

ENVIRONMENTAL FORENSICS COLUMN

# The Use of Alkyl Leads in Gasoline Age-Dating Investigations: New Insights, Common Investigative Techniques, Limitations, and Recommended Practices

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## INTRODUCTION

The United States consumes more than 300 million gallons of gasoline per day or more than about 40% of the worldwide consumption (Harper, 2000). With the advent of the sports utility vehicle, gasoline consumption increased close to 20% over the 1990s and, consequently, the amount of product flowing through service stations and the number of underground storage tanks (USTs) have escalated. It seems that, at least in the northeastern United States, there is a gasoline service station on every corner.

According to the U.S. Environmental Protection Agency's (USEPA's) website, there are presently more than two million USTs in the United States. As of 2002 about 170,000 gasoline service stations exist in the United States, each normally having three to six USTs. On the other hand, more than 200,000 stations were present in the 1960s, indicating that presently many abandoned sites are likely to exist (Stout et al., 2006).

Leakages from USTs occur frequently and, according to the New Jersey Department of Environmental Protection (NJDEP), they receive close to five new UST release cases per day. The USEPA states that more than 400,000 UST releases have been confirmed across the country since records started being kept. With the low interest rates and the many property transactions over the past decade, numerous problems have been uncovered and countless have ended up in litigation. The costs associated with cleanups can be in the hundreds of thousands to millions of dollars. Therefore, identifying additional

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or past potential responsible parties has become an important part of any environmental investigation at a gasoline service station.

## AGE DATING

Age dating is the assessment of when a contaminant release occurred. Forensic scientists are often requested to perform age-dating evaluations as part of a gasoline-release investigation. The results are often used to identify potential parties or obtain insurance coverage and may be used in litigation proceedings. Furthermore, the age-dating results may be used to allocate costs between several responsible parties (Graves et al., 2000). Numerous methods are available to the forensic investigator to age date gasoline releases and they include:

- Site history and eyewitness testimony (Stout et al., 1998; Oudijk, 2005a)
- Rates of gasoline weathering (Senn and Johnson, 1987; Stout et al., 2006)
- UST corrosion models (Morrison, 2000a)
- Stable lead isotopes (Hurst et al., 1996; Hurst, 2002)
- Diagnostic ratios such as the concentrations of dissolved benzene, toluene, ethylbenzene, and *o,m,p*-xylenes (BTEX) in groundwater samples (Kaplan et al., 1997)
- Dendroecology and tree-ring studies (Balouet and Oudijk, 2006; Balouet et al., 2007)
- Groundwater flow calculations and contaminant transport models (Fetter, 1993; Morrison, 2000b)
- Temporal trends in refining and blending (Schmidt et al., 2002; Schmidt et al., 2003; Kaplan, 2003)
- Age dating of gasoline-impacted groundwater with atmospheric contaminants (Oudijk, 2005b)
- Gasoline additives and/or index chemicals (Kaplan and Galperin, 1996; Davidson and Creek, 1999; Oudijk, 2005a)

An index chemical is a manufactured substance with a known usage time frame. For example, many of the gasoline additives are index chemicals, such as methyl-*tert*-butyl ether (MTBE) introduced in 1979 or *tert*-butyl alcohol (TBA) introduced in 1969.

In this article, we will describe the use of index chemicals added to gasoline, in particular the alkyl-lead additives, to aid in the estimation of release time frames. Because of the many service stations in the country, the number of historical releases, and the frequency of impacted environmental receptors, forensic investigations of these sites will likely be with us for many

years to come. Morrison (2000c) previously provided details on the use of alkyl leads in age-dating investigations; however, additional information has come to light since that publication and further clarification is needed. Our findings are based on over 20 studies completed at gasoline service station sites in New Jersey. We will further discuss the history of alkyl-lead usage, limitations of these age-dating methods, the potential rates of error, and their validity within the courtroom. Furthermore, many of the issues detailed in this paper, and the references cited at the end, have been points of discussion and subjects of cross-examination in trials. Two case studies, where alkyl leads were employed in litigation cases, are also provided as examples.

## THE HISTORY OF ALKYL-LEAD USAGE

Gasoline is a complex mixture of hydrocarbons that boils below 180°C (355°F) or, at most, below 200°C (390°F). The hydrocarbon constituents in this boiling range are those that have 4 to 12 carbon atoms in their molecular structure (Speight, 1991). These hydrocarbons fall into three general groups: paraffins, olefins, and aromatics.

Beginning in 1923, alkyl leads were added to gasoline to reduce knocking in automotive engines and increase the octane rating (Gibbs, 1990). An alkyl is a group obtained by removing a hydrogen atom from an alkane, such as a methyl group derived from methane having the general formula  $C_nH_{2n+1}$ , which forms part of the molecule. Examples are the methyl group ( $CH_3$ ) or the ethyl group ( $C_2H_5$ ). The most common alkyl lead is tetraethyl lead (TEL), which is a lead atom with four ethyl groups attached ( $Pb(C_2H_5)_4$ ). TEL has also been known as tetraethylplumbane and lead tetraehide (Morrison, 2000a). The formulation of TEL in the early 1920s by General Motors, Standard Oil (now ExxonMobil), and DuPont was hailed as a great industrial achievement because it allowed the production of more powerful engines.

