Forensic Investigations Using Compound Specific Isotope Analyses

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When evaluating complex subsurface contamination with possible overlapping plumes and multiple potential responsible parties, it is often desirable to determine if in a given area multiple sources of contaminant can be identified. Historically this has meant that each potential source must be characterized in detail, elucidating unique combinations or ratios of compounds which could be used to uniquely identify one source in the presence of another. In the case of two potential sources of similar products such as gasoline from two adjacent service stations, the presence of an additive unique to Station A but not to Station B could serve to identify the source of offsite contamination. Where unique additives are not present, the detailed GC fingerprint of the complex petroleum mixture may be characteristic of one product over the other, however the effects of weathering, particularly for product which has been present in the environment for extended periods may often demand the "opinion" of experts to suggest responsibility. Such evaluations are often the best that can be done given the particular situation and the tools available to the forensic investigator at the time.

There is another class of forensic evaluation for which there may be "advanced tools" available to provide source identification. This is the case when a single compound which is in common use in a variety of industries or in products common to multiple manufacturers has entered the groundwater. An example is perchlorate, ClO4 , which is a propellant contained in virtually all ammunition, in rocket fuel, in fireworks, road flares, automobile air bags, etc. Perchlorate also occurs naturally in mineral deposits in the southwestern US, in nitrate fertilizers imported from Chile, and is formed in the atmosphere and rains down generally across the countryside. Perchlorate has been detected in groundwater in 35 states, has impacted thousands of wells, and has been found by the FDA in common foods such as milk, lettuce, carrots, cantaloupes and spinach. Ingestion of perchlorate by humans inhibits iodide uptake in the thyroid and the effects of low level exposure are the subject of intense debate. There is no Federal MCL, but state levels range from 1 – 32 ppb. The Department of Defense is the largest user and has directed a large amount of effort to at least narrow the field of perchlorate contamination for which it is responsible. This effort has been focused on the fact that there are several different isotopically unique species of perchlorate: $^{35}Cl\ ^{16}O_4$, $^{37}Cl\ ^{16}O_4$, and $^{35}Cl^{16}O_3{}^{18}O$. Both the natural and anthropogenic sources of perchlorate are made up of mixtures of these unique perchlorate isotopologues and it has been determined, as shown in Figure 1, that the natural and anthropogenic sources are isotopically distinguishable.

The synthetic or anthropogenic perchlorate has heavier chlorine and lighter oxygen than natural perchlorates. This isotopic analysis then is very valuable to the DOD, particularly since it distinguishes most of the lower level perchlorate contamination as resulting from natural causes which are not the responsibility of the DOD.

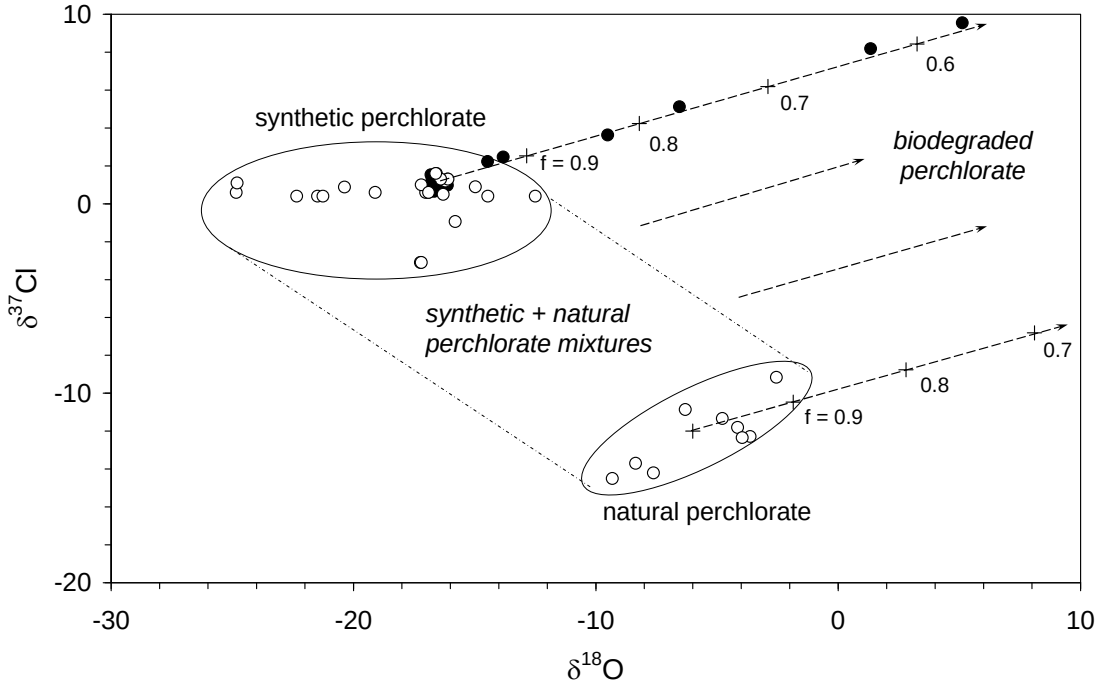

Figure 1. Dual Isotope Study of Perchlorate (Sturchio, et.al.)

Using knowledge of how perchlorate degrades isotopically, paths for its fractionation during degradation can be calculated as a function of "f ", the fraction of product remaining. These paths are shown as dashed lines in Figure 1 and demonstrate that even as the natural and anthrogenic perchlorate degrade over time, these products will always be distinguishable. Indeed, as shown in Figure 2, samples of perchlorate contamination which were isotopically unique from the two groups shown in Figure 1, was shown to be explainable as due to biodegraded synthetic perchlorate based on the degradation paths calculated.

