

A large, light green graphic element on the left side of the page, consisting of a thick, curved line that starts from the bottom left and curves upwards and to the right. A smaller, darker green line loops around a black dot at the top left, resembling a stylized orbit or a path.

Pace Analytical[®]

Advanced Tools for Subsurface Sampling and Analysis



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Advanced Tools

TABLE OF CONTENTS:

1. Table of Contents
2. Introduction
3. PAES Specialty Services
4. Compound Specific Isotope Analysis
5. Molecular Biological Tools
6. Dissolved Gas Analysis
7. RSK 175
8. Volatile Fatty Acids
9. Total Inorganic Carbon
10. Anions and Cations
11. Interpretive Reports
12. Remediation Test Panel

Introduction

The subsurface environment is heterogeneous and geologically complex. Pace Analytical Energy Services provides unique technologies to improve the understanding of complex environmental and geotechnical issues. Since 1984, we have helped to lead the industry in better understanding the fate and transport of chemicals in the subsurface through innovations in analytical sampling and technology.

Pace Analytical provides complete traditional environmental laboratory services. Pace Energy takes the next step to provide performance-based analyses which facilitate a comprehensive understanding of the coupled geochemical and microbiological processes in the subsurface environment. This information allows our clients to make better decisions regarding remediation, monitoring and closure.



General PAES Services

Specialty Geochemistry

- Dissolved Gases including Hydrogen
- Light Hydrocarbons (RSK-175)
- Anions/Cations
- Volatile Fatty Acids
- Total Inorganic Carbon
- Vapor Analysis

Compound Specific Isotope Analysis

Molecular Biological Tools

Petroleum Fingerprinting

Interpretive Reporting/Expert Witness

Pace Energy Services is established as an environmental services company that applies technologically advanced methods for both data collection and assessment to assist our clients in developing robust technical platforms for site management. Throughout our history, we have achieved significant results:

- Built a series of sampling and analytical tools for assessing geo- and bio-chemistry that underpin efforts to monitor, predict and control subsurface processes.
- Developed the ability to accurately identify subsurface redox processes and a sampling device to ensure the sample was representative of the aquifer.
- First US commercial laboratory to develop and offer Compound Specific Isotope Analysis.

Specialty Analyses

PAES offers a series of specialty analyses to quantify the presence of specific suites of analytes. Each analytical series is designed to accurately and reliably evaluate subsurface processes.

Analyses Supporting Monitored Natural Attenuation and Enhanced Biodegradation

Monitored Natural Attenuation (MNA) is the monitoring of the decrease of contaminant concentration resulting over time from the processes of dispersion, sorption, volatilization, abiotic and biotic degradation.

- PAES combines exceptional analytical services and insight into the data to understand your MNA projects.
- The dissolved gas and anion/cation analyses provide data to delineate redox zones which influence contaminant degradation pathways in the subsurface. This data is integral to the design and operation of in-situ remediation projects.

Interpretive Reporting

One of the reporting options offered includes graphical representations that plot analytical results for each sample point. This report provides insight into the capacity of the groundwater to degrade organic and inorganic constituents. The report is ideal for use in support of sites that are using MNA, stimulant injection and other remediation technologies.

Parameters can include:

- Dissolved Gases including Hydrogen
- Anions/Cations
- Volatile Fatty Acids
- CSIA
- Petroleum and Chemical Fingerprinting

Demonstrating Microbial Activity

With the proliferation of enhanced biodegradation as a remediation technology, PAES recognizes the need to provide analytical methods to demonstrate microbial activity:

- Developed volatile fatty acid (VFA) analysis using ion chromatography rather than gas chromatography. This methodology has significantly lowered detection levels and is ideal for remediation approaches using the addition of organic substrates.
- The difference in total organic carbon (TIC) before and after stimulated degradation is the amount of converted organic carbon during the process. PAES developed an analytical method that takes the guess work out of calculating TIC across a site.

Testing for Microbial Contaminant Degraders

Pace now offers full service molecular biological analyses including the BER Microbial Remediation Array, Next Generation Sequencing, PCR/qPCR and Microbial Growth Tests. These techniques identify contaminant degrading microbes and provide an additional line of evidence for contaminant destruction.

