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CO_2 Radiocarbon Analysis to Quantify Groundwater Contaminant Fuel Degradation at OU-8, Naval Base Kitsap, WA

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bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, xylene (common gasoline contaminants)
CH	chlorinated hydrocarbons
COI	contaminants of interest
COC	contaminants of concern
cVOC	chlorinated volatile organic compound
$\delta^{13}C$	Delta C-13 (stable isotope ratio)
$\Delta^{14}C$	Delta C-14 (radiocarbon isotope ratio)
DIC	dissolved inorganic carbon (dissolved CO_2)
DNAPL	dense non-aqueous phase liquid
DO	dissolved oxygen
DoD	U.S. Department of Defense
EPA	U.S. Environmental Protection Agency
EVO	emulsified vegetable oil
IR	Installation Restoration
LNAPL	light non-aqueous phase liquid
LTM	long-term monitoring
MNA	monitored natural attenuation
NAVBASE	Naval Base
NAVFAC LANT	Naval Facilities Engineering Command Atlantic
NAVFAC Northwest	Naval Facilities Engineering Command Northwest
NAVFAC Southwest	Naval Facilities Engineering Command Southwest
Navy	U.S. Navy
NRL	Naval Research Laboratory
OU	Operable Unit
QA	quality assurance
QC	quality control
ROD	Record of Decision
RPM	Remedial Project Manager
SAP	Sampling and Analysis Plan
SOP	standard operating procedure
TCA	trichloroethane
TCE	trichloroethylene
VOC	volatile organic compound
ZOI	Zone of Influence

Keywords: biodegradation, petroleum-source, fossil end-member, radiocarbon, radiocarbon-depleted, monitoring well, headspace.

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Abstract

This interim report summarizes efforts to characterize petroleum natural attenuation at OU 8 at Kitsap-Bangor Naval Base, WA, where monitored natural attenuation (MNA) is the long-term management alterative for persistent groundwater petroleum contamination. A brief description of the methods for implementing natural abundance radiocarbon to determine *in situ* petroleum hydrocarbon degradation rates is presented. This effort seeks to quantify the petroleum hydrocarbon portion natural attenuation and determine if it impacts the contaminant plume. Additionally, data will be used to determine if MNA is making progress toward attaining Washington State Model Toxics Control Act (MTCA) groundwater Method B cleanup standards for contaminants of concern (COCs) that include benzene and toluene. This study does not focus on chlorinated solvents – just petroleum. The radiocarbon method cannot distinguish between these classes of compounds. The radiocarbon method uses two main types of data, CO_2 radiocarbon content and respiration rate (CO_2 production over time), to determine hydrocarbon degradation rate: Petroleum degradation ranged from non-detect to 135 µg L^{-1} d^{-1} and displayed seasonality (highest rates in the summer, lowest in early spring). Spatially, rates were highest at the plume fringe – and upgradient. Downgradient wells may have been influenced by EVO injections adding modern carbon to the system. Two limited samplings were done before and after soil vapor extraction at the site (not included in this report) to determine how a disruptive event alters the relatively stable biogeochemical processes on-site. Another limited sampling after a year of quiescence would be useful to determine if the site conditions return to a previous state - and thus allow long-term attenuation prediction(s).

Introduction

The Department of Defense (DoD) faces billion-dollar expenditures for environmental cleanup in the United States. Prohibitive cleanup costs make treatment strategies such as monitored natural attenuation (MNA), enhanced passive remediation (EPR) or low-cost engineered solutions attractive remediation alternatives for reaching Response Complete (RC) status. Several lines of converging evidence are seen as necessary to establish reasonable evidence for *in situ* bioremediation or natural attenuation. Indirect "lines of evidence" approaches when used to determine natural attenuation rates are plagued by uncertainty. The main difficulty is trying to translate indirect measurements with the actual in situ contaminant conversion to a harmless end-product, *i.e.* CO_2.

Natural abundance radiocarbon analysis in respiration products serves as an excellent assessment tool because the method targets contaminant backbone carbon, so ^{14}C-depleted respiration CO_2 can be directly linked to petroleum hydrocarbons or petroleum-derived industrial chemicals. Because petroleum sources have been sequestered from the active carbon cycle (through burial and diagenesis), they are completely devoid of ^{14}C (which has a ~6,000 year half life). The radiocarbon signature (or lack thereof) is spread evenly throughout the contaminant mass, so there is no need to worry about tracer dilution effects (as one would with an added tracer compound).

Groundwater radiocarbon analysis has long been used to trace aquifer water age and associated recharge rate(s) because once intercalated through soils to an aquifer, meteoric water begins aging

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without atmospheric CO_2 exchange. A field site with organic solvent contamination was essentially "discovered" because radiocarbon results were anomalously depleted - far more than one would expect with normal aging groundwater. ^{14}C-depleted CO_2 was found in areas where organic solvents had been released (*1*). This provided a direct tie between the contaminant carbon backbone and contaminant respiration. CO_2 radiocarbon content soon after started being used to confirm hydrocarbon degradation at fuel and chlorinated hydrocarbon contaminated sites (*2-9*). Petroleum-derived CO_2 within the groundwater CO_2 pool can be calculated using a simple isotopic mixing model (*6, 9*). Background sites are used for the natural $^{14}CO2$ age on site (natural organic matter and root respiration).

Recently, we have measured CO_2 respiration rates in tandem with CO_2 radiocarbon content to determine the actual contaminant hydrocarbon degradation rate (*8-11*). This coupling is the most definitive means to determine the actual degradation rate on-site as it follows the actual contaminant's transfer from native form (*e.g.* contaminant) to CO_2 in both time and space. These measurements allow environmental managers to factor in the actual contaminant degradation rate to satisfy regulators and stakeholders and to plan further assessments or remedial actions. In this study, CO_2 radiocarbon and respiration analysis were used to confirm natural attenuation as a significant factor removing fuel hydrocarbons at OU-8.

Objectives

This project's objective is to combine CO_2 respiration and CO_2 radiocarbon content to calculate hydrocarbon degradation occurring at OU-8. Radiocarbon analysis will measure the fraction of petroleum-source in the CO_2 pool. To determine COI degradation rate, we will measure the CO_2 production rate using short-term incubations with collected groundwater. Using the respiration rate (CO_2 produced per unit volume per unit time) and the radiocarbon age of the CO_2 being respired, the contaminant degradation rate can be determined over both time (seasonal sampling) and space (multiple wells). This provides two key answers for site management and remediation efficacy (both active and passive) that have not been available:

- Is remediation occurring? We will be able to track the amount (percentage basis) of the degradation end product (CO_2). On the basis of this one measurement, a site manager will be able to definitively state whether (*bio*)degradation is occurring or not.
- At what rate is the remediation occurring? By measuring the proportion of fossil fuel-derived CO_2 and the CO_2 production rate over time, we will be able to calculate the rate of (*bio*)degradation occurring on-site. Using groundwater transport models and given an estimated size or volume of source material and plume dimensions, a much more accurate estimation of the time for remediation can be predicted:

$$\left(\frac{\text{unit time (i.e. } days)}{g\ CO_2 \text{ from contaminant}}\right)\left(g \text{ source contaminant}\right) \cong \text{time to remediate}$$

Technical Approach

The technical approach for the project is relatively well defined. It involves measuring the CO_2 production over unit time (respiration) and determining a radiocarbon age for that respired product. If the CO_2 is radiocarbon-depleted relative to a background site where natural organic matter is the only respiratory substrate, the radiocarbon-depleted CO_2 must be derived from the petroleum-sourced contaminant. By coupling the respiration rate and the differential respiration product derived from the contaminant, a contaminant degradation rate can be determined. Developing a model based on site hydrogeologic parameters which determines the volume sampled during each respiration measurement allows scaling contaminant degradation rate spatially and interpolation between wells sampled as above allows site-wide contaminant degradation estimates.

With a respiration rate (mg CO_2 degraded L^{-1} day^{-1}) and the CO_2 radiocarbon percentage, a straightfoward calculation for the degradation rate at each well was made (*e.g.* mg cVOC carbon degraded m^{-3} d^{-1}). The rates were then interpolated over the entire sampled area using estimates for plume dimensions to calculate the cVOC mass degraded over the entire site in time. Through NAVFAC contracting, additional biogeochemical analysis were made to better understand site conditions by Sealaska. Details are in the Sealaska Tier II SAP.

Results and Discussion

Due to cost constraints, all sampled wells were not assayed for radiocarbon (8MW24, 8PS-A1, 8PS-C2, and 8MW06). For May 2019 samples, 8MW05, 8MW47, 8PS-C1 and 8PS-F1 were also not able to be analyzed. If additional funding becomes available, these samples will be analyzed by NOSAMS. For the May 2019 samples for which no radiocarbon values were available, the average from pervious samples for a given well was used. At present, these are estimated values.

