Principles and Practices of Water Quality Monitoring

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Introduction

There are many activities in forest management that may affect water quality, i.e., timber harvesting, road building, mechanical and chemical site preparation, release operations, fuel reduction, wildlife opening maintenance, etc. How severely they affect water quality depends on how well the person in charge of the operation understands the activity itself, the potential problems, and how well that person manages or oversees the operation. Water quality monitoring provides basic information fundamental to the understanding of the condition of surface and ground water. It allows us to identify changes or trends in water quality over time, to establish baseline conditions for specific sites, determine whether program goals are being met, accumulate knowledge necessary for development of remediation programs, identify specific existing or emerging water quality problems, and identify and respond to emergencies. Some other reasons for monitoring include:

- National Environmental Policy Act of 1969
- Federal Water Pollution Control Act and Amendments of 1972
- Clean Water Act of 1972 and Amendments of 1977
- Safe Drinking Water Act of 1974
- National Forest Management Act of 1976
- Water Quality Act of 1987
- Risk Assessment
- Contract Validation
- Support For Or In Defense Of Litigation
- Good Stewardship

While all of these are good reasons for monitoring, the latter is the best. We in forestry serve the needs of society in a host of ways and it is incumbent upon us to be able to demonstrate that our management practices in forestry clearly do not degrade the environment whether terrestrial or aquatic and that we are leaving the land and water in a condition those generations that follow after us can enjoy. In order to accomplish this, it is first necessary to understand the potential magnitude of the problems.

US land use and pesticide use data indicate that over 1 billion pounds of pesticides are used on approximately 16 percent of the 3.6 million square miles of land in the United States annually. The most intensive use of pesticides occurs on land occupied by households. Households represent 0.4 percent of all land and receive 12 percent of all pesticides used in the US. Agricultural land (52 percent of all land) is the next most intensively treated receiving 75 percent of all pesticides used. Government and industrial land (16 percent of all land) receives 12 percent of all pesticides. The least intensive use of pesticides occurs on

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forest land (32 percent of the land) which receive less than 1% of all pesticides applied in the US annually (Michael, et al. 2000). Pesticides in general and especially those used in forestry have not been found to be important pollutants in the nation's rivers and streams. Rather, sediment is the most important pollutant affecting rivers and streams while pathogens (mainly bacteria), nutrients, oxygen-depleting substances, and metals are also important pollutants. The leading source of pollutants in streams and rivers is agriculture (59%). Urban runoff and storm sewer contributions are nearly double those from forestry. The latter is an extraordinary number considering that forests occupy approximately 80 times as much of the land base as urban areas (U.S. EPA, 1998). However, forestry activities can contribute to local impairment of water quality. Activities that can contribute to pollution load include road construction, harvesting, and site preparation and regeneration practices. Further, maintenance of rights-of-way and even wildlife habitat openings can potentially, if not managed properly, result in some degradation of water quality.

Sediment (suspended solids in water) is the single most important pollutant from forest sites (Elliott, 2000; Michael, et al. 2000). Sediment contributes to the cloudiness of water, especially evident after rainfall events, but it is most important for the impacts it has on aquatic communities and on drinking water quality. Sediment can clog fish gills causing health and reproductive problems as well as death. It can also reduce the amount of light penetrating the water column thus reducing algal photosynthesis rates and thereby dissolved oxygen content. Once water velocity slows sufficiently to allow sediment to settle out, sediment may smother bottom-dwelling organisms, cover breeding areas, and smother eggs of aquatic organisms. Indirect effects include elevated water temperature due to the increased heat absorbency of sediment particles versus that observed in clear water. In addition sediment may carry strongly adsorbed pesticides (chiefly insecticides which are less water soluble than most herbicides used in forestry) and high sediment loads increase costs of drinking water treatment by interfering with coagulation, filtration and disinfection. Sediment also adversely affects recreational and aesthetic enjoyment of water.

Increased nutrient loading and temperature of streams may also have detrimental effects on aquatic ecosystems. Elevated temperatures and nutrient levels increase algal communities, which bloom and then die. Concomitantly death and rotting of increased algal biomass results in increased CO_2 levels and decreased oxygen supplies and this sequence of events has been shown to result in fish kills and loss of other aquatic organisms. Thus it is important to maintain a high level of water quality.