TEL is reported to have harmful health effects, even at a dilution of 1000 to 1 (Rhue et al., 1992; Kovarik, 1994). It is believed to cause reproductive toxicity in humans (International Programme on Chemical Safety, 1993) and brain damage in children (Needleman, 2000). A series of refinery accidents in 1924 drew significant public attention to the use of alkyl leads and, in 1926, the U.S. Surgeon General recommended a maximum concentration of lead in gasoline of 3.17 grams per gallon (g/gal) (1 g/gal = 0.26 grams per liter). This maximum concentration was increased to 4.23 g/gal in 1959 (Kaplan, 2003). Many refiners offered in the 1970s a grade of low-lead gasoline with a content of 0.5 g/gal (Beall et al., 2002). Further details on the history of alkyl-lead usage are provided in Needleman (2000).

By 1970 it became apparent to government authorities that lead concentrations in automotive exhaust were a serious health concern and the USEPA began to mandate reductions of lead usage in gasoline. By 1978

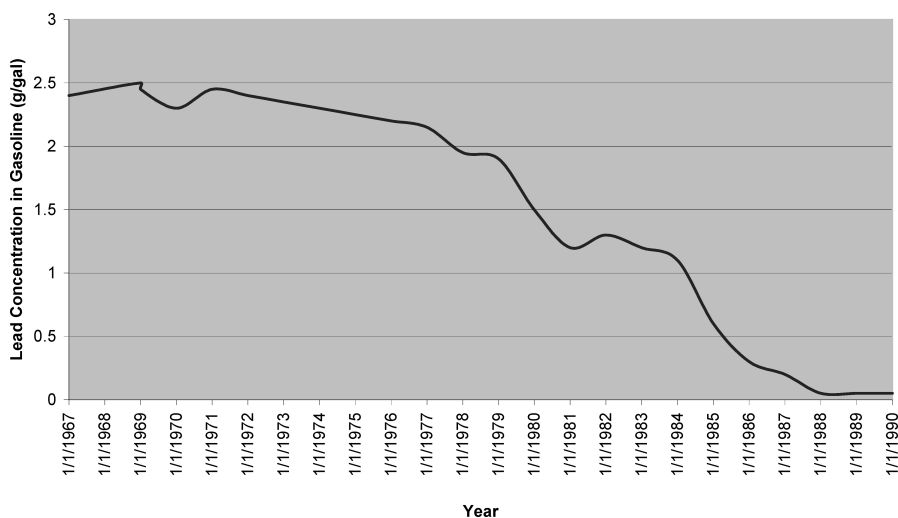


FIGURE 1. Historical trend of organic lead usage in gasoline (1967–1990). Source: redrawn from Kaplan et al. (1997).

the concentration was reduced to 0.8 g/gal for large refineries and 2.65 g/gal for small refineries. Kaplan (2003) provides a lengthy discussion on the allowable lead concentrations permitted through time; however, the following points can be used to describe the lead phasedown:

- Starting around 1970, the concentration of lead in gasoline steadily declined from an average of about 2.5 g/gal to less than 0.1 g/gal in 1988 (Fig. 1).
- The concentrations mandated by the government were for pool averages. Therefore, one particular batch of gasoline could have a concentration greater than the mandate. However, the average for the pool had to meet the government's number.
- At particular times, the government's mandates were less stringent for the smaller refineries. A small refinery is defined as one that produces less than 50,000 barrels per day (Needleman, 2000). Prior to the 1970s there were numerous small refineries across the country. These small refineries have been less common since that time.
- After about 1988, leaded gasoline was difficult to find. In January 1988 all banking and credits were exhausted. Leaded gasoline often had to be specially ordered or could be found only at particular service stations. Leaded gasoline was completely banned in California in 1992 and the rest of the country in 1996. The maximum allowable lead concentration in unleaded gasoline is presently 0.05 g/gal in both the United States and the European Union (CONCAWE, 1992). It is noted that in states such as Washington, Oregon, and New Mexico, where

cars can last a considerable amount of time, leaded gasoline could be found until the final ban.

Between the 1970s and 1990s, alkyl leads were essentially replaced in automotive gasoline by oxygenates, such as ethanol, methanol, MTBE, TBA, diisopropyl ether (DIPE), *tert*-amyl methyl ether (TAME), and ethyl-*tert*-butyl ether (ETBE), and through increased gasoline processing such as alkylation, isomerization, and catalytic reforming (Irwin et al., 1997; Schmidt et al., 2002).

Between the 1930s and the 1990s, the United States consumed two-thirds of the alkyl-lead production in the world (Thomas et al., 1997).