Respiration (CO_2 produced per unit time – per unit volume) was generally highest at the upper and western fringes of the plume. This was reasonably consistent between warmer seasons (Jul2017, Oct18, Figs. 3, 10) but in spring samplings (Apr18, May19) respiration was very low upgradient (8MW-47, -24, -08 and -05) and dominated by respiration at the southern end of the plume (Figs. 7, 13). Respiration was highest in the Jul17 sampling (460 µg C L^{-1} h^{-1}) followed by the May19 sampling (~160 µg C L^{-1} h^{-1}). Lowest rates were in Apr18 where only 9 of the 16 wells demonstrated measurable respiration.

Dissolved CO_2 age corrected for background and expressed as fraction petroleum derived or F_{pet} was highest at fringes and usually high (meaning more petroleum source) For instance, at 8MW-08 (upgradient east), F_{pet} was over 60% for all samplings (Figs. 4, 8, 11, 14). Well 8MW-47 (upgradient west) F_{pet} was 79-80% over the four samplings. Well 8MW-54, downgradient of the treatment area wells (8PS-XX) also had consistently old dissolved CO_2 – averaging 45% from petroleum sources. Treatment area well CO_2 (8PS-XX series) varied over the course of the study averaging around 32% from petroleum sources in Jul17 to only around 4% in Oct18 and May19. This may be a residual impact from modern carbon released as EVO in the region of the treatment wells. In conjunction perhaps, dissolved CO_2 at 8MW-33 (the farthest downgradient well) was modern during the Jul17 and Apr18 samplings (*e.g.* 0% petroleum sourced), but increased to ~17% petroleum sourced in Oct18 and May19. This could indicate

respiration product from contaminants being transported downgradient to this well. A similar observation was made for 8CB-8MW01 which was 7% petroleum sourced in Jul17, but increased to 19% in Apr18, and to 49% in Oct18. This well has not yet been analyzed for radiocarbon from the May19 sampling.

The highest petroleum degradation rates were recorded in Jul17 – up to 160 µg C L^{-1} h^{-1} (8PS-G1). Fringe areas, which had higher respiration and older CO_2 demonstrated the highest rates (Fig. 5). Rates in October were also relatively high throughout the site (Fig. 12) topping out at 26 µg C L^{-1} h^{-1}. Rates in April were low relative to other samplings only around 4 µg L^{-1} h^{-1}. Most degradation occurred downgradient of the treatment area (Fig. 9). In May19, most petroleum mineralization was upgradient of the treatment well region (Fig. 15) with the highest rate at 42 µg C L^{-1} h^{-1}.

These results confirm petroleum biodegradation at OU-8 with warmer months demonstrating the most degradation (up to ~120 g L^{-1} $month^{-1}$). Most wells on site with significant petroleum biodegradation showed more modest rates (5-50 g L^{-1} $month^{-1}$). These data have not yet been interpolated over the site and plume dimension estimate(s). That calculation could provide an idea of the total mass likely degraded from the plume over long periods (months to years). Results indicate the following:

- Biodegradation is occurring on-site. It is more significant in warmer months (*e.g.* when groundwater is warmer) than in cooler months.
- Biodegradation appears to be highest at the fringe areas of the sampling grid. Although there was significant petroleum biodegradation at the treatment well region during Jul17, subsequent samplings showed lower biodegradation.
- EVO injection may have introduced “younger” carbon in the system showing a residual effect on dissolved CO_2 during the course of the samplings. Dissolved CO_2 in wells downgradient of the treatment area got progressively older during the season sampling course.
- Respiration was difficult to measure during cooler months (very high standard deviation for replicate measurements and subtracted). Longer incubation times may help during any future samplings.

