Tools to Indicate Inappropriate Sources of Contaminants to Storm Drainage Systems

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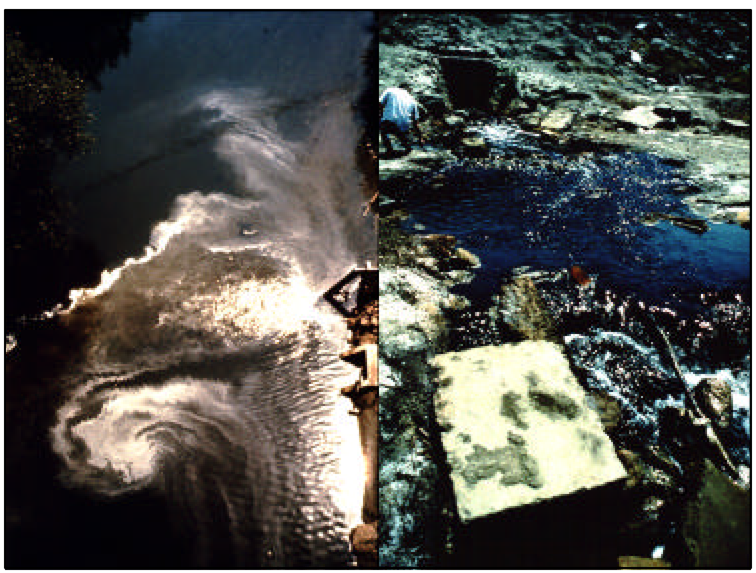
SCHOOL BUS



Summary

- Previously developed methods used to identify sources of contaminants in storm drainage systems.
- Reviewed emerging techniques that may also be useful.
- The original methods, along with selected new procedures, were tested using almost 700 stormwater samples collected from telecommunication manholes from throughout the U.S.

Development and Testing of Methods for Interpreting Field Screening Data

- Physical indicators of contamination
- Detergents as indicators of contamination
- Flow chart for most significant flow component identification
- Chemical mass balance at outfall to quantify flow sources

Previously Developed Approach: Tracers to Identify Sources of Contamination

- Purpose: Identify toxic/ pathogenic sources of water, typically raw sewage/industrial wastewaters, discharged to storm drain system.
- Ideal tracer to identify major flow sources has the following characteristics:
  - Significant difference in concentrations between possible pollutant sources;
  - Small variations in concentrations within each likely pollutant source category;
  - Conservative behavior (i.e., no significant concentration change due to physical, chemical or biological processes);
  - Ease of measurement with adequate detection limits, good sensitivity and repeatability.

Source Area Chlorine Values

	Shallow Groundwater	Sewage	Tap water	Irrigation water
	0.04	0.01	1.50	0.03
	0.00	0.03	1.26	0.05
	0.08	0.03	1.24	0.08
	0.02	0.01	0.40	0.02
	0.00	0.02	1.38	0.03
	0.01	0.00	0.19	0.00
	Cont.	Cont.	Cont.	Cont.
Average	0.02	0.01	0.88	0.03
Std. dev.	0.03	0.02	0.60	0.03
Coef. of var.	1.50	2.00	0.68	1.00

Source Area Potassium Values

	Tap Water	Sewage	Car Wash
	1.48	5.25	22.0
	1.55	4.79	22.0
	1.46	3.44	78.4
	1.50	3.09	40.7
	1.66	4.51	47.7
	1.58	5.88	35.4
	Cont.	Cont.	Cont.
Average	1.55	5.97	42.7
Standard dev.	0.06	1.36	15.9
Coef. of variation	0.04	0.23	0.37

Source Area Ammonia/Potassium Ratios

Source of Water	NH_3/K mean	NH_3/K range
Shallow groundwater	0.16	0.05 – 0.41
Springs	0.01	0.00 – 0.07
Household tap	0.02	0.01 – 0.03
Landscaping runoff	0.07	0.03 – 0.17
Laundry	0.24	0.18 – 0.34
Car Washes	0.01	0.00 – 0.01
Radiator flushing	0.01	0.00 – 0.04
Plating operations	0.16	0.00 – 0.65
Sewage	1.69	0.97 – 2.89
Septic tank discharge	5.18	3.19 – 15.4

