
Predictors of Water-soluble Organics (WSOs) in Produced Water— A Literature Review

Regulatory and Scientific Affairs

PUBLICATION NUMBER 4717
MARCH 2002

Predictors of Water-soluble Organics (WSOs) in Produced Water— A Literature Review

Regulatory and Scientific Affairs

PUBLICATION NUMBER 4717
MARCH 2002

PREPARED UNDER CONTRACT BY:

Jerry M. Neff and Scott Stout, Battelle, Duxbury, MA



**Helping You
Get The Job
Done Right.SM**

FOREWORD

API publications necessarily address problems of a general nature with respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precaution, nor undertaking their obligations under local, state, or federal laws.

Nothing contained in any API publication is to be considered as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any federal, state, or municipal regulation with which this publication may conflict.

Suggested revisions are invited and should be submitted to Regulatory and Scientific Affairs Department, American Petroleum Institute, 1220 L Street, N.W., Washington, D.C. 20005.

All rights reserved. No part of this work may be reproduced, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, N.W., Washington, D.C. 20005.

Copyright © 2002 American Petroleum Institute



Documents
Document Sharing Hub

ABSTRACT

Discharge of treated produced water to offshore waters of the United States is regulated by NPDES permits. Current general permits for the discharge of produced water to Federal offshore waters of the Gulf of Mexico have total oil and grease limits of 42 mg/L (ppm) daily maximum and 29 mg/L monthly average. EPA requires oil and grease concentrations in produced water to be monitored by EPA Method 413.1 or 1664. Both methods are gravimetric. The methods tend to overestimate the concentration of petroleum hydrocarbons in produced water, due to interference from dissolved non-hydrocarbon chemicals. The objective of this report is to evaluate the chemical composition of produced water from oil and gas wells, and identify the water-soluble organic chemicals (WSOs) in produced water that interfere with gravimetric determination of oil and grease. An initial assessment is made of the physical and chemical properties of the produced water and the associated fossil fuel reservoir, in an effort to predict which produced waters will contain high concentrations of WSOs.

Produced water may contain up to 1,000 mg/L total organic carbon (TOC), most of it in solution. Most of the dissolved organic carbon in produced water is accounted for by C₂ through C₅ organic acid anions, such as acetate, propionate, and butyrate. Acetic acid usually is the most abundant organic acid in produced water. These organic acids are identical to volatile organic acids produced by marine organisms and are not toxic or persistent in the marine environment.

A small fraction (usually less than 20%) of the dissolved organic matter in produced water is comprised of low molecular weight alkanes and aromatic hydrocarbons. The most abundant dissolved hydrocarbons in most produced waters are the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (BTEX). BTEX concentrations usually are in the range of 0.07 to 500 mg/L. Benzene usually is the most abundant. Low concentrations of low molecular weight alkanes (C₅ to C₂₀) and traces of a few polycyclic aromatic hydrocarbons (PAHs) also may be present in produced water. The concentration of total PAHs usually is less than about 2 mg/L. Naphthalene and alkyl naphthalenes usually are the most abundant.

Phenols usually are present in produced water at concentrations lower than 20 mg/L. Phenol, C₁-, and C₂-phenols usually are the most abundant. Other dissolved hydrocarbon-like chemicals containing oxygen, sulfur, or nitrogen usually are present at trace concentrations.

Produced water contains in solution most of the non-metal inorganic and metal ions found in seawater. Many produced waters, including most of those from the U.S. Gulf of Mexico, have a salinity (total dissolved solids concentration) greater than that of sea water ($\approx$ 35 g/kg). However, ionic ratios in produced water may be different from those in sea water. A few metals may be present in produced water from different sources at concentrations substantially higher (1,000-fold or more) than their concentrations in clean natural sea water. The metals most frequently present in produced water at elevated concentrations include barium, cadmium, chromium, copper, iron, lead, nickel, and zinc. Usually, only a few of these metals are present at elevated concentrations in a particular produced water sample. Produced water, particularly that from the Gulf of Mexico, contains radium isotopes (²²⁶Ra plus ²²⁸Ra) at concentrations up to about 2,800 pCi/L.

