MAJOR FINDINGS

Bacteria in the Upper Tennessee River Basin

Fecal indicator bacteria are the most frequent and widespread water-quality standard exceedances involving potential adverse effects to human health in the Upper Tennessee River Basin. The indicator bacteria themselves usually are harmless and easy to detect, but they are indicators of the presence of fecal material and have been shown to be associated with some waterborne disease-causing organisms. The presence of indicator bacteria, however, cannot be considered direct proof of any threat to human health, and research is underway to find better indicators.

Bacterial Counts Frequently Exceed Standards

The State of Tennessee’s current water-quality standards are based on a total fecal coliform level of 200 colonies per 100 milliliters of water, as a mean value.\(^9\) This value is commonly exceeded in agricultural and urban streams in the Upper Tennessee River Basin (fig. 10). In agricultural areas, livestock waste is the most likely bacterial source both from allowing livestock direct access to streams and runoff from animal-waste areas. Bacterial counts generally increase during higher streamflows associated with runoff events in the agricultural areas (fig. 11).

Deteriorated and leaky sewage systems, faulty sewage treatment plants, urban runoff, and combined sewer overflow systems are among the sources of bacterial contamination in many urban streams. For example, all of the urban streams draining the central Knoxville, Tennessee, area regularly exceed bacterial standards\(^{10}\) because of widespread leakage from very old and deteriorating sewer systems in the older parts of the city. Replacement in 1998 of an obsolete combined sewer overflow system for one city neighborhood, however, has improved conditions for that neighborhood and adjacent parts of Fort Loudon Reservoir. These conditions highlight the continuing need for infrastructure improvements, especially in older urban areas.

Livestock are a major contributor to fecal coliform levels in area streams.

In Upper Tennessee River Basin urban areas, deteriorated sewage systems and combined sewer overflows produce elevated fecal coliform levels.
Bacteria Frequently Are Detected in Domestic Wells and Springs

A common misconception is that untreated ground water from wells and springs generally is safe for consumption because percolation through the soil removes most contaminants. While the soil can act as a natural filter, this does not guarantee the absence of contaminants. In fact, about half of the waterborne-disease outbreaks in the United States since 1900 have involved contaminated ground water.\(^{(11)}\)

Ground-water systems such as the carbonate systems of the Upper Tennessee River Basin are particularly susceptible to contamination from surface sources. Ground-water flow paths in these systems usually are shallow, principally involving the upper 10 to 20 feet of highly fractured and heavily weathered rock. In addition, the common presence of bedrock outcrops, areas of thin overburden, and karst features such as sinkholes provide direct avenues for aquifer contamination (fig. 12). Other potential sources for bacterial contamination include faulty or poorly placed septic systems and poor well construction or sanitation practices.

For finished drinking water, the detection of as few as 4 coliform bacteria colonies per 100 milliliters (col/100 mL) or the detection of 1 col/100 mL of fecal coliform bacteria, or \(E.\ coli\), warrants concern for human health.\(^{(12)}\) Of 30 domestic wells used as sources for untreated drinking water, 11 (37 percent) exceeded the total coliform drinking-water standard and 9 (30 percent) exceeded the \(E.\ coli\) drinking-water standard (fig. 13). The highest \(E.\ coli\) value detected was 1,600 col/100 mL.

Total coliform values for 35 springs sampled in the Upper Tennessee River Basin ranged from 10 to 1,900 col/100 mL and \(E.\ coli\) ranged from 0 to 660 col/100 mL. All of the springs tested exceeded drinking-water standards for total coliform bacteria, and 95 percent of the springs exceeded the \(E.\ coli\) standard. Two springs exceeded the \(E.\ coli\) body-contact standard of 126 col/100 mL. Sixteen of the 35 springs are used as domestic water supplies and others are used for filling water containers by the roadside with what usually is believed to be “clean mountain spring water.”

**Figure 12.** Upper Tennessee ground-water flow systems can be affected by a number of potential contamination sources such as sinkholes, outcrops of bedrock, and areas with thin overburden. (Not to scale)

**Figure 13.** Coliform bacteria are often detected in Upper Tennessee River Basin ground water.

Most of the rural population in the Upper Tennessee River Basin depend on shallow domestic wells for water supply.

Although much of the public perceives them as clean sources of drinking water, springs are very susceptible to contamination.
Nutrients in the Upper Tennessee River Basin

Nutrients are nitrogen and phosphorus compounds that are essential for plant growth. When found at elevated concentrations, however, nutrients can degrade water quality. The enrichment of a water body with nutrients, called eutrophication, can result in dense, rapidly multiplying growths, or blooms, of algal species and other nuisance aquatic plants. These can clog water intake pipes and filters and interfere with recreational activities, such as fishing, swimming, and boating. Subsequent decay of algal blooms can overload water bodies with oxidizable debris and result in foul odors, bad taste, and reduced dissolved oxygen levels, which are harmful to other aquatic life.\(^{(13)}\)

Nutrients in the Upper Tennessee River Basin originate from point and nonpoint sources. Point sources are typically piped discharges from wastewater-treatment facilities and large urban and industrial stormwater systems. Nonpoint sources include stormwater runoff from urban and agricultural areas. In the Upper Tennessee River Basin, applications of synthetic fertilizers and manure are major sources.

