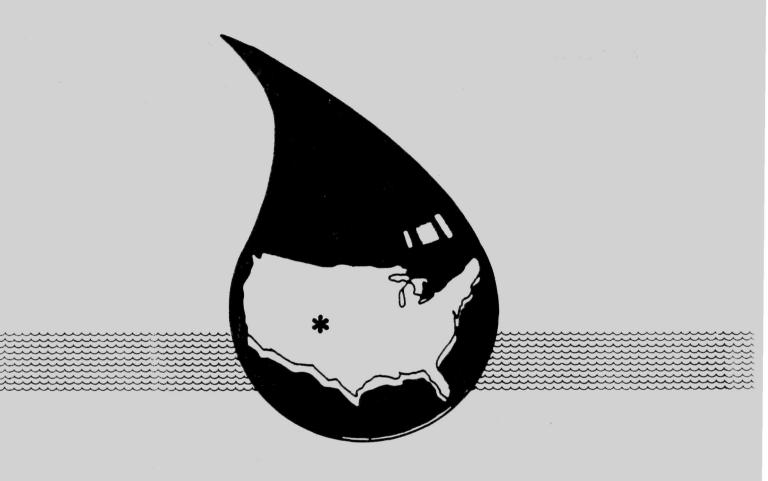
MONITORING STREAM WATER QUALITY FOR LAND-USE IMPACTS

A Training Manual for

Natural Resource Management Specialists





WATER RESOURCES DIVISION NATIONAL PARK SERVICE FORT COLLINS, COLORADO 80521 This training handbook is designed for use in training courses conducted by the National Park Service (NPS) Water Resources Division for NPS natural resource management specialists. As such, this training handbook is not a formal National Park Service publication. Use of trade names does not imply U.S. Government endorsement of commercial products.

MONITORING STREAM WATER FOR LAND-USE IMPACTS:

A Training Manual for Natural Resource Management Specialists

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PREFACE

Many parks and other units managed by the National Park Service (NPS) are confronted with threats of water pollution from sources within as well as outside their boundaries. In addition, many park units are considering the development of Water Resource Management Plans to add to other management documents. Park resource managers frequently contact the NPS Water Resources Division (WRD) for advice in identifying and interpreting pollution problems in their units and in evaluating the effects of various land uses on park water resources. In response to this need, we assembled this handbook as a starting point in answering some of the common questions concerning water quality and land-use impacts and as a guide for designing monitoring programs.

This handbook is limited to stream water quality monitoring, with little reference to lakes and impoundments or to ground water. Monitoring techniques for these water sources differ to the extent that each is a subject in its own right, and each could command a separate volume to cover the subject. Therefore, we concentrate on monitoring strategies for those water quality problems currently affecting stream waters in NPS areas.

In using this handbook, it is important to keep in mind the shortcomings inherent in making any monitoring recommendation. With so many water quality parameters in use today, it would be difficult to select the "magical few" that would apply in all cases or even to every situation of a certain type. Consequently, this volume is intended to assist the reader in designing a water quality monitoring program by providing information and ideas, not absolutes.

This document has been prepared as a primer on concepts and useful techniques for monitoring contamination in stream water in areas managed by the National Park Service. The recommendations in this report are purely technical in nature and do not necessarily bear any relation to legal requirements promulgated by state or federal agencies. Likewise, these technical recommendations are neither administrative directives of NPS nor indicative of NPS policy.

The authors would like to acknowledge the many individuals who contributed time, effort, and information that enhanced the quality and technical accuracy of this handbook. Technical review was generously provided by Dave DeWalle, Pennsylvania State University; Kirke Martin, Steve Workman, and Mike Richard, Colorado State University; Julie Van Stappen, National Park Service, Midwest Regional Office; Keith Yarborough, National Park Service, Southwest Regional Office; Leslie Vaculik, Sidney Covington, and William Nagle, National Park Service, Mining and Minerals Branch; Nancy Deschu, National Park Service, Alaska Regional Office; Cat Hawkins, Olympic National Park; Bob Krumenaker, Isle Royale National Park; and Dan Kimball, Gary Rosenlieb, and Ray Herrmann, National Park Service, Water Resources Appreciation also is extended to the Hach Company, Loveland, Colorado; the U.S. Forest Service; the U.S. Geological Survey; and the Atmospheric Deposition Program for providing materials, photographs, and maps.

It is with gratitude that we especially acknowledge the personal support of the late Thomas W. Lucke, who was Chief of the National Park Service Water Resources Division during most of the preparation of this

handbook. Because of his own particular interest in technical assistance to parks, he especially encouraged the development of materials of this nature. Without his support, this document could not have been completed.

ABBREVIATIONS

The following abbreviations are used throughout this handbook.

AA	atomic absorption	mL	milliliter
AMD	acid mine drainage	mS	millisiemen*
BOD	biochemical oxygen demand	μ mho	micromho*
°C	degrees celsius	μg	microgram
CaCO3	calcium carbonate	N	nitrogen
cfs	cubic feet per second	ng	nanogram
cfu	colony-forming units	N-NO ₃	nitrate as N
cm	centimeter	N-TKN	total Kjeldahl nitrogen as N
COD	chemical oxygen demand	NTU	nephelometric turbidity
DO	dissolved oxygen	NIO	unit
EDTA	ethylenediaminetetraacetic	P	phosphorus
		P-PO ₄	phosphate as P
EPA	Environmental Protection Agency	S	sulfur
FC bacteria	fecal coliform bacteria	so ₄	sulfate
FS bacteria	fecal streptococcal	TC bacteria	total coliform bacteria
	bacteria	TDS	total dissolved solids
g	gram	TFE	tetrafluoroethylene
HNO ₃	nitric acid	TSS	total suspended solids
JTU	Jackson candle turbidity unit	μeq	microequivalent
L	liter		
m	meter		
m^3/s	cubic meters per second		
meq	milliequivalent		
mg	milligram		

^{*}micromho - microsiemen - 0.001 millisiemen

^{*}micromho = microsiemen = 0.001 millisiemen

WATER QUALITY MONITORING PLAN: PHILOSOPHY

1.1 Purpose

The purpose of this handbook is to suggest strategies for designing and implementing simple, cost-effective surveys of water quality impacts resulting from land uses in and around National Park Service (NPS) units. Specifically, monitoring suggestions address various kinds of mining, oil and gas development, recreation, urbanization, and agricultural and forestry practices. This handbook provides a strategy for 1) designing a problemoriented water quality monitoring plan; 2) identifying sources of suspected water pollution caused by different land uses; and 3) recognizing, by means of a few basic analyses, when additional study of a water quality problem may be required. Three concepts form the basis of the strategy:

- NPS staff typically will conduct some of the field sampling and analytical work.
- 2. Certain analyses will necessarily be contracted out.
- A "focused" approach is used in which the minimum number of water quality parameters necessary is selected as indicative of specific impacts.

These concepts are explained below.

1.2 NPS Staff Role

The NPS resource manager plays a key role in identifying probable sources of water pollution that are or could be present. In preparing to assess these pollution sources, resource managers should have definite objectives in mind for the data to be collected. For example, they may need to identify and describe the severity of contamination caused by mining, so that these problems can be addressed in park planning, development, and mitigation efforts.

We recommend using park staff for certain analyses rather than contracting out the entire job (Fig. 1-1). The degree of analytical training needed for park staff involvement will depend upon the interest and skill levels of those involved. Park staff involvement in the sampling and field work typically will lower total costs, often markedly. More importantly, park staff will become familiar with analytical methods and terminology so that the data provided by outside laboratories can be interpreted, critiqued, and incorporated into park planning and management.

To enhance the understanding park personnel may have of water quality monitoring, and in view of the changes rapidly occurring in monitoring techniques, maintaining contact with specialists in the field is advised. Expertise is available within NPS as well as in other organizations and agencies, listed in Appendix A.



Fig. 1-1. Park ranger takes a stage reading, used for calculating stream discharge.

1.3 Linking Park and Contract Laboratory Data

A stronger set of water quality data for a particular stream or stream segment evolves by linking data collected by park staff with analyses from an outside, contract laboratory. For example, the outside facility can analyze for metals, acidity, sulfate, and other more analytically complicated constituents in water samples, while park staff can supplement these outside analyses with simpler field measurements such as pH, turbidity, and conductivity. For logistical and economical reasons, in-park measurements can be conducted on a more frequent basis than outside laboratory analyses, and relationships can then be drawn from analysis of both data sets. For example, pH (analyzed in park) normally relates to acidity (analyzed in contract laboratory); turbidity (in park) reflects total suspended solids (contract laboratory); conductivity (in park) correlates with the levels of total dissolved solids (TDS), metals, or other ionic substances (contract laboratory); and so on (Fig. 1-2). Knowing these relationships, park personnel can use the more frequently and simply measured parameters to estimate less frequently evaluated parameters analyzed by the contract laboratory. Estimation and extrapolation of data are then possible (Fig. 1-3). (All analyses should be conducted according to federally approved methods, which are described in Appendix B.)

1.4 A Focused Approach

By far the most important factor in monitoring is selection of indicator parameters for testing the water quality impacts of interest. The

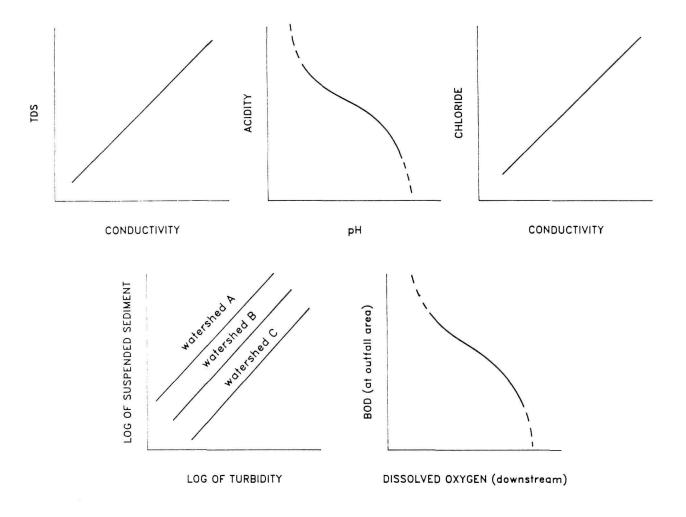
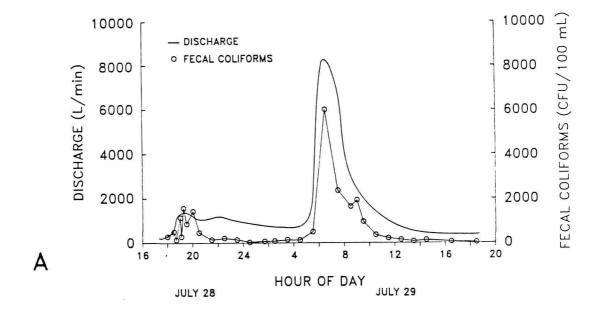


Fig. 1-2. Certain basic water quality parameters exhibit direct relationships with other parameters.

short lists of suggested monitoring parameters recommended in this handbook are based on our own experiences with field monitoring, plus information drawn from a thorough literature review (see especially Flora et al., 1984; McNeeley et al., 1984).

Most water quality questions could be answered with a "complete" water quality survey, using many physicochemical as well as biological indicators; however, the expense of such a "shotgun" water quality survey is in most cases prohibitive. Therefore, some researchers have attempted to develop shorter lists of parameters for general monitoring (Couillard and Lefebvre, 1985). Sherwani and Moreau (1975), for example, recommend measuring a relatively short set of parameters as a general water quality monitoring scheme, based largely on U.S. Environmental Protection Agency (EPA) studies. Their recommended water quality parameters are:

- biochemical oxygen demand (BOD)
- chemical oxygen demand (COD)
- chloride
- chlorophyll
- conductivity
- dissolved oxygen (DO)
- fecal coliform bacteria (FC)



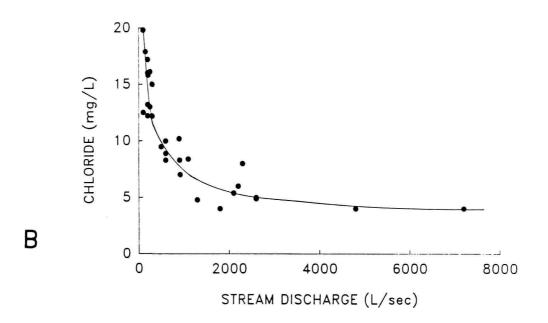


Fig. 1-3. Stream concentrations of substances from surface sources, such as bacteria from grazed lands, are often directly related to discharge since high flows flush them into the watercourse (A) (Kunkle, 1972b). On the other hand, substances originating from ground-water sources, such as chloride, are often inversely related to discharge, since high flows have a diluting effect (B) (Kunkle, 1972a).

- discharge
- nitrogen (ammonia)
- nitrogen (nitrate)
- nitrogen (organic)
- pH
- phosphorus (orthophosphate)
- phosphorus (total)
- total suspended solids (TSS)
- temperature
- total organic carbon (TOC)
- turbidity

These parameters together should effectively detect pollution, but even this limited number of tests--by no means a comprehensive analysis--will be expensive, costing about \$200 per sample in many laboratories. Moreover, a general monitoring list such as this one inevitably is more suited to detecting certain kinds of pollution at the expense of others. In this case, the above water quality parameters would detect sewage impacts well (BOD, bacteria, and nutrients are especially indicative) but be of little value for detecting coal mining impacts, where observations for metals, sulfate, and acidity would be important.

Many attempts have been made to develop a "water quality index" composed of a few select water quality parameters. One of these is the "National Sanitation Foundation Water Quality Index," which uses nine parameters, weights the measurements for each parameter, and from these figures derives a stream's index of water quality on a 0 to 100 scale (Ott, 1978). An index provides a useful way to rate the quality of water in streams for stream-to-stream comparisons or for following trends in water quality in a quantifiable way. However, indices are of limited interest from a park management viewpoint in that most are oriented toward evaluation of municipal sewage impacts.

Almost any impact on water quality can be detected with a few well-chosen measurements. This handbook presents short lists of parameters designed to assess the impacts of specific land uses commonly affecting NPS waters. A short, problem-focused list of water quality parameters offers the advantage of lowered analytical costs so that more samples can be gathered and more observations can be made. Generally, it is much better to spend money on biweekly observations of, say, three key water quality parameters than to buy quarterly analyses for a dozen less specific parameters. Since stream chemical concentrations can fluctuate drastically with hydrologic changes, more frequent sampling also helps define these hydrologic fluctuations and their effect on contamination levels.

One disadvantage to a focused approach to monitoring is that certain types of pollutants may be overlooked. To screen for unexpected contaminants, from time to time a few selected water samples can be analyzed more completely; this information would complement the data generated by focused monitoring.

1.5 Legal and Administrative Considerations

Since this handbook is intended as an introductory guide to the technical aspects of devising a water quality monitoring plan, the recommendations presented here are not intended to deal directly with the

legal considerations of water pollution or compliance monitoring. However, compliance and enforcement often come into play if water quality is to be protected. When specific legal questions or permit requirements are or could be of concern, then information on local, state, and federal regulations and permit requirements should be acquired from the appropriate agencies before monitoring is initiated. (Note: Under the Water Quality Act of 1987 [formerly the Clean Water Act], an NPS unit, even with exclusive jurisdiction, can be cited by the State for water quality infractions.) Some general information on permits and laws is provided in Appendix C; compliance monitoring is addressed separately in Appendix D.

The Environmental Protection Agency has developed water quality criteria that are summarized in the recently issued <u>Quality Criteria for Water</u> ("Gold Book") (USEPA, 1986). (These criteria are listed in Appendix E.) "Criteria" are research-based scientific judgments about the potential detrimental effect of individual water quality constituents on aquatic species and humans. State agencies use such water quality criteria as a basis for setting "standards," which are legally allowable levels of a constituent in water to protect a designated water use.

This handbook deals with stream monitoring, not drinking water; however, we might point out that under the Safe Drinking Water Act, Public Law 93-523, Section 1412, the EPA or states are required to regulate contaminants that may adversely affect public health. Standards for these contaminants, defined by the Safe Drinking Water Act, are included in Appendix E. The Public Health Service officers assigned to NPS Regional Offices are available to assist with monitoring drinking-water supplies and other health and safety questions.

1.6 Recommended Resources

Each of the chapters in this handbook contains a bibliography that includes references as well as publications considered useful for further reading on the topic covered. Highly recommended sources are listed in boldface. In addition, five books that we believe are essential references for anyone designing and implementing a water quality monitoring program should be purchased if at all possible. These references are listed below:

- American Public Health Association. 1985. (16th ed.) Standard methods for the examination of water and wastewater. Washington, DC. 1268 pp.
- Brown, G.W. 1983. (2nd ed.) Forestry and water quality. Oregon State University Book Stores, Inc., Corvallis, OR. 142 pp.
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- U.S. Environmental Protection Agency. 1983. Technical support manual: Waterbody surveys and assessments for conducting use attainability analyses. [Vol. I.] Office of Water Regulations and Standards, Washington, DC. 231 pp.

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HOW TO DESIGN A WATER QUALITY MONITORING PLAN

2.1 <u>Introduction</u>

This chapter presents an approach to designing a water quality monitoring plan and provides the framework for recommendations on specific land-use impacts discussed in succeeding chapters. These monitoring recommendations are based on four "facts of life" typical to many NPS units:

- 1. The park has limited staff for conducting water quality surveys.
- 2. Limited funds are available for water quality monitoring work.
- 3. Travel to stream monitoring sites involves logistical problems that will affect sampling frequency.
- 4. Park management will expect practical information, supported by reliable data, documenting water quality problems that may require management action.

The constraints imposed by these common conditions dictate a bias toward the simple and inexpensive.

Sampling design may be approached using the following seven-step procedure, adapted in part from Sanders et al. (1983):

- 1. <u>Define the objectives</u> of the monitoring program. Identify potential sources of pollution and other needs for monitoring.
- 2. <u>Determine sampling site locations</u>. Carefully review all existing information and try to link monitoring sites to any existing sites of other monitoring operations (Fig. 2-1).
- 3. <u>Select water quality parameters and sampling frequencies.</u> The sampling charts in chapters 4 through 9 recommend parameters and sampling frequencies for assessing impacts that may result from six common land uses.
- 4. <u>Decide on the methods needed to sample the selected parameters</u> to determine which parameters will be analyzed by park personnel and which will be contracted out. Then, select the equipment necessary for field and in-park analyses and--if needed--choose a suitable contract laboratory.
- 5. <u>Calculate costs</u> for the monitoring plan, including initial capital expenditures and recurring sampling costs.
- 6. <u>Determine the methods of data analysis</u> and the system of data storage and retrieval to be used. Preliminary sampling can aid in selecting appropriate analytical techniques.
- 7. <u>Decide what reports will be prepared and when they will be presented.</u> These reports should meet the objectives of the monitoring program and the information needs of park management.

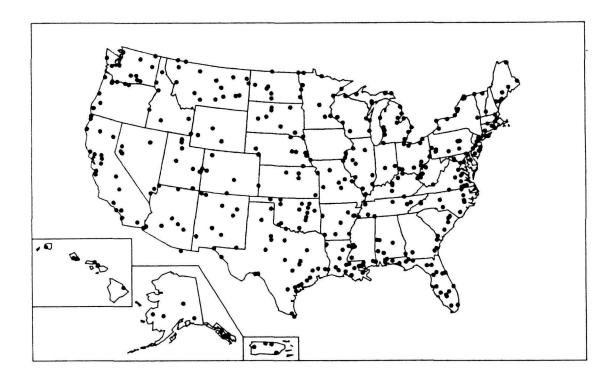


Fig. 2-1. Locations of the USGS National Stream Quality Accounting Network (NASQAN) stations in the 48 conterminous states as of 1987. (Map provided by USGS National Center, Reston, VA.)

These steps are discussed in detail below.

2.2 Monitoring Objectives

A vital first step in monitoring is to specifically define the monitoring objectives. For NPS units, such objectives almost always entail evaluation of one or more of the following:

- <u>impacts</u> caused by a particular land use or combination of land uses
- compliance with federal or state standards or legal requirements
- <u>baseline</u> or <u>background</u> <u>data</u> characterizing existing water quality for long-term records, general inventory, or pre-existing (historical) conditions

Whatever the objectives, it is important to clarify them with all cooperators--technicians, rangers, supervisors, contract laboratory personnel, and anyone else involved--to generate further ideas, ensure a well-thought-out program at the outset, and identify potential difficulties.

2.3 Sampling Site Location

The selection of stream sampling sites depends on the monitoring objectives, which usually entail the location of existing or potential impacts. Sampling stations can be established as:

- individual stations in a network
- a pair of sites above and below a suspected impact
- a single site for use before and after an activity of potential impact

These options are frequently combined.

A network of individual stations is most often used in monitoring programs. The stations may be concentrated in such key locations as swimming areas or river reaches, or they may be spread throughout entire river systems (Fig. 2-2). Often it is useful to select sites, such as bridges, that are easily accessible and can be reached throughout the monitoring period. However, this should not preclude selection of sites that will contribute to a more representative or complete data base. Collection of baseline water quality data will usually entail a network of stations designed to characterize streams and identify zones of pollution. This could include monitoring some watersheds at their mouths for the purpose of assembling profiles for basin-to-basin comparisons.

Where pollution occurs or is anticipated within a discrete area, stations sited above and below the area can either reveal the source of pollution or detect natural differences in water quality between the two sites. This scheme is particularly useful when the suspected pollution is from a "point source" such as sewage pipe outfall. Sampling below point sources must be below the mixing zone, i.e., at a point where the pollutant is mixed in, so that a representative sample can be collected.

Some water quality impacts occur as a result of an activity of limited duration, such as logging. In this situation, monitoring water quality at the same site before and after the activity can help identify an impact.



Fig. 2-2. Example of a network of sampling stations spread throughout a watershed.

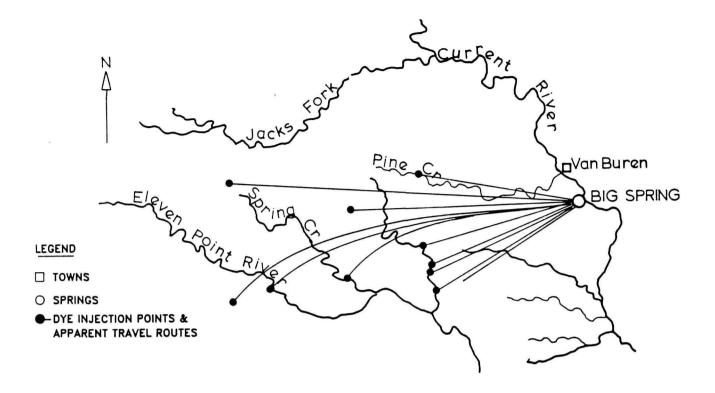


Fig. 2-3. Example of flow patterns in a karst area near the Ozark National Scenic River. Adapted from Mark Twain National Forest, unpublished Environmental Impact Statement, 1986. (Based on studies by T.J. Aley.)

In some areas, a paired watershed study may be an option for water quality monitoring, in which one watershed serves as a control and the other contains the potential or actual impact or land use. However, unless the two watersheds are carefully matched or are well-calibrated prior to the impact, the data can be misleading. Still, a nearby watershed can serve as a useful comparison. If, for example, a stream in watershed "A" with cattle grazing has ten times the coliforms of a stream in watershed "B," which is undisturbed, a pollution problem would be suspected.

A special case in site selection exists in limestone areas characterized by karst topography. These areas contain large springs, sinkholes, caves, and influent or "losing" streams where runoff can enter underground conduits. By these means, runoff from one watershed can emerge in a spring in a completely different watershed (Fig. 2-3). Water quality sampling in such areas should be accompanied by sampling of springs. Also, park staff will need to work with local hydrologists and geologists familiar with the karst hydrology of the area.

2.4 Selection of Water Quality Parameters

Each of chapters 4 through 9 presents a "sampling chart" containing recommended parameters. Each of the sampling charts divides the recommended parameters into three categories, as follows:

- 1. those that can be analyzed at the stream site;
- 2. those that can be analyzed in a park laboratory;
- 3. those best or necessarily analyzed by a contract laboratory.

Individual parameters appear under one of these three headings, with the exception of certain parameters that can as easily be analyzed in either of two sites; in these cases, the parameter is listed on the line dividing the two categories, and it is left to the judgment of park personnel which is the more suitable site of analysis. For example, pH is ideally measured at the stream site (especially in low ionic waters), turbidity can be measured using a turbidimeter purchased by the park or be contracted out, and metals are best contracted out.

In categorizing the recommended parameters, we considered several subjective factors, including the desirable extent of NPS staff involvement, capital and recurring costs, sample transport considerations, quality control, level of expertise or equipment required, and the nature of the analysis. However, common sense should always prevail: although we recommend, for example, that pH be measured on-site, if frigid weather conditions are likely to damage a pH meter, then rapidly returning samples to the park laboratory for analysis would be a more sensible approach.

2.4.1 <u>Parameter sampling techniques</u>. The purpose underlying a water quality monitoring program governs the field sampling procedures that should be followed. Commonly, the resource manager would like to know if the quality of stream water meets the quality recommended for that stream's designated use. This can be assessed by comparing parameter values from a stream sample to water quality criteria published (and periodically updated) by the EPA. These criteria are listed in Appendix E. Because most EPA criteria are based on the dissolved constituents in a water sample, field sampling techniques should include filtering the water that is to be analyzed for anions and cations. Field procedures should also follow proper sample preservation techniques, which are described in Appendix F.

Quality control during sampling should routinely be implemented to detect any data errors resulting from improper sampling or handling methods, poor sample preservation, or collection of nonrepresentative samples. These quality control procedures are also discussed in Appendix F.

2.4.2 <u>Discharge.</u> In any water monitoring effort, park personnel should obtain at least an estimate of stream flow, or discharge, in order to properly interpret water quality data. Wherever possible, stream gauging instruments should be used. Without discharge data, it may be impossible to distinguish pollution effects from normal variations caused by stream flow. For larger streams or rivers, discharge data is often available from USGS or other agencies (Appendix A). For watercourses lacking discharge data, park staff will need to make their own measurements or establish a stage (water depth)-discharge relationship. If no one on staff is experienced with stream gauging and calibration of stream cross-sections, the resource manager is referred to the National Handbook of Recommended Methods for Water-Data Acquisition (USDI, 1977) and to the USGS manuals by Buchanan and Somers (1968; 1969). Additionally, consultation with USGS or NPS Water Resources Division personnel, university specialists, or other hydrologists may be necessary.

2.4.3 <u>Biological measurements.</u> Although we emphasize moderately priced physical and chemical parameters for basic water quality monitoring, biological measurements can be used to supplement the physicochemical tests. The Environmental Protection Agency (USEPA, 1984) recommends such an integrated approach. Surveying aquatic communities, including benthic macroinvertebrate and fish surveys or bioaccumulation of contaminants in fish flesh, can yield the pollution "history" of a watercourse which point-in-time physicochemical sampling may not (Fig. 2-4). Other advantages are that biological sampling can reveal the effects of many known and unknown constituents; bioavailability of pollutants can be measured by toxicity testing; and pollutants can be assessed for which no adequate chemical tests are available. However, the expense of biological surveys is significant: a trained biologist must conduct species collection, identification, and data interpretation (Table 2-1). Also, biological indices and other ecosystem measures have yet to be standardized (Cairns, 1982; Perry et al., 1984).

In cases where a park staff biologist is able to carry out the laboratory work, sampling of aquatic life may be an economically viable option. In specific instances biological surveys are a useful supplement, costs notwithstanding, and these we have noted in the sampling charts where appropriate.

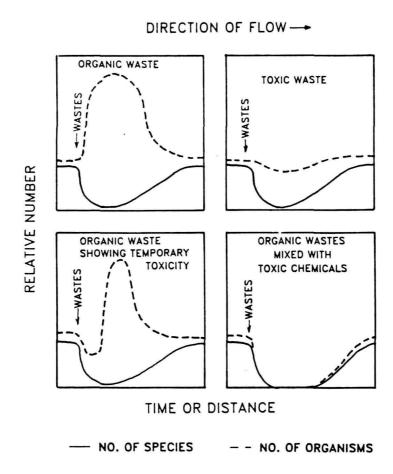


Fig. 2-4. Effect of different kinds of waste loading on species diversity and number of individuals in a stream. Adapted from Keup in USEPA, 1983b.

Table 2-1. Advantages and disadvantages of using macroinvertebrates and fish in evaluation of the biotic integrity of freshwater aquatic communities. Source: USEPA, 1983a.

MACROINVERTEBRATES

Advantages

- Fish that are highly valued by humans are dependent on bottom fauna as a food source.
- Many species are extremely sensitive to pollution and respond quickly to it.
- Bottom fauna usually have a complex life cycle of a year or more, and if at any time during their life cycle environmental conditions are outside their tolerance limits, they die.
- Many have an attached or sessile mode of life and are not subject to rapid migrations, therefore they serve as natural monitors of water quality.

Disadvantages

- They require specialized taxonomic expertise for identification, which is also time-consuming.
- Background life-history information is lacking for many species and groups.
- Results are difficult to translate into values meaningful to the general public.

FISH

- Life history information is extensive for most species.
- Fish communities generally include a range of species that represent a variety of trophic levels (omnivores, herbivores, insectivores, planktivores, piscivores) and utilize foods of both aquatic and terrestial origin. Their position at the top of the aquatic food web also helps provide an integrated view of the watershed environment.
- Fish are relatively easy to identify. Most samples can be sorted and identified in the field, and then released.
- The general public can relate to statements about conditions of the fish community.
- Both acute toxicity (missing taxa) and stress effects (depressed growth and reproductive success) can be evaluated. Careful examination of recruitment and growth dynamics among years can help pinpoint periods of unusual stress.

