



Risky bismuth: Distinguishing between lead contamination sources in soils



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HIGHLIGHTS

- Some urban soils contained high levels of Pb and trace levels of Bi.
- Some urban soils contained high levels of Pb but contained no Bi.
- These differences were linked to different sources of lead: paint or gasoline.
- Lead paint contained trace levels of Bi but leaded gasoline contained no Bi.
- XRF can detect low levels of Bi to reveal the origin of Pb in soils.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 10 January 2019

Received in revised form

30 May 2019

Accepted 10 June 2019

Available online 13 June 2019

Handling Editor: Petra Petra Krystek

Keywords:

Soil contamination

Lead

Bismuth

Leaded paint

Leaded gasoline

XRF

ABSTRACT

In a broad environmental study in St. Joseph County, Indiana, elemental data from ~2000 soil samples and ~800 paint samples were collected with X-ray Fluorescence (XRF) spectroscopy. The observed lead concentrations were compared to other elemental concentrations in these data. A strong correlation between lead and bismuth concentrations was observed in a subset of the soil samples and in nearly all of the paint samples, with lead levels approximately 150 times higher than bismuth. However, some soil samples contained lead with no bismuth present. Since most lead sources likely contain bismuth as an impurity from refining of native lead ore, but leaded gasoline does not contain any bismuth impurities due to the manufacturing process of tetraethyl lead, it may be possible to distinguish environmental lead sources by XRF. To test if leaded gasoline could be the source of lead in the subset of soil samples containing no bismuth, leaded paint samples were analyzed with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES), which confirmed the presence of bismuth in leaded paint. Aviation gasoline, which contains tetraethyl lead, was also analyzed by ICP-OES to confirm the absence of bismuth in leaded gasoline. This discovery suggests that XRF can be used to rapidly distinguish different legacy lead contamination sources from one another. For low lead concentrations, elemental measurements of bismuth by ICP-OES can be used in environmental forensics to distinguish leaded gasoline contamination from other sources of lead.

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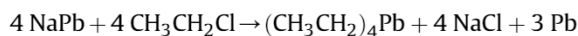
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1. Introduction

Lingering environmental lead contamination from the use of leaded paint and leaded gasoline plagues urban areas across the United States. Lead's adverse health effects are well known (Agency For Toxic Substances And Disease Registry (ATSDR), 2017; Binns et al., 2007; Dietrich et al., 2001; Lidsky and Schneider, 2003; Needleman et al., 2002; Wright et al., 2008) and it has recently come to light that South Bend, St. Joseph County, IN has extremely high rates of child lead poisoning (Pell and Schneyer, 2016). While the use of leaded paint and leaded gasoline was banned decades ago, legacy lead contamination remains a widespread issue in many urban environments across the country (Mielke et al., 2011; Mielke et al., 2001; Mielke, 1993; Mielke et al., 1985). Soil can become contaminated with leaded paint dust and paint chips from activities such as renovation, repainting, or demolition of homes and other painted structures, or from the historical combustion of leaded gasoline (Mielke, 1993). Contaminated soil is one of the main contributors to elevated blood lead levels in children. Strong seasonal variations were observed in children's blood lead levels (BLLs) in Indianapolis (Laidlaw et al., 2005). BLLs were higher in the summer, when children are more likely to be outdoors and exposed to contaminated soils, while BLLs were lower in the winter, when children are more likely to be indoors.

Since soil contamination can contribute to environmental lead poisoning, being able to readily identify the sources of the lead contamination could help residents reduce their lead exposure. Current methods for determining the sources of lead contamination in soil typically involve observing the particle morphology and chemical composition (Gulson et al., 2016; Harrison et al., 1981; Linton et al., 1980; Łobiński, 1995), or characterizing the isotopic composition of the lead (Cheng and Hu, 2010), though this method is primarily used for identifying the original location where the lead was mined, rather than directly identifying the source of the contamination as paint or gasoline. A common feature of these existing methods for identifying the origin of lead contamination in soils is that they require relatively time-consuming and technically challenging laboratory analysis techniques.

