Article 125

Feature Article from Watershed Protection Techniques. 3(1): 585 - 592

Use of Tracers to Identify Sources of Contamination in Dry Weather Flow

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For watershed managers, the location of potential sources of bacterial contamination is an important step in addressing urban water quality concerns. Inappropriate or illicit discharges may account for a significant amount of the pollutants discharged from storm sewerage systems (Pitt and McLean, 1986), including wastewater that can be an important source of fecal coliforms and pathogens. The development of screening techniques to detect these discharges is a valuable tool in the management of urban watersheds and in achieving water quality goals in receiving waters.

Urban stormwater runoff is often made up of not just the traditional precipitation that drains from city surfaces, but also waters from many other sources, including illicit and/or inappropriate flows into the storm drainage system. The EPA's Nationwide Urban Runoff Program (NURP) recognized the significance of the impacts of pollutants from inappropriate entries into urban storm sewerage (USEPA, 1983). The final NURP report concluded that the costs and complications involved with locating and eliminating such connections might pose a substantial problem in urban areas, but provides opportunities for dramatic improvement in the quality of urban stormwater discharges.

The following article contains a description of the procedures developed during research conducted on locating inappropriate discharges, especially the factors in selecting tracer indicators and identifying source waters. These methods can be used in any urban watershed, although the selection of specific tracers would vary depending on the likely source flows. An important premise for the development of this methodology was that the initial field screening effort would require minimal effort and expense, but would have little chance of missing a seriously contaminated outfall. This screening program would then be followed by a more in-depth investigation to better determine the significance and source of the non-stormwater pollutant discharges.

The screening approach is based on the identification and quantification of clean baseflow and the contaminated components during dry weather flows. If the relative amounts of potential components are known, then the importance of the dry weather discharge can be determined. As an example, if a dry weather flow is mostly uncontaminated groundwater, but contains 5% raw sanitary wastewater, it could still be an important source of pathogenic bacteria.

Tracers can be used to identify relatively low concentrations of important source flows in dry weather flows in storm drains. An ideal tracer should have the following characteristics:

- Significant difference in pollutant concentrations between possible source waters.
- Small variations in pollutant concentrations within each likely source water.
- Conservative behavior (i.e., concentrations do not change due to physical, chemical or biological processes).
- Ease of measurement with adequate detection limits, good sensitivity and repeatability.

Selection of Possible Tracers of Flow Sources

Table 1 compares the usefulness of candidate tracers to identify different potential non-stormwater flow sources. Generally speaking, natural and domestic waters should be uncontaminated. Sanitary sewage, septage, and industrial source waters can produce toxic or pathogenic conditions. Other source flows, such as wash and rinse waters and irrigation return flows, may cause nuisance conditions, or critically affect aquatic life. Field traces marked by a black circle can probably be used to identify the specific source flows by their presence. White circles indicate that the potential source flow probably will not contain the field tracer, and may help confirm the presence of the source by its absence.

Readers will note that bacteria, specifically the fecal coliform to fecal strep. bacteria ratio (FC/FS), has not been included as a candidate field tracer. Geldreich (1965) proposed this measures as a potential way to identify if a contamination source is human or nonhuman in origin (FC/FS > 4 = Human; <0.7 = Non-human). Die-off rates of the component bacteria, however, were found to vary over time and space, making this measure too undependable as tracer for sanitary sewage contamination (see Table 2). There may be some value in investigating specific bacteria types, biotypes or markers, but much care needs to be taken in the analysis and interpretation of the results.