- Sampling fish communities is selective in nature.
- Fish are highly mobile. This
 can cause sampling difficulties
 and also creates situations of
 preference and avoidance. Fish
 also undergo movements on diel and
 seasonal time scales.
- There is a high requirement for manpower and equipment for field sampling.

2.5 Sampling Frequency

Deciding when and how often to sample is a blend of art and science, seasoned by practical constraints and field conditions. In this handbook we distinguish between "key parameters," "supplementary parameters," and "special studies." The frequency recommendations for key and supplementary parameters suggest that a parameter be measured on a systematic schedule when not modified by seasonal needs and constraints. Extra sampling of certain parameters is critical during the hydrologic conditions described in the following sections. Monitoring frequencies for different stream types are described in Table 2-2.

- 2.5.1 <u>High-flow period</u>. Due to the diluting effects of high flow and pollutants introduced by runoff, high-flow periods are critical times to sample. Constituents best evaluated during high flow are those associated with nonpoint sources, such as the following:
 - sediment and turbidity originating from erosion of roads, clearcuts, surface mines, agricultural lands, and other areas lacking ground cover
 - road deicing chemicals
 - metals that adsorb onto and are transported by sediment particles

Heavy rains or snowmelt conditions carry accumulated surface substances such as these into watercourses (Fig. 2-5). In one northern New England study, 80 percent of the annual sediment yield occurred during the peak one-week period of spring snow melt (Kunkle, 1972). Although some chemicals, such as salts used for deicing, will be diluted by large volumes of water, it is still important to monitor them during high runoff when the total volume being transported is greatest.

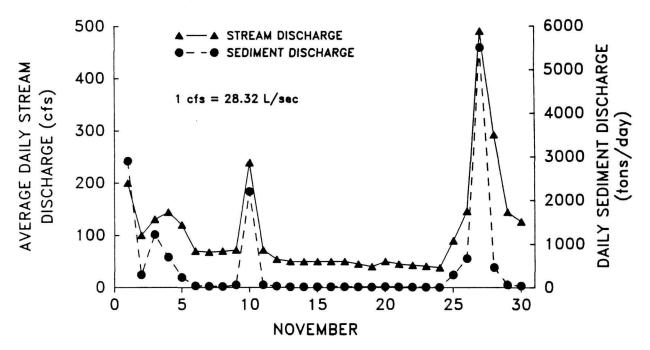


Fig. 2-5. Storm runoff delivery of sediment. Based on Lugo et al., 1976.

Table 2-2. Sampling frequencies for key and supplementary parameters. 1

Stream	Parameter T	ype
Type	Key	Supplementary
Perennial ²	Sample every 2 weeks during principal hydro- logic and impact periods; sample monthly or less during the remainder of the year. ⁵	Sample quarterly in conjunction with key parameters to cover a range of hydrologic conditions.
Intermittent ³	Sample every 2 weeks during principal hydro- logic and impact periods; sample monthly or less during the remainder of the flow period. ⁵	Sample quarterly in conjunction with key parameters to cover a range of hydrologic conditions.
Ephemeral ⁴	Sample at least twice a year during precipitation events that result in stream flow.	Sample at least once a year in conjunction with key parameters.

 $^{^{1}\}mathrm{Special}$ studies should be conducted as needed during the appropriate time of year or on a schedule that will produce the best results.

²Perennial streams are those that flow throughout the year.

³Intermittent streams flow seasonally.

⁴Ephemeral streams flow for short periods of time only in response to significant precipitation events or snowmelt.

⁵If the impact is of short duration during the year, increase sampling frequencies as needed to weekly or daily.

- 2.5.2 <u>Low-flow period</u>. Some stream-water constituents are best detected during the period of lowest flows when they become concentrated as a result of the low volume of water. The predominant source of stream flow during the low-flow periods is ground-water inflow from waters that have had the greatest residence time to contact mineral solids and mobilize constituents. Point-source pollutants, such as sewage outfalls, are especially easy to detect during low flow. Other contaminants or conditions best detected during low-flow periods are these:
 - ground-water inputs such as metals, organics, chloride, and silicon oxide
 - dissolved oxygen (DO) minimum values, especially when low flow and elevated water temperature coincide
 - BOD and COD maximum values, which occur when low flow coincides with higher temperatures (and therefore low DO)
 - leaking septic tank leach lines, leaking waste-water impoundments, and other sewage or waste inflow
 - feedlot contamination that has leached into the ground water contributing to a watercourse
- 2.5.3 <u>Storm periods.</u> Like the high-flow periods, storms create surface runoff that carries contaminants into watercourses. The difference is that they can occur any time of year; therefore, streams should be sampled during storm events. Constituents that are primarily storm-transported include these:
 - sediment from construction sites and from mining or logging operations
 - fecal bacteria from areas of livestock grazing, nitrogen and phosphorus from fertilizers, or pesticide residues
 - organic loading from bypassed sewage treatment systems and from overtopped tailing ponds or sewage lagoons

If sampling cannot personally be collected during storm runoff, automatic storm samplers can be utilized (see Appendix G).

- 2.5.4 <u>High recreational-use periods.</u> Heavy recreational use can result in increased contamination of stream water, especially from the following sources:
 - swimming, rafting, and other non-motorized water activity that bring human waste into a watercourse
 - backcountry use by hikers, horse-back riders, pack strings, or off-road vehicles
 - resorts and vacation homes that are producing increased sewage waste
- 2.5.5 <u>Periods of biological change.</u> Variations in nature can directly affect water quality. Algal blooms may depress DO levels in slow-moving

streams. In Eastern deciduous forests, water quality changes can result from heavy leaf fall in smaller streams. Migrations of wildlife, such as waterfowl or elk, can also have temporary but measurable effects on water quality.

- 2.5.6 <u>Periods of land disturbance.</u> Monitoring should be conducted before, during, and after periods of heavy land-use impact brought about by logging, mining, grazing, and farming so that the effects of these activities can be documented.
- 2.5.7 <u>Pollution slugs.</u> Instances occur wherein slugs of pollutants will course down a waterway as a result of clandestine dumping, spills, breaches in waste ponds, pipeline breaks, and other point-in-time occurrences. It is generally very difficult, if not impossible, to sample these pollution slugs, especially if their existence is not suspected. Usually, some type of continual-recording or -sampling equipment is needed if the slug cannot be anticipated. If ionic substances such as brine are entering a watercourse, a recording conductivity meter may reveal their presence. If regular night-time dumping is suspected, an automatic (clock-driven) water sampler might be used to detect the contamination. Biological indicators can be useful in revealing changes in aquatic life that suggest the periodic presence of contaminants. Analysis of sediment or other stream-bottom material can confirm the nature of the polluting substance(s).

Sampling frequency considerations relating to the above conditions are noted in each of the sampling charts. Monitoring recommendations for key parameters will usually result in 15-20 samples per year for these parameters considering the extra samples taken during the high- and low-flow periods, during one or more storms, and during periods of more intensive land or recreational use or other impact (Fig. 2-6). Quarterly sampling of supplementary parameters, if implemented, can be scheduled to coincide with periods of high or low flow or intensive land use. Taken together, this information is usually sufficient to reveal seasonal patterns and to identify the existence and severity of common water quality problems. Depending on the extent to which parameter values exceed acceptable levels, this information would also indicate any need for further study.

Every monitoring plan must be tailor-made, and it is important to combine systematic (e.g., monthly or quarterly) sampling with sampling that corresponds to important hydrologic seasons or land-use activities. The monitoring notes in the sampling charts will help the resource manager to devise a monitoring plan that will characterize the quality of a watercourse during important use or flow periods as well as during year-round conditions.

For research purposes, inferential statistics are often used to analyze water quality data. However, in these cases an unbiased method of sample frequency calculation, involving random sampling, should be used. In addition, sample number calculation should be based on each parameter's variability at a particular stream site. Although random sampling and sample number determination based on parameter variability are considered important for inferential statistics, they are typically not applied to stream-water monitoring. A random-sampling schedule might not be representative of hydrological conditions over the course of a year. Similarly, the extreme variability inherent in coliform bacteria analyses, for example, will frequently result in sample numbers that are economically and logistically infeasible (Sherwani and Moreau, 1975). Instead, systematic or

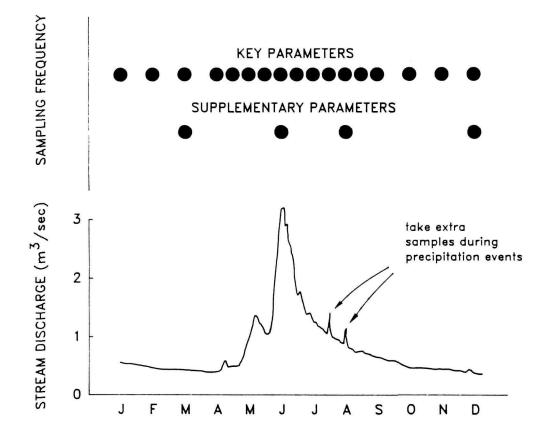


Fig. 2-6. Suggested sampling frequencies as they relate to stream hydrology over the course of a year.

routine sampling is characteristically used by USGS, EPA, and most states in their water quality monitoring activities. Many years of systematic monitoring have yielded a reliable history of information on water quality conditions.

2.6 Equipment and Contract Laboratory Selection

As mentioned earlier, recommendations are made in the charts relating to which parameters are best measured by whom. For those parameters that can be measured either by park staff or by contract laboratory, the resource manager must decide which is more expedient. Representative costs of field and laboratory equipment and parameter analyses are contained in Appendix H. In some parks, maintenance staff may rountinely analyze coliform, sediment, turbidity, or other parameters for sewage treatment plant operation. If this activity can be coordinated with your water quality monitoring program, some cost savings can be realized in equipment and service.

It is important to recognize that while field instruments such as pH and conductivity meters are relatively simple to use, obtaining valid data is not always easy. For example, a correct pH value may be difficult to obtain in the soft waters of many parks in the mountain and Great Lakes states and may require special procedures. Likewise, failure to properly standardize an instrument such as a conductivity meter--a common shortcutcan introduce major errors into the data. Selection of suitable

instrumentation is also critical. When purchasing a pH probe or conductivity cell (cell constant), the resource manager must ensure that these items will measure the data range routinely encountered in the waters in which they will be used. These concerns are further addressed in Kunkle and Wilson (1984).

Several points bear consideration in searching for a contract laboratory to conduct water quality analyses. Accessibility--by mail, if necessary--is one. Others include laboratory quality control, certification, analytical costs, and flexibility and timeliness.

- 2.6.1 <u>Laboratory quality control.</u> Quality control in the laboratory is based on practices that ensure a specified degree of confidence in the analytical results. A good analytical quality-control program involves a series of practices that considers at least the following (APHA, 1985):
 - use of standardized and approved analytical methods (federal regulatory inorganic test procedures are contained in Appendix B)
 - routine analysis of a standard sample along with analyses of unknown samples to check the accuracy of analytical techniques (internal quality control)
 - analysis of prepared reference samples provided by an outside agency (such as EPA or the National Bureau of Standards) as a means of evaluating analytical techniques (external quality control)
- 2.6.2 <u>Certification</u>. If a laboratory is EPA- or state-certified, quality control is typically acceptable although costs might be higher than at a non-certified facility. By the same token, non-certified laboratories that practice internal and external quality control can be equally suitable. In certain legal situations, an EPA- or state-certified laboratory may be preferable or necessary.
- 2.6.3 <u>Costs.</u> Meet with the laboratory supervisor to discuss your exact needs. Be sure to obtain a current price list to use for calulating your monitoring plan costs or for price comparisons with other laboratories: prices can vary enormously. (In one survey of laboratory costs conducted by the authors, some prices varied by as much as 400 percent.) Learn whether the laboratory will provide sample bottles, preservatives, and other necessities; usually it is more practical and effective for quality control if the laboratory provides these items.

It is essential to match a monitoring program's objectives with the analytical procedures to be used by a contract laboratory. Analysis sophistication should be adequate to provide the needed data and to allow the desired interpretations. Overly sophisticated analyses (analyzing to ppb when ppm would suffice) add unnecessary cost; by the same token, analyses at very broad levels could be useless. If litigation is involved, you must ensure that the lab's planned analyses meet the court's requirements. Since most chemical analyses can be conducted in one of several ways, decisions of this sort should be made at the program's inception. For example, metal analysis results can be provided in units of dissolved, total, total recoverable, acid extractable, or acid soluble forms.

Although analytical costs are often of primary importance in NPS areas, they should not be the only criterion for selecting a contract laboratory. If quality control is poor or nonexistent, your data could be unreliable. Still, a well-equipped and well-operated local laboratory may provide low-cost analyses that can amount to considerable savings over a better-known government-operated laboratory.

2.6.4 <u>Flexibility and timeliness.</u> Monitoring schedules can require sample analysis at times outside of normal business hours. When this is the case, you will need to know how flexible the laboratory staff can be in analyzing your samples at the necessary times. By the same token, turnaround time for analysis results should be suitable to your needs.

2.7 <u>Calculation of Monitoring Plan Costs</u>

Figuring a budget for your monitoring plan will entail consideration of initial capital costs (field and laboratory equipment for the park) and recurring costs (costs per analysis). Total sampling costs will include transport, labor, shipping, containers, etc. Analytical costs for an example monitoring plan are figured in Chapter 11, and representative costs of equipment and analyses are provided in Appendix H.

2.8 Data Analysis

You should determine how your data will be analyzed and presented early in the planning stages of your monitoring program. Two methods for assessing water quality monitoring results are 1) comparing parameter values with EPA criteria or state standards, and 2) using inferential statistics to compare parameter means between sites and over time.

As a means of evaluating whether a particular parameter exceeds acceptable levels for different stream uses, Appendix E provides a list of EPA criteria for parameters recommended in this handbook. (In some states, these criteria may be more stringent; refer to the appropriate state environmental agency for standards applicable in your state.) In using this table, be aware of natural background conditions in your area that may elevate or depress certain parameters independent of human-induced impacts (see Chapter 3).

For comparing sample means between sites or over time at the same site, the Cochran's Approximation to the Behren's-Fisher Student t-test and the Rank-Sum Test are often useful. Both statistical tests use a method that determines the differences between means based on a level of confidence. However, the t-test has been most commonly used in water quality statistical analyses. Snedecor and Cochran (1980) or Steel and Torrie (1980) can be consulted for actual calculations and a more detailed discussion of these two tests.

You may wish to add water quality data to an existing data-base system for the park or even a nationwide source such as Geographic Information Systems (GIS), maintained by the USGS. In such cases, it will be important to consult with the agency or unit maintaining the system on the proper format for submitting your park's data. The USGS uses GIS for such tasks as mapping stream basin characteristics and relating this information to changes in stream-water quality as a result of different land-use practices.

In this way, GIS can be used as a predictive tool for water resource managers that desire a more intensive sampling effort for selected stream reaches.

2.9 Report Preparation

When you are ready to present the results of your water quality monitoring to those needing the information, you need to be able to convey a water quality picture that is clear and easily comprehended. One way is to make effective use of graphics. A variety of graphical styles for presenting water quality data are described and depicted in Appendix I.

2.10 Summary

Much has to be considered in designing a water quality monitoring plan. In this chapter we have attempted to identify and discuss the most important aspects of monitoring plan design. In the ensuing chapters that address common land-use impacts, you will learn more about the specific impacts and their effects on water quality. Monitoring suggestions are made that will assess these impacts effectively but at relatively low cost. Even then, and keeping in mind the importance of a consistent protocol for long-term monitoring, shifts in plan design may have to be made. Averett (1978) offers perhaps the best counsel when he advises, "Define your problem well, select your water-quality parameters carefully and in a conservative manner, review your data frequently, and do not be afraid to discard or add parameters in the light of added knowledge."

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NATURAL BACKGROUND CONDITIONS

3.1 General Description

The following sections are meant to be general guidelines for understanding the processes that contribute to natural background qualities of stream water. Although these generalizations are not without exceptions, they are provided as a means of introducing the reader to the concept that natural environmental factors contribute to a stream's water quality. A graphical representation of the major factors that individually or collectively may influence stream water quality is presented in Figure 3-1.

Park resource management specialists should be aware of naturally occurring sources of contaminants that are unique to their parks. In some areas, background levels of certain parameters may exceed federal or state standards, yet they are not harmful to the organisms that have adapted to these conditions. In such cases, these natural background conditions must be taken into account to properly interpret data and to avoid confusing them with human-caused impacts.

One approach to obtaining background information on a particular stream is to review the USGS Water Resources data base for streams in the same area (Table 3-1). (Sources of USGS water quality data and other possible sources of stream water quality information are listed in Appendix A.) If the stream of interest is presently affected by land-use impacts, water quality data that was collected prior to the impact(s) should be sought. Be aware

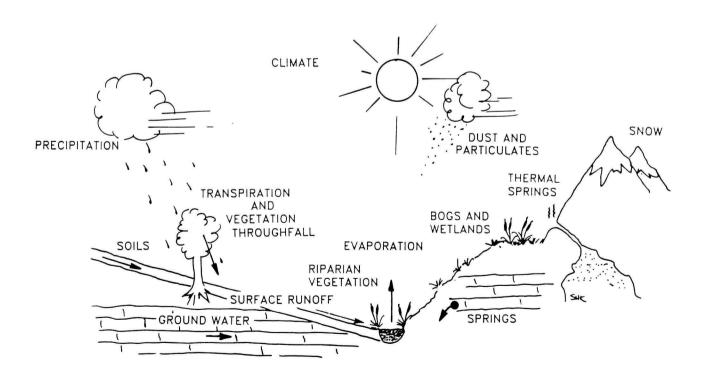


Fig. 3-1. Natural processes that may influence stream water quality.

 $\hbox{Table 3-1.} \quad \hbox{Examples of water chemistries for selected parameters and $USGS$ stream stations in the United States. }$

Parameter	Unit ¹	John Day River, Oregon ²	Cache La Poudre River, Colorado ³	Arkansas River, Kansas ⁴	Spruce Creek, Florida ⁵	Cattaraugus Creek, New York ⁶
рН	standard units	8.4	7.9	8.3	6.0	8.1
conductivity	μ mhos/cm at 25°C	323	54	2350	90	314
alkalinity	mg/L as CaCO ₃	150	22	160	16	110
temperature	°C	22.4	13.5	24.0	25.0	23.0
calcium	mg/L as Ca	24	5.9	200	11	47
magnesium	mg/L as Mg	13	1.5	86	1.7	8.5
sodium	mg/L as Na	26	2.3	270	7.5	8.3
potassium	mg/L as K	3.8	0.7	9.9	0.8	2.3
sulfate	mg/L as SO4	19	2.9	1200	11	31
chloride	mg/L as Cl	4.8	0.7	72	15	12
fluoride	mg/L as F	0.2	0.2	0.7	0.0	0.1
phosphorus	mg/L as P	0.02	0.01	0.10	*	0.00
silica	mg/L as SiO ₂	9.5	7.9	10	5.4	3.2
total dissolved solids	mg/L at 180°C	195	36	1990	154	209
nitrite + nitrate	mg/L as N	0.05	0.11	*	0.03	0.56
point discharge	cfs	283	626	26	58	255

* not analyzed

- 1 All ions (Ca, Mg, Na, K, SO₄, Cl, F, PO₄, Si, NO₂, NO₃) were analyzed as dissolved (i.e., field-filtered using a 0.45 micron membrane filter).
- ²Sample collected on August 21, 1979 for USGS station #014048000, John Day River at McDonald Ferry, Oregon. From USGS Water Resources Data for Oregon, Volume I. OR-79-1.
- ³Sample collected on August 15, 1979 from USGS station #06752000, Cache la Poudre River at mouth of canyon, near Fort Collins, Colorado. From USGS Water Resources Data for Colorado, Volume I. CO-79-1.
- ⁴Sample collected on August 28, 1979 from USGS station #07137500, Arkansas River near Coolidge, Kansas. From USGS Water Resources Data for Kansas, Volume II. KS-79-2.
- ⁵Sample collected on August 10, 1979 from USGS station #02248000, Spruce Creek near Samsula, Florida. From USGS Water Resources Data for Florida, Volume I. FL-79-1.
- ⁶Sample collected on August 8, 1979 from USGS station #04213500, Cattaraugus Creek at Gowanda, New York. From USGS Water Resources Data for New York, Volume I. NY-79-1.

that nearby streams as well as different reaches on the same stream may have dissimilar water quality characteristics. These differences can be natural or human-caused. A good practice to follow is to assemble all available information on a stream, then walk the length of the stream reach of interest in order to discover possible sources of water quality degradation.

3.2 Geologic Influences

The initial source of most dissolved constituents in stream waters is the minerals in rocks that water passes over or through as it moves into streams. A general indication of the geologic factors that may influence the quality of stream waters can be acquired through 1) a review of geologic maps (found at most major libraries) for the watershed of concern, and 2) general relationships between water quality and geology as exemplified in Table 3-2. This table is by no means an all-inclusive "geology versus water quality" index. However, the table does provide insight into the predominance of certain ions over others in stream waters draining specific project units.

3.3 Precipitation

Generally, as rainfall increases, dissolved solids in streams decrease. An example of this condition is found in semi-arid areas where stream discharge is partly controlled by low precipitation and high evaporation rates. Weathering of the underlying rock and soil is slow and the dissolved

Table 3-2. Typical chemical composition of waters (mg/L). Taken from R. H. Brown et al., 1977. Reprinted with permission.

	Place ²	Total dissolved salts	Ca	Mg	Na	K	Cl	SO ₄	HCO ₃	Fe
Granite	1	122	14	4.7			5.9	52	46	
	2	83 470	7 62	2 28	18 15		17 66	4 14	24 224	0.1
Basalt	4	169	27	10	13		6.2		128	0.08
Dasaic	5	165	15	8.9		3.0	5.0		109	0.01
	6	367	48	31	15	3.8	4.0		192	1.97
Calcarenites	7	437	107	12	42		61	36	355	
and others	8	540	132	25	34		72	101	355	
	9	884	157	38	99		171	245	342	
Compact	10	520	95	61	6		10	61	402	
crystalline	11	330	86	13	16		3.5	45	240	
Limestone	12	210	44	4.3	8		11	27	100	
Dolomites	13	890	103	82	83		141	303	336	
	14	440	68	46	29		90	58	147	
	15	662	87	56	68		142	207	192	
Shales	16	3,255	512	22	47		73	1,485		81
	17	2,236	235	138	394		936	282	504	
	18	1,667	145	106	304		583	353	342	
Sandstone	19	143	35	11	14		14	6.4	50	0.5
and pure	20	189	41	3.4			23	26	63	0.2
sands	21	140	10	8	25		36	45	18	7.0
Sands and	22	482	59	37	67		74	84	336	
ordinary	23	439	65	38	44		63	79	326	
sandstones	24	504	69	27	69		77	162	200	0.4
Evaporites	25	5,609	536	601	315		650	3,368	204	
	26	2,881	613	126	72		98	1,887	150	
	27	245,300	1,071	1,974	88,897		137,778	11,981	324	
Lignites	28	1,208	16	6.6			36	11	1,506	0.1
	28	472	7	8	13		20	16	200	7

¹The chemical composition of the water from each of these rocks may vary considerably from the typical composition shown, depending on hydraulic or weather conditions and the presence or absence of soil, etc.

²1, Butte, Montana, United States. 2, France. 3, San Diego, California, United States. 4, Mud Lake Region, Idaho, United States. 5, 6, The Dalles, Oregon, United States. 7, 8, 9, Tunisia. 10, 11, 12, France. 13, 14, 15, Tunisia. 16, France. 17, 18, Tunisia. 19, 20, France. 21, 22, 23, Tunisia. 24, France. 25, 26, 27, Tunisia. 28, France.

products are concentrated into the small amount of water available to streams. However, occasional floods in these areas may be low in dissolved constituents as a result of dilution and a significant bypass of water contact with soils and rocks during overland flow to streams. Stream-water samples collected under these conditions may have abnormally high TSS as a result of the scouring effect of high stream flows.

3.3.1. Precipitation quality. Dust particles and gases in the atmosphere adhere to water vapor droplets that fall to earth as precipitation. The most common gases are oxygen, nitrogen, and carbon dioxide, but many minor constituents appear as well. Precipitation that is intercepted by vegetation will pick up additional minerals and organics from leaves and branches. When this intercepted water reaches the land surface, it infiltrates the soil and rock interface to percolate through the weathered mantle. There the water further dissolves minerals and participates in various complex exchanges and chemical interactions between mineral, floral, and faunal components. Thus, water that enters streams as overland, subsurface, or ground-water flow has physical and chemical qualities that reflect the mineralogy of the watershed, the character of the precipitation, and the nature of the vegetatative cover, generally in that order.

Atmospheric deposition of chemicals -- which includes rain and snow as well as the fallout of dry materials -- can have a significant effect on stream-water quality in some NPS areas. Chemicals in the atmosphere coming from natural sources include dust, volcanic emissions, and salts. coastal areas, for example, precipitation, and therefore streams, will naturally contain higher levels of chloride. Atmospheric deposition can be quantified for the purpose of predicting its potential influence on stream water quality. The National Atmospheric Deposition Program established to monitor atmospheric deposition in the United States, maintains a data base from which levels of pH and other constituents likely to be found in local precipitation can be determined. The NADP was established in 1978 and has grown to include approximately 200 sites, of which NPS presently operates 29 (Fig. 3-2). At each site precipitation is collected and measured continuously, and ten parameters (calcium, ammonia, [field and laboratory], magnesium, sulfate, conductivity, sodium, nitrate, potassium, and chloride) are sampled weekly. This precipitation data is available to the public in report and digital forms. All established NADP sites receive semiannual NADP data for the entire network. Data is also provided for a fee to non-network individuals. Contact information is listed in Appendix A.

3.4 Soils

Soils are strongly influenced by the effects of both climate and vegetation. Although soils are derived from rock, a soil's structure and chemistry is altered during its formation and may display little resemblence to its parent rock. The quality of many natural waters is the result of chemical and physical reactions that occur as water passes through soil zones to a stream. An important process that occurs in soils is the production of carbon dioxide from respiration and decay. Levels of carbon dioxide in unsaturated soil air spaces can be many times higher than aboveground surface air. The formation of carbonic acid, from the chemical reaction of carbon dioxide and water, is considered to be the major agent in the weathering of minerals from rocks. Organic acids in soils are also viewed as possible weathering agents.

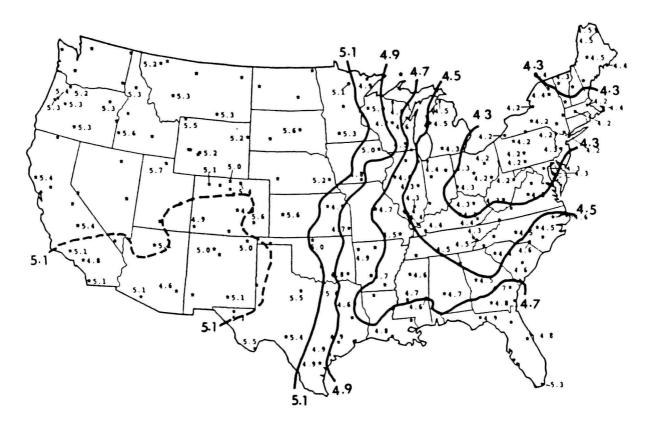


Fig. 3-2. Average pH values of precipitation in the United States. (Map provided by the National Atmospheric Deposition Program, Colorado State University, Fort Collins, CO.)

3.5 Other Factors Affecting Stream Water Quality

The effects of vegetation and topographic relief are difficult to evaluate with respect to increases or decreases of dissolved solids in stream water. Vegetation can increase weathering rates of minerals in contact with soil waters as a result of the production of carbonic and organic acids. However, vegetation also stabilizes soils, which can decrease physical erosion and thereby lessen the exposure of fresh rock to weathering processes. The effects of varying topographic relief are just as difficult to specify. An increase in relief would generally increase the rate of chemical weathering as a result of the instability of steep slopes and the consequent increase in weatherable fresh rock. However, increased relief also decreases the residence time of water passing through these soil-rock interfaces and therefore may decrease the rate of chemical weathering.

3.6 Springs, Seeps, and Bogs

Geothermal springs, sulfur springs, and similar mineral waters may naturally contain levels of metals, radioactive substances, or chemical compounds that are deleterious to aquatic life, drinking water, or the suitability of streams for recreation. Some watersheds contain natural oil seeps. Many western streams naturally are alkaline or saline, just as certain marsh or bog areas normally contain acidic waters. These natural background conditions can sometimes complicate data interpretation. For

example, mountain streams in West Virginia may contain acidity from natural bog conditions, from acidic precipitation, and from coal mining sources upstream, and it can be difficult to separate these three effects from one another.

Metals and other toxics of concern may bind to organic matter in water at roughly 1 μ eq of metal-binding capacity per mg of dissolved organic carbon (DOC). Organic carbon is indicative of the inputs of plant and soil organic matter into streams. Swamps, marshes, and bogs have the highest natural concentrations of DOC, in some cases 30 mg/L or more. At the other extreme, sea water will have only about 1-3 mg/L. Concentrations of DOC in streams lie somewhere between these values and are dependent on climate (Table 3-3).

3.7 Radioactive Substances

Radioactivity is the release of energy (i.e., alpha, beta, or gamma rays) from the disintegration of atomic nuclei. When an element such as radium decays, it yields radioactive substances (radionuclides) that can be an environmental concern. The greatest threat to park streams containing radionuclides is the detrimental effect on fish and wildlife species that rely on these streams for survival. Radionuclides are physical parameters because of their radioactive emissions; however, they are typically treated as chemical properties of water because sampling and analytical techniques for radionuclides are similar to those used for chemical parameters.

