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Environmental Risk Assessment of Paint Sludge from Ramapo/Ringwood, NJ

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Environmental Risk Assessment of Paint Sludge from Ramapo/Ringwood, NJ

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Abstract

A paint sludge sample from the Ramapough Indian Reservation in Ramapo, NJ, the site of chemical dumping by Ford Motor Company, was analyzed to determine its toxic components in order to perform a preliminary risk assessment of the site. The paint sludge sample was evaluated based on two major components: volatile and semi-volatile compounds, evaluated via gas chromatography-mass spectrometry (GC-MS), and heavy metals, evaluated via inductively coupled plasma optical emission spectrometry (ICP-OES). GC-MS headspace analysis of the paint sludge sample identified over 40 volatile organic compounds, consisting primarily of aromatic compounds such as xylenes and naphthalene. Leaching of heavy metals under different environmental conditions was simulated, including bioavailability (i.e., ingestion), short and long term exposure to surface and ground water on the site, and acidic landfill conditions. Pb, As, Cd, Cr, and Se were found at concentrations of 68,000 ppb, 122 ppb, 341 ppb, 33,000 ppb, and 38 ppb in the bioavailability extract, and 30 ppb, 10 ppb, 5 ppb, 90 ppb, and 21 ppb, respectively in the DI water extract, above accepted levels set by the EPA. Worst-case scenario risk assessments indicate that in the DI water, Soxhlet water, and bioavailability leachates, hazard quotients for As, Cr, Cu, and Pb are greater than 1, suggesting that these elements may pose a risk to the Ringwood residents in the future based on the current proposed remediation plans.

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1. Introduction

1.1 Love Canal and the Establishment of the Superfund

Love Canal in Niagara Falls, New York is a household name in the world of environmental disasters. This abandoned canal project was the site Hooker Chemical Company used as a chemical waste dump, disposing of around 22,000 tons of mixed chemicals from 1942 until 1953.[1] After their dumping was complete, Hooker Chemicals capped the site and sold it to the Board of Education for one dollar. Following this purchase, an elementary school was built on the site, as well as a multitude of single-family homes. By 1978, Love Canal was a fifteen-acre neighborhood composed of around 800 residential homes and 240 low-income apartments. Heavy precipitation in the late 1970s raised the water table and caused the leaching of the dumped chemicals into the sewer system, basements and yards of the local residents. Public awareness was brought to this disaster when residents in the area were diagnosed with unexplainable illnesses and health issues including epilepsy, asthma, migraines, nephrosis, miscarriages, and severe birth defects.[2]

For decades, numerous American businesses had disposed of hazardous wastes they produced irresponsibly and improperly, leading to the widespread contamination of water, land, and air. However, it wasn’t until the very public scare of the Love Canal disaster of 1978 that people began concerning themselves with the immediate and potential long-term threats to public and environmental health.[3] The media attention and panic surrounding Love Canal sparked American citizens into action, leading them to threaten Congress to do something about the pressing issue of hazardous sites. This public pressure resulted in the enactment of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980.[4] Under CERLCA, Federal authority was taxed with the responsibility of responding directly to such contaminated sites in two ways[4]: (1) short-term removals which require immediate response and (2) long-term remedial response actions which can only be conducted at sites listed on the EPA's National Priorities List (NPL). The NPL is the list of national priorities among known contaminated sites throughout the United States and its territories intended to guide the EPA in its decision of which of these sites require further investigation.[5] Also as part of CERCLA, the chemical and petroleum industries would be taxed and the resulting funds as well as additional federal funds would be allocated to an EPA trust fund for cleaning up abandoned and hazardous waste sites if no responsible party could be identified. This fund became known as the "Superfund" and hazardous sites remediated by this money became known as "Superfund sites". However, in 1995 Congress let the taxes on the oil and chemicals expire[6], and Superfund sites are now fully financed by taxpayers, as well as the parties identified by the EPA as potentially responsible for the contamination (PRPs).

This "polluters pay" policy, in which the responsible corporations are billed, has been criticized by many. While advocates of this policy maintain that it is effective because it forces corporations to be more responsible with their waste (cleaning up pollution costs millions of dollars, which isn't exactly economically incentivizing), critics argue that it is often difficult to identify responsible parties[7], and that when parties are identified, the extreme cost of cleanup causes them to delay remediation projects through endless red tape and litigation. In their article "Making Superfund Work", Robert Harris and Grover Wrenn state that the Superfund program was hampered by lawsuits from PRPs, citizens groups, and environmental organizations that delay cleanup efforts, while the EPA's management of the Superfund program not only drew widespread criticism but also was the subject of criminal investigation.[8] One such Superfund site (Ringwood Mines/Landfill Superfund Site) in northern New Jersey drew enough widespread criticism that a documentary was made detailing the current ongoing remediation struggle. *Mann V. Ford*[9] documents the plight of the Ramapo Indians, a state recognized Indian tribe, to gain compensation for the negative health effects and widespread contamination they suffered due to chemical dumping by Ford Motor Company. Plans are still currently being finalized for this site's ongoing remediation.

1.2 Ringwood Mines/Landfill Superfund Site

In Ringwood, New Jersey, about an hour's drive from New York City and a mere forty minutes northeast of Drew University, exists the Ramapough Indian Reservation, home to the Ramapough Lenape Indian Tribe, who have resided in the area for hundreds of years. This 500-acre, remote, mountainous region is comprised of vegetated and forested areas, abandoned mine pits and shafts, landfill and disposal areas, a municipal recycling center, and around 50 residential homes (Figure X).[10]

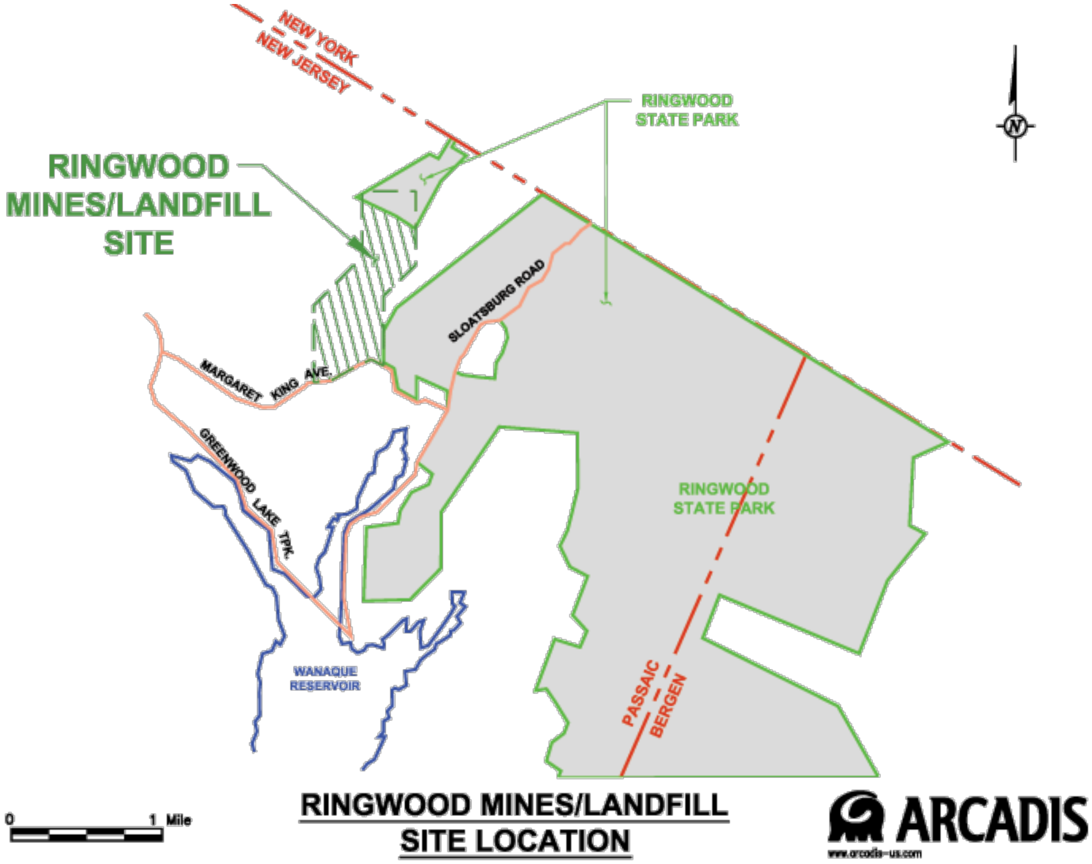


Figure 1. Map of the Ringwood Mines/Landfill Site Location. Image obtained from the Ringwood Site Update webpage powered by Ford. The Wanaque Reservoir is outlined in blue.

There are approximately 20 water supply wells in the area (although not directly on site), which draw from an aquifer located in the bedrock and provide water to various residences and industries nearby.[10] Although water beneath the site is not currently used as drinking water, as the residents are connected to the municipal water supply, groundwater below the site is discharged to surface streams as well as the Wanaque reservoir (Figure 1), which provides drinking water to about 2.5 million people, roughly ¼ the population of the state of New Jersey.

The site was the location of magnetite ore mines run by private owners from the 1700s until the early 1900s and after this time period until about 1931, the history of the site is not very well known. Some time around 1940, the U.S. government purchased the mines and associated properties, which were later sold to a series of successive owners. One of these owners was Ringwood Realty, a firm owned by Ford Motor Company[10]. O'Connor Trucking, a contractor of Ringwood Realty, ran a permitted landfill on various locations of the site from 1967 to 1971.[10] During this period of time, O'Connor was also contracted to remove wastes from Ford's automobile assembly plant in Mahwah, New Jersey. These wastes included wood, trash, paint sludge and metal drums, all of which were disposed of at the Ringwood Mines Landfill site, both on the ground and in the two abandoned mines on site, Peter's Mine and Cannon Mine.[11]

After a donation of 290 acres by Ringwood Realty in 1970, the Ringwood Solid Waste Management Authority was able to begin operating a permitted municipal disposal area on the site in 1972, which was later closed by the state in 1976[10]. There are many claims of other companies disposing of their wastes illegally as well[12], therefore it is important to note that Cannon Mine and other large portions of the land on site had been used as a disposal ground for discarded automobiles and other waste by entities not affiliated with Ford Motor Company prior to Ringwood Realty acquiring the property.

Attributing the Ringwood Mines Landfill site and the paint sludge contamination as the source, the Ramapough tribe has expressed their suffering from numerous health issues including but not limited to diabetes, heavy metal poisoning, bodily rashes, miscarriages, and numerous types of cancer, as well as an extremely high death rate of community members. Although it has been concluded that these adverse health issues can not be officially linked directly to Ford's disposal, the high exposure that these residents have had with the paint sludge leads many to have little doubt of the source. As vividly seen in the documentary *Mann V. Ford*[9], the Ramapoughs had direct contact with the dumped waste and sludge in numerous significant ways. Adults scavenged amongst the waste for copper, brass and other valuables companies dumped in the landfill to try to make a living. Children used the paint sludge to slide down the mountainside in the summertime, and they made mud pies with the colorful sludge and ate them. Most of the community lived off the land in a traditional way, hunting and consuming game such as rabbits, squirrels, and deer that fed off the contaminated vegetation on site. Many residents were also exposed to cancer-causing dioxin in the atmosphere when areas of the mine pits and landfill caught fire in the late 1970s and burned for weeks at a time.

In 1982, the New Jersey Department of Environmental Protection (NJDEP) conducted a site inspection that revealed levels of benzene, ethylbenzene, and xylene in water samples collected from Peter's Mine shaft. Due to these results, in combination with claims by the Ramapough calling for action, the EPA was brought onto the site to investigate and the Ringwood Mines/Landfill Site was added to the National Priorities List (NPL) in 1983, making it eligible for Superfund remediation. The EPA issued an administrative order to Ford Motor Company in March 1984 to determine the extent of contamination of the site. Along with Ford, the Ringwood Borough was also declared a potentially responsible party.

As part of the remediation process, the EPA issued a Record of Decision (ROD) in 1988, which set up long-term ground water monitoring wells for surface and groundwater across the site. Reports have indicated sporadic levels of what has been referred to as volatile organic compounds (VOCs) and metals above drinking water standards. The paint sludge itself is reported to contain a number of toxic contaminants, including lead, arsenic, and VOCs.[10] From 1987 to 1988, Ford removed an alleged 7,000 cubic yards of paint sludge and contaminated soils from the Ringwood site[10]. Some 60 or so drums of toxic waste were also removed after their discovery in 1990.[10] These drums were reported to contain polychlorinated biphenyls (PCBs) at concentrations above 50ppm. After this remediation, the EPA deemed the site to be free of all paint sludge and hazardous materials and the groundwater monitoring reports appeared acceptable. Due to this, the EPA removed the site from their Superfund list in 1994.[10] However, additional paint sludge was discovered and reported by a resident in April 1995, and five more cubic yards of were disposed of. In 1998, another resident reported the presence of more paint sludge, and one hundred more cubic yards of paint sludge were disposed of accordingly. Ringwood residents wrote to the EPA in 2003 expressing concerns over their exposure to paint sludge that had not been removed from the site, and in 2004 Ford removed even more paint sludge at identified locations across the site. After continued paint sludge discovery and complaints of health issues from the Ramapough tribe, in 2006 the EPA reinstated the site to the NPL (making it the first and only site to ever be reinstated to the list) and additional cleanup commenced by Ford, in accordance with EPA plans. The EPA admits that 80 percent of the toxins were missed in the original cleanup.[13]

Approximately 53,500 tons of paint sludge have been removed from the site by Ford since 2004, and remediation is still an ongoing process.