Compound Specific Isotope Analysis (CSIA)

CSIA is proving to be an invaluable resource for responsible parties and other stakeholders. Most often it is utilized to unambiguously prove that fractionation, and therefore contaminant degradation, is occurring or has occurred. It may also be used for a number of other remediation and forensic applications that include:

- Establishing multiple sources of a contaminant
- Determining the rate and extent of degradation
- Identify mechanisms of degradation
- Confirmation of Vapor Intrusion Pathways

Compound Specific Isotope Analysis

Compound Specific Isotope Analysis (CSIA) is a technique which generates isotopic characterization of individual compounds. The isotopic data can be used to more definitively characterize processes in groundwater which degrade contaminants of concern such as BTEX, MTBE, 1,4-Dioxane, CVOCs, etc.

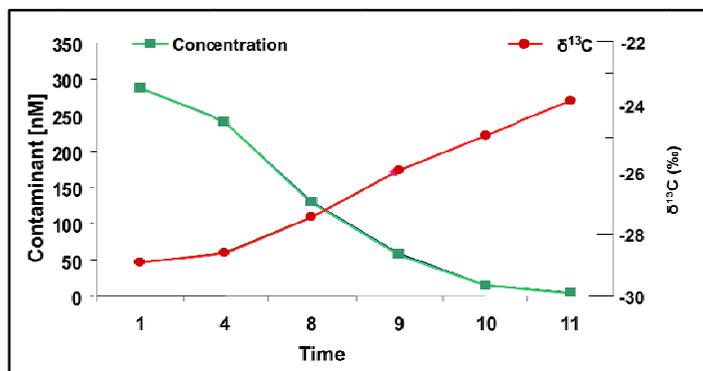
According to the USEPA, "isotopic fractionation unequivocally proves that contaminant degradation is occurring."

CSIA analyzes isotopic ratios of compounds of concern to demonstrate isotopic fractionation.

The data generated by CSIA can be used to:

- Prove biodegradation is occurring.
- Identify mechanisms of degradation.
- Determine the rate and extent of degradation.
- Establish multiple sources of a contaminant.

While processes like dilution, sorption and volatilization affect groundwater contaminants, they have very little or no isotope effects. Processes like biodegradation or abiotic degradation are associated with significant isotopic effects.



The study of isotopes in groundwater plumes of fuel oxygenates and chlorinated solvents has provided proof of their degradation, revealed the mechanisms of degradation and provided an in-situ measurement of degradation rates.

Applications of CSIA

- PCE, TCE and daughters
- Petroleum Hydrocarbons
- Fuel Oxygenates (MTBE)
- 1,4-Dioxane
- Vapor Intrusion Pathway Confirmation
- Fugitive Methane
- Select SVOCs
- Water
- Inorganic compounds: nitrate, sulfate

The isotopic data from CSIA can be a powerful tool in evaluating the progress of in-situ degradation. They are also extremely useful in determining the source of some compounds and establishing multiple sources of contamination.

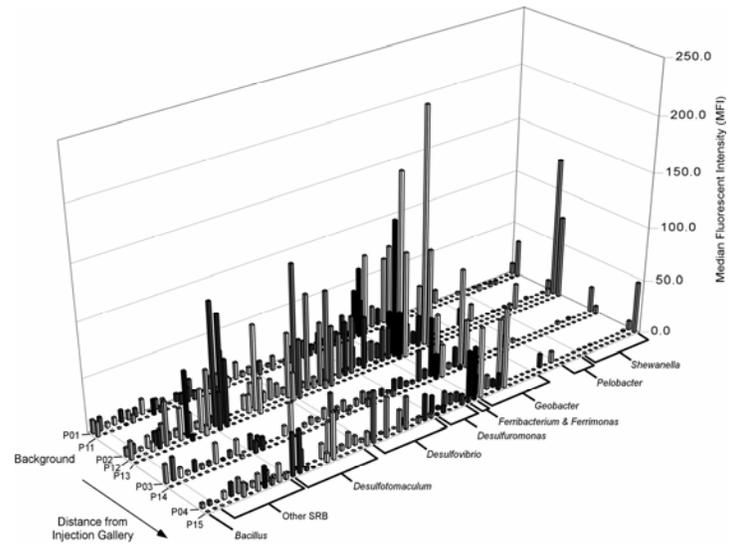
PAES currently offers analysis of stable carbon, chlorine, and/or hydrogen isotopes in groundwater for various contaminants of concern. As the technology continues to develop, more applications and contaminants will be offered. PAES is currently the only commercial laboratory in the United States offering a CSIA solution for vapor intrusion.

