

# A Simple Stream Monitoring Technique Based on Measurements of Semiconservative Properties of Water

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**ABSTRACT** / Correlative relationships exist among conductivity, alkalinity, and hardness in streams due to natural geological and climatological controls, but the relationships among these three water-quality factors can be altered strongly by inputs of ion-rich wastewaters. The degree of alteration can be monitored conveniently by use of a simple chemical perturbation index, computed by subtracting the

sum of rank pairwise correlations among the conductivity, alkalinity, and hardness (for observations on each of these variables, measured through time) from 3.0. The chemical perturbation index can be used to document or characterize spatiotemporal changes in stream water quality. This study explains the development of the index's concept and provides examples of its application in an extensive stream monitoring program used to assess ecological conditions in streams on the Department of Energy's Oak Ridge Reservation in east Tennessee, USA. The chemical perturbation index technique may be particularly useful in community-based stream monitoring programs because to its simplicity and low cost.

Many urban residents view surface water quality issues as important, but relatively few communities have the financial resources or extensive technical expertise to devote to stream monitoring. Within this context, the need for simple, place-based techniques that can help integrate science into community-based decision making, notably in relation to watershed management, has become increasingly evident (Rhoads and others 1999). A recent study demonstrates that one means to encourage this outcome is to emphasize broad-based decision making that incorporates education and collaborative planning rather than specific management actions and regulations that attack specific problems (Stein and others 1999). However, many of the technical tools currently available for obtaining information needed for community involvement and decision-making are not ideal for this purpose: methods originating from the domain of science are often crafted for application to specific problems by technical experts, such that the measurement and monitoring methods tend to be too specific, complex, and expensive.

For community-based stream monitoring programs, the use of costly or complex sampling and analysis methods is especially detrimental, for such methods encourage less-frequent sampling. In the context of a stream monitoring program, sampling frequency is important both for technical and societal reasons. Tech-

nically, conditions at a site within a stream can vary quickly in response to precipitation events. An inadvertent release of a toxic chemical or wastewater to a receiving stream can move through a site, cause significant ecological damage en route, and disappear downstream, all within a matter of hours. A sampling frequency that is low relative to the frequency of ecologically or toxicologically important events makes it difficult to reliably characterize stream ecological conditions within a meaningful cause-and-effect context (Stewart and others 1996). From a societal perspective, broad-based community interest in the condition of a flowing freshwater resource may be more sustainable if data are obtained and reported frequently, particularly if sampling, data analysis, and reporting efforts can be done using community resources (e.g., civic volunteer programs, high school students, etc.). Simple and reliable methods, routinely applied, are needed to achieve the fundamental objective of effective community involvement in efforts to help protect community freshwater resources.

Precipitation events result in streams in urban areas receiving inputs of various materials due to the influx of runoff from roads, construction sites, agricultural areas, lawns, and buildings. Many urban-area streams also are used, to a greater or lesser extent, as receiving systems for regulated point-source inputs of wastewaters. While some of the chemicals that enter urban streams from these sources may damage a receiving stream ecologically, even at low concentrations, many

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of the soluble chemicals that enter surface waters in the United States are relatively benign toxicologically, but quite abundant. Some nine billion pounds of sodium sulfate (a low-toxicity salt) enter US surface waters annually, from treated wastewaters, as does some nine million metric tons of rock salt, used to deice US roads during the winter (Stewart 1991).

The main premise of this paper is that communities might find it easier to implement and sustain stream water-quality monitoring activities, perhaps in association with school science programs or civic volunteer programs, if simple, low-cost, and technically sound procedures for tracking water-quality conditions in receiving streams become more widely available. In this paper, I describe a water-quality monitoring technique, referred to hereafter as the chemical perturbation index (CPI), that is particularly well-suited for stream monitoring programs in urban areas. The CPI method described here was developed and tested as part of an extensive stream-monitoring program that began more than a decade ago (Stewart and Loar 1994).

The CPI method involves simple inspection of the correlative relationships among conductivity, alkalinity, and hardness—water-quality factors that can be measured reliably and easily with minimal technical expertise. In this paper, I outline the conceptual basis for the CPI; explain how the CPI is calculated; and give examples to show how the CPI method can be used to monitor stream water-quality conditions through time. A simple graphing method for detecting stream water-quality changes based on the three parameters that are used in the CPI is also described.