Nutrient Loadings and Yields Vary among Upper Tennessee River Subbasins

Nutrient loadings in the Upper Tennessee River subbasins are primarily influenced by land use and streamflow conditions. Loads were estimated by using a constituent transport model and multiple regression to relate streamflow to the concentration of a water-quality constituent to derive loads.\(^{(14)}\) Twenty-three stations with adequate streamflow and chemical records were used for nitrogen calculations and 20 for total phosphorus.

Figure 14. Mean annual total nitrogen yields between 1973 and 1993 were highest in the upper French Broad and upper Clinch River Basins.

Figure 15. Mean annual total phosphorus yields between 1973 and 1993 were highest in the upper French Broad River Basin.

The highest yields in the study area for both nutrient species were detected in the French Broad River Basin, particularly the upstream portion that includes Asheville, North Carolina (figs. 14 and 15). The French Broad River, as a whole, accounted for about 40 percent of the 138,000 pounds per day (lb/d) average annual total nitrogen load\(^{(15)}\) and about 25 percent of the 13,500 lb/d average annual total phosphorus load,\(^{(16)}\) leaving the basin at Chattanooga, Tennessee. The Holston River Basin added another 22 percent of the total nitrogen load but only 8 percent of the total phosphorus load.

A combination of agricultural and urban runoff is probably responsible for conditions in the French Broad River. In addition, the French Broad River and its tributaries have a history of water-quality problems associated with industrial point-source discharges. These basins also had the highest yields and loadings in the Upper Tennessee River Basin for total ammonia and organic forms of nitrogen.

Nutrient loadings and yields generally were lowest in those basins with relatively low percentages of agricultural land use and at sites directly downstream from tributary reservoirs. The fate of nutrients in the reservoirs depends on the physical characteristics of the reservoir (volume, surface area, depth, and hydraulic retention time) and its trophic state.\(^{(17)}\) The tributary reservoirs in the Upper Tennessee River Basin commonly function as sinks for nutrient species by providing a favorable environment for nitrogen transformation and by efficiently trapping both dissolved and sediment-bound phosphorus. Outflow loads of total phosphorus below Norris Lake on the Clinch River, for example, were 37 percent of the inflow load from the Clinch and Powell River Basins. Load estimates for the Holston River upstream and downstream from...
Cherokee Reservoir similarly indicate that the reservoir traps about 46 percent of the incoming load of total phosphorus. In contrast, less trapping occurs in the main-stem reservoirs, which are predominantly flow-through systems with limited storage capacity and relatively short residence times. Outflow phosphorus loads downstream from Chickamauga and Watts Bar Reservoirs significantly exceeded the inflow loads from upstream drainages. The increased loads can be attributed to low rates of trapping as well as additional input from ungaged areas adjacent to the reservoirs.\(^{(16)}\)

**Nutrient Concentrations and Yields Vary with Land Use**

The relation between total nitrogen concentrations and land-use percentages was investigated for 87 sites in the Upper Tennessee River Basin and was found to be statistically significant. Stations in forested watersheds had the lowest concentrations of total nitrogen, whereas stations in agricultural areas had the highest. Concentrations of nitrogen in urban and mixed land-use areas were significantly greater than forested watersheds but were somewhat less than nitrogen concentrations in agricultural watersheds. Total nitrogen concentrations tended to increase with increased development whether agricultural or urban (fig. 16).\(^{(15)}\)

Nitrogen sources also were investigated by using regression analysis between annual basin yields and total annual inputs from fertilizer, animal waste, wastewater discharges, and atmospheric deposition. For total nitrogen, basin yields significantly and positively correlated with agricultural inputs but only weakly correlated with wastewater discharges and atmospheric inputs. This tends to identify agricultural land use as the major contributor to annual instream nitrogen yields.\(^{(18)}\)

The relation between total phosphorus concentrations and land-use percentages also were investigated for 83 sites in the Upper Tennessee River Basin. Although the relation was not quite as clear as with nitrogen, statistically significant increases in total phosphorus concentrations also accompanied increased development whether urban or agricultural (fig. 17). As with total nitrogen, the lowest phosphorus concentrations were detected at sites in predominantly forested watersheds, whereas sites in urban and agricultural areas had the highest phosphorus concentrations.\(^{(16)}\)

Phosphorus sources also were investigated by using calculated basin yields and total annual inputs from fertilizer, animal waste, wastewater discharges, and the atmosphere. Phosphorus yields were found to strongly correlate with wastewater discharges but not with the agriculturally related input categories. This suggests that wastewater discharges may account for most of the total phosphorus load in basin streams (J.F. Connell, U.S. Geological Survey, written comun., October 20, 2000). Agriculturally applied phosphorus may be assimilated quickly by area soils thereby reaching area streams slowly if at all.