This figure illustrates isotopic fractionation of a contaminant during biodegradation.

Molecular Biological Tools

To complete our service offering to the remediation market, PAES developed the molecular biological tools laboratory specializing in the analysis of microbes in the subsurface.

The tests and services offered cover several different microbial and biogeochemical tests for remediation, biofouling, biocorrosion, industrial hygiene and public safety. Many of these tests are performed using DNA, RNA or other biochemical constituents of microbial cells. In recognizing the need for a more cost-effective assay specific to remediation of CVOCs and hydrocarbons, PAES developed the BER Microbial Remediation Array.



BER Microbial Remediation Array

- Analyzes for 35 genera and 149 different species encompassing relevant organisms for the cleanup of contaminated sites.
- Contains targets for PCE, TCE, DCE and VC degradation.
- Useful for chlorinated aromatics, chlorinated alkanes, dichloromethane, BTEX, MTBE, perchlorate and metals.
- Nearly 150 different species for around half the cost of a single qPCR target.
- Includes Dehalococcoides, Dehalobacter, Geobacter.

Molecular Biological Tools Service Offering

Next Generation Sequencing

- These analyses provide a detailed overview of the microbes present in a sample. The analysis can be tailored to be broad or more focused depending on the specific project objectives.

Quantitative and Semi-Quantitative PCR

- Pace has a library of microbial PCR targets that can be analyzed quantitatively or semi-quantitatively depending on project needs.

Microbial Growth Tests

BER Microbial Remediation Array

- 35 genera, 149 species
- Useful for chlorinated solvents, chlorinated aromatics, chlorinated alkanes, BTEX, MTBE, perchlorate and metals.

Dissolved Gas Analysis

Both abiotic and biologically facilitated reactions of contaminants with components of groundwater often produce species that exist in groundwater as dissolved gases. Typical dissolved gas species are carbon dioxide, methane, ethene, ethane, hydrogen and acetylene.

The identification and quantification of these dissolved gases is often useful in:

- 1) Identifying the redox process that is predominant in a given volume of groundwater, thus determining the achievable rates of various transformations.
- 2) Verifying that degradation has taken place.
- 3) Identifying the path that degradation has taken.

PAES classifies three suites of dissolved gases:

- Permanent gases including methane, carbon dioxide, oxygen and nitrogen.
- Light hydrocarbons including methane, ethane, ethene, propane, propene, i-butane, n-butane and acetylene.
- Dissolved hydrogen.



PAES is the only certified laboratory that offers dissolved hydrogen analysis. Our analytical methods for dissolved gases are fully documented and have been reviewed by several state agencies and the USEPA.

- Each method includes all QA/QC that would be expected from promulgated USEPA methods.
- **Lowest Detection Levels in the Industry!**
- The PAES gas chromatograph is a customized instrument built in-house for this procedure. The instrument includes three detectors arranged so all three suites of analytes may be determined from the same sample.

This eliminates potential variables between separate samples due to sampling error. This is extremely important in the analysis of light hydrocarbons and permanent gases.

- PAES has a unique flame ionization detector for the analysis of light hydrocarbons that can achieve MDLs for ethane and ethene of 5 ng/L. This is three orders of magnitude lower than can be achieved on commercial FIDs.

At many sites, the levels of ethene or ethane are below the usual 5-10 ug/L detection limits of FIDs used by other laboratories. The reported NDs or <5.0 ug/L may suggest that vinyl chloride is not degrading when it may be.