Certain mineral springs and other natural waters can contain high levels of radioactive substances, principally dissolved uranium and radium. Although the radionuclides thorium and radon gas are present in significant quantities in the environment, natural stream-water concentrations are usually undetectable because of the low solubility of thorium and the degassing losses of radon. Because the analysis of radionuclides is very costly, we recommend analyzing for gross alpha and gross beta emissions as an indicator of overall radionuclide levels. These analyses in turn would indicate the need for more extensive studies.

Table 3-3. Mean DOC concentrations of watercourses in different climatic zones. (Adapted from Thurman, 1985.)

***************************************	Climatic zones	Mean DOC (mg/L)
	arctic and alpine	2
	cool	3
	arid	3
	wet tropics	6
	warm temperate	7
	taiga	10
	swamps and wetlands	25

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RECREATIONAL IMPACTS

4.1 General Description

All parks with surface-water resources are potentially subject to water quality impacts arising from recreational use. Especially in the more heavily visited parks, overuse or improper management of recreational activities may lead to water quality degradation. These activities include backcountry use; water-based recreation such as swimming, fishing, and boating (Fig. 4-1); campgrounds; and concession facilities and developments, all of which can produce a variety of water contaminants (Table 4-1).

4.2 Water Quality Impacts

Of special concern in areas of heavy recreational use is the threat of water contamination with waterborne pathogens, including parasites transmitted by humans and domestic animals. Some pathogens may spread via contact recreation in contaminated waters, which can result in gastrointestinal bacterial and viral infections, serious eye and ear infections, or more frequent nuisances such as "swimmer's itch." An additional concern is bacterial and viral infections such as salmonellosis and hepatitis, and parasites such as <u>Giardia</u>, that can infect backcountry recreationists who consume improperly treated water. A listing of the more common waterborne diseases is presented in Table 4-2.



Fig. 4-1. This marina in Glen Canyon National Recreation Area, Arizona-Utah, can be a source of fuel and oil contamination.

Table 4-1. A summary of common sources and impacts of stream pollution associated with recreational activities.

Pollution Source	Characteristics and Impacts
Backcountry recreationists	Human and animal wastes contaminate water with bacteria, viruses, and parasites which in turn may infect those who drink the water. Erosion from trails, roads, and ski slopes may cause increased turbidity and sediment loading in streams and lakes.
Marinas, boating, and boat camping	Water quality in marinas is often degraded by runoff from parking areas and boat maintenance areas, careless fuel handling procedures, boat motor operation, and the improper disposal of sewage. Direct discharge of the non-sewage "gray water" (sink and shower water) may also cause aesthetic degradation in heavily used houseboat anchorages.
Beaches and swimming holes	Contamination from inadequate sewage systems or improper sanitary practices at heavily used beaches and swimming holes may result in bacteriological contamination of contact recreation waters and the transmission of various waterborne pathogens during swimming activities.
Resorts, campgrounds, recreational housing, and stables	Resorts, campgrounds, recreational housing, and stables may contaminate waters with bacteria, pathogens, viruses, and parasites. Organic loads (BOD) may depress stream dissolved oxygen (DO) levels. Salts, detergents, spilled fuels, oils, or litter may pollute streams. An increase in nutrients (N and P) from golf courses or lawn maintenance can result in algal blooms. High chlorine concentrations may be evident below sewage treatment facilities.

Pollution may also come from recreational facilities, including park facilities and concessions. Bacterial contamination from faulty septic systems in recreational housing is a common water quality problem in many NPS units. Organic wastes and nutrients such as phosphorus and nitrogen compounds from sewage plants, septic tanks, and the fertilization of lawns and golf courses can cause algal blooms that consume vital dissolved oxygen, altering the ecosystem (Fig. 4-2).

Finally, erosion from overused hiking and riding trails, poorly maintained roads, neglected ski slopes, and off-road vehicle and snowmobile trails can lead to maintenance and safety problems, reduced aesthetics, and siltation of watercourses.

Table 4-2. Common waterborne diseases and their agents. Taken from Martin et al., 1985.

DISEASE

BACTERIAL DISEASES

AGENT

Legionnaire's disease Legionella pneumophila

Colibacillosis Escherichia coli enteropathogenic

Cholera Vibrio cholera

Typhoid fever Salmonella typhi

Enteric fever Salmonella paratyphi

Salmonellosis Salmonella typhimurium

Bacillary dysentery Shigella species

Meliodidosis Pseudomonas pseudomallei

Leptospirosis Leptospira species

Yersiniosis Yersinia entercolitica

Campylobacteriosis Campylobacter jejuni

VIRAL DISEASES

PARASITIC DISEASES

Hepatitis Hepatitis A virus

Polio Polio virus

Enteroviral gastroenteritis Enterovirus

Norwalk syndrome Norwalk virus

Rotavirus

Rotavirus gastrointestinal syndrome

Intestinal roundworm Ascaris

Blood flukes Shistosoma

Amoebic dysentery Entamoeba histolytica

Lung flukes Paragonimus

Giardiasis Giardia lamblia

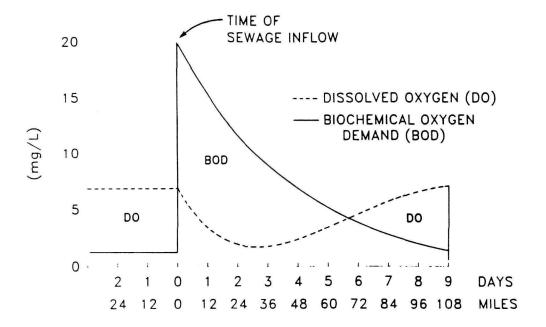


Fig. 4-2. Temporal and spatial changes in DO and BOD in a receiving stream as a result of sewage loading. Adapted from Bartsch and Ingram, 1982.

4.3 Controlling Recreational Impacts

More so than many other land-use impacts, recreational impacts can be mitigated. Park managers might consider the following actions:

- In locating outhouses, bivouac areas, horse corrals, and other contamination sources, allow a large enough filter strip so that contaminants do not enter nearby surface waters. Filter strip size is determined considering soil type, depth to water table, and slope. In any case, such facilities should be at least 100 feet from surface water sources, a distance normally adequate to filter out any bacteria and viruses (Fig. 4-3).
- Educate recreationists via pamphlets and other means on the hazards of poor sanitation practices in the outdoors and their effect on water. Educate on how to properly dispose of wastes to facilitate decomposition by soil microbes.
- Require portable toilet facilities on boats or rafts.
- Designate swimming areas in locations that have good circulation and sandy bottoms. Coves and sheltered areas tend to lack circulation and have a tendency to allow enteric bacteria to reach dangerous levels (Burton, 1982).
- Locate boat ramps away from swimming areas because water turbulence from boat launching can resuspend sediments and pathogens into the water column (Horak, 1974).
- Monitor water quality to detect problems and impacts, setting up minor laboratory facilities, as needed, to measure fecal coliform bacteria or other indicators of human wastes.



Fig. 4-3. Building a concrete liner for an outhouse will help protect nearby streams from fecal contamination.

- Control numbers of users in recreation areas so that the capacity for waste assimilation or disposal is not exceeded.
- Maintain trails to reduce erosion (e.g. install drains and water bars) and restrict off-road vehicles and snowmobiles to designated sites.
- Assure good drinking water wherever feasible and advise hikers on practical ways to adequately treat raw water.

The actual risk of contracting a waterborne illness from contaminated waters is uncertain; however, the public health risks involved often dictate monitoring in areas of heavy contact recreation. The monitoring design will depend upon the usage of the area (hiking, boating, contact recreation, etc.), the type of water body (lake, stream, etc.), and the source(s) of pollution.

4.4 Monitoring Recommendations

Because of the wide range of potential pollution sources associated with recreational water quality, the most effective monitoring programs will be designed with the specific problems, hydrological setting, and park management objectives in mind. For instance, the overall goals for water quality protection in the major recreational areas along the Colorado River Basin might require sophisticated monitoring programs well beyond the objectives and financial capabilities of the National Park Service. In

these instances, major river and lake monitoring programs by the U.S. Geological Survey, Bureau of Reclamation, U.S. Fish and Wildlife Service, and state agencies may be a source of important background data to the resource management specialist. However, smaller-scale problems such as beach monitoring, the impact of recreational developments, or back-country water use are usually neglected by the other agencies and therefore may constitute an important monitoring role for park staff. The most efficient resource management specialist will actually promote liaison among the various agencies that may have data and experience relating to the affected resource.

Limnological (lake) study designs, which are not discussed in this handbook, are quite different from stream and river assessments presented here. Generally, limnological studies are more costly and will require additional specialized assistance.

Parameters indicative of recreational impacts are listed in Table 4-3, followed by monitoring recommendations in Table 4-4. Note that the fecal coliform (FC) and fecal streptococcal (FS) bacteria analyses are used together to help identify whether contamination is from animal or human sources. The concentration of FC per 100 ml divided by the concentration of FS per 100 ml provides an index known as the FC/FS ratio. Generally, a ratio under 0.7 indicates animal fecal contamination, over 4.0 indicates human fecal contamination, and between 0.7 and 4.0 is a mixture of the two.

Table 4-3. Parameter selection rationale for recreation.

Parameter	Rationale
chloride	an indicator of sewage or animal wastes
chlorine	often associated with sewage treatment plants, residual chlorine releases may be toxic to downstream aquatic life
conductivity	an estimator of TDS
dissolved oxygen (DO)	may indicate pollution loads as well as show basic suitability of waters for fish habitat
fecal coliform (FC) bacteria	an indicator of fecal contamination caused by humans or animals, often associated with poorly functioning septic tanks or urban storm runoff; the standard for swimming waters most often is based on FC bacteria and will vary from state to state but usually is similar to the EPA criteria, where FC level should not exceed a log mean of 200 colonies per 100 ml, with not more than 10 percent of the total samples within 30 days exceeding 400 colonies per 100 ml (USEPA, 1976)
fecal streptococcal (FS) bacteria	FC:FS ratios may indicate whether fecal contamination is of human or animal origin
nutrients (including soluble reactive phosphorus, total phosphorus, nitrate and nitrite nitrogen, total nitrogen)	indicators of nutrient enrichment which in severe situations may cause algal blooms or lake eutrophication; sources of these nutrients are not usually associated with recreational activities, but problems may result from small sewage treatment facilities associated with recreational developments or excessive fertilization of golf courses
oil and grease	generally the presence of oil and grease can be detected by the sheen on the surface of the water; however, a moderately expensive analytical test is available to quantify the contaminant concentration; at times this may be appropriate in marinas or in response to a fuel spill into recreational waters
parasites (esp. <u>Giardia</u>)	may be appropriate in determining the suitability of recreational waters as a water supply
pH, temperature	valuable measurements in determining the basic suitability of waters for fish habitat

Table 4-3. Continued.

Parameter	Rationale
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning habitat
total coliform (TC) bacteria	an indicator of fecal contamination often associated with poorly functioning septic tanks; however, the total coliform group contains more soil organisms and other naturally occurring bacteria, so is not always indicative of pollution; the test helps as a quality control check on the FC as well
turbidity	indicator of erosional impacts caused by development of recreational facilities or the overuse of backcountry roads and trails

TABLE 4-4. Suggested parameters for identifying water quality impacts from recreational activities. 1,2

		T		
	Stream Site	Park Lab	Contract Lab	Sampling Notes
50	discharge pH temperature			 Discharge should be measured on each sampling occasion (see Section 2.4). Temperature is necessary for pH and conductivity calibrations
KEY PARAMETERS	conduc D	_		 DO can be field-metered; or, "fix" in field, titrate in lab.
PAR				 Measurement of bacteria is imperative in contact recreation water.
			cteria	5. Sample turbidity primarily during storm flows.
		TC bacteria ◀ turbidity		 Sample chlorine if downstream of sewage treatment facility.
ARY		chlo FS ba	rine cteria	 Sample FC bacteria concurrently with FS bacteria when animal contamination is possible.
SUPPLEMENTARY PARAMETERS				 Evaluate nutrients when excessive nutrient loading is suspected.
SUPPL			total N total P	9. When excessive erosion is suspended, sample settleable solids during high-flow or storm-flow periods.
-110			soluble reactive P	10. Special nutrient studies may be advisable if excessive nutrient loading is causing eutrophication.
SPECIAL STUDIES			nitrate+nitrite N oil and grease	ll. Oil and grease can be assessed near marinas.
SPI STI			parasites	12. Parasites should be sampled where untreated surface water is used by backcountry travelers or in heavily used swimming areas.

LEGEND: 2For sampling frequencies, refer to Table 2-2 in Chapter 2.

Boldface indicates suggested parameters for initial field reconnaissance.

Indicates usual site of analysis

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URBAN IMPACTS

5.1 General Description

Many National Park Service units located in or near urban areas are encountering increasing encroachment of subdivision development and other urban expansion. As these developments expand, significant portions of watersheds that drain into NPS units may be altered (Fig. 5-1). Urban runoff, the presence of active or abandoned land fills, and sewage and industrial wastewater are additional sources of water quality degradation.

5.2 Water Quality Impacts

Over an extended period of time, much of the pollution deposited on impervious surfaces will eventually end up in surface runoff, which in turn will carry the pollutants into local streams. Also, as larger and larger sections of a watershed become urbanized, the capacity for rainfall to



Fig. 5-1. Subdivision development is a source of sediment loading in Richmond National Battlefield Park, Virginia.

percolate into the soil is lessened, resulting in increased surface runoff during storms. Abnormally high flows can cause erosion and channel scouring when stream channel capacity is exceeded (Fig. 5-2). Water quality problems associated with urban encroachment include increased sediment loading; contamination from road salts, oil and other chemicals; accelerated enrichment from lawn fertilization; and possible contamination from pesticides, sewer line rupture, and fuel or chemical spills. The sediment load carried by streams can increase by orders of magnitude when urban development takes place (Table 5-1). Water quality degradation resulting from urban and suburban development is also associated with alterations in natural runoff patterns and the increased loading of pollutants brought about by intensive use and development.

Surfaces that once allowed the natural infiltration of rainfall often are covered with asphalt or other impervious materials, which reduces the infiltration and thereby increases storm-water runoff. Urban storm-water runoff (considered nonpoint-source pollution) can transport large quantities of collected residues to the nearest watercourse. While problems associated with urban storm-water runoff are common to many units of the National Park Service, the problems can be greatest near large population centers and older urban areas because of the density of development and the greater likelihood of having combined sewers (storm-water runoff and sewage).

A number of conservation measures can be applied to reduce sediment and turbidity coming from urban-suburban construction sites, including:

• reseeding, sodding, straw mulching, and "hydroseeding" to protect bare soil from erosion



Fig. 5-2. Stream-bank erosion is caused by upstream development at Petersburg National Battlefield, Virginia.

Table 5-1. A comparision of sediment yields among various land uses. Taken from Tourbier and Westmacott, 1981.

Watershed	Sediment Yield (tons/sq mi/year)
Woodland	100 forestry
Mixed Rural	300 agriculture
Farm Land	500 agriculture
Light Development	10,000 } urbanization
Heavy Development	10,000 100,000 urbanization

- using filter devices, such as bales of hay or plastic barriers, to keep sediment from washing away
- avoiding development of areas that are too steep or implementing special erosion controls, such as terracing, in such areas
- leaving undisturbed areas or "buffer strips" along streams and runoff areas
- rip-rapping runoff areas

In addition to the common sources and problems associated with urban runoff (Table 5-2), a study by the Nationwide Urban Runoff Program (NURP) (USEPA, 1984) has shown that heavy metal contamination is also common in urban storm-water runoff (Table 5-3). Heavy metals and other inorganic contaminants associated with urban runoff have great potential for long-term impacts on aquatic life.

It is beyond the scope of this paper to discuss point-source pollutants associated with industries that usually are located in urban areas. The undesirable characteristics of industrial wastes can include most of those mentioned in Table 5-2, as well as more complex contaminants such as toxic soluble organics, thermal pollution, radioactive wastes, and pathogenic substances (Cross, 1975). Most of these are organic pollutants that appear in the EPA's "Priority Pollutant" list. (An overview of this list is contained in Multer and Hindman [1986] and National Research Council [1982].) Discharge of these pollutants is usually usually under the jurisdiction of the National Pollutant Discharge Elimination System (NPDES) administered by the state water pollution control agencies and/or the U.S. Environmental Protection Agency (USEPA, 1985). Monitoring of such wastes should be in conjunction with specialists from these agencies.

5.3 Monitoring Recommendations

Because a wide variety of pollution sources can affect waters flowing through urban NPS units, monitoring programs should be designed with respect

to specific impacts and management objectives. The parameter rationales found in Table 5-4 and the sampling recommendations in Table 5-5 will help the resource manager to select the best indicators for specific pollution problems.

If organic toxics or mixed toxic substances present a health hazard, EPA may advise use of bioassay techniques (using live aquatic organisms) as described in Peltier and Weber (1985). Because they are expensive and complicated, however, bioassay tests necessarily are conducted by specialists.

Table 5-2. A summary of common sources and impacts of stream pollution associated with urban development.

Pollution Source	Characteristics and Impacts
Subdivision development	Development reduces infiltration areas, which can increase storm-water runoff and alter discharge and hydrologic patterns. This in turn can lead to additional sediment loading and channel scour in the receiving stream. Improperly designed development on steep slopes can also increase surface erosion and sediment load. Fertilizers and pesticides from lawn maintenance can cause water quality degradation.
Roads and parking areas	Urban storm-water runoff from roads and parking areas are frequently contaminated with chemicals used for road deicing, fuels, and particulate and heavy metal contaminants associated with vehicle exhaust. Leaks from service station storage tanks also may eventually enter surface waters.
Road salting	Runoff from deiced areas leads to increased levels of sodium and chloride in surface and ground waters.
Airborne pollutants	Airborne pollutants generated from power plants, refineries, wood burning stoves, and vehicle exhaust may contribute large quantities of particulate matter, acids, and heavy metals, which can degrade regional water quality.
Sewage treatment facilities	These facilities may contribute organic loading, nutrients, chlorine, and other contaminants to receiving water.
Landfills	Organic loading, nutrients, heavy metals, and a variety of toxic contaminants are often associated with poorly designed or maintained landfills. Abandoned dumps are a problem in some parks.
Domestic animals	Fecal bacteria from dogs and other domestic pets can produce localized water quality problems, especially in or near urban parks.

Table 5-3. Most frequently detected Priority Pollutants in the Nationwide Urban Runoff Program (NURP). Taken from USEPA, 1984. 1, 2, 3

Detection Rate	Inorganics	Organics
Detected in 75% or more of the NURP samples	Lead (94%) Zinc (94%) Copper (91%)	None
Detected in 50-74% of the NURP samples	Chromium (58%) Arsenic (52%)	None
Detected in 20-49% of the NURP samples	Cadmium (48%) Nickel (43%) Cyanides (23%)	Bis 2-ethylhexyl phthalate (22%) α-Hexachlorocyclohexane (20%)
Detected in 10-19% of the NURP samples	Antimony (13%) Beryllium (12%) Selenium (11%)	α-Endosulfan (19%) Pentachlorophenol (19%) Chlordane (17%) γ-Hexachlorocyclo- hexane (Lindane) (15%) Pyrene (15%) Phenol (14%) Phenanthrene (12%) Dichloromethane (methyl chloride) (11%) 4-Nitrophenol (10%) Chrysene (10%) Fluoranthene (16%)

 $^{^1\}mathrm{Based}$ on 121 sample results received as of September 30, 1983, adjusted for quality control review. Does not include special metals samples.

²Percentages indicate frequency of detection, not concentration. Analysis of concentration shows that concentrations of copper, lead, and zinc were the highest of any priority pollutant.

³Analyses for metals are based on total recoverable metals.

Table 5-4. Parameter selection rationale for urban development.

Parameter	Rationale
benthic macroinvertebrates	can be used as reliable indicators of water quality degradation in areas that may be affected by "exotic mixtures" of pollutants
biochemical oxygen demand (BOD)	an indicator of potential lowering of dissolved oxygen concentration due to decomposition of organic wastes by microbes; frequently associated with organic loading from sewage plants or certain industries
chemical oxygen demand (COD)	similar to BOD, COD is an indicator of the potential lowering of dissolved oxygen; COD is sometimes measured to document severe degradation due to urban storm-water runoff, and must be used in place of BOD if mining or industrial wastes are present which are toxic to bacteria; COD is also elevated by certain industrial wastes
chloride	an indicator of sewage, animal wastes, and road salt
chlorine	often associated with sewage treatment plants, residual chlorine releases may be toxic to downstream aquatic life
conductivity	an estimator of total dissolved solids
dissolved oxygen (DO), pH, and temperature	valuable measurements in determining the basic suitability of waters for fish habitat
fecal coliform (FC) bacteria	an indicator of fecal contamination caused by humans or animals, often associated with poorly functioning septic tanks or urban storm runoff; the standard for swimming waters most often is based on FC bacteria and will vary from state to state, but usually is similar to the EPA criteria, where FC level should not exceed a log mean of 200 colonies per 100 ml, with not more than 10 percent of the total samples within 30 days exceeding 400 colonies per 100 ml (USEPA, 1976)
fecal streptococcal (FS) bacteria	FC:FS ratios may indicate whether fecal contamination is of human or animal origin

Table 5-4. Continued.

Parameter	Rationale
heavy metals (including arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, zinc)	often found in particulate form in urban storm- water runoff, these contaminants can potentially affect aquatic life as well as human health
nutrients (including soluble reactive phosphorus, nitrate and nitrite nitrogen, total nitrogen)	indicators of nutrient enrichment which in severe situations may cause algal blooms or lake eutrophication; sources of these nutrients include small sewage treatment facilities and excessive fertilization of lawns and golf courses
oil and grease	generally the presence of oil and grease can be detected by the sheen on the surface of the water; however, a moderately expensive analytical test is available to quantify the contaminant concentration
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning habitat
surfactants	an indicator of detergents from sewage
total coliform (TC) bacteria	an indicator of fecal contamination often associated with poorly functioning septic tanks; however, the total coliform group contains more soil organisms and other naturally occurring bacteria, so is not always indicative of pollution; the test helps as a quality control check on FC bacteria
turbidity	indicator of erosional impacts caused by development of recreational facilities or the overuse of backcountry roads and trails

TABLE 5-5. Suggested parameters for identifying water quality impacts from urban activities. 1,2

	Stream Site	Park Lab	Contract Lab	Sampling Notes
KEY PARAMETERS	discharge pH temperature conduc t	o ≪ chlor FC bac	c teria cteria	 Discharge should be measured on each sampling occasion (see Section 2.4). Temperature is necessary for pH and conductivity calibrations DO can be field-metered; or, "fix" in field, titrate in lab. Sample FC and TC bacteria during storm flows and recreational periods. Sample turbidity during storm flows. Sample chlorine if sewage plant effluent is
SUPPLEMENTARY PARAMETERS	settleab	chlor FS bac		present. 7. Sample FS bacteria concurrently with FC bacteria. 8. It may be necessary to determine COD in lieu of BOD if toxic substances are affecting microbiological communities.
SPECIAL STUDIES			COD oil and grease macroinvertebrates metals: Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn	

LEGEND: ¹/₂For sampling frequencies, refer to Table 2-2 in Chapter 2.
Boldface indicates suggested parameters for initial field reconnaissance.

^{◄ -} Indicates usual site of analysis.

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AGRICULTURAL AND FORESTRY IMPACTS

6.1 General Description

Agricultural or forestry activities and maintenance of powerline or other rights-of-way in or adjacent to parks can be problematic wherever chemical spraying, machinery use, irrigation return-water flow, grazing, tree harvesting, road construction, and related actions affect streams in or upstream from the parks (Table 6-1).

Most agricultural and forestry pollutants are from nonpoint sources, which enter a watercourse from land areas in a diffuse manner. Most phosphorus and nitrogen in rivers come from nonpoint sources, especially agricultural lands. During storms, runoff from agricultural lands or areas where logging is taking place figures prominently in the pollution of local streams (Fig. 6-1).

The EPA recently conducted a survey in which the 50 states, Puerto Rico, and Virgin Islands were asked to rank agricultural problems in order of priority (USEPA, 1984). The results, presented in Table 6-2, serve as an example of the kinds of pollution problems associated with agriculture that can affect water quality.



Fig. 6-1. Agricultural pesticides applied to these crops threaten water quality in Everglades National Park, Florida.

Table 6-1. A summary of common sources and impacts of stream pollution associated with agriculture and forestry.

Pollution Source	Characteristics and Impacts	
Logging and road construction	Erosion leads to increased turbidity and sediment in streams and lakes. Flood peaks may increase in areas of heavy logging. Contamination may result from human wastes or fuel spills.	
Overgrazing	An increase in turbidity and sediment can result from eroded areas. Bacterial levels may increase due to animal wastes.	
Irrigation and drainage	Erosion from fields may increase turbidity and sediment. Irrigation return waters or drainage may contain nutrients (N, P, K) from fertilizers which stimulate algal blooms, as well as elements (Se, Hg, As, Cd) toxic to fish and wildlife.	
Pesticides and herbicides	Water can be contaminated by chlorinated hydrocarbons (e.g., DDT); organophosphate pesticides; metals (e.g., Cu, Hg) from herbicides used in orchards and in forestry, agriculture, and powerline maintenance activities; insecticides used for mosquito control; and rodenticides. Appendix J provides more specific information on pesticides.	
Road salts	Runoff from salted areas leads to increased levels of sodium and chloride in ground and surface waters.	
Aquatic weed control	Chemicals such as copper sulfate used to control weeds upstream may cause damage to aquatic life in downstream areas.	

6.2 Water Quality Impacts

Toxic chemicals, pesticides, and herbicides used primarily in agriculture and in clearing powerline paths and other rights-of-way can be harmful or toxic to aquatic life and humans. Irrigation can introduce such toxic substances into watercourses, where they flow downstream and affect wetlands and wildlife areas. (This has been a problem in the Central Valley area of California, for example, where selenium has contaminated critical waterfowl habitat.) These chemical compounds produce either acute effects or long-term chronic effects, with the possibility of bioaccumulation and biomagnification in the food chain. (Pesticides and their effects are further discussed in Appendix J.) Fish may accumulate undesirable metals or other substances until their flesh is unsafe for human consumption. Fertilizers and other nutrients can lead to downstream algal blooms in lakes, causing ecological and aesthetic impacts. Nitrogen in agricultural runoff is a common problem. Commonly used commercial fertilizers include:

Table 6-2. Ranking of agricultural problems by the 50 states, Puerto Rico (PR), and the Virgin Islands (VI). From USEPA, 1984.

Problem	Number of States	
Erosion/sedimentation	46 states, PR, VI	
Nutrients	28 states, PR	
Pesticides	22 states, PR	
Small feedlots/animal waste	19 states, PR	
Fertilizers	15 states, PR	
Salinity	10 states	

•	nitrogen (N)	anhydrous ammonia ammonium nitrate ammonium sulfate urea natural organics
•	phosphorus (P)	ammonium phosphate "super phosphates" natural organics
•	potassium (K)	potassium chloride potassium magnesium sulfate potassium sulfate natural organics

(Colorado Crop and Livestock Reporting Service, 1985. Toxicities for many of these chemicals are listed in USEPA, 1976.)

Logging practices and grazing can reduce or remove ground cover, leading to siltation problems in waterways. Increased siltation in turn can cause local flooding, harm to riverine forests, increases in stream and lake turbidity, and siltation of reservoirs. Deforestation can trigger the release of various chemicals into streams via cessation of nutrient uptake by trees and interference with other movements and reactions of chemicals in the forest ecosystem. Therefore, higher levels of turbidity, sediment, and certain chemicals often appear in nearby streams following logging operations. Bormann and Likens (1981) found that during a three-year period of deforestation, total net losses of dissolved substances from a clearcut watershed were nearly eight times greater than those from a forested watershed. Nitrogen increases were evident in higher concentrations of ammonia and nitrate nitrogen. In particular, nitrate nitrogen in the receiving waters increased from near zero before clearcutting to over 40 mg/L following the operation. However, elevated concentrations of such substances decrease rapidly once regrowth begins and may approximate concentrations found in control watersheds within five years.

The temperature of small streams is affected by the presence or absence of shade (Brown, 1985). In many states, water quality standards permit only small changes in water temperature; thus, logging near streams must be conducted so that the necessary streamside shading remains. If such shading is lost, this in turn can cause higher water temperatures in affected streams.

Animal waste runoff may carry numerous pathogens that can contaminate drinking water sources or swimming areas (Fig. 6-2). Feedlots and barnyards produce enormous volumes of the nutrients nitrogen (N) and phosphorus (P), as well as bacteria (Table 6-3). A herd of 50 swine, for example, can produce over a ton of nitrogen a year and over a third of a ton of phosphorus, which potentially could cause algal blooms downstream. A cow will produce about $5{,}400 \times 10^6$ fecal coliforms per day (Geldreich, 1966); several of these animals in or near a watercourse can contribute considerable numbers of bacteria.

The degree of any impact is influenced by the presence or absence of buffer strips (also called filter strips). These are protective bands of vegetation that are left undisturbed along stream channels during logging, grazing, or other activities on watersheds. The purpose of a buffer strip is to protect water from increases in turbidity, temperature, nutrients, and contaminants. Studies have shown that contributions of bacteria to streams, even in heavily grazed watersheds, are negligible if cattle are restricted from stream environs by a buffer strip (Kunkle, 1972).



Fig. 6-2. Livestock can foul watercourses used as drinking water sources by recreationists in backcountry areas. Photo courtesy of the National Agricultural Library, Forest Service Photo Collection.

Table 6-3. Total nitrogen and phosphorus produced by weight of various livestock. Taken from Novotny and Chesters, 1981.