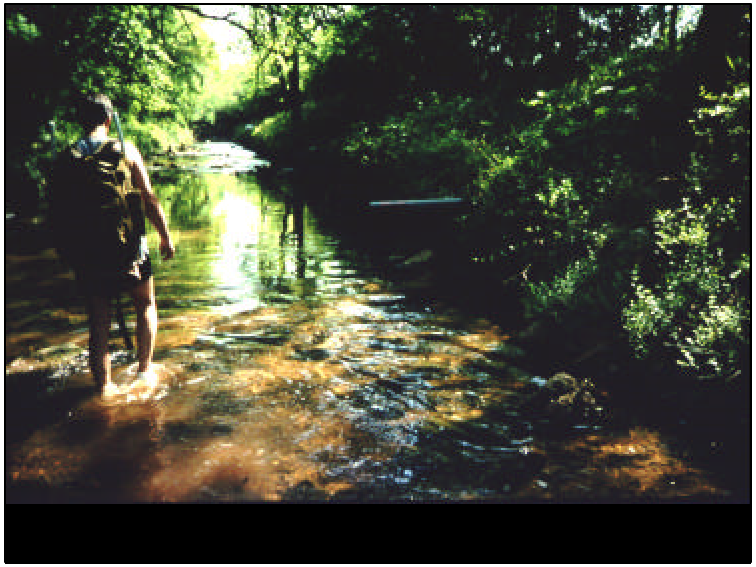
Detergents to Indicate Contamination

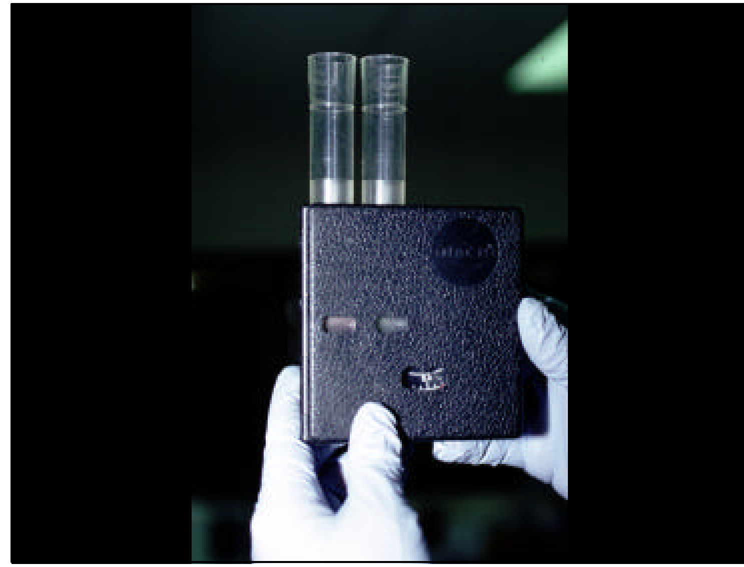
Water Source	Detergent, mean (mg/L)	Detergent, range (mg/L)
Shallow groundwater	0.00	All < 0.00
Springs	0.00	All < 0.00
Household tap	0.00	All < 0.00
Landscape runoff	0.00	All < 0.00
Sewage	1.50	0.48 – 4.40
Septic tank discharge	3.27	0.15 – 12.00
Laundry	26.9	17.0 – 37.0
Car washes	49.0	38.0 – 56.7
Radiator flushing	15.0	13.5 – 18.3
Plating wastes	6.81	1.45 – 15.0