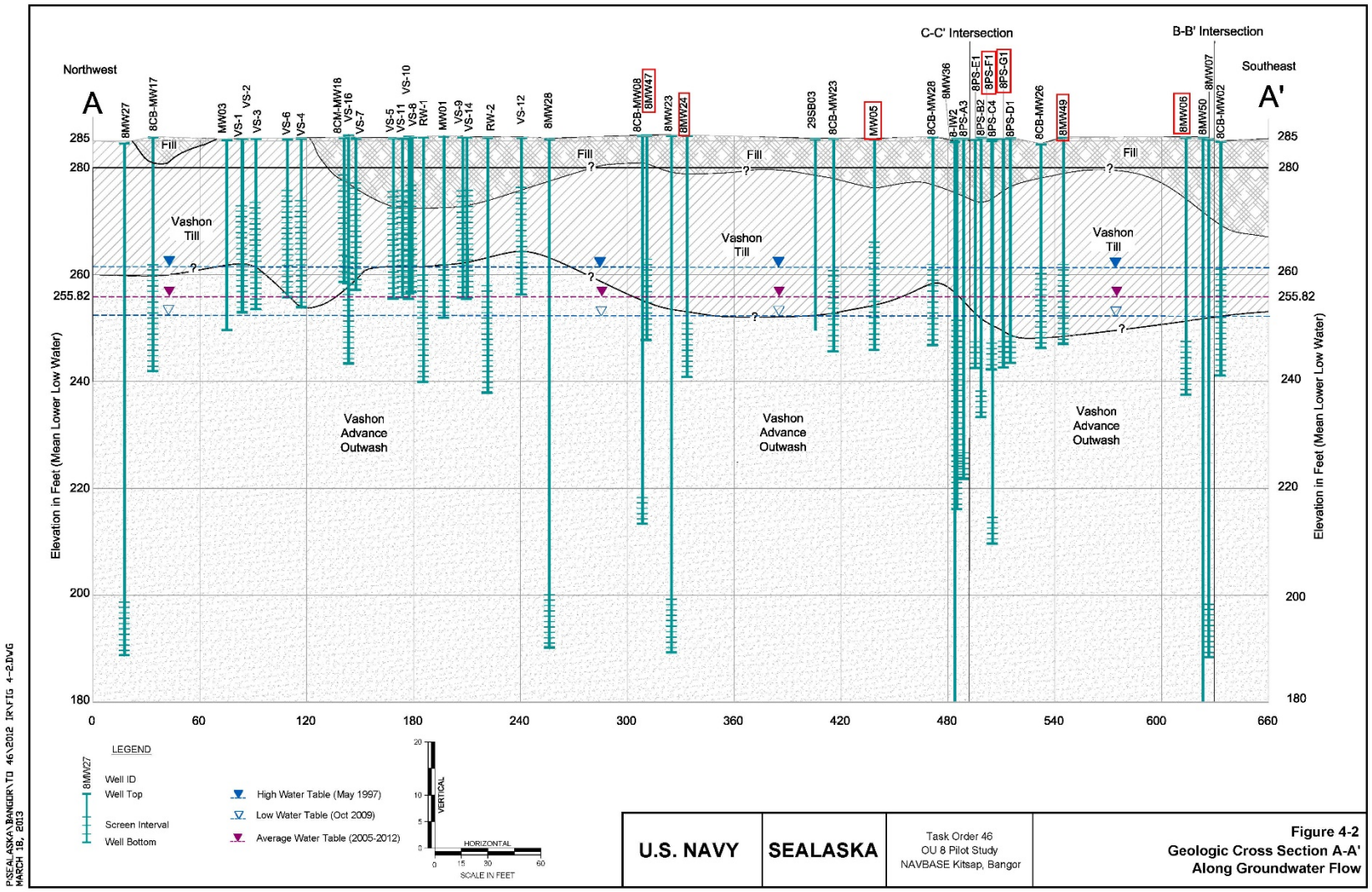


Figure 1. Well cross sections OU-8

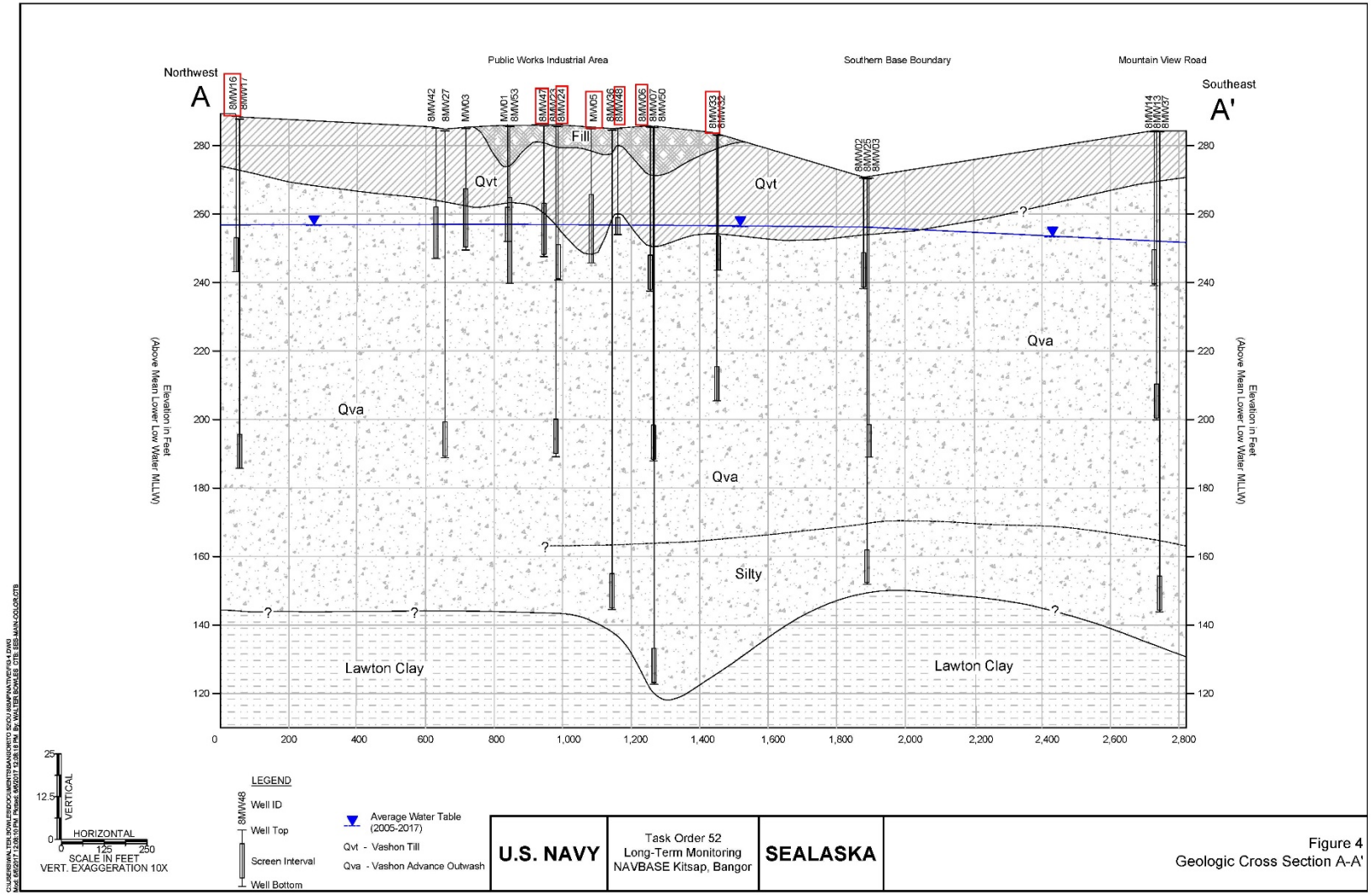
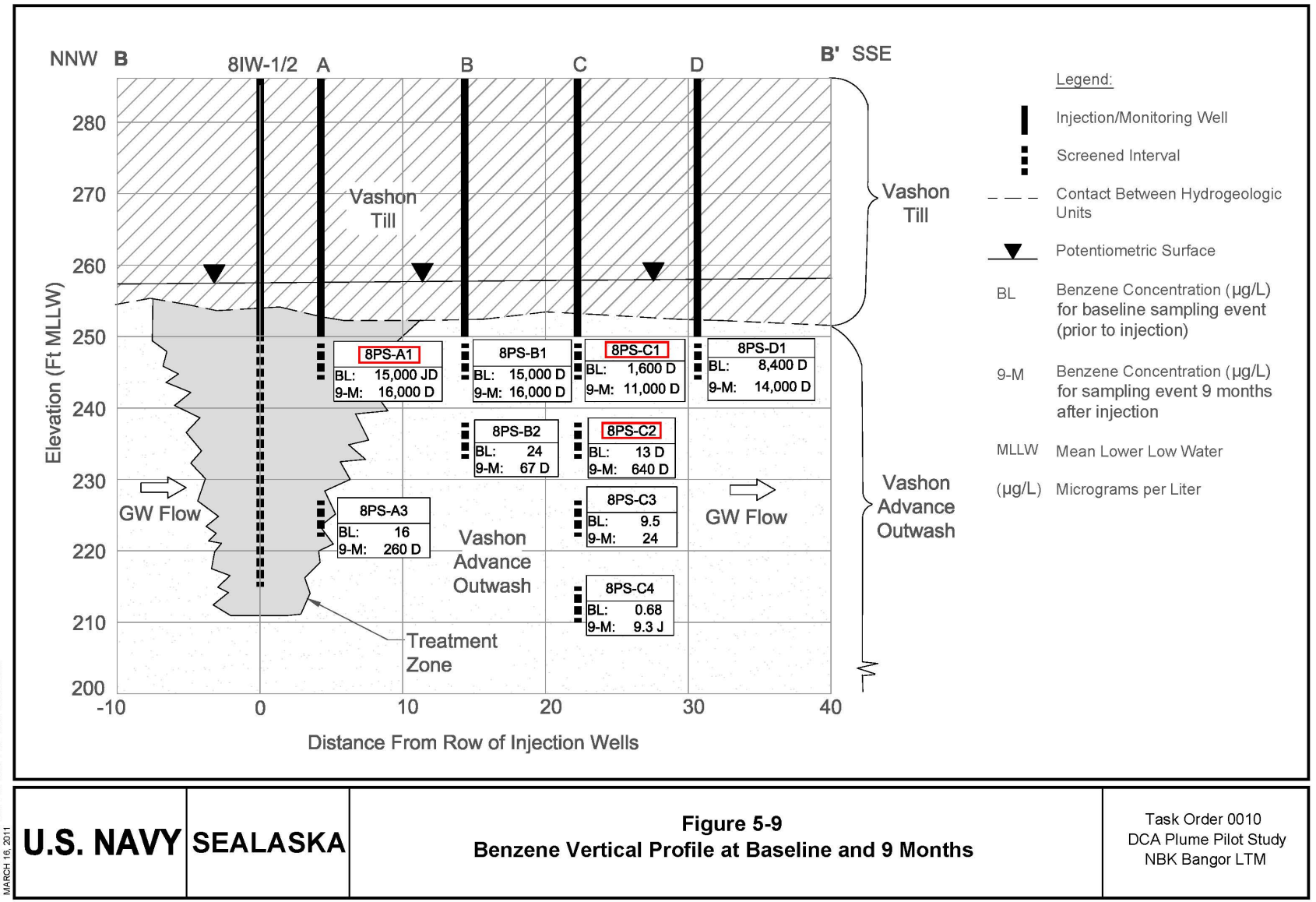


Figure 2. Well cross sections OU-8 (cont)



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MARCH 16, 2011

U.S. NAVY SEALASKA	Figure 5-9 Benzene Vertical Profile at Baseline and 9 Months	Task Order 0010 DCA Plume Pilot Study NBK Bangor LTM

Figure 3. Well cross sections OU-8 (cont)