### Conceptual Basis for Chemical Perturbation Index

The CPI requires time-matched data for conductivity, alkalinity, and hardness. Each of these three properties is conservative or semiconservative, that is, the three factors typically are not influenced strongly by biota. Conductivity, alkalinity, and hardness levels instead are governed predominantly by geology of a stream's catchment, weathering, precipitation events, etc. I outline the concept for how conductivity, alkalinity, and hardness can be used to monitor water-quality status and water-quality changes after briefly defining each of the three parameters below.

#### Specific Conductivity

All natural waters contain at least trace quantities of dissolved ions, chief among which are sodium, potassium, calcium, magnesium, carbonate, bicarbonate, sul-

fate, and nitrate. The ability of a water sample to conduct an electric current depends upon the types and concentrations of the ions in solution. Thus, measurement of a water's conductivity (or specific conductance) at standard temperature (25°C) provides (non-specific) information about the water's total ion content. Biologically productive freshwaters typically have conductivity values between 100–500  $\mu\text{S}/\text{cm}$ . Very low levels of conductivity (e.g.,  $<100 \mu\text{S}/\text{cm}$ ) suggest oligotrophic (nutrient-poor) conditions, and levels of conductivity that approach or exceed about 1000  $\mu\text{S}/\text{cm}$  can indicate saline situations that are less than ideal for most species of freshwater organisms. Conductivity can be easily, reliably, and rapidly measured by use of a simple field-portable meter-and-probe device. Such instruments are robust and easily standardized; measurement error for conductivity is typically less than 1% of the measured value.

#### Alkalinity

Simply expressed, alkalinity is a measurement of a water sample's capacity to neutralize a strong acid. Alkalinity can be determined by titrating a known volume of water with a standard solution of a strong acid to a specified pH (typically, to pH 4.4 or 4.5). Usually, either 0.01 normal hydrochloric acid or 0.02 normal sulfuric acid is used for this purpose. For most waters, a fixed-pH end point (for example, 4.50) for the titration can be used, with the end point being determined with a pH-sensitive dye (e.g., a mixed bromcresol green-methyl red indicator), or a pH meter and an appropriate probe (Wetzel and Likens 1991). If alkalinity levels are less than about 20 mg/liter as  $\text{CaCO}_3$ , Gran titration techniques may be more appropriate (Wetzel and Likens 1991). By convention, alkalinity can be expressed as the concentration of calcium carbonate (in milligrams per liter) that would be needed to account for the amount of acid consumed in the titration, even though materials other than calcium carbonate contribute to the water's acid-neutralizing capacity (Hutchinson 1975, Wetzel and Likens 1991). Alkalinity can be very low in some natural streams (near or less than zero, for example, in Smoky Mountain streams that are influenced by pyritic geology). In streams that flow through limestone-rich catchments, alkalinity values can be 200–300 mg/liter (Stewart 1988, Neel 1985). For alkalinity, measurement error can be  $<2.5\%$  of the measured value if the titration is performed carefully.

#### Hardness

Hardness is a measure relating best to the concentration of divalent cations (chiefly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) in

the water. Usually, contributions to hardness due to the presence of metals such as iron are very minor. Total hardness can be determined by use of a simple titration method (APHA 1989). Eriochrome black T, a dye that appears reddish in color in the presence of calcium and magnesium ions at a pH of  $10.0 \pm 0.1$ , is added to a pH-adjusted, freshly collected 50- or 100-ml water sample. The sample is then titrated immediately with a standard solution of ethylene diamine tetraacetic acid (EDTA). The EDTA is a metal-binding chemical that out-competes the dye for the calcium and magnesium ions. When an amount of EDTA just sufficient to bind all of the calcium and magnesium has been added, the dye changes color, from wine red to blue (APHA 1989). The titrant volume, the titrant normality, and the volume of water sample are then used to calculate hardness. Total hardness, like alkalinity, is commonly expressed as the concentration of calcium carbonate (in milligrams per liter) that would be needed to account for the measured level of hardness, even though constituents other than calcium can titrate as hardness. Many stream water samples analyzed for hardness in the Oak Ridge National Laboratory's Toxicology Laboratory, as part of our internal quality assurance-quality control activities, had hardness values ranging from 20 to 200 mg/liter. These measurements can be made to within 5% of the true value with minimal practice. The environmental significance of hardness is that it provides aquatic animals with some protective benefits from the deleterious effects of toxic metals such as copper, lead, cadmium, and zinc (Rand and Petrocelli 1985).