Dissolved Gas Detection Limits

Hydrogen	0.088 nM
Methane (FID)	0.037 ug/L
Ethane and Ethene	0.004 ug/L
Carbon Dioxide	0.27 mg/L
Oxygen	0.097 mg/L
Nitrogen	0.203 mg/L

RSK 175 – Low Level

It is often stipulated that a particular method be used to measure dissolved methane, ethane and ethene (MEE). The technical reason for that measurement is straightforward: the methane is a byproduct of the reactions that facilitate reductive dechlorination, and the ethane and ethene are the end-products of dechlorination. The choice of method is considerably less straightforward.

RSK 175 describes a procedure particular to the R.S. Kerr USEPA Laboratory in Ada, OK. It is not a promulgated method. The work-group that develops methods for the EPA is tasked with developing methods to measure hazardous contaminants, and MEE is not hazardous. However, the scientists at Ada developed RSK 175 as a high quality, defensible and documented way to measure MEE and have been gracious enough to share it with many laboratories.

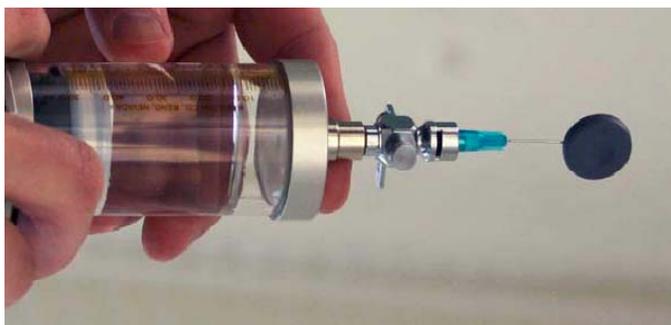
PAES scientists realized that it was important to look at concentrations below those measurable with RSK 175. AM20Gax was developed to measure very low MEE concentrations, but because it was not strictly an RSK 175 method, many practitioners could not use it.

RSK 175 – Low Level Reporting Limits	
Methane	0.5 µg/L
Ethane	0.2 µg/L
Ethene	0.2 µg/L

Pace Energy’s RSK 175 is a combination of the technology behind the high sensitivity of AM20Gax and the quality control program of RSK 175.

Our RSK 175 technique gives the superior sensitivity and the more widely recognized quality assurance of RSK 175.

The reporting limits of AM20Gax are still lower than the RSK 175 Low Level. For that reason, PAES routinely recommends AM20Gax for MEE. However, if RSK 175 is required, we can supply it whenever requested with superior detection limits.



Volatile Fatty Acids

With the proliferation of enhanced biodegradation as a remediation technology, PAES recognized the need to provide analytical support to clients using organic substrates to stimulate anaerobic biodegradation.

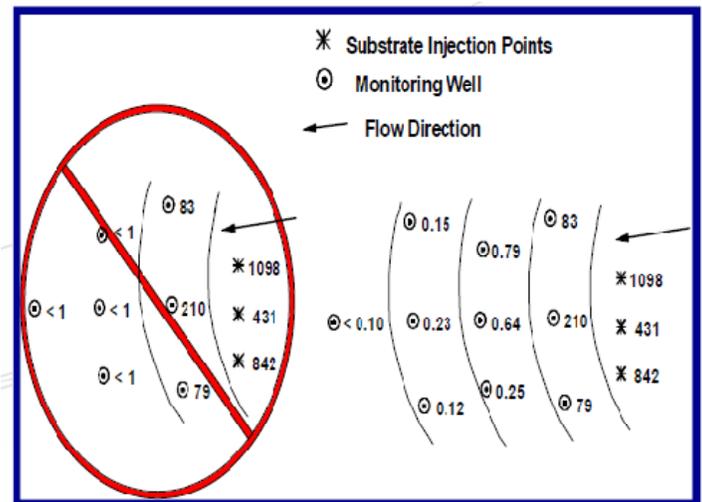


Injected substrates are fermented by the in-situ microbial community into volatile fatty acids. The presence of these acids after the addition of a Substrate is evidence of activity of the microbial process. This rather unique suite of so called volatile fatty acids (VFAs) is also a convenient tracer to monitor where the treated water flows.

PAES developed a new methodology for analysis of VFAs which uses ion chromatography (IC) instead of gas chromatography (GC). This method has achieved significantly lower detection levels in the range of a few tens of ug/L.