Organic acids are the quantitatively most important WSOs in produced water that interfere with the gravimetric methods for determination of total oil and grease. Although they are not extracted efficiently with the organic solvent used in the gravimetric methods (Freon[®] or hexane), their concentrations in most produced waters are high enough that they contribute substantially to the mass of organic matter extracted from produced water. Treatment of the extract with silica gel (an option in Method 1664) decreases the amount of interfering non-hydrocarbon WSOs in the extract.

Organic acids in petroleum or produced water are thought to form by thermal degradation of oxygenated organic matter in source rocks or by hydrous pyrolysis of hydrocarbons. Organic acid anions are more soluble in water than in oil and, so, partition into produced water from the oil in the reservoir. The optimum temperature for these processes appears to be in the range of 80°C to 120°C. At lower reservoir temperatures, microbial degradation of organic acids decreases their concentrations in the produced water. At higher reservoir temperatures, organic acids are unstable and undergo thermal decarboxylation, forming CO₂ and low molecular weight hydrocarbons (natural gas).

Because of these thermal processes, concentrations of total volatile organic acids in produced water tend to increase with increasing temperature below about 80°C, reach highest levels in reservoirs with temperatures between about 80°C and 120°C, and decline in reservoirs with higher temperatures. However, many secondary factors influence the concentration of organic acids in any given produced water. Thus, the relationship between temperature and organic acid concentration in produced water is only approximate. It is not possible to use reservoir temperature alone to predict the concentration of organic acids in produced water. The main secondary factors affecting organic acid concentrations in produced water include the nature and amount of organic matter in source rocks, the age of the reservoir, the geology and migration distance between source rocks and the reservoir, and the sources of connate water in the reservoir.

The following recommendations are based on the results of this review:

- The optional silica gel cleanup step in Method 1664 should be used to remove most of the polar organic chemicals that interfere with oil and grease measurement; and,
- Consistent correlations between organic acid concentrations in produced water and physical/chemical properties of the hydrocarbon-bearing formation, the crude oil or gas, and/or the produced water itself are needed, although the necessary composition and property data are rarely available. If such information can be obtained from operators, it may be possible to model the occurrence of organic acids and total WSOs in produced water.

ACKNOWLEDGMENTS

The following participants are recognized for their contributions to this work:

API STAFF CONTACT

Roger Claff, Regulatory Analysis and Scientific Affairs Department

MEMBERS OF THE API OIL AND GREASE WORKGROUP

Syed Ali, ChevronTexaco Corporation

Kris Bansal, Conoco, Incorporated

Larry Henry, ChevronTexaco Corporation

Sung-I Johnson, Phillips Petroleum Company

Tim Nedwed, ExxonMobil Upstream Research Company

Bhagwandas Patel, Equilon Enterprises, LLC

James Ray, Shell Oil Company

Larry Reitsema, Marathon Oil Company

Joseph Smith, ExxonMobil Upstream Research Company

Donna Stevison, Marathon Oil Company

Zara Khatib, Shell Oil Company

TABLE OF CONTENTS

Section	Page
1 INTRODUCTION.....	1
2 CHEMICAL COMPOSITION OF PRODUCED WATER.....	2
2.1 Origins of Produced Water.....	2
2.2 Organic Chemicals in Produced Water.....	3
2.3 Inorganic Chemicals in Produced Water.....	8
2.4 Production Chemicals in Produced Water.....	12
3 NATURE OF THE WATER-SOLUBLE ORGANIC MATTER IN PRODUCED WATER.....	13
3.1 WSOs in Produced Water.....	13
3.2 Interference of WSOs with Oil & Grease Analysis.....	14
4 GEOCHEMISTRY OF ORGANIC ACIDS IN PRODUCED WATER.....	15
5 RECOMMENDATIONS.....	18
6 REFERENCES.....	18