#### Development of the CPI Concept

The three water-quality factors described above are related but not identical. For example, if calcium sulfate rather than calcium carbonate is a significant component of the ionic load in a stream, then hardness and conductivity might be high, although alkalinity could be low. Conversely, alkalinity can be high and hardness can be low if a stream receives inputs of acid-neutralizing compounds such as sodium carbonate or sodium bicarbonate. In natural stream systems that do not receive inputs of ion-rich wastewaters, conductivity, alkalinity, and hardness are affected somewhat differently from one another by rainfall events that are large enough to affect streamflow. And due to natural phenomena such as rainfall events and periods of drought, each of the three factors varies through time (Mulholland and others 1990, Hill 1993, Newbold and others 1995). Nevertheless, the levels of the three factors in natural streams tend to vary in concert through time, implying control of the three parameters by un-

derlying geological conditions and natural biogeochemical processes. The CPI method makes use of this fundamental tendency for natural covariance among the three parameters.

It is also important to note that most wastewaters contain common ions (including sodium, calcium, chloride, and sulfate) that can alter the natural associations among conductivity, alkalinity, and hardness. Additionally, runoff from developed areas or effluents that enter streams usually are ion-rich compared to water in the receiving system (Johnson and others 1997, Stewart 1996). Thus, changes in the strength of the associations among conductivity, alkalinity, and hardness, for stream water samples analyzed through time, can provide information about stream water-quality conditions. For example, if stream sites located upstream and downstream of an effluent source are monitored routinely for the three parameters, one may quantify the degree of chemical perturbation caused by the wastewater inputs. As shown below, it is also possible to discern in-stream changes in water chemistry patterns by use of the CPI, both spatially and through time.

#### Computation of CPI

In its simplest form, a CPI can be computed as the sum of the three pairwise Spearman (rank) correlation coefficients among conductivity, alkalinity, and hardness, for observations over time. The sum of these three correlation values is subtracted from 3.0, so as to express greatest impact with a larger value, and lesser impact with a smaller value. A reasonably large number of time-matched observations of each parameter (e.g.,  $\geq 25$ ) should be used for the computation of the correlation coefficients. In most cases, the three parameters tend to vary together, so each of the three correlation coefficients is positive and large in nonperturbed streams (i.e.,  $>0.7$ , with an upper bound of 1.0). Thus, the sum of the three coefficients can approach 3.0 in a nonperturbed system. If perturbation is severe due to large inputs of wastewaters that are chemically distinctive in terms of conductivity, alkalinity, or hardness, one or more of the pairwise correlations can be negative. In such instances, the sum of the three coefficients could in theory approach  $-3.0$ . If one or more negative correlations occur, they increase the CPI, because the CPI is computed by subtracting the sum of the correlations from 3.0. Two examples of the computation are given below to show how the technique accommodates positive or negative correlation values.

*Example 1.* Assume that the correlations between alkalinity and hardness, alkalinity and conductivity, and hardness and conductivity are  $-0.18$ ,  $-0.83$ , and

-0.67, respectively. The sum of these three values is -1.78. The CPI in this instance is 3.0 minus (-1.68), or 4.68, indicating a strongly perturbed system.

*Example 2.* Assume that the correlations between alkalinity and hardness, alkalinity and conductivity, and hardness and conductivity are 0.72, 0.84 and 0.79, respectively. The sum of these three correlations is 2.35. The CPI in this instance is 3.0 minus (2.35), or 0.65—a low value, indicative of near-natural conditions.

In practice, the correlation between conductivity and hardness or between conductivity and alkalinity is almost always positive for streams that are not dominated by effluents, because bicarbonate-rich waters (which constitute the majority of natural waters in the United States) have an innate tendency to assume a positive near-unity relationship between alkalinity and hardness (Cole 1994, Stewart 1988). Accordingly, for nonperturbed waters, the correlation for any pair of the three parameters is rarely lower than about 0.4 or 0.5, and more often approaches 0.8 or 0.9, for  $N \approx 25$ . Correlation analysis techniques are included with virtually all commercially available statistical software packages for use on personal computers.