Water quality is defined in a number of ways, depending on the end use. In forestry, the many facets of water quality include transported materials, either dissolved (pesticides, nutrients, etc.) or suspended; physico-chemical attributes (temperature, pH, turbidity, alkalinity, etc.) and biological attributes (pathogens, periphyton, macroinvertebrates, fish, and measures of the ability of different trophic levels to function in the test water).

The principles and practices of water quality monitoring are defined by the definition driving the monitoring process and on the end use projected for the water. This paper will deal primarily with monitoring for endogenous (naturally occurring nutrients) and exogenous (pesticides, fertilizers, etc.) dissolved pollutants and for entrained materials (i.e., suspended sediment).

Principles of Water Quality Monitoring

Sampling is the weakest link in any monitoring program. Samples taken at random without regard to environmental influences, without understanding of the *in situ* behavior of the compound or condition of interest, or just for the sake of monitoring will be worse than worthless. They will be an unnecessary expense, a waste of human resources and may be your worst nightmare come true. There are only a few principles needed to govern and insure a successful monitoring program:

- Monitoring must occur when the compound or condition of interest will be present
- Samples must be representative of the environment being monitored
- A monitoring protocol designed to insure the required data will be collected is essential. The protocol should at the minimum:
    - Clearly state monitoring goals and objectives
    - Provide for collection of sufficient baseline samples to aid in interpretation of chemical or other analyses
    - Identify chemical or other analyses to be conducted and who will do it
    - Identify data and statistical analysis
    - Determine equipment needs, frequency and volume of sampling
    - Provide for sanitary handling of samples and identify necessary personal protective equipment
    - Describe required sample documentation, handling, storage, and chain of custody procedures
    - Provide for quality assurance/quality control procedures. In the case of chemical analysis, these must include provisions for blank and spiked samples.

Timing is Everything. It may not always be possible to know when the compound or condition of interest is present. However, there are some guidelines that will be helpful. Concentration of endogenous dissolved nutrients seldom changes significantly with precipitation except following a site disturbance that releases these nutrients. A good example is the application of tire to harvested sites prior to planting or the use of tire to manipulate fuel loads or vegetation. Under such conditions fire releases nutrients, which may show some increased values during the first 2-5 storms following the bum. Typically, the increased concentrations observed in runoff occur at or near peak stream discharge as is also true for exogenous dissolved compounds and for sediment (Figure 1).

Samples Must be Representative. The collection of representative samples is sometimes a very difficult operation. It has already been shown that the maximum observable concentration of exogenous compounds and in some cases endogenous compounds occurs at or near peak storm discharge. This is also true of suspended sediment, however, suspended sediment is a collective term describing particulate matter that exists over a range of particle sizes and densities. Therefore, they are stratified in the water column of a flowing stream according to the energy of the flowing water at different depths. Different energies are associated with different depths because of the drag imposed on moving water by the roughness of stream channel bottoms and sides. Stream depths of less than 0.75 meters (2.5 feet) have a mean flow velocity at 0.6 of the stream depth from the surface and it is here that a point sample is best taken (Brakensiek et al. 1979).