Between 1923 and 1933, TEL was added only to premium-grade gasolines (Beall et al., 2002). Between 1923 and 1960, TEL was the only alkyl-lead additive used in automotive gasoline. In 1960 Chevron (then Standard Oil of California) formulated tetramethyl lead (TML) and various lead “packages” were developed and introduced into the market. These packages included both physical mixtures and reacted mixtures of TEL and TML. Stout et al. (2002) provides a thorough description of the different physical and reacted mixtures. The reacted mixtures are the end products of a catalyzed TEL:TML reaction that results in the formation of five organic-lead compounds: TML, trimethylethyl lead (TMEL), diethyldimethyl lead (DEDML), methyltriethyl lead (MTEL), and TEL (Stout et al., 2002). The use of the mixtures began in 1960, but it does not appear that they gained popularity quickly. In 1962 TEL production was 494 million pounds versus 18 million pounds for TML (Stout et al., 2006). The use of the lead mixtures began to be reduced after about 1980. The year 1980 cannot be used as a cutoff date, but it can be considered as a time of reduced usage. This reduced usage was likely caused by costs. The mixed-lead packages were more expensive than the TEL-only package and the quantity of leaded gasoline being sold was declining significantly; automobiles running on leaded gasoline had not been manufactured since 1975. By 1985, less than 35% of the gasoline manufactured contained alkyl leads (USEPA, 2000b). Accordingly, it can be said that, after 1980, TEL was the predominant alkyl lead, in comparison to the mixtures, and after 1985 the mixtures were generally no longer used.

Two lead scavengers were added to gasoline since the late 1920s: ethylene dibromide (EDB) and 1,2-dichloroethane (DCA). The purpose of these additives was to reduce the adverse effects of lead oxide in the engine after fuel combustion (Kaplan et al., 1997). The scavengers allowed the lead to vaporize and be released with the exhaust, thus causing the health problems suspected in the 1920s but only dealt with in the 1970s. Between 1923 and 1926, triethylbromide, carbon tetrachloride, and trichloroethylene were used as lead scavengers. In 1925 chloronaphthalene was also added as a scavenger. Between 1926 and the early 1940s, EDB was the only scavenger used. Since the early 1940s leaded gasoline contained EDB and DCA in proportion to

the amount of TEL with a molar ratio of Pb:Cl:Br of 1:2:1 (Thomas et al., 1997; Falta, 2004; Falta et al., 2005). It is reported that this ratio was constant until completion of the lead phase-out (Beall et al., 2002). In some countries, dibromopropane was also used as a scavenger. Falta (2004) provides an in-depth discussion of the history of lead-scavenger usage and the amounts added historically to gasoline.

## **PRESENT USAGE OF LEADED GASOLINE**

As of 2006, alkyl leads are still used in the United States in aviation gasoline; some racing gasolines for automobiles and boats; recreational marine fuels for boats, all-terrain vehicles, and snowmobiles; and some lawn, farm, and construction machinery fuels. Between the early 1990s and 2006, the vast majority of alkyl-lead usage has been in aviation gasoline; TEL is the only alkyl lead added to aviation gasoline, while TML can be found in some of the remaining fuels cited above. Aviation gasoline has a maximum TEL concentration of about 4 g/gal, while most commonly it is about 2 g/gal. Alkyl leads are not added to jet fuels, while aviation gasoline, used solely in airplane piston engines, amounts to less than 1.5% of the aviation fuel market and 0.25% of the total gasoline market (Thomas et al., 1997; USEPA, 2005). According to Web sites for CITGO and Conoco Phillips (76), racing gasolines have an alkyl-lead concentration ranging from 3 g/gal to 4 g/gal and it appears that leaded gasoline is still quite common in the racing industry. However, NASCAR reportedly plans to switch completely to unleaded fuels by 2008 (Bernstein, 2006). Alkyl leads have not been manufactured in the United States since 1994 and any alkyl leads used in the country since that time were imported (USEPA, 2000a). The largest producer of lead alkyls worldwide is presently Innospec, Inc. of Great Britain, owned by Great Lakes Chemical (Thomas, 1995).

As of the late 1990s, leaded gasoline could still be found in numerous countries, such as in the Middle East, some parts of Eastern Europe, New Zealand, South Africa, and India (World Bank, 1998). Over 90% of the gasoline in Africa and the Middle East and 30% in Asia and South America still contain lead. Unleaded gasoline is not available in many of these countries. European countries such as Romania, Croatia, and Macedonia continue lead usage at maximum concentrations of about 3 g/gal. More recently, many of these countries have been changing over to unleaded gasoline through the help of the United Nations and the World Bank. North and Central American countries using only leaded gasoline include Belize, Cuba, Dominican Republic, and Honduras; however, some South American countries, such as Brazil, converted in the 1980s because of their significant ethanol production. China is still using lead additives, but they are also using some substitutes such as ferrocene and methylcyclopentadienyl manganese tricarbonyl (MMT).