## Streams, Sampling Sites, and Methods

The CPI method was formulated and tested as one aspect of stream biological monitoring programs for Department of Energy facilities near Oak Ridge, Tennessee, USA. These monitoring programs included studies on stream ecological condition, with attention being given specifically to stream water chemistry in relation to ambient toxicity, periphyton, benthic macroinvertebrate communities, fish health, and fish community structure. Over a 13-year period, the studies collectively involved more than 55 sites on 16 streams (Figure 1) and have resulted in more than 80 open-literature publications (Adams and others 1992, Ham and others 1997, Teh and others 1997, Hill and others 1995, Kszos and others 1997, Napolitano and others 1994, Smith and Beauchamp 1999, Southworth and others 1994).

Data used in the CPI examples given below are from five of these streams (East Fork Poplar Creek, Melton Branch, White Oak Creek, First Creek, and Fifth Creek; Figure 1). Historical hydrologic data are available from United States Geological Services (USGS) weirs on East Fork Poplar Creek (site ID 03538250), Melton Branch (site ID 03537100), White Oak Creek (site IDs 03536320, 03536380, and 03536550), and First Creek (site ID 03536450), on the World-Wide Web (<http://waterdata.usgs.gov>). Grab samples of water were collected from the indicated streams and sites daily, for

seven consecutive days, between 09:00 and 11:00 h. The seven-day sampling campaigns occurred on a once-per-month basis or a once-per-quarter basis, in accordance with the Biological Monitoring and Abatement Program sampling plans for the Oak Ridge National Laboratory and the Oak Ridge Y-12 Plant. The water samples were taken to the ORNL Toxicology Laboratory, where they were analyzed for (among other things) conductivity, alkalinity, and hardness. Details of the types of chemical data obtained from the stream sampling programs are given in several other publications (e.g., Stewart and others 1990, 1996).

## Examples of CPI

### White Oak Creek, First Creek, and Fifth Creek

For 80 to 84 samples collected during a one-year period (March 1986 through March 1987; the number of sampling events varied slightly among these three streams), individual pair-wise Spearman (rank) correlations between conductivity, alkalinity, and hardness for reference sites in upper White Oak Creek, First Creek, and Fifth Creek (upstream of Oak Ridge National Laboratory operations; see Figure 1) were strong, ranging from 0.85 to 0.95. For this observation period, the sums of the three pairwise correlations for these three sites was 2.65 for upper Fifth Creek, 2.79 for upper First Creek, and 2.86 for upper White Oak Creek. Thus, the CPI for each of the three reference sites was low (0.35 for Fifth Creek, 0.21 for First Creek, and 0.14 for White Oak Creek). In each of these streams, the CPI increased with distance downstream, as the streams received wastewaters from ORNL operations. For First Creek, Fifth Creek, and for a mid-reach segment for White Oak Creek, the rates of CPI increase were 14.6%/km, 39.4%/km, and 59.9%/km, respectively (Stewart 1990), compared to CPI values at the corresponding upstream reference site. The increases in CPI with distance downstream resulted from stream-specific inputs of treated wastewaters (a sewage treatment plant, a nonradiological waste-treatment plant, and a coal-yard runoff treatment facility, in White Oak Creek, for example) (Ashwood 1994, Stewart and others 1990).

To show how spatial and temporal changes in stream water quality can be depicted by CPI, I plotted CPI versus distance downstream for six sites in White Oak Creek for two time-periods (1986–1989, and 1991–1992) (Figure 2). The values of correlation coefficients are sensitive to the number of observations used in their computation, and CPI values could potentially be influenced by time of year due to





**Figure 1.** Biological Monitoring and Abatement Program sampling sites on streams on the Oak Ridge Reservation in east Tennessee. Triangles are reference sites (upstream of effluent release points), circles are sites downstream of the influence of operations at Department of Energy facilities. Open symbols (triangles or circles) designate sites yielding

data used to compute chemical perturbation index (CPI) values in the present study; closed symbols are sites providing data not included in the present study. In the insert, PWTP, CYRTF, and STP indicate effluent entry points into White Oak Creek from a process waste treatment plant, a coal yard runoff treatment facility, and a sewage treatment plant, respectively.