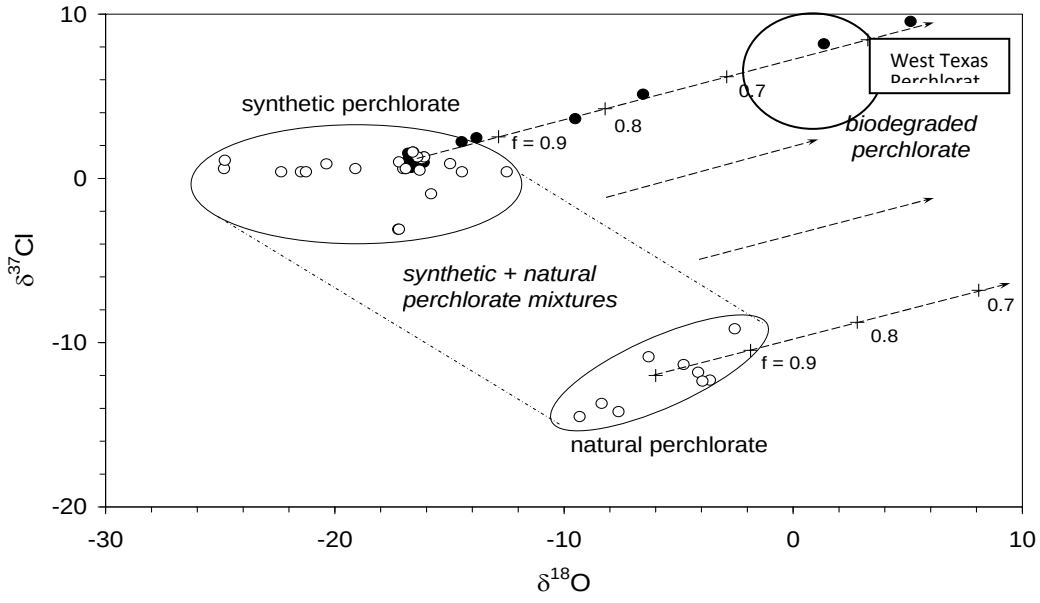

Figure 2. Dual Isotope Study of Perchlorate (Sturchio, et. al., & Paul Hatzinger, private communication)

While all perchlorate is composed of one chlorine atom and four oxygen atoms, not all perchlorate is identical when isotopic composition is considered. Based on these unique and identifiable perchlorate compositions, different sources of perchlorate can be identified. This is also true for other compounds and classes of compounds of interest in forensic analyses.

A second class of compounds which have unique isotopic composition are the chlorinated solvents such as PCE, TCE, 111TCA and daughter products. The results of an isotopic analysis of several product (undegraded) TCE and TCA samples is shown in Figure 3. Clearly the isotopic composition in terms of carbon and chlorine isotopes is unique for different manufacturers and could be used to differentiate undegraded products.

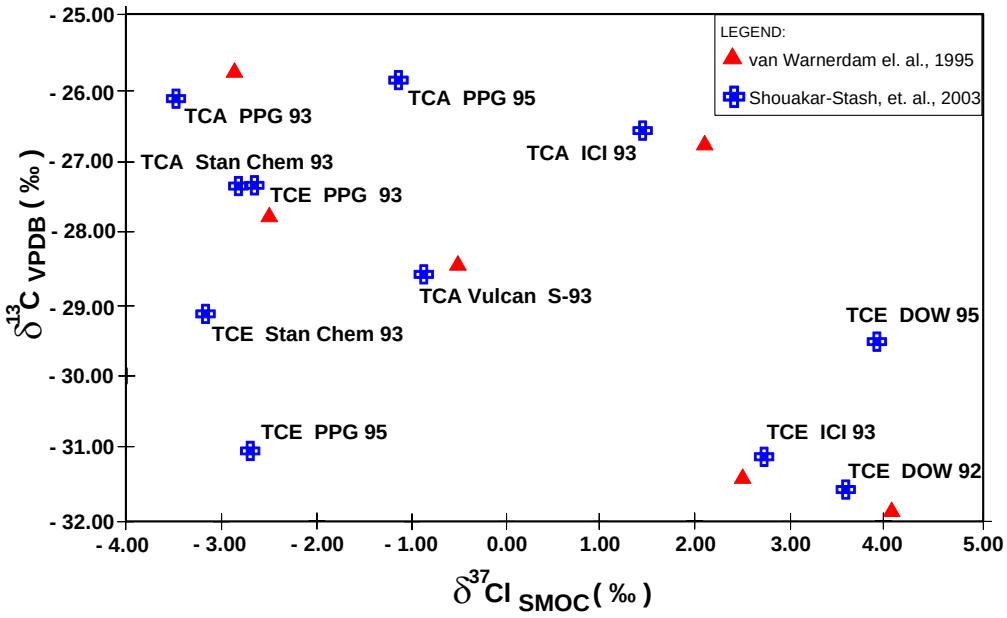

Figure 3. Dual isotope study of chlorinated solvents (Shoukar-Stash, et.al.)

Goldman, et.al. have reported the determination of 3 unique sources of TCE in groundwater samples from an aquifer at the Orion Public Housing Area near Moffett Field Naval Air Station in California, as shown in Figure 4. Although no explanation was given regarding the detailed interpretation of this data, as plotted the data suggest that Source 1 may have evolved along the heavy black line shown in Figure 4. If this is true, the data points shown in blue and within the blue circle shown in Figure 5 represent a less fractionated state of Source 1 and could be representative of the δ_o for Source 1. Such an interpretation is similar to that for perchlorate, shown in Figures 1 & 2, which is based on the fact that unique sources of a species, each degrading by the same mechanism, follow parallel paths of isotopic enrichment. Based on this, the West Texas perchlorate was determined not to be a unique source, but rather likely to be a degraded anthropogenic perchlorate.

