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Title: Using X-ray Fluorescence (XRF) to Detect Automobile Heavy Metal Pollution in Los Angeles Soils with Copper and Palladium as Indicators

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## Abstract:

This project evaluates the effectiveness of using portable X-ray Fluorescence (XRF) to detect soil composition matrices that show patterns of anthropogenic influence. We explore 26 areas within Los Angeles County, California, that have various amounts of traffic; classifying each locale as Urban or Recreational. The main elements of interest are copper and palladium. These indicators are largely theorized to originate from brake pad wear-and-tear and vehicle emissions. Wildfires and the degradation of city related infrastructures provide additional context to the concentrations of copper that are found within each area.

In all samples, copper was reliably detected with an average concentration of  $29.35 \pm 24.74$  parts per million (ppm). Elevated copper levels were notably associated with areas of high traffic density. This supports its use as an elemental marker for vehicle brake-pad pollution. Palladium, by contrast, was detected at an average of  $19.54 \pm 9.63$  ppm across the region. However, higher relative measurement uncertainty and a lack of clear spatial variability suggest that these measurements may be affected by instrumental noise or soil matrix interference. Furthermore, the difference between concentrations found here and previous studies from around the world makes palladium less reliable for environmental assessment. Overall, these findings support the use of portable x-ray fluorescence for rapid screening of copper for tracking automobile activity; while highlighting limitations in its ability to accurately quantify trace levels of palladium.

# **Introduction:**

Heavy metals from vehicle traffic are continuously released into the environment, accumulating along roadsides and into soil every day [1]. More generally, research on chemical contamination in densely populated areas often focuses on elements such as lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), and nickel (Ni) [2,3,4]. This is due to toxicity risks, environmental persistence, and widespread variability related to human activities. Palladium (Pd), on the other hand, remains comparatively understudied despite its emerging ecological relevance [5,6]. This trace metal is used in automobile catalytic converters during redox reactions that convert toxic gases into less harmful substances [7]. It was introduced in the 1970s in automobiles as a way to replace platinum providing cleaner exhaust emissions [8]. Despite the overall benefit of palladium in vehicles, some of the metal is gradually released into the environment, where it could be posing health, occupational, and ecological risks [9, 10].

This research identifies copper and palladium as key heavy metal indicators for environmental monitoring. Previous research has shown how palladium can impact plant and fungal networks [11,12]. This in turn can influence the food chain [13,14]. Copper is often introduced into the environment through brake pad wear [15], urban infrastructure degradation [16], and fire related events [17,18]. The effects of copper on human health have been noted [19, 20] in addition to ecological contamination [21].

For baseline references: a 2017 study by Leopold et al. in Germany found average concentrations of palladium in roadside dust to be 311µgkg-1 with a maximum 193µgkg-1 level in topsoil layers [22]. This converts to approximately 0.311 ppm and 0.193 ppm respectively. Their findings pointed to palladium being highly mobile through soil, even to depths of 25 to 30cm. This was determined using an S2 Picofox total reflection X-ray fluorescence (TXRF) instrument. Another project from 2018 in South Africa used Inductively Coupled Plasma Quadrupole Mass Spectrometry (ICP-QMS) and Differential Pulse Adsorptive Stripping Voltammetry (DPAdSV) along two roads [23]. They detected minute amounts for Pd ranging from 0.00048 to 0.00544 ppm.

Copper tends to be at higher levels while staying below hazardous limits unless a contamination event occurs. For background analysis, a 2009 project showed copper by gravel roadsides remaining below the Lithuanian hazardous concentration limit of 100ppm [24]. To compare, a 2024 study sampled soil near a copper mine ranged between 84.9 and 2554.3 ppm [25].

For our research project, soil samples were gathered from specific zones in Los Angeles County that were categorized as either urban or recreational environments. Despite previous findings showing trace amounts of palladium, our research is meant to see if the levels are high enough to be detected using a portable X-ray fluorescence (XRF) spectrometer. This is due to the accessibility of the equipment and its ease of use.