Agricultural land uses appear to account for most of the total nitrogen loads to area streams.

Wastewater discharges appear to account for most of the total phosphorus in Upper Tennessee River Basin streams.
Nutrient Concentrations in Upper Tennessee River Basin Surface Waters Generally Are Lower Than National Median Concentrations

Although nutrient concentrations and loadings are a concern in parts of the Upper Tennessee River Basin, concentrations generally are low for most area subbasins when compared with national averages. Mean total nitrogen concentrations exceeded or equaled the national median values only for three agricultural sites: Big Limestone Creek (83 percent agricultural), Copper Creek (51 percent agricultural), and the Nolichucky River (39 percent agricultural). Similar results were obtained for total phosphorus at Big Limestone Creek and the Nolichucky River, but the French Broad River flowing into Tennessee from North Carolina also exceeded the national median value. Although relatively low, mean total phosphorus concentrations at most sites exceeded the U.S. Environmental Protection Agency (USEPA) goal of 0.05 mg/L total phosphorus for surface water entering reservoirs.

Nitrogen Species Changed by Wastewater Treatment

Prior to the widespread implementation of wastewater treatment, nitrogen loadings for most Upper Tennessee River Basin streams primarily consisted of reduced species such as ammonia and various organic forms. These nitrogen species generally are undesirable in surface water because of associated color changes and decreases in dissolved oxygen levels. In addition, under certain conditions, ammonia nitrogen can be highly toxic to aquatic life. Wastewater-treatment facilities convert these undesirable forms to the oxidized species, nitrite and nitrate.

At the Tennessee River at Chattanooga, Tennessee, as with most major streams in the Upper Tennessee River Basin, the ratio of reduced to oxidized nitrogen species began to change in the late 1970s (fig. 18), corresponding to the implementation of wastewater-treatment facilities. By about 1983, the oxidized nitrogen species, nitrate and nitrite, became the predominant forms of nitrogen discharged from the basin, a trend which has continued to the present.

Figure 18. The predominant nitrogen species changed at the Tennessee River at Chattanooga, Tennessee, between 1970 and 1998.
### Loading Trends Increase in Parts of the Upper Tennessee Basin

Trend analyses for 56 stations using the seasonal Kendall statistical analysis test indicated significant increases in total nitrogen at seven sites in the Upper Tennessee River Basin and significant decreases at eight sites (fig. 19). Sites showing decreases were all on relatively major streams (average drainage area, 2,600 square miles) or below major impoundments. Of the seven sites showing increases, six are in the Blue Ridge physiographic province and six drain basins with forests accounting for more than 75 percent of the total land use. The exception is Beaver Creek, which drains the Bristol, Tennessee and Virginia, urban area in the Valley and Ridge Province. The average area of basins showing nitrogen increases was only 276 square miles.\(^{(15)}\)

Of the seven sites showing increases, five are in the Blue Ridge in North Carolina—two sites on the French Broad River and one each on the Little Tennessee River and tributaries to the Hiwassee and Pigeon Rivers. Much of this area is undergoing nonurban residential development in the form of vacation homes. Nitrogen loads are probably increased by the sewage and fertilizer use associated with this development.

Similar trend analyses for 42 sites to detect changes in total phosphorus concentrations yielded only one site with significant increases (fig. 20). West Chickamauga Creek, which drains a major industrial and urban setting, showed high concentrations for the entire period of record. Most (33) sites showed no trend, and eight sites showed significant decreases. These sites are dominated for the most part by pasture and forest; however, three sites are downstream from major wastewater discharges.\(^{(16)}\) For sites in these more urbanized basins, improvements in wastewater-treatment processes are clearly responsible for the downward phosphorus trends.

### Figure 19. Total nitrogen increased in parts of the Upper Tennessee River Basin between 1970 and 1993.

![Map of the Upper Tennessee River Basin showing nitrogen trends](image)

Nonurban residential development in the Blue Ridge Mountains is most likely the largest contributor to increasing total nitrogen concentrations.

### Figure 20. Total phosphorus decreased or remained unchanged in the Upper Tennessee River Basin between 1970 and 1993.

![Map of the Upper Tennessee River Basin showing phosphorus trends](image)
Nutrient Concentrations Generally Are Low in Upper Tennessee River Basin Ground Water

All of the nutrients measured in the Upper Tennessee River Basin ground water were relatively low, as is usually typical of ground water. Most nutrient species are retained by soil particles or organic matter, taken up by plants, or utilized by soil bacteria and never enter the ground-water flow system. Exceptions are the nitrate and ammonia forms of nitrogen; however, only nitrate has a drinking-water standard, which is 10 mg/L. Drinking water containing nitrate concentrations higher than the standard can cause methemoglobinemia, a life-threatening illness in infants.