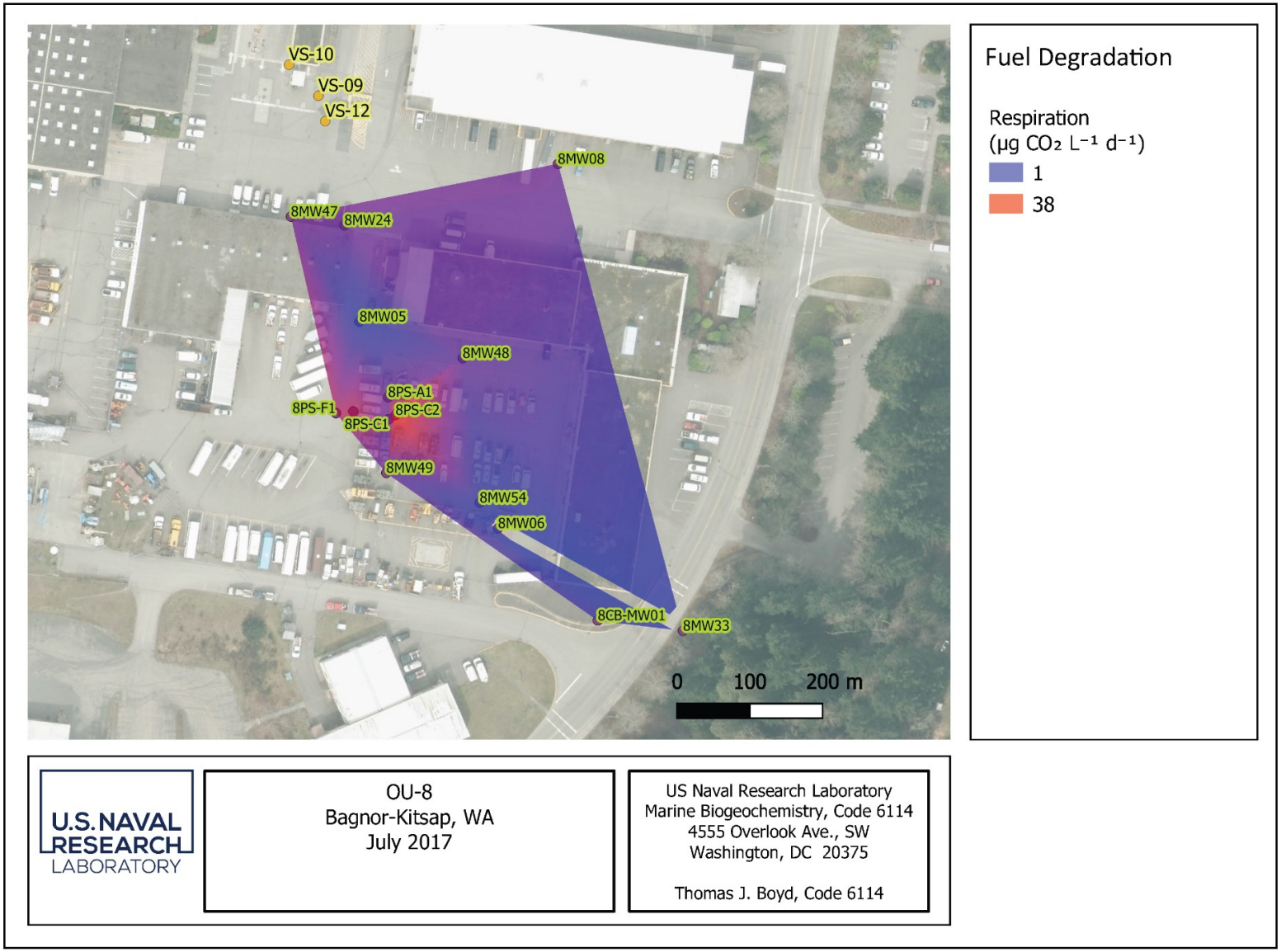

Figure 4. July 2017 Respiration

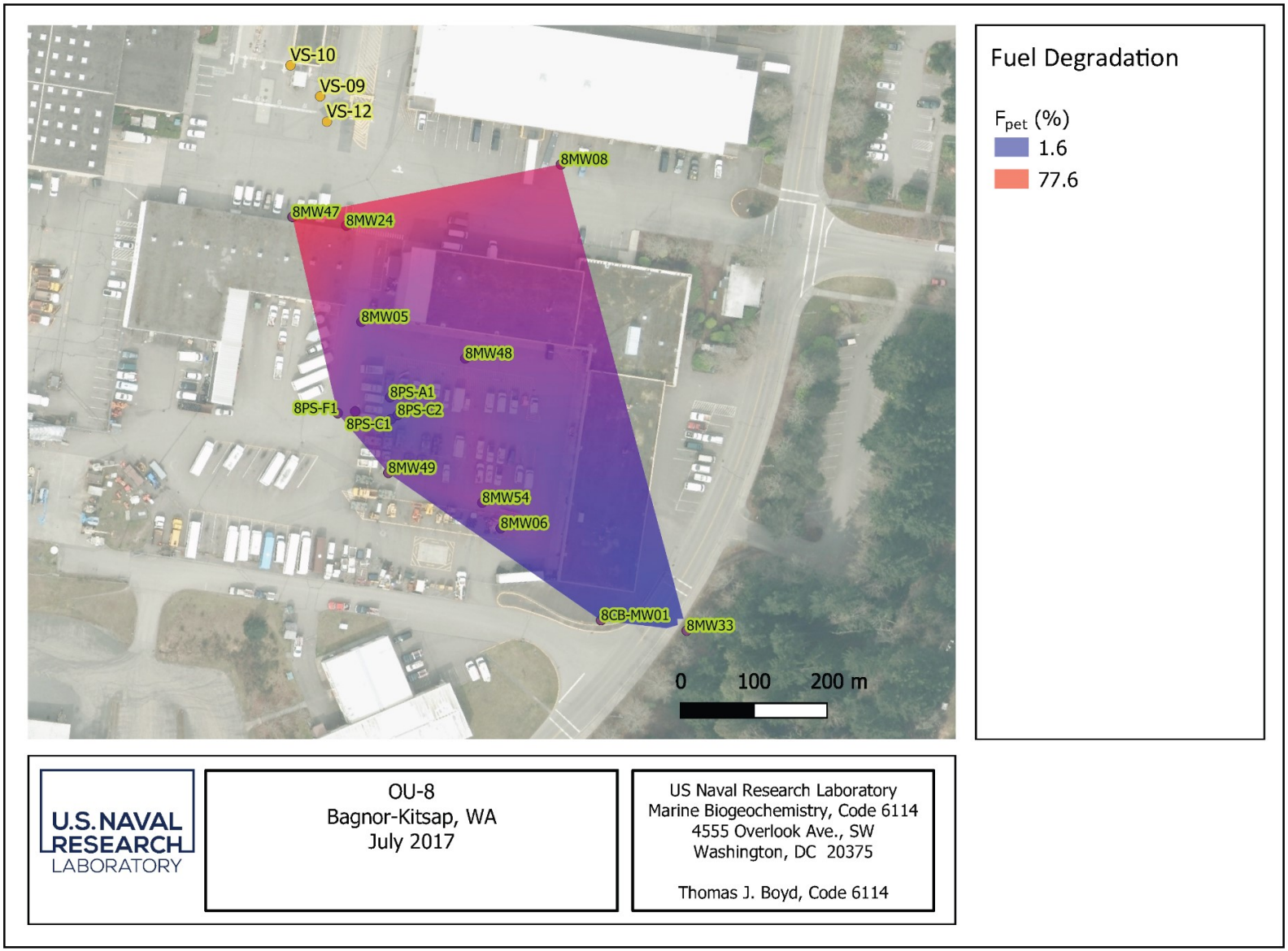

Figure 5. July 2017 DIC Fraction Petroleum

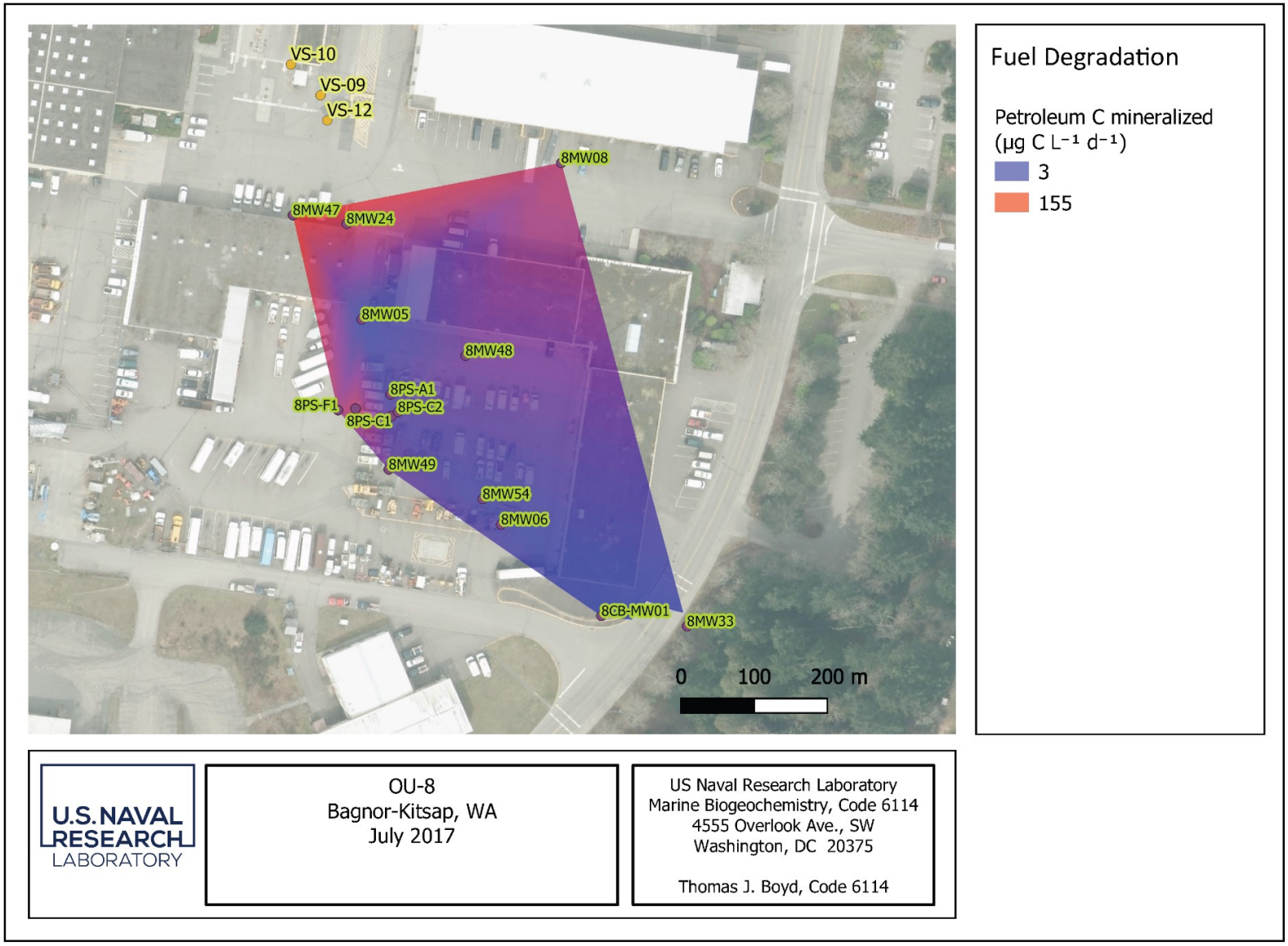

