

# National Water Research Institute

Independent Advisory Panel Final Report

## **BDOC as a Performance Measure for Organics Removal in Groundwater Recharge of Recycled Water**

*Prepared for:*

**CALIFORNIA DEPARTMENT OF PUBLIC HEALTH**





**NATIONAL WATER RESEARCH INSTITUTE**

**Final Report**

*of the*

**Independent Advisory Panel**

*for the*

**California Department of Public Health**

**BDOC as a Performance Measure for Organics  
Removal in Groundwater Recharge of Recycled Water**

September 26, 2012  
Fountain Valley, California

## **ABOUT NWRI**

A 501c3 nonprofit organization, the National Water Research Institute (NWRI) was founded in 1991 by a group of California water agencies in partnership with the Joan Irvine Smith and Athalie R. Clarke Foundation to promote the protection, maintenance, and restoration of water supplies and to protect public health and improve the environment. NWRI's member agencies include Inland Empire Utilities Agency, Irvine Ranch Water District, Los Angeles Department of Water and Power, Orange County Sanitation District, Orange County Water District, and West Basin Municipal Water District.

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## **DISCLAIMER**

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## 1. PURPOSE OF THE PANEL

### 1.1. Explanation of the Issue

In 2011, the California Department of Public Health (CDPH) requested that the National Water Research Institute (NWRI) of Fountain Valley, California, form an Independent Advisory Panel (Panel) to provide expert peer review on whether biodegradable dissolved organic carbon (BDOC) is a suitable performance measure to assess the removal of unregulated wastewater-derived organics from recycled water used for groundwater recharge via surface spreading. The use of BDOC as a performance measure, if found to be suitable, could provide an alternative to the currently considered use of total organic carbon (TOC) as a performance measure.

CDPH has prepared Draft Groundwater Recharge Reuse Regulations (draft regulations) for the recharge of groundwater with recycled water. The most current – not published – version of the draft regulations is dated November 21, 2011<sup>1</sup>. Section 60320.116 in the draft regulations establishes the provisions for groundwater recharge reuse projects to establish the Recycled Water Contribution (RWC) based on TOC, where TOC is used as a surrogate for unregulated organic chemicals. As currently drafted, the draft regulations specify that:

$$TOC_{max} = \frac{0.5 \text{ mg/L}}{RWC}, \quad (1)$$

Where, RWC is the proposed maximum RWC.

Compliance is determined in the recycled water or in the recycled water after soil-aquifer treatment (SAT) not influenced by dilution water (see Section 60320.114).

SAT is a subsurface treatment process that is composed of two components: 1) primarily vertical movement of recycled water from a surface spreading basin through the vadose zone, and 2) primarily horizontal movement through the saturated zone. The extent of both zones to the point of water abstraction for a given project can vary widely. Attenuation of contaminants does occur in both components of a SAT system; however, the majority of BDOC is usually removed in the initial phase of infiltration.

Existing water quality regulations for waste discharges and drinking water supplies do not address all chemicals that may be present in wastewater. The measurement of TOC in recycled water is currently used to assess the effectiveness of the treatment process in removing the bulk of organic chemicals. The use of alternatives to TOC in determining the RWC is allowed in Section 60320.118(h) of the draft regulations, pending CDPH approval, if the chemical(s) used in lieu of TOC can:

- Be quantifiable in the wastewater, recycled municipal wastewater, groundwater, and throughout the treatment process, and;

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<sup>1</sup>CDPH (2011). *Groundwater Recharge Draft Regulations*. November 21, 2011. Sacramento, CA.

- Have identifiable treatment performance standards as protective of public health as the TOC standards.

The use of TOC as a surrogate for unregulated organics of wastewater origin has a long history with regard to the development of groundwater recharge regulations and in establishing RWCs for permitted groundwater recharge project in California. However, the removal of TOC via wastewater treatment or SAT does not necessarily relate to the removal of specific organic chemicals of wastewater origin that are of health concern. The TOC approach also has a limiting effect on the RWC calculation and the allowable amount of recycled water that can be used for a project inasmuch as there may be some recalcitrant TOC (i.e., humic substances) that is primarily derived from the drinking water source that ultimately becomes wastewater (Drewes and Fox, 2000).

One alternative that has been suggested to CDPH is the use of BDOC in concert with specific chemical indicators to assess the removal of unregulated wastewater-derived organic chemicals for groundwater recharge projects using surface spreading. In this case, indicator chemicals are defined as individual compounds occurring at quantifiable levels that can represent certain physical, chemical, and biodegradative characteristics that are relevant to fate and transport during treatment (where treatment includes above ground treatment and SAT). BDOC is a measure of dissolved biodegradable organic matter that is consumed or otherwise altered by indigenous bacterial populations within a given time period. The use of BDOC by measuring  $\Delta$ TOC (i.e., the differences between recycled water TOC before and after transport through the soil column) in combination with specific chemical indicators may be able to serve as a performance measure for the absence of biodegradable organic compounds that are not derived from humic substances (i.e., organic matter originating from soil or drinking water).

## **1.2. Charge to Panel**

Specifically, the Panel was to:

- Assemble information and research relevant to TOC, BDOC, and trace organic indicator chemicals related to the use of recycled water for groundwater recharge via surface spreading.
- Review this information to:
  - Evaluate if available research demonstrates that BDOC can be used to measure the performance of a SAT system and, if so, can be described by (1) measuring the BDOC in recycled water, and (2) showing that the degradable organic carbon in recycled water effluent has been fully degraded by SAT by the time it reaches monitoring wells hydraulically downgradient of recycled water spreading basins.
  - Evaluate various methods/approaches available to quantify BDOC in recycled water and in water that has been recharged, and to recommend an approach for measuring the  $\Delta$ TOC where organic matter is removed by biological processes.
  - Evaluate whether measuring TOC in absolute concentrations may be ill-defined due to recalcitrant TOC contributions from dilution water and native groundwater.
  - Provide specific recommendations to CDPH on the use of BDOC.

- Develop recommendations for agencies to implement BDOC.

Panel members include:

- *Chair*: Professor Dr.-Ing. Jörg Drewes, Colorado School of Mines (Golden, CO)
- Richard Bull, Ph.D., MoBull Consulting (Richland, WA)
- James Crook, Ph.D., P.E., Environmental Engineering Consultant (Boston, MA)
- Jean-François Debroux, Ph.D., Kennedy/Jenks Consultants (San Francisco, CA)
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- Professor Shane Snyder, Ph.D., University of Arizona (Tucson, AZ)
- Dennis Williams, Ph.D., P.G., CHG, GEOSCIENCE Support Services, Inc. (Claremont, CA)

A short biography of each Panel member is included in **Appendix A**.

### **1.3. Panel Process**

In preparation of the NWRI Independent Advisory Panel meeting, the Panel members discussed the Panel charge and scope of work during a kick-off conference call in January 2012. A report was prepared by the Panel Chair to summarize background information regarding previous research on the concept of using BDOC as a treatment performance measure of biological activity. The Panel members reviewed this background report prior to the Panel meeting. A 1-day meeting of the NWRI Advisory Panel was held on March 21, 2012, at CDPH's facilities in Sacramento, California. Representatives from CDPH participated in the meeting. The complete meeting agenda for the March 2012 meeting is included in **Appendix B**. A complete list of meeting attendees is included in **Appendix C**. A follow-up conference call was conducted on September 12, 2012, between the Panel Chair and representatives from CDPH and NWRI to discuss a draft of this report.



## **2. FINDINGS REGARDING THE USE OF TOC TO ASSESS PERFORMANCE OF GROUNDWATER RECHARGE FACILITIES AND BDOC AS A MONITORING ALTERNATIVE**

### **2.1. History of Using TOC as a Treatment Performance Measure**

In California, the use of TOC as a performance measure of groundwater recharge operations has a long tradition to assess the removal of unregulated wastewater-derived organic chemicals from recycled water. While this Panel was charged to evaluate the use of BDOC as an alternative performance measure that is equally protective of public health, it is important to understand the reasoning and underlying assumptions why TOC was originally selected as a performance measure. The following sections summarize the evolution of the draft groundwater recharge regulations and reasoning for specifying certain absolute TOC values for monitoring purposes.

#### ***2.1.1. Background***

Up until the mid-1970s, the gross parameters used to indicate quantities of organic substances in water supply sources were biochemical oxygen demand (BOD), chemical oxygen demand (COD), TOC, and carbon chloroform extract (CCE) or carbon alcohol extract (CAE). As the TOC analytical instrumentation improved through the years (greater accuracy, lower quantification limits, ease of use), it soon became the preferred technique to measure bulk organic content in water samples. Some of the reasons cited for using TOC as the preferred monitoring tool for measuring the concentration of organic matter in water are as follows:

- BOD and COD do not lend themselves to accurate measurements of small amounts of organic matter.
- Many synthetic chemicals are not biodegradable, thus limiting the applicability of the BOD test. Also, dissolved oxygen will react with some oxidizable materials, such as ferrous iron, sulfide, and sulfites, and provide misleading results.
- The COD test fails to measure all organic compounds either because of failure to oxidize them or because of loss of volatile material before it can be oxidized. While the COD analytical technique does not oxidize some common biodegradable compounds, such as benzene, toluene, and pyridine, it does oxidize some biologically non-degradable organic chemicals such as phenols.
- In the 1970s, the TOC measurement was accurate to about 1 milligram per liter (mg/L), but the measurement was subject to interferences. TOC analytical techniques have vastly improved since the 1970s and today can accurately measure concentrations as low as 0.1 mg/L.
- The carbon adsorption method (CCE-CAE) is more specific in that it differentiates between compounds that are soluble in either chloroform or ethanol. The test determines the quantities of organic substances that are adsorbed onto activated carbon columns and subsequently extracted with the two solvents, chloroform and ethanol.
- Some disadvantages of the carbon adsorption method are that waters high in organic compounds yield CAE fractions having significant inorganic content, the carbon does not adsorb all of the organic matter present in the water, and the total analysis took at least 24 hours.

### **2.1.2. California Draft Groundwater Recharge Regulations**

#### **1976 Draft Groundwater Recharge Regulations (for Spreading Only)**

In 1976, CDPH developed draft groundwater recharge regulations for surface spreading only (injection projects were not considered to be acceptable at that time). It was an internal document and was not widely circulated to outside agencies. The draft regulations included the following requirements:

- Minimum of secondary treatment and granular activated carbon (GAC).
- $\geq 10$ -foot depth of vadose zone.
- Meet drinking water standards.
- $\text{COD} \leq 5.0$  mg/L.
- $\text{TOC} \leq 3.0$  mg/L in reclaimed water.
- One-year residence time underground.