The first country to restrict the use of leaded gasoline was the Soviet Union in 1967; leaded gasoline was banned in cities such as Moscow, Kiev, and Leningrad. However, as of the mid-1990s, the former Soviet countries were some of the largest users of lead additives. Japan was the first country to completely eliminate lead usage in 1980 (Thomas, 1995; Thomas et al., 1999). Other countries such as Germany, Sweden, Canada, South Korea, and Brazil do not permit alkyl leads in any fuels (UNEP, 1998). Based on the data presented in Thomas et al. (1999), the rollback schedules implemented in many countries were similar to the schedule applied in the United States.

## GASOLINE AGE-DATING INVESTIGATIONS

Alkyl-lead additives have been used as tracers by forensic scientists for several decades, in particular in the field of arson investigation (Frank, 1980). Alkyl leads can be helpful to the environmental forensic scientist when performing an age-dating investigation in three manners:

- The federal rollback schedule, as depicted in Fig. 1, can sometimes be useful to bracket the age of spilled gasoline.
- The presence of the reacted mixture, with compounds such as TML, TMEL, DEDML, and MTEL, reveals that the gasoline was produced after 1960. However, the cutoff date for usage is a little more tricky and sometimes cannot be concluded with certainty.
- The presence of the lead scavengers EDB and/or DCA reveals that a leaded gasoline is or was present and, therefore, the release may have begun during the time frame of leaded-gasoline usage.

The concentration of total organic lead (TOL) can be determined for samples of separate-phase, for example a layer of gasoline found in a monitoring well. Soil samples can also be collected and analyzed for TOL. The original TOL concentration in the gasoline ( $TOL_g$ ) can be estimated by dividing by the soil's gasoline content. The  $TOL_g$  concentration can then be compared to the federal rollback schedule depicted in Fig. 1. Stout et al. (2006) recommend a review of local data to assess  $TOL_g$  concentrations for a specific time period. The Department of Energy (DOE) has produced reports providing these data on a regional basis. There are numerous limitations to these methods and they are described in the following paragraphs.

The minimum that alkyl leads can provide a forensic investigation is that their presence represents a pre-1992 release in California and a pre-1996 release in the rest of the country. A review of state or even local regulations may help refine these dates as some localities had specific regulations concerning the sale of leaded gasoline. Furthermore, site documents and historical records may help to pinpoint when leaded gasoline was dispensed at a specific site.

The methods described herein have been used for several years, have been accepted by the scientific community, and have been detailed in the scientific literature (Morrison, 2000c; Healey et al., 2002).

Because similar rollback schedules were implemented, these forensic methods can also be employed in many countries outside of the United States.

## ALKYL-LEAD WEATHERING

Several studies have been completed over the past two decades on the potential weathering rates of alkyl leads in the subsurface. Weathering in soil consists predominantly of three processes: dissolution, volatilization, and biodegradation; however, as will be shown below, other processes, such as photodecomposition and hydrolysis, may significantly impact alkyl leads.

TEL is very unstable in soil because of its highly hydrophobic nature; however, it is highly stable in hydrophobic solvents, such as gasoline, benzene, or hexane, under dark conditions (Mulroy and Ou, 1998). Hydrophobicity is the property that defines a material as being water-repellent. TEL and TML are very sensitive to light and are subject to rapid photodecomposition. Byproducts of TEL and TML degradation include triethyl lead (TREL), trimethyl lead (TRML), and diethyl lead (DEL). The presence of these by-products in environmental samples would reveal that at least some weathering is occurring.

Macaskie and Dean (1990) found that TML could be treated biologically through the use of certain microbes and fungus. However, these experiments were completed solely on the alkyl lead without a separate gasoline phase. Ou et al. (1995) and Mulroy and Ou (1998) found that alkyl-lead weathering was more commonly a chemical process, probably caused by hydrolysis, where hydrolysis is when ions from water replace equivalently charged ions from a contaminant. They further found that TEL and TML could be rapidly degraded in soil if a separate gasoline phase is not present. However, if gasoline is present, the TEL and TML weathering can be significantly retarded.

Teeling and Cypionka (1997) found that TEL could be significantly degraded if heat was present and sufficient oxygen available. However, once again, these experiments were completed without a separate gasoline phase. Gallert and Winter (2003) found that the limiting factor in the chemical and biological decomposition of TEL and TML was the oxygen content of the soil. In cases where sufficient oxygen was present, complete removal of TEL and TML was possible. However, Gallert and Winter's weathering experiments were conducted without a gasoline phase and they acknowledged Mulroy and Ou's 1998 findings that a gasoline phase would retard weathering. Douglas et al. (2006) found that alkyl leads were particularly susceptible to hydrolysis reactions, but only if the quantity of separate-phase gasoline was small. Oudijk (2005a) provided a case study from a tropical location and a shallow water table where significant degradation of alkyl leads had occurred, possibly

through hydrolysis and/or photodecomposition. Stout et al. (2006) cited unpublished laboratory data where soil samples were spiked with hydrocarbons containing the five alkyl leads and allowed to sit undisturbed for 24 hours. Extraction recoveries were found to be only 0 to 40%. Stout et al. (2006) also presented field data that demonstrated the potential chemical degradation of TEL from separate-phase gasoline samples collected from monitoring wells. However, these findings were based on only two samples.