Nitrate was present in all wells and springs sampled in the Upper Tennessee River Basin but usually at concentrations of 3 mg/L or less. This included all of the 30 domestic wells used for drinking-water supply that were sampled and the 35 springs sampled across the basin. The median nitrate concentration for domestic wells was 0.59 mg/L, slightly more than the 25th percentile value nationally; the median nitrate concentration for springs was 1.16 mg/L, which was significantly lower than the national 50th percentile. The higher concentrations detected in springs most likely reflect the predominance of relatively short ground-water flow paths associated with localized recharge and runoff. No nitrate concentrations in excess of the 10-mg/L standard were detected in any domestic wells or springs.

Nitrate concentrations in excess of the 10 mg/L standard were detected in 5 of the 30 wells installed during the study period to monitor shallow ground-water quality under and adjacent to tobacco fields. Tobacco is the main cash crop in the Upper Tennessee River Basin and is usually grown in small but intensively fertilized and cultivated plots. In general, fertilizer applications for tobacco cultivation are much greater than for any other row-type crop raised in the Upper Tennessee River Basin.

The median nitrate concentration in the shallow agricultural monitoring wells, however, was 0.68 mg/L—only slightly more than the median concentration for domestic wells and the national 25th percentile. Among the concentrations found nationally for agricultural and urban land uses, this value falls in the lower end of the medium range as shown in the accompanying figure.

The results indicate that nitrate contamination of extensive areas of ground water in the Upper Tennessee River Basin is very unlikely. High nitrate concentrations relative to the 10 mg/L drinking-water standard were detected only in shallow ground water directly under heavily fertilized tobacco plots. Tobacco fields typically cover only about 2 acres and are widely scattered across the study area. The potential for nitrate contamination of drinking-water sources is, therefore, very low outside of the immediate vicinity of tobacco fields.
Pesticides in the Upper Tennessee River Basin

Pesticides are widely used in the Upper Tennessee River Basin to control insects, fungi, weeds, and other undesirable organisms. These compounds vary in their toxicity, persistence in the environment, and transport characteristics. Use of some of the more persistent organochlorine compounds, such as DDT, chlordane, dieldrin, and aldrin has been discontinued in the United States, but their residues are still detected in the environment. Although pesticides usually are applied to specific areas and directed at specific organisms, these compounds often become widely distributed and pose hazards to nontarget organisms. Of 18 sites sampled for organochlorine residues in bottom material and biota in the Upper Tennessee River Basin, chlordane was detected at three sites and dieldrin and DDT-related residues at two sites.

Pesticides were Frequently Detected in Surface Water

Pesticide use in the Upper Tennessee River Basin is primarily for agricultural purposes. Herbicides, including atrazine and its degradation product, deethylatrazine, had some of the highest application rates and were also among the most frequently detected pesticides in the basin. Herbicides were detected in 98 percent of the 428 surface-water samples collected; atrazine was found in 91 percent and deethylatrazine in 86 percent. Metolachlor and simazine were detected in 62 and 40 percent, respectively. Tebuthiuron and prometon, which are used most commonly in noncrop areas, were also among the most frequently detected herbicides (in 58 and 31 percent of the samples collected, respectively). The most frequently detected insecticides were diazinon (12 percent), carbaryl (10 percent), and chlorpyrifos (10 percent), all of which are used on a variety of crops to control pests.

Detection frequencies for 27 pesticides detected at 3 intensively sampled agricultural sites in the Upper Tennessee River Basin (fig. 21) generally illustrate the results obtained at all 13 Basic Fixed Sites from which surface-water samples were collected. Overall, a total of 32 pesticides were detected. Chlorothalonil, alpha-BHC, and terbacil each were detected once and ethoprop was detected twice.

Some differences among the three sites are notable and probably reflect different agricultural practices and hydrologic conditions. For example, at the Nolichucky River site, compounds generally not found at other sites such as cyanazine, alachlor, DCPA, metribuzin, bromacil, and diazinon, were detected. Molinate, trifluralin, and p,p'-DDE were detected only at the Copper Creek site, which also had a significantly higher frequency of detection for tebuthiuron. Pesticide detection frequencies at Big Limestone Creek and the Nolichucky River were, as expected, similar for several compounds including metolachlor, simazine, prometon, and napropamide. Big Limestone Creek is a tributary to the Nolichucky River, and both drain the same general agriculturally dominated area. The Big Limestone Creek drainage basin, however, contains more dairy operations than other parts of the Nolichucky drainage basin, which may account for some of the differences between the two sites.