Figure 6. July 2017 Petroleum Degradation Rate

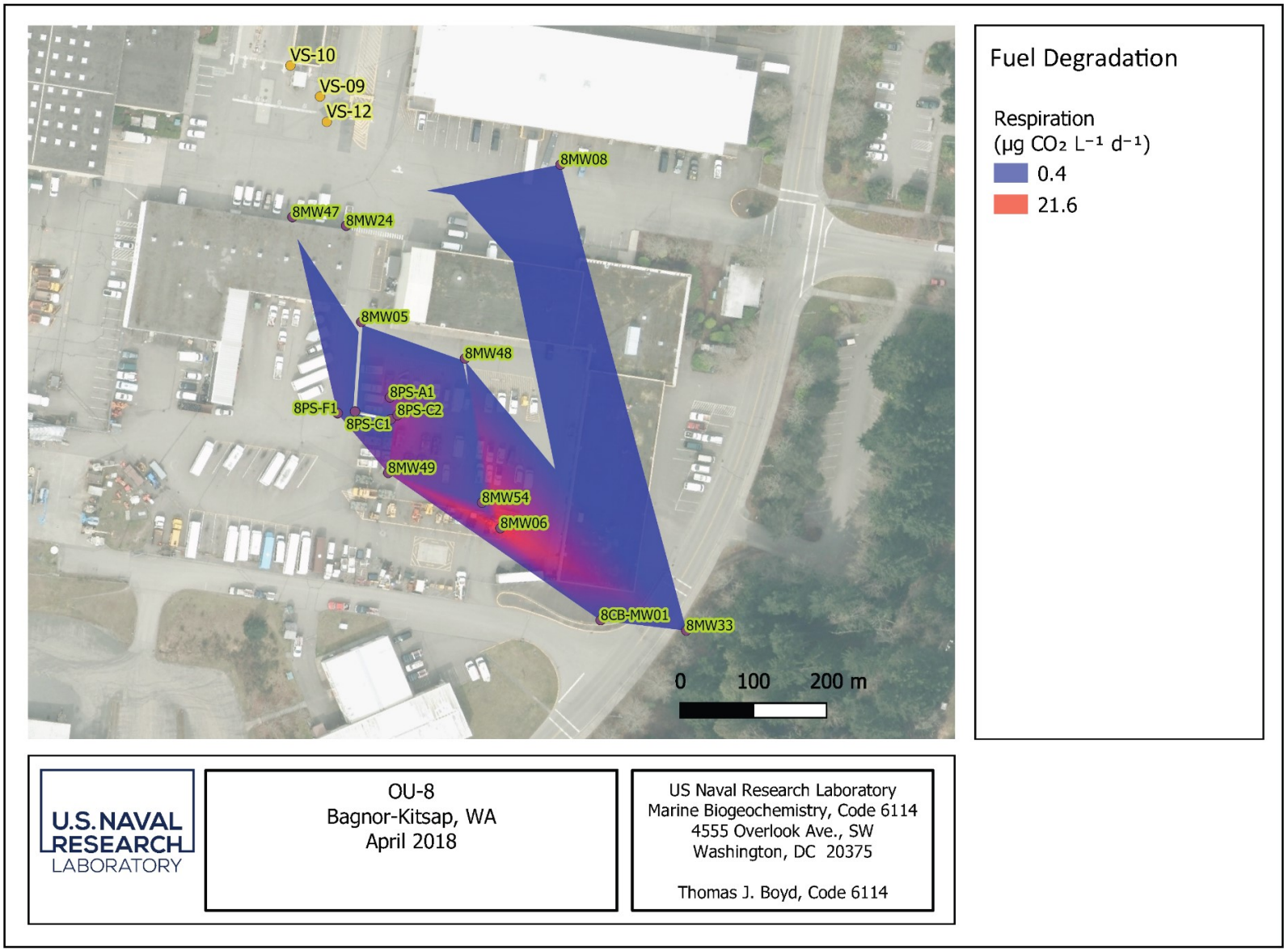

Figure 7. April 2018 Respiration

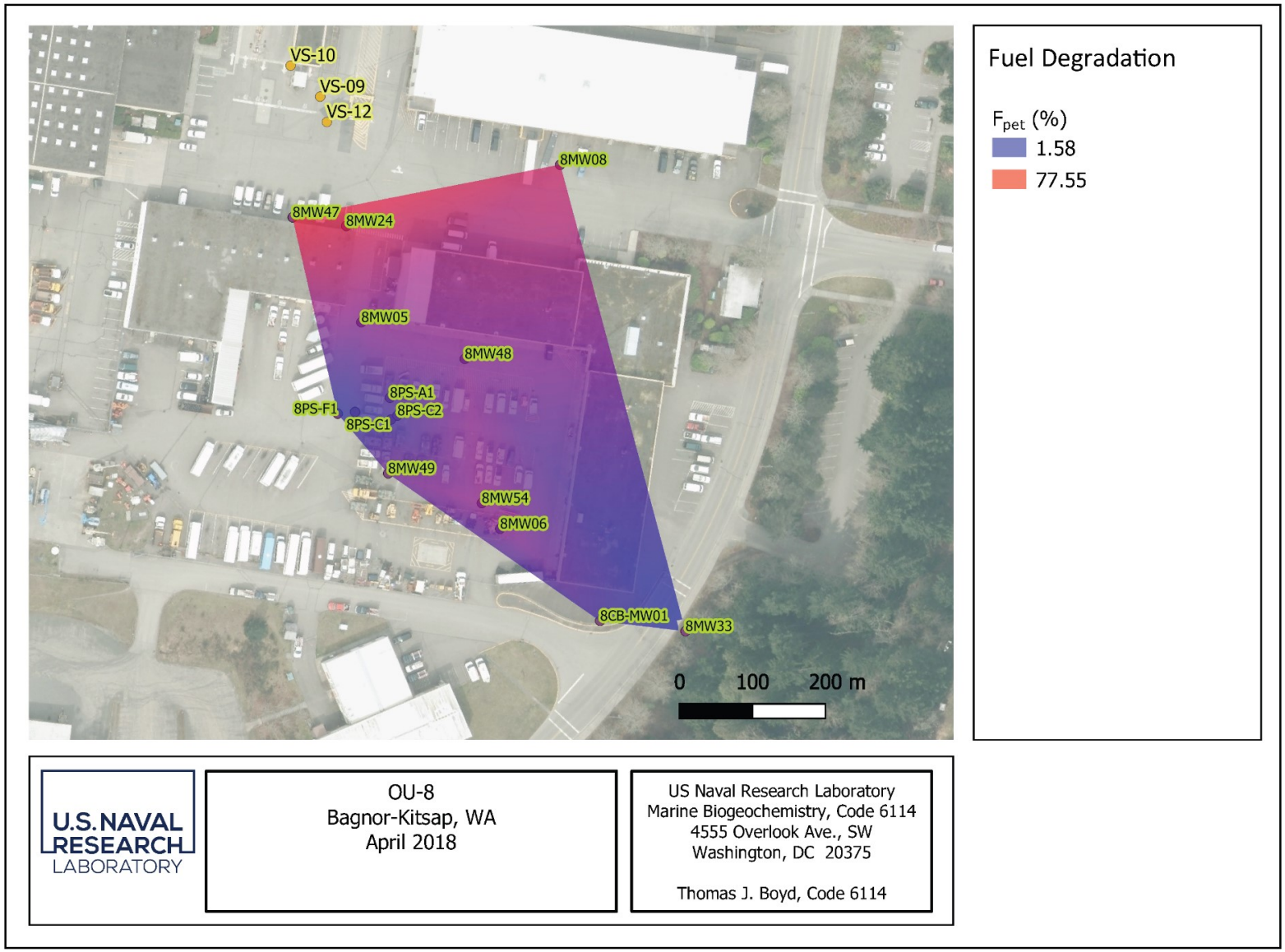

Figure 8. April 2018 DIC Fraction Petroleum

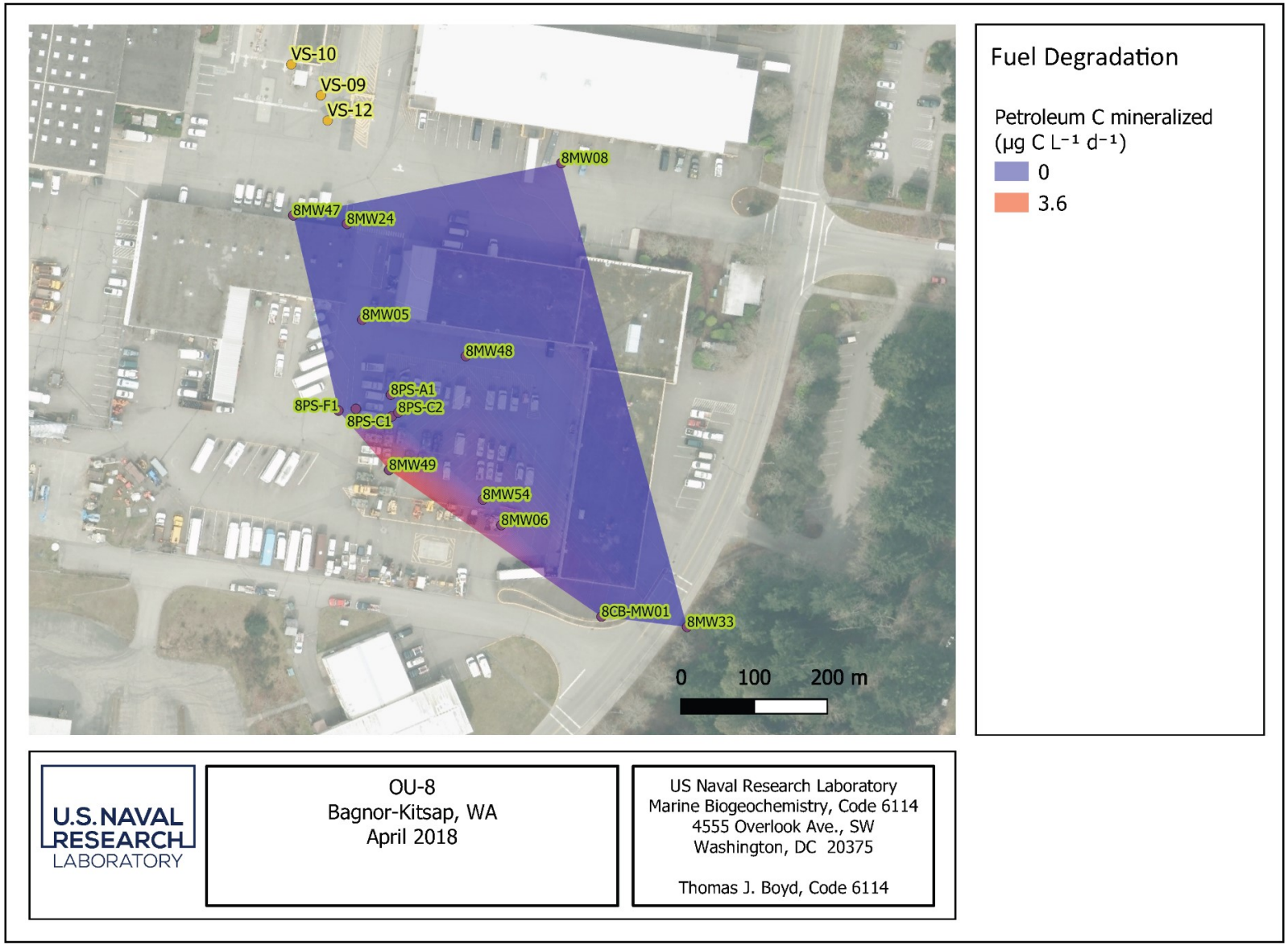