Based on the above findings, soil samples collected for TOL or alkyl lead analysis should contain significant quantities separate-phase gasoline. As stated by Mulroy and Ou (1998), in the absence of a separate-phase, alkyl leads are strongly adsorbed to soils, limiting the extraction process needed by the laboratory to perform the analysis. Furthermore, samples that have been subjected to minimal weathering are preferred and obviously these will be found within zones of significant separate-phase gasoline. Therefore, soil samples containing significant amounts of gasoline at, or close to, saturated conditions are needed.

Alkyl leads are converted to vapor-phase lead oxides during combustion in the pistons and expelled with the exhaust with the help of the lead scavengers. Furthermore, they are rapidly decomposed in sunlight. Accordingly, it is unlikely that alkyl leads found in soil or within separate-phase samples could be derived from atmospheric deposition.

In summary, it can be concluded that normally alkyl leads are not easily weathered, especially if they are within a separate-phase. However, in cases where separate phase is lacking or minimal, degradation can be significant.

## LIMITATIONS

There are numerous limitations involved with using alkyl leads in a forensic investigation. Each limitation should be evaluated and considered whenever formulating conclusions. Furthermore, it should be assumed that a cross-examining attorney will be familiar with these limitations and will question the expert witnesses tirelessly on these points.

- Gasoline found in the subsurface, for example a layer of separate-phase on the water table, often represents a mixture of many ages. Because the soil surrounding a leaking UST can retain close to 50% of the gasoline, a concept known as “residual saturation,” the ages determined through any of the methods described above would be an average. Moving away from the source would cause the gasoline to become more “age discrete” (Oudijk et al., 2006) and more distant sampling locations would provide a better chance of uncovering the maximum age. Unfortunately, these more distant locations are more susceptible to weathering and, therefore, uncertainty with these results may be much increased.

- With regard to the federal rollback schedule, it is important that investigators understand that many variables are at hand, including concepts such as lead credits, lead banking, whole- and leaded-gasoline pool averaging, and summer versus winter gasoline (Stout et al., 2002; Stout et al., 2006). Therefore, the values presented in Fig. 1 are averages and there may be significant play in these numbers. Accordingly, caution is needed when using these methods and we recommend that additional age-dating techniques be employed congruently. However, one advantage of the average values depicted in Fig. 1 is that they are being compared to average values in the subsurface. As discussed in the paragraph above, the calculated ages of spilled gasoline are likely to be averages and, therefore, these techniques would encompass a comparison between two averaged values.
- The presence and concentration of TEL in a soil or separate-phase sample will be dependent on numerous factors, such as the initial TEL concentration in the gasoline, the biodegradation potential of the soil and/or groundwater, aqueous-, separate-, and solid-phase partitioning, and the amount of gasoline in the soil (saturated versus nonsaturated). As stated above, Mulroy and Ou (1998) found that TEL could be rapidly degraded in soil if gasoline was not present. However, as long as gasoline remained in the soil, TEL would also remain in the gasoline phase. It is stressed that a careful assessment of environmental conditions is required whenever this type of analysis is to take place. Accordingly, a thorough understanding of the geological, hydrological, and biochemical conditions is needed to assess the potential for alkyl-lead weathering. As discussed by Kaplan (2003), exposure to the following environmental conditions will increase the uncertainty associated with any age-dating evaluation: (1) water with unknown chemical composition; (2) fluctuation in temperature; (3) microbiota present in the water or soil where the residues reside; (4) solar ultraviolet radiation, and (5) atmospheric oxygen. It is apparent that the longer the alkyl leads reside in the environment, the greater the uncertainty in interpreting the causes for the measured changes in their chemical composition.
- The presence of a certain gasoline additive, such as a lead package, cannot be used to assign a certain oil company to the gasoline. As a result of exchange agreements, a branded retailer may sell a competitor's gasoline that contains different additives than the producer would add at its own refinery (Stout et al., 2006). Gasoline is a commodity being bought and sold on the market every day. Therefore, an individual oil company's recorded use of certain additives may not be indicative of the additives present in the gasoline in their USTs. Needless to say, a private service station owner can purchase gasoline from any source

and the type of additives in their gasoline could change virtually on a daily basis.