#### **1976 Report of the Consulting Panel on Health Aspects of Wastewater Reclamation for Groundwater Recharge**

In 1976, the California State Water Resources Control Board, Department of Water Resources, and Department of Health (now CDPH) convened a Consulting Panel on the “Health Aspects of Wastewater Reclamation for Groundwater Recharge.” A pertinent conclusion in the Panel report regarding TOC is given below:

*“Present wastewater treatment technology can produce water containing as little total organic carbon (TOC) as 1 to 2 milligrams per liter (mg/L). Although such concentrations approach that of high quality unpolluted ground waters, and although it has not been established that there is a health hazard associated with these organic residues (such studies have not been performed), there very likely may be a need to remove TOC (or components thereof) to even lower levels in both wastewater reclamation and in water purification. Processes for study would include:*

- A. Adsorption onto activated carbon and specific soils.*
- B. Other methods, including biological oxidation, ion exchange, membrane processes, and chemical treatment.”*

#### **1976 Draft Groundwater Recharge Regulations (for Spreading Only)**

CDPH developed a more definitive set of criteria in 1976 – again, only addressing surface spreading projects. The pertinent requirements in this draft set of criteria (see below) included a TOC limit of  $\leq 3$  mg/L in the product water after recharge.

- Minimum of secondary treatment and GAC.
- 10-foot vadose zone (minimum).
- Meet drinking water standard.
- $\text{COD} \leq 5$  mg/L.
- $\text{TOC} \leq 3$  mg/L.

- Dilution:  $\leq 50$ -percent reclaimed water.
- One-year residence time underground.

### **1987 Report of the Scientific Advisory Panel on Groundwater Recharge with Reclaimed Water**

A Scientific Advisory Panel commissioned by the California State Water Resources Control Board, Department of Water Resources, and Department of Health Services (now CDPH) was charged with defining the health significance of using reclaimed water for groundwater recharge, evaluate the benefits and risks associated with such recharge, and provide information needed to establish statewide criteria. Significant Panel conclusions related to TOC are provided below:

- *“In the context of the charge given, the Panel concluded after reviewing the Health Effects Study that it was comfortable with continuation of the current Whittier Narrows groundwater replenishment project and with the safety of the product water.”*
- *“Using reverse osmosis membranes will reduce the total dissolved organic carbon below 1 mg/L and essentially all identifiable trace organic compounds of significance should be absent in detectable concentrations.”*

### **First DHS Groundwater Recharge Committee Draft Regulations (for Surface Spreading Only) – February 1988**

In this draft regulation (and all subsequent versions), dilution of the treated reclaimed water to meet the TOC requirement is acceptable. It should be noted that there have been many versions of draft groundwater recharge from 1988 to the present time. Only those that significantly revised the TOC requirements are summarized in this document.

- Minimum treatment: oxidation, filtration, disinfection, carbon adsorption.
- GAC not required if dilution  $\leq 20$  percent.
- Meet drinking water standards.
- Total N  $\leq 10$  mg/L.
- COD  $\leq 5$  mg/L.
- TOC  $\leq 3$  mg/L.
- One-year residence time underground.
- Distance to withdrawal = 500 feet.

### **Some Changes Made in 1989 Version of the Draft Groundwater Recharge Regulations**

- GAC or reverse osmosis (RO) were specified as the required organics removal treatment processes.
- Requirements for direct injection included for the first time.
- Used formulas/tables to determine TOC requirement for spreading.
- TOC  $\leq 1$  mg/L for injection.

- TOC of 1 mg/L based on Scientific Advisory Panel finding and data indicating (erroneously, perhaps) that the Montebello Forebay project had 70-percent TOC removal due to SAT and, thus, the TOC of the mix was less than 1 mg/L.

### **By 2001, GAC Treatment Is No Longer Acceptable as the Sole Organics Removal Process for Injection (RO Became the Required Organics Removal Process)**

### **2002 Draft Groundwater Recharge Regulations Reduced TOC Limit from 1 mg/L to 0.5 mg/L**

The reduction of the acceptable TOC limit from 1.0 mg/L to 0.5 mg/L was principally due to a finding that N-Nitrosodimethylamine (NDMA) and 1,4-dioxane found in groundwater were caused by the recharge of recycled water at an operational groundwater recharge project. CDPH concluded that the use of cellulose acetate RO membranes contributed to the presence of these chemicals in the product water and has stated that: *“The performance standard was changed to 0.5 mg/L to assure use of TFC [thin-film composite] polyamide RO membranes that had been shown to effectively remove many types of organic chemicals found in wastewater.”* CDPH has also stated that: *“The Montebello Forebay recharge project was the subject of health effect studies and was not found to result in adverse effects. The project resulted in a maximum TOC contribution of reclaimed wastewater to the water supply of 0.54 mg/L when calculated in a manner consistent with the approach used in the regulation....”*

### **2.2. Characterizing Water Quality Changes during Groundwater Recharge Using Various Chemical Parameters**

When recycled water percolates through recharge basins into the vadose and saturated zones of the underlying aquifer, various physical, chemical and biological processes result in the attenuation of constituents of concern present in secondary and tertiary treated effluents, including pathogens, TOC, nitrogen species, and chemicals of emerging concern (CECs). This treatment process is referred to as SAT.

A significant amount of research has been conducted to understand the performance of SAT systems in removing pathogens, disinfection byproduct (DBP) precursors (i.e., TOC), nutrients, and CECs (Drewes and Fox, 1999; Drewes and Fox, 2000; Leenheer et al., 2001; Fox et al., 2001, 2006; Drewes et al., 2003a,b; Drewes et al., 2006a,b; Hoppe-Jones et al., 2010; Rauch-Williams et al., 2010). Many studies indicate that several factors affect the quality of the recovered water and performance of SAT systems. Besides the wastewater quality, spreading basin characteristics, subsurface conditions, and the degree of blending with native groundwater, operating conditions are important for the final product water quality.

Effluent pretreatment above ground directly influences the concentration of organic carbon applied to a spreading basin and the redox conditions under which organic carbon is transformed (Fox et al., 2006). The bulk of TOC in tertiary treated effluents is composed of easily biodegradable materials and refractory organic carbon. The levels of easily biodegradable organic carbon in applied effluents are a function of the efficiency of biological pretreatment above ground. Refractory dissolved organic carbon (DOC) in applied effluents is assumed to be



composed of residual natural organic matter (NOM) (largely humic acids) from the drinking water, some soluble microbial products, and some anthropogenic and natural trace organic chemicals (including some CECs). NOM of drinking water origin appears to persist during effluent pretreatment; therefore, the levels appear to be independent of conventional biological nutrient removal (BNR) processes, but dependent upon the type of source water used for drinking water supply in the service area (Drewes and Fox, 2000). For tertiary effluent qualities generated by nitrifying/denitrifying water reclamation facilities, TOC levels usually vary between 5 and 10 mg/L (Fox et al., 2006; Laws et al., 2011).

The correlation between the TOC content of post-SAT water and the TOC in drinking water supplies provides evidence that the absolute TOC concentration in recharged water is independent of the degree of treatment (Drewes and Fox, 2000). A comparison of results from SAT studies in Europe and the United States inspired the research to prove that absolute TOC concentrations were independent of treatment. Studies in Berlin, Germany, demonstrated that SAT could effectively transform DOC and the DOC concentrations could be reduced to 5-6 mg/L, which was similar to the native groundwater used as a drinking water supply (Fox et al., 2006). Ozonation was capable of decreasing the DOC concentration after SAT. The ozonation was effective since the recalcitrant TOC concentration in the drinking water source was high. Similar studies on SAT conducted in Tucson, Arizona, also showed that DOC could be transformed effectively. In these studies, the initial TOC concentration in the recycled water could be relatively high (15 mg/L), but the post-SAT concentration was 1-2 mg/L. Ozonation could increase the kinetics of DOC transformations, but there was no effect on the post-SAT concentration. The drinking water source in Tucson is a pristine groundwater with DOC concentrations less than 1 mg/L; thus, the recycled water did not contain much recalcitrant DOC of drinking water origin. While SAT can provide the same level of treatment in terms of protecting public health in both Germany and Arizona, the use of an absolute TOC concentration would greatly limit groundwater recharge in Germany, while the TOC concentration requirement would easily be met in Arizona. The use of BDOC as a performance measure could be applied equally and uniformly in both locations.

Above ground treatment indirectly affects the predominant redox conditions during SAT. The residual DOC in a tertiary treated effluent has a direct demand for oxygen during percolation through the infiltration zone of a SAT facility, and the quantity of DOC – along with residual ammonia – thus determine to what extent oxygen is removed during SAT. Redox conditions also appear to affect the kinetics of DOC removal; the fastest removal was observed under aerobic conditions, whereas the slowest removal usually occurs under anoxic conditions (Fox et al., 2006).

Inorganic nitrogen species that are relevant to human health are nitrite and nitrate. SAT or riverbank filtration facilities usually achieve additional nitrification of remaining ammonia in the initial phase of infiltration (Fox et al., 2001). Depending on the availability of organic carbon and predominant redox conditions in the subsurface, denitrification is achieved that usually results in total nitrogen concentrations of less than 5 mg N/L after SAT (Hoppe-Jones et al., 2010; Laws et al., 2011). The organic carbon that is used during denitrification is derived from DOC present in tertiary treated effluent, as well as the soil-bound carbon pool present in the infiltration zone of SAT facilities. This carbon pool is replenished by the degradation of

particulate organic carbon delivered through recycled water, as well as biomass generated by the active biofilms in the vadose zone that is decomposed during SAT.

Recycled water can contain thousands of chemicals originating from consumer products (e.g., household chemicals, personal care products, pharmaceutical residues), human waste (e.g., natural hormones), industrial and commercial discharge (e.g., solvents, heavy metals), or chemicals that are generated during water treatment (e.g., transformation products). Previous studies have characterized the transformation and removal of select trace organic chemicals during SAT for travel times ranging from less than 1 day to more than 8 years (Drewes et al., 2003b; Montgomery-Brown et al., 2003; Grünheid et al., 2005; Amy and Drewes, 2007; Massmann et al., 2008; Laws et al., 2011).

### ***2.1.2. Performance Measures of Biological Treatment of SAT and Their Correlation to Removal of CECs***

Traditional water quality methods of measuring bulk organic matter in wastewater, such as measurements of COD, TOC, total organic halides (TOX), or conductivity, continue to be used in monitoring programs, even though their ability to serve as surrogates for the removal of CECs has only been demonstrated very recently (Drewes et al., 2008; Dickenson et al., 2009; Drewes et al., 2011). These studies demonstrated that changes in certain bulk parameters do correlate with changes of indicator chemicals in the subsurface or during RO treatment leading to direct injection (Drewes et al., 2011).