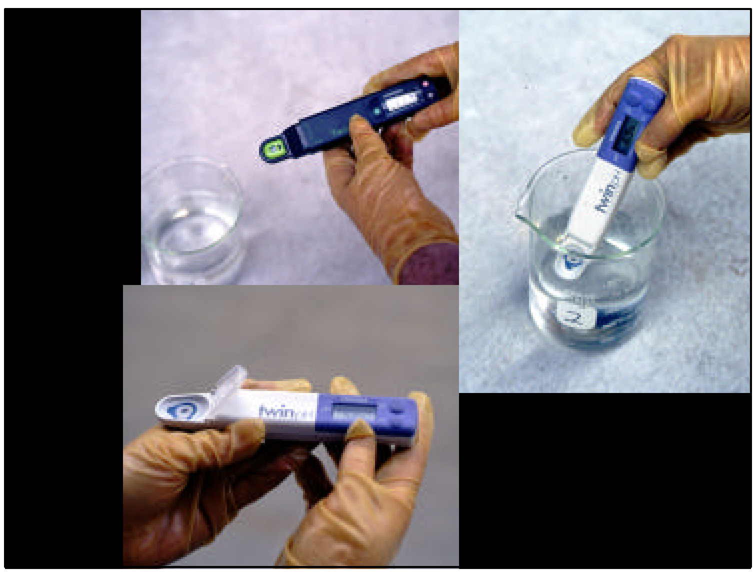
Field Screening Method Verification

- Completely developed 4,500 acre urban watershed (Village Creek) in Birmingham, AL.
- 83 stormwater outfalls, with samples collected during at least 8 visits over 30 months.

	Outfalls from large subwatersheds	Outfalls from creek-side businesses	Total
Always flowing	17%	11%	16%
Intermittently flowing	9%	33%	14%
Always dry	74%	56%	70%



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Results of Field Verification Tests

Drainage areas for 10 outfalls were studied in detail in order to verify actual sources of contamination.

Data analysis method	Information obtained	Percentage of false negatives	Percentage of false positives
Physical indicators	Some contaminated outfalls missed and some uncontaminated outfalls falsely accused.	20%	10%
Detergents	All contaminated outfalls correctly identified!	0	0
Flow chart	All major contaminating sources identified correctly!	0	0
Chemical mass balance	All contaminated outfalls correctly identified, and most sources correctly identified and reasonably well quantified!	0	0

Verification of Inappropriate Sources in Drainage System

- Know what to look for based on outfall screening surveys
- Flow and chemical analyses in upstream drainage system to locate affected section/reach
- Video evaluations to locate specific entry points
- Dye tracer studies of candidate connections

Developing Technologies for Inappropriate Discharge Investigations

- Fecal Sterol Compounds
- Caffeine
- Detergent Compounds
- Pharmaceuticals
- DNA Analyses
- Stable Isotope Analyses

Coprostanol and Other Fecal Sterol Compounds

What they are:

- **Fecal sterols, such as coprostanol and epicoprostanol, analyzed using GC/MSD.**
- **Discharged in feces from carnivores.**

Coprostanol and Other Fecal Sterol Compounds

Where successfully used to trace sanitary sewage:

- **New York bight sediments for mapping sewage sludge disposal areas (Eaganhouse, *et al*. 1988).**
- **Particulates and sediments collected from coastal areas in Spain and Cuba (Grimalt, *et al*. 1990).**
- **Sediment cores from Santa Monica Basin, CA, and effluent from two local municipal wastewater discharges (Venkatesan and Kaplan 1990).**

Coprostanol and Other Fecal Sterol Compounds

Where successfully used to trace sanitary sewage:

- Sediments and mussels in Venice, Italy (Sherwin, *et al*. 1993).
- CSOs, stormwater, and receiving waters in King County, WA, along with caffeine and heavy metals (Shuman and Strand 1996).
- Stormwater and the sea-surface microlayer (Nichols, *et al.* 1996).

Coprostanol and Other Fecal Sterol Compounds

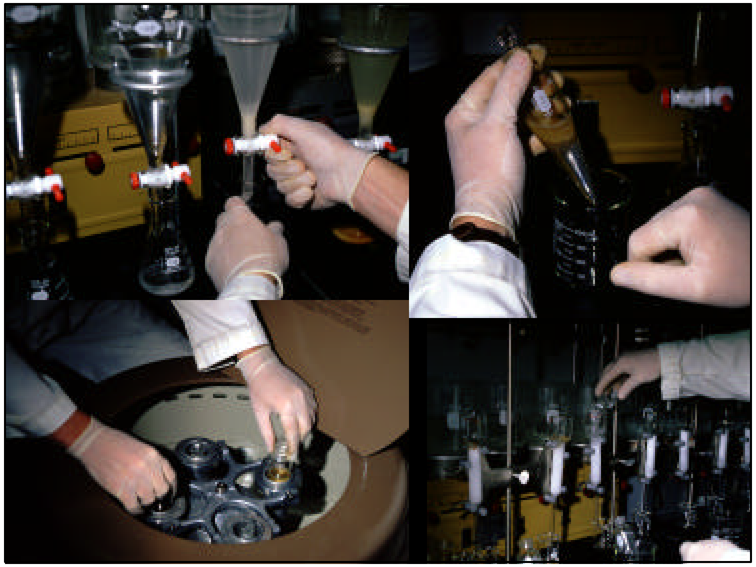
Where successfully used to trace sanitary sewage:

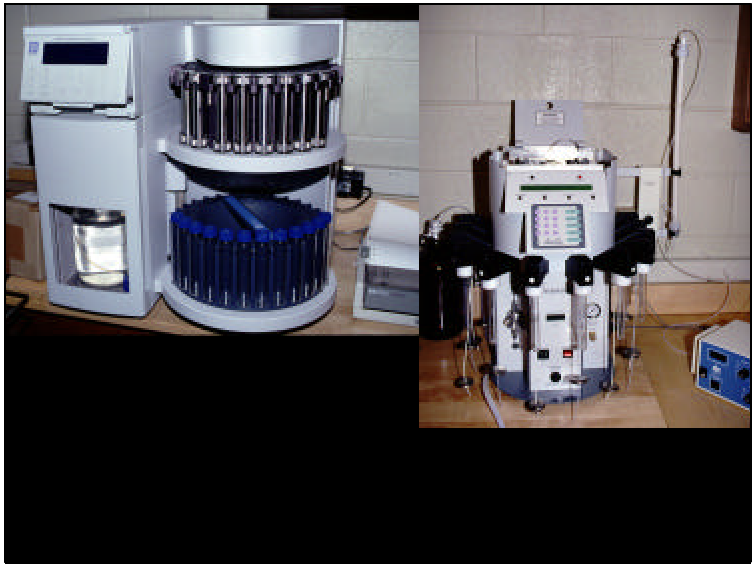
- Estrogenic chemicals recognized using TIE approach and then specifically identified with GC/MSD (Routledge, *et al.* 1998; Desbrow, *et al*. 1998).
- Water, particulate, and sediment samples near the Cocoa, FL, domestic wastewater treatment plant analyzed for saturated hydrocarbons with 16-18 carbons, and saturated hydrocarbons with 16-21 carbons, in addition to coprostanol (Holm, *et al.* 1990).

Coprostanol and Other Fecal Sterol Compounds

Problems:

- Not specific to humans.
- Long lasting (confuses recent contamination with historical or intermittent contamination).
- Commonly available analytical methods are expensive and time consuming, but not very sensitive.
- Best used for particulate-bound material and sediments, not water column measurements.





Coprostanol and Other Fecal Sterol Compounds

Suggestions for better use for tracing inappropriate discharges:

- **Utilize more sensitive instrumentation (research grade MS).**
- **Concentrate particulates from water column.**
- **Use in conjunction with other indicators (such as total sterols, some saturated hydrocarbons, caffeine, and heavy metals) to separate background levels and for plume tracing.**

Caffeine

What it is:

- Caffeine has been used as an indicator of sewage contamination by several investigators (caffeine content of regular coffee about 700 mg/L).

Where successfully used to trace sanitary sewage:

- Caffeine (representing dissolved CSO constituents) and coprostanol (representing particulate bound CSO constituents), along with heavy metals and conventional analyses (representing stormwater), used to identify contributions to the Duwamish River and Elliott Bay, King County, WA (Shuman and Strand 1996).
- Caffeine (7 μg/L) found in Boston Harbor *US Water News* (1998).

Caffeine

Problems:

- Very low concentrations.
- Requires expensive and time consuming analytical methods.

Suggestions for better use for tracing inappropriate discharges:

- Possible confirmation for the presence of sewage, when used in conjunction with other tracers.

Detergent Compounds

What they are:

- Detergents (using MBAS tests) most successful individual tracer to indicate contaminated water in storm sewer dry-weather flows (Pitt, *et al*. 1993; Lalor 1994).
- Linear alkylbenzene sulphonates (LAS) and linear alkylbenzenes (LAB) have been used to indicate sewage.
- LAS can be measured using HPLC with fluorescent detection (after solid phase extraction) to very low levels.

Detergent Compounds

What they are:

- Fujita, *et al*. (1998) developed an efficient enzyme-linked immunosorbent assay (ELISA) for detecting LAS at levels from 20 to 500 μg/L.
- Boron, a major historical ingredient of laundry chemicals, can also be potentially used.

