Environmental Aspects of Two Volatile Organic Compound Groundwater Treatment Designs at the Rocky Flats Site – 13135

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ABSTRACT

DOE's Rocky Flats Site in Colorado is a former nuclear weapons production facility that began operations in the early 1950s. Because of releases of hazardous substances to the environment, the federally owned property and adjacent offsite areas were placed on the CERCLA National Priorities List in 1989. The final remedy was selected in 2006. Engineered components of the remedy include four groundwater treatment systems that were installed before closure as CERCLA-accelerated actions. Two of the systems, the Mound Site Plume Treatment System and the East Trenches Plume Treatment System, remove low levels of volatile organic compounds using zero-valent iron media, thereby reducing the loading of volatile organic compounds in surface water resulting from the groundwater pathway. However, the zero-valent iron treatment does not reliably reduce all volatile organic compounds to consistently meet water quality goals. While adding additional zero-valent iron media capacity could improve volatile organic compound removal capability, installation of a solar powered air-stripper has proven an effective treatment optimization in further reducing volatile organic compound concentrations. A comparison of the air stripper to the alternative of adding additional zero-valent iron capacity to improve Mound Site Plume Treatment System and East Trenches Plume Treatment System treatment based on several key sustainable remediation aspects indicates the air stripper is also more "environmentally friendly." These key aspects include air pollutant emissions, water quality, waste management, transportation, and costs.

INTRODUCTION

DOE's Rocky Flats Site (the Site), near Denver, Colorado, began operations as part of the nation's nuclear weapons complex in the early 1950s. Because of releases of hazardous substances to the environment, the federally owned property and adjacent offsite areas were placed on the CERCLA National Priorities List in 1989. When the nuclear production mission ended in the 1990s, DOE changed the plant's mission to cleanup and closure.

The cleanup and closure of the Site were completed in late 2005. The final CERCLA, RCRA, and Colorado Hazardous Waste Act response actions were approved in the *Corrective Action Decision/Record of Decision for Rocky Flats Plant (USDOE) Peripheral Operable Unit and the Central Operable Unit* (CAD/ROD)[1]. The response actions selected for the Central Operable Unit (OU) are institutional controls, physical controls, and continued monitoring and maintenance.

The *Rocky Flats Legacy Management Agreement* (RFLMA)[2], among DOE, the Colorado Department of Public Health and Environment, and EPA, provides the regulatory framework for implementing the final response action in the Central OU. Engineered components of the remedy include four groundwater treatment systems that were installed before closure as CERCLA-accelerated actions. Their continued operation, maintenance, and monitoring were incorporated into the CAD/ROD and RFLMA.

All utilities, including line power, were removed from the Site during closure. Any continuous power that may be needed to implement the remedy in the Central OU must be provided by application-specific solar photovoltaic (PV) systems.

CURRENT TREATMENT FOR VOCs AT THE SITE

Three groundwater treatment systems at the Site treat for volatile organic compounds (VOCs): the Present Landfill Treatment System (PLFTS), the Mound Site Plume Treatment System (MSPTS), and the East Trenches Plume Treatment System (ETPTS). The PLFTS is a passive air stripper system in which VOC-contaminated seep water flows over a series of steps, allowing the very low concentrations of VOCs in the seep water to volatilize into the air. This system is effective at reducing VOC concentrations in effluent to meet RFLMA surface water standards.

The Mound Site Plume and East Trenches Plume contain VOCs at levels that are several orders of magnitude greater than those the seep water treated by the PLFTS. Table I lists the main VOCs that the ETPTS treats, and the influent concentrations reported in October 2011 monitoring results.

The MSPTS and ETPTS use zero-valent iron (ZVI) media to treat VOCs. Each system has a groundwater intercept barrier downgradient of the VOC plume source area, and gravity feeds the collected groundwater through two ZVI-filled treatment cells (each cell is approximately 3 meters in diameter and 3.7 meters tall). The treated groundwater is discharged into the subsurface via discharge galleries. Groundwater subsequently discharges into surface water in the Central OU as base flow.

The original (1998-1999) objective of the MSPTS and ETPTS was to reduce the loading of VOCs in surface water resulting from the groundwater to the surface water pathway. Conversely, the RFLMA objective (2007) is to operate and maintain the systems so that treated effluent meets surface water standards in RFLMA Attachment 2, "Legacy Management Requirements," Table 1, "Surface Water Standards" [2].

Treatment of contaminated groundwater by the MSPTS and ETPTS results in the removal of the vast majority of the VOC contamination load from the influent groundwater. But treatment typically does not result in complete removal of VOCs, and a few VOCs remain in the systems' effluent at levels above RFLMA surface water standards.