Table 1: Candidate Field Tracers to Identify Flow Sources in Dry Weather Flow

Candidate Tracer	SOURCE WATER							
	Natural water	Potable water	Sanitary sewage	Septage water	Industrial water	Wash water	Rinse water	Irrigation water
Fluoride	❍	●	●	●	▲	●	●	●
Hardness change	❍	▲	●	●	▲	●	●	❍
Surfactants	❍	❍	●	❍	❍	●	●	❍
Florescence	❍	❍	●	●	❍	●	●	❍
Potassium	❍	❍	●	●	❍	❍	❍	❍
Ammonia	❍	❍	●	●	❍	❍	❍	❍
Odor	❍	❍	●	●	●	▲	❍	❍
Color	❍	❍	❍	❍	●	❍	❍	❍
Clarity	❍	❍	●	●	●	●	▲	❍
Floatables	❍	❍	●	❍	●	▲	▲	❍
Deposits and stains	❍	❍	●	❍	●	▲	▲	❍
Vegetation change	❍	❍	●	●	●	▲	❍	●
Structural damage	❍	❍	❍	❍	●	❍	❍	❍
Conductivity	❍	❍	●	●	●	▲	●	●
Temperature change	❍	❍	▲	❍	●	▲	▲	❍
pH	❍	❍	❍	❍	●	❍	❍	❍

Note: ❍ implies relatively low concentration; ● implies relatively high concentration; ▲ implies variable conditions

Tracer Characteristics of Local Source Flows

Table 3 summarizes tracer measurements for Birmingham, Alabama by Pitt *et al.* (1993). It can be viewed as a "library" that describes the tracer conditions for each potential source category. The table includes the median and coefficient of variation (COV) values for each tracer for each source category. The COV is the ratio of the standard deviation to the mean. A low COV value indicates a much smaller spread of data compared to a data set having a large COV value. It is apparent that some of the generalized tracer relationships shown on Table 1 did not always exist during the demonstration project, which stresses the need to obtain local data to develop a local source water library.

Good tracers have significantly different concentrations for each source water category. In addition, effective tracers also need low COV values within each flow category. The study indicated that the COV values were quite low for each category, with the exception of chlorine, which had much greater COV values. Chlorine is therefore not recommended as a quantitative tracer to estimate the flow components. Similar data must be collected in each community where these procedures are to be used. Recommended field observations include color, odor, clarity, presence of floatables and deposits, and rate of flow, in addition to the chemical tracers shown on Table 3.

Visual Field Screening

Visual parameters can indicate obvious problems at the stormwater outfall during field screening. These are important because they are the simplest and fastest method to identify grossly contaminated dry weather outfall flows. The visual examination of stormwater outfall characteristics includes unusual flow, odor, color, turbidity and other conditions. Table 4 presents a summary of visual indicators, along with narratives of the descriptors to be selected in the field.

Visual screening methods do not quantify flow components and can result in incorrect determinations (missing outfalls that have important levels of contamination). Visual screenings are most useful for detecting gross contamination. Only the most significant outfalls and drainage areas would therefore be recognized from this method. More intensive chemical tracing is needed to quantify the flow contributions and to identify the less obvious contaminated outfalls.

Table 2: Problems With Using Fecal Coliform to Fecal Strep Ratios to Identify Sources of Bacteria Contamination

- ***Shifting ratios***. Feachem (1975) reported that if bacteria is from human sources, the FC/FS ratio will start out high (> 4) and decrease over time. If non-human in origin, the ratio starts out low (<0.7) and increases over time. This shifting ratio problem undermines the usefulness of the FC/FS ratio as an indicator measure for bacteria contamination. Shifting is caused by:
  - ***Changing physical and chemical conditions.*** Ambient conditions, including water temperature, pH, organic nutrients and toxic metals, affect die-off rates of the component bacteria. (Geldreich, 1965; Geldreich and Kenner, 1969).
  - ***Aging***. Geldreich and Kenner (1969) caution that for the FC/FS ratio to useful, samples must be taken within 24 hours following the deposition of feces. For most sampling programs, the time it takes for bacteria to travel from its point of deposition to the location where sampling occurs is unknown (under both wet and dry weather scenarios). Consequently, it is impossible to determine "freshness" of the bacteria.
  - ***Sample location***. Because of the aging problem, samples must be taken relatively near where feces are deposited so that bacteria can be collected as "fresh" samples. Geldreich and Kenner (1969) recommended that samples be taken at wastewater outfalls, since this is where large numbers of fecal organisms recently discharge from warm-blooded animals would be located. Pitt (1983) found that samples collected in runoff source areas usually have the lowest FC/FS ratio in a catchment, followed by urban runoff, and finally the receiving water. In any case, however, there will likely be a mixing of fresh and "not-so-fresh" bacteria which undermines the meaning of the ratio.