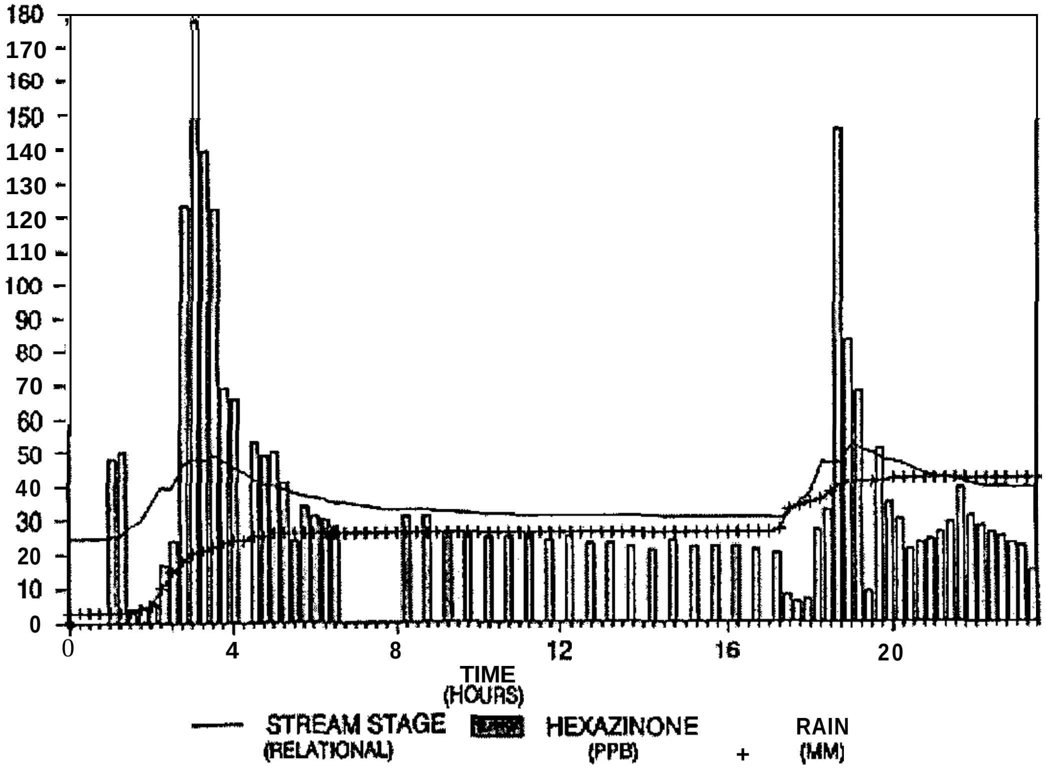

Figure 1. Stream flow samples from a clear-cut forest site at 15-minute intervals through two precipitation events demonstrate the pulsed inputs normally observed for exogenous compounds (in this case hexazinone applied at 3 times the prescription rate and flown directly into the stream). Peak concentrations are strongly correlated with peak stream discharge. (relational, absolute units are not given; ppb, parts per billion is equivalent to micrograms per liter; mm, millimeters of accumulated precipitation)

A Monitoring Protocol is Essential. Monitoring protocols should be sufficiently detailed that a relative neophyte can take the protocol and go to the field to conduct sampling. While this sounds a little overstated, it gives notice to all of us that it is essential that all protocols be well thought out, succinctly written and each step easily justifiable. Goals and objectives should give not only a philosophical idea of what is being monitored and why, but exactly what use is intended for the monitoring data.

Samples collected after disturbance or treatment may contain a number of false-positive samples, There is only one easy and inexpensive way to get around this problem: take pretreatment or predisturbance baseline samples so they can be analyzed along with the post-treatment samples and give some idea as to how a particular data point should be interpreted. Baseline samples can also be sent to the chemist for analytical methods development and refinement. When monitoring spans a long time, it should be remembered that season might be reflected in dissolved materials content so a separate set of similar control samples may be seasonally necessary.

Additional aspects of the monitoring protocol fall more appropriately under the heading of monitoring practices and are discussed below.

Practices of Water Quality Monitoring

*Equipment Needs, Frequency and Volume **of** Sampling.* The techniques and equipment required for water quality monitoring will largely depend on the monitoring goals and objectives. If the objective is to establish current conditions for endogenous compounds, establish water temperature, pH, alkalinity, etc., the equipment required can be fairly simple. However, if the monitoring is to determine whether there is an increase in streamflow loads of exogenous compounds or sediment, the equipment may have to be more sophisticated. Water sampling should be performed in turbulent points in the stream where possible to insure adequate mixing. It is also a good idea, where possible to place the sample intake line at a point 0.6 of the stream depth from the surface, especially if suspended sediment or turbidity is being attempted with either grab or sipper samplers (Brakensiek et al. 1979).