BDOC has been previously proposed as a surrogate measurement for assessing the performance of SAT systems (Drewes and Fox, 1999; Drewes and Jekel, 1998; Fox et al., 2001; Drewes and Fox, 2000). As expected, BDOC measurements have been strongly correlated with the distribution of biomass in the infiltration zone of surface spreading operations (Rauch-Williams and Drewes, 2006). The results of a study reported by Drewes et al. (2011) also demonstrated that changes in TOC correlated with concentration changes of indicator compounds in the subsurface. However, based on laboratory soil-column experiments using feed water with a low carbon concentration (~0.2 mg/L), the same indicator compounds exhibited similar substantial reductions despite no changes in TOC concentrations being observed. This demonstrates that for sites using feed water qualities that are characterized by a low TOC concentration (<1 mg/L), differential TOC ( $\Delta$ TOC) monitoring would not be a sufficient surrogate parameter to assess the removal of CECs during spreading-basin operation. Therefore,  $\Delta$ TOC monitoring coupled with the monitoring of additional indicator compounds has been suggested by a Science Advisory Panel (Anderson et al., 2010). To ensure the proper performance of unit operations (including SAT regarding the removal of CECs), a combination of appropriate surrogate parameters and performance indicator CECs can be selected that are tailored to monitor the removal efficiency of individual unit processes comprising an overall treatment train. Performance indicators and surrogate parameters are defined as follows:

- **Indicator** – An indicator compound is an individual chemical occurring at a quantifiable level that represents certain physicochemical and biodegradable characteristics of a family of trace organic constituents that are relevant to fate and transport during treatment.

- **Surrogate** –A surrogate parameter is a quantifiable change of a bulk parameter that can measure the performance of individual unit processes (often in real-time) or operations in removing trace organic compounds.

In 2012, the California State Water Resources Control Board (SWRCB)<sup>2</sup> endorsed this concept following the recommendations of the Science Advisory Panel as a suitable monitoring approach to ensure the proper performance of SAT operations regarding the removal of trace organic chemicals (Anderson et al., 2010). The SWRCB suggested a combination of appropriate surrogate parameters and health-based and performance-based indicator chemicals for the monitoring of SAT projects. Monitoring requirements suggested by Anderson et al. (2010) are summarized in Table 1.

**Table 1. Health-Based and Performance-Based CEC Indicators and Performance Surrogates for SAT Practices Suggested by the Science Advisory Panel (Adopted from Anderson et al., 2010)**

Reuse Practice	Health-Based Indicator	MRL (ng/L)	Performance-Based Indicator	Expected Removal <sup>8</sup>	MRL (ng/L)	Surrogate	Method	Expected Removal <sup>8</sup>
SAT	17β-estradiol <sup>1</sup>	1	Δgemfibrozil <sup>5</sup>	>90%	10	Δammonia	SM	>90%
	Triclosan <sup>2</sup>	50	ΔDEET <sup>6</sup>	>90%	10	Δnitrate	SM	>30%
	Caffeine <sup>3</sup>	50	ΔCaffeine <sup>3</sup>	>90%	50	ΔDOC	SM	>30%
	NDMA <sup>4</sup>	2	Δiopromide <sup>5</sup>	>90%	50	ΔUVA	SM	>30%
				ΔSucralose <sup>7</sup>	<25%	100		

<sup>1</sup>Steroid hormones; <sup>2</sup>Antimicrobial; <sup>3</sup>Stimulant; <sup>4</sup>Disinfection byproduct; <sup>5</sup>Pharmaceutical residue; <sup>6</sup>Personal care product; <sup>7</sup>Food additive; <sup>8</sup>Travel time in subsurface 2 weeks and no dilution, see details in Drewes et al., 2008; SM – Standard Methods; MRL – Method reporting level.

This Panel notes that the characterization of caffeine in recycled water as a useful health-based indicator is not supported by the scientific literature assessing hazards and benefits of this compound. Health Canada concluded that adults can safely consume 400 milligrams per day (mg/day) and children and women of childbearing age could consume 300 mg/day (Nawrot et al., 2003). Epidemiological studies too numerous to cite have shown that coffee consumption either does not affect or significantly reduces morbidity and mortality from chronic diseases (see, for example, Sugiyama et al., 2010; Wedick et al., 2011; Mesas et al., 2011).

Selecting multiple indicators representing a broad range of properties and amenability for biotransformation can elucidate how changes in retention time affect the degree of removal achieved during SAT. Multiple indicators with various properties will also account for compounds currently not identified (“unknowns”) and new compounds that may enter the environment in the future (e.g., new pharmaceuticals) provided they fall within the range of properties covered.

<sup>2</sup>State Water Resources Control Board (2012). *California Water Recycling Policy – Amendment A: Requirements for Monitoring Constituents of Emerging Concern for Recycled Water* (Draft). April 23, 2012. Sacramento, CA.

Both field monitoring efforts as well as controlled laboratory studies have demonstrated that SAT systems can effectively remove a wide range of CECs (Amy and Drewes, 2007; Drewes et al., 2008; Laws et al., 2011), including CECs with demonstrated health relevance, such as N-nitrosamines (Drewes et al., 2006b). This attenuation during SAT is mainly attributed to biologically-driven processes in which the available BDOC supports the growth and metabolism of microorganisms that are also capable of transforming CECs. The BDOC serving as the carbon source for microbial activity during SAT is also being transformed and, with time, becomes more similar in character to NOM present in native groundwater. It is important to note that any biotransformation of CECs in SAT systems usually result in metabolites of the parent compounds rather than complete mineralization. The health relevance of these metabolites requires further discussions and is beyond the scope of this Panel. This issue is also independent of whether SAT performance is assessed using TOC or BDOC as a performance measure.

### 2.2.2. Overview of Available Methods to Quantify BDOC

Biodegradable organic matter consists of organic compounds that undergo microbial biotransformation and mineralization to grow and maintain biomass. Different methods for measuring the biodegradability of the organic matter present in water have been developed. These techniques measure either assimilable organic carbon (AOC) or BDOC. Tables 2 and 3 summarize the original methods, as well as published modifications for AOC and BDOC measurements, respectively. A detailed description of these methods is provided in Appendix D. Parameters (i.e., time, inoculum) of the measurements are summarized in Table D.1 (see Appendix D).

**Table 2. Modifications of the Original AOC Method (Adapted from Page and Dillon, 2007)**

Improvement Sought	Modification	Reference
Original method	Standardized AOC method based on stepwise inoculation with <i>Pseudomonas fluorescens</i> P-17 and <i>Spirillum</i> NOX	van der Kooj et al. (1982); APHA (1998)
Increased speed	Incorporation of four species in the inoculum	Kemmy et al. (1989)
	A single fast growing <i>Acinetobacter</i> used for the inoculum	Kang et al. (1997)
	Simultaneous inoculation with <i>Pseudomonas fluorescens</i> P-17 and <i>Spirillum</i> NOX	van der Kooj (1990)
	Increased inoculation density	Frias et al. (1994)
	Increased incubation temperature	LeChevallier et al. (1993)
	ATP bioassay of organisms	LeChevallier et al. (1993)
Reduction of contamination potential	Rapid macroscopic technique	Bradford et al. (1994)
	Rapid technique based on flow cytometry	Hammes and Egli (2005)
	40 mL vials batched instead of 1 L flask	Kaplan et al. (1993)
Greater sensitivity	Natural microbial consortium used for inoculum	Hammes and Egli (2005)
Greater biostability	Samples heated to 72°C then cooled on ice instead of pasteurization	Escobar and Randall (2000)
	Use of membranes to sterilize the water instead of pasteurization	Yoro et al. (1999)

**Table 3. Modifications of the Original BDOC Method  
(Adapted from Page and Dillon, 2007)**

Improvement Sought	Modification	Reference
Original method	Standardized BDOC method based on measurement of DOC	Servais et al. (1987); APHA (1998)
Increase size of measured BDOC pool	Use of attached bacteria	Joret and Levi (1986); Park et al. (2004)
	Increase incubation time	McDowell et al. (2006)
Increased speed	Use of attached bacteria	Trulleyová and Rulík (2004); Park et al. (2004)
	Use of recirculating batch reactor	Gimbel and Mälzer (1987); Lucena et al. (1990)
	Use of a plug flow bioreactor	Volk et al. (1997)
Reduction of contamination potential	Pre-filtering of test water	Kaplan et al. (1994)

The use of BDOC or AOC for managed aquifer recharge systems serves as a surrogate of the presence of organic compounds that are not derived from humic substances, which are assumed to be refractory. However, AOC and BDOC are conceptually different. While BDOC can be considered to represent the portion of the DOC that can be mineralized by indigenous heterotrophic microorganisms, AOC is the portion of the DOC that can be converted to biomass (Huck, 1990; Frias et al., 1995). The parameter measured to determine AOC is the biomass formed as a consequence of biodegradable carbon assimilation. BDOC is an operationally defined parameter that depends upon the underlying protocol of measurement and experimental conditions (particularly contact time, biomass, and redox conditions). AOC is based on the metabolic capability of two known bacteria species (i.e., *Pseudomonas fluorescens* P-17 and *Spirillum* strain NOX), while BDOC is based on the metabolic activities of an unknown but larger number of species. For recycled water, in which a large variety of compounds may be present, an acclimated mixed culture should provide a better indication of the biodegradable organic carbon than any specific strains of bacteria. The bacteria for the BDOC assay often originate from the test water; thus, it can be assumed that acclimation and the selection for particular metabolic pathways has already occurred. The original BDOC test (Servais et al., 1989) consisted of an oxic and continuously mixed batch system that contained inoculum derived from the water sample and a water sample where the DOC is monitored in the aqueous phase over time. The BDOC value corresponds to the difference between the initial DOC and the minimum final concentration reached in that period. The BDOC test was modified over the years to increase the quantity of microbes and decrease the time required to complete the test. Columns containing media with attached microbes could decrease the time required from 30 days to less than 1 day; however, the complexity of column reactors made reproducibility problematic. The BDOC test was modified specifically for assessment of SAT systems by using an oxic mixed batch reactor with microbes attached to soil (Cha et al., 2004). In the methods for determining AOC, the biomass can be measured by means of heterotrophic plate count, concentration of intracellular Adenosine Triphosphate (ATP), or turbidity increase.

Theoretically, concentrations as low as 1 microgram ( $\mu\text{g}$ ) C/L can be detected with the AOC method; however, in practice, the detection limit is closer to 10  $\mu\text{g}$  AOC/L as the AOC bioassay is extremely sensitive to organic carbon contamination (APHA, 1998). The particular

advantages of the AOC bioassay are that it is sensitive, precise, standardized by employing certain bioassay organisms, generally has a response parameter (colony forming units per milliliter) that exceeds the blank by an order of magnitude (high signal to noise ratio), and gives a measure of the potential to form new biomass. The disadvantages of the AOC method include its sensitivity to organic carbon concentration, a response parameter in units of substrate C equivalencies, and the length of time required (several days to weeks) to perform the test.

Detection limits of DOC are in the range of 100 microgram per liter ( $\mu\text{g/L}$ ), depending upon the analytical instrumentation employed (APHA, 1998), but if the BDOC is calculated as the difference between two DOC analyses, the detection limit for BDOC is closer to 200  $\mu\text{g/L}$ . A distinct advantage of using direct measurements of DOC is that the values are in units of carbon; also, information is provided on the proportion of DOC that is non-biodegradable. In general, the main problem of the batch system methods to measure the BDOC is the long period of incubation during the test, which will not allow properly monitoring responses to sudden changes in water quality. However, to overcome this limitation for online monitoring, a continuous plug flow bioreactor has been developed (Lucena et al., 1990; Kaplan and Newbold, 1995; Volk et al., 1997; Søndergaard and Worm, 2001; De Vittor et al., 2009) that allows measurement results within a few hours, the time it takes the water to travel through the reactor. This enables the monitoring of BDOC concentrations in nearly real-time and repetition of samples. One major disadvantage of a plug flow bioreactor is that it requires considerable time ( $\sim 100$  days) for colonization of bacteria prior to use. The other major disadvantage is the complexity of the reactor system decreases the reliability of the test (Khan et al., 1998).