Table 1. Major pesticides used in the Upper Tennessee River Basin, listed in order of estimated total pounds of active ingredient applied annually (1991-94) (18)

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<thead>
<tr>
<th>Insecticides</th>
<th>Herbicides</th>
<th>Fungicides</th>
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<tr>
<td>Oil .......... 256,000</td>
<td>Atrazine ...... 116,000</td>
<td>Methyl bromide 423,000</td>
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<tr>
<td>Acephate .... 80,700</td>
<td>2,4-D .......... 55,600</td>
<td>1,3-D ........ 342,000</td>
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<td>Chlorpyrifos .... 71,500</td>
<td>Metolachlor ....... 46,300</td>
<td>Captan ........ 108,000</td>
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<td>Carbarly .......... 27,200</td>
<td>Alachlor ........ 40,900</td>
<td>Ziram ........... 69,500</td>
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<td>Fenamiphos .... 17,200</td>
<td>Pethate ........ 31,400</td>
<td>Sulfur .......... 58,700</td>
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<tr>
<td>Carbofuran ...... 17,000</td>
<td>Pendimethylalin ... 25,200</td>
<td>Chloropicrin ....... 45,100</td>
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<tr>
<td>Formetanate ..... 16,300</td>
<td>Butylate ........ 24,800</td>
<td>Mancozeb .......... 40,400</td>
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<tr>
<td>Azinphos-methyl .... 14,400</td>
<td>Simazine ......... 23,800</td>
<td>Metalaxyl ....... 28,100</td>
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<tr>
<td>Phosmet ........ 9,420</td>
<td>Glyphosate ....... 16,100</td>
<td>Manab .......... 21,500</td>
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</table>

Figure 21. Pesticide detections at three agriculturally dominated sites followed similar patterns.
Mixtures of Pesticides Are Common

Pesticides were seldom detected alone in surface-water samples and usually occurred as mixtures of several compounds. Generally, the effects of pesticide mixtures on biota or humans are not included in water-quality criteria, which are most commonly based on single-species, single-chemical toxicity tests conducted under laboratory conditions. As a result, potential adverse effects on biota may be underestimated.

Of the 163 samples collected at the three intensive sites, only 2 samples at Copper Creek contained only one detectable pesticide compound, and only 5 total samples contained only two compounds (fig. 22). Among the intensively sampled sites, samples from the Nolichucky River at Lowlands, Tennessee, generally contained more detectable pesticide compounds than samples from the other sites, but usually at lower concentrations. This reflects the larger drainage area of the Nolichucky River (1,687 square miles) as compared to the drainage areas of the other intensive sites (79 and 106 square miles for Big Limestone and Copper Creeks, respectively). Similarly, more pesticides also were detected in samples from Big Limestone Creek, which has a larger percentage of agricultural land use and a greater variety of crops than the Copper Creek Basin in Virginia.

Peak Pesticide Concentrations Are Seasonal

Pesticide concentrations were found to be seasonal and closely related to land use. The highest concentrations occurred in the more heavily agricultural basins in late spring and early summer, coinciding with crop applications. Results of weekly sampling results at the three intensively sampled agricultural sites illustrate the seasonality and short-lived nature of the peak concentrations in streams draining agricultural areas (fig. 23). Peak concentrations coincided with the first substantial runoff event following agricultural applications in May 1996, after which concentrations declined relatively rapidly to near-background levels. Less frequent sampling would have made it less likely to have noted the existence of the peaks. Because these streams are “flashy” in that peak discharges come and go very quickly, it is possible that even higher concentrations can occur for short periods of time. Seasonality also was evident at sites not characterized or directly influenced by intense agricultural activities. Atrazine and metolachlor concentrations at Clear Creek at Lilly Bridge, a predominantly forested watershed and part of the Obed National Wild and Scenic River watershed, also showed a distinct seasonality but with much lower concentrations (fig. 24). The seasonal pattern at this site is more gradual, suggesting atmospheric input more than runoff from agricultural activity.
Pesticide Concentrations Usually Meet Guidelines

Although most of the water samples collected contained detectable concentrations of one or more pesticides, no concentrations exceeded any drinking-water standards or guidelines. Only 20 of the 31 pesticides detected, however, have established guidelines. Of the 15 compounds that have aquatic-life guidelines, four were detected at concentrations higher than the guidelines. Carbaryl concentrations in excess of the 0.20-µg/L (micrograms per liter) aquatic-life criterion were found in four samples—two each from the Guest River near Millers Yard, Virginia, and the Nolichucky River at Lowlands, Tennessee (fig. 25). Lindane, an organochlorine used primarily for the protection of tobacco transplants, was above the 0.01-µg/L criterion in three samples from three different sites, two of which were in the same subbasin - Little Limestone Creek and the Nolichucky River at Lowlands, Tennessee.

An atrazine concentration higher than the 0.18-µg/L criterion also was detected in one sample taken at the Nolichucky River at Lowlands, Tennessee, in May 1996. This was the only criterion exceedance noted for any herbicide even though herbicides were detected much more frequently than the other pesticide types. One sample collected at the Guest River near Millers Yard, Virginia, contained a diazinon concentration that was not only greater than the aquatic-life guideline of 0.08 µg/L but approached the USEPA lifetime health advisory level of 0.60 µg/L for drinking water.