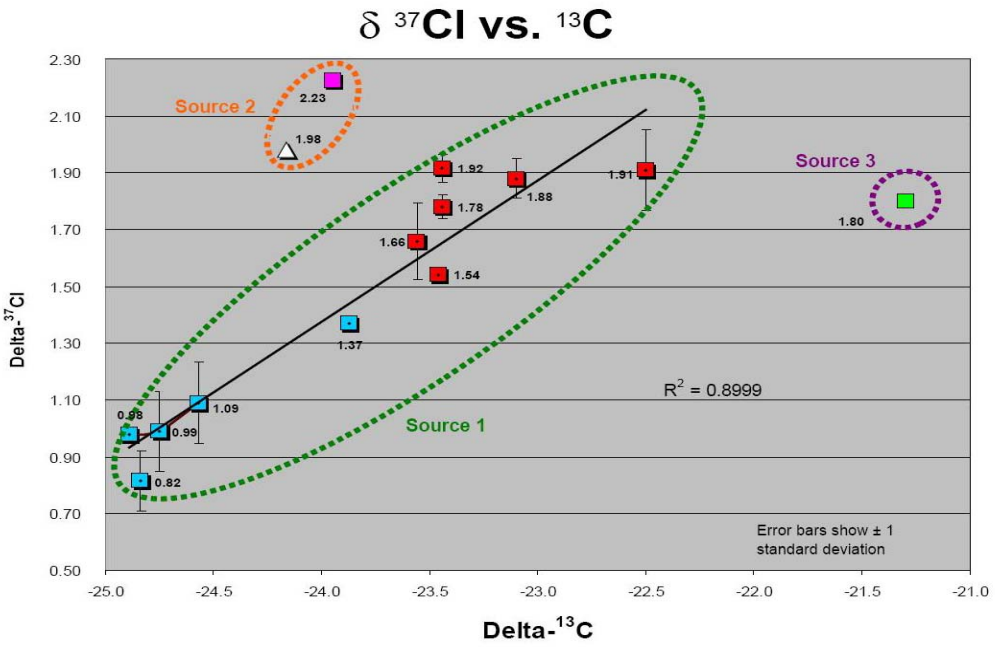

Figure 4. Stable Isotope Study Orion Public Housing Area, Moffett Field (Goldman et. al.)

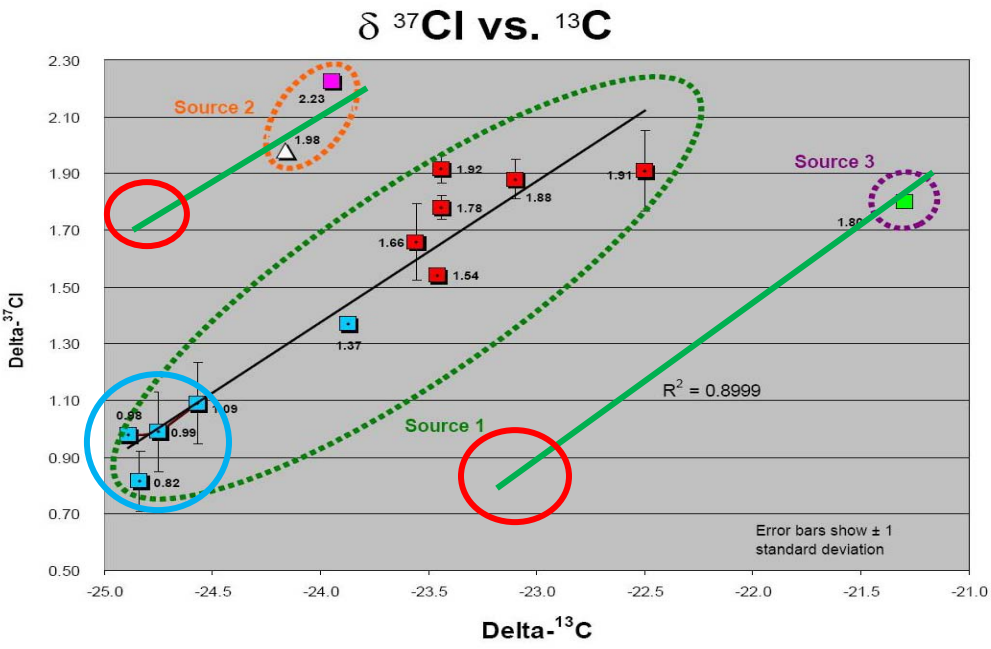

Figure 5. Potential Enrichment Paths for 3 Sources at Moffett Field (after Goldman, et. al.)

Using a similar reasoning, it is reasonable to interpret the data points attributed to Source 2 and Source 3 as unique, since it appears that they could not have evolved from Source 1. It is reasonable to interpret these data points as either un-degraded unique sources or enriched versions of their respective Source δ_o 's . Their present isotopic composition then would be interpreted as having evolved along the parallel green lines shown on Figure 5. This

interpretation assumes of course that the degradation mechanism has been the same for all three potential sources.

The conclusions from this work were**: *"Stable isotope analysis provided the only line-of-evidence that there are three isotopic ratio signatures, thus three distinct TCE sources affecting the groundwater beneath the housing area at Moffett Field. At least two and likely three of the sources originate off-site and up-gradient of the housing area. This analysis has provided the Navy with the data necessary to defend to the regulatory agency that the contamination beneath the housing area originated off-site, potentially saving the Navy millions of dollars."***

Chlorinated solvent plumes often migrate over substantial distances from their source and it is useful to inquire into the effects of that transport on isotopic composition. Hunkeler, et. al. have studied two chlorinated ethene plumes in Ontario, Canada in which the groundwater geochemistry suggested only marginal or no potential for biodegradation. Under these conditions physical processes such as NAPL dissolution and diffusion can be studied where the effects of degradation on isotopic fractionation are minimal. These studies are useful to determine if isotopic composition can be used to link contaminant plumes to their source.

At the first site near Kitchener, shown in Figure 5, the contaminant is TCE apparently caused by a former manufacturing plant about which little was known. TCE concentrations up to its solubility limit were measured near the bottom of the aquifer. DNAPL was collected from one high concentration zone. A laboratory experiment using this DNAPL revealed that only slight isotopic fractionation (0.26 ‰) occurs during dissolution of TCE.

Depth discrete delineation of the carbon isotope ratio was done across cross-sections perpendicular to the plume direction as shown in Figure 6. The source cross-section near the release site and a down-gradient (~120 m) cross-section are shown in Figure 6.

Isotopic composition in the high concentration zones is near -24.2 ‰ which is the composition of the source DNAPL. Slightly enriched compositions are found mostly near the aquitard and could result from some biodegradation and/or preferential diffusion of lighter TCE into the aquitard. Indeed the presence of daughter products, while limited, occurs only near the aquitard.