Detergent Compounds

Where has it been successfully used to trace sanitary sewage:

- Sanitary sewage traced using LAS from synthetic surfactants, which degrade rapidly (Terzic and Ahel 1993).
- Complete biodegradation of LAS requires several days (Fujita, *et al*. 1998).
- Sanitary sewage tracing using nonionic detergents, which do not degrade rapidly (Zoller, *et al*. 1991).
- Distribution and fate of LAS (having carbon ratios of C12 and C13 compared to C10 and C11, plus ratios of phosphates to MBAS and the internal to external isomer ratio) in urban stream in Korea (Chung, *et al*. 1995).

Detergent Compounds

Where has it been successfully used to trace sanitary sewage:

- LAS was strongly sorbed to particulates and had a significant vertical stratification (much higher in surface layer) in the Bay of Cádiz off the southwest of Spain (González-Mazo, *et al.* 1998).
- LAB was measured, along with polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons (AHs) to indicate the relative pollutant contributions of wastewater from sanitary sewage, nonpoint sources, and hydrocarbon combustion sources off San Diego (Zeng and Vista 1997; Zeng, *et al*. 1997).
- The type of fluorescent whitening agents (FWAs) found can be used to distinguish laundry, textile finishing, and paper production wastewater sources (Poiger, *et al.* 1996; Kramer, *et al.* 1996).

Detergent Compounds

Problems:

- Simple colorimetric detergent methods use hazardous organic solvents (chloroform or benzene) as an extraction step.
- LAS, etc., measurements commonly done by HPLC, a relatively expensive and time consuming method

Detergent Compounds

Suggestions for better use for tracing inappropriate discharges:

- Boron has the advantage of being relatively easy to analyze, while LAS requires chromatographic equipment.
- Fluorescent analyses can perform very sensitive measurements of detergent “brighteners,” can also be done rapidly in the field in real time, but require expensive instrument.

Pharmaceuticals

What they are:

- Various pharmaceutical substances have been found in receiving waters and in public water supplies originating from sanitary sewage discharges and these anthropogenic substances have been suggested as a sewage tracer.

Where has it been successfully used to trace sanitary sewage:

- Numerous pharmaceutical substances (such as clofibric acid, aspirin, and ibuprofen) in sewage effluents and in receiving waters in Berlin (Halling-Sørensen, *et al.* 1998).

Pharmaceuticals

Problems:

- Expensive and time consuming laboratory analyses required.
- FDA guidance mandates that the maximum concentration of a pharmaceutical substance, or its active metabolites, at the point of entry into the aquatic environment be less than 1 mg/L (Hun 1998).

Suggestions for better use for tracing inappropriate discharges:

- Possible use for confirmation in conjunction with other sewage tracers that are easier to detect.

DNA Analyses

What they are:

- DNA patterns in fecal coliforms vary among organisms, and it is relatively straight-forward to distinguish between human and non-human sources of bacteria.
- Several investigations have cataloged the DNA of *E. coli* to identify their source in water. This rapidly emerging technique seems to have great promise in addressing a number of nonpoint source water pollution issues (Kratch 1997).

DNA Analyses

Where successfully used to trace sanitary sewage:

- Virginia Polytechnic Institute and State University using DNA of *E. coli* identified bird population as source of bacteria contamination of a shellfish bed in Chesapeake Bay (instead of suspected failing septic tanks).
- Wright State University researchers have used randomly amplified polymorphic DNA polymerase chain reaction (RAPD-PCR) techniques on populations of snails, pill bugs, violets, spiders, earthworms, herring, and some benthic macroinvertebrates (Krane, *et al*. 1999).

DNA Analyses

Problems:

- Currently a highly specialized procedure, but can be inexpensive.

Suggestions for better use for tracing inappropriate discharges:

- May be a significant tool in watershed management.
- Procedures need to be simplified for more common use.

Stable Isotope Analyses

What they are:

- Naturally occurring stable isotopes of oxygen and hydrogen can be used to identify waters originating from different geographical sources.
- Depletion of heavy isotopes occur with rain during water vapor transport from equatorial regions to higher latitudes.
- Stable isotopes have been recommended as an efficient method to identify illicit connections to storm sewerage.
- Ma and Spalding (1996) used stable isotopes to investigate recharge of groundwaters by surface waters.

