data, the ±33% average uncertainty of McCarthy et al. (2008) and the ±34% uncertainty of the "good" data quality scenario (Harmel et al. 2016a) are readily achievable with proper QA/QC and good sampling conditions. Q = flow. TSS = total suspended solids. NO_3-N = nitrate-nitrogen. PO_4-P = orthophosphate-phosphorus.
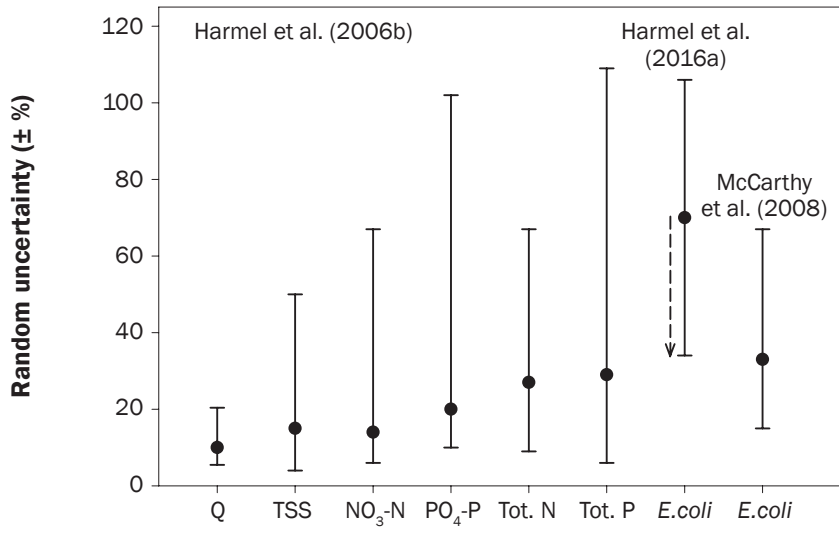
Current Research and a Glimpse into the Future

The increasing importance of water quality data to evaluate the benefits of conservation practices and address high-profile water quality impairments demands further improvement in the quantification of water quality at the EOF. Thus, lower cost systems, practical improvements, and enhanced in situ sampling are driving current research and will likely dominate the field of EOF monitoring in the coming years. For the same reasons, enhanced understanding and communication of the "quality" or uncertainty of that data is increasingly important in modeling and decision making.

Additionally, as investment decisions related to EOF monitoring are made and scrutinized, projects that serve multiple purposes should receive priority in terms of resource allocation. EOF projects can and should be designed to not only collect data but to answer questions about conservation efforts and water quality that are facing researchers, policy makers, stakeholders, and land managers. For instance, what is the efficiency of a conservation practice or suite of practices? What are the efficiency trends in loss over time? What are the regional differences in practice efficiency?

Lower Cost Systems and Practical Improvements. Recently scientists have developed a prototype EOF runoff monitoring gauge designed to minimize financial and technical barriers to EOF monitoring in northern climates. The prototype system includes low-cost hardware components (i.e., custom electronic data logger, original equipment manufacturer (OEM) stage sensors, low-cost peristaltic pump, and low-profile flume) and innovative system designs (i.e., flume heaters, equipment enclosures, and integrated systems) intended to reduce equipment and installation costs as well as reduce the cost of operating and maintaining gauging stations (Mentz et al. 2016).

Initial results of prototype field tests have proved successful and also highlighted components of the prototype system that could be improved. Low-cost ultrasonic stage sensors produced accurate estimates of flume stage when compared to time-lapse photos of in flume staff gauges ($R^2 = 0.97$). The modified flume is designed to gauge larger discharge events at lower heads, therefore lowering the height of berms and wing walls and installation costs. In laboratory tests, the flume performed well overall; however, turbulent flow resulted in less accurate stage readings at high discharge rates. Integrated flume heaters and gauge enclosures, while increasing equipment costs, significantly decreased the time and effort required to prepare stations for monitoring winter snowmelt events, and

improved working conditions for technicians maintaining the gauging stations. The low-cost sampler produced similar estimates of suspended sediment (R^2 = 0.95) and nitrate-N (NO_3-N) (R^2 = 0.89) when compared to a conventional automated sampler. Several iterations of the data logging hardware have been developed and field tested in an effort to address deficiencies and increase capabilities and reliability.

In Situ Sensors. In situ sensors have been conceptualized, developed, and deployed for decades in attempts to overcome limitations of traditional sampling methods and analytical procedures. Ideally, in situ sensors would circumvent difficulties associated with sample collection, transportation, storage, processing, and analysis. Zhang and Zhang (2014) provide a thorough discussion of these sensors and the potential for them to be rapidly and easily deployed and provide continuous in situ data. Rode et al. (2016) provide insightful discussion of in situ sensors, the impacts of high frequency, high density data on models, limitations of current technology, and future directions.

