Estimating the age of leaded gasoline releases using stable lead isotopes: The ALAS Model

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Estimating the year gasoline was released into the environment has been difficult. Methods relying upon gasoline additive chronologies and/or presumed rates of biodegradation do not provide adequate age resolution. Lead isotopic analyses of gasoline-impacted southern California marine sediments by Patterson demonstrated the presence of systematic isotopic variations in gasoline lead between 1940 and 1978. Circa 1990, Hurst surmised that if these temporal variations in gasoline lead isotope ratios were real and could be calibrated, an improved method of age-dating gasoline releases might result.

By acquiring samples of archived leaded gasoline and gasoline-impacted sediment, a calibration curve, the ALAS Model (Anthropogenic Lead ArchaeoStratigraphy), has been developed, and has been used to estimate the age of leaded gasoline releases. Systematic increases in $^{206}Pb/^{207}Pb$ ratios observed in the ALAS Model curve (1965-1990) are caused by the increased use of radiogenic lead from Mississippi Valley-Type ores ($^{206}Pb/^{207}Pb \approx 1.30$) in the production of alkyllead additives. The ALAS Model calibration curve exhibits minimal scatter, which is attributed to the use of very similar proportions of lead by major alkyllead manufacturers (e.g. Ethyl Corporation, DuPont) from 1965 through 1990. Correlations between ALAS Model ages and known release ages are excellent ($R^2 = 0.97$), warranting the continued investigation of lead isotopes as tracers of lead pollution by hydrocarbons.

A forensic geochemical technique for estimating release dates of petroleum products

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Background

In 1993 Christensen and Larsen (C-L Model) proposed that the degradation of normal heptadecane (nC17) relative to pristane (nC17/Pr ratio) could be used to estimate the age of diesel fuels released to the environment. The C-L Model indicated a linear relationship between the nC17/Pr ratio of the petroleum and the time since the release. Given the importance of accuracy and scientific defensibility of techniques for estimating the age of petroleum releases, it is not surprising the the C-L Model has been the subject of much debate. Concerns are that variations and unknowns in the subsurface conditions, starting (initial) nC17/Pr ratios of the petroleum released and the rate of degradation contribute to uncertainties in the C-L Model age determinations.

Middle distillate degradation model

In order to address the uncertainties in the C-L Model, measured initial nC17/Pr ratios of ~4500 worldwide crude oils and 90 domestic petroleum products, the C-L Model was integrated with more than 50 additional data points for comparitive linear regression analyses and new data from documented distillate and crude oil releases from diverse geographic regions to assess variations in subsurface temperature and conditions. The culmination of these data is the MDD Model for estimating the age of ditillates, fuel oils and crude oil releases up to ~20 years with substantially more certainty than the C-L Model.

Conclusions

The MDD Model can be used to estimate petroleum release ages in ranges from plus or minue 1.5 years under optimal conditions to plus or minus 5 years in a worst case scenario. Where little information is available about the site and the initial nC17/Pr ratios is unknown, then it may only be possible to estimate that the release is older or younder than 10 years, whereas a 3 year window would be reasonable under optimal conditions using due diligence and care.