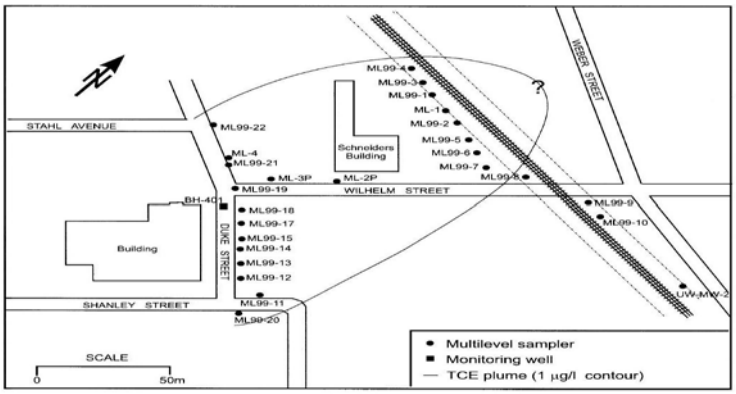

Figure 5. Manufacturing site near Kitchener, Ontario. (Hunkeler, et. al.)

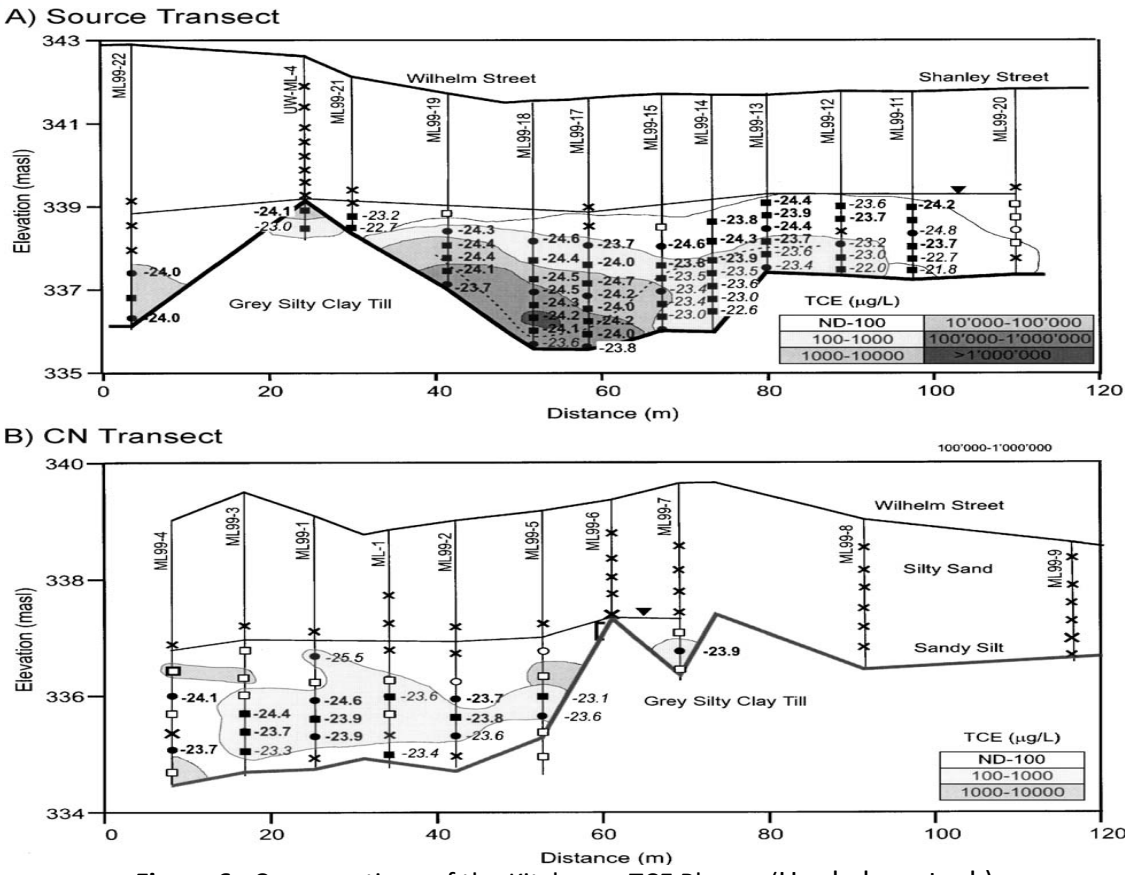

Figure 6. Cross-sections of the Kitchener TCE Plume. (Hunkeler, et. al.)

In the down-gradient cross section, 10 of 17 of the determined isotopic values are near the isotopic composition of the source. Most of the other data is slightly enriched, again suggesting some minimal biodegradation and/or diffusion. The behavior of the isotopic composition is shown in Figure 7 which illustrates the $\delta^{13}C$ values for the sampling point with the highest TCE concentration in a transect in the direction of plume advance.

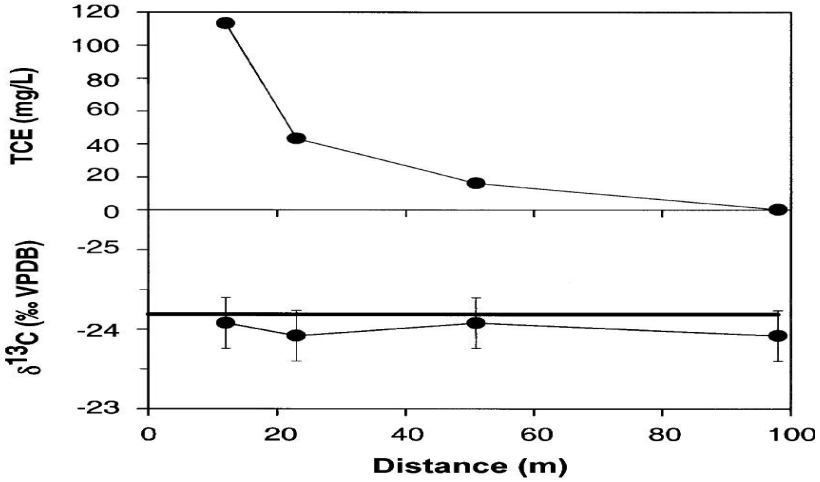

Figure 7. TCE concentration and $\delta^{13}C$ of TCE for sampling point with highest TCE concentration in ML99-19, ML-3P, ML-2P, and ML99-7 as a function of distance from source at the Kitchener site. (Hunkeler, et. al.)