At present, no absolute measure of biodegradable organic matter can be used as a standard for all other assays as all methods differ in their minimum detection limits and applicability. Attempts to identify the entire pool of organic matter in water are complicated by the fact that biodegradation is a function of both bacterial enzymes and the character of dissolved organic matter. BDOC assays attempt to quantify as much of the biodegradable organic matter as possible. Comparative studies between different AOC and BDOC methods concluded (Kaplan et al., 1994; Volk et al., 1994; Charnock and Kjønne, 2000) the following:

- AOC method estimated biodegradable organic matter concentrations are lower than concentrations obtained in BDOC methods.
- BDOC methods based on suspended bacteria result in less BDOC than those using attached bacteria.

Comparisons between the AOC and the BDOC assays are not necessarily valid because the yield coefficient for the AOC bioassay organisms must be assumed, and these vary depending upon the character of the biodegradable organic matter tested. The reason for the differences between the BDOC measurements using suspended and attached bacteria is not always apparent, but may result from differences in the diversity of the metabolic pathways by the bacterial communities or the bacterial density. Both BDOC techniques use the indigenous bacterial communities; however, the bacterial species collected in a single grab sample may differ from those present in a continuous flow bioreactor. This refers to not only the initial strains of bacteria that colonize the media, but also to the seasonally changing populations within the bacterial community that have the potential to colonize the bioreactor. Additionally, the presence of the media for the

attached bacteria should establish a greater variety of niches for species colonization. The use of attachment media should also better simulate microbial activity in a SAT system.

Correlations between methods of the same type (i.e., two ways of measuring BDOC) tend to be strong, but correlations between AOC and BDOC measurements tend to be variable. The observation that AOC estimates of biodegradable organic matter are less than BDOC is universal. This can be explained by the differences in the metabolic capabilities of the bacteria, as mentioned previously. However, Tihomirova et al. (2011) demonstrated in laboratory experiments that adaptation of soil columns to the different concentration of organic matter in water samples is necessary to decrease the bias in BDOC measurements when using columns tests.

Nevertheless, BDOC measurements could be a feasible surrogate parameter to assess SAT performance. During start-up of a spreading operation, the baseline DOC and BDOC levels of the surrounding groundwater have to be determined. Furthermore, dilution and mixing of the infiltrated recycled water with the native groundwater based on tracer tests and groundwater flow paths should be quantified. Foulquier et al. (2010) showed in their study regarding stormwater infiltration that the observed reduction in DOC below the groundwater table at recharge sites was essentially caused by mixing effects with native groundwater rather than biological uptake because of the low biodegradability of the DOC and the short transit time of stormwater in the upper layers of groundwater.

In spreading basins using reclaimed water, the BDOC quality that is applied is usually consistent since the municipal wastewater sources and above ground treatment processes do not vary significantly with time. This allows the SAT system to become acclimated to the organic compounds, and the soil filtration system becomes an effective biofiltration system. Fox and Makam (2009) asserted that SAT systems with silt, sand, or gravel aquifer materials could have similar surface areas for biofilm attachment when similar travel times are used for design. Because travel time is a common design criterion, the similarity in SAT performance with respect to the removal of organic compounds is expected for common types of aquifer materials. Clearly, the removal of BDOC is evidence that the SAT system is functioning as an effective biofiltration system, provided that samples are not diluted by native groundwater.

Direct evidence that the removal of BDOC implies the removal of CECs is limited (see the discussion in Section 2.2.1). Nalinakumari et al. (2010) used BDOC tests to evaluate the removal of NDMA and compared the results to soil column tests. The removal of NDMA occurred in the BDOC tests at rates comparable to the soil column testing. The method used for the BDOC test was an oxic batch test with sand as an attachment media for microorganisms, while the column tests had a residence time of approximately 30 days. The removal of BDOC was correlated with the removal of NDMA by Nalinakumari et al. (2010). Since it is unlikely that NDMA can directly support microbial growth even at elevated concentrations, the removal of BDOC was apparently necessary to support the removal of NDMA.

The removal of BDOC during SAT could be used as a performance measure provided data on indicator organic compounds supports that the system is working as an effective biofiltration system. The removal of BDOC provides direct evidence that the system is removing the

majority of biodegradable organic carbon. The removal of indicator compounds provides evidence that biofiltration during SAT is removing compounds of health concern with different structures and functionality. The removal of both BDOC and indicator compounds implies that the microbial community has adapted to remove a broad spectrum of organic compounds, and the removal can be sustained as long as a similar source of BDOC is provided. Waters with low BDOC concentrations, such as RO-treated waters, might not provide sufficient BDOC to sustain the removal of a broad spectrum of organic compounds. Therefore, it is recommended that the removal of BDOC should be coupled as previously suggested with the removal of indicator compounds to measure performance.

The use of BDOC measurements has largely been used as a research tool, and BDOC measurements have not been standardized. If BDOC measurements are to be used for measuring SAT performance, a standardized test should be used that can represent SAT performance and provide a uniform measurement method. In general, three different methods have been used to measure BDOC. The original method used suspended microorganisms under oxic conditions in a mixed batch test. The microorganisms were collected from the water to be tested to ensure the microbes were adapted. However, the time required to complete the test was 30 days, and the length of time was considered too long. Although the microbes were adapted, they were not necessarily adapted to the conditions of the BDOC test. The use of recirculating plug-flow reactors is an effective method to measure BDOC over short time scales. A large population of adapted microorganisms can be attached to media in a plug-flow reactor, allowing for rapid measurement of BDOC. It can take months to develop a large population of adapted microorganisms, and maintaining the reactors to measure BDOC is difficult. The complexity of maintaining plug flow reactors makes them impractical to develop into a uniform BDOC measurement method. The BDOC method that uses sand as an attachment media in oxic mixed batch tests appears to be the best method to assess SAT performance. An adapted microbial population can be developed in a month, and the adapted population can be easily maintained. The population can be adapted to the specific reclaimed water used during SAT, and the majority of microbes are attached similar to an SAT system. The test can still require 30 days to complete, which is the major drawback; however, the simplicity of the test allows many replicates to be run and the test is reproducible. The residence time in SAT systems is much longer than 30 days, and these times are often necessary for the removal of more difficult to degrade compounds.

### **2.3. Alternative Option 1 – Maintain RWC and Measure BDOC Instead of Absolute TOC**

Considering the current regulatory framework and opportunities, such as BDOC as an alternative performance measure, the Panel concluded that two potential options exist for how the BDOC concept could be adopted in lieu of TOC to assess proper performance of surface spreading operations. Water quality impacts and equivalency of public health protection for these two options are addressed in the following sections.

For Option 1, discussed here, the recharge volume of surface spreading operations would still be restricted through a predetermined RWC value. Project permits based on the current draft Groundwater Recharge Regulation limits the maximum RWC for surface spreading operations to 35 percent. For Option 1, the required TOC monitoring would be replaced by measuring BDOC or  $\Delta$ TOC rather than an absolute TOC concentration divided by an approved RWC value (see



Equation 1). BDOC in this context is defined as the difference between recycled water applied to a spreading basin and the TOC in the shallow groundwater directly downstream of the spreading operation, but BDOC could also be determined both in recycled water and groundwater using published methods. If BDOC is measured using the *in situ* TOC concentration difference between the recycled water and a hydraulically downgradient groundwater well, this well might also contain some DOC and potentially BDOC that originated from native (diluent) groundwater, which needs to be accounted for.

### ***2.3.1. Review Feasibility of Option 1 to Measuring $\Delta$ TOC where TOC Is Removed by Biological Processes***

Coupling BDOC laboratory tests to field tests is necessary to assess SAT performance. In essence, the field-scale SAT system itself is analogous to a BDOC reactor system that uses biomass attached to porous media. In both systems, the BDOC concentration decreases in the presence of adapted microbes as a function of time. The difference between the systems is the microbial population in a SAT system will change as a function of space and time, while the microbial population can only change as a function of time in a BDOC reactor. The performance of an SAT system could be assessed based on the BDOC content of the applied water. The  $\Delta$ TOC measured in the SAT system would be the difference between applied water TOC content and the TOC measured at a monitoring point prior to dilution with native groundwater. If the  $\Delta$ TOC is greater than the BDOC content of the water, the SAT system should be performing as an effective biofilter, and the BDOC content could be used as a performance measure. Appropriate blanks can be used to account for any background BDOC in a system. A set of indicator compounds can be added to assure that the use of BDOC as a performance measure is a reliable surrogate parameter for the attenuation of a broad set of biodegradable CECs.

### ***2.3.2. Conclusions Regarding Viability and Protection of Public Health of Option 1***

The main assurance that public health is being protected derives from 1) demonstrating that there are not unusual concentrations of toxicants in the wastewater, 2) monitoring to ensure that the wastewater being introduced into the basins is of a consistent quality, and 3) demonstrating that SAT will produce consistent removal of contaminants. An initial monitoring period should consider variables that could contribute to an inconsistent wastewater quality, such as the day of the week and seasonal variations. Once it is clear that the wastewater has a sufficiently consistent composition, a longer term monitoring program should be instituted. The frequency of this monitoring should be established based upon the variability observed in the initial period. Parameters to be considered include BDOC and selected organic contaminants discussed as CEC indicators elsewhere in this document.

Such a monitoring approach has been recently adopted and proposed by the State Water Resources Control Board (see Footnote 2) in its most recent draft Amendment A to the Water Recycling Policy. Monitoring for both health-relevant and performance-indicator CECs and surrogate parameters for surface spreading projects is divided into an initial assessment phase with more frequent monitoring requirements (i.e., CECs quarterly; surrogates weekly to monthly), a baseline phase with intermediate monitoring frequencies (i.e., CECs semi-annually;

surrogates weekly to quarterly), and a standard operation with less frequent monitoring requirements (i.e., CECs semi-annually to annually; surrogates weekly to quarterly).

With respect to the protection of public health, the Panel concluded that both monitoring approaches (TOC vs. BDOC) have limitations, as discussed above, to serve as safeguards to public health. In that respect, the equivalency of these two methods is that one cannot say that one or the other produces more public health protection.