Some Pesticides Were Detected More Frequently in the Upper Tennessee River Basin Than Nationally

Three herbicides consistently were detected more frequently in the Upper Tennessee River Basin than in other basins across the Nation. Atrazine and deethylatrazine were detected in 99 and 98 percent, respectively, of samples from agricultural basins in the Upper Tennessee River Basin and in 94 and 95 percent, respectively, of samples from mixed land-use basins - significantly more frequently than the national averages of about 80 and 60 percent, respectively. Tebuthiuron also was detected in about 60 percent of the Upper Tennessee River Basin samples as opposed to an overall average of about 20 percent nationally. Detection frequencies for most of the other herbicides probably reflect different herbicide-use patterns in the Upper Tennessee River Basin resulting from particular crop patterns. The three most commonly detected insecticides in the Upper Tennessee River Basin - diazinon, carbaryl, and chlorpyrifos - were detected less frequently than the national averages in all land-use categories.
Pesticides Were Detected at Low Levels in Ground Water

Pesticides were detected in Upper Tennessee River Basin ground-water samples more often than not, but generally at concentrations less than 0.01 µg/L. Pesticide concentrations in ground water did not exceed any drinking-water standards or guidelines. Usually, however, pesticides occur in mixtures for which criteria are not available. In addition, 5 of the 11 pesticides detected have no established guidelines or criteria.

Pesticides were detected in springs significantly more often and in more pesticide detections per sample than in other ground-water sources sampled (fig. 26). This probably reflects the greater vulnerability of springs to surface contamination either from the immediate area or karst features in the carbonate bedrocks. More frequent detections also may reflect the larger drainage areas from which springs capture ground water as opposed to wells. Of the 35 springs sampled, 24 (69 percent) contained detectable pesticide concentrations, and 12 (34 percent) contained detectable quantities of three or more different compounds. Detection frequencies in agricultural and domestic wells, by contrast, were significantly lower and similar to one another; 12 of 30 (40 percent) agricultural wells and 13 of 30 (43 percent) domestic wells contained detectable pesticide concentrations. Of these detections, only three (10 percent) samples from agricultural wells had detections of three or more pesticides. Eight (27 percent) domestic wells, however, had detections of three or more compounds.

Atrazine and its degradation product, deethylatrazine, were the pesticides most commonly detected in all ground-water samples but were detected twice as frequently in springs as in other ground-water sources (fig. 27). Tebuthiuron, the third most frequently detected pesticide, also was detected more than twice as frequently in springs as in domestic wells. The different pesticide mixtures typical of the agricultural wells sampled reflect the focus on tobacco in this phase of the study. In general, a different suite of pesticides are used for tobacco than for most other crops. For example, atrazine and other broadleaf herbicides are toxic to tobacco.
Volatile Organic Compounds Were Frequently Detected in Ground Water

Ground-water samples were collected from 30 domestic wells and 35 springs tapping carbonate strata in the Upper Tennessee River Basin. Volatile organic compounds (VOCs) were detected in most of the ground-water samples (fig. 28) but generally at very low concentrations—often in orders of magnitude below the established reporting limit. Twenty-eight different VOCs were detected during sampling, 12 of which have drinking-water standards. No measured concentrations, however, exceeded these standards.

VOCs were detected more frequently in springs (86 percent) than in domestic wells (67 percent) and generally at slightly higher concentrations. Of the 20 samples with one or more concentrations greater than 0.1 µg/L, 14 were taken from springs and only 6 from wells. Similarly, of the 28 compounds detected, 22 were detected in spring samples and only 18 were detected in domestic wells.

The most frequently detected VOCs were trichloromethane (51 percent), chloromethane (28 percent), styrene (23 percent), tetrachloroethane (18 percent), carbon disulfide (11 percent), and trichloroethene (9 percent). The remaining 22 compounds were detected in three or fewer samples (less than 5 percent).

Other than the greater detection frequencies for spring samples, no areal or other occurrence patterns could be found. As is the case nationally, the source for many of the most common VOCs detected in ground water, such as trichloromethane, is unclear. The greater occurrence of detections in springs as well as the widespread but random pattern of occurrence suggests the possibility of atmospheric origins, but no definite source can be identified at present.

Detection frequencies in Upper Tennessee River Basin wells for the 10 most commonly detected VOCs nationally were similar to national detection frequencies found for ambient ground water in all land-use settings. All compounds were assessed at a common detection level of 0.1 µg/L. Trichloromethane was the most commonly detected compound nationally as well as in the Upper Tennessee River Basin but typically was detected at concentrations far below drinking-water standards. The results are consistent with the mixed urban and rural land uses surrounding most Upper Tennessee River Basin ground-water sites.
Water-Quality Influences of Industry and Mining

Industrial and mining activities prior to the passage of the Clean Water Act in 1972 have left a legacy of contaminated sediment that continues to affect water quality in parts of the Upper Tennessee River Basin. The most widespread contaminants are PCBs (polychlorinated biphenyls) and mercury, mostly from industrial activities dating from 1950 to 1972. Sources for some of the other contaminants, however, such as those affecting the Pigeon and Ocoee Rivers date back as far as 1908 and 1843, respectively.