Because both bismuth and lead are co-produced radiogenically in the earth's crust from uranium and thorium natural decay series, bismuth is often a byproduct of lead mining (Jasinski, 1995). The chemical similarities of these two elements means that they are costly to separate, so most industrial uses of lead minerals involve trace levels of bismuth as well. However, one of the largest sources of environmental lead was the widespread use of tetraethyl lead in automotive gasoline between 1920 and 1980. An unusual feature of tetraethyl lead is that it was commercially manufactured by reacting chloroethane with a sodium–lead alloy, followed by distillation of tetraethyl lead (Seyferth, 2003):



Thus the industrial manufacturing process effectively removes any trace bismuth from the lead (Frey and Cook, 1960). Compared to any other sources of environmental lead, leaded gasoline should contain the lowest levels of bismuth impurities.

X-ray fluorescence (XRF) spectrometric analysis of 2018 soil samples and 820 paint samples have been used to verify a potential method to distinguish between sources of environmental lead contamination. By measuring trace levels of bismuth in the lead samples, it is possible to distinguish legacy sources of lead contaminants with instrumentation that could be used in the field, or with more sophisticated instrumental analysis performed on soil samples sent to a lab. This novel method for distinguishing between lead contamination sources could shed light on whether

legacy paint or gasoline contributes more to elevated BLLs today, several decades after both have been discontinued, as well as enabling more efficient remediation strategies; if the source of contamination is identifiable it can be removed and halt the addition of more lead contamination to the soil.

2. Materials and methods

2.1. Ethical approvals

Institutional Review Board approval for the sample collections described in this work were obtained through the University of Notre Dame (IRB # 17-01-3522 08 June 2017–14 March 2018, IRB #18-03-4538 15 March 2018–14 March 2019).

2.2. Sample collection

During 2017, 2018, 2018 soil samples and 820 paint samples were collected throughout St. Joseph County, IN, by students at John Adams High School, community health workers at the Near Northwest Neighborhood Center, and Notre Dame faculty, graduate, and undergraduate students. All participants received a training session on how to collect the samples, record the locations of the samples, and a kit of pre-labeled bags. Soil samples were collected with small plastic spoons into 0.002-inch thick resealable low-density polyethylene bags (Uline S-1291). Paint chips were collected with double sided tape and placed into the same type of resealable bags.

2.3. XRF analysis

The samples were analyzed with a handheld SciAps X-100 XRF Spectrometer which was calibrated each day with an alloy cap and regularly checked against a NIST leaded soil standard (NIST SRM 2586). The spectrometer was set upright on a benchtop and each sample was placed on top of the device; all samples remained inside the thin-walled resealable bags during analysis. The limit of detection for lead was typically about 12 ppm and the limit of detection for bismuth was about 2 ppm. Replicate measurements of the NIST standard showed that accurate soil lead results were obtained through the thickness of the plastic sample bag. For this study, the XRF was configured to measure 19 elements simultaneously. The elements measured and their relative limits of detection (in ppm) are listed together with the operating parameters in the Supporting Information (Table S1).

2.4. Preparation of gasoline for ICP-OES

Leaded aviation gasoline, Avgas 100 Low-Lead (blue), was obtained from the Indiana Flight Center in Elkhart, IN. Following the method detailed by Mansell and Hiller (1973), 5 mL of Avgas and 5 mL of concentrated hydrochloric acid were combined in a Teflon cup, placed in a hydrothermal reactor, and put in the oven for 3 h at 115 °C. After 3 h, the hydrothermal reactor was removed from the oven and allowed to cool for several hours. After cooling, the contents within were washed into a beaker and placed on a heating plate at about 50 °C until the solution had evaporated. The resulting residue was then dissolved in 1 mL of concentrated nitric acid and again allowed to evaporate. The final residue was then dissolved in 5% nitric acid and this solution was used for analysis with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). This procedure was repeated after spiking 5 mL of the leaded gasoline with 100 µL of 1000 ppm bismuth (theoretical concentration 20 ppm Bi), to determine the percent recovery of bismuth in a leaded gasoline solution.

2.5. Preparation of paint chips for ICP-OES

A leaded paint chip that had been collected from a residence in South Bend, IN was weighed and placed in a 50 mL conical tube. 50 mL of 5% nitric acid was added to the tube and the solution was then placed on a KJ-201 BD Orbital Shaker for 2 h. This solution was then filtered through 90 mm 1 Whatman filter paper then analyzed with ICP-OES.