## **2.4. Alternative Option 2 – Replacing the TOC RWC Equation with BDOC**

Under Option 2, discussed here, projects can request that the recycled water contribution for surface spreading operations can be increased from the current maximum value of 35 percent. For these cases, performance monitoring would still rely on BDOC instead of absolute TOC concentrations, as outlined under Option 1. Water quality impacts for various constituents of concern are being discussed in this section if the RWC is gradually increased from 35 percent to 50 percent, 75 percent, and 100 percent. As a baseline of comparison and to address the question of equivalency of public health protection, water qualities of a “pristine” groundwater supply, a groundwater supply that is recharged with imported surface water, and a groundwater supply that is recharged with different amounts of recycled water are being contrasted. For both options, additional monitoring of performance- and health-based indicator CECs would be required similar to the current draft Groundwater Recharge Regulations and the proposed Amendment A to the Water Recycling Policy.

### **2.4.1. How is RWC Determined under Option 2?**

Determining the RWC for a given project will follow the existing draft Groundwater Recharge Regulations. The definition of RWC is provided in Section 60301.705. Section 60320.116(a) to (f) specifies RWC requirements. Since RWC calculations under Option 2 are decoupled from dividing a TOC value of 0.5 mg/L by the approved RWC percentage through the introduction of BDOC as a performance measure, the Panel suggests modifying section 60320.116(d). This section currently reads:

- (d) A GRRP [groundwater recharge reuse project] may increase its maximum RWC, provided that:
1. The increase has been approved by the Department and RWQCB [Regional Water Quality Control Board];
  2. For the previous 52 weeks, the TOC 20-week running average, as monitored pursuant to section 62320.118, has not exceeded 0.5 mg/L divided by the proposed maximum RWC; and
  3. The GRRP has received a permit from the RWQCB that allows operation of the GRRP at the increased maximum RWC.

The following modification for this section is suggested:

- (d) A GRRP may increase its maximum RWC, provided that:
1. The increase has been approved by the Department and RWQCB;

2. For the previous 52 weeks, the BDOC 20-week running average, as monitored as TOC concentration difference between recycled water applied to surface spreading basins and a downstream groundwater monitoring well, has been consistent and steady (i.e.,  $\pm 20$  percent for the last 20 week running average); and
3. The GRRP has received a permit from the RWQCB that allows operation of the GRRP at the increased maximum RWC.

This revised proposed language does not imply that a project could just go to 100-percent RWC as long as the BDOC remains the same. Higher RWC will affect the groundwater quality (as illustrated in Section 2.4.2), and CDPH should consider these impacts while approving an increase in RWC.

#### ***2.4.2. Different Recharge Scenarios and Their Impact on Water Quality***

To illustrate potential differences in water quality for different recharge situations, three scenarios were adapted. As a baseline, Scenario 1 assumes a pristine groundwater quality. It is acknowledged that a pristine groundwater quality does not likely exist in urban groundwater basins; however, it was selected here to describe relative water quality changes that might be associated with different groundwater recharge practices using surface spreading basins. Scenario 2 assumes groundwater that is recharged by (imported) surface water, and Scenario 3 represents a groundwater that is impacted by recharge using recycled water. In this section, these water quality changes are being discussed for key water quality parameters, such as select inorganics, dissolved organic nitrogen (DON), DBPs and DBP formation potential, predominant redox conditions in the subsurface and impacts on water quality, and CECs.

#### **Inorganics/Dissolved Organic Nitrogen (DON)**

In general, the total dissolved solids (TDS) concentration in recycled water tends to be higher than other water sources. During municipal water use, the primary reason for the increase in TDS concentration is the addition of sodium chloride from a variety of sources. Industrial pretreatment programs effectively control the addition of most other inorganics. The bromide concentration in recycled water can be significantly greater than other water sources. The increase in bromide has important implications for DBP formation. The addition of inorganics can vary considerably between the service areas of municipalities, but an increase in concentration is always expected. Potential changes in inorganic water quality due to geochemical interactions are discussed in a separate section on the role of redox conditions.

Both Colorado River water and recycled water will have DON concentrations that are higher than pristine groundwater. Colorado River water will have higher DOC simply because the NOM concentration will be greater, and a portion of the NOM will contain dissolved organic nitrogen. The DON content of recycled water will be significantly higher because the effluent organic matter (EfOM) contains a variety of organic compounds of microbial origin (i.e., soluble microbial products) that contain nitrogen (Westerhoff et al., 2007).

Expected changes for the three recharge scenarios (i.e., pristine groundwater, surface water vs. recycled water spreading) are illustrated for select inorganic constituents and DON in Table 4.

During SAT, no significant changes in TDS content occur and the TDS in recharge water will increase with increasing RWC. Microbial transformation during SAT will transform both DOC and DON. Transformations can result in DOC concentrations similar to pristine groundwater. The same transformations also reduce the DOC concentrations; however, it is uncertain how the DON concentrations would compare with pristine groundwater.

**Table 4. Changes in Water Quality for Select Inorganics/DON For Different Recharge Scenarios**

	Inorganics	DON
NOM (Pristine)	Comparison Point	Comparison Point
NOM (Colorado River Water)	TDS ↑	DON ↑
NOM/EfOM (RWC = 35%) (post-SAT)	TDS ↑	DON→↑
NOM/EfOM (RWC = 50%)	TDS ↑	DON→↑
NOM/EfOM (RWC = 75%)	TDS ↑	DON→↑
NOM/EfOM (RWC = 100%)	TDS ↑	DON→↑

→ = No difference between NOM (pristine) water and listed water

↑ = Potential increase in constituent in listed water compared to NOM (pristine) water

→↑ = Undetermined difference but suspected possible increase

### DBP-Formation Potential

The character of organic matter and the concentrations of key inorganic ions in drinking source waters can have an impact on the quantity and speciation of DBPs formed during drinking water disinfection. In addition, residual DBPs present in source drinking waters due to previous exposures to disinfectants can contribute to the overall concentration of finished water DBPs. Expected changes for the three recharge scenarios are illustrated for the DBPs and DBPs formation potential (FP) in Table 5.

The reactivity of organic matter to form regulated DBPs (i.e., trihalomethanes [THMs] and select haloacetic acids [HAA5]) can be estimated by the physical-chemical characteristics of the organic molecules that collectively make up the organic matter. Greater aromatic content of organic matter has been shown to yield greater THMs, all else equal, than organic matter with more aliphatic content (Reckhow et al., 1990). In addition, more HAA5 has been observed when organic matter of lesser aromatic content (and greater aliphatic content) has been exposed to free chlorine (Debroux, 1998). Aromatic content has been shown to positively correlate with specific ultraviolet absorbance at 254 nm (SUVA<sub>254</sub>).

EfOM is more aliphatic than most typical NOMs. Although both EfOM and NOM are precursors to DBPs and generate DBPs in similar quantities, there is limited data that suggests that when water with EfOM is chlorinated, a greater HAA5/THM ratio will result as compared to NOM bearing waters (Debroux, 1998). Elemental analysis on organic matter from different

sources indicates that EfOM has higher concentrations of nitrogen than most NOM samples. This is believed to be due to the source of the organic matter (McKnight et al., 1994, 2001; Debroux, 1998). Organic matter that is derived from more plant like material, which can be high in lignins, has less nitrogen than organic matter derived from algae or bacteria. It has been hypothesized that this additional nitrogen in the organic matter could result in more nitrogenous DBPs, but currently the literature does not support this claim.

EfOM is subject to transformations during SAT. The biodegradable fraction (i.e., BDOC) of EfOM is quickly utilized by bacteria that reside in soil pores. Over time, the resulting organic matter begins to resemble a typical NOM signature (Drewes and Fox, 1999). The organic matter becomes more aromatic and less aliphatic during subsurface transport and, during significant periods in the subsurface, the bulk organic carbon becomes indistinguishable from the groundwater NOM (Drewes and Croue, 2002).

**Table 5. Changes in Water Quality for DBP-Formation Potential (FP)**

	DBP-FP	TOX
NOM (Pristine)	Comparison Point	Comparison Point
NOM (Colorado River Water)	HAA/THM → TOBr→↑	TOCl, TOBr, TOI →
NOM/EfOM (RWC = 35%) (post-SAT)	HAA/THM → TOBr↑ TOI ↑ DBP-N →↑	TOCl, TOBr, TOI →↑
NOM/EfOM (RWC = 50%)	HAA/THM → TOBr↑ TOI ↑ DBP-N →↑	TOCl, TOBr, TOI →↑
NOM/EfOM (RWC = 75%)	HAA/THM → TOBr↑ TOI ↑ DBP-N →↑	TOCl, TOBr, TOI →↑
NOM/EfOM (RWC = 100%)	HAA/THM → TOBr↑ TOI ↑ DBP-N →↑	TOCl, TOBr, TOI →↑

→ = No difference between NOM (pristine) water and listed water

↑ = Potential increase in constituent in listed water compared to NOM (pristine) water

→↑ = Undetermined difference but suspected possible increase

Bromide and iodide are known to be inorganic precursors for DBPs, as chlorine (i.e. hypochlorous acid) reacts with bromide and iodide to form the brominated or iodated analog oxidant. When these oxidants react with organic matter, the bromine and iodine atoms are incorporated into the DBP much like chlorine is when hypochlorous acid reacts with organic matter. Greater levels of bromide and iodide in the source water lead to greater levels of brominated and iodated DBPs when the water is chlorinated. This DBP species shift is important for two reasons: 1) regulated brominated DBPs weigh more per mole than their chlorinated analogs, therefore resulting in greater concentration per mole than their chlorinated analogs, and 2) possible human health risks associated with the ingestion of water with brominated and iodated DBPs – as yet undefined.

When water is used by society, the salt content of the water (i.e., inorganic ion total dissolved solids) increases. An increase of 250 to 300 mg/L TDS concentration has been observed and is considered typical. This added TDS concentration can contain bromide and iodide ions, which can act as precursor to DBPs. Low levels of bromide and iodide (i.e., 10s to 100s of  $\mu\text{g/L}$ ) are needed to shift speciation to more brominated and/or iodated DBPs. This said, natural waters and not only recycled water may contain elevated levels of bromide and/or iodide due to mineral dissolution or contact with intruded seawaters.

Recycled waters have typically been exposed to disinfectants at least twice during drinking water treatment and wastewater treatment. These disinfection steps generate DBPs. Regulated DBPs (i.e., THMs and HAA5) can comprise 50 percent of the total organic halide (TOX) (Krasner et al., 1989). THMs are volatile and will not remain in the recycled water, but HAA5 and other non-volatile halogenated organics may remain in solution. HAA5 have shown to biodegrade in the subsurface (Matucha et al., 2003; Bayless and Andrews, 2008) and non-regulated DBPs are likely to be attenuated during SAT. Fox et al. (2000) demonstrated that TOX at a recharge site in Arizona decreased rapidly and correlated well with the fate of biodegradable CECs during SAT.

### **Redox Potential**

As the percentage of reclaimed water increases, the potential for developing anoxic conditions increases. Most groundwater recharge sites in California that are used for indirect potable reuse maintain oxic conditions because the applied reclaimed water is blended with native groundwater (Fox et al., 2006). Even a high quality effluent treated with advanced biological treatment with a BDOC concentration of 2-3 mg/L can cause an aquifer to become anoxic. For example, this occurs in Mesa, Arizona, where advanced biological treatment produces an effluent quality with low BDOC concentrations and a total nitrogen concentration of less than 10 mg/L. The total oxygen demand of an effluent includes both carbonaceous BOD and nitrogenous BOD. Since 1 mg/L of ammonia nitrogen can exert over 4 mg/L of oxygen demand, a low BDOC level will not prevent the development of anoxic conditions. Once oxygen is exhausted from water applied to an aquifer, the anoxic conditions will be maintained until water with oxygen is used to replenish the aquifer.