Figure 9. April 2018 Petroleum Degradation Rate

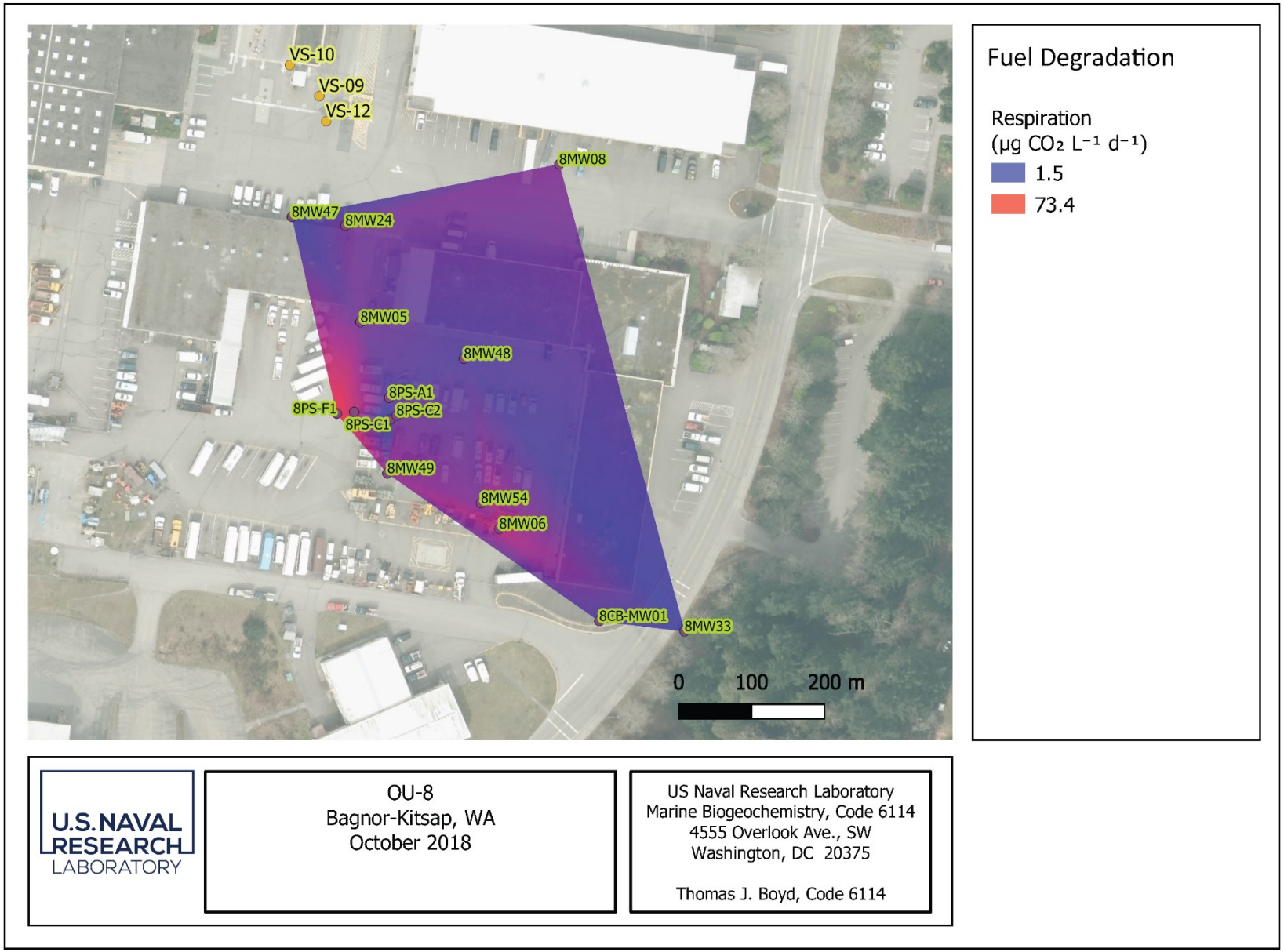

Figure 10. October 2018 Respiration

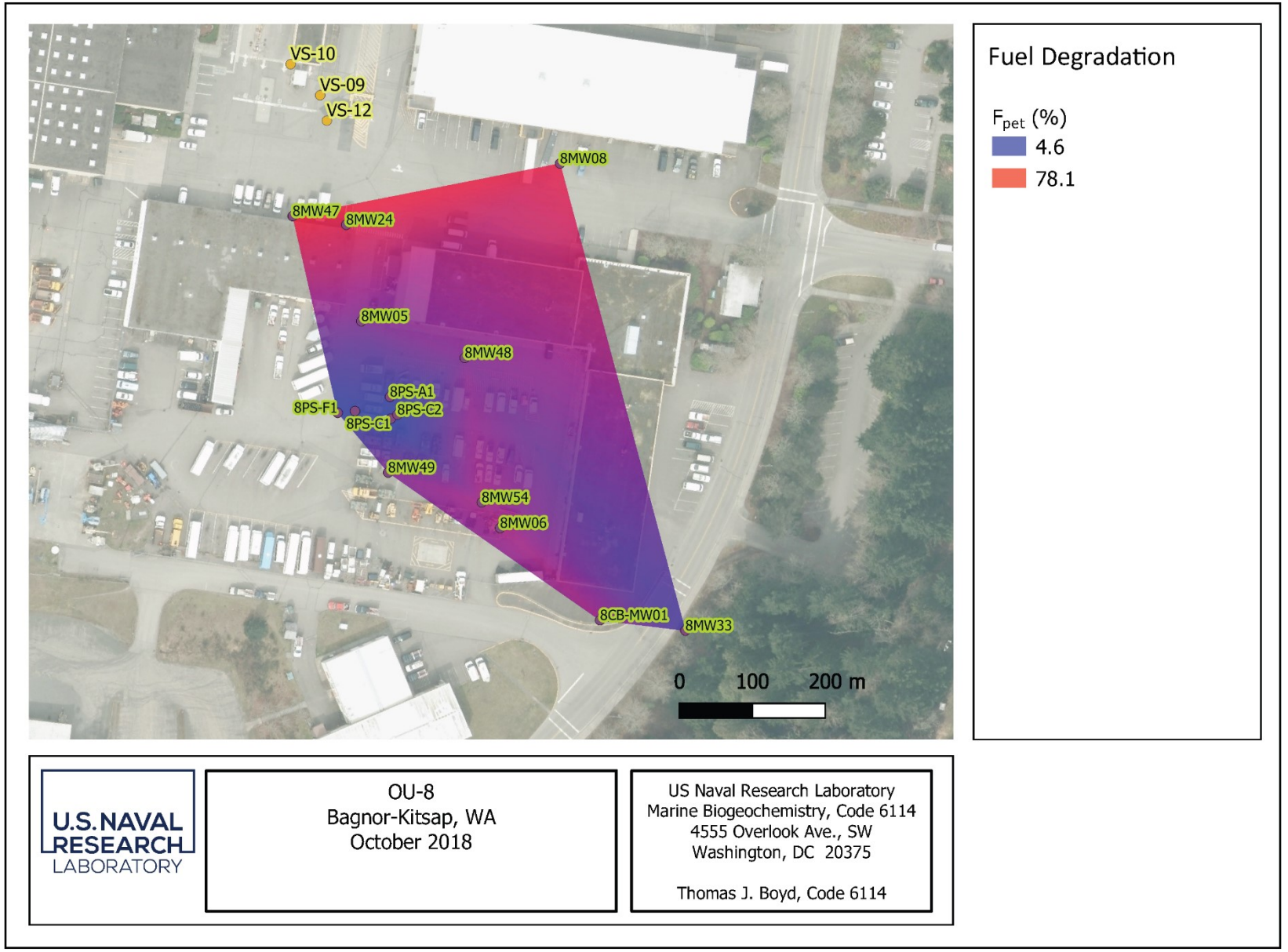

Figure 11. DIC Fraction Petroleum