2.6. ICP-OES analysis

ICP-OES analysis was performed on a PerkinElmer Optima 8000 instrument. Measurements were taken with both axial and radial viewing optics with 2 replicate measurements, with yttrium as the instrument's internal standard. Standards were prepared for both lead and bismuth in 5% nitric acid to match the matrix of the samples. The LOQ for lead was 0.023 ppb and the LOQ for bismuth was 0.071 ppb using the 220.35 nm wavelength for lead and the 223.06 nm wavelength for bismuth. Operating parameters for these analyses are listed in the Supporting Information.

3. Results and discussion

The measured lead concentrations were plotted against all other measured elemental concentrations. An initial scatter plot of the observed lead and bismuth concentrations of 2018 soil samples (Fig. 1) showed 3 distinct categories of samples: lead accompanied by a correlated bismuth concentration, lead concentrations with no measurable bismuth, and bismuth with no (or low) lead concentrations. Of the 2018 samples, one soil sample was omitted because it contained nearly 7% lead. This sample also contained measurable Bi, with 0.035% Bi. The soil samples were mostly homogeneous, and this excluded sample may have contained a solid piece of lead or highly leaded paint chips in it.

To help explain the relationship between lead and bismuth in the soil samples, a scatter plot of the lead and bismuth concentrations found in 818 paint samples is shown in Fig. 2. The lead and bismuth concentrations are strongly correlated, with an R^2 of 0.945 from a simple linear fit through the origin. The slope of the correlation (149 ± 104) is similar to the slope of the correlation found in the soils. Two paint samples were omitted from this plot, each of which contained high bismuth levels with no lead. Upon further investigation, it was found that these two paint chips came from the same home (and the same location in the home) and was determined to be the pigment bismuth vanadate (BiVO_4), as it was bright yellow and XRF analysis showed both bismuth and vanadium.

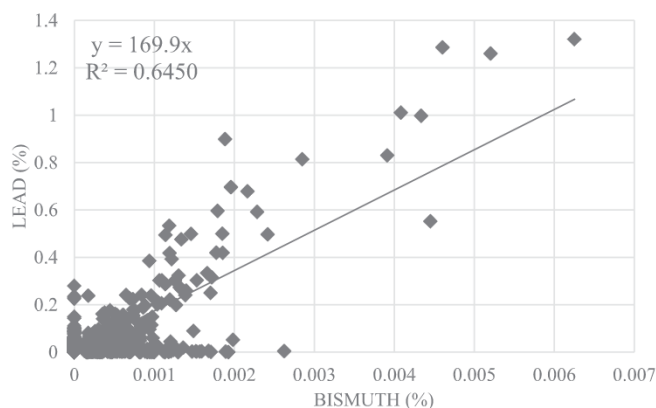


Fig. 1. Scatter plot of bismuth and lead concentrations (w/w %) in soil.

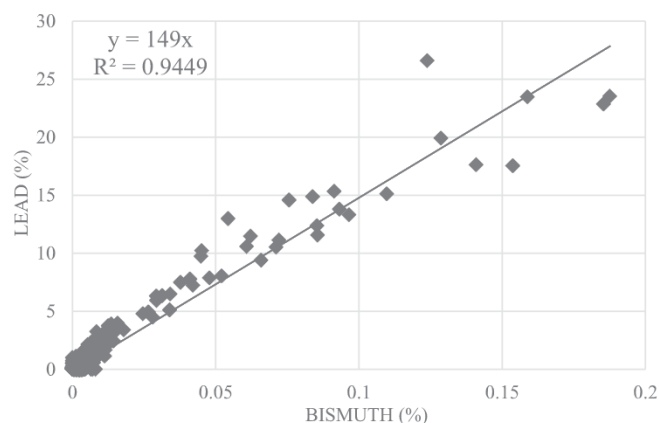


Fig. 2. Scatter plot of bismuth and lead concentrations (w/w %) in paint.