Tables

1 Volumes of treated produced water discharged to the ocean from production platforms in several parts of the world. Volumes are liters/day.	3
2 Concentration ranges of several classes of naturally-occurring organic compounds in produced water worldwide. Concentrations are in mg/L (parts per million). From Neff (1997).....	3
3 Concentrations of total dissolved organic carbon (DOC) and total C ₂ through C ⁵ organic acids in produced water from several geologic basins. Age and temperature of the formation are given. Concentrations of DOC and organic acids are mg/L. From Fisher (1987).....	4
4 Mean concentrations of the main organic fractions in produced water from three offshore production facilities in the Norwegian Sector of the North Sea. BTEX (C ₆ -C ₈ aromatics) are not included. Concentrations are mg/L. From Strømgren et al. (1995).....	4
5 Maximum reported concentrations of several organic acids in produced waters. Concentrations are mg/L. From MacGowan and Surdam (1988).....	4
6 Range of concentrations of several low molecular weight organic acids in produced water from three locations. Concentrations are mg/L. From MacGowan and Surdam (1988).....	5
7 Range of concentrations of organic acids, aliphatic acids, and phenols in produced water from Seven produced water treatment facilities in coastal Louisiana. Concentrations are mg/L. From Rabalais et al. (1991).....	5
8 Concentrations of phenol and different alkylphenol groups in produced water from three production facilities in Indonesia. From Neff and Foster (1997). Concentrations are mg/L.	6
9 Concentrations of BTEX and other selected monocyclic aromatic hydrocarbons in produced water from four platforms in the U.S. Gulf of Mexico (OOC, 1997; DOE, 1997) and from three offshore production facilities in Indonesia (Neff and Foster, 1997). Concentrations are mg/L.	7

Section	Page
10 Concentrations of n-alkanes in produced water from two platforms in coastal Louisiana and two platforms in Thailand. Concentrations are mg/L. From Neff et al. (1989) and Battelle (1994).	8
11 Concentrations of individual PAHs in seven produced waters from the U.S. Gulf of Mexico (DOE, 1997; OOC, 1997), three produced waters from Indonesia (Neff and Foster, 1997), and one produced water from Thailand (Battelle, 1994). Concentrations are mg/L.	9
12 Concentration ranges of selected cyclic alkanes and heterocyclic compounds in produced water from three production treatment facilities in Indonesia. Concentrations are mg/L. From Neff and Foster (1997).	10
13 Concentrations of several elements and inorganic ions in produced waters from different geologic ages. Concentrations are mg/kg (ppm). From Collins (1975).	11
14 Concentration ranges of several metals in produced water from seven platforms in the northwestern Gulf of Mexico. From DOE (1997) and OOC (1997). Concentrations are mg/L.	11
15 Activities of natural ²²⁶ Radium and ²²⁸ Radium in produced water from the U.S. Gulf of Mexico. Activities are pCi/L. 1 picocurie (pCi) = 0.037 bequerels (BQ). From Neff (1997).	11
16 Amounts of production chemicals used on production platforms in the North Sea and amounts discharged with produced water to the ocean or injected into a well. Masses are metric tons/year. Table from Hudgins (1994)	13
17 Aqueous solubilities and values for log K _{ow} for several low molecular weight petroleum hydrocarbons. Concentrations are mg/L. From TPH Criteria Working Group (1997).	14
18 Factors potentially influencing the concentration of organic acids in produced water	16

PREDICTORS OF WATER-SOLUBLE ORGANICS (WSOs) IN PRODUCED WATER—A LITERATURE REVIEW

1 Introduction

The U.S. Environmental Protection Agency (EPA) or a state agency designated by EPA issues region wide (general) or site-specific National Pollutant Discharge Elimination System (NPDES) permits to regulate discharges of treated produced water to State and Federal offshore waters of the United States. Produced water intended for ocean discharge is first treated in various oil/water separation devices to remove dispersed oil droplets. Current general permits for Federal offshore waters of the Gulf of Mexico have limits for total oil and grease in produced water of 42 mg/L (ppm) daily maximum and 29 mg/L monthly average.