- The mixing of gasoline plumes is a common occurrence, especially when multiple USTs from one or more sites are leaking. When the mixing of gasoline plumes occurs, the deciphering of the resulting data is often extremely difficult to impossible and alternative age-dating techniques may be warranted. The only productive conclusion that mixed data may provide is that one or more leaded-gasoline releases had occurred in the past. We are presently working on a study in northern New Jersey where a known unleaded-gasoline release occurred in 2005, but separate-phase samples from five locations contained TEL. It was only later discovered that a release had occurred at the same site in the mid-1970s. We have also completed several studies where the separate-phase was a mixture of gasoline and diesel and analyses for GRO and DRO were required to perform the  $TOL_g$  calculations. Obviously, these mixtures will produce additional error to the calculations.
- Several investigators have claimed that the cutoff date for the use of the physical and reacted mixtures is 1980 (Hurst et al., 1996; Stout et al., 1998; Morrison, 2000a). However, there is evidence that these mixtures were used after 1980 (Stout et al., 2002). Accordingly, it can only be concluded that the use of these mixtures after 1980 was limited and, in general, discontinued after 1985. It is reported that, by 1985, 90% to 95% of the lead used in gasoline was solely TEL (Stout et al., 2006). It is further noted that the lead mixes were more commonly used in premium-grade gasolines (Wakim et al., 1990). Premium-grade leaded gasolines were, for the most part, removed from the market after 1981 (Gibbs, 1990). Therefore, it can be concluded that use of the lead mixes was much reduced after 1981. Furthermore, the largest producer of TML, the Nalco Corporation, significantly reduced its TML production in 1983 (Anonymous, 1982).
- The use of EDB and DCA is often helpful in forensic investigations. However, EDB is a common agricultural chemical (a fumigant), while DCA is a common industrial solvent and chemical feedstock (Falta et al., 2005). Therefore, their presence is not always indicative of a gasoline release. Furthermore, EDC and DCA are somewhat soluble in water and, therefore, they may migrate more readily. The lack of EDC or DCA in a sample is not evidence of an unleaded gasoline.
- Leaking abandoned USTs are a particular limitation to these age-dating methods. USTs abandoned in place, but still containing gasoline, were a common occurrence prior to the many UST regulations enacted in the 1980s. Accordingly, an UST containing old gasoline may have initiated leakage at some date after abandonment. The methods

described herein can only assess when the gasoline was produced and not when it was actually released to the environment.

## SAMPLING PROCEDURES AND LABORATORY ANALYSES

Samples of separate-phase and soil are often collected during investigations of gasoline releases. These same samples can be used to help evaluate the time frame of the release. Groundwater samples are usually not helpful because alkyl leads have a low aqueous solubility and it is unlikely that they would be found in a water sample.

There are several laboratories across the country and worldwide that can perform these analyses. In particular, the analyses needed are total organic lead (TOL) and alkyl leads. It is noted that the TOL analysis is considered to be a “specialty” analysis. Normally, laboratories analyze for total lead, which would not be appropriate in this case (Wade, 2004). The alkyl lead analysis is performed by GC/MS in select ion monitoring (SIM) mode (TML:  $m/z$  253, 223; TMEL:  $m/z$  253, 223; DEDML:  $m/z$  267, 223; MTEL:  $m/z$  281, 223; TEL:  $m/z$  295, 237)(Stout et al., 2002). If soil samples are collected, an analysis for gasoline-range organics (GRO) will be needed to calculate the total organic lead content of the original gasoline ( $TOL_g$ ). If additional petroleum products are suspected in the sample or a mix of gasolines is possible, it may be wise to also conduct a diesel-range organics (DRO) analysis and/or a full scan with a gas chromatograph equipped with a flame-ionization detector (GC/FID) and/or, in some cases, a purge and trap gas chromatograph/mass spectrometry (GC/MS) analysis for the “PIANO” compounds (*Paraffins, Isoparaffins, Naphthenes, Aromatics, and Olefins*). The PIANO analysis may also help to assess the magnitude of weathering to the gasoline. Furthermore, a volatile organic compound (VOC) scan will be needed to detect the presence of EDB and DCA. It is noted that not all laboratories include EDB in their VOC scan and this compound may need to be requested separately.

There are presently no mandated holding times for laboratory analysis of TOL and alkyl leads. However, to prevent potential conflicts and debates, possibly in a courtroom setting, it is recommended that the samples be analyzed within two weeks of collection.

As discussed above, samples collected closer to the gasoline source will be less age discrete or contain a mixture of ages. Therefore, sampling at some distance away from the source is often preferable. A drawback is that these samples may be less impacted and more susceptible to weathering.

When interpreting the data, it is important that only samples containing significant quantities of gasoline be considered. As interpreted through the findings provided in Mulroy and Ou (1998), the weathering of gasoline hydrocarbons in some cases could skew the calculated  $TOL_g$  concentrations, either higher or lower. When a significant layer of separate phase exists, interaction

between the TEL and the ambient environment is likely to be exceedingly slow (Kaplan et al., 1997). Therefore, to avoid zones where weathering could be substantial, sampling within highly-contaminated locations is preferable.

The following points should be kept in mind whenever a sampling plan is being developed for alkyl-lead analysis:

- Separate-phase samples, such as a layer of gasoline floating on the water table, are preferred over soil samples. However, in many cases the collection of separate phase is not possible and the media to be sampled will be dictated by site conditions. Zones with the greatest separate-phase thickness are preferred, keeping in mind that the thickness found in a monitoring well will be greater than the actual formational thickness.
- Samples collected at depth are often less susceptible to weathering caused by volatilization or photodecomposition.
- Samples collected beneath impervious surfaces are less susceptible to dissolution or volatilization.
- Soil samples collected from within fine-grained sediment are preferred over coarser-grained zones because weathering is often less.
- Smear zones, pockets of separate-phase trapped beneath the water table and areas with significant fluctuations of the water table are more susceptible to weathering processes such as dissolution.
- Because lead alkyls are highly susceptible to photodecomposition, it is recommended that the jars containing the separate-phase or soil samples be immediately covered with an opaque wrapper, such as aluminum foil, after sampling is completed.