Livestock	Total N (kg/animal/yr)	P (kg/animal/yr)
chickens	0.5	0.2
ducks	5.8	0.35
swine	23.0	8.0
dairy cattle	38.0	25.0
beef cattle	53.0	13.0
sheep	11.0	2.0

Although this handbook deals with surface water, it must be mentioned that ground-water contamination is a special concern in agricultural areas, because nitrogen, pesticides, and several other toxic substances can infiltrate ground-water aquifers (Kimball, 1985). These substances are able to percolate through the soil into the ground water since they do not become trapped in or adsorbed to soil. Ultimately, they can appear not only in wells but also surface waters into which the ground water flows.

6.3 Monitoring Recommendations

Tables 6-4 and 6-5 present the suggested parameters and sampling chart recommendations for assessing impacts resulting from agricultural and forestry practices. Appendix J discusses pesticide monitoring considerations.

Table 6-4. Parameter selection rationale for agriculture and forestry.

Parameter	Rationale	
benthic macroinvertebrates	a biological analysis that integrates changes in physical and chemical water quality conditions	
biochemical oxygen demand (BOD)	an indicator of potential lowering of dissolved oxygen levels due to decomposition of organic wastes by microbes	
chemical oxygen demand (COD)	a quick estimate of BOD; should be substituted for BOD if pulp plant wastes are suspected which are toxic to bacteria	
chloride	a good indicator of sewage and animal wastes	
conductivity	a simple estimator of TDS and an index of inorganic pollutants	
dissolved oxygen (DO)	an indicator of depressed oxygen levels caused by organic sediment loading	
fecal coliform (FC) bacteria	an indicator of contaminants caused by human or animal wastes	
fecal streptococcal (FS) bacteria	FC:FS ratios may indicate whether fecal contamination is of human or animal origin	
herbicides	analyze for locally-applied herbicide(s)	
nitrate as nitrogen $(N-NO_3)$	an indicator of nitrogen-containing fertilizer or pesticide (high in N) contamination	
pesticides	analyze for locally-applied pesticides	
phosphate (total)	an indicator of phosphate-containing fertilizer contamination	
рН	a valuable measure for interpreting solubility ranges of chemical parameters	
temperature	a requirement for pH and conductivity and a valuable measure for interpreting solubility ranges of chemical parameters	
total coliform (TC) bacteria	an indicator of fecal contamination often asso- ciated with poorly functioning septic tanks; however, the total coliform group contains more soil organisms and other naturally occuring bacteria, so is not always indicative of pollution; the test helps as a quality control check on the FC as well	

Table 6-4. Continued.

Parameter	Rationale
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals
turbidity	a simple estimator of TSS

TABLE 6-5. Suggested parameters for identifying water quality impacts from agricultural and forestry activities. 1,2

		r	T	
	Stream Site	Park Lab	Contract Lab	Sampling Notes
KEY PARAMETERS	discharge temperature conduc D O	BOD of chlored	r COD > ride cteria cteria cteria NO3 SS > idity total P	 Discharge should be measured on each sampling occasion (see Section 2.4). Temperature is necessary for pH and conductivity calibrations DO can be field-metered; or, "fix" in field, titrate in lab. Use BOD generally, COD if industrial wastes are affecting biological communities. Storm-flow samples usually reveal maximum values for TSS and turbidity. Bacteria maximums can occur both during high
SUPPLEMENTARY PARAMETERS	рН		TDS	flows (surface washing) and low flows (input from streamside feedlots, farms, and grazing areas). 7. Sample P-total at stream inflows to lakes. 8. Herbicide and pesticide analysis is discussed in Appendix H.
SPECIAL STUDIES			macroinvertebrates herbicides pesticides	

LEGEND: 1/2 For sampling frequencies, refer to Table 2-2 in Chapter 2.
Boldface indicates suggested parameters for initial field reconnaissance.

✓ - Indicates usual site of analysis.

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VII

OIL AND GAS DEVELOPMENT IMPACTS

7.1 General Description

In the exploration, drilling, and production phases of oil and gas development, many operations take place that may alter the watershed or otherwise adversely affect water resources. Roads and trails cut during the exploration survey can cause erosion and increase sediment loading into local waters. Significant resource degradation may occur during site preparation when vegetation is removed, access roads are constructed, and the drilling pad is graded (Figs. 7-1 and 7-2). A proper plan of operation will take into account road and drilling pad placement in order to ensure that damage to sensitive resources is kept to a minimum and that natural flow patterns are not disrupted. Care must be taken to protect surface and ground water from contamination, especially during the drilling process when large amounts of produced water (brines), drilling fluids, drilling muds, and oil may be in contact with the surface and ground water. Finally, the plan of operation must ensure that during the long-term production phase, spill contingency plans are adequate to minimize any impact that may result from an accidental spill of oil or brines, either at the well head or along the transportation or transmission corridor (Fig. 7-3).

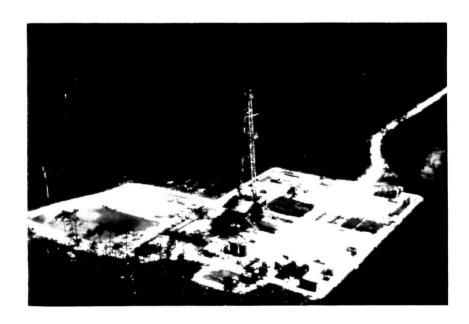


Fig. 7-1. A large-scale oil drilling pad in Big Cypress National Preserve, Florida.

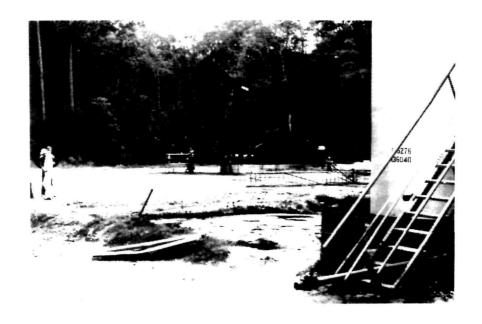


Fig. 7-2. A small-scale, "mom and pop" oil operation can be hard to control from an environmental protection viewpoint. This one is in Big Thicket National Preserve, Texas.



Fig. 7-3. Oil-absorbing "diapers" are used to soak up oil following a spill in Big Cypress National Preserve, Florida.

7.2 Water Quality Impacts

Once drilling and pumping for oil are underway, the potential exists for spills and leaks of drilling fluids, muds, oil, or produced waters. The drilling fluids and natural ground water encountered in the drilling process are often high in dissolved salt content (especially sodium, calcium, magnesium, and chloride) and sometimes contain heavy metals such as barium, cadmium, chromium, lead, strontium, and zinc (American Petroleum Institute. Bicarbonates, carbonates, sulfates, sulfides, and oil may also be associated with produced waters and drilling fluids. The potential also exists for spills or leaks of such substances as detergents, fuels, machinery fluids, and toxic chemicals. Trucks transporting oil or produced water pose further spill hazards, and storage tanks or pumping stations sometimes rupture. Herbicides sprayed for brush control along pipelines and other cleared areas can enter streams by way of storm runoff. Finally, fallout of airborne particles (such as dust) can contribute to water pollution problems. Water quality impacts commonly associated with oil and gas developments are outlined in Table 7-1.

Oil shale and tar sand extraction experiments have recently been conducted in the Colorado River Basin, where large deposits of oil-bearing shales and tar sands are found. At some future time, these deposits may be developed as important sources of hydrocarbon fuels. After the rock and sand materials are processed in the extraction phase, problems may arise in the disposal of the large amounts of spoils and waste rock. Additional watershed disturbance problems are inherent given the steep topography, the arid to semi-arid conditions, and the shortage of water needed for processing in areas where the deposits are found. Heavy metals associated with oil shale deposits, including aluminum, arsenic, cadmium, lead, mercury, and selenium, can harm aquatic life at low concentrations. Erosion from these spoil piles may also contribute to increased turbidity and sedimentation in the receiving waters.

7.3 Monitoring Recommendations

Oil and gas exploration and development pose a special challenge to park managers. Mineral rights ownership in some NPS areas allow oil and gas extraction; in these cases, a manager might wish to monitor oil developments with a view toward minimizing damage and helping to design better oil development guidelines for environmental protection. The more progressive companies will likely seek cooperation with affected parks in developing these guidelines. Less responsible companies or individuals may warrant close monitoring to guard against environmental damage.

In many cases, properly conducted operations will require less monitoring than those lacking an adequate plan of operation. Also, the drilling fluid and mud systems utilized may dictate some of the specifics of the monitoring program devised. A number of fluids and chemicals involved in oil and gas development are potentially toxic to natural ecosystems and to humans. (A listing of some of the chemical components of drilling fluids are presented in "Oil and Gas Technology and Associated Environmental Effects," recently released by the NPS Energy, Mining and Minerals Division [Tetra Tech, 1987].) Oil is the most visible pollutant. It is immediately toxic and can dangerously depress dissolved oxygen levels following a spill, because the biochemical oxygen demand of oil is caused by oxygen consumption of microorganisms that decompose the oil. Oil can also continue to harm aquatic organisms many months after a spill.

Table 7-1. A summary of common sources and impacts of stream pollution associated with oil and gas extraction.

p. 11	
Pollution Source	Characteristics and Impacts
Storage tanks, pipelines, natural seeps	Oil spills or natural oil seeps resulting from the area geology may coat stream channels and beds and riparian soils and vegetation. Fish and wildlife may be affected. Depressed dissolved oxygen levels may also result from oil spills.
Holding ponds	Leaking or breached ponds may introduce brine, drilling mud, or other fluids containing chlorides, Fe, Mn, NH ₄ , or other chemicals into streams. Sometimes detergents are evident. Conductivity, sodium, turbidity, heavy metal, and TDS levels may rise. (In some cases, though, brines may actually reduce turbidity by helping to coagulate the sediment.)
Roads, pads, pipelines, seismic lines	Erosion resulting from these and other sources cause increased turbidity and sediment and possibly localized flooding.
Right-of-way maintenance	Herbicides resulting from careless spraying may affect stream biota.

Contamination from oil operations outside a park can also present resource problems, as can offshore mineral operations for coastal parks. Therefore, resource managers need to be aware of oil and gas operations within a regional context, not just within NPS boundaries. In many cases, developing cooperative monitoring efforts with other agencies is an effective strategy.

Tables 7-2 and 7-3 present the suggested parameters and sampling chart recommendations for monitoring water quality impacts related to oil and gas development. (A simple procedure for detecting the presence of oil has been suggested by R. Clark of the National Oceanic and Atmospheric Administration in Seattle [C. Hawkins, Mt. Rainier National Park, 1987, personal communication]: nearly fill a jar with water sample, leaving some air space. Place the jar in the sun to warm for a short time, then open it and smell; the human nose is generally capable of detecting oil odors at very low concentrations. An additional suggestion is to obtain, if possible, a "fingerprint" sample from the source of an oil spill or leak for later use in identifying or confirming the exact nature and source of any oil found in nearby park waters.)

Table 7-2. Parameter selection rationale for oil and gas extraction.

Parameter	Rationale		
alkalinity	a measure of stream buffering capacity		
biochemical oxygen demand (BOD)	an indicator of potential lowering of dissolved oxygen levels due to hydrocarbon decomposition by aquatic microbes		
calcium	elevated levels may be evidence of produced water contamination from the drilling and production operations		
chloride	(see calcium)		
conductivity	a good index of brine leakage; a simple estimator of TDS		
dissolved oxygen (DO)	may be depressed by microbial action following an oil spill		
herbicides	may appear in nearby watercourses as a result of brush control around drilling pads, roads, and pipelines		
magnesium	(see calcium)		
metals	may be associated with drilling fluids and muds; if analysis of metals is found to be desirable the metals monitored should be those related to the drilling fluid and mud systems utilized		
oil & grease	a measure of contamination from petroleum spills and seepage; residual hydrocarbons in sediments may be quantified (if appropriate) utilizing the PAH (polyaromatic hydrocarbons) in the sediments		
phenols	an indicator of drilling waste waters		
рН	a valuable measure for interpreting solubility ranges of chemical parameters		
sodium	(see calcium)		
sulfate	(see calcium)		
surfactants	an indicator of pollution from wetting agents and detergents used in oil drilling processes		
temperature	a requirement for pH and conductivity and a valuable measure for interpreting solubility ranges of chemical parameters		

Table 7-2. Continued.

Parameter	Rationale
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentration (e.g., dissolved toxic metals)
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals
turbidity	a simple estimator of TSS, turbidity can increase as a result of watershed disturbances associated with oil and gas development; however, turbidity may decrease following a produced-water spill

TABLE 7-3. Suggested parameters for identifying water quality impacts from oil and gas development activities. 1,2

	Stream Site	Park Lab	Contract Lab	Sampling Notes
KEY PARAMETERS	discharge pH temperature conduc	alkalinity BOD > calcium > chloride magnesium > sodium > sulfate > turbidity oil and grease		 Discharge should be measured on each sampling occasion (see Section 2.4). Temperature is necessary for pH and conductivity calibrations. Sampling during low flow will reveal maximum concentrations for BOD, calcium, magnesium, and sodium. Sampling during storm flow usually reveals maximum TSS and turbidity values. Oil and grease can be inspected visually. DO can be field-metered; or, "fix" in field, titrate in lab. Metals analysis can entail a total ICP
SUPPLEMENTARY PARAMETERS	DO	meta pher Ti	als ► nols ► DS ► SS ► surfactants	package for unforeseen contaminants. 8. Herbicide analysis is discussed in Appendix H.
SPECIAL			herbicides	

LEGEND: ¹/₂For sampling frequencies refer to Table 2-? in Chapter?

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VIII

COAL MINING IMPACTS

8.1 General Description

Coal mining operations, whether conducted above or below ground, can seriously pollute nearby watercourses if not properly reclaimed or closed. Such is the case in a number of parks located in or near coal reserves in the continental U.S. (Fig. 8-1).

Strip mining involves removing the layers of soil, subsoil, and rock above a coal seam followed by removal of the coal. Overburden materials are either dumped aside in spoil piles or are replaced and reclaimed. Spoil piles in unreclaimed strip-mine sites often contain toxic materials such as iron pyrites that prevent revegetation and contaminate runoff water. Oxidation of the pyritic materials leads to the formation of sulfuric acid, which lowers the pH of water and can mobilize toxic metals that would not dissolve in water at higher pH levels. Also, reddish iron hydroxide [Fe(OH)₃] precipitates can be formed that coat stream bottoms and destroy aquatic habitat. Water flowing through coal mining areas can be very acidic due to acid mine drainage. Although recent legislation requires return of top soils to the surface and revegetation of the mine site, old strip-mine areas that were never reclaimed generate acid for decades and continue to contaminate nearby waters (Fig. 8-2).

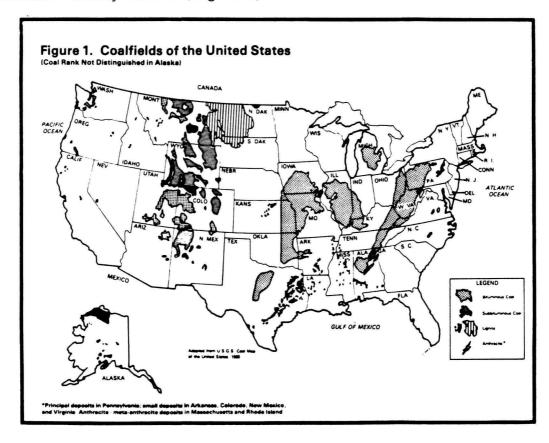


Fig. 8-1. Coal reserves of the continental U.S. Taken from Slatick, 1980.

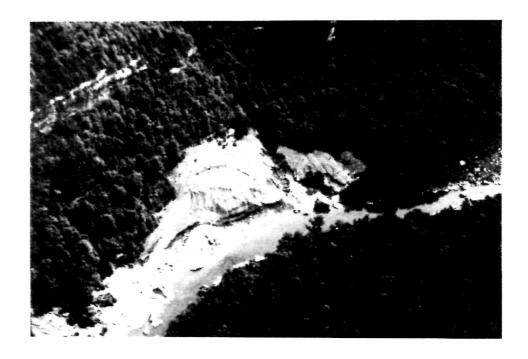


Fig. 8-2. Unrestored coal mining areas can add acids, metals, and other pollutants to streams. These spoil piles are in the Big South Fork National River and Recreation Area, Kentucky-Tennessee.

Deep mines are also sources of acid mine drainage. Subsurface waters trickle into abandoned shafts, contact and are contaminated by pyrites or other toxic materials, and flow out into a stream at some lower-elevation shaft opening. Deep mines abandoned decades ago often continue to pollute for years (Fig. 8-3), and some parks have begun to seal old mines to prevent pyrite oxidation.

8.2 Water Quality Impacts

Coal mining and its associated activities create numerous threats to water quality (Table 8-1). Many pollutants emanating from strip mines are toxic to fish, wildlife, and riparian vegetation (Fig. 8-4). Low pH levels also are unsuitable for most aquatic life. High color values, high turbidity, excessive siltation, and dead riparian vegetation not only diminish aesthetic values but also may seriously harm biological communities associated with the waterway and its riparian zone.

Treatment or use of municipal, domestic, and industrial water supplies can be impaired by high levels of salt, heavy metals, hardness, iron and manganese (strong taste and discoloration problem), sulfur (unpleasant odor), and acid-caused corrosion of pipes. Similarly, mine-contaminated water can be too salty or acidic for irrigation, livestock use, or park purposes. Sediment from erosion of the unvegetated spoil piles can contribute to local flooding, create turbidity-caused treatment problems for municipal waters, harm aquatic habitat, and fill in reservoirs.

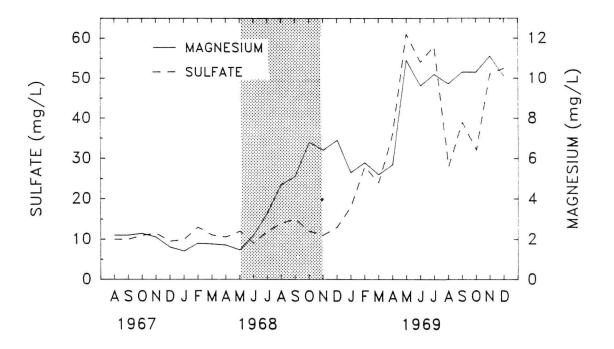


Fig. 8-3. Coal mining can contaminate waters long after mining activity ceases. Here, sulfate and magnesium content in stream flow rise during the period of mining operations (shaded area) and remain high. Adapted from Curtis, 1973.



Fig. 8-4. Abandoned coal mines can release acid mine drainage strong enough to kill riparian vegetation, as it has in Friendship Hill National Historic Site, Pennsylvania.

Table 8-1. A summary of common sources and impacts of stream pollution associated with coal mining.

Pollution Source	Characteristics and Impacts
Mine shafts	Seeps from improperly sealed mine shafts may have an orange to yellow color, low pH (<3.0), high conductivity, and high concentrations of substances such as sulfate, iron, aluminum, manganese, and chloride.
Strip mines	Erosion from barren strip-mined areas will increase turbidity downstream following precipitation. Seepage from the spoil areas may have the same characteristics as mine shaft seepage.
Ponds	Runoff water from strip-mined areas that accumulates in ponds is typically coffee-colored and acidic, and it contains the high metal concentrations typical of acid mine drainage.
Roads	Both new and abandoned roads can erode, causing landslides and high turbidity and/or high sediment loads in streams.
Flooding and high flows	Polluted streams that are choked with fallen vegetation and sediment will flood during periods of high stream flow and kill more vegetation. Also, mining activity can increase peak flows by a factor of 3 to 5 in small watersheds (Poe and Betson, 1983).

8.3 Monitoring Recommendations

Park resource management specialists, especially in the eastern and midwestern U.S., may encounter problems of both active and abandoned coal mines in or near their units and will need to determine the sources and extent of pollution in various streams. In the western U.S., which is now a major coal-mining region, water quality monitoring is vital for maintaining environmental protection during mining and for ensuring the success of restoration measures.

Table 8-2 lists parameters particularly suitable for monitoring coal mining effects. Table 8-3 presents the sampling chart recommendations for monitoring coal-mining impacts. A few parameters that are especially indicative of coal mining, such as TSS, pH, sulfate, conductivity, TDS, iron, and manganese (Rikard et al., 1986), are the heart of the sampling chart. Macroinvertebrate analysis is suggested as a special study for coal mining impacts because some aquatic insects are severely affected by acid mine drainage (Herricks and Cairns, 1974). Intolerant species include those in the orders Odonata (dragonflies and damselflies), Ephemeroptera (mayflies), and Plecoptera (stoneflies). More tolerant groups of insects include Diptera (true flies), some Chironomidae (over 2,500 species), and certain Megaloptera (alderflies, dobsonflies, and fishflies).

Table 8-2. Parameter selection rationale for coal mining.

Parameter	Rationale
acidity	a measure of the strength of acids and aluminum and iron sulfates released during mining
alkalinity	a measure of stream buffering capacity
aluminum	an indicator that depressed stream pH levels are mobilizing metals, a major component of clays
benthic macroinvertebrates	a biological test that integrates changes in physical and chemical water quality conditions
chloride	an indicator of mobilized alkaline earths and other chloride-bearing minerals
color	an indicator of dissolved metallic compounds (e.g., iron and manganese)
conductivity	a simple estimator of TDS
hardness	a factor in aquatic toxicity interpretation, reflects increased metal mobilization
iron	an indicator of iron oxide mobilization
manganese	an indicator of manganese oxide mobilization
mercury	an indicator of mercuric sulfate mobilization
рН	a valuable measure for interpreting solubility ranges of chemical parameters
potassium	an indicator of potassium-bearing rock mobilization
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning beds
sulfate	a predominant anion that indicates the weathering of pyrite to sulfuric acid
temperature	a requirement for pH and conductivity, and a valuable measure for interpreting solubility ranges of chemical parameters
total dissolved solids (TDS)	an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)

Table 8-2. Continued.

Parameter	Rationale
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals
turbidity	a simple estimator of TSS
zinc	an indicator of zinc sulfide mobilization

TABLE 8-3. Suggested parameters for identifying water quality impacts from coal mining activities. 1,2

	Stream Site	Park Lab	Contract Lab	Sampling Notes
KEY PARAMETERS	discharge pH temperature conduc	discharge pH		 Discharge should be measured on each sampling occasion (see Section 2.4). Temperature is necessary for pH and conductivity calibrations. Low-flow sampling may reveal maximum values for acidity, alkalinity, iron, and sulfate. Storm-flow sampling reveals maximum values for turbidity and TSS. Color is likely to vary seasonally. Low-flow sampling will best detect aluminum,
SUPPLEMENTARY PARAMETERS	settleab			 chloride, manganese, mercury, potassium, and zinc emanating from ground-water sources (e.g., mine shaft seepage). 7. Benthic macroinvertebrate sampling is discussed in Section 2.4. 8. Fish surveys are conducted relative to season.
SPECIAL STUDIES			macroinvertebrates fish	

LEGEND: ${1 \over 2}$ For sampling frequencies, refer to Table 2-2 in Chapter 2. Boldface indicates suggested parameters for initial field reconnaissance.

^{◄ -} Indicates usual site of analysis.

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PLACER MINING IMPACTS

9.1 General Description

Placer mining is a special concern of several parks in Alaska, where gold is sought in alluvial deposits in and along stream channels. In commercial operations, heavy equipment such as bulldozers, scrapers, loaders, and draglines are employed near the stream channel to move gravel and alluvial materials to sluice boxes or other gravity separation devices where the gold is removed (Fig. 9-1). Large washing operations may use thousands of gallons of water per minute. Though uncommon today, hydraulic stripping (use of water under high pressure) was often used in the past to forcefully remove the overburden.

9.2 Water Quality Impacts

Removal of gravel from the stream channel, washing of the alluvial materials, and deposition of spoil materials in the past have created severe water quality and fisheries degradation (Table 9-1). The EPA (1985) has found that the wastewater of commercial placer mines is characterized by high levels of turbidity, settleable solids, and total suspended solids. In addition, heavy metals such as arsenic that are released via overburden removal, sediment loading, and ore oxidation and runoff are sometimes

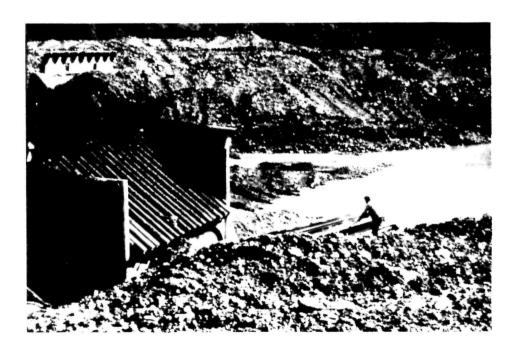


Fig. 9-1. Sluice box outfall in a placer-mining operation in Nome Creek near Fairbanks, Alaska.

Table 9-1. A summary of common sources and impacts of stream pollution associated with placer mining.

Pollution Source	Characteristics and Impacts
Hydraulic stripping	The removal of overburden by hydraulic pressure has been responsible for heavy loading of sediments into streams, severely degrading water quality and fisheries habitat.
Ore-bearing materials removal	Use of trucks and heavy equipment in and around the stream channels can damage vegetation and wetland habitat in the riparian zone, destabilize the stream bank, alter stream hydraulics and ground-water flow, damage fish spawning areas, and contribute to water quality degradation by increasing turbidity and sediment loading. Water temperatures may increase, and fluctuations in dissolved oxygen levels can result from organic materials loading.
Washing/sluicing operations	These activities greatly increase turbidity, settleable solids, and total suspended solids. Alaska state water quality regulations necessitate that most sluicing operations utilize settling ponds to control settleable solids and reduce turbidity. The EPA has recently proposed effluent guidelines that, when adopted, will put into place new effluent limitation guidelines for gold placer mining.
Settling pond construction and spoils disposal	The creation of settling ponds to reduce water pollution and the disposal of mine spoils can alter both the riparian zone and stream channel, causing loss of critical habitat. Although the construction of settling ponds is not allowed within the stream channel, poorly constructed ponds, unstable spoil piles, and diversions can contribute to increased sediment loading in the receiving water.
Enhanced recovery	Enhanced recovery operations such as cyanide heap leaching are presently being considered in Alaska. These operations have to be carefully monitored on a site-specific basis to assure that toxic chemicals or heavy metals do not pollute local surface or ground waters.
Abandonment	Leaching from old mine tailings may produce metals, acids, cyanide, or solids. Recreational use, habitat, and aesthetic values may be adversely affected with the loss of natural stream features.

resuspended in the water column during the mining operation. Fortunately, these metals are often bound to particulate matter and can be removed with the efficient removal of settleable solids and with substantial reduction of total suspended solids, if these processes are part of the pollution-control operations. Temporary holding ponds are often constructed along the stream (an unacceptable practice) rather than above the floodplain for settling the turbid wash water (Fig. 9-2). However, throughout the mining process, original vegetative cover will likely be destroyed by stream diversion and other movement of earth, and organic materials commonly are introduced into the stream (Fig. 9-3). A major problem in Alaska results from mine abondonment with no reclamation or stabilization work, leading to long-term sediment deposition. Other impact sources include roads (sometimes on extremely sensitive tundra), diversion channels, small airstrips, camp or cabin sites, dams for water storage, and the movement of heavy machinery. Temporary living areas can be sources of human contaminants, solid wastes, and fuel, oil, or chemical leaks.

9.3 Monitoring Recommendations

Table 9-2 lists the parameters particularly suited for identifying placer-mining impacts, and Table 9-3 presents monitoring recommendations. In many Alaskan parks, water quality monitoring at or near placer mine sites has been conducted for enforcement purposes. In these cases, compliance with state water quality standards has been a critical factor. Appendix D explains monitoring procedures for compliance cases.



Fig. 9-2. Temporary holding ponds may be constructed for settling turbid wash water from placer operations. Breaches in these ponds are evident.



Fig. 9-3. Aerial view of placer mining operation near Wrangell-St. Elias National Park, Alaska. Here, wash water is being discharged directly into the receiving stream.

Table 9-2. Parameter selection rationale for placer mining.

Parameter	Rationale		
arsenic	arsenic-bearing rocks are typically found with gold deposits; dredging oxidizes and mobilizes arsenic		
benthic macroinvertebrates	a biological analysis that integrates changes in physical and chemical water quality conditions		
color	a general indicator reflecting chemical changes caused by mining		
conductivity	a simple estimator of TDS		
copper	dredging oxidizes and mobilizes copper		
dissolved oxygen (DO)	an indicator of depressed oxygen levels caused by organic sediment loading		
hardness	influences the toxicity of heavy metals to aquatic organisms		
iron	dredging oxidizes and mobilizes iron		
lead	dredging oxidizes and mobilizes lead		
mercury	used in amalgamation of free gold; dredging oxidizes and mobilizes mercury		
рН	a valuable measure for interpreting solubility ranges of chemical parameters		
settleable solids	a simple indicator of the presence of materials that would settle on the stream bottom and potentially damage fish spawning habitat		
sulfate	an indicator of mining impacts in areas high in pyrite		
temperature	a requirement for pH and conductivity and a valuable measure for interpreting solubility ranges of chemical parameters		
total dissolved solids (TDS)	<pre>an index of inorganic pollutants in streams, TDS increases with increased ion concentrations (e.g., dissolved toxic metals)</pre>		
total suspended solids (TSS)	an indicator of stream sediment transport, which can carry sorbed toxic metals		
turbidity	a simple estimator of TSS		

TABLE 9-3. Suggested parameters for identifying water quality impacts from placer mining activities. 1,2

	Stream Site	Park Lab	Contract Lab	Sampling Notes
KEY PARAMETERS	discharge pH temperature conduc settleab	le solids ⋖ hard ∢ turb	ness idity DS ► SS ► arsenic	 Discharge should be measured on each sampling occasion (see Section 2.4). Temperature is necessary for pH and conductivity calibrations. Periods of in-stream operation usually reveal maximum TSS, settleable solids, arturbidity values. DO can be field-metered; or, "fix" in fietitrate in lab. Low-flow sampling will best detect copper iron, lead, and mercury that emanate from ground-water sources.
SUPPLEMENTARY PARAMETERS		color DO copper ► iron ► lead ► mercury ► sulfate ►		6. Streams with a history of mercury amalgamation methods especially should be sampled for mercury.7. Benthic macroinvertebrate sampling is discussed in Section 2.4.
SPECIAL STUDIES			macroinvertebrates	

LEGEND: $\frac{1}{2}$ For sampling frequencies, refer to Table 2-2 in Chapter 2. Boldface indicates suggested parameters for initial field reconnaissance.