Grab sampling, the practice of manually taking a single sample at a single point in time and space, is useful for periodic checks on endogenous compounds, pH, and alkalinity. However pH should be measured immediately after sample collection and may even be done *in situ* without the removal of a sample. This type of sampling is rarely suitable to description of changes in stream condition (as a result of disturbance) over short time periods. Since movement in the stream disturbs bottom material, sampling for suspended sediment is rarely accomplished with grab samples.

There are a variety of sipper samplers available and they are very useful for characterization of changes in stream condition over short to very long time periods. They can be placed on site, operated by battery and depending on the sophistication of the sampler either programmed to simply collect a time series (i.e., a sample every half hour, every hour, every 8 hours, etc.) of samples or programmed to collect samples which are either flow weighted (a subsample taken every time a specified volume has passed through the sampling point), time dependent, or stage dependent. Even the simplest of samplers can be connected to data loggers and external sensors (rain gages, pressure transducers to determine stream *stage, etc).* Information from the external sensors can be used by data loggers to prompt the samplers to begin taking samples at some specified event, for example when 1.0 cm of rain has fallen, or when the stream stage has increased by 0.5 cm, or even a combination of such events. This gives monitoring personnel the option of collecting samples to describe what happens during storm events, even when they occur at 2:00 am. Stream stage measurements allow us to select samples for analysis that will insure our ability to meet monitoring protocol objectives with a minimum of analytical costs. *Of* course, such samplers also allow the flexibility for compositing of samples and, therefore, the description of time- or flow-averaged values.

Splitter samplers are those that continuously collect a small percentage of the total stream output. Perhaps the best known is the Coshocton wheel which, depending on size collects 0.33, 0.5 or 1.0% of total flow and routes it to a holding tank for later analysis. The Coshocton wheel, designed for use with an H-flume, is probably the best system for detailed measuring and analysis of sediment. It can also be used effectively for measurement of endogenous and exogenous compounds moving in streamflow. Coupled with stage and therefore flow data from the stream, it is also possible to calculate total amounts of pesticides, nutrients, etc. moving off monitored sites.

Frequency of sampling is normally determined by the monitoring objectives, and volume collected is determined by the analytical procedures to be applied to the samples. If one is interested in whether an exogenous compound was applied directly into streams during an aerial application, samples taken on an hourly basis over the duration of the treatment phase should be sufficient; however, attempts to characterize the concentration profile associated with a storm will require much more frequent samples. As already mentioned, sampling for endogenous compounds, pH, and temperature do not normally require frequent sampling.

Sample volume is dependent on the analyses to be performed. For example, analysis for an herbicide by traditional solvent/solvent extraction and gas chromatography (GC) may require several liters of sample. Analysis for the same herbicide using solid phase extraction followed by GC or liquid chromatography may require as little as a few hundred milliliters and analysis by enzyme-linked immunosorbent assay (ELISA) may require fewer than 10 milliliters. The smaller the sample volume, the more critical it is to have a representative sample.

Sanitation is a must when it comes to sampling for exogenous compounds. It should be remembered that one normally walks through treated sites to get to the streams draining them, and it is very likely that monitored streams can be contaminated by those very people who are doing the monitoring. Equipment should also be thoroughly cleaned prior to use and after each use. Personal protective equipment and reentry periods should always be observed. In this regard, automatic sampling equipment solves a lot of problems we might otherwise experience in monitoring.

Sample documentation, handling, storage and chain of custody. If a sample is worth taking, it is worth taking good care of! Water quality monitoring samples may be handled by many people and taken many places before they are finally analyzed (i.e., collected in the field by one person, given to a technician for storage, moved from storage to shipping by another, shipped to an analytical laboratory where they are checked in by receiving, placed in storage by another person, removed from storage for analysis, extracted by a laboratory technician and finally analyzed by the chemist). Each stage is an opportunity for an error to occur. Each handling is an opportunity for a label to come off or be damaged beyond recognition. For this and many other reasons, documentation of samples should be obsessively observed. In our laboratory it is standard operating procedure to preprint labels with a unique sample number for each sample as well as description of the sample date, where and when and by whom it was collected. We then place at least two identical labels on each bottle. Sometimes we even go so far as to code the bottle cap. Field records are maintained in which we record each and every sample taken, its unique sample number, who took the sample, where it was taken and even any noteworthy conditions or peculiar appearance of any sample. When samples are brought back to the laboratory and stored, a storage notebook is also maintained which identifies the freezer in which a sample was placed and date. Removal from storage requires another entry in this storage book indicating who removed the sample, where it was taken and the purpose for which it was taken. A chain of custody document is prepared and maintained for any sample that leaves our control. This is especially important when samples are sent to contract laboratories for analysis and most laboratories require such documents.