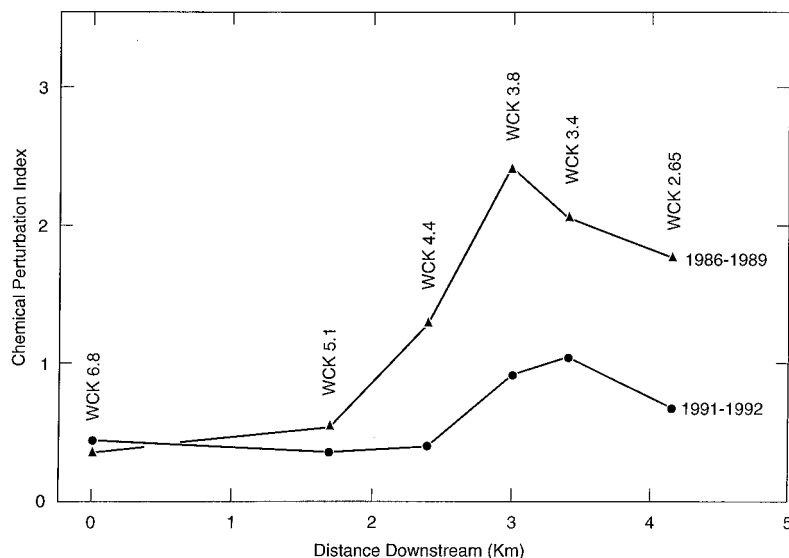
seasonal changes in hydraulic regime, so I controlled for these two factors by using seasonally matched data in the two assessment periods (1993).

Figure 2 shows that major changes have occurred in water-quality conditions in White Oak Creek between WCK 5.1 and WCK 2.65 through time. Chemical perturbation that was evident at WCK 4.4 during 1986–1989 was not detectable during 1991–1992. Additionally, during 1991–1992, the CPI at the three downstream sites (WCK 3.8, WCK 3.4, and WCK 2.65) was much lower than it was in the 1986–1989 assessment period. The changes in CPI that occurred at WCK 4.4, WCK 3.8, and WCK 3.4 between the 1986–1989 and 1991–1992 assessment periods resulted from an aggressive series of changes in wastewater treatment operations and pollution abatement activities at ORNL, driven by National Pollutant Discharge Elimination Sys-

tem permit requirements. A reduction in CPI at WCK 2.65, compared to WCK 3.4, was evident in both of the assessment periods (Figure 2). This reduction was due to the influx of chemically less-perturbed water from Northwest Tributary and First Creek, tributaries that join White Oak Creek between sites WCK 3.4 and WCK 2.65 (Figure 1). Substantial improvements in fish and invertebrate communities in downstream segments of White Oak Creek, First Creek and Fifth Creek also have occurred since 1986, demonstrating a general, long-term correspondence between CPI and stream biological status (Ashwood 1994).

#### Melton Branch

Melton Branch (MEK) is a 1.9-km-long tributary to White Oak Creek with a drainage area of about 3.83 km<sup>2</sup> (Loar 1994) (Figure 1). Streamflow in lower MEK



**Figure 2.** Chemical perturbation index values for six sites in White Oak Creek during 1986–1989 and 1991–1992. Numbers associated with stream site codes indicate the distance (kilometers) upstream from White Oak Creek’s confluence with the Clinch River.

was augmented by 23.3% to 43.9% [annual averages for 1991 (a wet year), and 1992 (a dry year), respectively] by periodic discharges of wastewaters from the Department of Energy’s High Flux Isotope Reactor. These discharges enter the stream at MEK 1.59. Three sites in MEK—one upstream of MEK 1.59 and two downstream of the effluent entry point—have been sampled periodically since March 1986, for computation of CPI values.

The High Flux Isotope Reactor did not operate from 19 February, 1987 to 20 December, 1989, so no wastewater was discharged from this facility to the stream during that period. Before reactor operations stopped, CPI values in Melton Branch downstream from the reactor were 3.52–3.67. When the reactor was on stand-by, the CPI values declined to natural levels (Table 1). When the reactor restarted after 29 March, 1990, CPI values for MEK downstream of the reactor increased again (Table 1). In Melton Branch upstream of the reactor’s influence, CPI values remained consistently low (range, 0.14–0.70; mean, 0.43) during the entire seven-year monitoring period (Table 1). Two points are evident from this example: (1) natural background CPI values for Melton Branch were low and relatively consistent (they ranged from 0.14 to 0.70; see Table 1), and (2) the influence of wastewater released from the reactor on CPI values for Melton Branch was large and clearly evident (Table 1).