^{◄ -} Indicates usual site of analysis.

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HARD-ROCK, SAND, AND GRAVEL MINING IMPACTS

10.1 General Description

Impacts from mining operations other than coal, oil, and placer deposits are also of concern to NPS resource managers. Included in this category is mining for base and precious metals, uranium, and sand and gravel. Water quality concerns related to these mining activities comprise many of the problems discussed in previous sections (Table 10-1).

10.2 Metals

Base metals include aluminum, antimony, copper, iron, lead, manganese, molybdenum, nickel, titanium, and zinc. Gold and silver are mined as precious metals. Quite often, gold and silver deposits are found in association with the base metals, and these mining operations are combined. Different methods can be employed to remove these metals from the ground, but the water quality concerns associated with each method are closely related and can be drastic.

10.3 Spoil Piles and Tailings Ponds

Erosion from spoil piles and seepage from tailings ponds are a concern if mining wastes are not properly contained. Erosion can cause an increase in sediment and turbidity values in a stream along with an increase in contaminants from the mining wastes. Along with the previously mentioned metals, higher concentrations of cadmium, arsenic, sulfate, and chloride may result from mining operations. Many of the metal elements will become attached to organic matter found in the stream's sediment load. Gibbs (1977) estimates that sediments transport over 97 percent of the total mass of transition metals (chromium, cobalt, copper, iron, manganese, and nickel) to the world's oceans. Low-pH water may also be discharged from mining operations or seep from settling ponds (Fig. 10-1).

10.4 Cyanide Leaching

Some mining operations use cyanide leaching methods to recover gold and silver (Fig. 10-2). Cyanide compounds of sodium and potassium are the most common leaching agents used in this form of mining. The cyanide solution is allowed to leach through the mined material and solubilize gold or silver, after which it drains into holding ponds or other structures. The precious metals are then recovered from the solution, while the waste cyanide solution may be recycled for later use.

Cyanide may seep into streams if holding structures are faulty or if eroded tailings containing cyanide are transported into the water (Stanton et al., 1986). While cyanide itself is highly toxic to humans and aquatic life, it breaks down rapidly at pH levels found in the natural environment. Therefore, toxicity to aquatic life might occur over a short distance downstream of a spill and would not be detected further downstream. A greater problem arises at cyanide leaching operations, where a spill could result in

Table 10-1. A summary of potential impacts associated with different mining activities.

Type of Mining	Potential Impacts
Base metals	Many different base metals can be released into a stream from mining operations, including Zn, Pb, Ni, Cu, Mn, Fe, Mb, and Al. Lower pH values may occur below mine sites along with higher turbidity values and increases in chloride, sulfate, and conductivity. The lower pH values cause the metals to become mobile, making the contamination more severe.
Precious metals	Mining for precious metals will have many of the same impacts mentioned above for base metals with another potential impact from cyanide leaching. Some precious-metal recovery operations use cyanide, which may seep into streams at some point during the lifetime of the mining project.
Uranium	Radioactive materials that may contaminate streams include uranium, thorium, and radium-226. Heavy metals may also be released, the most common ones being Zn, Al, Mg, Cu, and Fe. Additional problems may include higher concentrations of sulfate, nitrate, chloride, phosphate, and ammonia.
Sand and gravel	The major concern with sand and gravel mining is the increase in turbidity, suspended sediment, and color. These mining operations are generally quite close to stream channels, so the potential for contamination is relatively high. In some instances sand and gravel are recovered directly from stream beds, altering flow patterns and the sediment transport equilibrium in the stream.
Quarries	Quarry mining has similar impacts to sand and gravel mining. Increases in turbidity and suspended solids may occur downstream from the operation. If the quarry is located in a limestone-dominated area, pH may increase.
Oil shale and tar sands	Both oil shale and tar sands mining create water quality problems similar to those of oil and gas operations. Increased values of sulfate, chloride, TDS, conductivity, and metals may result from the mining activity. Oil and grease may also drain into streams. Increases in turbidity and suspended solids are possible due to erosion from spoil piles and access roads.

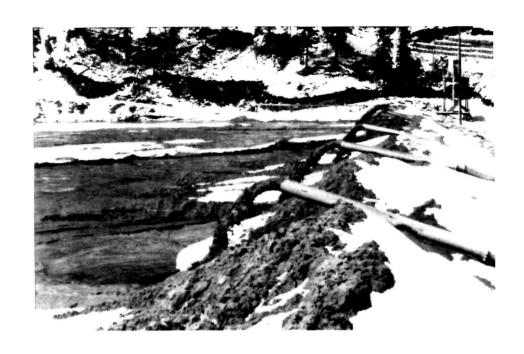


Fig. 10-1. Tailings ponds below a mining site in Climax, Colorado.



Fig. 10-2. Cyanide heap leaching operation in Colorado.

extensive heavy-metal contamination. Cyanide mobilizes a number of heavy metals associated with mine tailings, and the effect of such contamination would be felt much further downstream and for a longer period of time.

10.5 Radioactive Materials

Uranium ore mining and milling is a process that removes radioactive materials from their natural environment and places them on the land surface. Dispersion of radioactive contaminants, especially those deposited adjacent to lakes and streams, is inevitable due to erosion, seepage, and the possible failure of engineered systems during the life of the radioactive dump. The presence of thorium (half-life = 80,000 years) and its daughter element radium-226 (half-life = 1620 years) define the period of time during which these radioactive hazards can potentially contaminate surface and ground waters. Heavy metals present in the ore that will most likely appear in the tailings (a liquid/solid slurry containing ore wastes) include aluminum, copper, iron, magnesium, and zinc. Additional constituents mobilized by the milling processes include ammonia, chloride, nitrate, phosphate, and sulfate. Please note:

A SAMPLING PROGRAM THAT INCLUDES DETECTION OF POLLUTION RESULTING FROM THESE MINES IS BEST HANDLED BY OR IN COOPERATION WITH RADIOACTIVE WASTE EXPERTS DUE TO THE PUBLIC HEALTH HAZARDS ASSOCIATED WITH RADIOACTIVE CONTAMINANTS.

The USGS routinely samples for heavy metals, and periodically they make additional determinations of gross alpha, gross beta, radium-226, and uranium during water quality sampling at selected stations.

10.6 Sand and Gravel Mining

Sand and gravel excavations generally occur adjacent to or directly in river channels and their floodplains. Consequently, high turbidity values and sediment loads may appear downstream from a sand or gravel mining area. Other water quality constituents such as metals, pH, conductivity, dissolved solids, and chloride can be affected by sand and gravel operations, depending on the type of material being excavated.

One important problem associated with sand and gravel mining within the stream channel involves the channel hydraulics and sediment load of the stream. Mining will cause changes in slope and flow pattern in the stream as well as alter the armoring layer of the bed and banks. These changes can result in scouring and deposition of the channel and potential erosion problems as the river adjusts to a new course. In many cases, the affected river has completely bypassed a segment of its normal channel and created a new channel as a result of sand and gravel mining.

10.7 Monitoring Recommendations

To determine whether mining is adversely affecting water quality conditions, certain key parameters often will indicate a stream-water impact. For example, an increase in concentration of such dissolved ions as cadmium, chloride, sodium, and zinc is reflected in increased conductivity

values. Combining conductivity data with pH and total suspended solids data will yield basic information concerning mining-related impacts on stream water quality. A general review of the literature by Wildeman (1981) shows that certain simple-to-measure parameters are good indicators of impacts caused by most mining operations. These parameters are:

- pH
- conductivity
- discharge
- temperature
- total suspended solids

If noticeable changes occur in any of the above parameters and mining operations are located upstream, then more extensive water quality tests will be needed to better determine the cause of the changes.

No sampling chart has been developed for this section due to the wide variety of concerns associated with the different mining types. The sampling program implemented should be designed in response to one of the specific mining activities mentioned and in consideration of the specific impacts associated with that type of mining. For further information on these impacts and important parameters to monitor, refer to the sources in this chapter's bibliography.

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ESTIMATING ANALYTICAL COSTS

A method for figuring the costs of a monitoring program involves developing a "spread sheet" of sampling. The spread sheet example described here combines the sampling recommendations for coal mining (see Table 8-3) with estimates of equipment and laboratory costs from Appendix H. (Note: Miscellaneous expenses for analysis, such as buffer solutions, have been factored in. Because expenses such as transport and labor vary enormously [up to 50 percent of total costs], they are not included and should be added separately.)

Step 1. First, make two columns at the far left, one for the parameters to be measured, the other for capital costs. Then, determine the duration of your monitoring program (this will determine the width of your spread sheet).

Parameter	Capital Costs	Year 1	Year 2

Example: You want to conduct a two-year monitoring program. Add two columns to the right of the capital costs column.

Step 2. For each sampling site, select the parameters to be measured based on the sampling charts found in the respective land-use impact chapters, and list these in the parameter column at the far left.

Parameter	Capital Costs	Year 1	Year 2
acidity alkalinity conductivity discharge hardness iron pH sulfate TDS temperature TSS turbidity			

Example: The upstream land-use activity that may affect your stream is coal mining. Use the sampling chart in Chapter 8 (Table 8-3) to select water quality parameters. In this example, all key parameters from Table 8-3 will be used.

Step 3. Using the sampling frequency recommendations from Table 2-2, enter the number of samples you wish to collect for each parameter per year per site.

Parameter	Capital Costs	Year 1	Year 2
acidity		16	16
alkalinity		16	16
conductivity		16	16
discharge		16	16
hardness		16	16
iron		16	16
pН		16	16
sulfate		16	16
TDS		16	16
temperature		16	16
TSS		16	16
turbidity		16	16

Example: You decide to sample the key parameters as recommended in Table 2-2. In so doing, you will take two samples during the high-flow period, two during summer storms, two during low flow, and one during heavy mining activity. The rest of the year (nine months) you sample monthly. Thus, your total number of samples for each parameter for one year is 16. You will do the same during Year 2. Enter the total number of samples per year for each parameter.

<u>Caution</u>: Recurring costs in the park laboratory must allow for waste. This is important since often only part of a carton of chemicals or a purchased solution can be used before the expiration date requires the remainder to be discarded, thus increasing costs.

Step 4. Again using the sampling charts as a guide, determine the preferred site of analysis (stream site, park lab, or contract lab) for each parameter. Then fill in the appropriate cost for each parameter analysis. Next, multiply the sampling frequency by the cost per sample analysis, and add any capital costs. (Note: Capital costs are a one-time purchase for a monitoring plan. Some capital costs include equipment that analyzes more than one parameter.)

Parameter	Capital Costs	Year 11	Year 21
acidity	\$ 30	16 x\$0.15 = \$2.40	16 x\$0.15 = \$2.40
alkalinity	20	16 x 0.30 = 4.80	$16 \times 0.30 = 4.80$
conductivity	270	16 x 0.10 = 1.60	16 x 0.10 = 1.60
discharge	1700	16 x 0.00 = 0.00	16 x 0.00 = 0.00
hardness	135	16 x 0.40 = 6.40	16 x 0.40 = 6.40
iron	0	16 x 2.50 = 40.00	16 x 2.50 = 40.00
рН	210	16 x 0.20 = 3.20	16 x 0.20 = 3.20
sulfate2	0	16 x 2.50 = 40.00	16 x 2.50 = 40.00
TDS ²	0	16 x 4.00 = 64.00	16 x 4.00 = 64.00
temperature	8	16 x 0.00 - 0.00	16 x 0.00 = 0.00
TSS ²	0	16 x 3.00 = 48.00	16 x 3.00 = 48.00
turbidity	795	16 x 0.00 - 0.00	16 x 0.00 = 0.00

¹These calculations for recurring costs do not allow for waste (see "Caution" on preceding page).

Example: For turbidity, you are able to purchase a turbidimeter for \$795. With this purchase, there is no "cost per sample" per se, so that per-sample costs are \$0. TDS, on the other hand, is contracted out. Analytical costs are \$4 per sample, so for 16 samples the cost is 16 x \$4, or \$64 per year. For pH, 16 samples per year cost \$0.20 apiece (for buffers and breakage), or \$3.20, plus the initial cost of \$210 for a pH meter.

²These analyses are contracted out in this example.

Step 5. Finally, subtotal all columns to estimate all capital costs and the cost of sampling the stream annually; then add all subtotals to estimate the analytical cost of your two-year monitoring program.

Parameter	Capital Costs	Year 1	Year 2
acidity	\$ 30	$16 \times \$0.15 = \2.40	16 x\$0.15 = \$2.40
alkalinity	20	$16 \times 0.30 = 4.80$	16 x 0.30 = 4.80
conductivity	270	16 x 0.10 = 1.60	16 x 0.10 = 1.60
discharge	1700	$16 \times 0.00 = 0.00$	16 x 0.00 = 0.00
hardness	135	$16 \times 0.40 = 6.40$	16 x 0.40 = 6.40
iron	0	$16 \times 2.50 = 40.00$	16 x 2.50 = 40.00
pН	210	$16 \times 0.20 = 3.20$	16 x 0.20 = 3.20
sulfate	0	16 x 2.50 = 40.00	16 x 2.50 = 40.00
TDS	0	16 x 4.00 = 64.00	16 x 4.00 = 64.00
temperature	8	16 x 0.00 = 0.00	16 x 0.00 = 0.00
TSS	0	16 x 3.00 = 48.00	16 x 3.00 = 48.00
turbidity	795	16 x 0.00 = 0.00	16 x 0.00 = 0.00
Subtotal	\$ 3,160.00	\$ 121.60	\$ 121.60
Total		\$ 3,281.60 ¹	\$ 3,403.20 ²

 $^{^{1}}$ Capital costs + Year 1 analytical costs = total analytical cost for one stream site for one year.

²All subtotals combined = total analytical cost for two years.

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APPENDIX A

INFORMATION SOURCES

Many government agencies and organizations collect and store water quality and quantity data. Some of these sources are the following:

National Park Service Water Resources Division 301 S. Howes Street Fort Collins, CO 80521 303/221-5341

U.S. Geological Survey (USGS) National Center 12201 Sunrise Valley Drive Reston, VA 22902 703/648-4000

- NASQAN data base
- USGS water quality and discharge data (found in government documents section of libraries under classification number I-19, 53, XX [XX=state postal abbreviation])

U.S. Environmental Protection Agency (EPA) Criteria and Standards Division WH-585 401 M Street, SW Washington, DC 20460

• STORET data base: STORET User Assistance WH-553

401 M Street, SW Washington, DC 20460

800/424-9067

USDA Forest Service Contact a regional office in one of these nine cities:

Juneau, AK
San Francisco, CA
Lakewood, CO
Atlanta, GA
Missoula, MT

Albuquerque, NM
Portland, OR
Ogden, UT
Milwaukee, WI

National Atmospheric Deposition Program (NADP) Natural Resource Ecology Laboratory Colorado State University Fort Collins, CO 80523 National Bureau of Standards Office of Standard Reference Materials Room B311, Chemistry Building Gaithersburg, MD 20899 301/921-2045

• prepared standards available for purchase

State Agencies:

- Water Pollution Control Board
- Department of Health
- Department of Engineering
- Department of Environmental Quality
- Department of Natural Resources
- Geological Survey

City and County Agencies:

- Department of Health
- Department of Engineering
- Department of Water Resources

Colleges and Universities: contact departments specializing in water resources and hydrology

APPENDIX B

Table B-1. Federal regulatory approved inorganic test procedures. (From: Standard methods of analysis for water-quality parameters. Federal Register 51(125):23693-23700 [Monday, June 30, 1986]).

Parameter and Units	Method	Parameter and Units	Method
Acidity, as CaCO ₃ , alkalinity, as CaCO ₃ ,	Electrometric end point or phenolphthalein end point. Electrometric or	Color, platinum cobalt units or dominant wavelength, hue, luminance, purity.	Colorimetric (ADMI), or (Platinum cobalt), or Spectrophotometric.
mg/L	colorimetric titration to pH 4.5, manual, or Automated.	Copper - Total ¹ , mg/L	Digestion followed by AA direct aspiration,
Aluminum - Total ¹ , ng/L	Digestion followed by AA direct aspiration, AA furnace, Inductively coupled plasma, or Colorimetric (Eri- chrome cyanine R).		AA furnace, Inductively coupled plasma, Colorimetric (Neocuproine), or (Bicinchoninate).
Arsenic - Total ¹ , mg/L	Digestion followed by AA gaseous hydride, AA furnace, Inductively coupled plasma, or Colorimetric (SDDC).	Hardness - Total, as CaCO ₃ , mg/L	Automated colorimetric, Titrimetric (EDTA), or Ca plus Mg as their carbonates, by induc- tively coupled plasma or AA direct aspiration (see calcium and magnesium - Total).
Biochemical oxygen demand (BOD ₅), mg/L	Dissolved Oxygen Depletion.	Hydrogen ion (pH), pH units	Electrometric, measure- ment, or Automated electrode.
Cadmium - Total ¹ , mg/L	Digestion followed by AA direct aspiration, AA furnace, Inductively coupled plasma, Voltametry, or Colorimetric (Dithizone).	Iron - Total ¹ , mg/L	Digestion 1 followed by AA direct aspiration AA furnace, Inductively coupled plasma, or Colorimetric (Phenanthroline).
Calcium - Total ¹ , mg/L	Digestion 1 followed by AA direct aspiration, Inductively coupled plasma, or Titrimetric (EDTA).	Kjeldahl nitrogen - Total, (as N), mg/L	Digestion and distil- lation followed by Titration, Nesslerization, Electrode, Automated phenate, Semi-automated block
Chemical oxygen demand (COD), mg/L	Titrimetric, or, Spectrophotometric, magnish or automated.	1	digestor, or Potentiometric.
Chloride, mg/L	Titrimetric (silver micrate) or Mercuric nitrate), or Cclorimetric, manual or automated (ferricyanide).	Lead - Total ¹ , mg/L	Digestion 1 followed by AA direct aspiration AA furnace, Inductively coupled plasma, Voltametry 2, or Colorimetric (Dithizone).
Chlorine - Total residual, mg/L	fitrimetric Amperometric direct, Starch end point direct, Back titration either end point, or DPD-FAS; Spectrophotometric, DPD, or Electrode.	Magnesium - Total ¹ , mg/L	Digestion 1 followed by AA direct aspiration Inductively coupled plasma, or Gravimetric.

Table B-1. Continued.

Parameter and Units	Method	Parameter and Units	Method
Manganese - Total ¹ mg/L	Digestion followed by	Residue - filterable, mg/L	Gravimetric, 180°C.
	AA furnace, Inductively coupled plasma, or	Residue - nonfilter- able, (TSS), mg/L	Gravimetric, 103-105°C post washing of residue.
	Colorimetric (Persulfate), or (Periodate).	Residue - settleable, mg/L	Volumetric (Imhoff cone) or gravimetric.
Mercury - Total ¹ , mg/L	Cold vapor, manual or Automated.	Sodium - Total ¹ , mg/L	Digestion 1 followed by AA direct aspiration, Inductively coupled plasma, or
Nitrate (as N), mg/L	Colorimetric (Brucine sulfate), or		Flame photometric.
<i>5</i>	Nitrate-nitrite N minus Nitrite N (see Nitrate- nitrite).	Specific conductance, micromhos/cm at 25°C	Wheatstone bridge.
Nitrate-nitrite (as N), mg/L	Cadmium reduction, Manual or Automated, or Automated hydrazine.	Sulfate (as ${ m SO}_4$), mg/L	Automated colorimetric (barium chloranilate), Gravimetric, or Turbidimetric.
Oil and grease - Total recoverable, mg/L	Gravimetric (extraction).	Surfactants, mg/L	Colorimetric (methylene blue).
Orthophosphate	Ascorbic acid method,	Temperature, °C	Thermometric.
(as P), mg/L	Automated or Manual single reagent,	Turbidity, NTU	Nephelometric.
	or Manual two reagent.	Zinc - Total ¹ , mg/L	Digestion followed by
Oxygen, dissolved,	Winkler (Azide modifi-	Inc. Total , mg/ 2	AA direct aspiration,
mg/L	cation), or Electrode.		AA furnace, Inductively coupled
Phenols, mg/L	Manual distillation4		plasma, or Colorimetric
	followed by Colorimetric (4AAP) manual, or Automated.		(Dithizone or Zincon)
Phosphorus - Total, mg/L	Persulfate digestion followed by Manual or Automated ascorbic acid reduction, or Semi-automated block digestor.		
Potassium - Total ¹ , mg/L	Digestion followed by AA direct aspiration, Inductively coupled plasma, Flame photometric, or Colorimetric (Cobaltinitrate).		•

For the determination of total metals the sample is not filtered before processing. A digestion procedure is required to solubilize suspended material and to destroy possible organic-metal complexes. Two digestion procedures are given in "Methods for Chemical Analysis of Water and Wastes, 1979." One (Section 4.1.3), is a vigorous digestion using nitric acid. A less vigorous digestion using nitric and hydrochloric acids (Section 4.1.4) is preferred; however, the analyst should be cautioned that this mild digestion may not suffice for all sample types. Particularly, if a colorimetric procedure is to be employed, it is necessary to ensure that all organo-metallic bonds be broken so that the metal is in a reactive state. In those situations, the vigorous digestion is to be preferred making certain that at no time does the sample go to dryness. Samples containing large amounts of organic materials would also benefit by this vigorous digestion. Use of the graphite furnace technique, inductively coupled plasma, as well as determinations for certain elements such as arsenic, the noble metals, mercury, selenium, and titanium require a modified digestion and in all cases the method write-up should be consulted for specific instruction and/or cautions.

NOTE: If the digestion included in one of the other approved references is different than the above, the EPA procedure must be used.

Dissolved metals are defined as those constituents which will pass through a 0.45 micron membrane filter. Following filtration of the sample, the reference procedure for total metals must be followed. Sample digestion for dissolved metals may be omitted for AA (direct aspiration or graphite furnace) and ICP analyses provided the sample solution to be analyzed meets the following criteria:

- a. has a low COD (<20);
- b. is visibly transparent with a turbidity measurement of 1 NTU or less;
- c. is colorless with no perceptable odor; and
- d. is of one liquid phase and free of particulate or suspended matter following acidification.
- 2 The use of normal and differential pulse voltage ramps to increase sensitivity and resolution is acceptable.
- 3 The back titration method will be used to resolve controversy.
- 4 Just prior to distillation, adjust the sulfuric-acid-preserved sample to pH 4 with 1 + 9 NaOH.

APPENDIX C

PRINCIPAL LAWS AND REGULATIONS PERTAINING TO WATER QUALITY

by

Barbara J. West

CLEAN WATER ACT

The Clean Water Act, one of the first major pieces of comprehensive environmental legislation, established a complete regulatory system for the protection of water quality in the United States. Unlike many earlier responses to environmental problems, the Clean Water Act is equally applicable to activities on both federal and private lands.

Water Quality Standards

The act has general goals 1) to protect health; 2) to enhance the quality of water; and 3) to provide water quality for the protection and propagation of fish, shellfish, and wildlife in and on the water and for agricultural and industrial purposes. The Act provides for the States to establish water quality standards. These standards in each state are rules that determine the use or uses to be made of a water body or segment and the water quality criteria necessary to protect that use or uses. The criteria are usually expressed in terms of numerical limits. The standards are enforceable and are developed through a process that takes into account social, legal, economic, and institutional considerations. They also serve as the basis for water quality-based treatment controls.

The water quality standards of each State must also include an antidegradation statement or policy which is based on a three-tiered approach to maintaining and protecting various levels of water quality and uses. At its base, the existing uses of a water segment and the quality level necessary to protect the uses must be maintained. This establishes the absolute floor of water quality.

The second level provides protection of existing water quality in segments where quality exceeds levels necessary to support propagation of fish, shellfish, and wildlife and recreation in and on the water (that is, those segments meeting the "fishable/swimmable" goals of the Clean Water Act). In such segments, limited water quality degradation can be allowed after it has been shown through a demonstration process, which includes public participation, that quality will continue to support the "fishable/swimmable" uses.

Outstanding National Resource Waters

The third tier provides special protection for waters for which ordinary use classifications may not suffice and which are classified as "Outstanding National Resource Waters" (ONRW). The purpose of this special protection is to safeguard the State's highest quality waters

and also to maintain the quality of waters that have ecological importance.

The Environmental Protection Agency's (EPA) guidance in the Water Quality Standards Handbook states, "Where high quality waters constitute an outstanding National resource, such as waters of National and state parks and wildlife refuges and waters of exceptional recreational or ecological significance, that water quality shall be maintained and protected." For waters designated as Outstanding National Resource Waters, water quality must be maintained and protected, and only temporary and short-term changes may be permitted. The specific nature of the protection provided by ONRW designation differs by state but it often means that no new point-source discharges are permitted.

The selection of Outstanding National Resource Waters is based on the need to provide maintenance and protection to high-quality waters. Ordinarily, this category would be thought to protect only the highest quality waters and that is the policy's primary intent. However, the ONRW category also offers a means to protect waters of "ecological significance." These are water bodies that are important, unique, or sensitive ecologically, but whose water quality as measured by traditional parameters (dissolved oxygen, pH, etc.) may not be particularly high or whose character cannot be adequately described by these parameters. Such unique waters might include swamps or hot springs.

Effluent Limitations

The Clean Water Act prohibits the discharge of pollutants without a permit and provides for the development of effluent limitation by industrial category. If persons or companies intend to discharge pollutants, they must have a permit that prescribes the quantity and concentration of pollutants that can be discharged.

The National Pollutant Discharge Elimination System (NPDES) permit is the primary enforcement mechanism under the Clean Water Act. The majority of monitoring requirements are included as part of the NPDES permit. Dischargers are required to monitor and maintain records that show they are in compliance with the terms and conditions of their permits. In cases where the State has obtained primacy for enforcement, the exact requirements for monitoring are set by the State, either in regulation or as part of the permit terms and conditions.

Non-Point Source Pollution

In addition to the requirements that relate to point-source discharges, the Clean Water Act also prescribes that "best management practices" be followed by those conducting activities, such as agriculture or silviculture, that may result in non-point source pollution.

Wetlands and Floodplains

The Act also requires that all activities that would result in filling wetlands or dredging in the waters of the United States require permits (section 404 permits) from the Army Corps of Engineers. The program regulates discharges into virtually all surface waters--the use, degradation, or destruction of which could affect interstate commerce--along with all tributaries of such waters and all adjacent wetlands.

Wetlands are defined as "areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions." Executive Order 11990 requires that federal agencies take the lead to minimize the destruction, loss, or degradation of wetlands in managing activities on federal lands. The NPS Water Resources Division will be revising its guidelines on how to comply with this executive order as well as Executive Order 11988 which deals with federal activities in floodplains. Monitoring may be required to ensure that NPS actions do not adversely affect either floodplains or wetlands.

THE SAFE DRINKING WATER ACT OF 1986

This Act sets national minimum standards for drinking water and applies to all "public water systems." Generally, any water system that supplies water for human consumption for at least 25 people must comply with the requirements of the Act. Like the Clean Water Act, States may obtain primary enforcement responsibility if they can demonstrate that the state's program meets federal requirements. Federal agencies that operate public water systems are subject to State requirements and enforcement.

Operators of affected water systems are required to establish and maintain records, monitor activities, and provide information upon request that demonstrates that the water system is in compliance with the national standards. The monitoring requirements for systems are tailored to the individual systems and differ by such factors as system size, the source of the water, and the contaminants likely to be found in the system's drinking water.

RESOURCE CONSERVATION AND RECOVERY ACT OF 1976

This Act was passed in 1976 to close the last major environmental "loophole," that is, to provide for the safe disposal of hazardous materials. It provides "cradle-to-grave" standards for hazardous wastes.

The Act established federal criteria for sanitary landfills and defines those not meeting the standards to be "open dumps" which must either be eliminated or upgraded. It also defines "hazardous waste" in the statute and by regulation as any solid waste that may pose a substantial hazard to human health or the environment. Wastes may

qualify as hazardous by being specifically listed by EPA or because they have certain properties -- flammable, corrosive, toxic, etc.

Underground Storage Tanks

Of particular interest to the National Park Service is the program for Underground Storage Tanks. The program applies to any tank or combination of tanks that contain regulated substances, including petroleum products, ten percent or more of which is underground. The States are responsible for the programs; federal agencies, including NPS, that have jurisdiction over any underground storage tanks are subject to and responsible for complying with all Federal, State, local, and interstate requirements applicable to any other person. In NPS, the primary responsibility for the program rests with the Maintenance Division.

OTHER ACTS

Several other acts may affect NPS actions and influence management decisions or requirements for monitoring, depending on where and what types of activities are proposed. Among them are:

Wild and Scenic Rivers Act
Comprehensive Environmental Response, Compensation, and Liability
 Act (CERCLA, also called Superfund)
Federal Insecticide, Fungicide, and Rodenticide Act
Surface Mining Control and Reclamation Act
Nuclear Waste Policy Act
Coastal Zone Management Act
Outer Continental Shelf Lands Act
Toxic Substances Control Act
National Environmental Policy Act

APPENDIX D

SAMPLE COLLECTION PROCEDURES FOR ASSESSING PLACER MINING IMPACTS IN AN ENFORCEMENT CASE

by

Nancy Deschu, National Park Service, Alaska Regional Office Bub Loiselle, Environmental Protection Agency, Seattle, WA

Certain steps must be taken by NPS personnel in collecting valid water samples for potential enforcement action pursuant to the Water Quality Act of 1987 (Clean Water Act). By <u>carefully</u> following these steps and by prearrangement with EPA, NPS could relinquish the water samples to EPA for legal action.