EPA requires oil and grease concentrations in produced water to be monitored by EPA Method 413.1 or 1664 (EPA, 1983, 1995). Both methods are gravimetric. Nonpolar and slightly polar organic matter in produced water is extracted with Freon[®] (Method 413.1) or n-hexane (Method 1664). In Method 1664, the analyst has the option to treat the hexane extract with silica gel to remove polar interfering compounds. The extract is dried and weighed to derive a concentration of total extractable organic matter (total oil and grease).

Although the oil and grease methods are inexpensive and easy to perform, there are two technical problems that may have implications for the regulation of discharges of produced water to offshore marine waters. First, low-molecular-weight, volatile alkane and aromatic hydrocarbon (BTEX) analytes are lost by evaporation during sample processing. Second, many non-hydrocarbon organics, and possibly some metals, are extracted by the solvent and measured as part of the total oil and grease in produced water, even after extract cleanup with silica gel.

Loss of volatile hydrocarbons is not a concern, since these chemicals are not persistent in surface waters and so are unlikely to contribute to the toxicity of produced water plumes to marine animals (Neff, 1997). In a regulatory context, the second problem is more of an issue. The analytical methods may grossly overestimate the concentration of petroleum hydrocarbons in produced water if the concentration of non-hydrocarbon organic matter in the produced water is high (Brown et al., 1990, 1992; Otto and Arnold, 1996). Typical produced water from production platforms in U.S. Gulf of Mexico may contain 50 to more than 500 mg/L (ppm)¹ total organic carbon (TOC), of which approximately 8.5 to 16% is petroleum hydrocarbons (Neff et al., 1989). The remaining TOC is a mixture of non-hydrocarbon organics, including water-soluble production treatment chemicals, phenols, organic acids, alcohols, and ketones. These non-hydrocarbon organic fractions of produced water have not been well characterized. Some information is available about water-soluble production treatment chemicals, organic acids, and phenols (Neff, 1997).

If oil and grease concentrations in produced water from a platform exceed regulatory limits for oil and grease, the operator may be required to cease discharging produced water and upgrade the produced water treatment system on the platform. If most of the organic matter measured oil and grease is comprised of water-soluble organics and not true petroleum hydrocarbons, improvement of the efficiency of the oil/water separation system will not help to bring total oil and grease concentrations down below regulatory limits. Usually in such circumstances offshore compliance can only be accomplished by closing in the wells or reinjecting the produced water, both of which have substantial financial consequences, especially in a deep offshore environment. There are two approaches to resolving this problem:

- Develop and gain EPA approval of a new analytical method for total oil and grease that accurately measures the true concentration of produced water petroleum hydrocarbons, excluding non-hydrocarbon water soluble organics (WSOs); or,
- Develop and gain EPA acceptance of correlations or predictors of elevated concentrations of non-hydrocarbon WSOs in produced waters, so that these correlations might be used to adjust monitoring data in compliance determinations.

¹Concentration in parts per million should be expressed on a weight/weight basis as mg/kg; however, it often is expressed on a weight/volume basis as mg/L. The two values are essentially the same when the liquid is fresh water (specific gravity of 1.0 g/mL). However, many produced waters are concentrated brines with specific gravity of > 1.0. The error resulting from expressing ppm as mg/L is small and within the margin of error of the analytical method. For example, produced water with a salinity of 140 parts per thousand (specific gravity of 1.1009), containing 100 mg/L of a compound, actually contains 99 mg/kg of the chemical. In this document, concentrations in produced water will be expressed in mg/L, or µg/L, which are slightly greater than parts-per-million and parts-per-billion, respectively.