Because the average bismuth concentration for this set of samples is a very small fraction of the lead concentration (~150 times lower or approximately 0.67% of the lead concentration on average) and because the bismuth and lead L_{α} X-ray energy lines are close to each other, at 10.55 keV and 10.84 keV, it may be possible for the commercial peak-fitting software in the XRF to mistakenly assign a small value for a Bi reading, if the Pb peak is very large. To ensure that was not the case, the raw spectrum of a typical leaded paint chip is shown in Fig. 3. There is clear peak separation between the L_{α} peak of lead (10.55 keV) and the L_{α} peak of bismuth (10.84 keV), that the commercial software provided by SciAps can readily distinguish. This same paint chip was dissolved and analyzed with ICP-OES. ICP-OES results returned 353 ppm Bi in the paint sample with a lead concentration of 130,200 ppm (13% by weight) which can be seen in Table 1.

Bismuth is a common impurity in lead ores that is difficult to remove during smelting and refining because it is less reactive to oxidation than lead. Traces of bismuth should therefore be present in all lead objects and lead compounds, such as the lead carbonates, oxides, and hydroxides that were commonly used as paint pigments or drying agents in varnish. However, it is unlikely that bismuth would be a contaminant in tetraethyl lead, the anti-knocking agent in leaded gasoline, because the industrial process of making tetraethyl lead involves distilling the volatile tetraethyl lead (Frey and Cook, 1960), which effectively separates the lead from any bismuth impurity. Thus, the subset of soil samples in Fig. 1 that showed significant levels of lead with no bismuth could be

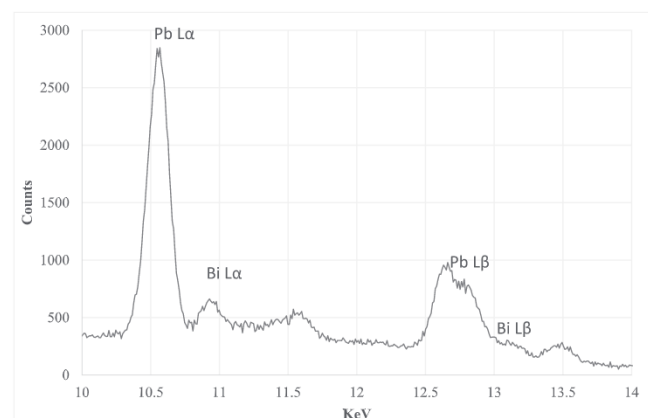


Fig. 3. Raw XRF spectrum of a leaded paint sample showing 13.8% Pb by weight and 932 ppm Bi.

Table 1

ICP-OES results from a leaded paint sample, an aviation gasoline sample, and aviation gasoline spiked with bismuth.

Sample	Pb ppm	Bi ppm
Paint Chip	130,200 ± 800	353 ± 101
Avgas	734 ± 10	0
Avgas-Bi Spiked	761 ± 19	19.2 ± 0.4

explained by contamination of soils from leaded gasoline.

Upon investigation for a common method for analyzing leaded gasoline, it was discovered that ASTM method D 5059-98, a standard test to analyze lead in gasoline with X-ray spectroscopy utilizes bismuth as the internal standard, further solidifying the hypothesis that bismuth would not be an impurity in leaded gasoline. To test this hypothesis, 100LL (blue) aviation gasoline (also known as avgas) was prepared and analyzed with ICP-OES. ICP-OES results (Table 1) showed that the 100LL aviation gasoline contained 734 ppm lead, and no bismuth. The gasoline sample was then spiked with 100 µL of 1000 ppm Bi to ensure the ICP digestion method used could recover it. The spiked aviation gasoline sample returned a result of 761 ppm Pb and gave a 96% recovery for the spiked bismuth, confirming the hypothesis that leaded gasoline does not contain trace amounts of bismuth.

It is acknowledged that lead was used industrially for many applications and can be contributed to the environment from more sources than simply paint and gasoline. It is suspected that lead from other sources besides gasoline (i.e. fishing sinkers, bullets, pipes, etc ...) will contain trace levels of Bi since lead metal usually contains traces of bismuth. However, legacy paint and gasoline are two of the largest contributors to environmental lead contamination especially in cities. Environmental lead contamination will no doubt be high in mining locations or near smelters – where this Pb and Bi correlation is less likely to be helpful as there will probably be Bi impurities from other lead sources – but in cities that do not have industrial lead contamination, leaded and paint and leaded gasoline are the main contributors. What is interesting about this study is that with a hand-held XRF, we are able to distinguish potential sources of lead in typical soils that are elevated to around the current EPA action limit on leaded soils (400 ppm). There are many contaminated sites where the inclusion of Bi as an analyte could be readily used to distinguish legacy lead sources with XRF technology.