Despite the marked decrease in TCE concentration with increasing distance from the source, the $\delta^{13}C$ of TCE in the high concentration core of the plume is not significantly different from the $\delta^{13}C$ of the source. Thus, in the absence of significant degradation, isotopic composition can be used to link plumes to their source.

In a second site, Hunkeler, et. al., examined a PCE plume in a sandy aquifer near a small town in Ontario as shown in Figure 8.

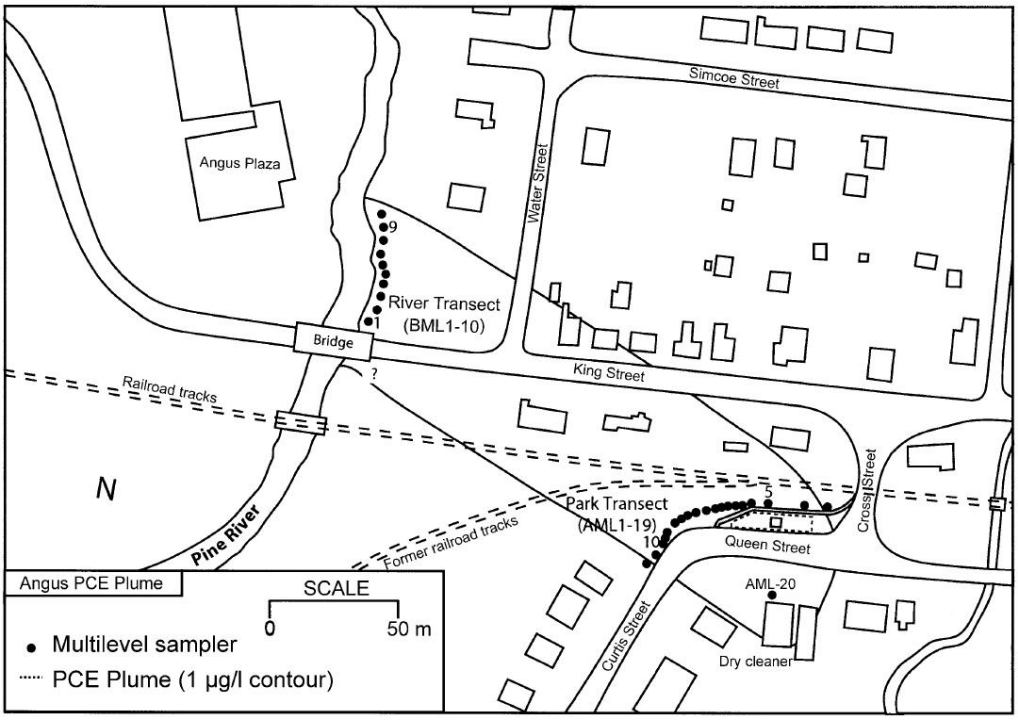

Figure 8. Dry Cleaner Site, Angus Field, showing multilevel sampler locations. (Hunkeler, et. al.)

The plume was very wide close to the presumed source area and they were able to distinguish three separate plume cores with unique carbon isotope ratios. They were able to conclude that these significantly different zones of unique isotopic composition, likely originated from 3 independent sources of PCE. A transect of the plume about 40 to 50 m down gradient of the source is shown in Figure 9.

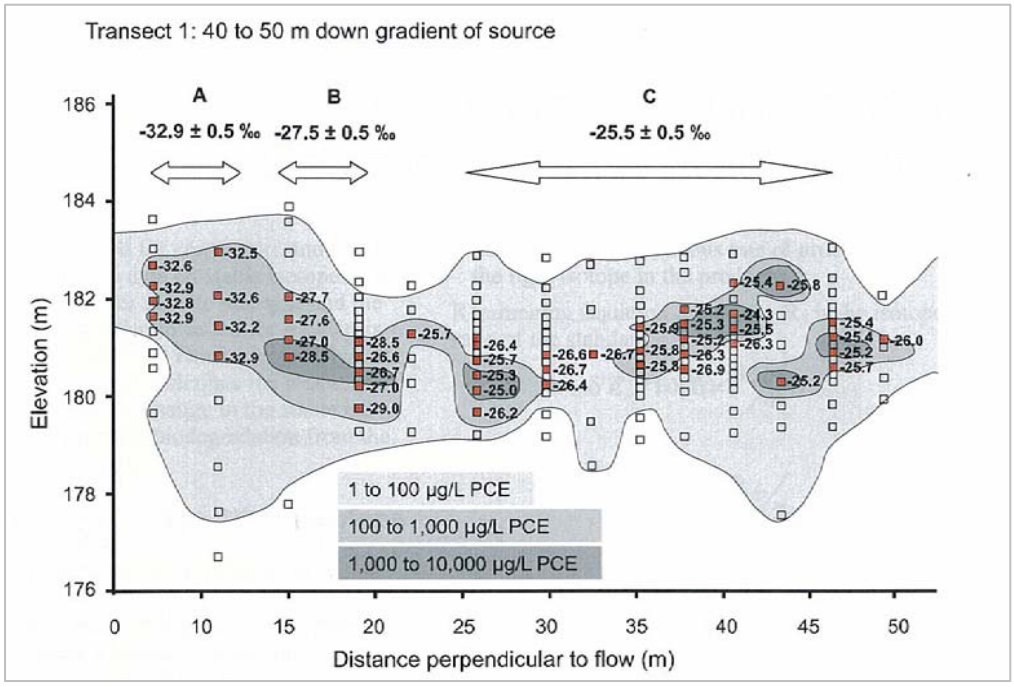

Figure 9. Park Transect, Angus Field (Hunkeler, et. al.)

A second transect about 220 m downgradient of the source is shown in Figure 10. Two of the three plume cores can still be identified at this down gradient transect.