#### East Fork Poplar Creek

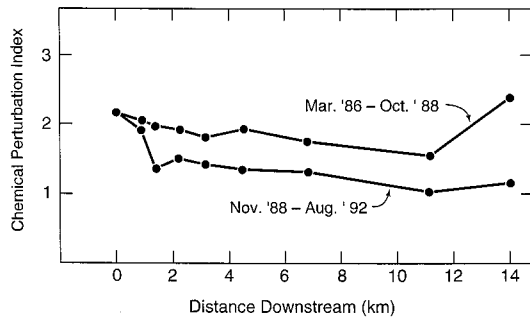
East Fork Poplar Creek (EFPC) is approximately 24.5 km in length and has a drainage area of about 77.2

Table 1. Chemical perturbation index values for three sites in Melton Branch

Dates	MEK 1.8	MEK 1.4	MEK 0.16
20 Mar, 1986–15 Jan, 1987	0.70 (36) <sup>a</sup>	3.52 (64)	3.67 (67)
19 Feb, 1987–20 Dec 1989	0.53 (56)	0.56 (56)	0.61 (63)
29 Mar, 1990–30 Jan, 1991	0.29 (63)	3.43 (68)	3.02 (88)
28 Feb, 1991–29 Apr, 1992	0.14 (34)	2.41 (35)	1.83 (83)
18 Jun, 1992–9 Dec, 1992	0.47 (28)	3.61 (28)	3.70 (28)

<sup>a</sup>Numbers in parentheses are the number of observations used to compute correlations. During the 20 March, 1986 to 15 January, 1987 assessment period, MEK 1.8 was frequently dry, and so was sampled less often than MEK 1.4 or MEK 0.16.

km<sup>2</sup> (Figure 1). The headwaters of this stream are located within the operating area of the Department of Energy’s Oak Ridge Y-12 Plant, and the stream has received diverse pollutants from this facility for many years. In 1986, a comprehensive monitoring program was established to assess biological conditions in EFPC, in relation to Y-12 Plant effluents and operations (Stewart and Loar 1994). As part of an ambient toxicity testing task, routine measurements were made of the conductivity, alkalinity, and hardness of water samples from various EFPC sites through time. CPI values were computed from these data to test for both spatial and



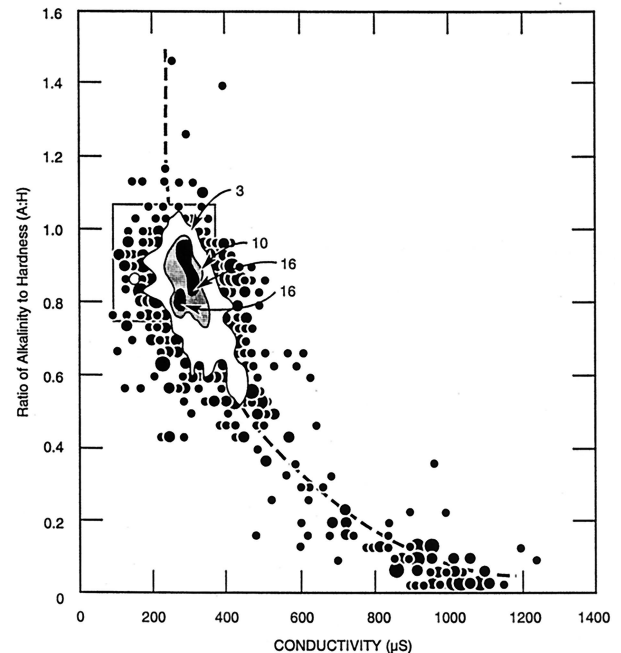
**Figure 3.** Chemical perturbation index values for nine sites in East Fork Poplar Creek during 1986–1988 and 1988–1992. Similar numbers of observations were used to compute correlations used for the CPI computation at each site in both assessment periods. Effluent from the Oak Ridge municipal sewage treatment plant enters East Fork Poplar Creek near distance 12 km, accounting for the increase in CPI between km 11.8 and km 14.

temporal changes (Figure 3). Based on similar numbers of seasonally matched observations in each assessment period, CPI values were greater at all sites in EFPC during the first assessment period (1986–1988) than they were later (1988–1992) (Figure 3).