It is uncommon to find a site where all of the above limitations are met and therefore the age-dating estimates need to be made with these considerations in mind.

### **CASE STUDY NO. 1**

In the late 1990s, a real estate developer purchased a gasoline service station near Atlantic City, New Jersey, in a sheriff's sale. The prior owner had purchased the property from an oil company about 1985. A service station had been present at the property since the 1940s. The property had been abandoned since about 1995, was paved, and had been used as a parking lot.

In 2001 several abandoned USTs were removed from the site, about 2,500 cubic meters of impacted soil excavated, and a thin layer of separate-phase gasoline was detected on the water table at about 2 meters (m) below ground surface. Field observations showed that the release originated from a line failure. We were subsequently requested to perform an age-dating

evaluation by the developer's attorney. To provide an objective opinion on the age of the release, we requested that the ownership details not be provided until the field data had been reviewed.

In late 2001 two boreholes were completed and soil samples collected from just above the water table (Fig. 2). Separate-phase samples could not be collected because of insufficient yield, although beads of separate were present on the water table. The soil samples were forwarded to a laboratory for analysis of alkyl leads and VOCs. One alkyl lead, TMEL, was detected in one sample (SB-1). Accordingly, a release of a substantial age was suspected and further investigation requested.

Between 2003 and 2006, twelve additional boreholes and one additional excavation were completed at the site (Fig. 2). Soil samples were collected from eight boreholes and three samples (1A, 1C, and 1D) were obtained from an excavation at depths from between about 0.5 m and 2 m for laboratory analysis of TOL, alkyl leads, GRO, GC/FID, and VOCs. The sampling locations were based on field observations, in particular the presence of separate-phase gasoline. Impacted soil and groundwater extended for at least 35 meters to the west of the USTs and most likely continued well into the street. Beads of separate-phase gasoline were observed on the water table at the property boundary, at 10 m to 20 m from the USTs.

Surficial soils within the first 1 to 2 m were fairly fine grained, reducing the possibility of evaporative losses. The ground surface was paved, reducing infiltration and limiting dissolution; however, dissolution was possible through contact with the groundwater.

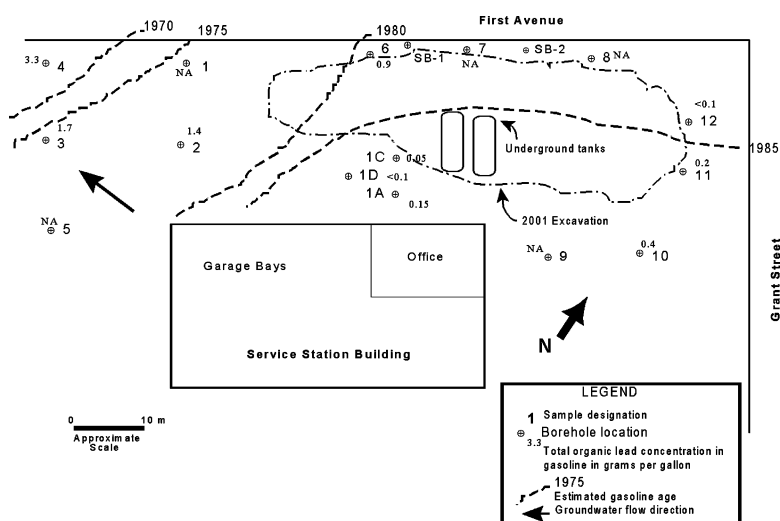


FIGURE 2. Location of soil samples for alkyl-lead and total-organic-lead concentrations, Case Study No. 1.

The GC/FID results revealed that a moderately-weathered gasoline was present in the samples, while the GRO analyses revealed organic concentrations in the percent range, indicating gasoline at saturated or close-to-saturated conditions. TEL was detected in five soil samples, while MTEL was present in two. Based on the presence of MTEL, it can be concluded that the gasoline release began prior to the mid-1980s. The  $TOL_g$  concentration was calculated by dividing the TOL concentration by the GRO concentration. Consequently,  $TOL_g$  concentrations were found to range from  $<0.1$  g/gal to about 3.3 g/gal. Contours of the calculated gasoline age, based on the  $TOL_g$  values, the values provided in Fig. 1, and local data obtained from DOE, roughly correspond to the groundwater flow direction with the age increasing downgradient.

Based on (1) the federal rollback values, (2) the presence of the mixed-lead additives, (3) the extent and quantity of impacted soil and groundwater, (4) the estimated gasoline migration rates, (5) the known environmental conditions, and (6) the age of the UST system, the gasoline release most probably began in the early 1970s (Figs. 1 and 2). Because contamination is known to have extended into the street, although site access issues prevented the evaluation of the downgradient portion of the impacted area, the release may have predated the early 1970s.