1.3 Risk Assessment

The most challenging aspect of the Ringwood Mines/Landfill Superfund site, or any hazardous waste site, is the ability to determine the risk that the site poses at any given point in time. To do this, a tool called risk assessment is often employed. To understand what a risk assessment entails, it is first important to explain exactly what a "risk" is in terms of the environment and human health. The EPA categorizes risk as "the chance of harmful effects to human health or to ecological systems resulting from exposure to an environmental stressor." A stressor, in turn, is defined as "any physical, chemical, or biological entity that produces an adverse response."[14] By most definitions, risk can be explained with a simple equation[15]:

$$\text{Risk} = \text{Hazard} \times \text{Exposure}$$

In other words, no matter how hazardous a chemical or substance may be or what risk it may potentially pose, it is only considered a risk if there is exposure to it. Risk assessment is a useful tool that systematically evaluates the magnitude of a risk from a specific hazard. However, it is important to note that there is always a degree of uncertainty when using such an assessment, and the answers provided can never be precise. This is largely in part due to the fact that there are often gaps of information and data missing about a potential hazardous site – and the job of a risk assessment is to fill these gaps in with educated assumptions and extrapolations.

The two main types of risk assessment are those pertaining to human health risks and ecological risks. Due to the nature of the Ringwood Mines/Landfill Superfund Site and the adverse health effects of the residents surrounding it, the human health risk assessment will be the main focus of this study. There are numerous protocols and methods for carrying out a health risk assessment of a chemical, but most (including the EPA's[16]) follow four main steps:

1. *Hazard Identification* – Is a particular chemical a hazard? If so, why?
2. *Exposure Assessment* – What is the extent of human exposure, if any?
3. *Dose-Response Assessment* – What is the relationship between exposure and the probable health effects of the chemical?
4. *Risk Characterization* – Uses a combination of the three above methods to quantify the magnitude of human risk, including uncertainty.

Marquita K. Hill, in her text *Understanding Environmental Pollution*[15], does a great job illustrating and explaining each of these steps in the risk assessment process.

The first step, *Hazard Identification*, utilizes resources available on the chemical in question to determine what makes the chemical a hazard. Common questions to consider are: In what ways does it harm the body (nervous system, respiration, immune system, birth defects, etc.)? How does exposure occur - through skin, ingestion, inhalation?

The second step, *Dose-Response Assessment*, is comprised of three sub steps. The first involves finding a dose of the chemical that is safe to laboratory animals. The goal is to find the highest dose that the animal can tolerate without displaying adverse health effects – this is called the "no observed adverse effect level" (NOAEL). Since the goal of a risk assessment is to determine possible harm to humans, not laboratory animals, this NOAEL value is divided by a safety factor, the second sub step of the dose-response assessment. To determine a safety factor, some assumptions need to be made. First, a human is assumed to be 10 times more sensitive to the chemical in question than an animal. Then, some humans are assumed to be 10 times more sensitive to the chemical than the least sensitive human. Taking these two assumptions into account, 10 is multiplied by 10, resulting in a safety factor of 100. One more assumption takes into account the validity of the animal dose-response study. If the study is deemed to be of low quality, another multiple of 10 is included to increase the safety factor to 1000. One last assumption takes into account exposure of the chemical to children. If a child is exposed, the safety is again increased by another factor of 10, resulting in a final safety factor of 10,000, although typical values used are much lower. The third sub step of the dose-response assessment is to determine a reference dose (RfD). To do this, NOAEL is divided by the safety factor. This reference dose is defined as the dosage safe for humans over a lifetime of exposure. RfD is sometimes also referred to as the acceptable daily intake (ADI). The smaller the value of an RfD, the more toxic the chemical is.

The third step in the risk assessment process, *Exposure Assessment*, is composed of five main sets of circumstances relating to a human's exposure to the chemical. The first set of circumstances revolves around the source of the chemical (i.e., factory emissions, motor vehicle exhaust, wastes leaching into groundwater, etc.). The second set of circumstances takes into account the route of exposure (If through drinking water, what's the concentration? How much water does an average person drink? If through soil, what's the concentration? How much soil is ingested or inhaled (as dust) by an average person? How long does the exposure occur?). The third set of circumstances involves the most highly exposed population to the chemical (if the chemical in question is radon, people who live in rural areas and drink from wells most likely have the highest exposure; people who live in a city may have the highest exposure to exhaust from motor vehicles; people who live near a hazardous waste site will have the highest exposure to the chemicals on site, etc.). The fourth set of circumstances gives special consideration to the exposure of children. The fifth set of circumstances uses worst-case scenarios. Due to the fact that there usually isn't enough information for a perfect or even good evaluation of exposure, worst-case assumptions are often used to make a risk assessment. The worst-case assumption refers to the greatest exposure that could possibly occur.

The fourth and final step in the risk assessment process, *Risk Characterization*, ties together all of the information from the first three steps in order to quantify the chemical's risk. Risk is often referred to quantitatively as a chemical's hazard quotient. There are two main considerations taken into account when determining a chemical's hazard quotient. The first is extremely relevant to a hazardous waste site or any situation where more than one chemical is being evaluated. In cases such as these, the individual hazard quotients for each chemical are added together to yield a higher risk. The second is relevant if there are multiple pathways of human exposure to a chemical (i.e., water plus soil, or air plus water). In these cases, the pathways of exposure are added together to yield a higher risk. According to the EPA, a chemical is considered a risk if its hazard quotient is greater than 1.

Summary of steps in the Risk Assessment Process

1. Hazard Identification

In what ways does it harm the body?
(nervous system, respiration, immune system, birth defects, etc.)

How does exposure occur?
(through skin, ingestion, inhalation, etc.)

2. Dose-Response Assessment

1. Identify NOAEL (no observed adverse effect level)
2. Determine Safety Factor (multiples of 10)
3. Determine RfD (dosage safe for humans over a lifetime of exposure)

3. Exposure Assessment

1. Source
2. Route of exposure
3. Most highly exposed population
4. Children
5. Worst-case assumption

4. Risk Characterization

HQ < 1 = no risk
HQ > 1 = risk

Figure 2. Summary of steps in the risk assessment process.

1.4 Current Remediation Plans

Remediation plans for the Ringwood Mines/Landfill Superfund Site have yet to be officially finalized. On June 30th, 2014 the EPA published a Record of Decision (ROD), which presents the final plans that were selected to address the three areas of contamination of the Superfund Site: Peter's Mine Pit, Canon Mine Pit, and the O'Connor Disposal Area (Figure 3).

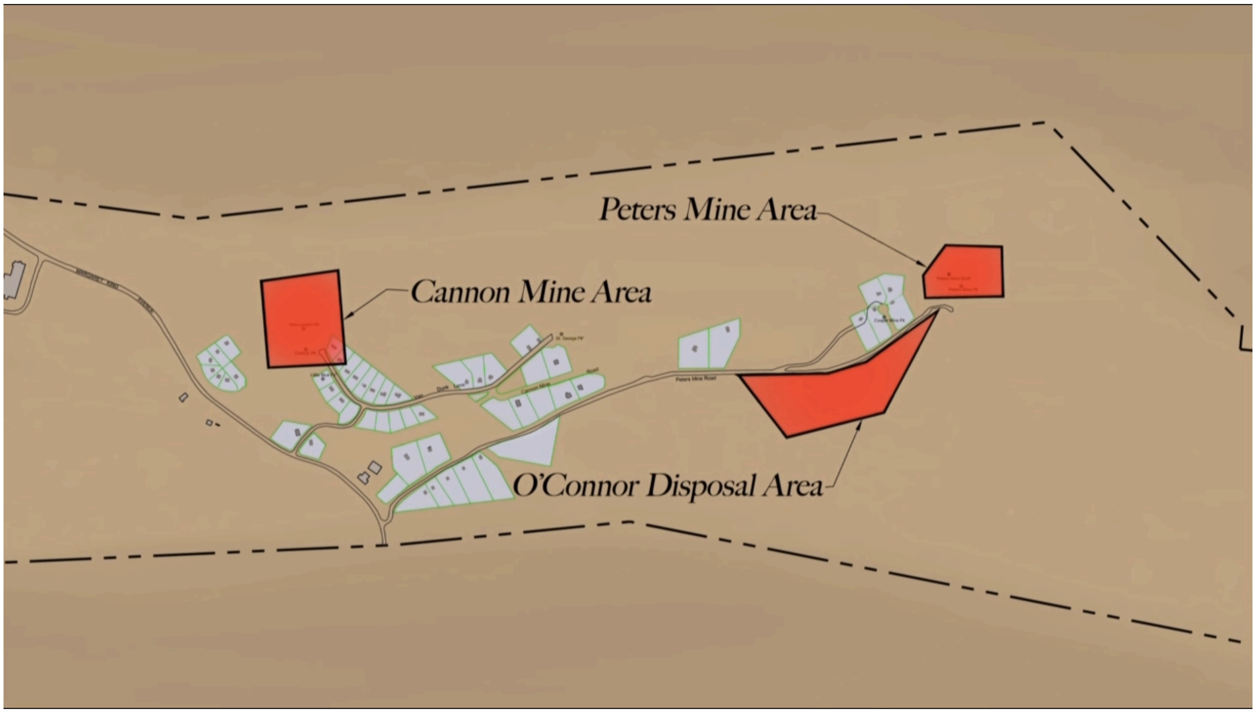


Figure 3. The three main areas of concern on the Ringwood Mines/Landfill Site location are highlighted within the red boxes: Peter's Mine Pit, Cannon Mine Pit, and O'Connor Disposal Area. Image is a screenshot from Mann V. Ford Documentary.

These three areas are referred to as operable unit 2 (OU2). The first phase (OU1) was the original remediation plan set forth when the site was first added to the NPL in 1983. The third phase (OU3) is still in the works, but these remediation plans will address the groundwater contamination across the site. Costing an estimated $45 million and financed by Ford and the Borough of Ringwood, the OU2 plan includes capping the two mine pits after removal of contaminated soil and other materials, and excavation of the O'Connor Disposal Area with the possibility of capping if the Ringwood Community decides to make the area the site of their new recycling center. Detailed descriptions of the remediation, as summarized from the EPA's ROD, for each of the three areas are provided below.

Peter's Mine Pit

Water from the pond in the Peter's Mine Pit will be removed and disposed of offsite. The soil and fill material from the area surrounding the Pit will be excavated and any drums of waste or paint sludge encountered in the process, as well as the excavated fill, will be disposed of offsite. If any of the fill is non-hazardous, it will be used to re-fill the excavated area or the Pit. Clean fill will be compacted in the Peter's Mine Pit with the goal of raising the elevation at least two feet above the average surface water elevation of the pond that was removed. The surface of the Peter's Mine Pit will be recontoured and prepared for the fitting of a geotextile fabric and cap, and clean fill and topsoil will be deposited on the cap to an elevation at least three feet above the surrounding area to ensure drainage away from the cap onto surrounding terrain. Indigenous trees and vegetation will be planted to restore the Peter's Mine Pit Area so it may be used for recreational purpose as part of Ringwood State Park. The cap will receive long-term monitoring and maintenance and the groundwater quality in the area will be monitored long-term until an OU3 remediation plan for groundwater is selected.

Canon Mine Pit Area

The Canon Mine Pit will be filled in with fill material surrounding the pit, as well as with clean fill material, to raise the elevation and promote drainage away from the pit. Any waste or drums of paint sludge encountered during this process will be disposed of offsite. The Canon Mine Pit will be capped with geotextile fabric and clean topsoil and indigenous vegetation will be plant to secure the surface of the cap. Fencing and other engineered controls such as boulders will help restrict access to the capped area. The cap will be monitored and maintained long-term, as will the groundwater quality of the site until an OU3 remediation plan for groundwater is selected.

O'Connor Disposal Area

The soil and fill material in the O'Connor Disposal Area will be excavated until the mine tailings beneath are reached and the removed fill will be disposed of and/or recycled offsite. Topsoil will be deposited in the excavated area and any wetlands in the area that are disturbed by this process will be restored. The groundwater quality of the site will be monitored until an OU3 groundwater remediation plan is selected. The Borough of Ringwood owns the land that contains the O'Connor Disposal area and wishes to construct a new recycling center on the site. The EPA has created a remediation plan that will accommodates the borough's wishes and will agree to go through with it if the borough provides the EPA with documentation (including detailed engineering plans, financial assurance, and assurance that the plan will fit within the time frame of the rest of the ROD) within 6 months of the publication of the OU2 ROD.