The Y-12 Plant made numerous and extensive changes in existing waste-treatment operations and brought several new waste-treatment facilities on-line after the earlier assessment period. These changes greatly reduced pollutant loading to the stream and account for the reduction in CPI values in EFPC. The reduction in pollutant loading to EFPC also resulted in improvements in biotic communities in the stream: studies have shown a gradual increase in the numbers of fish species, a large increase in fish abundance, and an increase in the number of pollution-sensitive fish species (M. G. Ryon, Environmental Sciences Division, ORNL, personal communication). Thus, as was noted previously for streams in the White Oak Creek watershed, there is a good general correspondence between CPI and stream biological status.

#### Graphical Method for Using Conductivity, Alkalinity, and Hardness Data to Characterize Streams

As noted previously, a positive, near-unity relationship exists between alkalinity and hardness in many surface waters, and runoff from developed areas or waste-treatment systems that remove pollutants by means of acid-base reactions, incineration, or ion-exchange reactions tend to create ion-rich wastewaters that can increase the wastewater's conductivity relative



**Figure 4.** Relationships between conductivity and the ratio of alkalinity to hardness for water samples from 15 sites on streams near the Oak Ridge National Laboratory, in the White Oak Creek watershed (see Figure 1). Each site was sampled 84 times over a 12-month period. The size of the data point reflects the number of over-plots (none, one, or two). The areas bounded by irregular solid lines designate regions where over-plotting consistently exceeded 3, 10, or 16 per point. The area inside the square encloses all data from three upstream reference sites. The dashed line shows the nonlinear relationship between the ratio of alkalinity to hardness (A:H) and conductivity.

to the receiving system. These two considerations indicated that deviations from the natural relationships among conductivity, alkalinity, and hardness in stream water might be visualized by means of a simple graph. This idea was explored by plotting the ratio of alkalinity to hardness (A:H) versus conductivity for water samples from 15 sites in five streams near ORNL. Data for each site were from 80 to 84 samples collected during a 12-month period (Stewart 1990).

The resulting plot included a clustering of points near  $A:H = 0.8-1.0$ , particularly for headwater reference sites upstream of ORNL operations (Figure 4). However, numerous samples with low values for A:H, many of which had conductivity values  $>500 \mu S$ , also were clustered together. Most of the later observations were for samples from sites in Melton Branch downstream of the High Flux Isotope Reactor. When observations from three upstream headwater reference sites ( $N = 252$ ) are considered together, every A:H value

was between 0.74 and 1.08, and every conductivity value was between 80  $\mu\text{S}$  and 380  $\mu\text{S}$ . Thus, observations potentially indicative of wastewater inputs could be identified easily relative to the upstream reference sites. This result shows that it should be possible to establish statistically sound threshold values indicative of potentially adverse changes in conditions among the three water-quality factors. Such exceedances, in turn, could be used to trigger decisions about the need for additional monitoring, testing, or treatment.

## Discussion and Conclusions

The ability to detect trends and evaluate water-quality patterns at low cost, with minimal expertise, and with good reproducibility is an important prerequisite for effective, sustained management of urban freshwater streams. The CPI approach described here has these attributes and thus may help encourage the development of community-based stream monitoring programs.

Numerous other studies show that chemical water-quality data can be analyzed statistically to resolve sources of groundwater to surface-water streams (Perry and Clark 1990), determine export of nutrients and major ions from catchments (Cook and others 1994, Newbold and others 1995), or characterize groundwater-surface-water interactions (Valett and others 1997). Trilinear diagrams (Piper 1944, Morris and others 1983) also can be used to visually display differences and similarities among waters, based on specific cation and anion concentrations, but it is costly to analyze numerous samples for specific anions, cations, or nutrients. For this reason, it is sometimes difficult to sustain a chemical-based, water-monitoring program that incorporates a sampling frequency great enough to permit much insight into stream condition or function.

Even when data on specific ions or nutrients are available, it can be difficult to assign particular biological or geological significance to a particular level of change in a particular analyte. As an example, assume that the potassium concentration in water at a stream site is 40% greater in one sampling period than it was in the preceding sampling period. Why? And what are the ecological implications of this change? In the context of stream monitoring, the inability to unambiguously assign causality to, or consequences of, changes in a well-measured constituent detracts from the value of the measured constituent, because value depends in part on the ability of those making the measurements to interpret the results and convey them clearly and unequivocally to society (Karr 1994).