PROCEDURES FOR FIELD NOTES

It is important that detailed field notes are recorded in ink in a weatherproof field notebook. Do not erase any field notes (single line cross out only, with initials). Do not tear out pages from the notebook. Log the date and the time of arrival, sample collection, and departure. Make a note of weather (particularly current and recent precipitation), and soil type if possible. Sign your full name at the bottom of the last page of notes for each site visit. Document your inspection trip with still photography or videotape.

Determining Who Is Discharging

Questions to ask are:

- Who is in charge on site? Is this individual(s) the claim holder? a lessee? a sub-lessee?
- If the claim holder is not on site, what is the name of the claim holder? Is it an individual, partnership, corporation, or association?
- What are the summer and winter addresses of the operator and claim holder?
- · What are the names of the employees on site?

Determining the Mining Activity

Questions to ask are:

- What is the location of activity? Record section, range, and township, quad map name, claim name(s), receiving water.
- How are they gaining access to the mining site?

- What is the physical set-up of the operation? Record the size, number, and condition of settling ponds, size of sluice box, length of runways (if any), type and number of pieces of heavy equipment.
- · How are they removing overburden and how is it being stored?
- · How much paydirt are they processing?
- · What is the water volume being used?
- Is the discharge entering the receiving stream from the sluice box, settling ponds, or raceway?
- · How are they handling their fuel supply?
- How are they handling the camp sewage? pit toilet? leachfield?
- · How long have they been operating?
- · What is the likelihood of continuing activity?
- · Do they have the necessary state and federal permits?
- From whom did they obtain permits?

COLLECTING SAMPLES

What to Record

Record the exact location, the time, and the number of samples collected. A sketch of the mine site is valuable in pinpointing the sampling sites and must be included in the field notebook as part of each site survey.

Collect the water samples in new polyethylene "cubitainers" (available, with prior arrangement, from EPA). Each sample should be labelled on the cubitainer using an indelible marking pen. The labels should include:

- Lab Number: e.g., 8721001
- Date/Time: e.g., 8707051300
- · Analysis Required: e.g., arsenic
- Samplers: e.g., Jane Smith, John Black

Note: The last section of this appendix explains how to derive your Lab Number and your Date/Time codes.

Turbidity

To be consistent with current EPA NPDES permits, turbidity samples should be collected 1) from the effluent prior to entering the receiving stream and 2) in the receiving stream above the mining operation at a location that is representative of natural stream conditions. If several mines are operating on a stream, a sample should be collected immediately above each operation to assess the impact of one operation on the next. Additionally, to determine compliance with state water quality standards, samples should be collected in the receiving stream at a location where the effluent and receiving stream water are well mixed (generally 500 feet downstream from the point where the effluent enters the receiving stream). Due to variations at each mine site, samples should be collected:

- · above all mining activity
- · immediately above a particular mining operation
- in the effluent prior to discharge into the receiving stream (at the end of the raceway; or, if applicable, at the end of the pipe)
- in the receiving stream 500 feet downstream from the effluent entry point (the "point" is the effluent pipe or the mouth of the raceway, whichever is appropriate) (Fig. D-1).

Turbidity samples should be analyzed as soon after collection as possible. If necessary, samples can be stored on ice $(4^{\circ}C)$ for up to 24 hours.

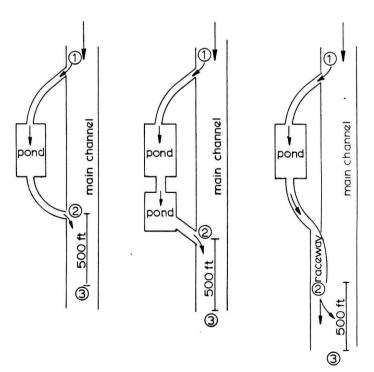


Fig. D-1. Examples of sampling sites.

Currently (1987), NPDES permits limit turbidity to an increase of 5 NTU above background level in the receiving water. Where verifiable dilution factors are provided to EPA, a limit higher than 5 NTU may be granted.

Arsenic

- Samples for total recoverable arsenic should be collected at the same locations as those prescribed for turbidity samples.
- The arsenic water samples should be stored on ice in a dark place, and shipped immediately to a certified laboratory (or EPA laboratory if prearranged) for analyses. If immediate shipping is not possible, arsenic samples (total, dissolved, or suspended) can be preserved with ultra-pure nitric acid to a pH of less than 2. The holding time for samples preserved this way is six months.

Currently (1987), the maximum allowable concentration of total recoverable arsenic is 0.05 mg/L (50 μ g/L) measured at the point of discharge.

Settleable Solids

Settleable solids should be measured at the same three sampling locations as turbidity and arsenic.

- 1. Fill an Imhoff cone to the one liter mark with a thoroughly mixed sample.
- 2. Settle for 45 minutes, then gently stir with a rod, or by spinning the cone.
- 3. Settle 15 minutes longer, then record the volume of settleable matter in the cone as milliliters (mL/L/hr).
- 4. Do not estimate floating material.

It is best to measure settleable solids immediately after collection. However, settleable solids samples can be held for 24 hours with no preservatives, if necessary.

Currently (1987), NPDES permits limit settleable solids to an instantaneous maximum of $0.2\ \text{mL/L/hr}$.

PROPER FORM COMPLETION

"Field Sample Data and Chain of Custody" Sheet

Carefully complete the Field Sample Data and Chain of Custody Sheet. You need to fill in the following information:

 Name/Location: Kantishna Mining District Denali National Park, AK mine operator or owner creek name

- Enforcement/Custody: (check this box)
- · Notes: "collected by NPS personnel for EPA analysis"
- Samplers: your name and names of any others participating in sampling
- · Recorder: name of person recording data
- Source Code: select sample source code from back of data sheet (most often the code will be 12, 34, or 37)
- · Matrix: check "water"
- # containers and preserv.: check "unpress"
- Lab Number: Year record last two digits of year (e.g. 87)

 Week record the week number according to the

 Julian calendar, which begins on a

 Sunday; i.e., Jan 1-7 = 01, Jan 8-15 =

 02, Dec 25-31 = 52
 - Seq consecutive numbering system; (sequence
 numbers available from EPA Region 10
 Laboratory)
- Station Description: describe your sample location on the stream (don't forget to sketch a map in your field notebook)

"Laboratory Analysis Required" Sheet

Two "Laboratory Analysis Required" sheets must be completed for each sample set. There is one laboratory analysis sheet for "general analysis," and one for "metals analysis." Transfer the appropriate Lab Number from the Field Sample Data Sheet to the far left column of the laboratory analysis sheets. Check off the desired tests (i.e., arsenic, turbidity, settleable solids). Describe the sampling location, and date and sign the lab sheet.

Other Field Measurements

If you do take depth, temperature, pH, conductivity, or other miscellaneous measurements, record them in the lower left-hand blocks on the Field Sample Data and Chain of Custody Sheet. Copy your exact Lab Number from the upper block, to the lower block Lab Number; now fill in your extra field measurements accordingly. If you take no extra field measurements, leave these lower data blocks empty.

Chain of Custody Record

When the person who collects the field samples releases them to another person, both the relinquisher and the receiver must sign,

date, and record the time on the Chain of Custody Record (lower right-hand corner of Field Sample Data Sheet). This record must be completed each time the samples are transferred between people. The record is not complete until the lab analyst has signed as the receiver. Before shipping samples, check with EPA on appropriate methods for custody seals on shipping containers.

PHOTOGRAPHIC DOCUMENTATION OF SITE INSPECTIONS

Photographs are very helpful in documenting impacts associated with placer mining, especially if settlement negotiations or other legal proceedings are or might be involved. Specifically, photographs of the following should be included:

- site overview (when possible)
- · mine cut area
- sluice site/recovery site
- · sampling locations
- control locations (e.g., natural conditions above the mine site)
- · treatment facilities
- staging areas (used for fuel storage, vehicle or equipment maintenance, etc.)
- discharge locations
- tailing and/or waste disposal sites
- · reclaimed (or unreclaimed) areas
- general environmental impacts associated with any given mine site

The same type of quality control measures used for sample collection apply also to photographs: be sure to note for each photograph the date, time, location, subject matter, and photographer.

Reference: U.S. Environmental Protection Agency. 1979. Methods for chemical analyses of water and wastewater. EPA 600/4-79-020. Environmental Monitoring and Support Laboratory, Cincinnati, OH. 431 pp.

EPA Region 10 Office 1200 6th Ave. Seattle, WA 98101 (206) 442-1412 EPA Region 10 Laboratory P.O. Box 549 Manchester, WA 98103 (206) 442-0370

APPENDIX E

EPA WATER QUALITY CRITERIA

The following summary chart for water quality criteria contains excerpts from Quality Criteria for Water: 1986 (USEPA, 1986), which summarize available information on toxicities and criteria levels for chemical elements, man-made compounds, and the natural constituents or characteristics found in water. These criteria levels reflect the latest knowledge on the effects of surface-water and ground-water pollutants on health and welfare.

A brief explanation for interpreting the summary table follows. For a complete explanation of the derivations used in computing the chemical criteria shown, refer to appendices A through C in the original document (USEPA, 1986).

Pollutant levels for fresh water are divided into chronic and acute toxicity levels. Where information is sufficient, acute (short-term) toxicity levels are given that estimate the highest one-hour average concentration or a single grab sample concentration that should not produce unacceptable effects on aquatic organisms. Likewise, chronic (long-term) toxicities are diplayed when enough information is available to estimate the highest four-day average concentration (or the average concentration of several samples collected and analyzed over a period of time) that should not cause unacceptable toxicity during a long-term exposure. Both chronic and acute toxicity levels for many parameters are related to water quality characteristics such as pH, salinity, or hardness, and the toxicity concentration levels are a function of these pertinent character-istics. The criteria levels are maximum values except in the case of alkalinity, which is based on a minimum concentration needed to support fisheries unless background levels are naturally lower.

The categories for 1) water and fish ingestion and 2) fish consumption only refer to the effects of consumption of the constituents on human health. The concentrations shown here represent daily intake limits for each water quality parameter; that is, a constituent would be considered a health hazard to humans if ingested via untreated stream water or fish in a concentration greater than the criterion given.

It should be noted that a number of chemical parameters listed have exceedingly small criteria levels reported for human health considerations, and many are given in fractions of a nanogram (ng). In routine water quality sampling, very few laboratories are able to measure chemicals to this level of accuracy. These low levels indicate the high toxicity and potential health hazards of these chemicals and suggest that any amount found in a water sample requires that more extensive testing be done, and the proper authorities should be notified immediately.

The EPA and its predecessor agencies began publishing information on ambient water quality criteria beginning in 1968, followed by revisions in 1972 and 1976. The latest update of Quality Criteria for

 $\underline{\text{Water}}$ (USEPA, 1986) can be obtained (for a fee) by writing to the following address:

U.S. Government Printing Office Superintendent of Documents N. Capitol and H. Street N.W. Washington, D.C. 20401

The EPA is continuously updating and revising existing criteria and recommendations as well as developing new ones. These releases will also be made available to the public as they are completed. Questions regarding criteria level determinations or applicability can be addressed by contacting the following:

U.S. Environmental Protection Agency Criteria and Standards Division WH585 401 M Street SW Washington, D.C. 20460

REFERENCE

U.S. Environmental Protection Agency (USEPA). 1986. Quality criteria for water 1986. U.S. Government Printing Office, Washington, DC. 265 pp.

U.S. Environmental Protection Agency Office of Water Regulations and Standards

U.S. Environmental Protection Agency Office of Water Regulations and Standards Standards Branch (WH-585)		N2	CONCENTRATIO	NS IN µg/L	v	NITS PER LITER		
401 M Street S.W. Washington, D.C. 20460 update 1.0 September 2, 1986	PRIORITT POLLUTANT	CARCINOGEN	FRESH ACUTE CRITERIA	FRESH CHRONIC CRITERIA	WATER AND FISH INGESTION	FISH CONSUMP- TION ONLY	DRINKING WATER H.C.L.	DATE/ REFERENCE
ACENAPTHENE ACROLEIN ACRYLONITRILE ALDRIN	Y Y Y Y	N N Y Y	*1,700. *68. *7,550. 3.0	*520. *21. *2,600.	320.µg 0.058µg** 0.074ng**	780.µg 0.65µg** 0.079ng**		1980 FR 1980 FR 1980 FR 1980 FR
ALKALINITY APPIONIA ANTIHONY ARSENIC	N N Y Y	N N N Y	CRITERIA ARE	20,000. pH AND TEMPER *1,600.	ATURE DEPENDENT - 146.µg 2.2ng**	SEE DOCUMENT 45,000.µg 17.5ng**	0.05mg	1976 RB 1985 FR 1980 FR 1980 FR
ARSENIC (PENT) ARSENIC (TRI) ASBESTOS BACTERIA	Y Y Y N	Y Y Y N	*850. 360. FOR PRIMARY	*48. 190. RECREATION AND	30k f/L** SHELLFISH USES -	SEE DOCUMENT	<1/100ml	1985 FR 1985 FR 1980 FR 1986 FR
BARIUM BENZENE BENZIDINE BERYLLIUM	N Y Y Y	N Y Y Y	*5,300. *2,500. *130.	*5.3	1.mg 0.66µg** 0.12ng** 6.8ng**	40.µg** 0.53ng** 117.ng**	1.0mg	1976 RB 1980 FR 1980 FR 1980 FR
BHC CADMIUM CARBON TETRACHLORIDE CHLORDANE	Y Y Y Y	N N Y Y	*100. 3.9+ *35,200. 2.4	1.1+	10.μg 0.4μg÷* 0.46ng**	6.94µg [⊹] * 0.48ng [⊹] *	0.010mg	1980 FR 1985 FR 1980 FR 1980 FR
CHLORINATED BENZENES CHLORINATED NAPHTHALENES CHLORINE CHLOROALKYL ETHERS	Y Y N Y	Y N N	*250. *1,600. 19. *238,000.	*50. 11.	488µg			1980 FR 1980 FR 1985 FR 1980 FR
CHLOROETHYL BIS-2 CHLOROFORM CHLOROISOPROPYL (BIS-2) CHLOROMETHYL ETHER (BIS)	Y Y Y Y	Y Y N N	*28,900.	*1,240.	0.03µg** 0.19µg** 34.7µg 0.00000376ng**	1.36µg ^{**} 15.7µg ^{**} 4.36mg 0.00184µg ^{**}		1980 FR 1980 FR 1980 FR 1980 FR
CHLOROPHENOL 2 CHLOROPHENOL 4 CHLOROPHENOXY HERBICIDES (2,4,5,-TP) CHLOROPHENOXY HERBICIDES (2,4-D)	Y N N	N N N	*4,380.	*2,000.	10.μg 100.μg			1980 FR 1980 FR 1980 FR 1976 RB
CHLORO-4 METHYL-3 PHENOL CHROMIUM (HEX) CHROMIUM (TRI) COLOR	N Y N	N N N	*30 16. 1,700.+ NARRATIVE ST	11. 210.+ ATEMENT - SEE	50.µg 170.mg DOCUMENT	3,433.mg	0.05mg 0.05mg	1980 FR 1985 FR 1985 FR 1976 RB
COPPER CYANIDE DDT DDT METABOLITE (DDE)	Y Y Y Y	N N Y Y	18.+ 22. 1.1 *1,050.	12.+ 5.2 0.001	200.µg 0.024ng**	0.024ng**	_	1985 FR 1985 FR 1980 FR 1980 FR
DDT METABOLITE (TDE) DEMETON DIBUTYL PHTHALATE DICHLOROBENZENES	Y Y Y Y	Y N N	*0.06 *1,120.	0.1 *763.	35.mg 400.μg	154.mg 2.6mg		1980 FR 1976 RB 1980 FR 1980 FR
DICHLOROBENZIDINE DICHLOROETHANE 1,2 DICHLOROETHYLENES DICHLOROPHENOL 2,4	Y Y Y N	Y Y Y N	*118,000. *11,600. *2,020.	*20,000. *365.	0.01µg** 0.94µg** 0.033µg** 3.09mg	0.02µg** 243.µg** 1.85µg**		1980 FR 1980 FR 1980 FR 1980 FR
DICHLOROPROPANE DICHLOROPROPENE DIELDRIN DIETHYL PHTHALATE	Y Y Y Y	N N Y N	*23,000. *6,060. 2.5	*5,700. *244. 0.0019	87.µg 0.071ng** 350.mg	14.1mg 0.076ng** 1.8g		1980 FR 1980 FR 1980 FR 1980 FR
DIMETHYL PHENOL 2,4 DIMETHYL PHTHALATE DINITROTOLUENE 2,4 DINITROPHENOLS	Y Y N Y	N N Y N	*2,120.		313.mg 0.11µg 70.µg	2.9g 9.1µg** 14.3mg		1980 FR 1980 FR 1980 FR 1980 FR
DINITROTOLUENE DINITRO-O-CRESOL 2,4 DIOXIN (2,3,7,8-TCDD) DIPHENYLHYDRAZINE	И Ү Ү Ү	Y N Y N	*330. *A0.01	*230. *0.00001	13.4µg 0.000013ng** 42.ng***	765.µg 0.000014ng** 0.56µg**		1980 FR 1980 FR 1984 FR 1980 FR
DIPHENYLHYDRAZINE 1,2 DI-2-ETHYLHEXYL PHTHALATE ENDOSULFAN ENDRIN	Y Y Y	N N N	*270. 0.22 0.18	0.056 0.0023	15.mg 74.µg 1.µg	50.mg 159.μg	0.0002mg	1980 FR 1980 FR 1980 FR 1980 FR
ETHYLBENZEME FLUORANTHENE GASES, TOTAL DISSOLVED GUTHION	Y Y N N	N N N	*32,000. *3,980. NARRATIVE ST	ATEMENT - SEE	1.4mg 42.µg DOCUMENT	3.28mg 54.µg		1980 FR 1980 FR 1976 RB 1976 RB
HALOETHERS HALOMETHANES HEPTACHLOR HEXACHLOROETHANE	Y Y Y N	N Y Y Y	*360. *11,000. 0.52 *980	*122. 0.0038 *540	0.19µg [:] * 0.28ng ^{::‡} 1.9µg	15.7µg:* 0.29ng** 8.74µg		1980 FR 1980 FR 1980 FR 1980 FR
HEXACHLOROBENZENE HEXACHLOROBUTADIENE HEXACHLOROCYCLOHEXANE (LINDANE) HEXACHLOROCYCLOHEXANE - ALPHA	Y Y Y Y	N Y Y	*90. 2.0	*9.3 0.08	0.72ng** 0.45µg** 9.2ng**	0.74ng	0.004mg	1980 FR 1980 FR 1980 FR 1980 FR
HEXACHLOROCYCLOHEXANE - BETA HEXACHLOROCYCLOHEXANE - GAMMA HEXACHLOROCYCLOHEXANE - TECHNICAL HEXACHLOROCYCLOPENTADIENE	Y Y Y	Y Y Y	* 7.	*5.2	16.3ng** 18.6ng** 12.3ng**	54.7ng** 62.5ng** 41.4ng**		1980 FR 1980 FR 1980 FR 1980 FR

WATER QUALITY CRITERIA SUMMARY

Office of Water Regulations and Standards Standards Branch (WH-585)		CEN	CONCENTRATI	ONS IN UE/L	u	NITS PER LITER		
401 M Street S.W. Washington, D.C. 20460 update 1.0 September 2, 1986	PRIORITY POLLUTANT	CARCINOGEN	FRESH ACUTE CRITERIA	FRESH CHRONIC CRITERIA	WATER AND FISH INGESTION	FISH CONSUMP- TION ONLY	DRINKING WATER H.C.L.	DATE/ REFERENC
RON SOPHORONE EAD MALATHION	N Y Y	N N N	*117,000. 82.+	1,000. 3.2+ 0.01	0.3mg 5.2mg 50.µg	520.mg	0.05mg	1976 RB 1980 FR 1985 FR 1976 RB
ianganese Ercury Ethoxychlor Herx	N Y N	N N N	2.4	0.012 0.03 0.001	50.µg 144.ng 100.µg	100.µg 146.ng	0.002mg 0.1mg	1976 RB 1985 FR 1976 RB 1976 RB
ONOCHLOROBENZENE APHTHALENE ICKEL ITRATES	Y Y Y N	N N N	*2,300. 1,800.+	*620. 96.+	488.µg 13.4µg 10.mg	100.µg	10.mg	1980 FR 1980 FR 1980 FR 1976 RB
KITROBENZENE KITROPHENOLS KITROSAMINES KITROSODIBUTYLAMINE N	Y Y Y	N N Y	*27,000. *230. *5,850.	*150.	19.8mg 0.8ng** 6.4ng**	1240.ng** 587.ng**		1980 FR 1980 FR 1980 FR 1980 FR
NITROSODIETHYLAMINE N NITROSODIMETHYLAMINE N NITROSODIPHENYLAMINE N NITROSOPYRROLIDINE N	Y Y Y	Y Y Y			0.8ng** 1.4ng** 4,900.ng** 16.ng**	1,240 ng** 16,000 ng** 16,100 ng** 91,900 ng**		1980 FR 1980 FR 1980 FR 1980 FR
OLL AND GREASE OXYGEN DISSOLVED PARATHION CCBs	N N N Y	N N Y		TATEMENT - SER ND COLDWATER (0.04 0.014	E DOCUMENT CRITERIA MATRIX - S 0.079ng**	EE DOCUMENT		1976 RB 1986 FR 1976 RB 1980 FR
PENTACHLORINATED ETHANES PENTACHLOROBENZENE PENTACHLOROPHENOL H	Y Y Y N	N N N	*7,240. *55.	*1,100. *3.2 6.5-9	74.µg 1.01mg	85.µg		1980 FR 1980 FR 1980 FR 1976 RB
PHENOL PHOSPHORUS ELEMENTAL PHOLITE ESTERS POLYNUCLEAR ARCHATIC HYDROCARBONS	Y N Y	N N N	*10,200. *940.	*2,560. *3.	3.5mg 2.8ng**	31.lng**		1980 FR 1976 RB 1980 FR 1980 FR
SELENIUM SILVER SOLIDS DISSOLVED AND SALINITY SOLIDS SUSPENDED AND TURBIDITY	Y Y N	N N N	260. 4.1+ NARRATIVE S	35. 0.12 TATEMENT - SEI	10.µg 50.µg 250.mg E DOCUMENT		0.01mg 0.05mg	1980 FR 1980 FR 1976 RB 1976 RB
SULFIDE-HYDROGEN SULFIDE TEMPERATURE TETRACHLORINATED ETHANES TETRACHLOROBENZENE 1,2,4,5	N N Y Y	N N N	SPECIES DEP	2. ENDENT CRITER	IA - SEE DOCUMENT	48.µg		1976 RB 1976 RB 1980 FR 1980 FR
TETRACHLOROETHANE 1,1,2,2 TETRACHLOROETHANES TETRACHLOROETHYLENE TETRACHLOROPHENOL 2,3,5,6	Y Y Y	Y N Y	*9,320. *5,280.	*2,400. *840.	0.17μg** 0.8μg**	10.7µg** 8.85µg**		1980 FR 1980 FR 1980 FR 1980 FR
THALLIUM TOLUENE TOXAPHENE TRICHLORINATED ETHANES	Y Y Y	N N Y	*1,400. *17,500. 1.6 *18,000.	*40. 0.013	13.µg 14.3mg 0.7lng**	48.µg 424.mg 0.73ng**	0.005mg	1980 FR 1980 FR 1980 FR 1980 FR
TRICHLOROETHANE 1,1,1 TRICHLOROETHANE 1,1,2 TRICHLOROETHYLENE TRICHLOROPHENOL 2,4,5	Y Y Y	N Y Y	*45,000.	*9,400. *21,900.	18.4mg 0.6µg** 2.7µg** 2,600.µg	1.03g 41.8µg** 80.7µg**		1980 FR 1980 FR 1980 FR 1980 FR
TRICHLOROPHENOL 2,4,6 Vinyl Chloride Zinc	N Y Y	Y Y N	320.+	*970.	1.2μg ^{±-‡} 2.μg ^{±-‡}	3.6µg*** 525.µg**		1980 FR 1980 FR 1980 FR
g = grams Y = YES mg = milligrams N = NO µg = micrograms ng = nanograms f = fibers	* :	INS IS HUML THR	UFFICIENT DATA THE L.O.E.L AN HEALTH CRIT	LOWEST OBSER	00 mg/L used) RITERIA. VALUE PRI VED EFFECT LEVEL. INOGENS REPORTED FO ENTED IS THE 10-6	ESENTED DR	FR = FEDERAL I RB = QUALITY (WATER, 19 L. = HAXIMUM (LEVEL	CRITERIA FOR 974 (REDBOOM

NOTE: This chart is for general information; please use criteria documents or detailed summaries in "Quality Criteria for Water 1986" for regulatory purposes.

¹These criteria concentration levels are identical to the drinking water standards set forth in the EPA Interim Primary Drinking Water Regulations as required by the Safe Drinking Water Act. The listed values are applicable to situations in which untreated stream water is consumed by humans.

The following parameters not included in this summary are also part of the interim Regulations. Their H.C.L.s are in parenthesis: fluoride *4 mg/L); turbidity (1-5 NTU); total trihalomethanes (0.1 mg/L); gross alpha (15 pci/L); and radium 226 + radium 228 (5 pci/L).

APPENDIX F

SAMPLE COLLECTION AND PRESERVATION TECHNIQUES AND QUALITY CONTROL

Field sample collection, preservation, and quality control must be properly conducted in order to obtain water quality samples that yield reliable data. To the casual observer, the collection of samples from a stream may appear to be a relatively simple and easy task. This manner of thinking may be the reason that sampling is often the major source of error in water quality monitoring studies. Faulty field sampling negates all results, even if laboratory and data analyses are flawless and "certified."

The optimum approach to collecting water quality information would be to analyze all parameters of interest at the field site, within the stream. Because this approach is logistically impossible for most parameters, the EPA has recommended preservation techniques to minimize changes in parameter levels prior to laboratory analysis.

The following sections contain excerpts from government publications that separately address sample collection, sample preservation, and quality control procedures. The first excerpt, "How to Collect a Field Sample," is taken from Curtis et al. (1986), A Manual for Training Reclamation Inspectors in the Fundamentals of Hydrology. "Quality Control for Field Sampling" and "Sample Preservation" are both excerpted from USEPA (1979), Handbook for Analytical Quality Control in Water and Wastewater Laboratories. These excerpts can serve as a guide for proper sample collection in any water quality monitoring plan.

HOW TO COLLECT A FIELD SAMPLE

Excerpted with permission from: Curtis, W. R., K. L. Dyer, and G. P. Williams, Jr. 1986. A Manual for Training Reclamation Inspectors in the Fundamentals of Hydrology. USDA Forest Service, Northeastern Forest Experiment Station, Berea, KY. 56 pp.

Sampling

A great variety of water sources must be sampled by inspection personnel. Therefore, a knowledge of many water-quality sampling techniques will be useful. Collecting a sample from a discharge pipe requires one technique, whereas collecting a sample from a flowing stream requires another.

Guidelines for Representative Samples

A sample is worthless unless it adequately represents the water in the stream or impoundment being sampled. To obtain representative samples, follow these guidelines:

- Collect the sample where the water is well mixed, if
 possible immediately downstream from a point of
 hydraulic turbulence such as a waterfall or flume. Samples may also be collected from free-falling water (as
 in a small waterfall); however, care should be taken to
 move the sampling device through the full thickness
 of the falling water at several points so that a fully
 representative sample is obtained.
- Avoid sampling where floating solids and oil tend to accumulate, such as downstream from certain types of weirs and flumes.
- 3. In a well-mixed stream, collect the sample in the center of the channel at from 4 10 to 6/10 of its depth where the velocity of flow is average or higher than average. This depth avoids the inadvertent collection of part of the stream bottom or top-floating materials such as oil, grease, or debris. In streams that may not be well mixed, force the mouth of the sampling vessel across the entire cross section of the stream to the fullest extent possible without collecting bottom materials or surface scum and debris. If the surface scum, oil, or grease is flowing with the stream (not just accumulated in a stagnant area) there may be need to include a representative portion of these materials in the sample—but only if the analysis is to include these parameters.
- 4. To avoid contaminating the sample, collect samples with the mouth of the sample bottle pointed upstream. Keep hands and other potential contaminants away from the mouth of the bottle.
- 5. Do not walk on, or in any way disturb, the stream bottom upstream from the sampling site.
- Do not sample backwaters or deep standing pools found along the stream.

- 7. Do not sample streams immediately below tributaries or other significant points of inflow. Sample far enough downstream for thorough mixing to have occurred, or sample both main stream and tributary just above their confluence.
- 8. Wide shallow streams should be sampled using the equal width increment (EWI) technique described later in this section. Shallow lakes or impoundments should be sampled at several points and the samples analyzed either as individual samples or as a composite sample.
- Water quality can vary with depth so deep lakes or streams should be sampled with depth-integrating samplers, or samples should be taken at different depths for analysis as individual or composite samples.
- 10. Collect sufficient sample volume to allow duplicate analyses and quality assurance testing. The required sample volume is the sum of the volume required for each analysis requested. Refer to the laboratory director for minimum volumes to be collected.
- 11. Not all sample containers should be filled to the same level. Sample bottles should be filled completely if the samples are to be analyzed for O₂, CO₂, H₂S, free chlorine, volatile organics, oil and grease, pH, SO₂, NH₃, NH₄, Fe⁺⁺, and acidity or alkalinity. Full bottles must be protected from freezing. When sampling for bacteria or suspended solids, it is desirable to leave an airspace in the sample container to facilitate mixing before subsampling in the laboratory. In depthintegrated sediment samples it is essential that the sample bottles not be filled more than ³/₄ full.
- 12. If samples are taken from a closed conduit via a valve or faucet, allow sufficient flushing time to insure that the sample is representative of the supply, taking into account the diameter, length of the pipe to be flushed, and the velocity of the flow.
- 13. Maintain an up-to-date log book in which to note possible interferences, environmental conditions, and problem areas.