Stable Isotope Analyses

Where has it been successfully used to trace water sources:

- Sources of arsenic contaminated sediments in the Hylebos Waterway in Tacoma, WA, determined through dating of sediments using ^{137}Cs and conducting optical and electron microscopic studies (Davis, *et al*. 1997).
- Differences in origin between the domestic water supply, local surface waters, and the local groundwater was used to identify sanitary sewage contributions to the separate storm sewerage in Detroit (Sangal, *et al.* 1996).

Stable Isotope Analyses

Where has it been successfully used to trace water sources:

- Rieley, *et al*. (1997) used stable isotopes of carbon in marine organisms to distinguish the primary source of carbon being consumed (sewage sludge vs. natural carbon sources) in two deep sea sewage sludge disposal areas.
- Platte River water is heavily influenced by snowmelt from the Rocky Mountains, while groundwater in parts of Nebraska is mainly contributed from the Gulf air stream. The origins of these waters are sufficiently different and allow good measurements of the recharge rate of the surface water to the groundwater (Ma and Spalding 1996).

Stable Isotope Analyses

Problems:

- Few laboratories can analyze stable isotopes, requiring shipping and a long wait for the analytical results. Sangal, *et al*. (1995) used Geochron Laboratories, in Cambridge, Massachusetts.
- Stable isotope analyses would not be able to distinguish between sanitary sewage, industrial discharges, washwaters, and domestic water, as they generally all have the same water origin, nor would it be possible to distinguish sewage from local groundwaters if the domestic water supply was from the same local aquifer.

Stable Isotope Analyses

Suggestions for better use for tracing inappropriate discharges:

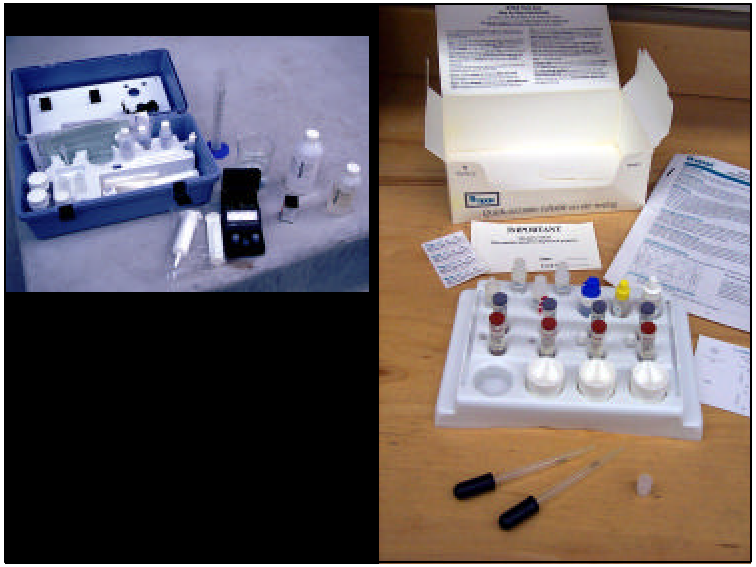
- This method works best for situations where the water supply is from a distant source and where separation of waters into separate flow components is not needed. It may be an excellent tool to study the effects of deep well injection of stormwater on deep aquifers.

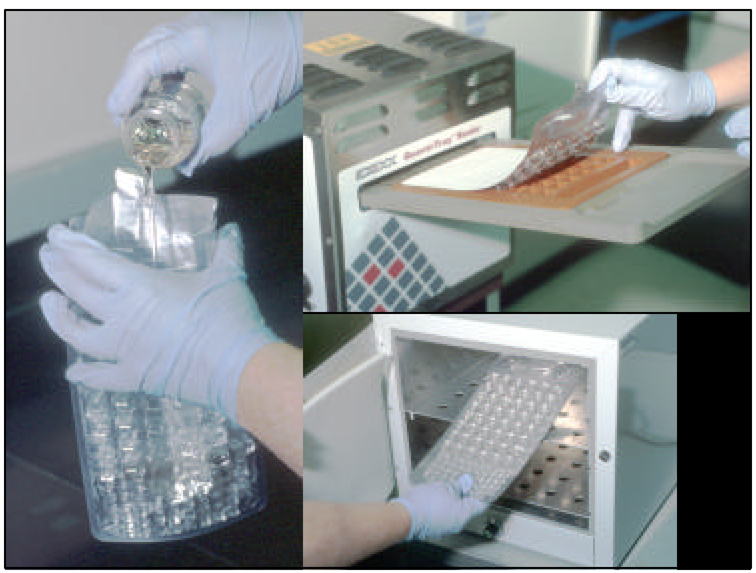
Recent Field Evaluations of Selected Indicator Parameters