It is inherently difficult to relate changes in water-

quality conditions to changes in biological conditions in receiving streams for several reasons. First, the concentrations of ions (or pollutants) in streams can vary nonlinearly with stream discharge because dissolved materials can enter the stream episodically as a consequence of wet-weather events through various hydrologic flow-paths (Mulholland 1993). Second, effluent release rates can vary with time, as can within-stream biotic and abiotic conditions that can alter the forms, concentrations, or biological availability of pollutants. These conditions make it difficult to accurately characterize exposure regimes of stream biota to pollutants (Stewart and others 1996). Finally, the responses of stream organisms to a given change in water-quality conditions can vary, depending upon factors such as the species of organism, the current and preceding environmental conditions (Ham 1994), the organisms' pollutant-exposure history (Ham and Peterson 1994, Lotts and Stewart 1995), and the age, life stage, and metabolic condition of the organisms (Rand and Petrocelli 1985, Ham 1994). Collectively, these factors may discourage community efforts to develop and sustain stream monitoring programs that include measurements of biological status and chemical conditions.

In short, variation in measured factors tends to work against routine incorporation of specific chemical water-quality measurements in urban stream monitoring. The CPI method, however, uses data on easily measured and inexpensive (but relatively nonspecific) water-quality parameters. The CPI method also intrinsically incorporates temporal variation in water-quality conditions by requiring the collection of samples through time, yet examining how the measured parameters change in relation to each other, without specific association to time. The collection of samples through time, in turn, requires multiple visits to the stream site(s) being monitored, which increases the likelihood for ancillary inspection of stream condition and, thus, increases the chance for detecting unusual conditions that may warrant closer attention.

Natural background values for conductivity, alkalinity, and hardness will vary with climate and a stream catchment's geology. For this reason, system-specific background ranges and appropriate threshold values for conductivity, alkalinity, and hardness would need to be established for each stream of interest if the CPI method is to be used effectively. Due to these site-specific differences, it is not possible to offer a technically sound recommendation about the magnitude of change in a stream's CPI status that would appropriately be used as a trigger to justify further attention, but statistically determined tolerance intervals (Guenther 1977, Smith and oth-



ers 1998) can be computed for measured water-quality factors, so as to set the bounds for normal conditions with a specified level of confidence. Such bounds, in turn, allow the determination of nonnormal conditions, with a specified level of confidence, for any of the three parameters.

For community use, I discourage the statistical-bounds approach and advocate instead use of the plotting method (Figure 4) in conjunction with the CPI method. When enough data have been obtained to graphically define and bound normal conditions for the stream being monitored, atypical data can be identified easily by eye as soon as they have been plotted. Three successive sampling events yielding “outlier” values could be taken as evidence for a change in water-quality conditions that may warrant additional attention. The farther away the outlier points are from the normal bound, the more attention they might deserve. In many cases, the most appropriate response to an apparent adverse change in water-quality conditions would be to increase sampling frequency, so as to develop confidence in the stream’s status. Since the CPI method aggregates data through time (for  $N = 25$  observations), CPI values are most easily used to compare sites or to detect long-term changes in conditions at one or more sites.

Systematic measurements of key biological indicators can provide a better estimate of a stream’s ecological condition, compared either to CPI or specific-constituent assessments, for many reasons (Norris 1995). Chief among these is the fact that stream-dwelling organisms simultaneously integrate and assess all relevant water-quality and habitat factors. However, measurements of most relevant biological parameters are significantly more time-consuming, specialized, or costly than measurements of conductivity, alkalinity, and hardness. Biological parameters may have substantial spatial and temporal variation, and time-lags may occur between short-term exposures to pollutants and resulting biological effects, as noted previously. For community-based stream monitoring programs in particular, the use of more costly or complex sampling and analysis methods inevitably encourages less frequent sampling, which can derail program intent—that of community involvement, and a broader, collective appreciation of the need to help protect freshwater resources. Thus, some of the inherent limitations in biological monitoring and specific-constituent monitoring, as components of stream monitoring programs, can be at least partly overcome by use of techniques such as the CPI method.

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