

Potential Chemical Indicators for Recreational Water Quality

Water Quality Program
Department of Environmental Health
County of San Diego

ABSTRACT

This general review provides information about potential chemical indicators of natural water contaminated by various pollution sources including wastewater. Basic background information about and measurement methods for caffeine and detergents are introduced briefly to the reader, with a focus on their distribution and concentration in water. Steroids, caffeine, and detergents are detected in many natural waters, but their contents are usually low. It appears that scientists are more interested in caffeine and steroids than other chemical indicators in recreational water. Caffeine and sterols seems to be related to sewage contamination, however, only a few reports have indicated a correlation between the concentration of pollutants (e.g., caffeine or sterols) and the level of bacterial indicators (e.g., *E. coli* or enterococcus) in water.

1. INTRODUCTION

A recent U.S. Geological Survey report is an informative resource for the potential chemical indicators of natural waters contaminated by wastewaters (Kolpin *et al.*, 2002). USGS used five newly developed analytical methods to measure concentrations of 95 organic wastewater contaminants (OWCs) in water samples from a network of 139 streams across 30 states during 1999 and 2000. The selection of sampling sites was biased toward streams susceptible to contamination (i.e. downstream of intense urbanization and livestock production). OWCs were prevalent during this study, being found in 80% of the streams sampled. The compounds detected represent a wide range of residential, industrial, and agricultural origins and uses with 82 of the 95 OWCs being found during this study. The most frequently detected compounds were **coprostanol** (fecal steroid), **cholesterol** (plant and animal steroid), ***N,N*-diethyltoluamide** (insect repellent), **caffeine** (stimulant), **triclosan** (antimicrobial disinfectant), **tri(2-chloroethyl)phosphate** (fire retardant), and **4-nonylphenol** (nonionic detergent metabolite). Measured concentrations for this study were generally low. The detection of multiple OWCs was common for this study, with a median of seven and as many as 38 OWCs being found in a given water sample.

In this brief review, we will focus on detergents and caffeine that could be potential chemical indicators for fecal contamination of recreational waters.

2. DETERGENTS

2.1. Background

Detergent, a cleaning agent, consists of a number of components, which is referred to as surface-active agents, or it's abbreviation surfactants. Using special active ingredients

that give detergents their unusual properties, detergents can be classified as cationic, non-ionic, amphoteric, and anionic.

The detergency of cationic detergents is in the cation, which can be a substantially sized molecule. Strong acids are used, such as hydrochloric acid to produce Cl anion as the “neutralizing” agent, although in essence, no neutralization takes place in the manufacturing process. Non-ionic detergents have no ionic constituents. They are “ionically” inert. Amphoteric Detergents contain both acidic and basic groups in their molecule, and can act as cationic or anionic detergents, depending on the pH of the solution, or as both cation and anion.

The detergency of the anionic detergent is vested in the anion. The anion is neutralized with an alkaline or basic material, to produce full detergency. Dealing with the common anionic detergents, we can place these detergents into the following main groupings:

1) Alkyl aryl sulfonates

Linear alkyl benzene sulfonate would be the highest quantity used of any detergent in the world, and the alkyl aryl sulfonates as a group would represent more than 40% of all detergent used. They are cheap to manufacture, very efficient, and the petroleum industry is a starting point for the base raw material. The most important alkyl aryl condensate is DDB (dodecyl benzene). DDB is sulfonated to DDBSA (dodecyl benzene sulfonic acid), and this in turn is used as a detergent base, where it is neutralized with a base, such as sodium hydroxide, monoethanolamine, triethanolamine, potassium hydroxide, etc.

2) Long Chain (Fatty) Alcohol Sulfates

Made from fatty alcohols, and sulfated, these are used extensively in laundry detergents. They can be produced with varying carbon chain lengths, but a C12 - C18 alcohol sulfate is a good choice.

3) Other groups

These include olefine sulfates and sulfonates, alpha olefine sulfates and sulfonates, sulfated monoglycerides, sulfated ethers, sulfosuccinates, alkane sulfonates, phosphate esters, alkyl isethionates, and sucrose esters.

The anionic detergents are used extensively in most detergent systems, such as dishwash liquids, laundry liquid detergents, laundry powdered detergents, car wash detergents, shampoo's etc.