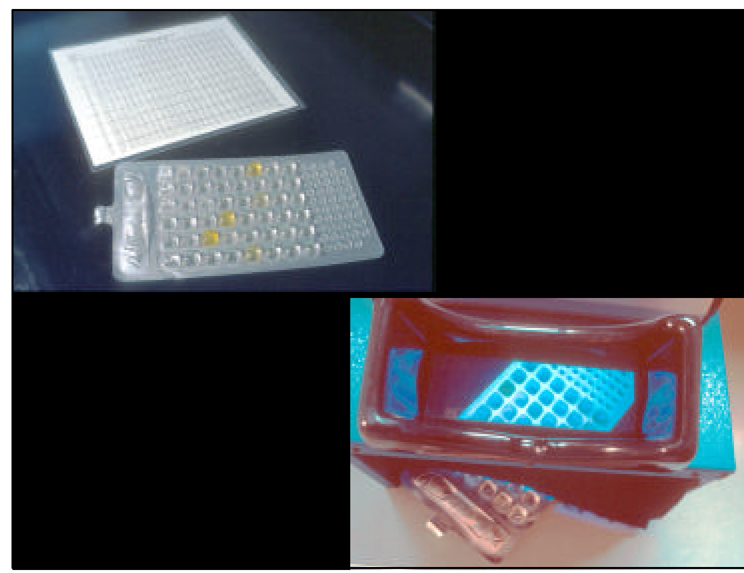
- Recent tests examined several of these potential tracers during a project characterizing stormwater that had collected in telecommunication manholes, funded by Telcordia (previously Bellcore), AT&T, and eight regional telephone companies.
- About 700 water samples were evaluated from throughout the US during all seasons.

Recent Field Evaluations of Selected Indicator Parameters

- **Numerous conventional constituents, plus major ions and toxicants, were measured, along with candidate tracers to indicate sewage contamination of this water.**
- **Boron, caffeine, coprostanol, *E. coli*, enterococci, fluorescence (using specific wavelengths for detergents), and a simple test for detergents were evaluated, along with the use of fluoride, ammonia, potassium, and obvious odors and color.**







Recent Field Evaluations of Selected Indicator Parameters

- Coprostanol found in about 25 percent of water samples (but in about 75% of the 350 sediment samples analyzed).
- Caffeine only found in <0.5% of the water samples.
- Elevated *E. coli* and enterococci concentrations observed in about 10% of the samples.

Recent Field Evaluations of Selected Indicator Parameters

- Strong sewage odors detected in about 10% of the water and sediment samples.
- About ten percent of the samples estimated to be contaminated with sanitary sewage using these methods, similar to what is expected for most stormwater systems.

Recent Laboratory Analyses of Potential Sewage Indicators

- Laboratory tests (funded by the University of New Orleans and EPA) examined sewage and laundry detergent samples.
- Boron poor indicator of sewage, possibly due to changes in modern laundry detergents' formulations.
- Fluorescence (using specialized "detergent whitener" filter sets) excellent indicator of sewage, but not very repeatable.
- UV absorbence at 228 nm excellent sewage indicator (very little background absorbence in local spring waters, but strong response factor with increasing sewage strengths).

Conclusions

- Previously evaluated methods still recommended as most useful procedure for identifying contamination of storm drainage systems, with possible addition of specific tests for *E. coli* and enterococci, plus UV absorbence at 228 nm.
- Most newly emerging methods require exotic equipment and unusual expertise and therefore not very available, especially at low cost and with fast turn-around times. For now, these emerging methods therefore more useful for special research projects than for routine screening of storm drainage systems.

New Research Project

- EPA 104(b)3 funded project for 2001 – 2003 to Center for Watershed Protection and the University of Alabama.
- Review Phase 1 cities experience in inappropriate discharge investigations
- Develop and test updated protocol
- Prepare guidance manual for Phase 2