Groundwater recharge in Fresno, California, with recycled water has resulted in an anoxic plume (Fono et al., 2009). Anoxic conditions can cause changes to water quality as Fe, Mn, and As can be released from native aquifer materials. This occurs in the anoxic plume in Fresno, California. On the edges of the plume where oxic conditions exist, the Mn and As concentrations decrease as the water equilibrates with the native aquifer materials. A similar situation exists in Mesa, Arizona, whereas concentrations are at a peak directly below the recharge basins and decrease in the recycled water plume as the water moves downgradient (Aboshanp, 2006).

Currently, it is known that recharge with a RWC content of 35 percent should maintain oxic conditions based on existing sites in California where dilution water does not contain significant oxygen demand. It is also known that anoxic condition will develop with recharge with 100-percent RWC, even if the above ground treatment is highly effective. The expected changes for the three recharge scenarios are illustrated for the predominant redox conditions in Table 6, and

expected impacts on water quality constituents are noted. There is uncertainty over how redox conditions will change if the RWC equals 50 percent, since 50 percent of the water would be dilution water that can add oxygen to the aquifer. Ammonia nitrogen can adsorb to clays and continue to exert oxygen demand during drying cycles and periods when dilution water is added. Therefore, one would expect anoxic conditions will develop for a RWC of 75 percent. Actually, increases in arsenic (As), manganese (Mn), and other inorganics will depend on the native aquifer materials, and the effects will be site-specific. In terms of health risks, an increase in As concentration can overshadow most other health concerns associated with groundwater recharge (Nellor et al., 2012).

**Table 6. Changes in Water Quality as a Function of Redox Conditions**

	Redox Conditions	Consequences
NOM (Pristine)	Comparison Point	Comparison Point
NOM (Colorado River water)	Oxic	Mn→ As→
NOM/EfOM (RWC = 35%) (post-SAT)	Oxic	Mn→ As→
NOM/EfOM (RWC = 50%)	Oxic	Mn→ As→
NOM/EfOM (RWC = 75%)	Anoxic	Mn↑ As↑
NOM/EfOM (RWC = 100%)	Anoxic	Mn↑ As↑

→ = No difference between NOM (pristine) water and listed water

↑ = Potential increase in constituent in listed water compared to NOM (pristine) water

→↑ = Undetermined difference but suspected possible increase

### Chemicals of Emerging Concern (CECs)

CECs are present in all wastewaters. The concentrations of specific CECs in wastewater samples are highly dependent upon treatment processes employed, season/weather, and sewage quality (i.e., population served and municipal/industrial contributions). To compare the occurrence levels of CECs under different RWC scenarios, a limited set of indicator species were selected (Table 7). These constituents are frequently detected in municipal WWTP effluents, including recycled water in California, and also have largely different biodegradation potentials. Table 7 considered occurrence data gathered by a Science Advisory Panel convened by the State of California to evaluate CECs in potable water reuse applications (Anderson et al., 2010). For these occurrence data, the 90<sup>th</sup> percentile values from the SAP report were adopted (Anderson et al., 2010).

Table 7 demonstrates the expected concentrations of indicator CECs for the different scenarios based simply on dilution and assuming a diluent water with non-detectable background concentrations of indicator CEC (again, acknowledging that such a pristine groundwater quality usually does not exist in urban settings). Also noted in Table 7 is a general biodegradation potential during SAT based simply upon empirical data from previous studies.

**Table 7. Indicator Compound Concentrations in Recycled Water and After Different Recharge Scenarios Assuming Zero Attenuation and Diluent Water with Non-Detectable Concentrations**

Constituent	CA CEC 90th Percentile Eff. (ng/L)	75% RWC (ng/L)	50% RWC (ng/L)	35% RWC (ng/L)	Biodegradation Potential
Carbamazepine	400	300	200	140	Low
DEET	1520	1140	760	532	High
17β-Estradiol	8.4	6.3	4.2	2.9	High
Estrone	72	54	36	25.2	High
Gemfibrozil	3550	2663	1775	1243	High
Iopromide	2174	1631	1087	761	High
Meprobamate	430	323	215	151	Moderate
NDMA	67.7	50.8	33.9	23.7	Moderate
PFOA	28	21	14	9.8	Low
PFOS	90	67.5	45	31.5	Low
Primidone	264	198	132	92.4	Low
Sucralose	26390	19793	13195	9237	Low
Sulfamethoxazole	1400	1050	700	490	Low
TCEP	688	516	344	241	High
T CPP	5920	4440	2960	2072	High
Triclosan	485	364	243	170	High

### CEC Concentrations Using Colorado River Water as Diluent

A summary is provided in Table 8 of the same selected CECs with concentrations as monitored in the Colorado River, as well as blends with the same water as shown in Table 7. This scenario considers low level detects of CECs in Colorado River water. Essentially, concentrations of selected CECs for the different blending scenarios are comparable such that blends result in only meager differences in predicted concentrations. Thus, the Colorado River will not provide a significant loading of CEC from use as diluent water.

### Measured SAT Performance

A full-scale water reclamation facility in California employing SAT was evaluated as part of WateReuse Research Foundation (WRRF) Project 06-006. Two pre-SAT samples and four post-SAT samples were collected in 2008. It should be noted that the travel times within the subsurface to the well shown in Table 9 has been estimated to be 21 months. Therefore, influent data is not likely representative of actual conditions exiting when a blend of stormwater and recycled water was actually infiltrated. Regardless, the trend for certain compounds is obvious. TOC concentrations were included in this study and provided in Table 9, yet considering the same caveat of non-paired sampling according to travel time in the subsurface.



**Table 8. Indicator Compounds in Colorado River and Resulting Concentrations if Used as Diluent Water for SAT Assuming Zero Attenuation**

CEC	Colorado River (ng/L)	75% RWC (ng/L)	50% RWC (ng/L)	35% RWC (ng/L)
Carbamazepine	4.4	301	275	209
DEET	7.1	1142	1045	793
17 $\beta$ -Estradiol	<0.5*	6	6	4
Estrone	<0.2*	54	50	38
Gemfibrozil	0.69	2663	2441	1853
Iopromide	<10*	1633	1495	1135
Meprobamate	13	326	296	225
NDMA	<2.5*	51	47	35
PFOA	2	22	19	15
PFOS	1.1	68	62	47
Primidone	3.7	199	182	138
Sucralose	400	19893	18168	13779
Sulfamethoxazole	19	1055	964	731
TCEP	<10*	519	474	359
TCP	<100*	4465	4076	3091
Triclosan	4	365	334	253

\* Represents <MRL.

**Table 9. Results from Sampling of Full-Scale SAT Facility in California**

CEC	Infiltration Water (ng/L)	Groundwater Well (after 21 months of travel)
Carbamazepine	210	111
DEET	138	<1
17 $\beta$ -Estradiol	<0.5	<0.5
Estrone	1.6	<0.2
Gemfibrozil	625	<0.25
Iopromide	755	<10
Meprobamate	345	7
NDMA	NM	<2
PFOA	95	18
PFOS	27	59
Primidone	130	71
Sucralose	NM	NM
Sulfamethoxazole	230	99
TCEP	385	<10
TCP	1200	<100
Triclosan	5.5	<1
TOC (mg/L)	6.6	1.3

NM = Not measured.

### ***2.4.3. Chemical Residuals of Health Concern***

Chemicals of health concern will be among biodegradable and recalcitrant organic matter of the water before and after SAT. Removal of indicator compounds provides a basis for extrapolating removals to other chemicals that are of health concern that fall within the range of chemical and physical properties covered by the indicator compounds. Following an evaluation of performance with indicator compounds to ensure that it remains consistent over time, it can be concluded that BDOC removal will reduce health risk from a variety of unmeasured but biodegradable chemicals with comparable physical-chemical properties. From this perspective, BDOC reduction is much superior to measuring residual TOC in the receiving water. As an example, the Panel compiled a list of CECs (Table 10) that represent different degrees of biodegradability of which a subset could be selected to serve as suitable CECs to assess the proper performance of an SAT operation in conjunction with BDOC measurements.

Obviously, removal of BDOC provides no assurance that chemicals of health concern that are recalcitrant to biodegradation are no longer present. However, attempts at estimating TOC residual from wastewater in the receiving water does not address this either. Therefore, analysis of chemicals in water following SAT needs to focus on chemicals of health concern that are recalcitrant. Of course, they are of little interest unless they are known to occur in wastewater, but it must be admitted that identifying such chemicals is a guessing game. It can progress only as the chemical composition of wastewater becomes better defined. However, one must consider the probability of a non-biodegradable chemical occurring in wastewater at concentrations that are harmful to human health. The volumes of water that are involved in recycling wastewaters are very large and even very toxic compounds would have to be produced and discharged to the wastewater in large quantities to be of health concern. While a precise estimate of the probability of such an event is not possible based on the limited data that are available, experience suggests that it is very low. Examples do exist. Perhaps the most relevant has been NDMA, which was discovered as a byproduct of the disinfection of water containing appropriate precursors in direct injection projects in California using highly treated recycled water (i.e., RO). NDMA as well some other nitrosamines are highly carcinogenic compounds, and are of concern in the nanogram per liter (ng/L) range. NDMA has not been detected at relevant levels in production wells of SAT facilities. Other chemicals have been identified that are not easily biodegradable (Table 10), but their occurrence in wastewater is well below any concentrations deemed of health concern.

In summary, relying on BDOC removal alone is not the ideal measure for ensuring the safety of water derived from an SAT operation. However, if properly validated with indicator CEC removals, it is a much superior measure of health protection than estimates of wastewater TOC residuals in the receiving water. As pointed out in previous sections, this latter measure is ambiguous at best with respect to the protection of health.