Streams

Grab Samples

Grab sampling, collecting a single-point, instantaneous sample, is generally not considered a good method for sampling a flowing stream unless the stream is very narrow (5 feet or less) or very shallow (10 inches or less). But since most mine effluents are smaller than this, grab sampling will of necessity be the method most commonly used by

mine inspectors. Normally a grab sample should be collected near the center of the main flow of the stream. When the stream is not well mixed, some attempt should be made to make the sample as representative as possible by moving the collecting bottle across flowing portions of the stream. More information relevant to grab samples can be found in the first seven guidelines for representative samples in the preceding section.

Point Sampling

For streams with a stable cross section and a rather uniform lateral distribution of suspended solids, sampling at a single vertical (near the center of the stream) will usually be adequate.

Equal Width Increment (EWI) Samples

To collect an equal width increment (EWI) sample, the width of a stream is divided into segments, each segment is sampled and its discharge is measured, then volumes of these samples are measured out proportional to the flow of their respective stream segments. The samples are combined to give the composite EWI sample.

Depth Integrated Samples

For a sample from a deep stream, lake, or impoundment to be representative, it usually must be depth-integrated. Samples for total suspended solids or other constituents, such as total iron and total manganese, may be collected with a US-DH-48 depth-integrating suspended-sediment sampler or similar sampler when the water is deep enough. If a Teflon nozzle and O-ring are used with the DH-48 sampler, the sample can be analyzed for almost any chemical pertinent to coal mining situations. However, if nozzles and fittings are of other materials — brass, aluminum, etc. — analysis may be somewhat restricted. More than one bottle of water may be required, depending upon the laboratory determinations to be made and the preservation techniques employed in the field. The following procedure should be used when collecting samples for subsequent analyses:

- Place a clean bottle in the US-DH-48 sampler.
- Lower the sampler into the water and collect a small amount of sample.
- Rinse bottle thoroughly and discard the water, making sure no solids remain.
- Replace bottle, lower sampler at a uniform rate from the surface to the bottom, then raise it at a uniform rate. DO NOT STRIKE BOTTOM.
- Repeat previous step at all verticals necessary for representative sample.
- Fill the bottle no more than ¼ full. If it is filled beyond that volume, all water must be discarded and a new sample collected.

High velocity, floating debris, very shallow water, or other conditions may preclude the use of a sediment sampler. In that case, grab samples should be collected in a clean, rinsed container. When grab samples are collected in wide, relatively shallow streams, it is important that several verticals be sampled because the distribution of suspended solids is probably uneven. A single bottle may be filled through quick dips at several verticals, avoiding the necessity of compositing samples or collecting multiple samples.

Flow Proportional Compositing

A flow-proportional composite sample should represent the total volume of water flowing past the sampling site during a given period of time. This composite sample is composed of a number of discharge-weighted subsamples collected at uniform time intervals, perhaps a day or a week apart. For example, the composited portion of a subsample collected at a discharge of 15 ft³/s would have 5 times the volume of the composited portion of a subsample collected at a discharge of 3 ft³/s.

Sequential Compositing

A series of small samples collected at uniform time intervals is combined to produce a sequential-composite sample representative of the period of time over which the individual samples were collected. The main advantage of sequential compositing is economy. However, this type of sampling is limited by its "averaging" effect, which tends to mask the influences of significantly large changes in both streamflow and water quality.

Springs, Seeps, and Very Shallow Streams

Unless pools are present, samples cannot be dipped in the normal way from springs, seeps, and very shallow streams. Water may be collected with a syringe from shallow water as long as it does not draw up particulate matter from the bottom. It is frequently necessary to place a clean flat rock or piece of glass on the stream bottom, so the syringe tip will not be close to the loose bottom materials. Sometimes it is necessary to excavate a small pool or depression so the water will be deep enough to sample. After disturbing the stream bed in any way it will be necessary to let the flowing stream wash itself clean of sediment and turbidity before samples are taken.

Water flowing over a smooth rock face can be especially difficult to sample; however, a straw or a stick can usually be used to lead it to the sample container.

Springs and seeps in unconsolidated material may sometimes be sampled using a slotted pipe as described in the later section on sampling equipment.

QUALITY CONTROL FOR FIELD SAMPLING

Excerpted from: U.S. Environmental Protection Agency. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA-600/4-79-019. Environmental Monitoring and Support Laboratory, Cincinnati, OH.

Quality control during sampling should be implemented to detect any data errors resulting from improper sampling or analytical methods, inadequate sample preservation, or collection of non-representative samples. The following EPA quality control samples should be collected, analyzed, and reported every 10 to 20 samples in order to determine the reliability of sampling techniques used in a monitoring program.

<u>Duplicate</u> <u>samples</u>. At selected stations on a random time frame duplicate samples are collected from two sets of field equipment installed at the site, or duplicate grab samples are collected. This provides a check of sampling equipment and technique for precision.

<u>Split samples</u>. A representative subsample from the collected sample is removed and both are analyzed for the pollutants of interest. The samples may be reanalyzed by the same laboratory or analyzed by two different laboratories for a check of the analytical procedures.

<u>Spiked samples</u>. Known amounts of a particular constituent are added to an actual sample or to blanks of deionized water at concentrations at which the accuracy of the test method is satisfactory. The amount added should be coordinated with the laboratory. This method provides a proficiency check for accuracy of the analytical procedures.

<u>Sample preservative blanks</u>. Acids and chemical preservatives can become contaminated after a period of use in the field. The sampler should add the same quantity of preservative to some distilled water as normally would be added to a wastewater sample. This preservative blank is sent to the laboratory for analysis of the same parameters that are measured in the sample and values for the blank are then subtracted from the sample values. Liquid chemical preservatives should be changed every 2 weeks—or sooner, if contamination increases above predetermined levels.

SAMPLE PRESERVATION

Excerpted from: U.S. Environmental Protection Agency. 1979. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA-600/4-79-019. Environmental Monitoring and Support Laboratory, Cincinnati, OH. 164 pp.

SAMPLE PRESERVATION

Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural waters, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition. Therefore, as a general rule, it is best to analyze the samples as soon as possible after collection. This is especially true when the analyte concentration is expected to be in the low ug/1 range.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and freezing.

The recommended preservative for various constituents is given in Table 1. These choices are based on the accompanying references and on information supplied by various Quality Assurance Coordinators. As more data become available, these recommended holding times will be adjusted to reflect new information. Other information provided in the table is an estimation of the volume of sample required for the analysis, the suggested type of container, and the maximum recommended holding times for samples properly preserved.

TABLE 1

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT⁽¹⁾

Measurement	Vol. Req. (ml)	Container ²	Preservative 3,4	Holding Time ⁵
100 Physical Properties				
Color	50	P,G	Cool, 4°C	48 Hrs.
Conductance	100	P,G	Cool, 4°C	28 Days
Hardness	100	P,G	HNO_3 to $pH < 2$	6 Mos.
Odor	200	G only	Cool, 4°C	24 Hrs.
pН	25	P,G	None Req.	Analyze Immediately
Residue				······································
Filterable	100	P,G	Cool, 4°C	7 Days
Non- Filterable	100	P,G	Cool, 4°C	7 Days
Total	100	P,G	Cool, 4°C	7 Days
Volatile	100	P,G	Cool, 4°C	7 Days
Settleable Matter	1000	P,G	Cool, 4°C	48 Hrs.
Temperature	1000	P,G	None Req.	Analyze Immediately
Turbidity	100	P,G	Cool, 4°C	48 Hrs.
200 Metals				
Dissolved	200	P,G	Filter on site HNO ₃ to pH < 2	6 Mos.
Suspended	200		Filter on site	6 Mos. (8)
Total	100	P,G	HNO ₃ to pH < 2	6 Mos.

TABLE 1 (CONT)

	Vol.			
Measurement	Req. (ml)	Container ²	Preservative ^{3,4}	Holding <u>Time</u> ⁵
Chromium+6	200	P.G	Cool, 4°C	24 Hrs.
Mercury Dissolved	100	P,G	Filter HNO ₃ to pH < 2	28 Days
Total	100	P,G	HNO_3 to $pH < 2$	28 Days
300 Inorganics, Non-Me	tallics			
Acidity	100	P,G	Cool, 4°C	14 Days
Alkalinity	100	P,G	Cool, 4°C	14 Days
Bromide	100	P,G	None Req.	28 Days
Chloride	50	P,G	None Req.	28 Days
Chlorine	200	P,G	None Req.	Analyze Immediately
Cyanides	500	P,G	Cool, 4°C NaOH to pH >12 0.6g ascorbic acid ⁶	14 Days ⁷
Fluoride	300	P,G	None Req.	28 Days
Iodide	100	P,G	Cool, 4°C	24 Hrs.
Nitrogen				
Ammonia	400	P,G	Cool,4°C H_2SO_4 to $pH < 2$	28 Days
Kjeldahl, Total	500	P,G	Cool, 4° C H_2SO_4 to $pH < 2$	28 Days
Nitrate plus Nitrite	100	P,G	Cool, 4° C H_2SO_4 to $pH < 2$	28 Days
Nitrate ⁹	100	P,G	Cool, 4°C	48 Hrs.
Nitrite	50	P,G	Cool, 4°C	48 Hrs.

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container ²	Preservative ^{3,4}	Holding Time ⁵
Dissolved Oxygen Probe	300	G bottle and top	None Req.	Analyze
Winkler	300	G bottle and top	Fix on site	Immediately 8 Hours
Phosphorus Ortho-			and store in dark	
phosphate, Dissolved	50	P,G	Filter on site Cool, 4°C	48 Hrs.
Hydrolyzable	50	P,G	Cool, 4° C H_2SO_4 to $pH < 2$	28 Days
Total	50	P,G	Cool, 4° C H_2SO_4 to $pH < 2$	28 Days
Total, Dissolved	50	P,G	Filter on site Cool, 4°C H ₂ SO ₄ to pH < 2	24 Hrs.
Silica	50	P only	Cool, 4°C	28 Days
Sulfate	50	P,G	Cool, 4°C	28 Days
Sulfide	500	P,G	Cool, 4°C add 2 ml zinc acetate plus NaOH to pH >9	7 Days
Sulfite	50	P,G	None Req.	Analyze Immediately
400 Organics				immediately
BOD	1000	P,G	Cool, 4°C	48 Hrs.
COD	50	P,G	Cool, 4°C H ₂ SO ₄ to pH < 2	28 Days
Oil & Grease	1000	G only	Cool, $4^{\circ}C$ H_2SO_4 to $pH < 2$	28 Days
Organic carbon	25	P,G	Cool, 4° C H_2SO_4 or HCl to $pH < 2$	28 Days
Phenolics	500	G only	Cool, 4°C H ₂ SO ₄ to pH <2	28 Days

TABLE 1 (CONT)

Measurement	Vol. Req. (ml)	Container ²	Preservative ^{3,4}	Holding Time ⁵
MBAS	250	P,G	Cool, 4°C	48 Hrs.
NTA	50	P,G	Cool, 4°C	24 Hrs.

- 1. More specific instructions for preservation and sampling are found with each procedure as detailed in this manual. A general discussion on sampling water and industrial wastewater may be found in ASTM, Part 31, p. 72-82 (1976) Method D-3370.
- 2. Plastic (P) or Glass (G). For metals, polyethylene with a polypropylene cap (no liner) is preferred.
- 3. Sample preservation should be performed immediately upon sample collection. For composite samples each aliquot should be preserved at the time of collection. When use of an automated sampler makes it impossible to preserve each aliquot, then samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.
- 4. When any sample is to be shipped by common carrier or sent through the United States Mails, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements of Table 1, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.30 or less).
- 5. Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still considered valid. Samples may be held for longer periods only if the permittee, or monitoring laboratory, has data on file to show that the specific types of sample under study are stable for the longer time, and has received a variance from the Regional Administrator. Some samples may not be stable for the maximum time period given in the table. A permittee, or monitoring laboratory, is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample stability.
- 6. Should only be used in the presence of residual chlorine.

- 7. Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before the pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by the addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.
- 8. Samples should be filtered immediately on-site before adding preservative for dissolved metals.
- 9. For samples from non-chlorinated drinking water supplies conc. H₂SO₄ should be added to lower sample pH to less than 2. The sample should be analyzed before 14 days.

APPENDIX G

AUTOMATIC STORM-WATER SAMPLING DEVICE

Source: Kunkle, S., N. Cowdin, J. Wilson, J. Grondin, T. Ricketts, and M. Flora, 1985. Field survey of <u>Giardia</u> in streams and wildlife of the Glacier Gorge and Loch Vale basins, Rocky Mountain National Park. Natural Resources Report Series 85-3. National Park Service, Water Resources Division, Fort Collins, CO.

The automatic storm-water sampling device, or "storm sampler," was developed by the staff of the NPS Water Resources Division for use in remote areas. This inexpensive, simple-to-construct device proved effective in collecting storm runoff samples during the water quality investigations conducted in Rocky Mountain National Park.

The storm sampler operates in the same way as existing suspended sediment samplers, whereby rising stream water resulting from storm runoff causes the sample bottles to fill. Once the bottle is filled, a ping-pong ball inside the bottle floats to the top and seals the opening, which prevents further exchange of water. Tests conducted under laboratory conditions, in which a dye-filled sampler was submerged in water for a 24-hour period, showed that only 1 ml of water from the sample bottle was lost to the outside in that time.

The storm sampler is constructed from steel angle iron, aluminum strips, plastic tubing, hose clamps, polyethylene bottles, rubber stoppers, screen, funnels, bicycle water bottle holders, and ping-pong balls (Fig. G-1). Assembled, the sampler weighs approximately 2.5 kg (5.5 lbs) and is about 1 m (3 ft) in height, but the height can be varied to suit individual needs. Materials cost about \$25, and construction requires three to four hours.

The sample bottles are fitted with a rubber stopper, into which a small funnel has been inserted upside down (Fig. G-2). The wide end of the funnel provides a sealing seat for the ping-pong ball in the bottle to press against when water entering the bottle floats the ball to the top. The bottle, thus sealed, allows no more water in or out of the sample bottle. The narrow end of the funnel, through which the water enters, is covered with 1 mm-size screen to keep particulate matter from entering the bottle or clogging the water intake. The screen is coneshaped to insure against air lock and to allow the bottle to fill freely. Sample bottles were also covered with aluminum foil to protect the contents from direct sunlight, since ultraviolet radiation is bactericidal. By this means the water samples were also kept cool until collected for analysis.

The sample bottles are set above normal stream level but at a height where they would be inundated in the event of storm runoff. More than one bottle may be used, and two or more may be set at different levels on the stand. We used two bottles and set them approximately 10 to $15~\rm cm$ (4 1/2-6 in) apart in order to accommodate both lower and higher runoff flows. The minimum stream depth needed for the sampler to operate is about 30 cm (1 ft).

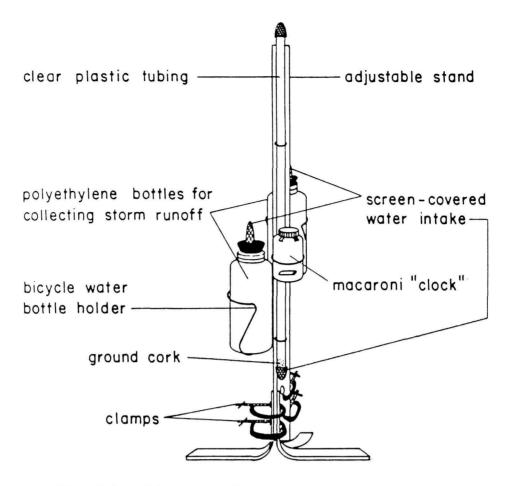


Fig. G-1. Schematic of automatic storm-water sampler.

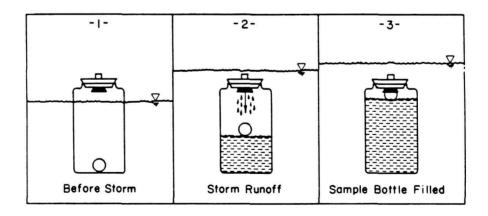


Fig. G-2. Operation schematic.

Attached along the axis of the sampler stand is a length of hollow plastic tubing which is covered at the base with screen. Inside the tube is some ground cork, which rises with an influx of water and sticks to the side of the tube at the height the water reached during the storm runoff. Thus, it can be estimated how high the stream rose when the storm water sample was collected.

In order to determine the approximate age of the storm sample, we developed what came to be known as the "macaroni clock," so called because it incorporates a piece of macaroni in a small (250 ml), separate polyethylene bottle also attached to the sampler unit. A piece of mostaccioli about 4 cm in length and 0.7 cm in diameter works well. The bottle that contains the single mostaccioli piece contains small holes in the neck of the jar to take in water during storm runoff at the same time one or more sample bottles are filling. Once wet, the noodle will gradually absorb water and indicate the age of the water sample. In cold (5°C) water, the noodle behaves as follows: after 12 hours, the noodle is swollen and soft. After 18-24 hours, it swells 1 1/2-2X its dry diameter. In 36 hours the noodle appears even more distended, and disintegration is visible at both ends. After 48 hours, disintegration is advanced. In this way, the "clock" enabled field personnel to distinguish day-old storm samples from two-day or older samples. (The timing is important so that bacterial analysis is valid, since old samples are subject to bacteria die-off.) Thus, we could be fairly sure that the samples automatically collected by the storm sampler and retrieved for analysis were from storms that occurred during the previous afternoon and not from old events.

APPENDIX H

LABORATORY AND FIELD EQUIPMENT AND PARAMETER ANALYSIS COSTS

Field and laboratory equipment for water quality analyses vary according to make, supplier, and the sophistication of the instruments. "Make and supplier" is too vast a topic for the present document, but instrument sophistication can be generally described. Table H-1 presents necessary equipment for those water quality parameters in the sampling charts that can be assessed at the stream site or in a park laboratory. Where choice of analytical tool exists, options are grouped under the same number.

Contract laboratory prices can vary considerably, as can reasons for the variation. For example, a university with a "paid-for" ICP spectrophotometer may be able to analyze for a suite of 15 or more metals at \$25 per suite, as compared to a firm amortizing new equipment that may charge much more. Variation in cost can also depend on cost of labor when conducting a labor-intensive analysis (of macroinvertebrates, for instance). Overhead varies considerably, and costs for quality assurance and proper standardizing will be higher for a top-quality, certified laboratory.

The analytical instruments a laboratory uses also determine the costs of using that laboratory. If a laboratory analyzes low-level sulfates on an ion chromatograph (IC), then for almost no additional cost they can provide data on orthophosphate, nitrate, and certain other anions concurrently tested by the IC. Thus, it is advisable to discuss various tests with laboratory personnel to understand all the "package deals" offered, while avoiding purchase of any unnecessary parameters. A survey of four laboratories in the Rocky Mountain Region yielded the prices and other information contained in Table H-2.

Both Tables H-1 and H-2 can be used for estimating water quality monitoring expenses.

Table H-1. Summary of principal costs for equipment commonly used in NPS units.

PARAMETER	PRICE
<pre>Bacteria (fecal coliform) 1. water bath OR special aluminum block incubator 2. filtration equipment*, pump, and accessories 3. recurring costs (petris, filters)</pre>	\$ 500-1000 \$1000-1500 \$ 500-800 \$ 5/sample
 Bacteria (total coliforms or fecal streptococci) 1. incubator 2. filtration equipment*, pump, and accessories 3. recurring costs (petris, filters, etc.) 	\$ 350-600 \$ 500-800 \$ 5/sample

Table H-1. Continued.

PARAMETER	PRICE
Colorimeter Tests (for nitrates, phosphates, color, certain metals, and sulfates)	
 field reconnaissance kits colorimeter (filter photometer quality) OR spectrophotometer, nonautomatic (such as 	\$ 25 \$ 300
Bausch and Lomb Spec 20 type) OR spectrophotometer, automatic features recurring costs (chemicals)	\$ 600-800 \$1500-2500 \$ 1/sample
Conductivity 1. portable meter	\$ 300-800 \$ 0.35 (apprair)
2. recurring costs (solutions) Dissolved Oxygen	\$ 0.25/sample
1. simple kit (Hach dropper type) OR more sensitive kit (Hach titration type) OR DO meter	\$ 50 \$ 150 \$ 400-800
2. recurring costs (chemicals, membranes)	\$ 1/sample
 pH papers or solution kits OR portable meter recurring costs (chemicals, probe replacements) 	\$ 20-30 \$ 300-600 \$ 0.50-1/sample
<pre>Settleable Solids 1. Imhoff cones (set of 4, plus</pre>	\$ 100
Stream Discharge 1. current meter with accessories	\$ 500-2000
Titration Equipment (for acidity, alkalinity, chloride, and hardness) 1. titration device (digital) or buret 2. recurring costs (chemical)	\$ 100 \$ 0.50/sample
Turbidity 1. meter 2. recurring costs (standards, bulbs)	\$ 500-800 \$ 0.25/sample

 $[\]star$ filtration equipment the same for all types of bacteria

Table H-2. Lowest and highest costs for parameter analyses at four selected laboratories in 1986.

Parameter	Labor-				Highest-Priced Laboratory			
	atory*	Method of Analysis	Reporting Level	Cost per Sample	Labor- atory*	Method of Analysis	Reporting Level	Cost per Sample
acidity	CSUL	titration	1 mg/L	\$ 5.00	USGS	titration	0.1 mg/L	\$ 9.25
alkalinity	CSUL	titration	1 mg/L	2.50	USGS	titration	0.1 mg/L	5.00
aluminum	CSUL	ICP	100 ug/L	2.50	USGS	AA	10 ug/L	20.50
arsenic	CSUL	hydride generator	0.5 ug/L	8.00	USGS	hydride generator	1 ug/L	20.60
BOD	WYDL	5-day incubate	1 mg/L	7.00	RMAL	5-day incubate	2 mg/L	40.00
bacteria	WYDL	millipore	1/100 mL	2.00	RMAL.	millipore	1/100 mL	30.00
COD	WYDL	colorimetric	25 mg/L	10.00	RMAL	colorimetric	5 mg/L	25.00
calcium	CSUL	ICP	0.01 mg/L	2.50	USGS	AA	0.01 mg/L	10.05
chloride	CSUL	IC	0.1 mg/L	2.50	USGS	IC	0.1 mg/L	4.15
chlorine	WYDL	colorimetric	0.5 mg/L	3.00	RMAL	colorimetric	0.5 mg/L	15.00
color	WYDL	colorimetric	5 units	1.00	RMAL	colorimetric	5 units	10.00
copper	CSUL	ICP	10 ug/L	2.50	USGS	AA	0.2 ug/L	30.00
hardness	CSUL	Ca + Mg (ICP)	1 mg/L	5.00	RMAL	Ca + Mg (AA)	5 mg/L	15.00
iron	CSUL	ICP	10 ug/L	2.50	USGS	AA	10 ug/L	4.60
lead	CSUL	ICP	100 ug/L	2.50	USGS	AA	0.3 ug/L	30.00
magnesium	CSUL	ICP	0.01 ug/L	2.05	USGS	AA	0.01 ug/L	10.05
manganese	CSUL	ICP	10 ug/L	2.50	USGS	AA	0.2 ug/L	30.00
mercury	CSUL	cold vapor, AA	0.5 ug/L	8.00	USGS	cold vapor, AA	0.1 ug/L	20.60
N-NO.	CSUL	colorimetric	0.01 mg/L	2.50	USGS	IC	0.05 mg/L	4.80
N-TKN	CSUL	colorimetric	0.1 mg/L	6.00	USGS	colorimetric	0.1 mg/L	12.60
oil+grease	WYDL	freon extract	0.1 mg/L	10.00	USGS	freon extract	1 mg/L	28.25
P-PO	CSUL	colorimetric	10 ug/L	3.50	USGS	colorimetric	1 ug/L	7.50
P-total	CSUL	colorimetric	10 ug/L	5.50	USGS	colorimetric	10 ug/L	12.95
phenols	WYDL	colorimetric	2 ug/L	7.50	USGS	acid extract	1 ug/L	23.55
potassium	CSUL	AA	0.01 mg/L	2.50	USGS	AA	0.01 mg/L	7.50
sodium	CSUL	AA	0.01 mg/L	2.50	USGS	AA	0.01 mg/L	7.20
sulfate	CSUL	IC	1 mg/L	2.50	USGS	IC	0.2 mg/L	7.10
surfactants	WYDL	colorimetric	0.01 mg/L	10.00	RMAL	colorimetric	0.1 mg/L	25.00
TDS	CSUL	gravimetric	1 mg/L	4.00	USGS	gravimetric	1 mg/L	12.10
TSS	WYDL	gravimetric	1 mg/L	3.00	USGS	gravimetric	1 mg/L	12.10
turbidity	CSUL	nephelometric	0.1 NTU	2.50	USGS	nephelometric	0.05 NTU	4.90
zinc	CSUL	ICP	10 ug/L	2.50	USGS	AA	0.05 ug/L	30.00

*Abbreviations: CSUL - Colorado State University Soils Lab

RMAL - Rocky Mountain Analytical Lab

USGS - United States Geological Survey Water Quality Laboratory
WYDL - Wyoming Department of Agriculture, Division of Laboratories

AA - Atomic absorption

ICP - Inductively-coupled plasma spectrometry

IC - Ion chromatography

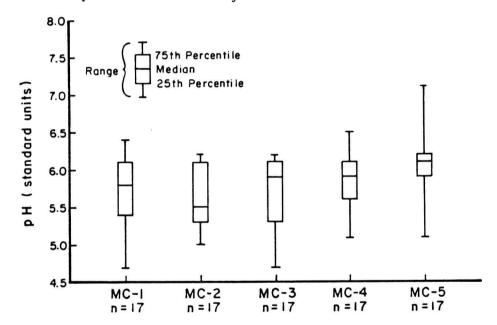
APPENDIX I

DATA DISPLAY

Compiled by
Jeff Hughes
National Park Service
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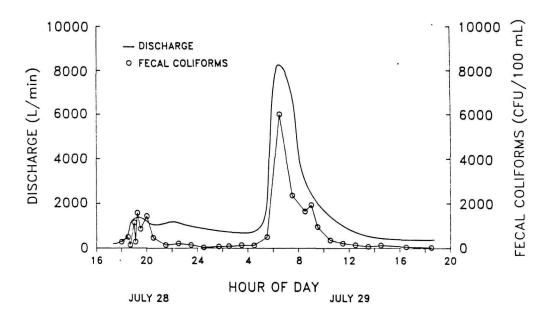
Graphs, tables, and charts serve as useful devices for organizing, summarizing, simplifying, and presenting data in a readily understood format. All graphics should be self-explanatory: that is, a reader should be able to understand the figure without any explanatory text. Graphics should not present an overwhelming amount of information but should remain simple. Two graphs may be easier to understand than one, given the same information.

The following examples represent some of the basic graphics used to present data. Refer to Snedecor and Cochran (1980) for a review of statistical parameters and analysis.



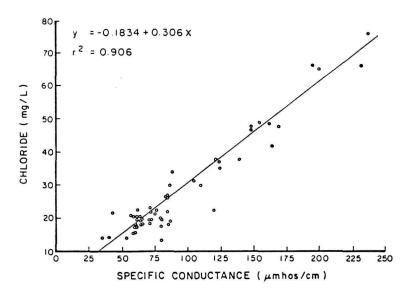
Median and range of pH levels for five sampling sites. Taken from Hughes et al., 1986.

This is a bar-and-whisker graph that displays some simple statistical parameters for sampling sites. It is effective for summarizing a large amount of information in an easily understandable format.



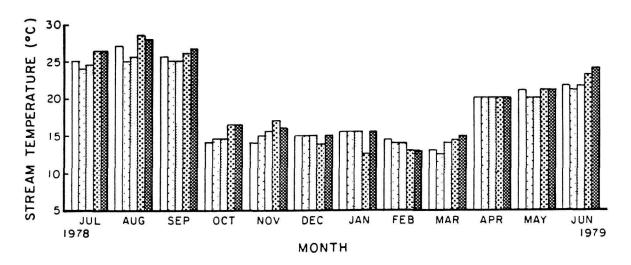
Storm hydrograph and bacterial indicator concentrations. Adapted from Kunkle, 1972.

A graph may show more than one variable on an axis. In this example, the Y-axis has two variables (discharge and total coliforms) to show a relationship over a period of time.



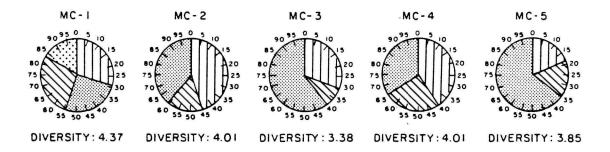
Relationship between chlorides and specific conductance values. Taken from Hughes et al., 1986.

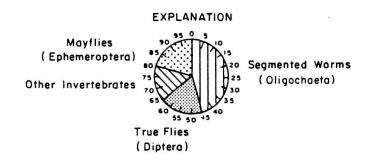
Regression lines are useful for illustrating the correlation between two variables. In this graph, the strong relationship between chloride and specific conductance is apparent.



Seasonal profile of stream temperatures (1978-1979) for five sampling sites. Taken from Hughes et al., 1986.