1.5. Present Study

The EPA's assessment of the site is that "actual or threatened releases of hazardous substances from the Site, if not addressed by implementing the response action selected in this ROD, may present an imminent and substantial endangerment to public health, welfare, or the environment".[17] However, many sources have expressed concern over whether capping without complete excavation is the best course of remediation for long-term assurance of safe ground-water levels of contaminants, especially in the mine pits, where the dangers and necessary resources of complete excavation have been stated to outweigh the benefits. While the groundwater in these areas has been monitored long-term since the 1980's and levels of contaminants have been stable thus far, there are still concerns about the possibility of contaminants leaching into the ground in the three main areas of concern, and whether these "safe" levels might not remain so safe in the future.

This study proposes to explore the possibility of long term leaching and health effects by conducting a risk assessment of organic and inorganic components of a single paint sludge sample collected near the site (Figure 3).

Figure 4. Original paint sludge sample obtained from Ramapo, NJ. Photo taken by Dr. Molly Crowther, Department of Chemistry, Drew University.

The first goal was to identify the composition of the paint sludge sample. To do this, the paint sludge was analyzed for its organic components (volatile organic compounds) and its inorganic components (heavy metals). The volatile organic compounds present in the paint sludge sample were identified via gas chromatography-mass spectroscopy (GC-MS) and the health risks associated with some of the most harmful compounds were qualitatively explored. The heavy metals present in the paint sludge sample were identified via inductively coupled plasma optical emission spectroscopy (ICP-OES) and the concentrations found were used to quantify a hazard quotient for each of the most toxic elements found using the four steps of a risk assessment explained in section 1.3 of this study. This risk assessment, while not wholly conclusive, may have possible implications for the long-term effects on the site as a whole.

2. Paint Sludge Emits Volatile Aromatics

2.1 Selection of Methods

In order to determine what volatile organic compounds are present in the paint sludge sample, gas chromatography-mass spectrometry (GC-MS) was used as the primary method of analysis. Two methods most commonly used to analyze volatile organic compounds (VOCs) in environmental samples are static headspace (SHS) or purge and trap (P&T) extraction.[18] Both use GC-MS as their method of separation and identification, however they differ slightly in their collection and sample preparation methods. Purge and trap is designed to extract and concentrate all solutes present in an adsorbent trap, after which they are thermally desorbed from the trap for introduction into GC-MS.[19] In static headspace, equilibrium is established between the sample and the gas phase above it in a sealed vial after a heating period. A portion of the gas phase is then taken up in a gas syringe and injected into the GC-MS for analysis. While P&T is more sensitive than SHS and is the preferred method for analyzing VOCs in water in ppb, P&T is much more complicated to run and maintain than SHS which offers fewer problems related to carryover and cross-contamination.[19] Due to these benefits, static headspace was the chosen method for VOC analysis in this study.

Another method used to extract organic compounds from the paint sludge sample in this study is the Soxhlet extraction. This technique is considered the benchmark of solid-liquid extraction techniques and has been the standard for over a century.[20] The Soxhlet technique uses a reflux and condensing system to separate leached compounds from a solid sample based on the polarity of the extraction solvent. Figure 5 shows the general set up of a Soxhlet extraction apparatus.

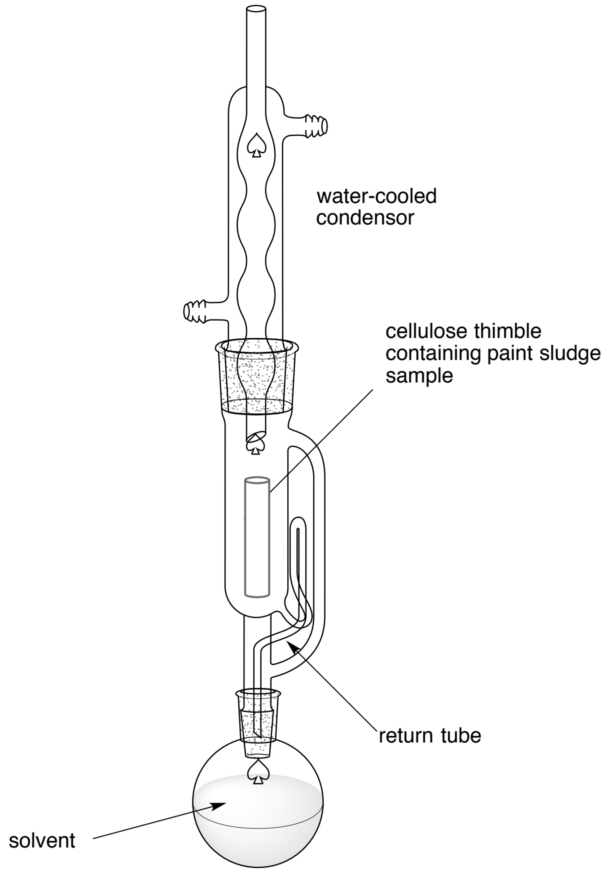


Figure 5. Soxhlet extraction set up.

Various studies have compared Soxhlet extraction to other extraction techniques such as sonication extraction and microwave-assisted extraction. In many cases Soxhlet measures up to these other techniques in terms of recoveries of individual compounds.[21] While the Soxhlet extraction has been used widely in many laboratories, as with any technique there are some disadvantages including a long extraction time (approximately 24 hours), a large solvent volume (often up to 500 mL), non-selectivity, as well as the need to concentrate the resulting extract.[22] There are newer extraction methods such as supercritical fluid extractions (SFE) that are much faster, use a smaller solvent volume, and have a greater recovery of compounds, but there is a high initial equipment cost.[23] For the purpose of this study which was primarily to identify the major organic components of the paint sludge sample, the Soxhlet extraction was an easy to use, readily available, and reliable technique.

2.2 Headspace Analysis Results

Over 40 volatile organic compounds were identified via GC-MS analysis of static headspace. Most of these compounds were aromatic, including all three forms of xylene, and naphthalene, both of which are often used in the automotive industry as components in paint resins.[24] The fact that so many volatile organics were able to be identified is both surprising and alarming considering the paint sludge sample is over 40 years old. Drew University obtained the paint sludge sample in 2011, and prior to this, the sample had been exposed to natural elements on the Ringwood site since the time of dumping in the late 1960s.

Due to the nature of exposure that the paint sludge sample had on the site (weathering and erosion, exposure to running streams and stagnant water), we thought it was necessary to evaluate the sample for volatile organics under various conditions to see if the results of what compounds we discovered varied. For the headspace analysis, four different preparation techniques were used to evaluate the paint sludge samples: dry powder, dry chunk, aqueous powder, and aqueous chunk. Samples referred to as powder consisted of finely ground paint sludge sifted through a metal mesh, while samples referred to as chunk consisted of larger particles, approximately 1-3 mm in diameter. All samples were approximately 0.16 g in mass. Dry powder and chunk samples were placed in a glass vial alone, while aqueous samples were placed in a glass vial and 1 mL of distilled water was added. All samples were oven heated for 15 minutes at 105°C and introduced into the GC-MS via manual injection.

Gas chromatography mass spectrometry (GC-MS) is composed of two components, the gas chromatograph (GC) and the mass spectrometer (MS). The gas chromatograph separates compounds in a mixture based on their individual volatility. A small volume of the mixture, in this case 20μL of the gaseous headspace sample, is injected into the GC injection port where the temperature is elevated to ensure immediate vaporization of the sample. Helium gas carries the sample through a column where the individual compounds are separated based on their different chemical properties and affinity for the stationary phase of the column. This interaction between the column and the molecules causes them elute from the column at different times, referred to as the retention time. As a compound, or molecule, elutes from the column it enters an ionization chamber where a beam of electrons collides with the molecule, breaking it into ionized fragments, which are then accelerated into a mass analyzer. These ions each have a particular mass to charge (or M/Z) ratio, which is the mass of the fragment divided by the charge. Most fragments will have a charge of +1, and so the M/Z essentially represents the molecular weight of the fragment.

The GC-MS used in this study is a quadrupole mass analyzer, containing four parallel metal rods between which voltage can be applied. As ions are accelerated down the quadrupole between the rods, the mass analyzer is able to control the voltage applied, such that only those ions with a certain M/Z will reach the detector, while others are deflected. The quadruples will cycle through different voltages many times a second in order to cover a wide range of M/Z ratios. Each of these cycles is called a scan, and the computer will record a graph, or mass spectrum, for each of these scans. The mass spectrum plots the signal intensity (or abundance) of each fragment collected during the scan against the M/Z ratio. Since the mass spectrum is generally the same for a compound every time, it can be used as a "fingerprint" to identify the compound. When all of the mass peaks of the individual compounds in a sample are added together, the total ion current, or summed intensity, is obtained. This total ion current can be plotted against the retention time of the compounds to produce a Total Ion Chromatogram (TIC).

Once the GC-MS provides the TIC for a sample, the composition of the sample can be determined by matching the mass spectrum of each peak of the chromatogram to library spectra. In this study, spectra were compared to library data provided by the National Institute of Standards and Technology (NIST), and the most probable structure of the compound matching the mass spectrum was provided. Figure 6 is an example of this process, displaying the TIC (6a) for one of the dry powder paint sludge headspace samples that were analyzed via GC-MS. The peak boxed in red corresponds to the mass spectrum (6b) for 1,2,4,5-tetramethylbenzene, the structure of which is embedded in the spectrum. The GC-MS software was able to identify this compound with a 20.6% certainty. All compounds identified in the paint sludge were identified in this manner.

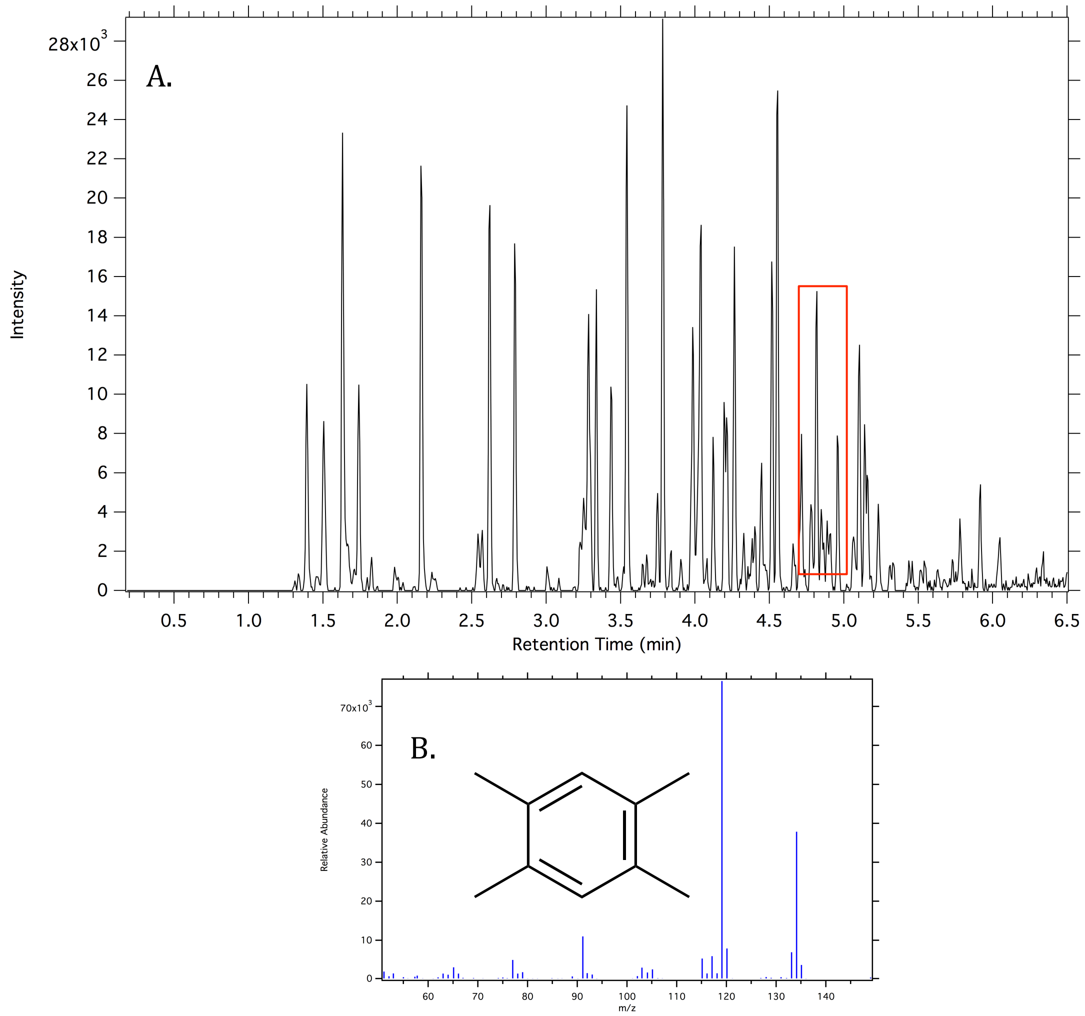


Figure 6. **Example of the identification process of organic compounds from GC separation and mass spectrometry library data**. **A.** The total ion chromatogram for a dry powder paint sludge sample is shown. The mass spectrum that corresponds to each peak (compound) in the chromatogram was matched with library data from the National Institute of Standards and Technology (NIST) the most probable structure of that compound was provided. **B.** The peak boxed in red corresponds to the mass spectrum for 1,2,4,5-tetramethylbenzene (structure provided.