**Table 10. Examples of Indicator CECs that Could Be Used to Assess Performance of SAT Operations in Conjunction with BDOC Monitoring**

<b>Chemicals of Emerging Concern</b>	<b>CA CEC 90th Percentile Eff.<sup>a</sup> (ng/L)</b>	<b>Biodegradation Potential</b>	<b>Concentrations of Potential Health Concern (ng/L)</b>	<b>Reference</b>
Carbamazepine	400	Low	10,000	Bruce et al., 2010
DEET	1520	High	2,500,000	AUS guidelines, 2008
17 $\beta$ -Estradiol	8.4	High	0.9	USEPA, 2009
Estrone	72	High	350	USEPA, 2009
Gemfibrozil	3550	High	45,000	AwwaRF, 2008
Iopromide	2174	High	90,000	Bull et al., 2011
Meprobamate	430	Moderate	200,000	Bull et al., 2011
NDMA	67.7	Moderate	0.69	USEPA, 2009
PFOA	28	Low	1,100	USEPA, 2009
PFOS	90	Low	200	USEPA, 2009
Primidone	264	Low	10,000	Bull et al., 2011 <sup>b</sup>
Sucralose	26390	Low	50,000,000	U.S. FDA ADI FR/63. No 64 April 3, 1998
Sulfamethoxazole	1400	Low	35,000	AUS guidelines, 2008
TCEP	688	High	2,500	USEPA, 2009
TCP	5920	High	2,500	Structurally and chemically related to TCEP, value adopted from TCEP
Triclosan	485	High	21,000,000	EPA Health Relevance Level

<sup>a</sup> Adopted from Anderson et al. (2010); <sup>b</sup> Lowest therapeutic dose for 10 kg child (10 mg/kg/day)= 100 mg. 100 mg/10,000 as human teratogen = 10,000 ng/L (Bull et al. (2011). Reg. Toxicol. Pharmacol.60:1-19). NA – Not Available.



### 3. SUMMARY OF RECOMMENDATIONS TO CDPH ON THE USE OF BDOC

In California, the use of TOC as a surrogate for unregulated organic chemicals of wastewater origin has a long history with regard to the development of groundwater recharge regulations and in establishing RWCs for permitted groundwater recharge projects. However, the removal of TOC via wastewater treatment or SAT may not always directly relate to the removal of specific organic chemicals of wastewater origin. The TOC approach currently favored by regulators in California also has a limiting effect on the RWC calculation and the allowable amount of recycled water that can be used for a recharge project inasmuch as there may be some recalcitrant TOC that is primarily derived from the drinking water source that ultimately becomes wastewater, and has no significance in terms of regulating organics of wastewater origin.

One alternative that has been suggested to CDPH that use of BDOC, in concert with monitoring water quality for specific indicator chemicals, could be used to assess the removal of unregulated wastewater-derived organic chemicals for groundwater recharge projects using surface spreading. The Panel was specifically charged to address the following issues:

- Evaluate if available research demonstrates that BDOC can be used to measure the performance of a SAT system, and if so can be described by (1) measuring the BDOC in recycled water, and (2) showing that the degradable organic carbon in recycled water effluent has been fully degraded by SAT by the time it reaches monitoring wells down gradient of recycled water spreading basins.
- Evaluate various methods/approaches available to quantify BDOC in recycled water and in water that has been recharged, and to recommend an approach for measuring the differential TOC ( $\Delta$ TOC) where TOC is removed by biological processes.
- Evaluate whether measuring TOC in absolute concentrations may be ill-defined due to recalcitrant TOC contributions from dilution water and native groundwater.
- Provide specific recommendations to CDPH on the use of BDOC.
- Develop recommendations for agencies to implement BDOC.

The Panel has reviewed the relevant sections of the most recent draft Groundwater Recharge Regulations (dated November 21, 2011). The Panel's recommendations listed in this report are strictly in the context of CDPH's proposed Groundwater Recharge Regulations.

#### **BDOC as Performance Measure for SAT vs. Measuring TOC in Absolute Concentration**

The bulk of TOC in tertiary treated wastewater effluents is composed of easily biodegradable materials and refractory organic carbon. The levels of easily biodegradable organic carbon in recycled water applied to groundwater recharge projects are a function of the efficiency of biological pretreatment above ground. Refractory dissolved organic carbon in applied effluents is assumed to be composed of NOM of drinking water origin, soluble microbial products, and anthropogenic and natural trace organic chemicals (including CECs). Effluent pretreatment above ground directly influences the concentration of organic carbon applied to a spreading basin and the redox conditions under which organic carbon is transformed.

Previous studies have demonstrated the direct impact of drinking water TOC on both concentration and composition of TOC present in recycled water. The assumption is that TOC in finished, disinfected drinking water remains unaltered while it is used by water consumers. Previous research confirmed that assumption (see Drewes and Fox, 2000; Fox et al., 2001; Drewes and Fox, 2001). These studies suggest that the character of TOC in drinking water is mainly comprised of fulvic and humic acids (NOM), whereas effluent organic matter in recycled water is comprised of fulvic and humic acids, soluble microbial byproducts formed during the biological decomposition of organic material, and naturally-occurring and anthropogenic trace organic chemicals. Previous studies have demonstrated that the chemical character of fulvic and humic acids from a corresponding drinking water is very similar to fulvic and humic acids found in recycled water (Drewes and Croue, 2002; Drewes et al. 2003a; Drewes et al. 2006a).

The use of an absolute TOC concentration would greatly limit groundwater recharge in areas with elevated TOC drinking water levels while the TOC concentration requirement would easily be met in areas characterized by low TOC concentrations in their drinking water supply, while SAT can provide the same level of treatment in terms of protecting public health in both areas. However, the use of BDOC as a performance measure could be applied equally and uniformly in both locations.

Both field monitoring efforts as well as controlled laboratory studies have demonstrated that biologically active SAT systems can effectively remove a wide range of CECs and provided evidence that changes in TOC correlated with concentration changes of certain (biodegradable) indicator CECs in the subsurface.

The removal of BDOC provides direct evidence that the system is removing the majority of biodegradable organic carbon. Monitoring for the removal of indicator compounds provides evidence that biofiltration during SAT is removing compounds of health concern with different structures and functionality. Neither TOC nor BDOC measurements will provide complete evidence that SAT can remove all known and unknown CECs, but monitoring of BDOC has the advantage to represent evidence of the biological function of a SAT system, which is not evident by just monitoring absolute TOC concentrations. Therefore, BDOC has the added benefit that it correlates with the removal of biodegradable CECs.

### **Methods to Quantify BDOC**

If BDOC measurements are to be used for measuring SAT performance, a standardized test should be used that can represent SAT performance and provide a uniform measurement method while not necessarily reflecting performance and conditions that are fully representative of a field-scale surface spreading operation.

In general, three different methods have been used to measure BDOC. The original method used suspended microorganisms under oxic conditions in a mixed batch test. The microorganisms were collected from the water to be tested to ensure the microbes were adapted. However, the time required to complete the test was 30 days and the length of time was considered too long. The use of recirculating plug-flow reactors is an effective method to measure BDOC over short time scales. The complexity of maintaining plug flow reactors makes them impractical to

develop into a uniform BDOC measurement method. The BDOC method that uses sand as an attachment media in oxic mixed batch tests appears to be the best method to assess SAT performance. An adapted microbial population can be developed in a month, and the adapted population can be easily maintained. The population can be adapted to the specific reclaimed water used during SAT, and the majority of microbes are attached similar to an SAT system. The test can still require 30 days to complete, which is the major drawback; however, the simplicity of the test allows many replicates to be run and the test is reproducible. The residence time in SAT systems is much longer than 30 days, and these times are often necessary for removal of more difficult to degrade compounds.

BDOC measurements using one of these methods could be a feasible surrogate parameter to assess SAT performance. During the start-up of a spreading operation, the baseline DOC and BDOC levels of the surrounding groundwater have to be determined. Furthermore, dilution and mixing of the infiltrated recycled water with the native groundwater based on tracer tests and groundwater flow paths should be quantified.

### **Specific Recommendations Regarding the Use of BDOC**

- CDPH should consider BDOC as an alternative performance measure to assess the efficiency of surface spreading operations since published research and monitoring results from ongoing SAT operations demonstrated that SAT systems are working as an effective biofiltration system.
- The removal of BDOC provides no assurance that chemicals of health concern that are recalcitrant to biodegradation are no longer present. However, attempts at estimating TOC residual from wastewater in the receiving water does not address this either and both measures are ambiguous at best with respect to protection of public health. The advantage of BDOC over measuring absolute TOC concentrations as a surrogate measure is that BDOC directly correlates with the removal of biodegradable CECs. If there is evidence for BDOC removal, there is assurance that biodegradable trace organic chemicals are also removed. Measuring an absolute TOC concentration would not provide that piece of evidence.
- Following an evaluation of performance with indicator compounds to ensure that it remains consistent over time, it can be concluded that BDOC removal will reduce health risk from a variety of unmeasured chemicals with comparable physical-chemical properties. Thus, if properly validated with indicator chemical removals, BDOC is a much superior measure of health protection than estimates of wastewater TOC residuals in the receiving water.
- Adopting the BDOC concept does not imply projects can go to 100 percent RWC as long as they still meet the same BDOC level. Higher RWC will have an effect on the downstream groundwater quality (as illustrated in this report). Thus, CDPH should consider other water quality parameters and acceptable changes while approving higher RWCs.
- If BDOC is adopted, each project should demonstrate during an initial phase of operation that the removal of both BDOC and indicator CECs is consistent during a predefined travel time, implying that the microbial community has fully adapted to remove a broad spectrum of organic compounds.

- Waters with low BDOC concentrations, such as RO-treated waters, might not provide sufficient BDOC to sustain the removal of a broad spectrum of organic compounds. Thus, while BDOC removal for these projects might be small, BDOC monitoring coupled with monitoring for indicator CECs will provide evidence for proper performance.



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## APPENDIX A: PANEL BIOGRAPHIES

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### **JAMES CROOK, Ph.D., P.E.**

*Environmental Engineering Consultant (Boston, Massachusetts)*

Jim Crook is an environmental engineer with more than 37 years of experience in state government and consulting engineering arenas, serving public and private sectors in the U.S. and abroad. He has authored more than 100 publications and is an internationally recognized expert in water reclamation and reuse. He has been involved in numerous projects and research activities involving public health, regulations and permitting, water quality, risk assessment, treatment technology, and all facets of water reuse. Crook spent 15 years directing the California Department of Public Health's water reuse program, during which time he developed California's first comprehensive water reuse criteria. He also spent 15 years with consulting firms overseeing water reuse activities and is now an independent consultant specializing in water reuse. He has served on several advisory Panels and committees convened by the National Academy of Sciences, NWRI, and others. Among his honors, he was selected as the American Academy of Environmental Engineers' 2002 Kappe Lecturer and the WaterReuse Association's 2005 Person of the Year. Crook received a B.S. in Civil Engineering from the University of Massachusetts and both an M.S. and Ph.D. in Environmental Engineering from the University of Cincinnati. He is a registered professional engineer in California and Florida.

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### **RICHARD BULL, Ph.D.**

*Consulting Toxicologist*

*MoBull Consulting (Richland, Washington)*

Since 2000, Richard Bull has been a Consulting Toxicologist with MoBull Consulting, where he conducts studies on the chemical problems encountered in water for water utilities, as well as federal, state, and local governments. Bull is a retired Professor of Pharmacology/Toxicology from Washington State University, where he maintains Adjunct Professor appointments in the College of Pharmacy and the Department of Environmental Science. Formerly, he served as a senior staff scientist at DOE's Pacific Northwest National Laboratory, Professor of Pharmacology/Toxicology at Washington State University, and Director of the Toxicology and Microbiology Division in the Cincinnati Laboratories for the U.S. Environmental Protection Agency. Bull has published extensively on research on central nervous system effects of heavy metals, the carcinogenic and toxicological effects of disinfectants and disinfection by-products, halogenated solvents, acrylamide, and other contaminants of drinking water. He has also served on many international scientific committees convened by the National Academy of Sciences, World Health Organization, and International Agency for Research on Cancer regarding various contaminants of drinking water. Bull received a B.S. in Pharmacy from the University of Washington and a Ph.D. in Pharmacology from the University of California, San Francisco.