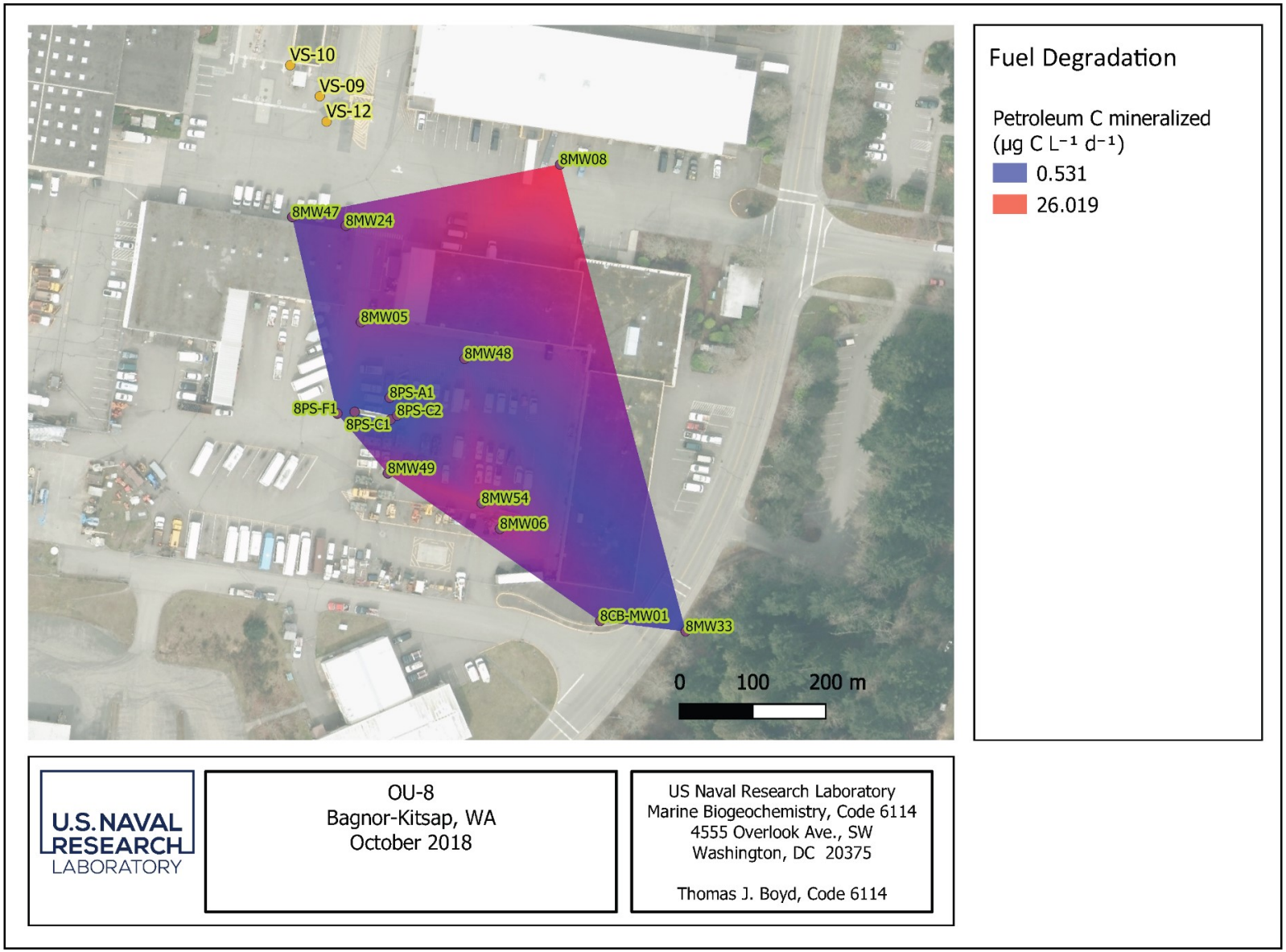

Figure 12. October 2018 Petroleum Degradation Rate

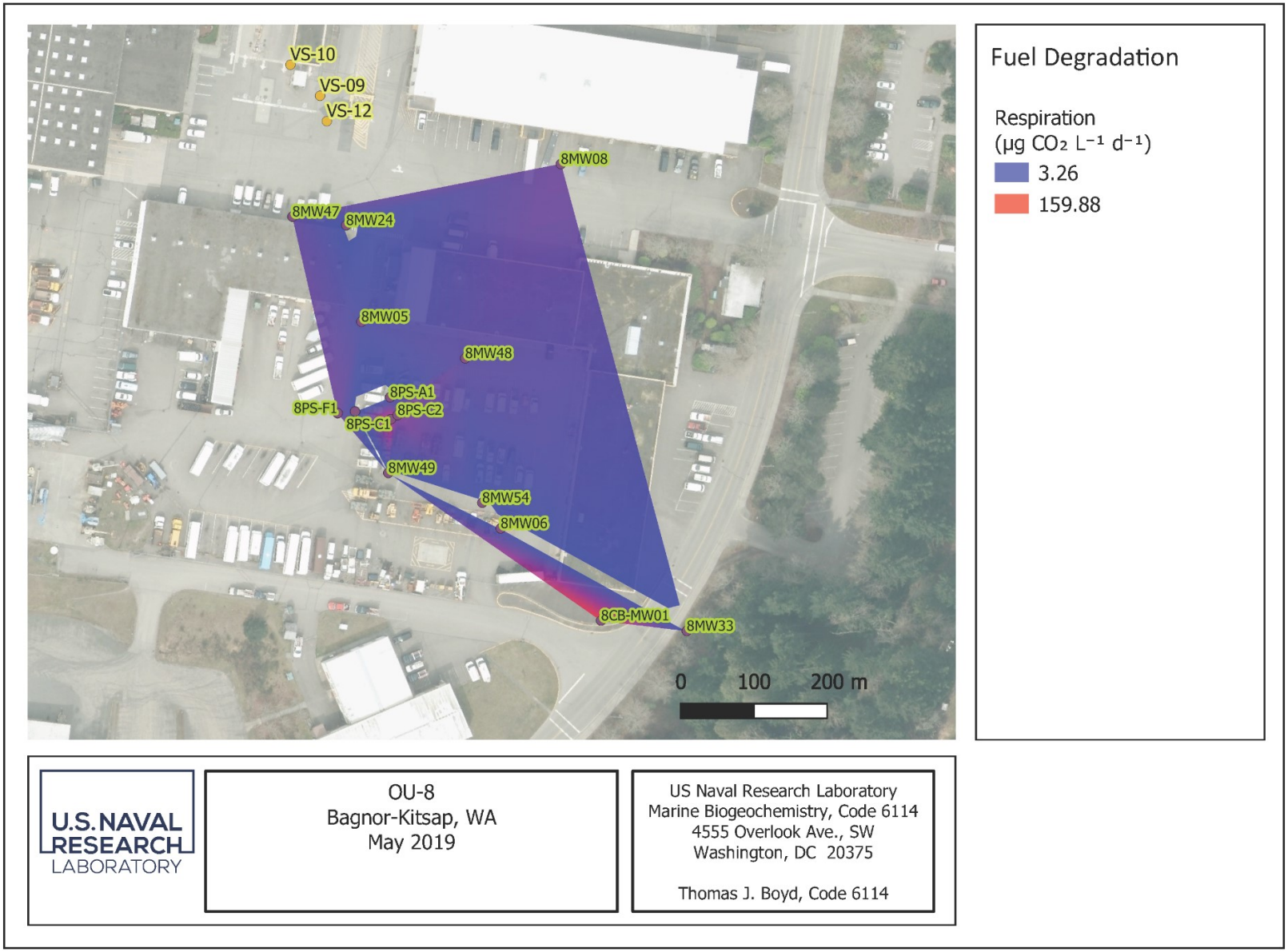

Figure 13. May 2019 Respiration

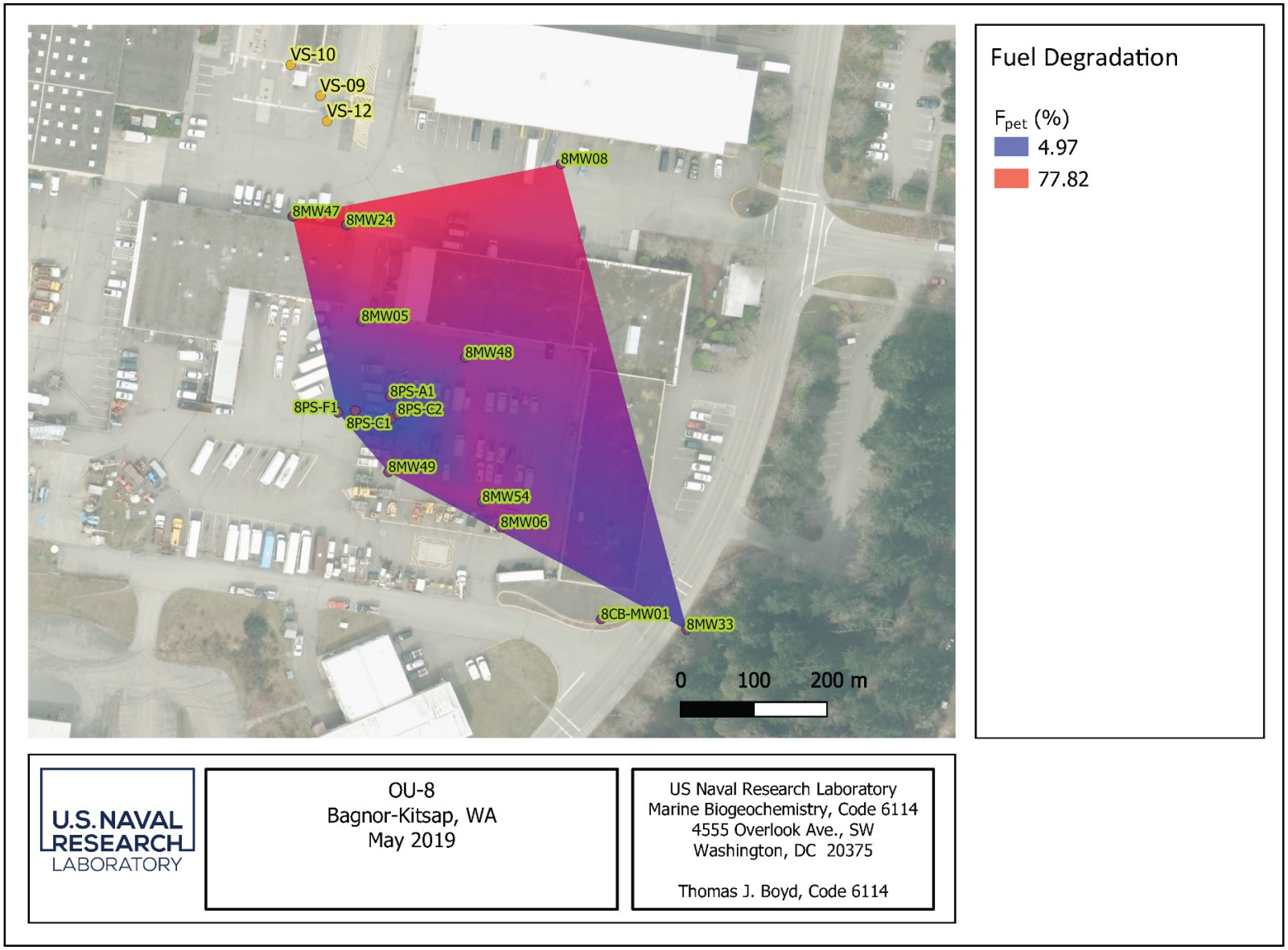

Figure 14. May 2019 DIC Fraction Petroleum