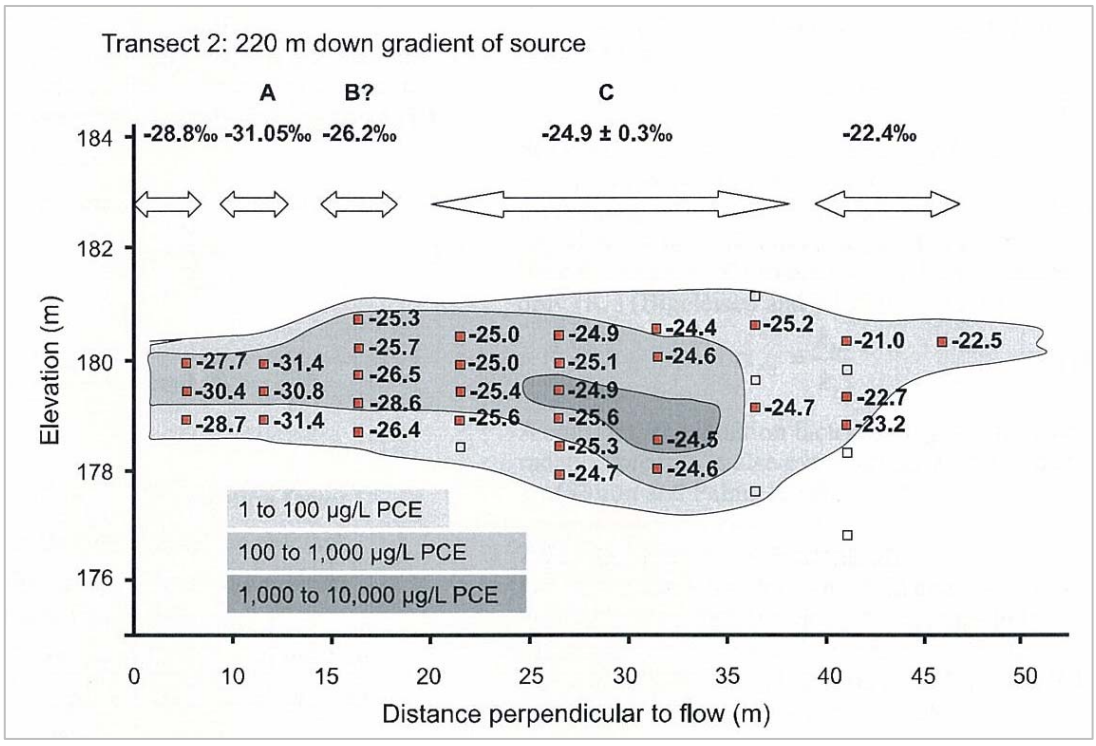

Figure 10. River Transect, Angus Field (Hunkeler, et.al.)

On the basis of the results from these two sites, one can conclude that in the absence of significant degradative fractionation, the isotopic signatures of sources, including DNAPL sources, persist without significant modification in the high concentration zones of plumes, even over significant distances. This persistence under these circumstances suggests the effects of dispersion and diffusion are not influential in the isotope composition of PCE and TCE.

Morrill et.al. have also studied the dissolution of PCE close to emplaced pure phase PCE in a control model aquifer. They found that in the absence of degradation, PCE isotope values of the dissolved PCE were within experimental error of that of the pure phase product. This further suggests that the process of dissolution is not significant in the isotopic composition of dissolved PCE.

Blessing, et. al. investigated an old industrial site in southwestern Germany where there had been widespread use of chlorinated solvents. There were multiple suspected and known sources. They used a multiple line of evidence approach including historical, hydrological, geochemical and isotopic data. The site is shown in Figure 11, where several parts of the various plumes are depicted as Areas A – G. To illustrate the approach, we will consider Areas E and C.

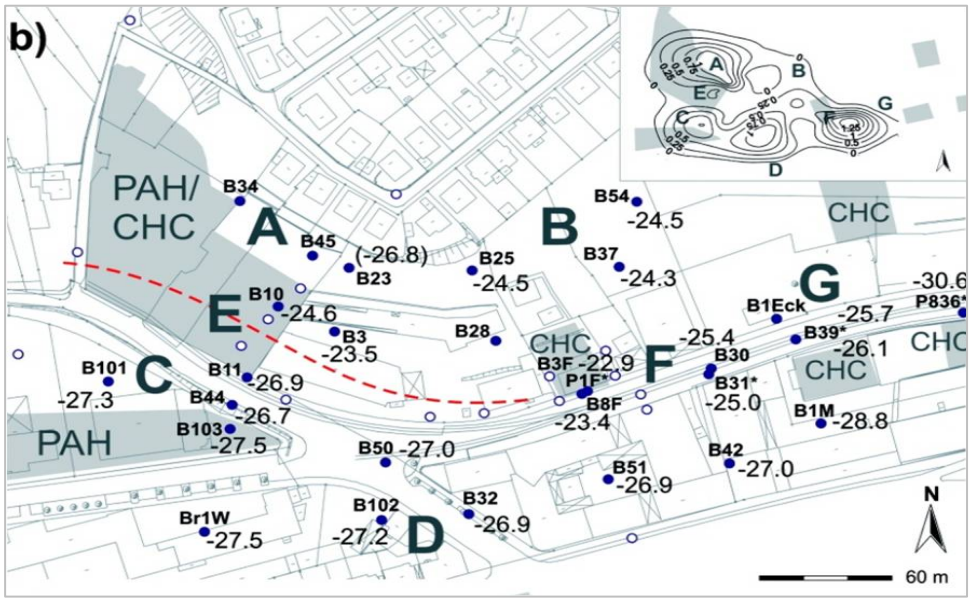

Figure 11. Industrial Site, Southwestern Germany, (Blessing, et. al.)

In Area E, as highlighted in Figure 12, $\delta^{13}C$ of PCE in wells B10 and B3 was found to be -24.6 and -23.5 ‰. Groundwater in this area is aerobic, thus under these conditions PCE will not degrade and it is therefore concluded that these values represent the isotopic composition of the original contaminant.