XRF works by using X-rays to excite atoms in a sample with enough energy to knock electrons out of the inner shells (K or L shells). When an inner-shell electron is removed, the atom has a vacancy in a low-energy orbital. This allows for electrons from higher shells to drop down to fill the gap. When those higher-energy electrons drop down, the extra energy is released as an X-ray photon. This is unique to the element, which acts like an atomic fingerprint. XRF equipment detects those photons. [26]

Our hypothesis is that palladium will be detectable because of decades of heavy traffic in Los Angeles county, but it will be less reliable as an environmental monitoring marker when compared to copper or zinc due to expected concentrations.

# **Methods:**

Soil for each location was gathered using a metal soil core sampler over a 12 day period (6/19/25 - 6/30/25). Depending on the composition of the soil, rough sampling amounts were collected averaging approximately 70.63 grams per site. Photos of each area were recorded with GPS locations for visual and mapping purposes.

Locations were chosen based on local traffic patterns, tourist hotspots, industrial environments, neighborhoods, and areas affected by recent wildfire events (Figure 1). As fires can increase concentrations of heavy metals, a few places included both burned buildings and burned cars to determine if palladium spikes occurred there. Some were found using photos from damage inspection maps created by the Los Angeles County government after the Eaton Canyon and Palisades fires that occurred on January 7, 2025.

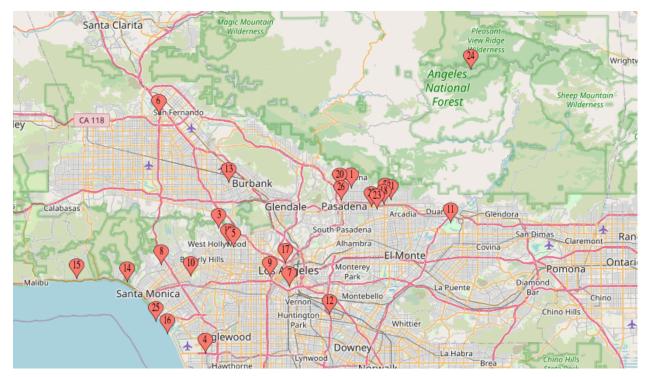


Figure 1: Map of where 26 soil samples were gathered within Los Angeles County.

The soil samples were stored at room temperature and then transferred to a Geology Lab at Pasadena City College. Using a portable BRUKER S1 Titan X-ray Fluorescence (XRF) machine elements were detected after calibration. With the GeoExploration setting, each bag was processed for approximately 85 seconds. A Python program was developed to clean up the raw data, organize the elements, and convert the information into a new .csv file. This preserved the original file as version control, establishing a robust software platform. All the code and charts were published to Github for open-source use.

Information for each location was arranged by type (Urban and Recreational). The elemental concentrations were adjusted using z-score normalization within a custom Python pipeline. This turned the raw data into a standardized form where deviations are easy to evaluate. Using the pandas and matplotlib coding libraries, the results were processed into two Principal Component Analysis (PCA) variables from an N-dimensional array. This transformed complex multi-element relationships into a 2D representation which highlights correlations between samples across the entire dataset. Individual elements were then grouped together using the same PCA variables allowing for the visualization of potential anthropogenic trends and contamination events.

# **Results:**

Our research showed higher concentrations of palladium than expected (Figure 2). This is despite existing research studies showing only minute amounts of palladium along roadsides [22,23]. The average level of all 26 samples in Los Angeles County was  $19.54 \pm 9.63$  ppm.

Copper concentrations had much lower error rates (Figure 3), suggesting that the XRF can pick up copper amounts with more accuracy when compared to palladium. The variability was more sporadic with copper based on sample location and the surrounding environment.