Once all of the compounds present in a particular paint sludge sample (dry powder, aqueous chunk, etc.) TIC were identified, it was then necessary to determine the most abundant compounds in the paint sludge overall. To determine the most abundant compounds present throughout the paint sludge, the five most abundant compounds in each sample were recorded based on their peak intensity in the TIC. This peak intensity can be considered approximately equal to the relative abundance of the compound in the paint sludge sample.

Figure 7 is a graph showing the overlayed spectra of the four different paint sludge sample types (A. dry powder, B. aqueous powder, C. dry chunk, D. aqueous chunk). While this figure shows only one spectrum for each sample type, triplicates were run for each. In all three trials of each sample type, the GC-MS chromatograms contained relatively the same peaks (See Figure 8, Methods, Section 6). This shows the reproducibility of the experimental procedure and validates the identities of the organic compounds determined from the NIST archives. In Figure 7, it is interesting to note that while the chromatograms for the four sample types are largely similar, there are subtle differences when comparing powder and chunk samples. The intensities of the powder samples seem to be overall slightly higher than the intensities of the chunk samples. This may be due to the increased surface area of exposure created by the crushing of the paint sludge into powder. Compounds that would otherwise be trapped in the paint sludge may have been released upon this crushing. The pattern and retention times of the peaks in the chromatograms of the powder and dry samples were largely identical, however.

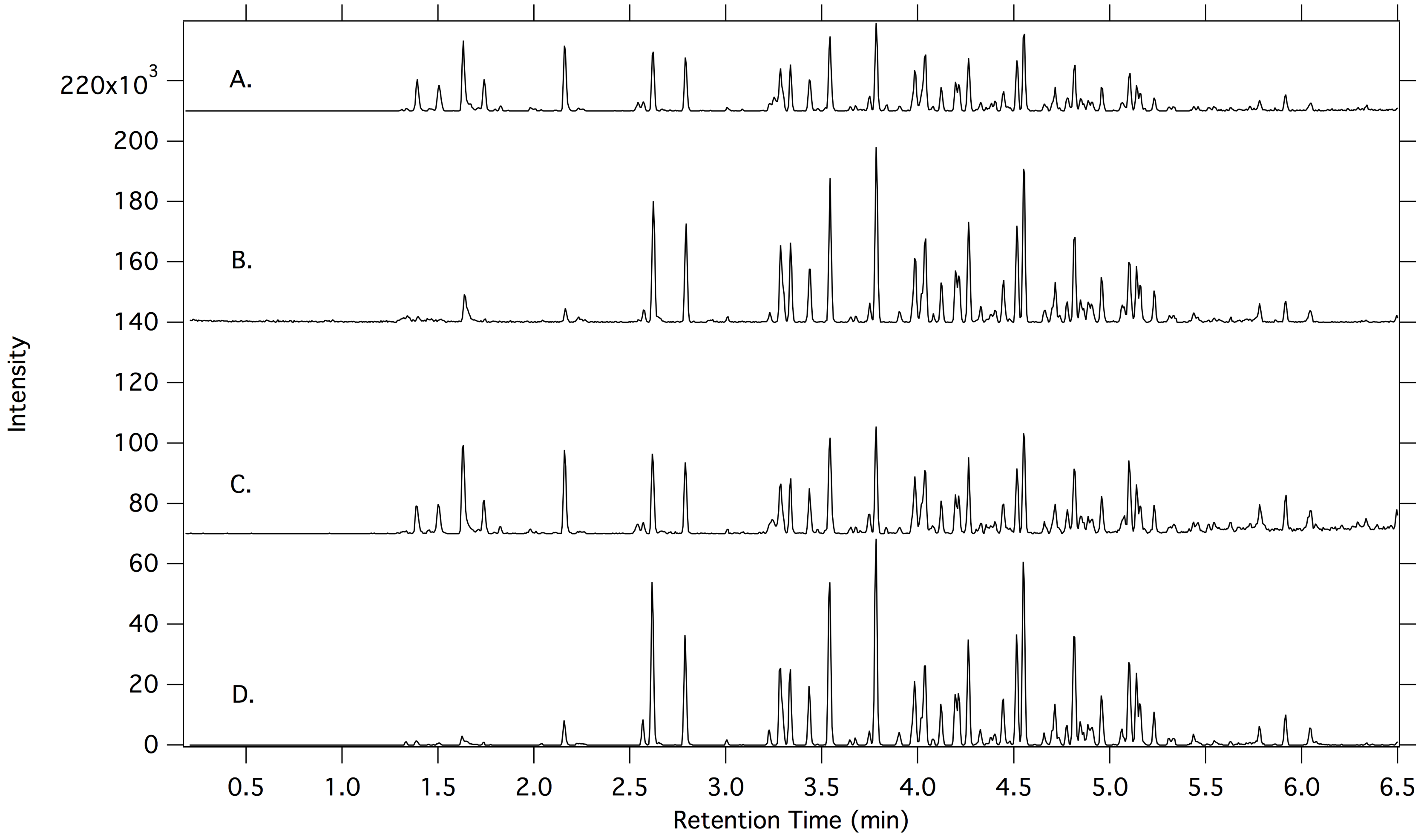


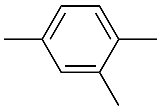
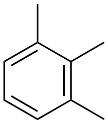
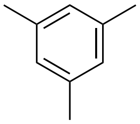
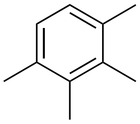
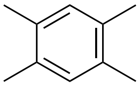
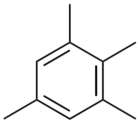
Figure 7. **Overlayed total ion chromatograms of the four paint sludge sample types.** A representative total ion chromatogram of each paint sludge sample type (A. dry powder, B. aqueous powder, C. dry chunk, D. aqueous chunk) is plotted. The four chromatograms are offset from the y-axis by intervals of 7.0 x 10^5 in order to show the full intensity range of each. Peaks are essentially the same in all four chromatograms with the exception of those compounds which eluted at a retention time of approximately 1.5 minutes.

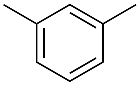
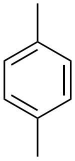
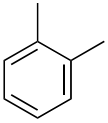
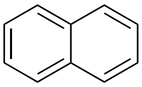
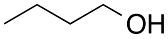
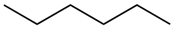
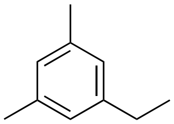
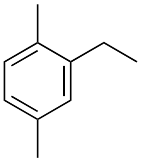
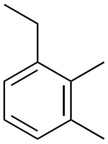
This indicates that the same compounds were present throughout the paint sludge sample as a whole. Out of all of these compounds, it was necessary to determine which were most abundant in the paint sludge. To determine the most abundant compounds present throughout the twelve samples overall, the number of times a compound occurred in each sample was recorded. Table 1 highlights the fifteen most abundant compounds that were present in all four paint sludge samples. Almost all of these compounds are some form of methyl or ethyl benzene, varying only in the placement and number of substituents. For many compounds identified, multiple isomers were present in the paint sludge.

The table lists the RfD values for the compounds identified. The RfD value, or reference dose, of a chemical estimates the minimum daily exposure to the chemical that would not likely cause serious health effects to humans over a lifetime. While the extent of this study is not quantitative in that we did not set out to determine the concentrations of organics present in the paint sludge, it is important to note just how low these threshold RfD values are. The compounds identified in the paint sludge are still around after more than 40 years. Over this period of time, the Ramapoughs had prolonged exposure to the chemicals within the paint sludge through their daily lives. Adults scavenged through the sludge to find metal scraps to sell, children ate the paint sludge because they though it was pretty. Therefore, while it is not possible to conclusively tie the negative health effects experienced by the Ramapoughs to the dumping of the paint sludge by Ford, it is clear that many of their symptoms overlap with those reported in toxicological data for the organic compounds identified (discussed in Section 2.3 below). It is also noteworthy that most of these compounds are used in the automotive industry.

Trimethylbenzene is used in the production of paint thinners, and tetramethylbenzene, xylene, and naphthalene, are all used in the production of paint resins[24].

Table 1. Percent Area Abundance and RfD values of the 15 most abundant compounds present in the paint sludge

Compound	Structure	Percent Area Abundance				RfD (mg/kg-day)
		powder dry	chunk dry	powder aqueous	chunk aqueous	
1,2,4-trimethylbenzene (pseudocumene)		3.786	3.875	3.786	0.000	N/A
1,2,3-trimethylbenzene (hemellitene)		3.544	3.544	0.000	3.339	N/A
1,3,5-trimethylbenzene (mesitylene)		0.000	0.000	0.000	0.000	N/A
1,2,3,4-tetramethylbenzene (prehnitene)		0.000	4.555	4.555	0.000	N/A
1,2,4,5-tetramethylbenzene (durene)		4.555	4.518	4.519	4.554	N/A
1,2,3,5-tetramethylbenzene (isodurene)		0.000	0.000	4.779	0.000	N/A

m-xylene		2.622	0.000	0.000	0.000	0.2
p-xylene		2.792	0.000	0.000	0.000	0.2
o-xylene		0.000	2.792	2.794	2.793	0.2
napthalene		5.106	5.104	5.104	5.104	$2.0x10^{-2}$
1-butanol		1.634	1.632	0.000	0.000	0.1
hexanal		2.163	2.126	0.000	0.000	N/A
1-ethyl-3,5-dimethylbenzene		0.000	0.000	4.268	4.267	N/A
2-ethyl-1,4-dimethylbenzene		4.040	4.040	0.347	0.000	N/A
1-ethyl-2,3-dimethylbenzene		4.819	4.518	4.041	0.000	N/A

*RfD values obtained from EPA's Integrated Risk Information System (IRIS)

2.3 Health Effects of Naphthalene and Xylene

All toxicological data used in this part of study was obtained from the Agency for Toxic Substances & Disease Registry (ATSDR). This organization reviews publically available studies to determine what health effects result from a period of prolonged exposure to chemicals. Information from the Centers for Disease Control and Prevention (CDC), as well as the EPA's Integrated Risk Information System (IRIS), and New Jersey Department of Health was also used. For the purpose of this study, two of the most toxic of these compounds, napthalene and xylene, will be highlighted for a qualitative risk assessment posed by the volatile organic compounds identified in the paint sludge.

Napthalene

Napthalene is a compound commonly found at hazardous wastes sites, identified at numerous sites on the NPL. When present as hazardous waste sites, napthalene has been found in drinking water when it dissolves in groundwater. Napthalene can also weakly attach to soil or leach through soil into groundwater. Although exposure to small amounts of napthalene is essentially harmless, exposure to large amounts may destroy red blood cells, potentially resulting in a condition called hemolytic anemia. Other effects of ingesting large amounts of napthalene include nausea, vomiting, diarrhea, bloody urine, and yellow skin tint. Lab animals that digested large amounts of napthalene have developed cataracts, and although it is uncertain whether this would occur in humans exposed as well, it has not been ruled out as a possibility. Based on results from these animal studies, the U.S. Department of Health and Human Services has concluded that napthalene is very likely carcinogenic to humans. The EPA assigned napthalene as a possible human carcinogen in their 1986 cancer guidelines. Levels of napthalene in drinking water set by the EPA state that for exposure lasting longer than 10 days, 7 years, and an average lifetime of 70 years, should not exceed 0.5 ppm, 0.4 ppm, and 0.1 ppm to be deemed potable.

Xylenes

There are three isomers of xylene (meta-xylene, ortho-xylene, and para-xylene) differing only in the placement of the methyl groups on the benzene ring. All three isomers were identified in the paint sludge sample in this study. Some of the most common uses for xylene are cleaning agents, paint thinners and varnishes, and the printing rubber, and leather industries. Due to its high volatility, unless there is a continuing source of contamination, xylene is rarely found in high concentrations in soil or surface water. However, if large amounts of xylene enter the soil, it can potentially contaminate drinking water wells. At hazardous waste sites, where large amounts of xylene are often present, humans can be exposed through drinking contaminated well water, inhalation, and direct skin contact. There are similar health effects for humans when exposed to any of the three isomers of xylene. With short-term exposure to xylene, the skin, nose, throat, and eyes and become irritated. People often experience difficulty breathing, stomach discomfort, loss of memory, visual response delays, as well as changes to their liver and kidney functions. Long-term exposure to high concentrations of napthalene, as well as short-term, can affect the nervous system, resulting in headaches, loss of muscle coordination, dizziness, confusion, and even death.