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**JEAN-FRANÇOIS DEBROUX, Ph.D.**

*Director, Advanced Technologies Group  
Kennedy/Jenks Consultants (San Francisco, CA)*

At Kennedy/Jenks Consultants, Jean Debroux serves as Director of the Advanced Technologies Group, which was formed to solve technologically challenging problems. Part of this effort includes performing pilot and field studies for regulated and emerging contaminants and evaluates the cost impacts of complying with Safe Drinking Water Act regulations. A water quality expert, Debroux has extensive experience and expertise working with water utilities and research organizations in water treatment and water reuse issues, and is an active member of the WaterReuse Foundation, where he serves on the Research Advisory Committee. Debroux received a B.S. in Chemical Engineering from the University of South Florida, and both an M.S. in Environmental Engineering and Ph.D. in Civil Engineering from the University of Colorado, Boulder. In addition, he attended the Environmental Management Institute at Tufts University and has served as a Post-Doctoral Research Fellow and Lecturer at Stanford University and as a Research Fellow at Université de Poitiers, France.

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**DR.-ING. JÖRG E. DREWES (Panel Chair)**

*Professor, Director of Research (NSF Engineering Research Center ReNUWIt)  
Colorado School of Mines (Golden, CO)*

Jörg Drewes has taught courses as in the Department of Civil and Environmental Engineering at Colorado School of Mines (CSM) since 2001. Dr. Drewes is the Director of Research for the NSF Engineering Research Center *ReNUWIt*. He also serves as Co-Director of CSM's Advanced Water Technology Center (AQWATEC), which is dedicated to advancing the research and development of novel water treatment processes and hybrid systems to enable sustainable and energy efficient utilization of impaired water sources to provide potable and non-potable water supplies. Drewes is actively involved in research in the areas of water treatment and non-potable and potable water reuse. Current research interests include treatment technologies leading to indirect potable reuse and the fate and transport of persistent organic compounds in these systems. He has published more than 200 journal papers, book contributions, and conference proceedings, and was appointed to the National Research Council Committee on Water Reuse as an Approach for Meeting Future Water Supply Needs. Drewes received a Cand. Ing. (B.S.), Dipl. Ing. (M.S.), and Doctorate (Dr.-Ing.) in Environmental Engineering from the Technical University of Berlin in Germany.

**PETER FOX, Ph.D.**

*Professor, School of Sustainable Engineering and the Built Environment  
Arizona State University (Tempe, AZ)*

Peter Fox is a Professor in the School of Sustainable Engineering and the Built Environment at Arizona State University (ASU) and serves as the coordinator of Environmental Engineering at ASU. He previously served as Director of the National Center for Sustainable Water Supply, which researched indirect potable reuse at numerous field sites in both Arizona and California. His professional interests include water reuse, biological treatment processes, and combined biological/adsorptive systems. For the last 14 years, he has focused his work on natural treatment systems and water reuse; recently, he has begun to expand his expertise on sustainable water systems to include desalination. Fox served as an Associate Editor of the American Society of Civil Engineering *Journal of Environmental Engineering*, and has published over 100 papers and presentations. He has also served on the National Academy of Science ad-hoc committee to assess Sustainable Underground Storage and was an executive committee member for the development of the national roadmap for desalination and water purification. Fox also authored the groundwater recharge chapter of the Metcalf and Eddy textbook, *Water Reuse*. Fox received a B.S. Chemical Engineering and both an M.S. and Ph.D. in Civil and Environmental Engineering from the University of Illinois.

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**SHANE SNYDER, Ph.D.**

*Professor, College of Engineering  
Co-Director, Arizona Laboratory for Emerging Contaminants  
The University of Arizona (Tucson, AZ)*

Shane Snyder joined the University of Arizona faculty in 2010, where he is a Professor in the College of Engineering. He is also the Co-Director of the Arizona Laboratory for Emerging Contaminants. For over 15 years, his research has focused on the identification, fate, and health relevance of emerging water pollutants. In 2000, he became the first R&D Project Manager at the Southern Nevada Water Authority (SNWA) and was a founding member of SNWA's Applied R&D Center. In 2008, he was one of six experts invited to testify before the U.S. Senate regarding pharmaceuticals in U.S. waters. He has since been invited to brief the U.S. Congress three additional times. Snyder has served two terms on the federal advisory committee to EPA's Endocrine Disruptor Screening Program and was an invited expert Panel member for the development of EPA's CCL3. He is also a member of the National Research Council's Committee on Water Reuse and has served two appointments on the California Chemicals of Emerging Concern Expert Panels. Snyder received a B.A. in Chemistry from Thiel College and a Ph.D. in Zoology and Environmental Toxicology from Michigan State University.

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**DENNIS E. WILLIAMS, PH.D., P.G., CHG**

*President  
GEOSCIENCE Support Services, Inc. (Claremont, CA)*

Dennis Williams is founder and president of GEOSCIENCE Support Services, Inc., which focuses on groundwater supply, development, management, and protection. He has over 35 years of experience in groundwater hydrology, specializing in groundwater planning, development, and management, with specific emphasis on the groundwater basins of Southern California. In particular, he has consulted to most of the major water districts and agencies in the Southern California area, as well as clients in South America, Europe, and the Middle and Far East. The author of numerous publications on groundwater, Williams is also a part-time research professor at the University of Southern California, where he has taught graduate level courses in geohydrology and groundwater modeling since 1980. Williams received a B.S. in Geology from the University of Redlands and both an M.S. and Ph.D. in Groundwater Hydrology from the New Mexico Institute of Mining and Technology. He is a registered California geologist, a certified hydrogeologist with the State of California, and a certified groundwater hydrologist with the American Institute of Hydrology.

APPENDIX B: MEETING AGENDA

**NATIONAL WATER RESEARCH INSTITUTE**  
**Independent Advisory Panel Meeting**

*Biodegradable Dissolved Organic Carbon (BDOC) as a Surrogate for  
Organics Removal in Groundwater Recharge*

**March 21, 2012**

California Department of Public Health  
1616 Capitol Avenue  
Room: 74.155  
Sacramento, CA 95899

**Final Agenda**

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**Panel Question:**

Is BDOC a suitable alternative surrogate to TOC to Assess the Removal of unregulated wastewater-derived organic chemicals from recycled water to be used for groundwater recharge via surface spreading?

**Meeting Objectives:**

- Regarding BDOC:
  - Determine if the available research demonstrates that BDOC can be used to measure the performance of a SAT system.
  - Evaluate various methods/approaches available to quantify BDOC in recycled water and in water that has been recharged, and to recommend an approach for measuring the  $\Delta$ TOC where TOC is removed by biological processes.
  - Evaluate the correlation between BDOC and removal of organics and the toxicological relevance of remaining organic compounds.
- Develop recommendations to CDPH on the use of BDOC.

Time	Topic	Presenter
8:30 a.m.	Welcome and Introduction <ul style="list-style-type: none"><li>• Introductions</li><li>• Overview of charge</li><li>• Review Panel process</li><li>• Review agenda</li></ul>	Jeff Mosher (NWRI) Jörg Drewes (Panel Chair)

Time	Topic	Presenter
8:50 a.m.	Discuss the use of BDOC as an alternative to TOC <ul style="list-style-type: none"> <li>• Role of TOC in Recharge Regulations</li> <li>• How has TOC worked as a surrogate?</li> <li>• Why BDOC?</li> </ul>	Jörg Drewes Bob Hultquist (CDPH)
9:20 a.m.	Research on BDOC as a measure of the performance of a SAT System <ul style="list-style-type: none"> <li>• Can this be described by measuring BDOC in recycled water?</li> <li>• Is the degradable organic carbon in the recycled water fully degraded by SAT prior to monitoring wells?</li> <li>• Evaluate the correlation between BDOC and removal of trace organic chemicals to assess SAT performance</li> </ul>	Jörg Drewes
10:00 a.m.	Evaluate various methods/approaches available to quantify BDOC in recycled water and in water that has been recharged, <ul style="list-style-type: none"> <li>• Review approach for measuring the <math>\Delta</math>TOC where TOC is removed by biological processes.</li> </ul>	Jörg Drewes
10:45 a.m.	Break	
11:00 a.m.	Evaluate the toxicological relevance of the refractory bulk organic carbon and remaining trace organic chemicals	Jörg Drewes
11:45 a.m.	Discussions of recommendations to CDPH on the use of BDOC	Panel
12:15 p.m.	<b>Working Lunch</b>	
12:45 p.m.	Discussions with CDPH (con't)	Panel
1:15 p.m.	<b>Break</b>	
1:30 p.m.	Closed Panel-Only Session <ul style="list-style-type: none"> <li>• Develop draft recommendations</li> <li>• Outline Panel report</li> </ul>	Panel
4:00 p.m.	<b>Adjourn</b>	

## **APPENDIX C: MEETING ATTENDEES**

### *Panel Members:*

- Chair: Dr.-Ing. Jörg E. Drewes, Colorado School of Mines (Golden, CO)
- James Crook, Ph.D., Water Reuse Consultant (Norwell, MA)
- Jean-François Debroux, Ph.D., Kennedy/Jenks Consultants (San Francisco, CA)
- Peter Fox, Ph.D., National Center for Sustainable Water Supply, Arizona State University (Tempe, AZ)
- Shane Snyder, Ph.D., Arizona Laboratory for Emerging Contaminants (ALEC), University of Arizona (Tucson, AZ)
- Dennis E. Williams, Ph.D., P.G., CHG, GEOSCIENCE Support Services, Inc. (Claremont, CA)

### *National Water Research Institute:*

- Jeff Mosher, Executive Director
- Gina Vartanian, Outreach and Communications Manager

### *California Department of Public Health (CDPH):*

- Robert Hultquist, P.E., Chief, Drinking Water Technical Operations Section (retired)
- Mark Bartson, CDPH
- Lynda Dyane, CDPH
- Leah Walker, CDPH

### *CDPH (On Phone):*

- Randy Barnard, PE, Division of Drinking Water & Environmental Management
- Cindy A. Forbes, PE, Division of Drinking Water & Environmental Management
- David Spath, Ph.D. CDPH
- Brian Bernados, P.E., Recycled Water and Treatment Technology Specialist





## **APPENDIX D: PUBLISHED METHODS TO DETERMINE BDOC/AOC**

There are three primary published methods to determine BDOC. They include the following methods:

- 1.) An oxic mixed batch test using suspended microbes (Servais et al., 1989).
- 2.) A recirculating oxic plug-flow reactor with microbes attached to media (Lucena et al., 1990).
- 3.) An oxic mixed batch test using microbes attached to media (Cha et al., 2004).







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