Correlation tests were conducted to identify relationships between outfalls that were known to have severe contamination problems and the visual screening indicators (Lalor, 1994). Pearson correlation tests indicated that high turbidity and odors appeared to be the most useful physical indicators of contamination when contamination was defined by toxicity and the presence of detergents

High turbidity was noted in 74% of the contaminated source flow samples, but in only 5% of the uncontaminated source flow samples. This represented a 26% false negative rate (indication of no contamination when contamination actually exists). Noticeable odor was indicated in 67% of flow samples from contaminated sources, but in none of the flow samples from uncontaminated sources. This translates to 33% false negatives, but no false positives. Obvious odors identified included gasoline, oil, sanitary wastewater, industrial chemicals or detergents, decomposing organic wastes, etc.

A correlation was also found to exist between color and Microtox™ toxicity. Color is an important indicator of inappropriate industrial sources, but was also associated with some of the residential and commercial flow sources. Color was noted in 100% of the flow samples from contaminated sources, and in 40% of the flow samples from uncontaminated sources. This represents 40% false positives, but no false negatives. Finally, a 63% correlation between the presence of sediments (assessed as settleable solids in the collection bottles of these source samples) and Microtox™ toxicity was also found. Sediments were noted in 34% of the samples from contaminated sources and in none of the samples from uncontaminated sources.

False negatives are more of a concern than a reasonable number of false positives when working with a screening methodology, since they are primarily used to direct further, more detailed investigations. False positives would be discarded after further investigation, but a false negative during a screening investigation results in the dismissal of a problem outfall for at least the near future. Missed contributors to stream contamination may result in unsatisfactory in-stream results following the application of costly corrective measures elsewhere.

Detergents as Indicators of Contamination

Lalor (1994) found that samples from dry-weather flow sources could be correctly classified as clean or contaminated based only on the measured value of detergent levels. Research showed that detergents can be used to distinguish between clean and contaminated outfalls simply by their presence or absence, using a detection limit of 0.06 mg/L. Nearly all samples analyzed from contaminated sources contained detergents in excess of this amount. No clean source water samples were found to contain detergents. Contaminated sources would be detected in mixtures with uncontaminated waters if they made up at least 10% of the mixture.

Flow Chart for Most Significant Flow Component Identification

The flow chart in Figure 1 describes an analysis strategy which may be used to identify the major component of dry-weather flow samples in residential and commercial areas. This method attempts to distinguish among four major groups of flow: (1) tap waters (including domestic tap water, irrigation water and rinse water), (2) natural waters (spring water and shallow ground water), (3) sanitary wastewaters (sanitary sewage and septic tank discharge), and (4) wash waters (commercial laundry waters, commercial car wash waters, radiator flushing wastes, and plating bath wastewaters). This method not only allows outfall flows to be categorized as contaminated or uncontaminated, but will allow outfalls carrying sanitary wastewaters to be identified. These outfalls should then receive highest priority for further investigation leading to source control. This flow chart was designed for use in residential and/or

Table 3: Chemical Tracer Concentrations Found in Birmingham, Alabama, Waters (Mean and Coefficient of Variation, Cov)