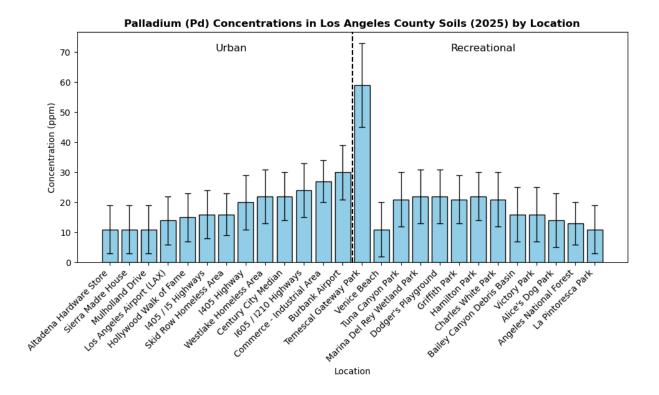


Figure 2: Palladium (Pd) concentrations (ppm) in soils collected from various urban, industrial, and natural sites across Los Angeles County in 2025. Error bars indicate measurement uncertainties reported by the X-ray fluorescence (XRF) instrument. Temescal Gateway Park is in an area that was affected by the Palisades Fire, but the actual sample was taken from an unburned spot.

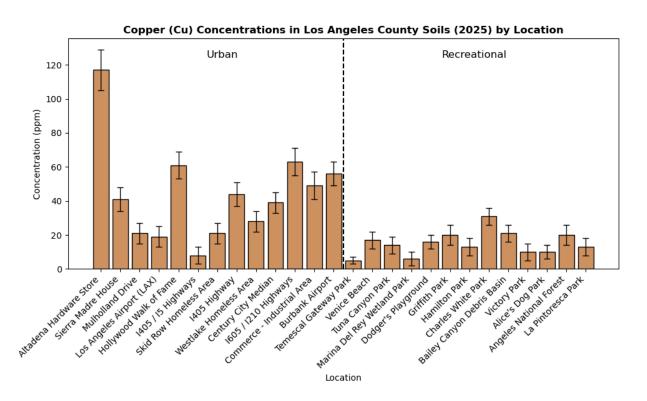


Figure 3: Copper (Cu) concentrations (ppm) in soils collected from various urban, industrial, and natural sites across Los Angeles County in 2025. Elevated copper concentrations are associated with urbanized and industrial sites, whereas lower concentrations are found in parks and natural areas. The Altadena Hardware Store and Sierra Madre House were both burned.

When comparing Urban and Recreational areas, palladium concentrations remained relatively consistent (Figure 4). The urban average was  $18.38 \pm 6.29$  ppm, and the recreational average was  $20.69 \pm 12.28$  ppm. The higher mean in recreational areas was due to one major outlier. In contrast, copper levels showed a more pronounced difference in variability across samples. Concentrations ranged from 1 ppm up to 117 ppm. Copper levels averaged  $43.62 \pm 28.01$  ppm for urban and  $15.08 \pm 6.99$  ppm for recreational in total; depicting a greater difference between the two zone types. Recreational areas had significantly lower copper concentrations than Urban environments overall by a factor of 2.89. The total standard deviation was approximately 24.74. These results showed that palladium was consistent across all samples regardless of location, while copper had much more variability.

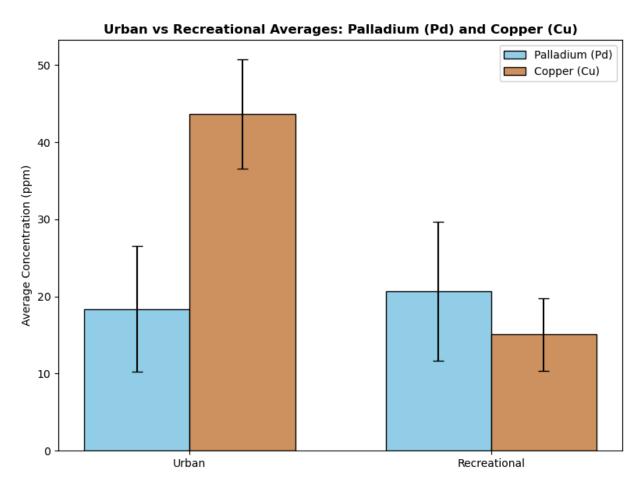


Figure 4: Comparison of average concentrations in parts per million of Palladium and Copper in urban and recreational environments within Los Angeles County (2025).