The older method for determination of VFAs was a gas chromatograph (GC) method with a detection level of about 15 mg/L for lactic acid, 5 mg/L for pyruvic and about 1 mg/L for the rest. Given these detection levels, VFAs could not be traced very far along the groundwater flow path before the concentration was below the detection level. Reports would often show reductive dechlorination in areas where VFAs were not detected, giving the impression that the engineered stimulation was not responsible for reductive dechlorination. Therefore, it became important to be able to look at very low concentrations of VFAs so the migration of the acids could be used as a tracer.

Additionally, Pace has extended the method to include the 5 and 6 carbon acids to accommodate clients who are using vegetable oils and other organic substrates.



Volatile Fatty Acid Reporting Limits

Compound Name	Acetic Acid	Propionic Acid	Butyric Acid	Pyruvic Acid	Lactic Acid	n-Pentanoic Acid	i-Pentanoic Acid	n-Hexanoic Acid	i-Hexanoic Acid
Low Level PQL (ppm)	0.10	0.10	0.10	0.10	0.20	0.10	0.10	0.20	0.20

Microbial Activity Analysis (TIC)

PAES has developed a method for analyzing microbial activity using Total Inorganic Carbon and methane that takes the guess work out of calculating TIC across a site.

There are three forms of inorganic carbon that exist in groundwater: carbon dioxide, carbonate and bicarbonate. They exist in groundwater in a pH dependent equilibrium.

If carbonate from soluble carbonate minerals in the soil matrix dissolves into the groundwater, there will be concentrations of all three forms of inorganic carbon at equilibrium. Since soluble carbonate minerals are common, there is almost always some background level of TIC, even in uncontaminated aquifers. In contaminated aquifers, there is almost always oxidation of organic material. Aerobic or anaerobic oxidation leads to the generation of inorganic carbon in the form of carbon dioxide in contaminant plumes. Therefore, when analyzing methane and TIC across a plume, one would find background concentrations over uncontaminated portions of the aquifer and anomalous concentrations of methane and TIC over contaminated portions.

Why Measure TIC?

- TIC is the final product of fuel oxidation.
- TIC analysis provides the most comprehensive look at inorganic carbon across a site.
- Mapping TIC across a site reveals the background TIC that results from aquifer sediments.
- Mapping TIC reveals the elevated TIC resulting from biooxidation of contamination.
- TIC combines bicarbonate, carbonate, carbonic acid and dissolved carbon dioxide into one analysis.

Reporting Limit for TIC:

1 mg CaCO₃/L

TIC can be determined from a groundwater sample if the sample is acidified before determining the dissolved carbon dioxide. Acidification causes the equilibrium to shift such that most of the inorganic carbon is in the form of carbon dioxide. The dissolved carbon dioxide measurement of an acidified water sample gives an excellent measure of TIC.

Some may feel that measuring alkalinity is sufficient and TIC is unnecessary. That's not true because inorganic carbon is present as both alkalinity and as carbon dioxide, and the ratio between the two can vary widely across a site depending on pH and dissolved solids. The crucial pH is near neutral, and the dissolved solids will increase dramatically as biological activity causes mineral dissolution. Thus, there can be wide swings across a site that alkalinity alone or carbon dioxide alone will not point out. Granted, by doing both tests, accounting for pH and TDS, and making many assumptions, TIC could be calculated. However, the method utilized by PAES provides TIC in one measurement and eliminates assumptions, multiple analyses and arduous interpretation.



Anions and Cations

There are a group of ionic species in groundwater whose concentration is also useful in characterizing chemical and biological degradative processes which are active in a contaminant plume.



Naturally Occurring Ionic Species:

- Nitrate
- Ferric Iron
- Sulfate

Products of Degradative Process

- Chloride
- Nitrite
- Ferrous Iron
- Manganese (II)

Pace Analytical has overcome this problem by utilizing glass vials with septa which preclude the diffusion of oxygen into the sample. The reduced state of these species may be preserved for long periods of time and laboratory analyses may be equally as reliable as the field methodologies.

Even in the laboratory, there are choices in methodologies that may be used to determine the concentration of each of these species. PAES has developed ion chromatography methods which monitor each ion independently and are generally superior in terms of reliability and detection limits.