Once a sample is collected, it must be properly handled. Most pesticides undergo photolysis, hydrolysis, or microbial degradation. The rate of these processes is affected by temperature, light, and frequently pH. A summary of the routes of degradation of some forestry herbicides is presented in Table 1. All of the most popular forestry herbicides are microbially degraded to some extent. Therefore is prudent to at least retiigerate all water quality monitoring samples suspected of containing any of the herbicides listed in Table 1. Some of the herbicides are also hydrolytically degraded. The process of hydrolysis can be very fast and the rate is often dependent on pH as in the case of the sulfonylureas (Fischer and Michael 1990). In handling the sulfonylureas it is necessary to stabilize the sample with some buffer to keep the pH on the alkaline side to reduce the speed of hydrolysis (Wells and Michael, 1987). Table 1 indicates that triclopyr acid does not undergo hydrolysis and that is true, however triclopyr amine and the ester of triclopyr do hydrolyze very quickly to the triclopyr acid that then undergoes photolysis. Obviously all water quality monitoring samples should be refrigerated as soon as they are taken to reduce microbial degradation. Refrigeration also slows hydrolysis, freezing stops it for as long as the sample is frozen. It is also obvious that samples should be protected from light to prevent photolysis. A good rule of thumb is: keep all water quality samples in the dark and frozen as much of the time between collection and analysis as is possible.

Table 1. Summary of the routes of degradation of some forestry herbicides.

Common Name	Trade Name	Photolysis	Hydrolysis	Microbial
Fosamine	Krenite	NO	NO	Very Fast
Glyphosate	Roundup	Yes	No	Yes
Hexazinone	Velpar	Yes	No	Yes
Imazapyr	Arsenal	Yes	Very Slow	Very Slow
Picloram	Tordon	Yes	NO	Yes
Sulfonylureas	Escort, Oust	NO	Yes	Yes
Triclopyr acid	Garlon	Very Fast	NO	Yes

Sample storage in our laboratory means freezing. We have conducted many studies *over* the years including forest dissipation studies required under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) for hexazinone, imazapyr, and sulfometuron. These studies frequently generate 20,000 to 30,000 samples each over a period of 1-2 years. Obviously these samples cannot be analyzed immediately as they come to the laboratory and storage is essential. We have conducted freezer storage stability studies for these herbicides and found that percent recovery was similar to that for the initially spiked samples over a period of several months. Specifically recovery for hexazinone was 99% after 25 weeks of frozen storage, 85% for imazapyr after 18 weeks and 92% for the sulfonylureas after 14 weeks. While the freezer storage stability studies have not gone beyond 6 months for any of our samples, it is highly unlikely any degradation would take place over extended storage periods, Our samples in these studies were all stored in high-density polyethylene plastic autosampler bottles (Isco). These bottles rarely crack, but when this happens the entire sample (even if still frozen) should always be discarded!

Quality Assurance/Quality Control. Baseline samples and/or control site samples serve to provide the basis for spike and blank samples required by most QA/QC programs. Chemists are not infallible, so it is a very good idea to have baseline, spike, and blank samples for submission to the chemist, It is also a good idea to meet with the chemist, discuss analytical methods and understand the chemist and analytical laboratory's capability. Norris (1986) sent replicate water samples containing picloram at a concentration of 10 ppb to ten analytical laboratories and asked them to analyze the water for picloram. Values reported from these ten laboratories ranged from ND (not detectable) to 780 ppb. One lab reported values ranging from 7-14 ppb while the worst lab reported values ranging from 160 to 780 ppb, ail based on samples with a true value of 10 ppb. Clearly an appropriate and replicated set of spikes and blanks should be included with any set of samples sent to analytical labs to allow one to interpret the laboratory's results.

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