Expanding outside the main scope of automobile pollution, additional elements beyond copper and palladium were evaluated for their potential as environmental markers. These were not detected in every sample. For instance, Gallium (Ga) had a slight increase in Urban areas on

average by 1.38 ppm, yet the error rates were relatively high. Nickel concentrations showed a more pronounced elevation with an average of 12.46 ppm from Urban samples and 4.31 ppm in Recreational soils.

Those with stronger anthropogenic indicator signals included Zinc which was consistently found in every sample with low error rates. Concentrations in Urban environments were greater on average (284.62 ppm) than Recreational (60.62 ppm) by a factor ~4.7. This was primarily due to a contamination event from a building fire that destroyed the Altadena Hardware store. Similarly, lead from this sample contained 1158 ppm which is approaching the 2020 EPA hazardous threshold in non-play areas in residential districts of 1200 ppm. Segmented accounts of total zinc and lead concentrations depict how contamination events can influence correlations in the overall dataset (Figure 5).

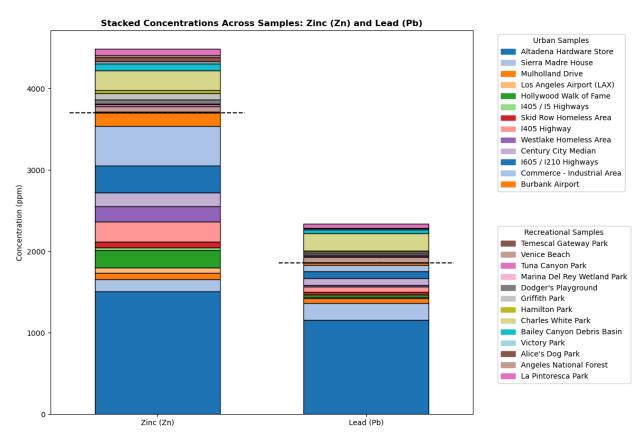


Figure 5: This chart shows how much of each sample affects the total amounts found across the entire collection. The Altadena Hardware Store contained high levels of both heavy metals Zinc and Lead due to contamination spurred on by the Eaton Canyon Fire as it burned the building and all the materials inside. The horizontal dotted line splits the total concentrations per element into Urban and Recreational categories. The range of colors help to differentiate each sample.

#### **Discussion:**

This research project provides a proof of concept establishing qualitative methods for heavy metal analysis of soil using XRF. This lays a foundation that can be repeated later on and proven via quantitative methods. The initial sample size of 26 is relatively small for such a large county like Los Angeles. Still, each spot was carefully chosen based on local knowledge of

traffic and population trends. Gathering larger amounts of samples in the future will help to provide a better understanding of areas affected by anthropogenic influence. As some elements can be increased by automobiles, fires, and other urban-related environmental processes. With additional research, these elements can become key environmental monitoring indicators for anthropogenic pollution.

Copper and zinc, in particular, serves as a reliable indicator of urban, industrial, and commercial influence due to its significant variability in concentration based on location. While trace amounts of copper are naturally present in soils, its levels tend to increase over time in areas with heavy human activity. Other elements, such as lead and nickel, are also found in elevated concentrations in urban environments, but they are generally absent or present in only trace amounts in natural areas. This makes them useful for urban monitoring but less effective in distinguishing between different environmental types.

Copper, however, stands out as a "keystone element," playing a crucial role in plant health and fungal activity at low concentrations. It is essential for processes like photosynthesis, enzyme function, and mycorrhizal growth. When concentrations rise too high, typically in urbanized areas, copper can become toxic to plants and microbes which has the potential to disrupt ecosystems. This dual nature of being both beneficial and harmful makes copper a unique marker of anthropogenic influence and a key element for understanding environmental health.