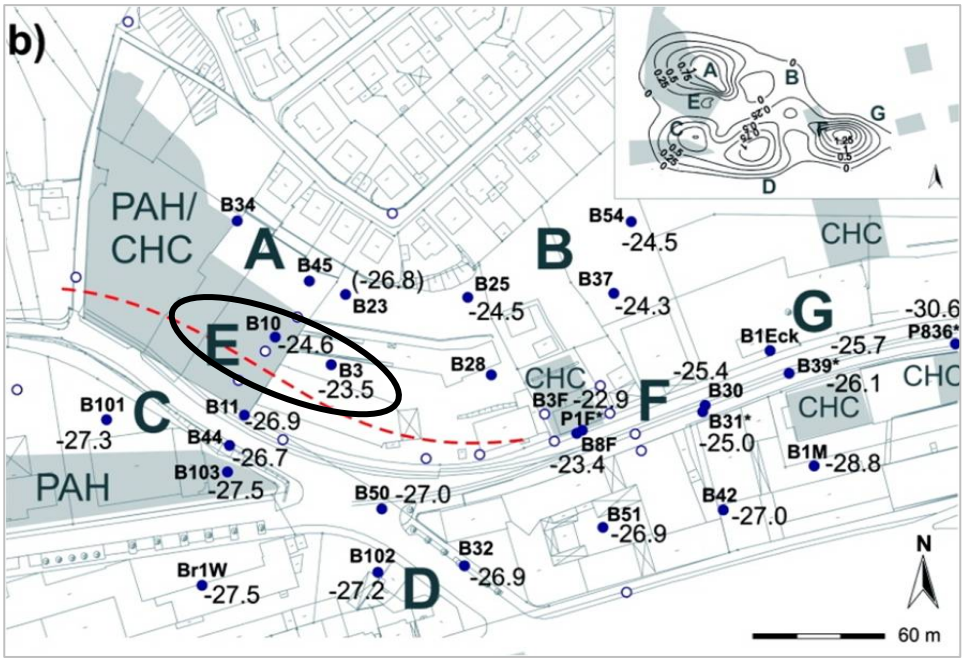

Figure 12. $\delta^{13}C$ of PCE Industrial Site, Southwestern Germany, Area E (Blessing, et. al.)

In the adjacent Area C, as highlighted in Figure 13, groundwater is weakly anaerobic and there is a significant presence of daughter products including cisDCE and VC. In wells B11, B44, B101, B103 and B50, $\delta^{13}C$ is found in the range - 27.5 to – 26.7 ‰ (all values are within experimental error). Given the presence of daughter products, reductive de-chlorination has occurred and thus fractionation of PCE must have also occurred. Thus the values of $\delta^{13}C$ of PCE found in Area C must be more positive than the source. If indeed this value represents significant fractionation relative to its source, then the source would have had a much lighter (more negative) $\delta^{13}C$ value. Since the $\delta^{13}C$ of the undegraded PCE in Area E was found to be more positive than the value found in Area C, it cannot be the source of the PCE in Area C, thus the conclusion is that Area's E and C have two separate sources of PCE.

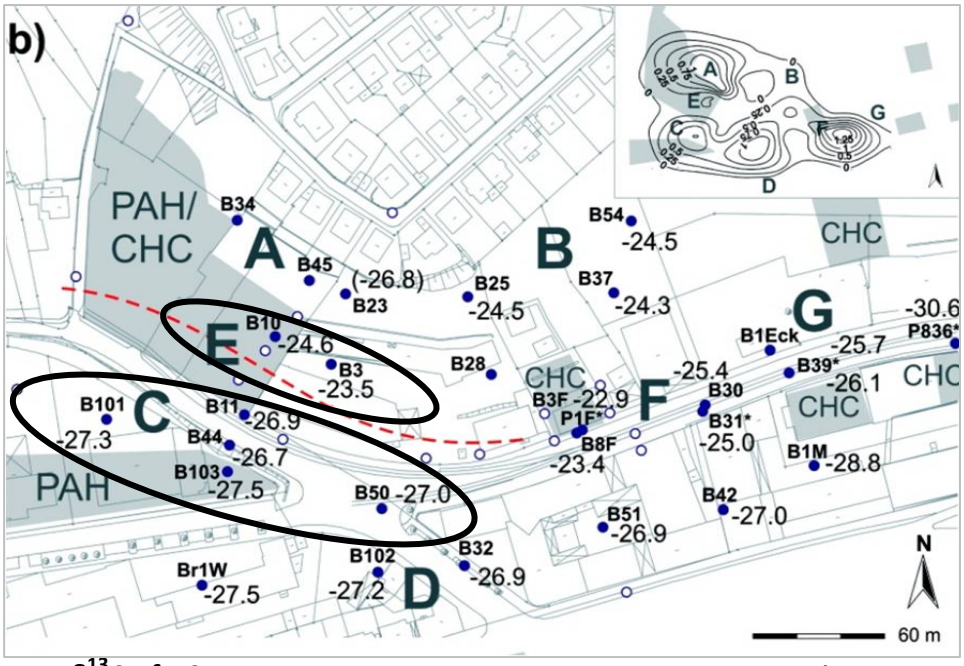

Figure 13. $\delta^{13}C$ of PCE, Industrial Site, Southwestern Germany, Area C, (Blessing, et. al.)

Given the background for forensic investigations discussed above, it is worthwhile to consider the potential to distinguish different sources of MTBE using CSIA. Kuder, et. al. have reported that the range of $\delta^{13}C$ for commercial MTBE is – 27.4 to – 33 ‰ , while $\delta^{2}H$ in commercial MTBE samples and from the source zones of MTBE plumes has been found in the range – 80 to – 125 ‰ . Data from individual samples were not presented. Given however that there were only four major domestic suppliers of commercial MTBE (J.E. Haas, private communication) the potential that these sources could be uniquely identified using both carbon and hydrogen CSIA seems reasonable.

Indeed, Smallwood et.al. have concluded from analyses of several commercial MTBE samples that purge and trap interfaced to a GCIRMS system was the most effective method for determining the carbon isotopic composition of MTBE in groundwater samples. Further they concluded, ***"…it is not proposed that this approach should be used in attempts to identify a specific manufacturer of MTBE. However where it will be invaluable is at sites where there may be several potential sources for MTBE in the groundwater. Determination of the isotopic composition of the MTBE in different parts of the plume will provide an indication as to whether there are multiple sources of MTBE."***

In a recently published paper McKelvie, et. al. have investigated the use of ^{2}H NMR to determine "site-specific" values of $\delta^{2}H$ in seven different commercially available MTBE products. "Site-specific" here means that this methodology is capable of independently determining $\delta^{2}H$ for the methoxy group and the t-butyl group. As shown on Table 1, the range of $\delta^{2}H$ for the methoxy groups in these products was -103 to -171‰ and for the t-butyl groups was -76 to -104‰. This no doubt reflects production of MTBE from methanol and isobutene, each of which could and almost certainly do have a range of $\delta^{2}H$.