Candidate Tracer	Spring water	Treated potable water	Laundry wastewater	Sanitary wastewater	Septic tank effluent	Car wash water	Radiator flush water
Fluorescence (% scale)	6.8 0.43	4.6 0.08	1,020 0.12	250 0.20	430 0.23	1,200 0.11	22,000 0.04
Potassium (mg/L)	0.73 0.10	1.6 0.04	3.5 0.11	6.0 0.23	20 0.47	43 0.37	2,800 0.13
Ammonia (mg/L)	0.009 1.7	0.028 0.23	0.82 0.14	10 0.34	90 0.44	0.24 0.28	0.03 0.3
Ammonia/Potassium (ratio)	0.011 2.0	0.018 0.35	0.24 0.21	1.7 0.31	5.2 0.71	0.006 0.86	0.011 1.0
Fluoride (mg/L)	0.031 0.87	0.97 0.02	33 0.38	0.77 0.23	0.99 0.33	12 0.20	150 0.16
Toxicity (% light decrease after 25 minutes, I_{25})	<5 n/a	47 0.44	99.9 n/a	43 0.59	99.9 n/a	99.9 n/a	99.9 n/a
Surfactants (mg/L as MBAS)	<0.5 n/a	<0.5 n/a	27 0.25	1.5 0.82	3.1 1.5	49 0.11	15 0.11
Hardness (mg/L)	240 0.03	49 0.03	14 0.57	140 0.11	235 0.64	160 0.06	50 0.03
pH (pH units)	7.0 0.01	6.9 0.04	9.1 0.04	7.1 0.02	6.8 0.05	6.7 0.03	7.0 0.06
Color (color units)	<1 n/a	<1 n/a	47 0.27	38 0.55	59 0.41	220 0.35	3,000 0.02
Chlorine (mg/L)	0.003 1.6	0.88 0.68	0.40 0.26	0.014 1.4	0.013 1.0	0.070 1.1	0.03 0.52
Specific conductivity (µS/cm)	300 0.04	110 0.01	560 0.21	420 0.13	430 0.72	485 0.06	3,300 0.22
Number of samples	10	10	10	36	9	10	10

Note: The fluorescence values are direct measurements from a fluorometers having general purpose filters and lamps and at the least sensitive setting (number 1 aperture). The toxicity screening test results are expressed as the toxicity response noted after 25 minutes of exposure using an Azur Environmental Microtox™ unit which measures toxicity using the light output from phosfluorescent algae. The I_{25} values are the percentage light output decreases observed after 25 minutes of exposure to the sample, compared to a reference. Fresh potable water has a relatively high toxicity response because of the chlorine levels present. Dechlorinated, potable water has much smaller toxicity responses.

Table 4: Visual Tests of Possible Contaminants in Dry Weather Flows

Odor - Most strong odors, especially gasoline, oils, and solvents, are likely associated with high responses on the toxicity screening test. Typical obvious odors include: gasoline, oil, sanitary wastewater, industrial chemicals, decomposing organic wastes, etc.

- *Sewage*: Smell associated with stale sanitary wastewater, especially in pools near outfall.
- *Sulfur ("rotten eggs")*: Industries that discharge sulfide compounds or organics (meat packers, canneries, dairies, etc.).
- *Rancid-sour*: Food preparation facilities (restaurants, hotels, etc.).
- *Oil and gas*: petroleum refineries or many facilities associated with vehicle maintenance or petroleum product storage.

Color - Important indicator of inappropriate industrial sources. Industrial dry-weather discharges may be of any color, but dark colors, such as brown, gray, or black, are most common.

- *Yellow*: Chemical plants, textile and tanning plants.
- *Brown*: Meat packers, printing plants, metal works, stone and concrete, fertilizers, and petroleum refining facilities.
- *Green*: Chemical plants, textile facilities.
- *Red*: Meat packers.
- *Gray*: Dairies.

Turbidity - Often affected by the degree of gross contamination. Dry-weather industrial flows with moderate turbidity can be cloudy, while highly turbid flows can be opaque. High turbidity is often a characteristic of undiluted dry-weather industrial discharges.

- *Cloudy*: Sanitary wastewater, concrete or stone operations, fertilizer facilities, automotive dealers.
- *Opaque*: Food processors, lumber mills, metal operations, pigment plants.

Floatable matter - A contaminated flow may contain floating solids or liquids directly related to industrial or sanitary wastewater pollution. Floatables of industrial origin may include animal fats, spoiled food, oils, solvents, sawdust, foams, packing materials, or fuel.