Mercury in the North Fork Holston River is a result of the operation of a chlor-alkali plant on the banks of the river from 1950 through 1971. An estimated 75 pounds of mercury per day were discharged either directly to the river or into unlined holding ponds along the riverbank. Although soils at the site have been remediated, the site continues to discharge mercury. Bed-sediment and tissue samples taken from the Holston River system (fig. 29) were the only samples taken during the study that were above the Canadian guideline for aquatic-life protection (0.486 micrograms per gram total mercury). Although tissue samples in the main-stem Holston River site at Surgoinsville were free of mercury, the bed-sediment results suggest that mercury may be migrating farther downstream than previously thought and may eventually reach Cherokee Reservoir.

Mercury is also a major contaminant in the drainages downstream from the Department of Energy’s 35,585-acre Oak Ridge Reservation (ORR), such as East Fork Poplar Creek, the White Oak Creek watershed, and the lower Clinch River - Watts Bar Reservoir. The ORR, established in 1942 as part of the Manhattan Project to develop the atomic bomb, encompasses three major facilities — X–10, originally for weapons research but now Oak Ridge National Laboratory (ORNL); Y–12, for the fabrication of nuclear weapons components; and K–25, for uranium enrichment by gaseous diffusion. As a result of these operations, about 527 sites covering approximately 15 percent of the total ORR area have been identified as contaminated with metals, including mercury, radionuclides, a variety of VOCs, and nitrates.

Most of the contamination has remained confined within the ORR, which was added in its entirety to USEPA’s National Priorities List in 1989. A number of contaminants, most notably mercury, PCBs, and cesium-137, however, have migrated to downstream areas. The State of Tennessee has posted a fish-consumption advisory for ORR drainages as well as Watts Bar Reservoir as a result of bioaccumulation of mercury and PCBs in some fish species.

A 1983 inventory estimated that about 2 million pounds (1,088 metric tons) of mercury was ‘lost’ from operations related to thermonuclear bomb development on the ORR. Most of this mercury is believed to have volatilized into the atmosphere, but much remains within ORR facilities and in Watts Bar Reservoir sediments. Analyses of sediment cores indicate that the highest discharges of mercury and cesium-137 occurred during the 1950s, and that about 76 metric tons of mercury has accumulated in Watts Bar sediments. About 91 percent of the 335

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<td>Watts Bar Reserve</td>
<td>PCBs</td>
<td>Not identified</td>
<td>Fish consumption advisory</td>
</tr>
<tr>
<td>Ft. Loudon Reserve</td>
<td>PCBs</td>
<td>Abandoned mining area</td>
<td>None</td>
</tr>
<tr>
<td>Tellico Reserve</td>
<td>Metals</td>
<td>Abandoned mining area</td>
<td>None</td>
</tr>
<tr>
<td>Parksville Reserve</td>
<td>Metals</td>
<td>Abandoned mining area</td>
<td>None</td>
</tr>
</tbody>
</table>

Figure 29. Mercury, in micrograms per gram, and organic contaminants persist in bed sediments and biological tissues in parts of the Upper Tennessee River Basin.
Tennessee portion of the Pigeon River are showing signs of recovery. Waterville Lake, however, still retains tons of contaminated sediments deposited since the dam became operational in 1930, and these sediments remain a potential source of dioxin and other contaminants.

Polycyclic aromatic hydrocarbons (PAHs) commonly are detected as pollutants in soils and sediments, occur naturally in crude oil and coal, and also can result from the incomplete combustion of fossil fuels and forest fires. In the upper Clinch River Basin, PAH concentrations reflect the presence of coal fines from upstream mining activities.

Twenty-nine PAHs were found in upper Clinch River bed-sediment samples and, with only a few exceptions, were not detected in the 12 samples taken from other parts of the Upper Tennessee Basin. Although PAHs are known to be toxic to fish, mussels, and aquatic insects, sediment-quality guidelines for the protection of aquatic life have been established for only 12 of the compounds detected. Of these, only two compounds—naphthalene and phenanthrene—exceeded their respective Canadian probable-effect levels of 391 µg/kg (micrograms per kilogram) and 515 µg/kg (fig. 30). The probable-effect levels define concentrations above which adverse effects are expected. A third compound, benzo(a)anthracene, occurred in concentrations very near its guideline of 385 µg/kg, and a number of compounds lacking guidelines were found at concentrations of 1,000 µg/kg or greater.