3. Risk Assessment of the Ringwood Mines/Landfill Site

3.1 Exploring the Leaching Potential of Heavy Metals from Paint Sludge

Due to the nature of contamination at the Ringwood Mines/Landfill Superfund Site and the fact that groundwater below the site is discharged to surface streams as well as the Wanaque reservoir, there is much concern that contaminants present in the paint sludge sample could leach into the soil and groundwater on site, contaminating the drinking supply. Considering the Wanaque reservoir provides potable water to a fourth of the state of NJ,[10] the possibility of heavy metals leaching into the groundwater is extremely serious. The groundwater has been monitored long-term during the site remediation process to ensure the contaminants present remain at an acceptable level. So far, sporadic levels of benzene and arsenic have been recorded in the groundwater monitoring wells, but overall levels have not posed a significant health threat to those in the area. However, there is concern for leaching potential in the future if the paint sludge remains on site. Due to the fact that it is considered too dangerous to excavate the mine shafts, contamination in these areas will not be removed· Therefore, there may be potential for contaminants located in the depths of the mine shafts to leach into the groundwater below as time goes on.

From an environmental standpoint, leaching is the process by which constituents are transferred from a solid to a contacting liquid or aqueous phase.[25] In terms of the paint sludge, leaching refers to the potential of heavy metals being transferred from the solid paint sludge matrix to the soil and groundwater below. If heavy metals are able to leach from the paint sludge into the groundwater on site, it is possible that they may end up in drinking water and pose serious health issues if they are present at high enough concentrations. Due to this concern, the concentrations of heavy metals present in water due to leaching of a point source are a large component of many risk assessment models.

3.2 Leaching Simulations

Since the risk assessment in this study deals with potential exposure and possible resulting health effects of residents on the site and surrounding area, the leaching methods chosen simulate exposure pathways most likely to be encountered by the residents in the area. Four different extraction fluids were used to simulate these possible exposure scenarios: TCLP, Bioavailability, DI Water, and Soxhlet extractions.

Due to the fact that a significant portion of the contamination at the Ringwood site was disposed of in the landfill on site, it was thought that a method that simulates an acidic landfill environment would provide useful and interesting leaching results. One of the most widely used leaching tests by the EPA is their toxicity characteristic leaching procedure (TCLP)[26]. This test uses acetic acid to simulate the leaching of solid wastes present in a municipal landfill. Water and other liquids present at a landfill can percolate through the solid wastes over time, reacting with these solids and potentially posing public and environmental health risks. TCLP is one of the primary regulatory methods utilized to determine if a solid waste is hazardous or not due to leaching of hazardous pollutants[27].

The second extraction, bioavailability, simulates the fraction of paint sludge components that would be biologically available if the paint sludge were to be ingested. This method was chosen based in part on methods from a study where hydrochloric acid

(HCl) and nitric acid (HNO_3) were used to determine the bioavailability of lead to sea birds.[28] In the present study, HCl acid was used as a means of quantifying the possible heavy metal exposure the children on site who eat the paint sludge might encounter. This acid was chosen due to gastric acid, or stomach acid, being composed primarily of hydrochloric acid. By determining the concentrations of heavy metals that leached from the paint sludge into the HCl, we're assuming that this is a representation of what might leach from the paint sludge by the stomach acid of the children who ingested it.

The third and fourth extraction fluids both simulate the leaching potential of heavy metals from the paint sludge into groundwater on site. The deionized water (DI) extraction fluid simulates a situation in which the paint sludge is in direct contact with surface water on the site. This method was chosen due to the large quantities of paint sludge that were sitting in streams and stagnant water at the Ringwood site. The Soxhlet extraction fluid also simulates direct exposure to water on site, but due to the fact that Soxhlet method uses high temperatures, this extraction fluid simulates long-term water exposure of the paint sludge.

All four of these extraction fluids were prepared and used in a laboratory-based leaching model. With the exception of the Soxhlet extraction, a small amount of both powder and chunk paint sludge sample (0.1 g) were placed separately into 20 mL of each extraction fluid and allowed to sit for a 24-hour period. Each leaching simulation was run in triplicate, for a total of six leachates for each extraction fluid: three powder samples and three chunk samples. The fluids were then filtered and the leachates were collected and the concentration of heavy metals present in each sample was analyzed via inductively coupled plasma optical emission spectroscopy (ICP-OES). The Soxhlet extraction (as described in Section 2.1 of this study) is a leaching method in and of itself. Heavy metals were leached from the crushed powder paint sludge under high heat for 24 hours, and the resulting leachate was introduced into the ICP-OES using the same method as the other three extraction fluids.

3.3 Heavy Metals Leach From Paint Sludge Above Standards Set by EPA

Table 2 provides the concentrations of all 15 elements that were present in the leachates, as determined via ICP-OES, from the four different extraction methods employed in this study. It is important to note that all the paint sludge samples analyzed were taken from the exterior of the paint sludge sample. Most of the concentrations of elements found in each leachate are extremely high, and this is after more than 40 years of paint sludge exposure to the elements (i.e., weathering and erosion) at the Ringwood site. It can be imagined that the concentrations of elements might be even higher if samples were taken from the interior of the paint sludge, which has not been exposed to the same weathering and erosion effects as the exterior of the paint sludge sample. While this comparison was not done in this study, it would be an interesting experiment to consider for the future.

When comparing the two types of paint sludge samples, on average, within each extraction fluid the concentrations of heavy metals in the powder paint sludge samples were higher than those of the heavy metals in the chunk paint sludge samples. This may be attributed to the larger surface area of paint sludge exposed to the extraction fluid, as well as the process of crushing the paint sludge sample aiding in releasing the elements within. Due to the nature of a risk assessment representing the worst-case scenario possible for a hazardous waste site, the higher concentrations from the powder samples were those chosen to quantify the risk these heavy metals may pose to residents at the Ringwood site.

Table 2. Concentration of heavy metals present in paint sludge leachates as determined by ICP-OES

Element	**DI Water Powder (ppb)**	**DI Water Chunk (ppb)**	**TCLP Powder (ppb)**	**TCLP Chunk (ppb)**	**Bioavailability Powder (ppb)**	**Bioavailability Chunk (ppb)**	**Soxhlet (ppb)**
Aluminum (Al)	8	0	253	12	27927	6168	2660
Arsenic (As)	**10**	**5**	**8**	**7**	**122**	**25**	**25**
Barium (Ba)	961	234	2313	1329	18698	10082	1438
Cadmium (Cd)	**5**	**4**	**28**	**7**	**341**	**221**	**7**
Cobalt (Co)	**49**	**28**	**184**	**58**	**943**	**369**	**70**
Chromium (Cr)	**89**	**11**	**315**	**85**	**32683**	**7444**	**162**
Copper (Cu)	9	0	41	0	1077	226	146
Potassium (K)	110	60	330	156	1382	450	1567
Manganese (Mn)	320	170	1046	267	3805	1122	1177
Molybdenum (Mo)	10	6	6	5	200	54	53
Nickel (Ni)	18	11	67	17	800	259	51
Lead (Pb)	**30**	**88**	**15234**	**474**	**67891**	**12127**	**463**
Selenium (Se)	21	15	39	15	38	48	40
Strontium (Sr)	76	13	204	44	2668	1060	238
Zinc (Zn)	1022	544	10172	24449	87529	28153	922

Although a total of 15 elements were analyzed in this study, in order to allow for a more in depth analysis of risk, only the five most toxic heavy metals out of the 15 were focused on. These elements and their data are bolded in Table 2 above, as well as in all subsequent tables. To determine the five most toxic compounds, we turned to the Agency for Toxic Substances & Disease Registry (ATSDR). Every two years along with the EPA, ATSDR publishes a Substance Priority List that ranks, in order of priority, the substances that are most commonly found at hazardous sites on the National Priority List

(NPL) and that pose the most significant potential threat to human health due to their potential exposure at the sites and the substance's known or suspected toxicity.[29] Based on the combination of these factors, each substance is scored with a point value; those with the highest total point values are at the top of the priority list. The total point score of a substance is determined using the following equation[30]:

$$\frac{Total\ Score}{(1800\ \mathrm{max}\ points)} = \frac{NPL\ Frequency}{(600\ points)} + \frac{Toxicity}{(600\ points)} + \frac{Potential\ for\ Human\ Exposure}{(300\ concentration + 300\ exposure\ points)}$$

Based on their ATSDR rank and total point score, the five most toxic compounds out of the fifteen elements in this study were determined to be arsenic, lead, cadmium, chromium, and cobalt, (Table 3).

Table 3. The ATSDR 2013 Substance Priority List

2013 Rank	Substance Name	Total Points	2011 Rank
1	As	1670.4	1
2	Pb	1529.2	2
7	Cd	1318.7	7
17	Cr	1146.9	17
51	Co	1011.7	52

*The 2013 Substance Priority List contains a total of 275 substances

Reporting only the concentrations found in each of these samples does not in itself provide a sense of the magnitude of leaching. In order to get a better understanding of these findings and what they imply about contamination, we thought it was relevant to display the concentrations of heavy metals found alongside the maximum contaminant levels (MCL) for each heavy metal as set by the EPA. The maximum contaminant level is the maximum concentration of a chemical that is allowed in public drinking water systems.[31] Table 2 displays the MCL, along with the concentrations of leachates from the powder paints sludge samples of five of the fifteen elements that were analyzed.

Table 4. Metal leachate concentrations in powder paint sludge samples above EPA drinking water standards

Element	**MCL (ppb)**	**DI Water (ppb)**	**TCLP (ppb)**	**Bioavailability (ppb)**	**Soxhlet (ppb)**
As	10	**10**	8	**122**	**25**
Cd	5	**5**	**29**	**341**	**8**
Cr	100	90	**315**	**33,000**	**162**
Pb	15	**30**	**15,000**	**68,000**	**463**
Co	N/A	49	184	943	70

*The EPA has not reported a maximum contaminant level for cobalt

Concentrations in the table that have been bolded are those that meet or exceed the maximum contaminant level for drinking water as set by the EPA. It is extremely alarming to note the magnitude of some of these concentrations. The concentration of lead that leached from the paint sludge into DI water, for example, is twice the MCL after only 24 hours of the paint sludge powder simply sitting in deionized water. The bioavailability of lead, which serves to represent the fraction of lead that may be biologically available to a child who ingested paint sludge, is a staggering 4,533 times greater than the MCL value. However, it is important to note that the levels in these leachates are not the actual levels of these elements that the community of Ringwood would necessarily be exposed to. In order to determine the actual exposure to the heavy metals that those near the Ringwood site would encounter, risk calculations were performed for the heavy metals present in the paint sludge. These calculations are described in detail in Section 3.5 of this chapter.

3.4 Microwave Digestion: Relative Percentage of Leaching from Paint Sludge

Microwave digestion is a method that uses concentrated acid under high temperature and pressure to dissolve most of the materials present in an environmental sample.[32] In this study, microwave digestion was used to digest the heavy metals present in the paint sludge sample, turning the solid paint sludge sample into a liquid. This liquid was filtered to remove any undigested particulates, diluted with 5% nitric acid, and introduced into the ICP-OES. By doing this, the total concentration of all heavy metals present in the paint sludge sample was able to be determined. By comparing the concentrations in these baseline measurements to the concentrations of the metals in the leachates, a relative measure of the fraction of each element that leached from the paint sludge into each extraction fluid was determined.

Table 4 provides the total elemental composition of the paint sludge as determined by microwave digestion. The sludge largely consists of aluminum, barium, chromium, lead, strontium, and zinc. Due to the heterogeneous composition of the paint sludge, in order to obtain the most accurate determination of the concentrations of the elements present, nine samples were taken from different areas of the paint sludge. Each of these samples were digested in a separate microwave digestion vessel, diluted to 50 mL in 5% HNO_3, and introduced into the ICP-OES as separate samples. The concentrations determined in each element from these nine samples were averaged in order to obtain the concentration of each element present in the paint sludge sample.