2.2. Detergents in Water

Industrial facilities that use detergents to clean machinery can discharge anionic detergents into the water supply. Soap manufacturers also discharge detergents. Other sources are household cleaners and personal care products. Environmental analysts often include a determination of anionic detergents when assessing surface water pollution. Anionic surfactants were studied in river waters during the 1950s to 1970s because they caused extensive foaming. Consequently, they have been measured for a long enough period (since 1958 in the Mississippi River) to provide an example of long-term trends in

water quality. The foaming was the result of high concentrations of branched-chained alkylbenzenesulfonates (ABS) that were resistant to biological degradation during wastewater treatment and residence in rivers. Concentrations were frequently above the foaming threshold of about 0.5 milligram per liter (mg/L) (ppm). Dilution was the primary attenuation mechanism for ABS. To remedy the foaming problem, the surfactant-manufacturing industry modified the chemical structure of the molecule to a more biodegradable linear side chain (LAS) which resulted in a significant decrease in concentrations during wastewater treatment and residence in rivers (Swisher, 1964). From 1959 to 1965, ABS concentrations in the Illinois River ranged from 0.4 to 9 mg/L; from 1965 to 1966, ABS+LAS concentrations ranged from about 0.2 to 0.3 mg/L. After 1968, LAS concentrations decreased to less than 0.1 mg/L even though surfactant consumption increased by more than 30 percent. This example shows that it is possible to reverse certain pollution effects, in this case by the compulsory introduction of a more biodegradable material.

Although the switchover from ABS to LAS occurred between 1964 and 1968, the concentrations of anionic surfactants in the Mississippi River continued to rise until 1971 or 1972, probably the result of increasing consumption rates and population density. Following 1972, concentrations decreased to the levels observed today, reflecting improvements in wastewater-treatment plants as the result of the Federal Water Pollution Control Act of 1972, which required secondary treatment of sewage effluents. The continued decrease of surfactant concentrations is observed during 1991-92.

2.3. Detergent Measurement

Detergents (anionic surfactants) can be measured in the laboratory using EPA method 425.1 (1983), APHA method 5540 C (1995), or ASTM D2330-02 method.

This test method covers the determination of compounds that react with methylene blue to form a blue colored complex that is extracted into an immiscible organic solvent. They are referred to as methylene blue active substances (MBAS), and are calculated and reported in terms of the reference material, linear alkyl benzene sulfonate (LAS). This test method is applicable for determining MBAS in water and wastewater.

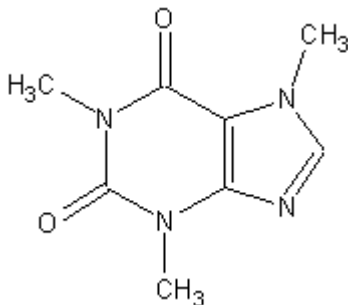
This test method is a simple, rapid, control procedure suitable for monitoring the effectiveness of a biodegradation or other linear alkyl benzene sulfonate (LAS) removal process. For a greater specificity, a pretreatment procedure for removal of interfering substances should be used. Data derived without the pretreatment procedure should be interpreted with care.

The ASTM D2330-02 method is applicable in the range from 0.03 to 1.5 ppm (mg/L) for a 100-mL sample. The EPA and APHA methods can be used to measure anionic detergents in the 0-3 ppm (mg/L) range.

3. CAFFEINE

3.1. Background

Caffeine has the following chemical structure: 3,7-Dihydro-1,3,7-trimethyl-1H-purine-2,6-dione (Figure).



It is a natural substance that is present in the leaves, seeds or fruits of more than sixty plant species worldwide. Many food and beverage products made with these ingredients naturally contain caffeine. In addition, caffeine is sometimes added to foods and beverages during the manufacturing process in order to enhance flavor or, in the case of medications, to enhance effectiveness.