These results suggest the potential for this new tool to contribute to source determination of MTBE and other compounds which contain hydrogen.

	δ^2H
methoxy group	-103 ‰ - -171‰
isobutyl group	- 76 ‰ - -104 ‰

Table 1. Site-Specific δ^2H of MTBE from ^2H NMR (McKelvie, et.al.)

The caveat here is that, at this point, this tool has only been applied to pure samples of MTBE and the method must now be extended to meaningful dissolved concentrations in groundwater. The results obtained however, when used to calculate overall MTBE δ^2H using weighted averages of the component groups have correlated well with overall δ^2H of these products obtained with traditional isotope ratio mass spectrometry. The ability to gain accurate information about the site-specific hydrogen isotopic composition within a molecule offers considerable promise as a new environmental tool to track the source and fate of environmental contaminants.

Finally, with regard to vapor intrusion, there is the potential to distinguish between sub-slab contaminants and those which originate from stored products within an enclosure. The concept is shown in Figure 15 where a dwelling overlies as subsurface TCE plume which has been fractionated due to in-situ degradation and has a $\delta^{13}C$ = -22‰. TCE from this groundwater plume is shown to have escaped into the vadose zone where it is found sub-slab with a $\delta^{13}C$ = -24‰ (assuming some liquid to vapor phase diffusive fractionation). From the sub-slab area it may or may not enter the breathing space of the dwelling through defects in the slab. Also shown is the potential for TCE to enter the dwellings breathing space as a result of escape from stored product within the dwelling itself. This TCE should not be degraded and should have $\delta^{13}C$ in the range of manufactured TCE which is for our purpose here, assumed to be - 32‰.

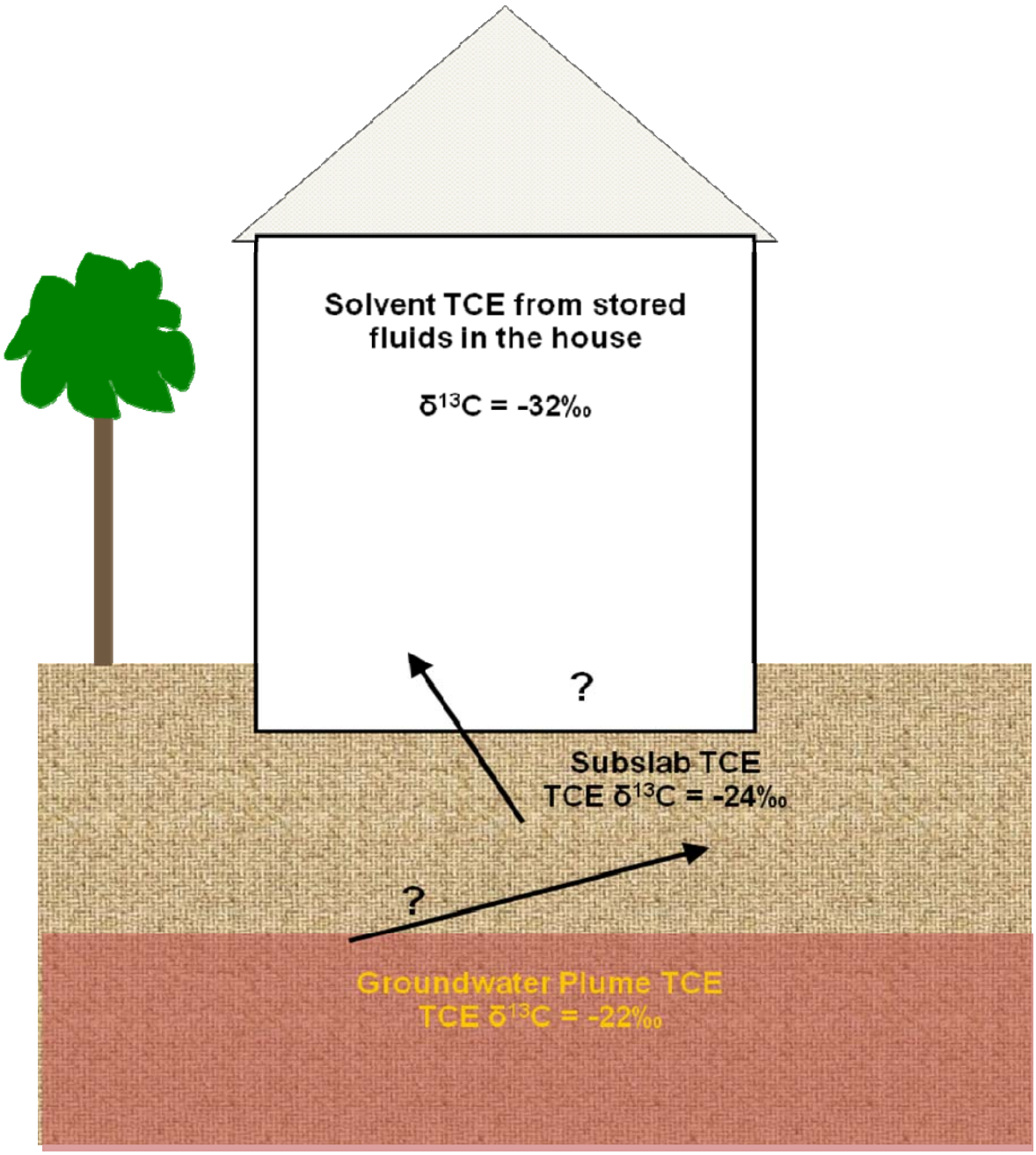

Figure 15. Application of CSIA to Vapor Intrusion (Burns, et.al.)

We believe that it is entirely reasonable that the two potential sources of TCE in the breathing space of this dwelling could be distinguished based on isotopic composition of the measured vapor. The potential success of this undertaking would be increased if both carbon and chlorine isotopic composition of the TCE could be determined. Microseeps is working on the means to accomplish this objective.

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