Peer Review Summary Document

(2/9/2021)

Peer Review Plan

https://www.usgs.gov/atom/100335 [80 KB PDF].

Title and Authorship of Information Product Disseminated

Groundwater Quality of Aquifers Overlying the Oxnard Oil Field, Ventura County, California, By Rosecrans, C.Z., Landon, M.K, McMahon, P.B, Gillespie, J.M., Kulongoski, J.T., Stephens, M.J., Hunt, A.G., Shimabukuro, D.H., and Davis, T.A.

Peer Reviewers Expertise and Credentials

Reviewer 1 holds a Ph.D. in Earth Science from Duke University and has 10 years' experience in aquatic and groundwater geochemistry research. The reviewer also has substantial experience in geochemical analysis of water interacting with hydrocarbon resources and evaluating mechanisms of groundwater quality impacts using geochemical and isotope tracers.

Reviewers 2 and 3 were anonymous reviewers selected by the journal for their expertise in the subject matter.

Charge Submitted to Peer Reviewers

The reviewers were asked to make an objective evaluation of the study methods, results, and conclusions described in the manuscript.

Summary of Peer Review Comments

Reviewer 1 had five major suggested changes as follows: (1) add statistical tests for correlations and comparison of selected geochemistry to potential explanatory factors; (2) reorganize the results section and sub-sections that outlines the occurrence of light hydrocarbon gases followed by sources and pathways of hydrocarbon gases; (3) move the Noble Gas discussion and figure to the main body of the report; (4) add a quantitative comparison plot of publicly available geochemistry from previous studies to the geochemical data collected as part of the Oxnard Regional Monitoring Program (RMP) to better distinguish/demonstrate the differences between Pleasant Valley and Oxnard Plain groundwater; and (5) update the conclusion that provides a synthesis and summary into a format that follows the same structure of the results sub-section and that includes suggestions for future refinements to better distinguish the pathways of detected thermogenic gases. The reviewer also made numerous editorial and terminology suggestions throughout the manuscript.

Reviewer 2 agreed with the interpretation that detections of thermogenic gas in groundwater indicate interaction of groundwater and hydrocarbon sources, but noted the need to stress that the low permeability units may be discontinuous throughout the Oxnard Plain groundwater basin and thus may partially allow gas to migrate upward following a

piezometric-downgradient direction. The reviewer did not agree with the Spearman's test for correlation results reported between methane and chloride. Reviewer #2 also remarked that the conclusions were too long and needed to be condensed.

Reviewer 3 did not agree with the sample design of the Oxnard RMP and commented that the 14 wells selected were not within an appropriate distance of active oil and gas wells and therefore surmised it would be difficult to find significant connections between sampled groundwater and oil and gas development.

Summary of USGS Response to Peer Review Comments

USGS response to Reviewer 1 comments: The authors found the reviewer's comments very helpful with respect to the suggestion for reorganizing the results and conclusions. In response to the reviewer's major suggestion 1: statistical analysis was added regarding correlations of observed thermogenic gases in available mud logs in relation to depth and oil shows (Spearman's rho test for correlation). However, due to the limited sampling density, correlation and comparison tests of selected geochemistry to potential explanatory factors did not reveal relevant information regarding the influence of the different explanatory factors considered in this study. In response to major suggestion 2: sub-sections in the results were reorganized to present the occurrence of light hydrocarbon gases followed by the sources and pathways. In response to major suggestion 3: a quantitative comparison plot depicting historical chloride concentrations in the Pleasant Valley and Oxnard Plain groundwater and samples collected as part of the Oxnard RMP was added with an expanded discussion that distinguishes differences and sources of high-chloride water between the Pleasant Valley and Oxnard Plain groundwater. In response to major suggestion 4: although the noble gas section was revised in the manuscript text and Supplementary Information section as suggested by Reviewer #1, the authors deduced that the results were not significant or didn't provide clear evidence that the thermogenic gases detected could be definitively tied to natural migration due to the limited density of the collected noble gas data. The pathways of thermogenic hydrocarbon transport to shallow Oxnard aquifers may be a result of diffusion from the underlying tar sands, but minor leakage from well field infrastructure cannot be ruled out as a possibility. For these reasons the noble gas figure and expanded details were retained in the Supplementary Information section. In response to major suggestion 5: The conclusions were condensed and suggestions for refinements in future studies were included. The authors accepted the editorial and terminology suggestions from the reviewer as they deemed appropriate.