4. Conclusions

These findings suggest that X-ray spectroscopy techniques capable of measuring both lead and bismuth at low concentrations can distinguish between leaded paint and leaded gasoline as sources of lead contamination in soils. This was confirmed in South Bend, IN, in soils that were elevated in lead. For soils with concentrations of lead below 400 ppm, or in a full environmental forensic analysis, ICP-OES methods could be used to identify the provenance of the legacy lead by including bismuth as a concurrent element to be analyzed. As local health departments use XRF to perform lead hazard assessments for families with lead-poisoned children, this technique could help offer remediation assistance more effectively. Knowing where the source of lead contamination in soil originates may allow for the source to be removed or at least the best mitigation technique to be used, ultimately helping to decrease lead exposure in urban environments. Additionally, this information could be used to understand whether legacy lead from paint or gasoline has a larger impact on BLLs today.

CRedit authorship contribution statement

Meghanne Tighe: Conceptualization, Investigation, Data curation, Formal analysis, Writing - original draft. **Heidi Beidinger:** Conceptualization, Funding acquisition, Project administration, Writing - review & editing. **Christopher Knaub:** Conceptualization, Investigation, Writing - review & editing. **Matthew Sisk:** Conceptualization, Funding acquisition, Writing - review & editing, Software, Formal analysis. **Graham F. Peaslee:** Conceptualization, Funding acquisition, Project administration, Supervision, Resources, Writing - review & editing. **Marya Lieberman:** Conceptualization, Funding acquisition, Project administration, Supervision, Resources, Writing - review & editing.

Acknowledgements

Funding is gratefully acknowledged from the University of Notre Dame College of Science, the Department of Chemistry and Biochemistry, and the Center for Social Concerns Ganey grant. This effort was also supported by the instrumentation provided by the Notre Dame Center for Environmental Science and Technology. The sample collection efforts were greatly assisted by the Near North-west Neighborhood organization, Mark Wilson, Dan Walsh, the John Adams High School science students, students of ND Chem 30331 Fall 2017 and Fall 2018, Adam Moeller and the ND student government, and Mulch Madness participants.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2019.06.077>.