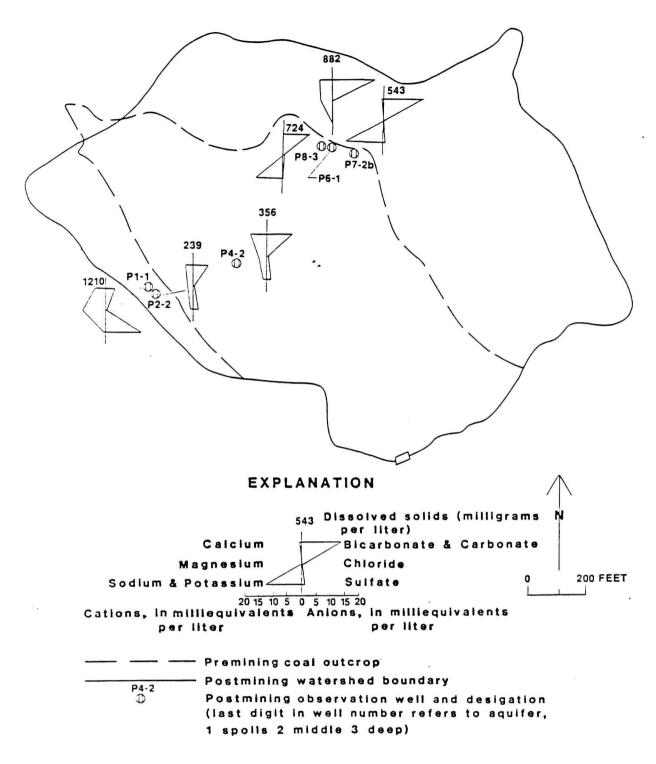
Bar graphs such as this one can be used in place of line graphs when numerous lines would be much more difficult to interpret than coded bars.





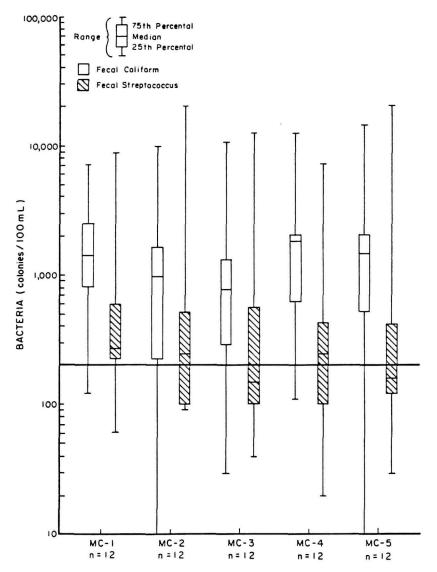
Annual percent distribution of aquatic macroinvertebrates for five sampling sites. Taken from Hughes et al., 1986.

Pie charts are useful for showing the abundance of a parameter or subtype relative to the total population measured.



Stiff diagram showing distribution of water types in post-reclamation spoils and middle aquifer. Taken from USDA Agricultural Research Service, 1983.

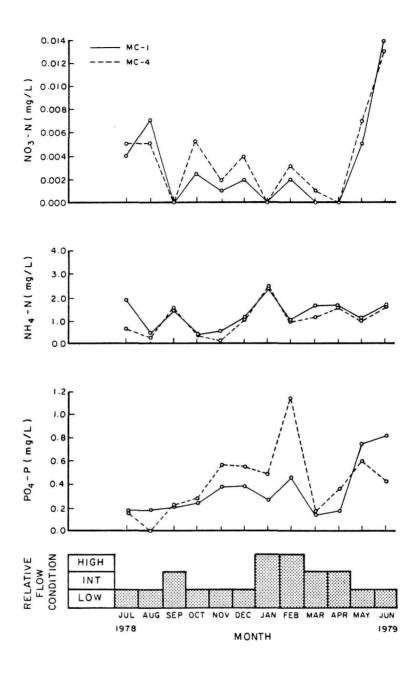
Stiff diagrams are a common means of illustrating anion and cation concentrations. This example indicates the differences in anions and cations around a mining area.



Note: The Y axis is expressed in a logarithmic scale

A profile of fecal coliform and fecal streptocococcal bacteria counts for five sampling sites. Taken from Hughes et al., 1986.

Logarithmic (log) scales are used for a variety of reasons. In this case, a standard scale would need to extend so far that the bulk of the data would be contained in a very small portion of the graph near the bottom. Log-log and semi-log graphs are also used to derive straight-line relationships if they would be nonlinear plotted together on a standard scale.



Seasonal relationship of discharge and NO3-N, NH4-N, and PO4-P for two selected sampling sites. Taken from Hughes et al., 1986.

This example combines a simple bar chart with line graphs to relate flow characteristics with nutrient concentrations. Again, much information is presented in a way that remains relatively simple to understand.

Table 2. Statistical information for total dissolved solids, specific conductance (at 25°C), and hardness for high- and low-flow periods in the Menard Creek Corridor Unit. Data taken from USGS (1965-1983) and TRA (n.d.).

Source and Flow Condition	n	Total Dissolved Solids (mg/L)	Specific Conductivity at 25°C (µmhos/cm)	Hardness (mg/L as CaCO ₃)
	Mean	132.0	243.4	33.6
USGS (1965-1983)	N	73	76	76
T C1	Std dev	104.4	213.4	24.8
Low flow	Range	34-579	49-1150	11-134
HCCC	Mean	83.4	165.3	26.1
USGS (1965-1983)	N	74	79	79
	Std dev	46.3	111.2	13.0
High flow	Range	37-275	50-557	11-72
	Mean	125.9	140.6	32.9
TRA (1975-1982)	N	31	31	26
Low flow	Std dev	41.3	60.6	40.2
LOW ILOW	Range	72-229	48-288	8-200
TDA	Mean	102.7	106.9	25.2
TRA (1975-1982)	N	27	30	28
	Std dev	21.9	36.5	18.4
High Flow	Range	25-131	30-172	1-86

If large amounts of information need to be presented at once, a table may be the best method. Too much information on a graph can appear cluttered and difficult to understand.

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APPENDIX J

PESTICIDES

by
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The purpose of a chemical pesticide is to prevent, retard, or destroy undesirable plant and animal life. Pesticides are classified chemically into several main groups that include both inorganic compounds (e.g., sulfur, copper, and arsenic) and organic compounds (e.g., organochlorines, organophosphates, and carbamates) as well as miscellaneous types (M. Richard, assistant professor, Colorado State University, 1987, personal communication). Classes of pesticides include fungicides, bactericides, miticides, acaricides, nematocides, insecticides, herbicides, and rodenticides. Most pesticides are synthetic organic compounds available in the form of sprays, granules, pellets, fumigants, and wettable powders.

The production and use of pesticides has increased almost 400-fold during the past forty years (Calvo and Raden, 1987). Some 50,000 pesticide products using 600 active ingredients are now registered with the U.S. Environmental Protection Agency (EPA) for use in the United States, with 200 pesticides in common use (Conservation Foundation, 1987; Holden, 1986). Furthermore, increased pesticide use is anticipated with the increasing demand worldwide for food and fiber (USDA, 1986).

The Impacts of Pesticides

Chemical pesticides pose a potential health hazard in waters contacting humans and wildlife; but as late as 1984, a complete health-hazard evaluation was possible for only 10% of all pesticides (Conservation Foundation, 1987). Furthermore, the "inert ingredients" in pesticides have recently gained attention as contaminants. In many cases these inert materials are considered "trade secrets," and neither they nor their effects are known by regulatory agencies (National Wildlife Federation, 1987). Specific health effects from pesticide exposure depend on properties of the chemical; the amount, duration, and route of exposure; and individual susceptibility (Calvo and Raden, 1987). In humans, long-term exposure to certain pesticides is known to cause liver, kidney, lung, heart, and thyroid damage; neurological damage; reproductive impairment; birth defects; and cancer (Conservation Foundation, 1987).

Sources of pesticides in surface waters may be from intentional or unintentional applications (McEwen and Stephenson, 1979; Richard, 1987). Intentional applications to control plant and animal life include those for algal blooms, fungus, weeds, insects, rodents, and fish. Unintentional applications include those from the following:

- atmospheric fallout: when dust and rain deposit pesticides that have entered the atmosphere by drift during application or by volatilization from treated soil, plant, and other surfaces;
- <u>soil erosion</u>: wherein 4 billion tons of sediment are deposited per year into water bodies in the U.S. (McEwen and Stephenson, 1979);
- <u>industrial effluent</u>: from pesticide industries and carpet and fabric manufacturing where pesticides are used for mothproofing;
- <u>disposal site leakage</u>: from municipal and industrial landfills and liquid waste lagoons;
- <u>sewage</u>: from both industry and private homes where pesticides might appear as fungicides and bactericides in soaps, cosmetics, and cleaners and from improper disposal of pesticides;
- <u>spills</u>: during manufacture, transport, storage, or application of pesticides.

Whatever the source, the amount and nature of the pesticide reaching surface waters within a park are functions of the pesticide properties, transport mechanisms from source to receiving waters, properties of the waters, and intensity and duration of pesticide application (Novotny and Chesters, 1981). These factors are discussed below.

Pesticide Properties and Transport Mechanisms

The solubility and persistence of a pesticide largely determine its mode of transport from source to receiving water and its final state in the receiving water, therefore greatly affecting environmental interactions. Pesticides that tend to be insoluble and persistent, such as the organochlorine insecticides, sorb (absorb or adsorb) to particles of soil, vegetative matter, or other solids. Because of these characteristics, the mode of transport for these pesticides is usually by wind and water erosion. Upon entering the receiving water the pesticide and its host particle become suspended sediment or bed material. Major inputs of organochlorine pesticides to surface waters usually correlate with major sediment influxes (Richard, 1987). Here in the sediment, degradation is slow and the integrity of the pesticide may remain unchanged for several years.

The more soluble and less persistent pesticides, such as the organophosphate insecticides and carbamates, are transported in solution via surface runoff from areas treated with pesticides, by percolation through soil containing pesticides, or by volatilization (vaporization) followed by atmospheric fallout. Once in the receiving water these pesticides begin to degrade by biological degradation, hydrolysis, and photolysis (Richard, 1987). The least persistent pesticides break down in days to weeks, the moderately persistent in weeks to months (USGS, 1985). Table J-1 lists the relative persistence of some pesticides in natural waters, and Table J-2 presents characteristics and uses of selected pesticides monitored by the U.S. Geological Survey (USGS) and the EPA.

Table J-1. Relative persistence of some pesticides in natural waters. Source: McEwen and Stephenson, 1979. The Use and Significance of Pesticides in the Environment. Copyright © 1979 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.

Non	Slightly	Moderately	Persistent ^d
Persistent ^a	Persistent	Persistent	
azinphosmethyl	aldrin	aldicarb	benomyl
captan	amitrole	atrazine	dieldrin
carbaryl chlorpyrifos demeton dichlorvos	CDAA CDEC chloramben	ametryne bromacil carbofuran carboxin	endrin hexachlorobenzene heptachlor isodrin
dicritoryos	chlorpropham	carboxin	monocrotophos
dicrotophos	CIPC	chlordane	
diquat	dalapon	chlorfenvinphos	
DNOC	diazinon	chloroxuron	
endosulfan	dicamba	dichlorbenil	
endothal	disulfoton	dimethoate	
fenitrothion	DNBP	diphenamid	
IPC	EPTC	diuron	
malathion	fenuron	ethion	
methiocarb	MCPA	fensulfothion	
methoprene	methoxychlor	fonofos	
methyl parathion	monuron	lindane	
mevinphos	phorate	linuron	
parathion	propham	prometone	
naled	Swep	propazine	
phosphamidon	TCA	quintozene	
propoxur pyrethrum rotenone	thionazin vernolate	simazine TBA terbacil	
temephos TFM 2,4-D		toxaphene trifluralin	

Half-life less than 2 weeks.

Half-life 2 weeks to 6 weeks.

Half-life 6 weeks to 6 months.

Half-life more than 6 months.

Table J-2. Selected characteristics and uses of pesticides monitored by the U.S. Geological Survey-U.S. Environmental Protection Agency Pesticide Monitoring Network, 1975 to 1980. Source: USGS, 1985; based on data from multiple sources. $[\mu g/L]$, microgram per liter; nd, no available data]

			Chara	cteristics		
Chemical	Detection limit ¹ (µg/L)		quality eria ² / <u>L)</u> Aquatic life	Solubility (µg/L)	Relative persistence within pesticide group ³	Principal uses and sources
		Or	rganochlo	rine insecti	cides	
Aldrin Dieldrin	0.01 0.03	0.0007	0.002 0.002	13 22	Low Medium	Corn Termite control, degradation product of aldrin.
Chlordane	0.15	0.005	0.004	56	High	Corn, termites, general purpose.
DDD	0.05	0.0002	0.001	5	High	Fruits and vege- tables, degra- dation product of DDT.
DDE	0.03	0.0002	0.001	10	High	Degradation pro- duct of DDT and DDD.
DDT	0.05	0.0002	0.001	17	High	Cotton, fruits, vegetables, general purpose.
Endrin	0.05	1	0.002	14	nd	Cotton, wheat.
Heptachlor epoxide	0.01	0.003	0.004	30	Low	Degradation pro- duct of hepta- chlor which is used on corn, and termite control.
Lindane	0.01	4	0.08	150	Medium	Livestock, seed treatment, general purpose.
Methoxychlor	0.10	100	0.03	3	nd	Livestock, alfalfa, gen- eral purpose.
Toxaphene	0.25	0.007	0.013	400	nd	Cotton, live- stock.

Table J-2. Continued.

		Characteristics					
Chemical	Detection limit ¹ (µg/L)	crit	quality eria ² /L) Aquatic life	Solubility (µg/L)	Relative persistence within pesticide group ³	Principal uses and sources	
		C	rganophos	phate insect	icides		
Diazinon	0.10	nd	nd	40,000	High	Corn, general purpose.	
Ethion	0.25	nd	nd	2,000	nd	Citrus fruits.	
Malathion Methyl	0.25	nd	0.1	145,000	Low	General purpose.	
parathion Methyl	0.25	nd	nd	57,000	Low	Cotton and wheat	
trithion	0.50	nd	nd	nd	nd	Not identified.	
Parathion	0.25	nd	0.04	24,000	Low	Wheat, corn, sorghum.	
Trithion	0.50	nd	nd	340	nd	General purpose.	
		Chlore	phenoxy a	and triazine	herbicides		
Atrazine	0.5	nd	nd	33,000	High	Corn.	
2,4-D	0.5	100	nd	900,000	Low	Wheat, rangeland general purpose.	
2,4,5-T	0.5	10	nd	240,000	Medium	Rice, rangeland, general purpose.	
Silvex	0.5	nd	nd	140,000	nd	Sugarcane, rice rangeland.	

 $^{^{1}}$ Detection limits shown are for water samples. Bed-sediment reporting limits are 10 times greater and are expressed in units micrograms per kilogram.

²U.S. Environmental Protection Agency Criteria. The human-health criteria for all pesticides except endrin, lindane, methoxychlor, 2,4-D, and 2,4,5-T represent the estimated average concentrations associated with an incremental increase in cancer risk of 10⁻⁵ (one additional cancer per 100,000 people over a lifetime of exposure). The aquatic-life criteria are for freshwater and are 24-hour average concentrations. ³Estimated relative persistence within each pesticide group.

Water Properties and Pesticide Application

Few specific studies have been done on water composition as it affects pesticides. However, it is known that higher temperatures generally increase the volatility, solubility, and degradation of a pesticide, whereas the effects of pH are variable (Richard, 1987). Organochlorine pesticides are largely unaffected by pH, whereas organophosphates and carbamates readily hydrolyze (degrade) at alkaline pH values. The most important mechanism for pesticide degradation are aquatic microorganisms (McEwen and Stephenson, 1979).

The intensity and duration of application, as well as the form of the pesticide, determine the amount and nature of the pesticide reaching surface waters. A concentrated, long-term application is more likely to contaminate surface waters than a dilute, brief application. Also, powders applied to foilage can easily drift into surface waters during application, whereas solutions injected into the soil would instead percolate into the ground water.

Bioconcentration and Biomagnification

Two concerns relating to the interaction between pesticides and the environment -- particularly for the insoluble, persistent pesticides -- are bioconcentration and biomagnification (Novotny and Chesters, 1981). Bioconcentration (or bioaccumulation) refers to the uptake and accumulation of contaminants by individual plants and animals. Exposure of this nature involves an organism's accumulation of pesticides over its lifetime. An organism exposed to a pesticide for a long period of time may take up enough of the pesticide to become debilitated or die. Table J-3 provides acute toxicity data with selected herbicides and wildlife.

Biomagnification, on the other hand, is a long-term, gradual intensification of toxin occurring through the food chain. Therefore, higher trophic-level organisms, such as game fish, may have higher concentrations of pesticides, while lower trophic organisms (such as algae) and water exhibit lower or undetectable concentrations. In some national parks game fish are of particular concern and pose a health hazard if consumed. Biomagnification can occur in the vicinity of a sediment deposit in which pesticides are available from the deposited particulate matter.

Monitoring

Monitoring for pesticides is a difficult task due to the large number of pesticides in use and the fact that testing for pesticides tends to be expensive, time-consuming, limited to certain pesticide classes, and/or lacking in sensitivity (Holden, 1986). Therefore, an understanding of pesticide application that may potentially reach a park's waters is essential for monitoring planning. For example, a large-scale vegetable farm whose tailwater is received by a park stream may apply pesticides prior to planting and intermittently throughout the growing season. With this knowledge, a monitoring program can be

Table J-3. Acute toxicity data for wildlife 1 . Source: USDA Forest Service, 1986.

Herbicide	Mallard LD 50 mg/kg	Quail LD 50 mg/kg	Bluegill LC 50 ppm	Rainbow Trout LC 50 ppm	Daphnia LC 50 ppm
Asulam	>4000	>2600	>3000	>5000	
Atrazine	>2000	>5000	26	12.6	3.6
Cacodylic	>2000	>2000 (P) ²	80-750 ³	96	>100
Dalapon	5600	>5000	105	>87	11.0
Dicamba	2000	673 (P) ²	>50	28	>100 (S) ²
Fosamine	>5000	>5000	670	>1000	1524 (48 hr)
Glyphosate	>4640 (ppm)	>4640 (ppm)	5.6	>1000	3.0
Hexazinone	>10,000 (ppm)	2258	505	322	>1000 (ppm)
MSMA	>5000 (ppm)	>5000 (ppm)	49.2	96	>100 (S) ²
Picloram	>2000	>5000	23.0	4.0-12.5	34.4
Simazine	>51,000 (ppm)	>5000	100	25	1.1
Triclopyr	1698	2935	148	117-140	133
2,4-D	>1000	>5000	0.5-7.5	1.0-3.1	1.2-6.4

 $^{^{1}\}text{All LC 50}$ values are for 96 hour tests, unless otherwise noted.

 $^{^{2}}P$ = pheasant or partridge

S = scud (a fresh water crustacean)

³A range is given when more than one formulation was tested.

developed in which sampling is conducted after heavy rains following pesticide application to determine peak concentrations in park waters.

Pesticide monitoring in surface waters should not be limited to the water. As discussed earlier, insoluble pesticides sorb to particulate matter and can be deposited with sediment, thereby becoming available for biomagnification. Sediment samples can be tested by a contract laboratory for roughly the same cost as a water sample (prices vary with each laboratory and the number and kind of analyses) (M. Aaronson, Assistant Professor, Colorado State University, 1987, personal communication).

Unfortunately, there are no simple indicators for pesticide contamination other than the obvious: fish kills, lack of algae growth, etc. Therefore, it is vital to investigate pesticide practices affecting park waters in order to predict the needed analyses prior to contacting a laboratory. It is also important to keep in mind the great variety and quantity of pesticides that may be used. This is a result of newly introduced pesticides, seasonality of pesticide use, and changing farm practices. Hence, information gathered from tributary areas regarding pesticide usage may become quickly outdated and may no longer be pertinent.

Because of the specialized nature of the analytical techniques used to test for pesticides, a contract laboratory will need to conduct the analyses. In addition to private and university laboratories, a number of government agencies (EPA, USGS, U.S. Fish and Wildlife Service) operate laboratories that conduct water quality testing for pesticides. Under direction from the selected laboratory, samples can be collected by park personnel to lower analytical costs. However, it is essential that samples submitted for pesticide analysis are properly identified for the pesticides suspected since different analytical procedures are used for each class of pesticide.

Finally, remedial action is much more costly than preventative measures. Any actions to either prevent unintentional applications or better inform pesticide users of the proper application procedures and potential dangers of pesticides should be the first steps in controlling pesticide contamination.

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APPENDIX K

PREDICTING PARAMETER CONCENTRATION IN RECEIVING WATER FROM A POINT-SOURCE DISCHARGE

The concentration of many types of so-called "conservative" chemical pollutants in streams is largely a function of dilution. ("Conservative" means the substance is not likely to react, combine, vaporize, or otherwise change.) Downstream pollution concentrations therefore can be estimated with a mixing equation. For example, if a tailings pond is expected to release 250 mg/L of iron in two liters per second of discharge into a stream (Fig. K-1), what will be the resulting concentration of iron in the stream when stream discharge is 150 liters per second? The stream's natural iron level is 0.5 mg/L of iron. The following mixing equation can be used to make the estimation:

$$QdCd = QtCt + QuCu$$

where Qd = stream discharge downstream (150 L/sec)

Qt = tailings pond discharge (2 L/sec)

Qu = stream discharge upstream (Qd-Qt)

Cd = concentration downstream, unknown

Ct = concentration of the tailings effluent (250 mg/L)

Cu = concentration upstream (0.5 mg/L)

Dividing by Qd:

$$Cd = \frac{QtCt + QuCu}{Qd}$$

Substituting known values:

$$Cd = \frac{[(2)(250) + (148)(0.5)]}{150},$$

$$Cd = 3.8 \text{ mg/L}$$

the iron concentration expected to appear in the stream during a $150\ \text{L/sec}$ stream discharge.

The above calculation is but one example of the way in which predictions can be made by employing a mathematical model. A more sophisticated model was used by Poe and Betson (1983) to predict, using only a few "critical decision constituents" (TSS, pH, TDS, dissolved manganese and iron, conductivity, and discharge), concentrations of eleven related parameters in response to acid mine drainage impacts. DeCoursey (1985) provides a review of a number of mathematical models pertaining to water resources and includes 42 references.

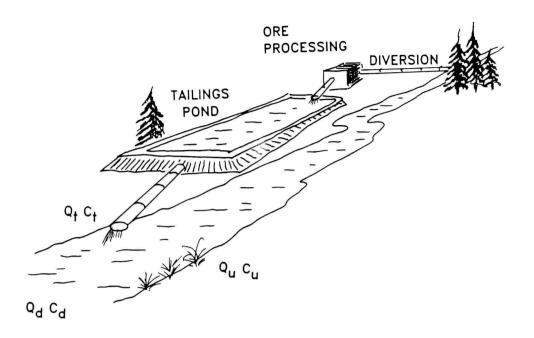


Fig. K-1. A tailings pond discharging into a stream with related variables to predict parameter concentration.

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APPENDIX L

PARAMETER DESCRIPTIONS

Excerpted from: Hach Co. 1985. Water analysis handbook. Loveland, CO. Reproduced with permission.

ACIDITY

a quantitative expression of a water's capacity to neutralize a strong base to a designated pH. The amount of acidity indicates the water's degree of corrosiveness.

ALKALINITY

refers to the capability of water to neutralize acids. The presence of carbonates, bicarbonates and hydroxides is the most common cause of alkalinity in natural waters.

ALUMINUM

the earth's most abundant metal, is present in natural waters from contact with rocks, soil and clay.

ARSENIC

may be found in water as a result of dissolution of minerals, contamination by industrial discharges or runoff from the application of insecticides. Arsenic poses a health hazard because of its high toxicity and the chronic effects of repeated ingestion.

BACTERIA

many of the microorganisms that cause serious disease, such as typhoid fever and dysentery, can be traced directly to polluted water. These disease-producing organisms are discharged along with fecal wastes and are difficult to detect in water supplies. Fortunately, less harmful, easily isolated bacteria called indicator organisms travel with the disease-producing microbes. [Total coliforms and fecal coliforms are two groups of bacteria commonly used as] a warning signal that more dangerous bacteria may be present.

BIOLOGICAL OXYGEN DEMAND an empirical measurement of the oxygen requirements of wastewaters and sewage. The test results are used to calculate the effect of waste discharges on the oxygen resources of the receiving waters.

CALCIUM

the fifth most common element, is found in most natural waters at levels ranging from zero to several hundred milligrams per liter. Calcium contributes to the hardness properties of water.

CHEMICAL OXYGEN DEMAND used widely to estimate the amount of organic matter in wastewater. When wastewater contains only readily available organic bacterial food and no toxic matter, the COD test results provide a good estimate of BOD (Biochemical Oxygen Demand) values.

CHLORIDE

present in all potable water supplies and in sewage, usually as a metallic salt. Chloride is essential in the diet and passes through the digestive system unchanged to become one of the major components of raw sewage.

CHLORINE

added to public drinking water supplies, sewage treatment plant effluents and swimming pools to destroy harmful bacteria. Chlorine can be present in water as free available chlorine and as combined available chlorine.

COLOR

in natural waters results from metallic salts, organic matter and other dissolved or suspended materials present. Specific colors are dependent on the pH of the water.

CONDUCTIVITY

as it applies to water analysis, is a measurement of water's capacity for conveying electrical current and is directly related to the concentrations of ionized substances in the water. Conductivity measurements are commonly used to determine the purity of demineralized water and as an empirical estimate of total dissolved solids.

COPPER

may occur in natural waters, wastewaters and industrial effluents as soluble copper salts or as precipitated copper compounds on suspended solids. More than 1 mg/L copper can impart a bitter taste to the water.

DISCHARGE

the volume of water passing a stream transect in a unit of time. Units can be cubic feet per second, cubic meters per second, or liters per second.

DISSOLVED OXYGEN

the effect of oxidation wastes on streams, the suitability of water for fish and other organisms, and the progress of self-purification can all be measured or estimated from the dissolved oxygen content.

HARDNESS

defined as a characteristic of water which represents the total concentration of polyvalent metal ions. Calcium and magnesium ions are the principal causes although iron, aluminum, manganese, strontium, zinc, and hydrogen ions are capable of producing the same effect.

TRON

natural waters contain variable but minor amounts of iron despite its universal distribution and abundance. Iron in ground waters normally is present in the ferrous (Fe⁺⁺) or soluble state which is easily oxidized to ferric (Fe⁺⁺) or insoluble iron on exposure to air. Iron can enter a water system by leaching natural deposits from acidic mine drainage.

LEAD

seldom found in ground waters in more than trace quantities and averages about 10 ug/L. Lead in water

normally indicates the intrusion of industrial, mine, or smelter wastes.

MAGNESIUM

an alkaline-earth metal that is an abundant element and a common constituent of natural waters. It is one of the two major components that constitute total hardness, the other being calcium.

MANGANESE

surface water may contain combinations of manganese in various oxidation states as soluble complexes or as suspended particles.

MERCURY

not commonly found in natural waters. It can enter the water system through agricultural pesticide, herbicide and fungicide residues.

NITROGEN (NITRATE)

represents the most completely oxidized state of nitrogen commonly found in water. High levels of nitrate in water indicate biological wastes in the final stages of stabilization or run-off from heavily fertilized fields. Nitrate-rich effluents discharged into receiving waters can degrade water quality by encouraging excessive growth of algae.

NITROGEN (TOTAL KJELDAHL)

the term "Total Kjeldahl Nitrogen" refers to the combination of ammonia and organic nitrogen.

OIL AND GREASE

oil may be present in natural waters from the decomposition of plankton and/or higher forms of aquatic life. Oil or grease in water generally indicates pollution from petroleum wastes.

pН

defined as the logarithm of the reciprocal of the hydrogen ion activity expressed in moles per liter. More simply, the pH value of a water sample expresses its tendency to accept or donate hydrogen ions on a scale of 0 (very acidic) to 14 (very basic).

PHENOLS

produced as waste in oil refineries, coke plants and some chemical manufacturing plants.

PHOSPHORUS

occurs in natural waters and in wastewaters almost solely as phosphates. Phosphates are used widely in municipal and private water treatment systems and are commonly grouped into three types: orthophosphate, condensed (pyro, meta or other poly) phosphate, and organically bound phosphate.

POTASSIUM

ranks seventh among the elements in order of abundance. Brines may contain more than 100 mg/L potassium.

SETTLEABLE SOLIDS

settleable solids is applied to the inorganic and organic particulate matter in water suspension and will

settle, under quiescent conditions, due to the influence of gravity.

SODIUM

the sixth most common element, is present in nearly all natural waters. Brines, hard water and water softened with sodium-form resin exchange units have high sodium concentrations.

SULFATE

appears in natural waters in a wide range of concentrations. Mine waters and industrial effluents frequently contain large amounts of sulfate from pyrite oxidation and the use of sulfuric acid.

SURFACTANTS

these are surface-active agents that act to lower the surface tension of liquids and permit increased wetting.

TEMPERATURE

the temperature of a water is primarily a result of the climatic regime, however, some land-use activities can modify water temperature.

TOTAL
DISSOLVED
SOLIDS

total dissolved solids is a measure of dissolved substances in a water. Conductance is often used as an empirically derived estimate of TDS.

TOTAL SUSPENDED SOLIDS total suspended solids is a measure of the suspended solids in a water. Suspended solids are those constituents of an unacidified water sample that are retained by a 0.45-micron membrane filter.

TURBIDITY

occurs in most surface waters as the result of suspended clay, silt, finely divided organic and inorganic matter, plankton and other microorganisms.

ZINC

commonly found in many natural waters. Industrial effluents may contribute large amounts of zinc, and gh concentrations suggest the presence of lead and cadmium.