3.2. Caffeine in the Environment

Caffeine may be released to the environment as a fugitive emission during its production or use and in wastewater effluent, landfill leachate, or incinerator fly ash. If released to soil, caffeine will display very high mobility. It will not volatilize from either moist or dry soil to the atmosphere. Limited data indicate that caffeine has the potential to biodegrade in soil. If release to water, caffeine will not volatilize from water to the atmosphere. It will not bioconcentrate in fish nor will it adsorb to sediment. Limited data indicate that caffeine has the potential to biodegrade in water. If released to the atmosphere, caffeine may undergo a gas-phase reaction with photochemically produced hydroxyl radicals at an estimated half-life of 2.5 hrs; however, caffeine will exist predominately adsorbed to particulates in the atmosphere, which may attenuate the rate of this process. Occupational exposure to caffeine may occur by inhalation of dust or dermal contact during its production, formulation or use. The general population will be exposed to caffeine by the ingestion of foods, medicines or consumer products in which it is contained.

Caffeine undergoes a complex metabolism in the human. Predominant metabolites include paraxanthine (1,7-dimethyl xanthine), theobromine (3,7-dimethyl xanthine) and theophylline (1,3-dimethyl xanthine), three monomethyl xanthines, and seven methylated uric acids. Only 3 percent of an administered caffeine dose is excreted unchanged making caffeine, and metabolites may therefore be potential indicators.

Caffeine is present in municipal wastewaters at levels up to 300 µg/L (ppb). Caffeine was detected in 1 of 10 secondary effluents taken at Illinois wastewater treatment plants, 1980. Caffeine was detected in 6 of 6 effluent samples obtained from 3 different publicly owned treatment works in NJ at concentrations of 3-20 ppb. It has been detected in 7 of 46 US industrial effluent samples. Caffeine has also been detected in Los Angeles County wastewater treatment plant effluent samples, 1980-81, at 40 ppb. It was detected in the

effluent from a municipal wastewater treatment plant in Vancouver, BC, Canada, at concentration of 16-292 ppb. Caffeine was identified in the leachate of a Barcelona, Spain, sanitary landfill. It was qualitatively detected in the fly ash samples collected from a municipal incinerator in Toronto, Canada. Found in primary domestic sewage plant effluent at 10-46 ppb.

Caffeine in natural waters ranges from sub-ppb to ppb levels. Caffeine was detected in 70% of 85 water samples at concentrations from 0.014 to 6 ppb (Koplin *et al.*, 2002). Caffeine was detected in 8 of 204 water samples obtained from waterway sites collected throughout the United States, 1975-6, at concentrations ranging from 1 to 6 ppb. It was detected in 4 of 13 samples taken from the Lake Michigan basin at concentrations ranging from 1-4 ppb. Caffeine was also detected in trace quantities in samples from the River Lee, UK, and the Delaware River, 1976. It was detected, but not quantified, in water samples from the lower Fox River, WI, 1976-77. The concentration of caffeine in the Rhine River, the Netherlands, was 0.1 ppb, 1979. Caffeine was detected in river water samples taken in the Kitakyushu area, Japan.

US EPA and other Federal and State agencies are interested in recreational water quality indicators other than bacteria. A recent USGS report summarized research results on chemical indicators and recreational water quality in Lake Erie. Preliminary results indicate that caffeine, 3-B coprostanol, pyrene, and fluoranthene are relevant to the concentration of *E. coli* in recreational water, but no solid correlation has been found.

Relations of sewage chemical indicators to log *E. coli* (Francy *et al.*, 2001)

	Analyte # Detects (n)	Pearson's r	Spearman's ?
Caffeine (USEPA)	19 (62)	0.402	0.445
Caffeine (USGS)	9 (14)	NS	0.739
Urobilin (USEPA)	2 (62)	NS	NS
Cholesterol	13 (14)	NS	NS
3-B coprostanol	2 (14)	0.656	0.564
NEPE01	7 (14)	NS	NS
NEPE02	0 (14)	-	-
Dichlorobenzene	2 (14)	NS	NS
Pyrene	7 (14)	0.659	0.605
Fluoranthene	7 (14)	0.582	0.590
Ethanol 2-butoxy-phosphate	5 (14)	NS	0.675