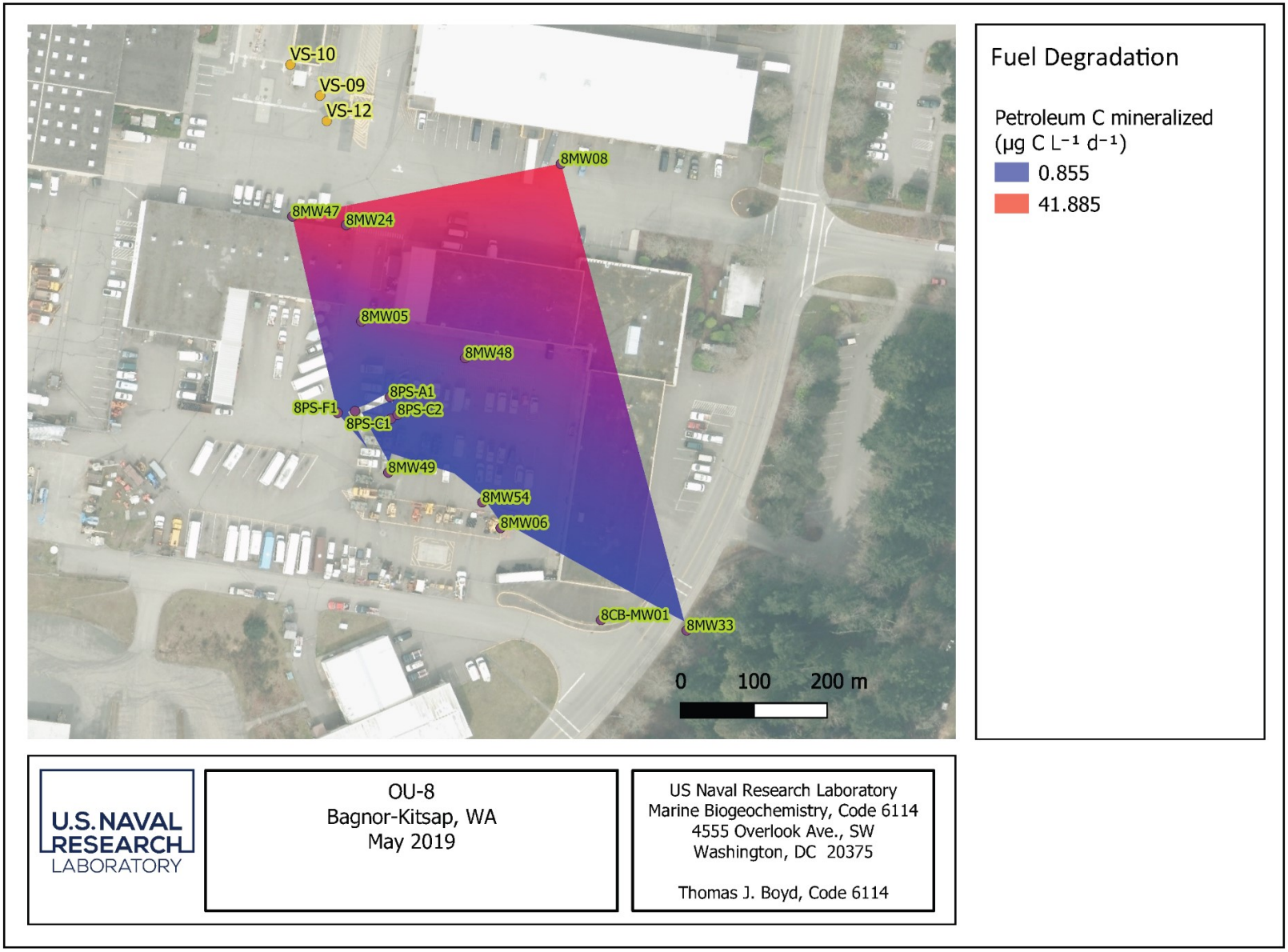

Figure 15. May 2019 Petroleum Degradation Rate

Appendix A. List of Cited Scientific / Technical Publications

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