- *Oil sheen*: Petroleum refineries or storage facilities and vehicle service facilities.
- *Sewage*: Sanitary wastewater.

Deposits and stains - Refer to any type of coating near the outfall and are usually of a dark color. Deposits and stains often will contain fragments of floatable substances. These situations are illustrated by the grayish-black deposits that contain fragments of animal flesh and hair which often are produced by leather tanneries, or the white crystalline powder which commonly coats outfalls due to nitrogenous fertilizer wastes.

- *Sediment*: Construction site erosion.
- *Oily*: petroleum refineries or storage facilities and vehicle service facilities.

Vegetation - Vegetation surrounding an outfall may show the effects of industrial pollutants. Decaying organic materials coming from various food product wastes would cause an increase in plant life, while the discharge of chemical dyes and inorganic pigments from textile mills could noticeably decrease vegetation. It is important not to confuse the adverse effects of high stormwater flows on vegetation with highly toxic dry-weather intermittent flows.

- *Excessive growth*: Food product facilities.
- *Inhibited growth*: High stormwater flows, beverage facilities, printing plants, metal product facilities, drug manufacturing, petroleum facilities, vehicle service facilities and automobile dealers.

Damage to Outfall Structures - Another readily visible indication of industrial contamination. Cracking, deterioration, and spalling of concrete or peeling of surface paint, occurring at an outfall are usually caused by severely contaminated discharges, usually of industrial origin. These contaminants are usually very acidic or basic in nature. Primary metal industries have a strong potential for causing outfall structural damage because their batch dumps are highly acidic. Poor construction, hydraulic scour, and old age may also adversely affect the condition of the outfall structure.

- *Concrete cracking*: Industrial flows
- *Concrete spalling*: Industrial flows
- *Peeling paint*: Industrial flows
- *Metal corrosion*: Industrial flows

commercial areas only, and investigations in industrial or industrial/commercial land use areas must be approached in an entirely different manner (EPA, 1983).

In residential and/or commercial areas, all outfalls should be located and examined. The first indicator is the presence or absence of dry-weather flow. If no dry-weather flow exists at an outfall, then indications of intermittent flows must be investigated. Specifically, stains, deposits, odors, unusual streamside vegetation conditions, and damage to outfall structures can all indicate intermittent non-stormwater flows. However, frequent visits to outfalls over long time periods, or the use of other monitoring techniques, may be needed to confirm that only stormwater flows occur. If intermittent flow is not indicated, then the outfall probably does not have a contaminated non-stormwater source.

If dry-weather flow exists at an outfall, then the flow should be sampled and tested for detergents. If detergents are not present, the flow is probably from a non-contaminated non-stormwater source. The lower limit of detection for detergent should be about 0.06 mg/L.

If detergents are not present, fluoride levels can be used to distinguish between flows with treated water sources and flows with natural sources in communities where water supplies are fluoridated and natural fluoride levels are low. In the absence of detergents, high fluoride levels would indicate a potable water line leak, irrigation water, or wash/rinse water. Low fluoride levels would indicate waters originating from springs or shallow groundwater. Based on the flow source samples tested in this research (Table 3), fluoride levels above 0.13 mg/L would most likely indicate that a tap water source was contributing to the dry-weather flow in the Birmingham, Alabama, study area.

If detergents are present, the flow is probably from a contaminated non-stormwater source, as indicated on Table 3. The ratio of ammonia to potassium can be used to indicate whether or not the source is sanitary wastewater. Ammonia/potassium ratios greater than 0.60 would indicate likely sanitary wastewater contamination. Ammonia/potassium ratios were above 0.9 for all septage and sewage samples collected in Birmingham (values ranged from 0.97 to 15.37, averaging 2.55). Ammonia/potassium ratios for all other samples containing detergents were below 0.7, ranging from 0.00 to 0.65, averaging 0.11.