In contrast, certain elements like molybdenum (Mo), tungsten (W), selenium (Se), and antimony (Sb) are less commonly found in natural environments but can serve as outliers for toxic contamination in specific industrial settings. These elements are often linked to pollution from mining, smelting, and manufacturing processes. Their presence in elevated concentrations, typically in regions near industrial sites or contaminated groundwater, makes them useful as toxicity markers. However, they are less ubiquitous across broader urban or recreational areas. These elements when found in elevated concentrations are more indicative of localized pollution sources rather than widespread environmental trends.

During this project, exact locations where the soil was sampled from most likely affected how much copper was found. For instance, the I405 and I605/I210 highway samples had more copper than the I405/I5 sample. This may be because the I405/I5 sample was at an emergency area that didn't get as much traffic comparatively. Although the Burbank Airport has less travelers per day compared to LAX, it had more copper probably because the sample was taken from the main entrance - while the LAX one was from a median on a side street about a mile away from the actual entrance.

Five samples were from fire affected areas from the Palisades and Eaton Canyon fires that occurred on January 7, 2025. The Altadena Hardware store was completely destroyed, leading to the higher levels of copper, zinc, and lead found. Natural recreation areas were affected by the fires too. For instance, Tuna Canyon Park was directly burned as well; while Charles White Park was not directly scorched, but the neighboring plots from the Eaton Canyon fire were. The Temescal Gateway Park was from an unburned area, even though much of the surrounding area was burned by the Palisades Fire. Copper levels look to be influenced by fire, while Palladium does not, even if there were burned cars nearby.

To confirm the validity of future XRF findings, it is worth looking into the other elements that would cause spectral interferences for palladium. Silver (Ag), Rhodium (Rh), and Cadmium (Cd) have X-ray emission lines within ~0.1–0.3 keV of palladium's L-lines. This proximity can lead to peak overlaps, especially when using lower-resolution detectors typical of portable XRF devices [27]. For this particular study in Los Angeles county, those elements were not consistently detected as palladium was. Therefore, high error rates of palladium could be due to complex soil matrices and composition instead. Because previous studies only showed trace amounts, further experimentation needs to occur. Increasing the analysis time and running triplicated per sample may reduce error rates for elements often found in trace amounts as well. Still, testing soil with other types of equipment like ICP-QMS will confirm the accuracy and precision of rapid screening of XRF.

The data analysis after initial XRF readings can also be tedious. Excel files automatically created by the BRUKER S1 Titan tool organize the columns based on the elements identified. If samples don't contain the exact compounds, then the data is misaligned with each other. Therefore, it takes considerable time to clean up and arrange the information properly manually. To speed the data processing up, python works well. Because error rates for each element per sample are provided by the XRF machine, creating charts to accurately represent individual error bars was challenging. In Excel, it is easier to show average error rates. Using Python methods allowed for individualized data sets to be visualized.

In addition, Principal Component Analysis (PCA) can reveal patterns and correlations among soil samples and elements which provide quantitative insight into why samples may have similar compositions. However, while PCA identifies associations, it does not by itself determine causal relationships between elements or environmental sources. Thus, correlation does not imply causation.

## **Conclusion:**

This research demonstrated that portable X-ray fluorescence (XRF) analysis can effectively detect and quantify copper concentrations in soils with relatively low error rates. This reflects its reliability for urban environmental monitoring specifically geared toward tracking automobile pollution. In contrast, palladium measurements exhibited higher error rates, likely due to soil matrix complexities and composition or the need for additional calibration specifically for this heavy metal.

Despite these limitations, palladium was consistently detected across both urban and recreational sites in Los Angeles County, suggesting its widespread environmental presence as a byproduct of catalytic converter abrasion. Copper concentrations, on the other hand, showed clear differentiation between urban and recreational areas. This was also true of zinc and lead, which all three were likely influenced by traffic density and recent wildfire impacts.

Future research with larger sample sizes and improved analytical calibration is recommended to better characterize palladium distribution. This will ultimately enhance our understanding of heavy metal pollution from vehicular sources in complex urban environments.

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