In order to quantify the relative percentage of each element that leached from the paint sludge sample into each extraction fluid, the concentration of element determined by the ICP-OES (mg/L) in the microwave sample was converted to the amount of element present in the 0.1 g paint sludge sample in mg/g. This value was considered to be the “total” amount of element present in the paint sludge sample. To obtain the fraction of that total amount of element that was leached from the paint sludge sample into the corresponding extraction fluid, the concentration of the element in the extraction fluid as determined by the ICP-OES (mg/L) was converted to mg/g. The amount of element present in the leachate (mg/g) was then divided by the total amount of element present in the paint sludge sample (mg/g) and multiplied by 100 to provide the percentage of the element that leached from the paint sludge sample into the leachate. A general scheme of these calculations is provided below.

$$\frac{X\ mg\ element}{L\ \ HNO_3}\ x\ 0.05\ L\ 5\%\ HNO_3=\frac{X\ mg\ element}{0.1\ g\ paint\ sludge\ sample}=\frac{X\ mg}{g}\ total\ element\ in\ paint\ sludge$$

$$\frac{X\ mg\ element}{L\ extraction\ fluid}\ x\ 0.02\ L\ extraction\ fluid=\frac{X\ mg\ element}{1\ g\ paint\ sludge\ sample}=\frac{X\ mg}{g}\ element\ leached$$

$$\frac{\frac{X\ mg}{g}\ element\ leached\ from\ paint\ sludge}{\frac{X\ mg}{g}\ total\ element\ in\ paint\ sludge}\ x\ 100=\%\ element\ leached\ from\ paint\ sludge$$

The total concentrations of all elements in the paint sludge sample, as well as the fractions of these that leached from the paint sludge into the extracts are shown in Table 5 below.

Table 5. Relative Percentage of elements leached from paint sludge sample

Element	**Total Concentration of Element in Paint Sludge (mg/g)**	**Percentage of Elements Leached from Paint Sludge Sample**						
		DI Water Powder	**DI Water Chunk**	**TCLP Powder**	**TCLP Chunk**	**Bioavailability Powder**	**Bioavailability Chunk**	**Soxhlet**
Al	2.7	<0.1	<0.1	0.2	<0.1	20.5	4.5	2.0
As	**<0.1**	**1.9**	**0.9**	**1.5**	**1.3**	**22.4**	**4.6**	**4.6**
Ba	23.1	<0.1	<0.1	0.2	0.1	1.6	0.9	0.1
Cd	**<0.1**	**0.3**	**0.3**	**1.8**	**0.4**	**21.4**	**13.9**	**0.5**
Co	**<0.1**	**2.7**	**1.5**	**10.0**	**3.2**	**51.3**	**20.1**	**3.8**
Cr	**1.6**	**0.1**	**<0.1**	**0.4**	**0.1**	**40.7**	**9.3**	**0.2**
Cu	<0.1	0.2	<0.1	1.1	<0.1	29.6	6.21	4.0
K	<0.1	5.1	2.8	15.4	7.3	64.5	21.0	73.1
Mn	0.2	3.8	2.0	12.4	3.2	45.1	13.3	14.0
Mo	0.4	<0.1	<0.1	<0.1	<0.1	1.2	0.3	0.3
Ni	<0.1	0.5	0.3	1.9	0.5	22.2	7.2	1.4
Pb	**3.1**	**<0.1**	**<0.1**	**9.9**	**0.3**	**44.0**	**7.9**	**0.3**
Se	<0.1	3.3	2.4	6.1	2.4	6.1	7.6	6.4
Sr	1.2	0.1	<0.1	0.3	<0.1	4.47	1.8	0.4
Zn	2.0	1.0	0.5	10.1	2.4	86.7	27.9	0.9

*total concentration of elements in paint sludge (mg/g) refers to the amount of mg of the element in the amount of g of paint sludge sample

3.5 Risk Assessment

While the concentrations of heavy metals that leached from the paint sludge sample are alarmingly high, it cannot be assumed that these concentrations pose a risk to, or are adversely affecting the health of residents at the Ringwood site. In order to determine what sort of risk long-term exposure to the concentrations reported in this study might pose, if any at all, it was necessary to perform calculations based on these values. The concentrations of heavy metals found in the DI water, Soxhlet, and bioavailability extracts were used to estimate the risk posed to the Ringwood site residents through two primary pathways of exposure: ingestion of heavy metals through drinking water, and ingestion of paint sludge by children who ate the paint sludge samples.

The quantitative assessment used to calculate risk in this study is a method employed by the EPA in Part A of their Risk Assessment Guidance for Superfund (RAGS).[33] RAGS Part A is a component of the EPA's human health risk assessment guidelines that provides a baseline risk assessment. This baseline risk assessment analyzes the potential current and future health effects caused by the release of substances at a hazardous waste site under the assumption of no action – that is, in the absence of any actions that would remediate the contamination at the site. Baseline risk assessments provide results that may be used to help determine whether remediation actions are necessary at a hazardous waste site, and to modify existing remediation plans. In light of the current remediation plans for the Ringwood site still being negotiated, the method of baseline risk assessment can provide useful evidence for the support or critique of these plans.

As mentioned previously in this study, the method used to quantify whether chemical substances pose a risk to human health is the four-step risk assessment process of hazard identification, dose-response assessment, exposure assessment, and risk characterization. The first step of this process, hazard identification, was determined in this study through the use of ATSDR's Substance Priority List. Since this list ranks the substances that are most commonly found at hazardous sites based on their most significant potential threat to human health due to their potential exposure at the sites and the substance's known or suspected toxicity, it does a great job answering the hazard identification question of, “Is a chemical a risk, and if so, why?” The second step, dose-response assessment, was utilized in this study through the reference dose (RfD) values of the heavy metals in question. These reference dose values are defined as the dosage safe for humans over a lifetime of exposure, and were obtained from two sources: the EPA’s IRIS site, and the Oakridge National Laboratory.

The third step in the risk assessment process, exposure assessment, was employed by taking into account the possible routes of exposure that Ringwood residents may have to the heavy metals found in the paint sludge. The two primary methods of exposure utilized in this study were ingestion of heavy metals through drinking water, and ingestion of heavy metals by children who ate the paint sludge. Another aspect that is part of the exposure assessment step is using worst-case scenario situations, which this study did by using the higher concentrations of heavy metals found in the powder paint sludge samples. The fourth step, risk characterization, was employed by calculating the potential risk to the health of residents using the EPA’s Risk Assessment Guidance for Superfund (RAGS) Part A. RAGS provides methods for calculating risk based on the two methods of exposure utilized in this study. Based on this fourth risk characterization step, a chemical poses a risk if its hazard quotient is larger than its RfD value.

According to RAGS, the non-cancer hazard quotient for a chemical can be calculated using the following equation:

$$\text{Non-cancer hazard quotient (HQ)} = \text{CDI}/\text{RfD}$$

The term CDI in this equation is referred to as the chronic daily intake, which is expressed in units of mg/kg/day. Residential exposure through the ingestion of chemicals in drinking water can be calculated using the following equation for CDI:

$$\mathrm{CDI} = \frac{\mathrm{CW \times IR \times EF \times ED}}{\mathrm{BW \times AT}}$$

The variables in this equation and their corresponding values as determined by the EPA in RAGS s are described in Table 6 below.

Table 6. Explanation of variables in the chronic daily intake (CDI) equation for residential exposure though drinking water

Abbreviation	**Definition**	**Units**	**Attributed Value**
CW	chemical concentration in water	mg/L	experimentally measured
IR	ingestion rate	liters/day	2
EF	exposure frequency	days/year	365 (for residents)
ED	exposure duration	years	70 (lifetime)
BW	average body weight	kg	adult: 70
			child (age 1-6): 16
AT	averaging time	days	ED x 365

Based on the values of these variables, CDI values were calculated for each heavy metal in the powder DI and Soxhlet water leachates. From these values, as well as the corresponding RfD values, a hazard quotient was calculated for each heavy metal. These values are reported in Table 7.

Table 7. Calculated CDI and HQ values for heavy metals in powder paint sludge DI and Soxhlet leachates

Element	**Concentration (mg/L)**		**CDI (mg/kg/day)**		**RfD (mg/kg/day)**	**HQ**	
	DI Water	**Soxhlet**	**DI Water**	**Soxhlet**		**DI Water**	**Soxhlet**
Al	7.9×10^{-3}	2.7×10^{0}	2.3×10^{-4}	7.6×10^{-2}	2.0×10^{-3}	0.1	**38.0**
As	**1.0×10^{-2}**	**2.5×10^{-2}**	**2.9×10^{-4}**	**7.2×10^{-4}**	**3.0×10^{-4}**	**1.0**	**2.4**
Ba	9.6×10^{-1}	1.4×10^{0}	2.8×10^{-2}	4.1×10^{-2}	2.0×10^{-1}	0.1	0.2
Cd	**4.9×10^{-3}**	**7.5×10^{-3}**	**1.4×10^{-4}**	**2.1×10^{-4}**	**1.0×10^{-3}**	0.1	0.2
Co	**4.9×10^{-2}**	**7.0×10^{-2}**	**1.4×10^{-3}**	**2.0×10^{-3}**	**N/A***	N/A	N/A

Cr	**8.9×10^{-2}**	**1.6×10^{-1}**	**2.6×10^{-3}**	**4.6×10^{-3}**	**3.0×10^{-3}**	0.9	**1.5**
Cu	8.9×10^{-3}	1.4×10^{-1}	2.5×10^{-4}	4.2×10^{-3}	1.0×10^{-3}	0.3	**4.2**
K	1.1×10^{-1}	1.6×10^{0}	3.1×10^{-3}	4.5×10^{-2}	N/A*	N/A	N/A
Mn	3.2×10^{-1}	1.2×10^{0}	9.2×10^{-3}	3.4×10^{-2}	1.4×10^{-1}	<0.1	0.2
Mo	9.9×10^{-3}	5.3×10^{-2}	2.8×10^{-4}	1.5×10^{-3}	5.0×10^{-3}	<0.1	0.3
Ni	1.8×10^{-2}	5.1×10^{-2}	5.3×10^{-4}	1.5×10^{-3}	2.0×10^{-2}	<0.1	<0.1
Pb	**3.0×10^{-2}**	**4.6×10^{-1}**	**8.6×10^{-4}**	**1.3×10^{-2}**	**3.5×10^{-3}**	0.2	**3.8**
Se	2.1×10^{-2}	4.0×10^{-2}	5.9×10^{-4}	1.2×10^{-3}	5.0×10^{-3}	0.1	0.2
Sr	7.6×10^{-2}	2.4×10^{-1}	2.2×10^{-3}	6.8×10^{-3}	6.0×10^{-1}	<0.1	<0.1
Zn	1.0×10^{0}	9.2×10^{-1}	2.9×10^{-2}	2.6×10^{-2}	3.0×10^{-1}	0.1	<0.1

*EPA and other sources were unable to provide an RfD value for potassium or cobalt
*HQ values bolded are those greater than 1 and signify the chemical poses a risk

Along with residential exposure through the ingestion of chemicals in drinking water, the residential exposure through the ingestion of paint sludge by children was also calculated. Since RAGS does not list an equation to calculate ingestion of paint sludge, the equation for ingestion of soil was modified to quantify this value instead. This substitution is based on the assumption that the factors that account for the ingestion of soil by children account for the ingestion of paint sludge by children as well. Residential exposure through the ingestion of chemicals in soil (paint sludge) can be calculated using the following equation for CDI:

$$\text{CDI} = \frac{\text{concentration of element in paint sludge x ingestion rate x fraction ingested}}{\text{body weight}}$$

The variables in this equation and their corresponding values as determined by the EPA in RAGS s are described in Table 8 below.

Table 8. Explanation of variables in the chronic daily intake (CDI) equation for residential exposure though drinking water

Abbreviation	Definition	Units	Attributed Value
CS	chemical concentration in soil (paint sludge)	mg/g	experimentally measured
IR	ingestion rate	g/day	1-6 years old: 0.2 >6 years old: 0.1
FI	Fraction ingested from	unitless	pathway specific

	contaminated source		value
BW	average body weight	kg	child (age 1-6): 16

*FI used was the percentage of elements that leached from paint sludge sample (Table 4)

In this study, the fraction ingested used in the above calculation was considered to bet he fraction of paint sludge biologically available to a child who may ingest it, as determined in Table 4 above. Percent leached was converted back to a fraction for this calculation. Based on the values of these variables, CDI values were calculated for each heavy metal in the powder Bioavailability leachates. From these values, as well as the corresponding RfD values, a hazard quotient was calculated for each heavy metal. These values are reported in Table 9.