Non-contaminated source water samples collected in Birmingham had ammonia/potassium ratios ranging from 0.00 to 0.41, with a mean value of 0.06 and a median value of 0.03. Using the mean values for non-contaminated samples (0.06) and sanitary wastewaters (2.55), flows comprised of mixtures containing at least 25% sanitary wastes with the remainder of the flow from uncontaminated sources would likely be identified as sanitary wastewaters using this method (Table 5). Flows containing smaller percent contributions from sanitary wastewaters might be identified as having a wash water source, but would not be identified as uncontaminated.

Summary

Tracers can be an important screening tool to detect bacterial and other contaminant sources to urban storm drainage systems. These tracers provide a method of identifying contaminated dry-weather flows in the field with a minimum of effort and expense. Those outfalls that are labeled as containing potential sources through this field screening would then receive a more intensive analysis to accurately pinpoint the specific sources contributing pollutant discharges. To be effective, a tracer needs to be easy to detect, not subject to substantial changes due to biological or chemical processes, and have concentration levels that vary significantly between possible pollutant sources but vary little within each source category.

Several visual criteria appear to function quite well as negative indicators of severe outfall contamination. These visual indicators provide a simple method of identifying grossly contaminated dry-weather outfall flows for field screening. The two most useful of these physical indicators are turbidity and odor. These two indicators had the highest correlation and smallest number of false negative results of all the parameters tested during examinations of contaminated and uncontaminated flows. Research also indicates that the presence of detergents is the most useful chemical indicator for distinguishing between contaminated and uncontaminated flows.

For the watershed manager, the detection of contaminant sources is a necessity in creating effective water quality plans. By providing a means of screening dry-weather flows for potential sources, tracers and negative indicators allow managers to direct source control planning measures in a more cost-effective and efficient way. The identification of the most significant components of flow permits watershed professionals to prioritize specific outfalls for more intensive investigation, thus providing a way to supply maximum treatment with limited staff and budget resources.