One type of in situ device is passive samplers, which rely on the diffusion of analytes through a diffusive surface onto an adsorbent. Passive samplers can be deployed for an extended period with little to no maintenance and provide time-weighted concentrations, especially for trace chemicals. Rozemeijer et al. (2010) provide valuable information on the testing, field operation, and comparative results for measuring NO_3 loads and concentrations with the passive sampler developed by De Jonge and Rothenberg (2005).

Miniaturized electronic devices capable of measuring temperature, pH, conductivity, and dissolved oxygen (DO) on a semicontinuous basis have been available since the 1980s. These multiparameter probes (or multiprobes) were later equipped with ion selective electrodes to measure inorganic constituent concentrations, such as NO_3-N. Although these sensors were successful in laboratory settings (Bakker et al. 1997; Bühlmann et al. 1998; Bobacka et al. 2008), they experienced substantial signal drift (Hanrahan et al. 2004) in field deployment forcing further correction (Scholefield et al. 1999, 2005; LeGoff et al. 2002, 2003). Since the 1990s, turbidity sensors have been utilized, either as stand-alone instruments or in multiprobes. Turbidity has been routinely used as a surrogate measure to estimate total

suspended solids (Gippel 1995; Brasington and Richards 2000; Birgand et al. 2004; Billotta and Brazier 2008; Minella et al. 2008; Navratil et al. 2011; Jones et al. 2011; Thompson et al. 2014) and total P concentrations (Jones et al. 2011). These estimates, however, rely on relationships with turbidity derived on a station by station basis, which introduces a potentially significant source of measurement uncertainty.

More recently, optical instruments measuring light absorbance and fluorescence have shown success. Spectrophotometers measuring absorbance (190 to 250 nm) have been used since the late 1980s to measure NO_3 concentrations (Crumpton et al. 1992). Absorbance at 254 nm has also been used to estimate dissolved organic carbon (C) (Brandstetter et al. 1996; Deflandre and Gagné 2001). The abundant information embedded in absorbance spectra has been used to develop a more robust relationship to predict not only parameters known to absorb light (e.g., NO_3, dissolved organic C, and total suspended solids) but others as well (e.g., phosphate [PO_4], organic N, bromine [Br], iron [Fe], and silicon [Si]) (Etheridge et al. 2014; Birgand et al. 2016). Even though all optical instruments (i.e., turbidity, absorbance, and fluorescence sensors) are subject to biological and chemical fouling (Etheridge et al. 2013), these in situ sensors are potentially transformative because they can ideally provide high frequency data and avoid many of the constraints associated with field sampling and laboratory analysis.

The importance of developing accurate, reliable, and affordable sensors for nutrients in water is highlighted by the US government-sponsored Nutrient Sensor Challenge, which is a global competition to incentivize development and production of NO_3-N and PO_4-P sensors. Specifically, the Nutrient Sensor Challenge is a market stimulation and innovation effort to accelerate development and deployment of affordable (<US$5,000), reliable, and accurate sensors that measure these constituents in water with the goal of commercial availability by 2017 (www.act-us.info/nutrients-challenge). The problem as expressed by the Challenge is that current methods for measuring nutrient loads are expensive and inadequate to capture the temporal and spatial variability within ecosystems. While we might not completely agree with the intent of this statement, the value of accurate, durable, and affordable

in situ sensors for nutrient concentrations could be tremendous; however, the need for and expense of flow measurement necessary for load determination with sensor-derived concentrations should not be overlooked.

Application of Measurement Uncertainty in Modeling. Research by Harmel and Smith (2007), Moriasi et al. (2007), and Harmel et al. (2010b) established methods to incorporate calibration/validation data uncertainty into model evaluation, and this topic is receiving a great deal of attention. The increased use of models in water resource policy, management, and litigation highlights the importance of uncertainty analysis (Shirmohamadi et al. 2006; Black et al. 2014; Harmel et al. 2014; Guzman et al. 2015). Numerous researchers including Abbaspour et al. (2007), McMillan et al. (2010), Arnold et al. (2012), Chen et al. (2014), and Yen et al. (2014, 2015, 2016) are working to better understand and quantify all sources of prediction uncertainty, including uncertainty in flow and water quality data. The benefits include (1) appropriately sharing burden of accurate prediction with data providers, (2) conducting more realistic evaluations of model performance, (3) helping prevent over fitting, (4) focusing model deficiency (where simulations do not fall within the uncertainty range of measured data or when model uncertainty is relatively high), and (5) accurately communicating model performance. Although most modelers would agree with these benefits of model uncertainty analysis, enhanced understanding is needed to communicate the value of model results and their limitations to stakeholders, policy makers, and regulators.