Table 9. Calculated CDI and HQ values for heavy metals in powder paint sludge Bioavailability leachate

Element	**Concentration (mg/L)**	**CDI (mg/kg/day)**	**RfD (mg/kg/day)**	**HQ**
Al	27.9	1.4 x 10^{-3}	2.0 x 10^{-3}	0.7
As	**0.12**	**6.8 x 10^{-6}**	**3.0 x 10^{-4}**	<0.1
Ba	18.7	7.6 x 10^{-5}	0.2	<0.1
Cd	**0.3**	**1.8 x 10^{-5}**	**1.0 x 10^{-3}**	<0.1
Co	**0.9**	**1.2 x 10^{-4}**	**N/A**	N/A
Cr	**32.7**	**3.3 x 10^{-3}**	**3.0 x 10^{-3}**	**1.1**
Cu	**1.1**	**7.9 x 10^{-5}**	**1.0 x 10^{-3}**	<0.1
K	1.4	2.2 x 10^{-4}	N/A	N/A
Mn	3.8	4.3 x 10^{-4}	0.1	<0.1
Mo	0.2	5.7 x 10^{-7}	5.0 x 10^{-3}	<0.1
Ni	0.8	4.4 x 10^{-5}	2.0 x 10^{-2}	<0.1
Pb	**67.9**	**7.5 x 10^{-3}**	**3.5 x 10^{-3}**	**2.1**
Se	<0.1	5.9 x 10^{-7}	5.0 x 10^{-3}	<0.1
Sr	2.7	3.0 x 10^{-5}	0.6	<0.1
Zn	87.5	1.9 x 10^{-2}	0.3	<0.1

*EPA and other sources were unable to provide an RfD value for potassium or Cobalt
*HQ values bolded are those greater than the RfD of that element

Risk characterization results indicate that in the DI water and Soxhlet water leachates, the hazard quotients for Al, As, Cu, and Pb are greater than 1, suggesting that these elements may pose a risk to the Ringwood residents if the levels present in drinking water were to be consumed. Cr was just below this threshold, with an HQ value of 0.9. Risk characterization results from the bioavailability leachates indicate that the hazard quotients for Cr and Pb are greater than 1, indicating that these heavy metals would pose a health risk to residents if ingested.

5. Big picture ramification of results in this study

In order to place the results of this study in a broader frame of analysis, it is necessary to compare the findings here to findings of similar studies. Although it is impossible to make a direct comparison, as paint sludge samples from this site have not been analyzed by others, there is still merit in seeing how the results from this study compare to results from others in terms of magnitude of heavy metal concentrations found, and the risk characterization determined. Literature studies of As, Cd, Co, Cr, and Pb will be the primary focus of this discussion.

TCLP leachate analysis of powder paint sludge samples revealed an average Pb concentration of 15.0 mg/L. In a separate study that used TCLP to determine the leachability of lead from cathode ray tubes[27], the authors found that 18.5 mg/L was the average concentration of Pb leached. The numbers found in this present study are certainly comparable, only 3 mg/L below the level found. Both of these studies found that levels of leached exceed the 5 mg/L regulatory limit of Pb as reported by the TCLP procedure.

A study of 153 soil samples collected from Changsha City, China collected to analyze the contents of As, Cd, Cr, and Pb, as well as other heavy metals, reported average concentrations of 18.98, 0.11, 74.21, and 36.5 mg/kg (mg element/kg soil), respectively.[34] The most direct comparison that can be made in this study is the concentrations of these four elements found in the microwave digestion results. When these concentrations are converted to mg/kg (mg element/kg of paint sludge), concentrations of As, Cd, Cr, and Pb are 11, 32, 1605, and 3088 mg/kg, respectively. While the concentrations of As and Cd are comparable to those found in the soil samples of the China study, the concentrations of Cr and Pb in this study are more than 21 and 84 times greater in magnitude, respectively, than those in the China study.

A study in Kohistan, Pakistan[35] was conducted to investigate the concentrations of Cd, Co, Cr, and Pb, along with other heavy metals, in drinking water in order to determine potential health risks posed to the local population of people. The average concentrations in μg/L (ppb) found in surface water at the site were 0.527, 0.523, 3.61, and 5.03 ppb for Cd, Co, Cr, and Pb, respectively. The average concentrations in μg/L (ppb) found in groundwater at the site were 1.11, 0.350, 7.83, and 9.64 ppb for Cd, Co, Cr, and Pb, respectively. The most direct comparison that can be made between this study and the Pakistan study would be to compare the concentrations they found to concentrations found in the DI powder water leachates of this study. The average concentrations in μg/L (ppb) found the DI powder water leachates were 4.88, 48.8, 89.3, and 30.0 ppb for Cd, Co, Cr, and Pb, respectively. The DI water concentrations are all more than three times in magnitude the surface and groundwater values reported in the

Pakistan study. Most were even greater in magnitude. For instance, the concentration of Pb in the DI water leachate is 6 times greater than surface water concentration and 3 times greater than the ground water concentration. The concentration of Co in the DI Water leachate is a staggering 93 times greater than surface water concentration and 139 times greater than the ground water concentration. The Pakistan study determined that none of the heavy metal concentrations present posed a risk to the local population.

5. Conclusion

The goal of this study was to determine the potential risk to humans posed by paint sludge samples at the Ringwood Mines/Landfill site. To do this, the paint sludge was evaluated for its composition of volatile organic compounds using headspace analysis and GC-MS, as well as its elemental composition, using ICP-OES. Volatile organic analysis of the paint sludge was qualitative and used to evaluate the possible health effects the paint sludge may pose to site residents due to the presence of two volatile organic compounds, naphthalene and xylene. Elemental analysis of the paint sludge was quantitative and used to perform preliminary risk assessment calculations of the site.

The elemental analysis was conducted in three steps: The first step was microwave digestion of the paint sludge sample in order to determine an average concentration of all heavy metals present in the paint sludge sample. The second step was to conduct four leaching tests (DI water, Soxhlet water, TCLP, and Bioavailability) to simulate the amount of heavy metals that could potentially leach from the paint sludge sample into soil and groundwater (or for bioavailability, the fraction ingested by a child that may become biologically available) under various conditions. The third step was to use the concentrations found in these leachates to perform quantitative risk calculations, based on an EPA Superfund risk assessment method, in order to determine if the concentrations of heavy metals found in this study pose a risk to site residents through exposure by drinking water or direct ingestion of paint sludge.

Risk characterization results indicate that in the DI water and Soxhlet water leachates, the hazard quotients for Al, As, Cu, and Pb are greater than 1, suggesting that these elements may pose a risk to the Ringwood residents if the levels present in drinking water were to be consumed. Cr was just below this threshold, with an HQ value of 0.9. Risk characterization results from the bioavailability leachates indicate that the hazard quotients for Cr and Pb are greater than 1, indicating that these heavy metals would pose a health risk to residents if ingested. Based on these results, it is suggested that any paint sludge remaining on site after remediation, in particular sludge left in the deep mine shafts, could potentially pose a health risk to site residents at a future date. These results also call into question whether simply excavating and capping the Ringwood site is the best method of remediation in terms of ensuring reduced exposure and mitigation of possible health effects.

It is my personal opinion, that although it appears to be the most cost effective and feasible plan for the remediation of the Ringwood site, that simply excavating and capping is perhaps not the best choice for long-term waste management. While capping the mine pit areas would prevent rainwater from moving through the soil beneath the geotextile fabric, it does nothing to prevent vertical movement of contaminants that may be already close to the water table in the mine pits. Although capping would prevent any direct contact between the site residents and the paint sludge, if high levels of contaminants were to find their way into the water supply, indirect contact may be inevitable regardless. Previously reported elevated levels of arsenic and benzene in the groundwater on site have helped to ensure long-term groundwater monitoring on site, which is perhaps the one aspect of the remediation plan that all parties involved agree on.

I am also curious as to know at what "off-site" location all of the contaminated water and soil that will be excavated is going to be disposed of. While the EPA's Record of Decision mentions off-site disposal frequently in the details of the Ringwood site remediation plan, the agency does not offer any explanation of what that process entails. Part of me wonders if the excavated materials are just going to be deposited at yet another location where a similar group of underrepresented people of a lower socioeconomic and social status are unfortunate enough to call home. Any time contamination is present at a hazardous waste site, so are issues of environmental justice. The contamination of the Ringwood site has been an ongoing disaster since the 1970s. After over more than 40 years, multiple governmental visits and remediation efforts, the Ringwood site is still not fully remediated. I don't feel that it is too presumptuous to insinuate that if the same contamination had occurred in a wealthy, primarily Caucasian town like Madison, NJ or The Hamptons in Long Island, not only would the site have been all over every major news outlet and a household name, it would have been remediated before the first drum of paint sludge even hit the freshly paved suburban street. More realistically, hazardous waste would never have been deposited there to begin with.

Although it was possible to determine the potential risk that paint sludge may pose to the Ringwood site, there are many limitations to this study and the results are not wholly conclusive. This study was conducted using only one paint sludge sample. Efforts were made to collect more samples from the Ringwood site, but unfortunately it was not possible in the time frame of this study. In order to gain a more significant understanding of potential risk, it would be necessary to collect more paint sludge samples, and perhaps even soil and water samples, from various locations at the Ringwood site. Along with the collection and analysis of a larger number of samples, it would be useful to calculate concentrations of volatile organic compounds present in the paint sludge sample in order to perform a more quantitative risk assessment of organics. It is also important to note that in this study, as well as in any risk assessment, there are inherent assumptions made that introduce a large amount of uncertainty in results. Therefore, results in this study are not definitive and no direct connections can be made to concentrations reported and health effects experience by the site residents.

Although this risk assessment is not wholly conclusive, and there are inherent uncertainties in the results, it still provides a method of analysis and insight into the potential future of the Ringwood Mines/Landfill Superfund Site. The paint sludge sample analyzed was over 40 years old and had been exposed to weathering and erosion at the Ringwood site for a majority of this time. Even if the results in this study cannot be directly correlated to any risk or health effects posed at the site, it is still extremely important to recognize that many of the concentrations of heavy metals found in this study are extraordinarily large in magnitude, even when compared to studies of a similar nature. Therefore, the results of this study should be kept in mind as remediation plans for the Ringwood site are finalized. Hazardous waste disposal has been and is still such a staggering and undertreated issue in this country. It is my hope that this study helps to bring attention to the Ringwood Mines/Landfill Superfund site, which although has been frequented in the media and the subject of a documentary, many individuals still have no knowledge of its existence.

6. Methods

6.1 Headspace Analysis

6.*1.1 Sample Preparation*

Four different categories of samples for headspace analysis were created to best determine the organic composition of the original sample: powder dry, powder aqueous, chunk dry and chunk aqueous. A total of twelve samples were analyzed, three from each sample category (Figure 8). The powder samples consisted of finely ground particles of the paint sludge sample, approximately the size of a grain of sand, while the chunk samples were larger particles, approximately 1-3 millimeters in diameter. The powder and chunk paint sludge samples classified as dry were placed in 1.5 mL amber GC vials and directly sealed. The powder chunk samples classified as aqueous were placed in 1.5 mL amber GC vials, approximately 1 mL of distilled water was added and the vials were sealed. Each sample was weighed out to approximately 0.16 g (Table 9). The samples were analyzed via direct injection gas chromatography-mass spectrometry, where the resulting spectra were matched with library spectra from the NIST database and the most probable organic composition of the paint sludge samples were determined.

Table 10. Characteristics of chunk and powder paint sludge samples

Sample Type	Vial Label	Mass (g)
chunk dry	C1D	0.1627
	C2D	0.1624
	C3D	0.1625
Powder dry	P1D	0.1629
	P2D	0.1628
	P3D	0.1626
chunk aqueous	C1A	0.1627
	C2A	0.1624
	C3A	0.1625
powder aqueous	P1A	0.1627
	P2A	0.1627
	P3A	0.1624

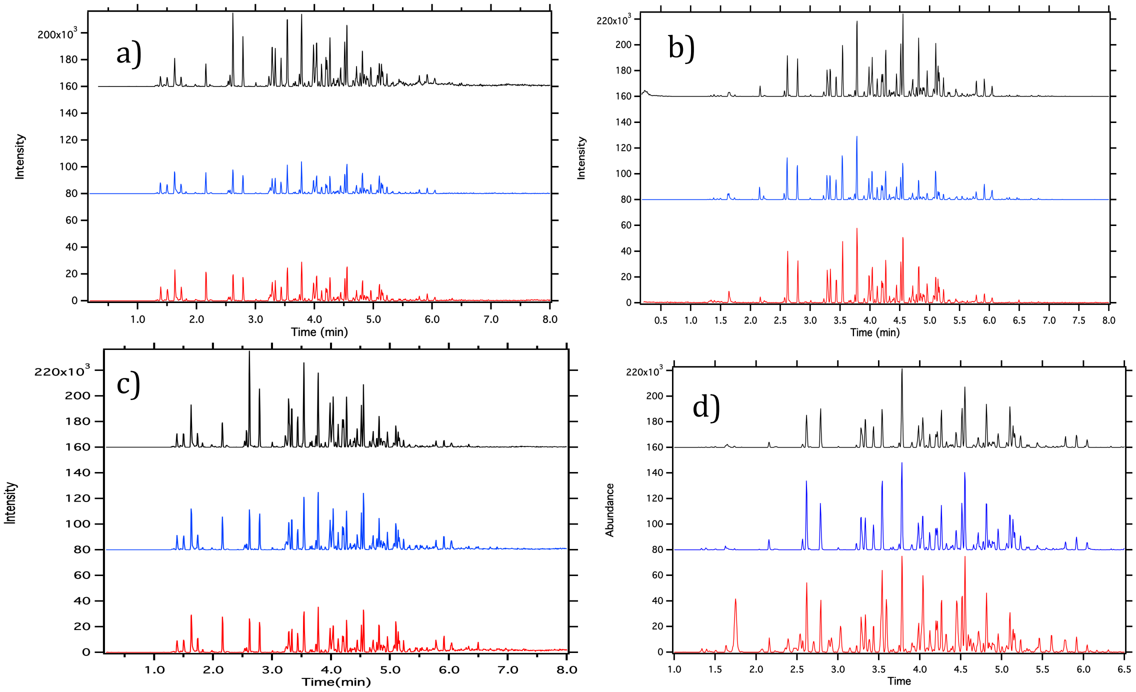


Figure 8. Overlayed total ion chromatograms for the headspace of a) dry powder, b) aqueous powder, c) dry chunk, and d) aqueous chunk paint sludge samples.