References

- Agency For Toxic Substances And Disease Registry (ATSDR), 2017. Lead Toxicity Case Studies in Environmental Medicine. *Case Studies in Environmental Medicine (Csem)*, WB2832, pp. 1–182. Retrieved from: https://www.atsdr.cdc.gov/csem/lead/docs/CSEM-Lead_toxicity_508.pdf.
- ASTM Standard D 5059-98, 2003. Standard Test Methods for Lead in Gasoline by X-Ray, Spectroscopy. ASTM International.
- Binns, H.J., Campbell, C., Brown, M.J., 2007. Interpreting and managing blood lead levels of less than 10 g/dL in children and reducing childhood exposure to lead: recommendations of the centers for Disease control and prevention advisory committee on childhood lead poisoning prevention. *Pediatrics* 120 (5), e1285–e1298. <https://doi.org/10.1542/peds.2005-1770>.
- Cheng, H., Hu, Y., 2010. Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environ. Pollut.* 158 (5), 1134–1146. <https://doi.org/10.1016/j.envpol.2009.12.028>.
- Dietrich, K.N., Douglas, R.M., Succop, P.A., Berger, O.G., Bornschein, R.L., 2001. Early exposure to lead and juvenile delinquency. *Neurotoxicol. Teratol.* 23 (6), 511–518. [https://doi.org/10.1016/S0892-0362\(98\)00184-2](https://doi.org/10.1016/S0892-0362(98)00184-2).
- Frey, F.W., Cook, S.E., 1960. The synthesis of tetraethyllead by reaction of tetravalent lead salts with triethylaluminum and other ethyl metal compounds. *J. Am. Chem. Soc.* 82 (3), 530–533. <https://doi.org/10.1021/ja01488a008>.
- Gulson, B., Chiaradia, M., Davis, J., O'Connor, G., 2016. Impact on the environment from steel bridge paint deterioration using lead isotopic tracing, paint compositions and soil deconstruction. *Sci. Total Environ.* 550, 69–72. <https://doi.org/10.1016/j.scitotenv.2016.01.083>.
- Harrison, R.M., Laxen, D.P.H., Wilson, S.J., 1981. Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils. *Environ. Sci. Technol.* 15 (11), 1378–1383. <https://doi.org/10.1021/es00093a013>.
- Jasinski, S.M., 1995. Bismuth from Mineral Commodity Summaries. Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., vol. IV.
- Laidlaw, M.A.S., Mielke, H.W., Filippelli, G.M., Johnson, D.L., Gonzales, C.R., 2005. Seasonality and children's blood lead levels: developing a predictive model using climatic variables and blood lead data from Indianapolis, Indiana, Syracuse, New York, and New Orleans, Louisiana (USA). *Environ. Health Perspect.* 113 (6), 793–800. <https://doi.org/10.1289/ehp.7759>.
- Lidsky, T.I., Schneider, J.S., 2003. Lead neurotoxicity in children: basic mechanisms and clinical correlates. *Brain* 126 (1), 5–19. <https://doi.org/10.1093/brain/awg014>.
- Linton, R.W., Natusch, D.F.S., Solomon, R.L., Evans, C.A., 1980. Physicochemical characterization of lead in urban dusts. A microanalytical approach to lead tracing. *Environ. Sci. Technol.* 14 (2), 159–164. <https://doi.org/10.1021/>

- es60162a004.
- Mansell, R.E., Hiller, T.A., 1973. Application of the Parr acid digestion bomb to decomposition of tetraethyllead. *Anal. Chem.* 45 (6), 975–975. <https://doi.org/10.1021/ac60328a042>.
- Mielke, H.W., 1993. Lead dust contaminated U.S.A. communities: comparison of Louisiana and Minnesota. *Appl. Geochem.* 8 (2), 257–261. [https://doi.org/10.1016/S0883-2927\(09\)80046-2](https://doi.org/10.1016/S0883-2927(09)80046-2).
- Mielke, H.W., Burroughs, S., Wade, R., Yarrow, T., Mielke, P.W., 1985. Urban Lead in Minnesota: Soil Transect Results of Four Cities.
- Mielke, H.W., Powell, E.T., Shah, A., Gonzales, C.R., Mielke, P.W., 2001. Multiple metal contamination from house paints: Consequences of power sanding and paint scraping in New Orleans. *Environ. Health Perspect.* 109 (9), 973–978. <https://doi.org/10.1289/ehp.01109973>.
- Mielke, H.W., Laidlaw, M.A.S., Gonzales, C.R., 2011. Estimation of leaded (Pb) gasoline's continuing material and health impacts on 90 US urbanized areas. *Environ. Int.* 37 (1), 248–257. <https://doi.org/10.1016/j.envint.2010.08.006>.
- Needleman, H.L., McFarland, C.E., Ness, R., 2002. Bone lead levels in adjudicated delinquency: a case-control study. *Neurotoxicol. Teratol.* 24, 11–17.
- Pell, M.B., Schneyer, J., 2016. The thousands of U.S. locales where lead poisoning is worse than in Flint. *Reuters* 1–17.
- Seyferth, D., 2003. The Rise and Fall of Tetraethyllead. 2. *Organometallics* 22 (25), 5154–5178. <https://doi.org/10.1021/om030621b>.
- Wright, J.P., Dietrich, K.N., Ris, M.D., Hornung, R.W., Wessel, S.D., Lanphear, B.P., Rae, M.N., 2008. Association of prenatal and childhood blood lead concentrations with criminal arrests in early adulthood. *PLoS Med.* 5 (5), 0732–0739. <https://doi.org/10.1371/journal.pmed.0050101>.
- Łobiński, R., 1995. Organolead compounds in archives of environmental pollution. *Analyst* 120 (3), 615–621. <https://doi.org/10.1039/AN9952000615>.