Application of Measurement Uncertainty in Decision Making. In spite of the fact that all measurements introduce uncertainty in the resulting value and the general agreement that uncertainty analysis does benefit hydrologic and water quality analyses, measurement uncertainty is still commonly ignored (McMillan et al. 2012), although less so in recent years. The justifications for ignoring measurement uncertainty in the past included tenuous philosophical concerns related to (1) the belief that scientists and engineers can understand uncertainty but not the public, stakeholders, and elected officials, and (2) the fear of negative perception of data with high uncertainty, although this is subjective, and even data collected with accepted protocols and trained personnel can

exhibit considerable uncertainty (Harmel et al. 2006b, 2009). The additional time and effort required to estimate and report uncertainty with measured data is likely another deterrent. However, another justification—the lack of adequate scientific understanding on the subject—is no longer valid due to the recent advances discussed previously. To maintain scientific integrity, scientists and engineers have a responsibility to accurately report what is known and what is unknown, including the quality of data reported.

As stated by Montgomery and Sanders (1986), "incorporation of uncertainty analyses in the decision making process is needed to help decrease the state of doubt as the best course of action…" This general statement presented in a conceptual framework to estimate uncertainty in measured water quality data highlights the value of data with corresponding uncertainty estimates to better inform regulation, policy, and resource decision making. More recently McMillian et al. (2012) stated that quantitative estimates are needed to communicate data uncertainty across disciplines' boundaries to data users, policy makers, and the general public. The direct benefits of considering measurement uncertainty in research and monitoring at the EOF and small watershed scales (1) allows technical staff to focus QA/QC attention on procedures with the greatest uncertainty; (2) highlights the benefits of preventative maintenance, training, and proper use of field and laboratory techniques; and (3) assists managers to better balance project expenditures and resource commitments with data quality goals. Filoso et al. (2015) stated that ideally, uncertainty in water quality measurements should be used to evaluate whether load reductions are scientifically defensible. Although they made this statement in the context of stream restoration, it also applies to field-scale evaluation of conservation practice effectiveness.

These benefits, along with expanding research, will likely further increase the application of uncertainty analyses in water quality monitoring projects; however, a couple of related topics warrant additional discussion. First, the long-standing practice of judging data values as "good" or "bad,"—for instance, in determining eligibility for inclusion in a state database—is erroneous. While we certainly recognize that there are bad data—defined as data collected with improper methods and/or data resulting

from mistakes in collection, procession, analysis, transcription, or other processes—all other data are valuable. Thus, we propose that all data collected with accepted methods and without mistakes should instead be presented with the corresponding measurement uncertainty. This will allow data users to determine the applicability of the data for a particular purpose based on an acceptable level of uncertainty. It will also avoid the incorrect and all too common assumption that data presented in reports and databases are without uncertainty, by acknowledging the fact that all measurements introduce uncertainty in the resulting value.

Second, all data users need to appropriately utilize data and corresponding uncertainty estimates. It is not adequate to acknowledge the fact that all measured data have some level of uncertainty and that for water quality data this uncertainty is contributed by collection, preservation, storage, and analysis procedures. Users should utilize the data and supplemental information (uncertainty) to evaluate the influence on important water quality decisions (e.g., development of QA/QC protocols, assessment of standards, and evaluation of model performance). All too common examples of misapplication include (1) flagging of data as bad or unusable if presented with high uncertainty, even though that level of uncertainty may be the lowest levels possible given technological or site limitations; (2) justifying the superiority of model predictions relative to measured data, especially without conducting comprehensive model uncertainty analysis; and (3) questioning data integrity when the data show a water quality impact not favorable to or desired by stakeholders. The uncertainty in measured data needs to be embraced, not disregarded or misused.

Third, the issue of uncertainty related to determination of water quality standards violation has been recently discussed in US Environmental Protection Agency (USEPA) and state agency meetings. While it is not appropriate for this research summary paper to advocate for specific regulatory processes, consideration of measurement uncertainty in evaluation of water quality standards attainment is supported by current science. In the simplest terms, this may involve differing regulatory actions depending on the confidence (uncertainty) in measured water quality data. For example, data with relatively low uncertainty that indicate a violation of standards

may warrant more strict or decisive action than do violations indicated with highly uncertain data.

Summary and Conclusions

This paper conveys decades of collective wisdom to those who are managing, designing, implementing, or operating water quality monitoring programs, particularly at smaller scales (field to headwater streams). The practical recommendations within are underlain by an honest acknowledgment that measuring water quality at the EOF and small watershed scales is difficult, time consuming, and expensive. In spite of the challenges, the data and understanding produced are increasingly important for determining conservation practice effectiveness, calibrating and validating water quality models, and designing effective nonpoint source policy considering soil, management, meteorological, and land use differences.

This manuscript presents background information, which sets the stage for recent developments and summarizes how those developments advanced the science of EOF water quality sampling. In addition, current and expected research and development related to lower cost systems, practical improvements, enhanced in situ sampling, and increased consideration of the uncertainty of EOF data in modeling and decision making are presented. Well-designed EOF monitoring efforts are a critical component to enhanced understanding of how management changes on the landscape influence water quality. This need underscores the importance of designing EOF monitoring to produce relevant data to equip scientists, stakeholders, land managers, and policy makers for addressing water quality problems at the EOF and downstream.

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