USGS response to Reviewer 2 comments: Text was added that clarifies a low permeability unit between the Oxnard upper aquifer system and the lower aquifer system does exist and, in some places, may be discontinuous with an appropriate citation. In addition, citations to historical studies that describe low permeability units in the Santa Barbara Formation that overly the Vaca Tar Sands were included. In response to the reviewer's disagreement with the interpretation of Spearman's test for correlation between methane and chloride concentrations, the authors believe the reviewer misinterpreted the reported p-value for that of a reported rho-value; therefore a p-value of 0.78 for a correlation test between methane an chloride concentrations in groundwater samples collected as part of the Oxnard RMP would not be considered significant. Revisions were made to the manuscript to remove the possibility of misinterpreting reported rho values indicating significant correlations with reported p-values indicating no significant correlation. As suggested by the reviewer, the conclusions were revised and condensed to a succinct summary.

USGS response to Reviewer3 comments: The Oxnard regional monitoring program study design was to sample available groundwater wells within and surrounding the Oxnard oil field boundary contingent on getting permission from well owners. From the over 35 well owners were contacted, permission was obtained from 14 of them. These 14 wells are in areas that capture key locations the authors reason adequately represent the groundwater quality surrounding the oil and gas wells within and surrounding the Oxnard oil field boundary. For example, 8 of the 14 wells are located within the oil field boundary, are in areas that have large densities oil and gas wells, are located both upgradient and downgradient of oil and gas wells, and include wells with depths greater than 380 m below land surface—an important consideration as the Vaca Tar Sand is a shallow hydrocarbon reservoir that occurs with 200 m (vertically) of sampled wells. Additionally, four wells are east of the oil field boundary in the Pleasant Valley groundwater basin—another important consideration as this groundwater basin has historically elevated concentrations of chloride and dissolved organic carbon unassociated with the oil and gas production activities in the Oxnard oil field. The reviewer commented that many of the selected wells are 3 km to 8 km from active wells, however this study sampled wells in 2017; during a period when this oil field was mostly "shut-in" following steam injection and few wells were producing from the Vaca Tar Sands production zone. Figure 4 depicts where the majority of oil and gas wells surrounding sampled groundwater wells with thermogenic gas detections (OXG-5, -6, -7, -2, -3) are "idle". Reviewer #3 also commented that the authors overlooked presenting groundwater quality results of wells OXG-4 and OXG-14 as these were the wells closest (lateral distance) to active oil/gas wells, however these active oils/wells, rather than being associated with the Vaca Tar Sand, are associated with the deeper Sespe formation found at depths greater than 2000 m below land surface; a hydrocarbon formation that is described and depicted in the manuscript text and/or Supplementary Information section. The manuscript states that "all wells were analyzed for the same suite of constituents in the manuscript, but not all constituents are reported," particularly if those wells did not have thermogenic gas detections. Citations for all water quality results in the data release that accompanies this manuscript (Rosecrans, et al., 2020; https://doi.org/10.5066/P99EHQ8H). The authors acknowledge that the sampling density of the study design is insufficient to definitively determine the sources and mechanisms for thermogenic gases present in groundwater in the manuscript conclusions; however multiple lines of evidence are provided throughout the Results and Discussion section that indicate pathways connecting groundwater to hydrocarbon sources exist and whether in oil-production zones or non-producing geologic zones. As suggested by the reviewer, suggestions for future refinements in subsequent investigations to broaden our understanding of potential risks of water-quality degradation in aquifers overlying zones of hydrocarbon production were included in the Conclusions and the Supplementary Information sections.

Dissemination

The published information product will be released by the journal *Science of the Total Environment*.