6.1.2 Soxhlet Extractions

Soxhlet: Water

Paint sludge was finely ground into a powder and sifted through a metal mesh (1 mm) to remove larger particulates. For the Soxhlet extraction, 5 g of paint sludge was homogenized with 5 g of the drying reagent anhydrous sodium sulfate (Na_2SO_4) and placed in the extraction thimble. 150 mL of deionized water was added to a round bottom flask containing boiling chips and the sample was extracted for 24 hours (8 hours a day for three days). To avoid injecting water into the GC-MS, the total water extract was separated into two equal volume aliquots and each aliquot was introduced to one of two organic solvents (dichloromethane and ethyl acetate) in a separatory funnel (10 mL of organic solvent and 20 mL of Soxhlet extract). The organic layer of each separatory funnel extract was transferred to a GC vial and analyzed via GC-MS, where the resulting spectra were matched with library spectra from the NIST database and the most probable organic composition of the paint sludge samples were determined.

6.1.3 Gas Chromatography-Mass Spectrometry (GC-MS) Analysis

For headspace analysis, the paint sludge samples were heated at 100°C for 15 minutes to volatize trapped organics. (Initial oven temperature 75°C; ramp rate 20°C/min; final oven temperature 180°C (holds at 180°C for 5 min); run time 11.25 min). At the end of the heating period, the sample was removed from the oven and 20 μL was introduced into the gas chromatographer via direct injection using a gas-tight syringe. The background was the gas-tight syringe containing no sample, only air.

The gas chromatographer used was an Agilent 7890A (inlet: 250˚C, flow rate: 1.2 L/min, split: 10:1, column: double check column type and add). The mass spectrometer used was and Agilent 5975C (MS source: 280˚C, MS Quad: 150˚C, total ion mode, electron ionization, threshold: 150, scan range from 50-300). The software program used for data analysis was Enhanced MSD ChemStation E.02.02.1431).

6.2 Heavy Metal Analysis

6.2.1 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

ICP-OES was used as the method for determining the presence and concentration of 16 elements in the paint sludge sample. Multi-elemental trace grade stock solution contained 50ppm of Al, As, Ba, Cd, Co, Cr, Cu, K, Mn, Mo, Ni, Pb, Se, Sr, and Zn. The standard solutions (ranging from 50 ppm to 1000 ppm) for the calibration curves of the 16 elements were prepared with 5% HNO_3 (Fluka trace select nitric acid).

The ICP-OES used was a Varian 710-ES (Thermo Scientific) with an axial plasma torch (RF power: 1 kW, pump rate: 15 rpm, plasma: 15 L/min, nebulizer: 200 kPa, auxiliary: 1.5 L/min). The software program used for data analysis was ICP Expert II version 1.1.3.

6.2.2. Microwave Digestion

The paint sludge was finely ground, homogenized and sifted through a metal mesh (1 mm). Approximately 0.1 g of the paint sludge powder was added to each of 9 microwave-closed vessels. 9 mL concentrated HCl (add specs) and 3 mL concentrated

HNO_3 (add specs) was added to each of the vessels (Temperature program: heat to 200˚C for 20 min, hold for 20 min). After the digestion procedure, the liquefied paint sludge was analyzed for heavy metals via inductively coupled plasma optical emission spectroscopy (ICP-OES).

The microwave digestor used was a 1.2 kW EthosEZ Microwave Digestion System with an SK-10 rotor for high pressure acid (Milestone).

6.2.3 Leaching Tests

Four leaching models (Soxhlet, DI, Bioavailability, TCLP) were employed to simulate different environmental conditions that the paint sludge might be exposed to in its natural environment. For each leaching method, with the exception of the Soxhlet extraction, two types of paint sludge samples were used: powder and chunk. The powder samples consisted of finely ground particles of the paint sludge sample, approximately the size of a grain of sand, while the chunk samples were larger pieces of paint sludge, slightly differing in size and shape. Both powder and chunk samples were weighed to approximately 0.1 g and placed in 20 mL of the corresponding extraction fluid (DI, Bioavailability, TCLP). The specifications of each leaching method are as follows:

Soxhlet extraction simulated long-term exposure to water that the paint sludge might be in contact with at the Superfund site. For the extraction, 5 g of paint sludge was homogenized with 5 g of the drying reagent anhydrous sodium sulfate (Na_2SO_4) and placed in the extraction thimble. 150 mL of deionized water was added to a round bottom flask containing boiling chips and the sample was extracted for 24 hours (8 hours a day for three days). The deionized water (DI) leaching method simulated natural conditions such as the paint sludge sitting in natural water such as a river, stream or puddle, or exposure to runoff (20 mL of deionized Millipore water). The bioavailability leaching method simulated ingestion of the paint sludge (20 mL of 1 N HCl). TCLP (Toxicity Characteristic Leaching Procedure) simulated the acidic conditions of a landfill (glacial acetic acid, Millipore water, 1 N NaOH). The leachates from each of these methods, as well as the Soxhlet extract, were analyzed via inductively coupled plasma optical emission spectroscopy (ICP-OES).

References

1. Love Canal Collections [Internet]. [Updated 2015]. University at Buffalo Libraries; [cited May 2015]. Available from: http://library.buffalo.edu/libraries/specialcollections/lovecanal/about/background.php

2. Love Canal: A Brief History [Internet]. [Updated 2013]. Geneseo The State University of New York; [cited May 2015]. Available from: http://www.geneseo.edu/history/love_canal_history

3. Superfund [Internet]. [Updated 2014 May 5]. United States EPA; [cited May 2015]. Available from: http://www.epa.gov/region02/superfund/

4. CERCLA Overview [Internet]. [Updated 2011 December 12]. United States EPA; [cited May 2015]. Available from: http://www.epa.gov/superfund/policy/cercla.htm

5. National Priorities List [Internet]. [Updated 2016 October 13]. United States EPA; [cited May 2015]. Available from: http://www.epa.gov/superfund/sites/npl/index.htm

6. Superfund [Internet]. [Updated 2014]. National Geographic; [cited May 2015]. Available from: http://www.nationalgeographic.com/superfund/

7. Hird, J. A. Environmental Policy and Equity: The Case of Superfund. *Journal of Policy Analysis and Management*. 1993. *12*(2), 323-343.

8. Harris H., et al. Making Superfund Work. *Issues in Science and Technology*. 1988. 36-41.

9. Mann V. Ford. Dir. Maro Chermayeff and Micah Fink. Show of Force Productions, 2010. DVD.U.S. EPA. Ringwood Mines/Landfill.

10. Ringwood Mines/Landfill Site [Internet]. [Updated 2015 March 3]. United States EPA; [cited May 2015]. Available from: http://www.epa.gov/region2/superfund/npl/ringwood/

11. U.S. EPA. *Environmental Justice Assessment for the Ringwood Mines/Landfill Area*. July 2013.

12. Barry J, Layton MJ, Nussbaum A, Troncone T, Washburn L, Williams B, Franklin TE. Ford, the feds, the mob: making a wasteland. *The Record*. 2005.

13. Schilling V. Toxic: Documentary chronicles battle between Ramapough Lenape and EPA http://indiancountrytodaymedianetwork.com/2011/08/26/toxic-documentary-chronicles-battle-between- ramapough-lenape-and-epa-49183

14. Basic Information: What is a risk? What is a stressor? [Internet]. [Updated 2012 July 31]. United States EPA; [cited May 2015]. Available from: http://epa.gov/riskassessment/basicinformation.htm#risk

15. Hill, Marquita K. Understanding Environmental Pollution. Cambridge: Cambridge UP, 1997. Print.

16. Risk Characterization Handbook [Internet]. [Update Unknown]. United States EPA; [cited May 2015]. Available from: http://www.epa.gov/spc/pdfs/rchandbk.pdf

17. Record of Decision: Ringwood Mines/Landfill Superfund Site Operable Unite 2. [Internet]. [Updated 2014]. United States EPA Region II; [cited May 2015]. Available from: http://www.epa.gov/region2/superfund/npl/ringwood/pdfs/ringwood_final_rod_063014_complete.pdf

18. Jacq K, David F, P Sandra. Analysis of volatile organic compounds in water using static headspace-GC/MS. Research Institute for Chromatography, Pres. Kennedypark 26, B-8500 Kortrijk, Belgium, and M. Klee, Agilent Technologies, Application Note, publication 5990-3285.

19. Lewis ET, Sensel AK. Fundamentals of Purge and Trap. Teledyne Instruments. Application Note, publication 3100-005.

20. Luque de Castro MD, Garcia-Ayuso LE. Soxhlet Extraction of solid materials: an outdated technique with a promising innovative future. Analytica Chimica Acta 369 (1998) 1-10.

21. Saim N, Dean JR, Abdullah MP, Zakaria Z. Extraction of polycyclic aromatic hydrocarbons from contaminated soil using Soxhlet extraction, pressurized and atmospheric microwave-assisted extraction, supercritical fluid extraction and accelerated solvent extraction. Journal of Chromatography A. 1997. 791:1-2:361-366.

22. Snyder JL, Grob RL, McNally ME, Oostdyk. Comparison of supercritical fluid extraction with classical sonication and Soxhlet extractions for selected pesticides. Anal Chem. 1992. 64(17):1940-1946.

23. Naude Y, et al. Comparison of supercritical fluid extraction and Soxhlet extraction for the determination of DDT, DDD and DDE in sediment. Water SA. 1998. 24(3): 205-214.

24. Waldie, John M. Surface Coatings. Vol. 1. Raw Materials and Their Usage: Oil and Colour. Chemists' Association, Australia 1974, 1983.

25. Background Information for the Leaching Environmental Assessment Framework (LEAF) Test Methods. [Internet]. [Updated November 2010]. United States EPA; [cited May 2015]. Available from: http://nepis.epa.gov/Adobe/PDF/P1009TQ9.pdf

26. Toxicity Characteristic Leaching Procedure (TCLP): EPA Method 1311. [Internet]. [Updated 1992]. United States EPA; [cited May 2015]. Available from: http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/1311.pdf

27. Musson SE, et al. Characterization of Lead Leachability from Cathode Ray Tubes Using the Toxicity Characteristic Leaching Procedure. Environ Sci Technol. 2000. 34:4376-4381.

28. Finkelstein ME, et al. Lead Poisoning of Seabirds: Environmental Risks from Leaded Paint at a Decommissioned Military Base. Environ Sci Technol. 2003. 37:3256-3260.

29. Priority List of Hazardous Substances. [Internet]. [Updated 2014 May 7]. Agency for Toxic Substances & Disease Registry; [cited May 2015]. Available from: http://www.atsdr.cdc.gov/spl/index.html

30. Support Document to the 2013 Priority List of Hazardous Substances That Will Be the Subject of Toxicological Profiles. [Internet]. [Updated 2014 April]. Agency for Toxic Substances & Disease Registry; [cited May 2015]. Available from: http://www.atsdr.cdc.gov/SPL/resources/ATSDR_2013_SPL_Support_Document.pdf

31. Drinking Water Contaminants: National Primary Drinking Water Regulations. [Internet]. [Updated 2014 October 29]. United States EPA; [cited May 2015]. Available from: http://water.epa.gov/drink/contaminants/

32. Bettinelli M, et al. Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. Analytica Chimica Acta. 2000. 424(2):289-296.

33. Risk Assessment Guidance for Superfund (RAGS) Part A. [Internet]. [Updated 2012 July 2013]. United States EPA; [cited May 2015]. Available: http://www.epa.gov/oswer/riskassessment/ragsa/

34. Chen, J. Q., Wang, Z. X., Wu, X., Zhu, J. J., & Zhou, W. Bin. (2011). Source and hazard identification of heavy metals in soils of Changsha based on TIN model and direct exposure method. *Transactions of Nonferrous Metals Society of China (English Edition)*, *21*(3), 642–651. doi:10.1016/S1003-6326(11)60761-9

35. Muhammad, S., Shah, M. T., & Khan, S. (2011). Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. *Microchemical Journal*, *98*(2), 334–343. doi:10.1016/j.microc.2011.03.003