The highest concentrations generally follow the results for naphthalene and phenanthrene and occurred in the major river sites nearest, on a relative basis, to upstream mining activities. For example, concentrations at the Powell River and Pendleton Island sites exceeded those found at the Clinch River near Tazewell, which is farther removed from active mining in terms of river miles. Higher gradients and water velocities in the tributaries to the major streams prevent the accumulation of fine-grained sediment and coal fines. The main river channels, however, contain large pools and backwater areas where fine-grained material and associated constituents are deposited.
Freshwater Mussels in the Clinch and Powell Rivers

Freshwater mussel species diversity has been slowly declining in the Clinch and Powell Rivers of Tennessee and Virginia over the past 100 years. The numbers of mussel species found in these rivers are shown in figure 31 for selected periods of time and illustrate the long-term trend in loss of species diversity. The numbers do not precisely show numbers of species lost but reflect difficulties in finding specimens as species decline and, in some cases, difficulty with basin access. For example, prior to 1915, the upper parts of the river basins were inaccessible and remained unsurveyed.

Although some forms were lost, survey results from 1963 to 1971 indicate that the fauna survived TVA impoundment largely intact. Mussel declines became apparent, however, in the mid-1970’s, and by that time many previously common mussel species had become rare, extirpated, or extinct.

The greatest declines in mussel abundance occurred during the record drought from 1983 to 1988 (fig. 32). Since that time, the Clinch River in Tennessee has shown remarkable recovery, both in mussel densities and species numbers. The Virginia parts of the Clinch and the Powell Rivers, however, have recovered to a little more than half the densities recorded in 1979, mostly reflecting recovery of the three most abundant species. Most of the rare and more sensitive species continue to decline in the Powell River and in the Virginia part of the Clinch River.(29)

Upper Tennessee River Biological Communities in a National Context

Three biological indicators, which typically respond to changes in stream degradation, illustrate the relation of Upper Tennessee River Basin sites to the overall range of NAWQA sites nationwide. For all indicators, higher values suggest a more degraded stream site.

Algal status focuses on the changes in the percentage of certain algae in response to increasing siltation. Within the Upper Tennessee River Basin, the only sites in the highest 25 percent nationally are Big Limestone Creek, which drains predominantly agricultural land use, and the Pigeon River, which has been heavily affected by industrial wastes.

Invertebrate status is the average of 11 invertebrate (primarily insects, worms, crayfish, clams) metrics that summarize changes in richness, tolerance, trophic conditions, and dominance commonly associated with water-quality degradation. Among the Upper Tennessee River Basin sites, the two that rank highest on the index are the Pigeon and French Broad Rivers. The Pigeon River is recovering from decades of receiving industrial wastes. The French Broad River is principally affected by urban development in the Asheville, North Carolina, area and agriculture in the lower part of the basin.

Fish status is the sum of scores of four fish metrics (percentage of tolerant, omnivorous, non-native individuals, and percentage of individuals with external anomalies) that tend to increase in association with water-quality degradation. The Holston River at Surgoinsville, Tennessee, which ranked highest on this index, is characterized by relatively high concentrations of mercury and copper in bed sediments, probably derived from upstream industrial activities.
Toxic Spills and Releases

The NAWQA Program, like most water-quality assessments, is designed to gather information on general water-quality conditions and analyze problems that tend to be chronic as opposed to episodic. Even though the NAWQA Program provides for sampling during storm events in order to achieve a more complete “picture” of water-quality conditions, detection of every instance of water contamination is clearly beyond the program’s defined scope. In general, this is true of every other ongoing State or Federal water-quality assessment.

In late May 1996, however, a toxic release was recorded at the Big Limestone Creek site (fig. 33, number 8) that resulted in a fishkill over several miles in the lower end of the stream. The apparent cause was excessive ammonia concentrations that were traced to agricultural activities upstream. If not for the sampling activity being conducted at the site, the kill most likely would have gone unreported. Given the relatively remote nature of many biologically diverse stream reaches in the Upper Tennessee River Basin, it is possible that many similar episodes go unreported as well.

The number of relatively rare and threatened aquatic species in the Upper Tennessee River Basin make accidental spills and releases a particular concern in parts of the basin. Habitat modifications resulting from human activities, such as impoundments and pollution, have restricted the greatest numbers and variety of aquatic fauna to only a few tributaries. In addition, impoundments have effectively separated once contiguous biological communities into smaller, more vulnerable subunits.

The upper Clinch and Powell watersheds are home to the most diverse fish and mussel fauna in the Upper Tennessee River Basin. These two subbasins are effectively separated from biological interaction, however, by Norris Lake and are very vulnerable to coal-fine spills from numerous active and abandoned mining sites in their headwaters. At least five coal-fine spills occurred during the 1995–99 study period (G. Heffinger, U.S. Fish and Wildlife Service, written commun., April 17, 2000).

Mussel species generally are of the greatest concern because of their lack of mobility and the longer times typically required for populations to recover. For example, data collected in 1971 following a very large 1967 fly-ash spill in the Clinch River found that fish and aquatic insects were reestablished relatively quickly. Mussels, however, have yet to recolonize the 9- to 10-mile reach directly downstream from the spill site.