Because soil samples were collected instead of separate-phase samples, some bias may have occurred, impacting the calculated  $TOL_g$  contents of the gasoline and thereby affecting the age-date estimates. Because of adsorption to soils and the many possible weathering processes described by Mulroy and Ou (1998) and Stout et al. (2006), the TEL concentrations in the soil samples have likely been reduced to some degree and the calculated  $TOL_g$  values could be skewed to a younger age. There is no evidence to suggest that TEL concentration could have concentrated within the separate-phase. Accordingly, the age-date estimates, as depicted on the contours of Fig. 2, are considered minimum values.

Litigation with the oil company ensued and the court accepted the use of alkyl leads as an age marker for gasoline. The court subsequently agreed that the gasoline release began during the oil company's ownership and an allocation of costs was ordered by the judge. The court's decision was also confirmed by an appellate court and the state supreme court declined a review of the case.

## **CASE STUDY NO. 2**

In the late 1970s a client purchased a gasoline service station near New Brunswick, New Jersey, from an oil company. According to the client's testimony, documents issued by the state and fire department records, leaded gasoline was never dispensed at the site during this client's ownership.

In 2002, the four gasoline USTs beneath the site were excavated and removed. The removed USTs were intact; leakage was not identified from these USTs. However, soils underlying the USTs exhibited evidence of severe gasoline contamination. The soils were stained black and exhibited odors of highly-weathered gasoline. Continued excavating of impacted soil revealed four additional USTs, previously unknown to the client. Gasoline was not present in these USTs. These additional USTs had rusted to the point where they could no longer hold any product. All eight USTs were removed and several hundred cubic meters of soil disposed of.

After the cleanup had been completed, we were asked by the client's attorney to perform an age-dating evaluation. Despite the removal of the impacted soil, we completed several boreholes with a drilling rig, but only found one location exhibiting residual gasoline contamination. A soil sample was collected and forwarded to a laboratory for analysis of VOCs, TOL, alkyl leads, and GRO.

TEL and EDC were present in the soil sample, indicating that a leaded gasoline had been present. The TOL<sub>g</sub> concentration was calculated to be about 2 g/gal. Despite only one sample being available, an argument was made that the gasoline contamination originated from the older, previously unknown USTs. The reasoning was that the older USTs, which were in use prior to the late 1970s, contained leaded gasoline, while the existing owner never dispensed leaded gasoline. Several pieces of evidence pointed in this direction and the presence of the alkyl lead further supported this conclusion. Furthermore, there was no evidence that the client's USTs sustained a release. A lawsuit was filed against the oil company to retrieve the cleanup costs, the court agreed that the contamination originated from the leaded-gasoline USTs and awarded the cleanup costs to the client. In this case, the mere presence of one sample containing an alkyl lead was sufficient to convince the court that the release originated from the older, leaded-gasoline UST system.

## **COURT ACCEPTANCE**

We are familiar with the two case studies cited herein where the county courts in New Jersey have accepted the use of alkyl leads as age-markers in gasoline-release cases. We are further aware of a case in New York State that reached the appellate division and alkyl leads were again accepted as an age marker (State of New York, 2005).

## **CONCLUSIONS**

The use of alkyl leads can be a powerful tool in forensic investigations, if used properly and within the limitations cited above. We have been involved in two litigation cases, both being decided in county courts in New Jersey, where

the presence of alkyl leads was a significant part of the argument. In both trials, as described in the above case studies, the decisions were favourable to the clients.

Because lead concentrations in manufactured gasoline varied within specific time periods, sometimes significantly, the range of error with this type of age-dating evaluation can often be considerable. As stated by Stout et al. (2006), blindly comparing the TOL<sub>g</sub> concentrations to the federal roll-back schedule severely oversimplifies a very complex analysis. Furthermore, degradation of alkyl leads can occur in the environment and an assessment of the weathering potential of the sampling location is necessary to interpret the data. Therefore, any investigator should evaluate the data with care and scepticism before reaching any final conclusions.

It is preferable to use the presence of alkyl leads as a way of bracketing the release time frame, instead of pinpointing a date. For example, the presence of MTEL could be used to establish that the release occurred between 1960 and 1985. Additional evidence, such as company records, could be used to further pinpoint the date.

As with any forensic study, a multidisciplinary approach is needed, which may include evidence such as site history, geological, hydrological, and biochemical conditions (all taken together to assess fate-and-transport) plus the gasoline chemistry. A study's conclusions should not be based on one piece of fragmentary evidence, but several lines of evidence should be presented. As shown in case study no. 2, several lines of evidence were provided to the court, such as the state's documents, the condition of the USTs, and eyewitness testimony, but it was the presence of the alkyl leads that put the nail in the coffin and sealed the court's decision. Accordingly, alkyl leads should be used as one line of evidence that can hopefully buttress several other lines and make a good argument even stronger.

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