For several of these species there are field kits and other field analytical tools which may be utilized depending on the needs of the client.

For species like ferrous iron and nitrate, which are in-situ reduction products of the active biological processes in the plume, there was a concern that they may reoxidize during transport to the laboratory. For that reason, field data was preferable to laboratory data.



Interpretive Reporting

When you need more than just numbers!

For some of the work that environmental professionals do, the number is the story... is it above or below the MCL? Is it within the limits of quality and reliability? Is it higher or lower than it was before?

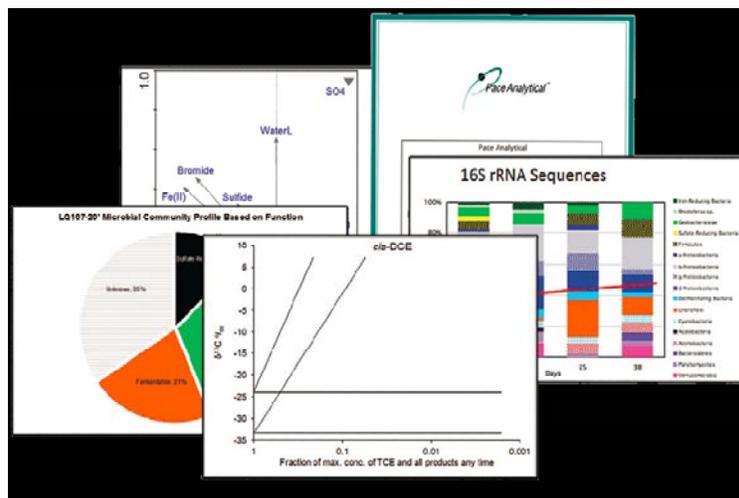
For most the work performed by Pace Energy Services, the number is only part of the story. Particularly when designing or implementing a remedial solution, it is the meaning of the numbers that can make the difference in the effectiveness of the entire project.

At PAES, we not only have the means to generate the numbers that will support a complex work plan, we have the insight and understanding to help you interpret the numbers. We can generate a report that clearly demonstrates results in such a way that clients and regulators understand their meaning and helps both when deciding how to proceed or when to stop.

Interpretive reports do not replace the standard reports that you usually receive. In fact, for our specialty analyses you will receive a report that is just numbers, results, QA/QC, etc. However, PAES will provide a report that can be used as an addendum to the standard report that provides insight and interpretation of the data. That understanding will be useful in the decision making process.

Interpretive reports are not standard. The scope and fee for developing them should be discussed and agreed upon in advance. However, if it becomes apparent that an interpretive report will be helpful, we can create it as part of a post project review.

For more information on how PAES can help in the reporting process or for an example interpretive report, please contact our customer service department.



Remediation Test Panel

Multiple Lines of Evidence

One of the main challenges to successfully implementing in-situ remediation is the need to cost-effectively collect and interpret data from multiple lines of evidence. In order to make this straightforward and uncomplicated, Pace has developed a Remediation Test Panel based upon EPA, ITRC and other guidance documents that consists of four data categories:

1) Contaminant Concentrations

- SW-846 methodology

2) Geochemical Setting

- Dissolved Gases
- Anions/Cations
- Total Organic Carbon
- Alkalinity

3) Microbial Contaminant Degraders

- 35 genera, 149 species
- Useful for determining the presence of a biodegradation pathway.

4) Compound Specific Isotope Analysis (CSIA)

- Dilution or Degradation
- Multiple Sources
- Degradation Rates
- Isotopic Mass Balance

The test panel includes all of the above to answer your most critical site questions. With the addition of an interpretive report, you gain expert oversight of your data and the decisions you make to move your project forward.



As regulators become more sophisticated, multiple lines of evidence may be needed to make progress on your site!

Questions Answered by the Remediation Test Panel Include:

- Which remediation strategy should be used?
- Are there multiple contaminant sources?
- Is the current remediation effort working?
- Will MNA be sufficient?
- Can monitoring be improved in terms of cost of effectiveness?
- Does the data support a transition from active treatment to MNA?
- Are additional lines of evidence needed to finalize closure?