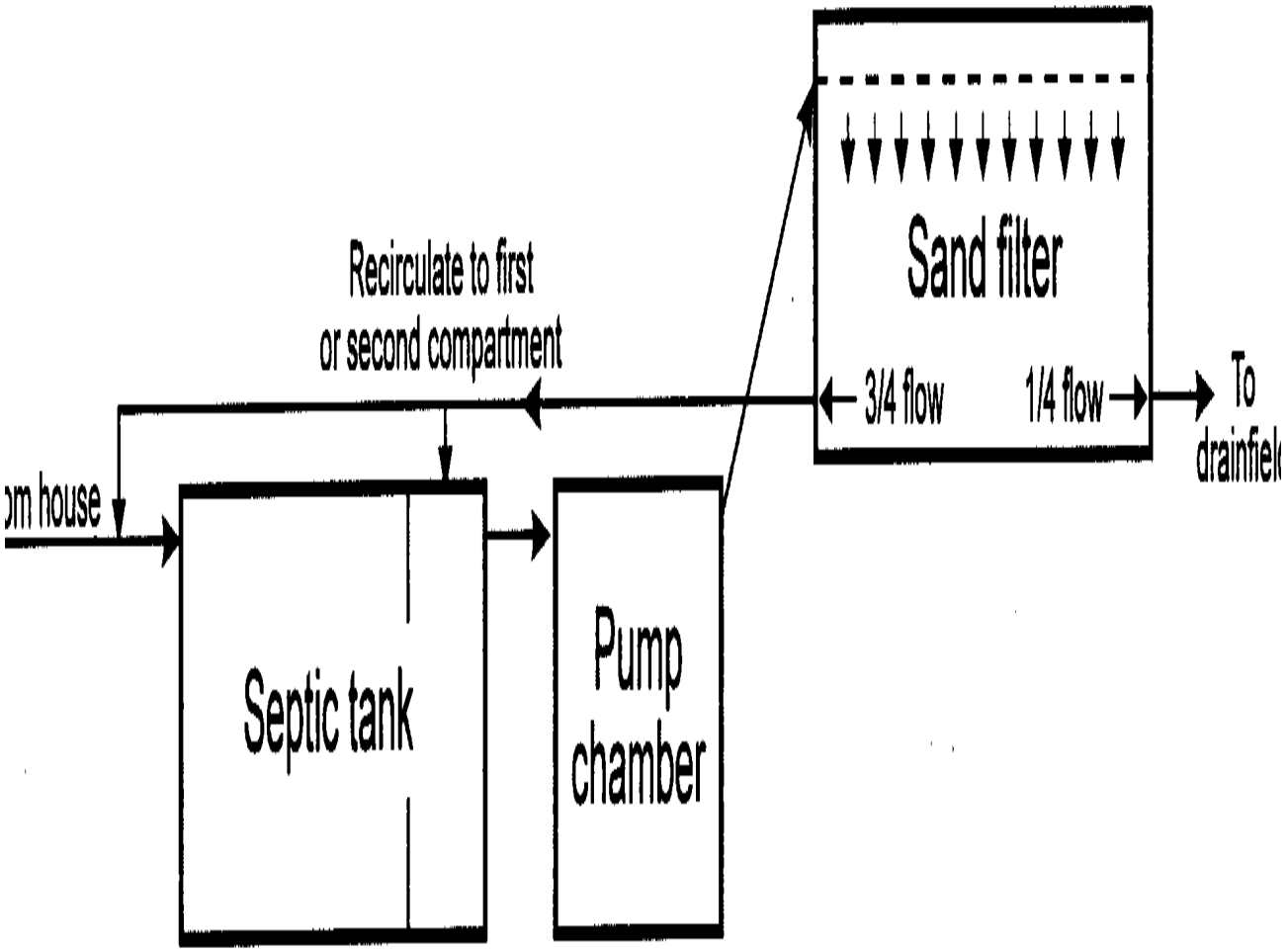

Figure 1: Flow Chart Methodology for Identifying Most Significant Flow Component (Lalor, 1993)

Table 5: Tracers for Identifying Treated Potable Water and Sanitary Wastewater

Treated Potable Water	Sanitary Wastewaters
• Variations in major ions or other chemical/ physical characteristics of the flow components may exist, depending upon whether the water supply sources are groundwater or surface water, and whether the sources are treated or not. Specific conductance may also serve as an indicator of the major water source. • Hardness may be used as an indicator if the potable water source and the baseflow are from different water sources. • If the concentration of chlorine is high, then a major leak of disinfected potable water is likely close to the outfall. Due to the rapid loss of chlorine in water (especially if some organic contamination is present) it is not a good parameter for quantifying the amount of treated potable water at an outfall. • Fluoride can often be used to separate treated potable water from untreated water sources. If the treated water has no fluoride added, or if the natural water has fluoride concentrations close to potable water fluoride concentrations, then fluoride may not be an appropriate indicator. If the drainage area has industries that have their own water supplies (quite rare for most urban drainage areas), then further investigations such as toxicity screening are needed to check for industrial non-stormwater discharges.	• Surfactant (detergent) analyses may be useful in determining the presence of sanitary wastewaters. However, the presence of surfactants could also indicate laundry wastewaters, car washing wastewater, or other industrial or commercial process waters. • The presence of fabric whiteners (as measured by fluorescence) may distinguish laundry and sanitary wastewaters. • Sanitary wastewaters often exhibit predictable trends during the day in flow and quality. In order to maximize the ability to detect direct sanitary wastewater, it would be best to survey the outfalls during periods of highest sanitary wastewater flows (mid to late morning hours). • The ratio of surfactants to ammonia or potassium concentrations may be an effective indicator. If the surfactant concentrations are high, but the ammonia and potassium concentrations are low, then the contaminated source may be laundry wastewaters. Conversely, if ammonia, potassium, and surfactant concentrations are all high, then sanitary wastewater is the likely source. Low surfactants concentrations and high potassium and ammonia concentrations may be characteristic of septic tank effluents, but must be confirmed by local characterization data for potential contaminating sources.

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