NS is not significant at alpha = 0.05

Caffeine has been detected in Boston Harbor seawater with concentrations ranging from 140 to 1600 ng L⁻¹, and in Massachusetts Bay seawater at concentrations from 5.2 to 71 ng L⁻¹ (Siegener and Chen, 2002). Sources of caffeine appear to be anthropogenic with higher concentrations in the seawater of Boston's inner harbor and in freshwater sources to the harbor. Charles River water and Deer Island sewage treatment plant effluent, the two major sources of freshwater to the harbor, contained 370 and 6700 ng L⁻¹ of caffeine,

respectively, in 1998. Sewage influent and effluent concentrations appear to be consistent with consumption estimates of caffeinated beverages for the Boston area and total organic carbon removal targets for treated sewage. Caffeine was inversely correlated to salinity in a transect from the mouth of Boston Harbor to Stellwagen Basin, indicating it may be a useful chemical tracer of anthropogenic inputs to marine systems.

3.3. Caffeine Measurement

EPA Method 553 can be used to measure caffeine. Analysis is based upon the extraction - high performance liquid chromatography (HPLC) method.

Organic compound, analytes and surrogates are extracted from 1 L of water sample by liquid-liquid extraction (LLE) with methylene chloride or by passing 1 L of sample water through a cartridge or disk containing a solid inorganic matrix coated with a chemically bonded C18 organic phase or a neutral polystyrene/divinylbenzene polymer (liquid-solid extraction, LSE). If LLE is used, the analytes are concentrated in methanol by evaporation of the methylene chloride and addition of methanol (solvent exchange). If LSE is used, the analytes are eluted from the LSE cartridge or disk with a small quantity of methanol and concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated methanol solution into a high performance liquid chromatograph (HPLC) containing a reverse phase HPLC column and interfaced to a mass spectrometer (MS) with a particle beam (PB) interface. Compounds eluting from the HPLC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by the same compound in a calibration standard (external standard). Surrogate analytes, whose concentrations are known in every sample, are measured with the same external standard calibration procedure. An optional isotope dilution procedure is included for samples that contain interfering matrix or coeluting compounds.

4. References

Burkhardt, M.R. et al. 1999. Determination of submicrogram-per liter concentrations of caffeine in surface water and groundwater samples by solid-phase extraction and liquid chromatography. *Journal of AOAC International*. 82:161-166.

Francy, Donna, Rob Darner, Amie Gifford, and Don Stoeckel. 2001. Evaluating water quality at public beaches for the protection of public health. Great Lakes Beach Conference - 2001 Proceedings. Chicago, February 6-8, 2001.
<http://www.epa.gov/waterscience/beaches/meeting.html>

Halling-Sorensen, B. et al. 1998. Occurrence, fate and effects of pharmaceutical substances in the environment – a review. *Chemosphere*. 36:357-393.

Kolpin, Dana W., Edward T. Furlong, Michael T. Meyer, E. Michael Thurman, Steven D. Zaugg, Larry B. Barber, and Herbert T. Buxton. 2002. Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999-2000: A National Reconnaissance. *Environ. Sci. Technol.*, 36 (6), 1202 – 1211.

Lu, J.F. et al. 1998. Simultaneous determination of five caffeine metabolites in human urine with reverse phase HPLC method. *Analytical Letters*. 31:613-620.

McNeill, A.R. 1992. Recreational Water Quality. pp. 193-216. In Connell, D.W. and D.W. Hawker (eds.). *Pollution in Tropical Aquatic Systems*. CRC Press, Boca Raton, FL.

Meade, R.H. 1995. Contaminants in the Mississippi River. Circular 1133. U.S. Geological Survey, Denver, CO.

Raloff, J. 1998. Drugged Waters. *Science News Online*. March 21, 1998. (www.sciencenews.org/sn_arc98/3_21_98/bob1.htm)

Rogers, I.H., Birtwell, I.K., and Kruzynski, G.M. 1986. *Can. J. Water Pollut. Res.* 21, 187-204. Spectrum Laboratories. 1998. Caffeine Fact Sheet. (www.speclab.com/compound/c58082)

Siegener, R. and R.F. Chen. 2002. Caffeine in Boston Harbor seawater. *Marine Pollution Bulletin* 44:383–387.

US EPA. 1996. Method 8321A Solvent Extractable nonvolatile compounds by high performance liquid chromatography/thermospray/mass spectrometry (HPLC/TS/MS) or ultraviolet (UV) detection.