The RFLMA parties began consulting in June 2010 regarding ways to optimize the VOC removal capability of the MSPTS and ETPTS. Because the MSPTS performance indicated that the media needed to be replaced with new ZVI, the MSPTS was the initial focus of the possible improvements. The following methods were considered: (1) installing a stepped concrete riffle air stripper similar to the one at the PLFTS, (2) adding a third ZVI cell to improve residence time of the VOC-contaminated groundwater with the media, or (3) adding a PV system-powered air stripper, either in the form of a pre-manufactured unit (e.g., stacked tray) or employing a pump and spray nozzles.

Due to the high costs of the other approaches, the spray-type air stripper method was selected to test its effectiveness; this method would also be fairly easy to implement quickly in the existing effluent manhole space, and the VOC removal effectiveness could be theoretically improved by adjusting air stripper flow rates and/or the number and type of spray nozzles. Constructing a sufficient number and overall length of concrete steps would be costly and difficult in the area available at the MSPTS, and would require a powered pump to deliver water to it; its effectiveness in the winter months and maintenance to keep the surfaces relatively clean, and in the winter free of ice, also presented major concerns. Adding a third ZVI cell would entail a significant and costly design and construction effort and the effectiveness of just one additional cell could not be predicted.

Commercially available air strippers are typically designed for flow rates and/or VOC concentrations that are much higher than those present at the MSPTS, and the cost to provide them with enough solar power would be prohibitive. In addition, the associated maintenance and potential for freezing posed concerns. Consequently, it was decided that a small, spray-aeration type solar-powered air stripper designed by the Stoller LMS Team technical staff should be tested at the MSPTS in the effluent manhole to gather performance data covering winter and summer conditions.

The prototype MSPTS air stripper was installed in early 2011. It consists of a sump pump to pump effluent (i.e., ZVI treated) water through inexpensive, commercially available engineered spray nozzles within the MSPTS effluent manhole, which allows the VOCs to volatilize into the air in the manhole headspace. This prototype air stripper was initially powered by a PV array sufficient for operations in daylight. The unit was expanded in 2013 for full-scale, full-time operation by upgrading the PV system to accommodate 24-hours-per-day operation, and installing a more robust, continuous-duty pump, which can accommodate a significantly higher flow rate.

Figures 1 and 2 show the prototype MSPTS air stripper PV array and effluent manhole, and Figure 3 shows one configuration of air stripper nozzles tested in the effluent manhole.

Figure 1. MSPTS PV array for air stripper.

Figure 2. MSPTS Air Stripper System; solar array (backside), air stripper manhole (white) and ZVI treatment cell (right side of photo).

Figure 3. MSPTS air stripper spray nozzles in the effluent manhole.

Since the installation of the MSPTS air stripper in March 2011, several tests have been run, and samples have been routinely collected to evaluate treatment. The MSPTS air stripper is performing well, and optimization is ongoing. A paper summarizing the features and performance testing of the prototype air stripper through the fall of 2011 was presented at the Waste Management 2012 conference[3].

Minor alterations of the air stripper, such as the number and design of nozzles, have made it possible to work towards optimizing the effectiveness of the air stripper system. Available data suggest that using a higher flow rate through the spray nozzles (dependent on voltage delivered to the pump) and more nozzles was a more would be a more effective way to strip the VOCs, most specifically vinyl chloride and *cis*-1,2-dichloroethene (*cis*-1,2-DCE).

SUSTAINABILITY EVALUATION

Based on the positive results of the MSPTS air stripper performance, DOE recently has decided to install at the ETPTS a solar-powered air stripper that is similar to the one at the MSPTS, but in the ETPTS influent manhole. This is intended to provide a reduction in the influent groundwater VOC concentrations that are subsequently treated by the ETPTS ZVI treatment media. It has the potential to allow the current volume of ZVI media to provide adequate VOC treatment so that all effluent concentrations are below RFLMA standards.

The PV system for the ETPTS air stripper is a modular design, being attached to and contained within a portable cargo container rather than set into the ground surface, so construction involved minimal soil disturbance.

The addition of a third ZVI media treatment cell to enhance the VOC treatment effectiveness at the MSPTS was considered during the 2010 evaluation before the MSPTS media change-out. A third cell would increase the residence time of the groundwater in the media, thereby improving treatment, but treatment results could not be accurately predicted. Therefore, such an approach was also eliminated from consideration for improvements to the ETPTS.

The following discussion is a semi-quantitative sustainability evaluation that compares the ETPTS air stripper to the addition of a third ZVI cell as alternative means to further reduce VOC concentrations. Because the ETPTS air stripper will treat influent water, the concentrations of VOCs potentially released to the air are much higher than for the effluent-treating air stripper at the MSPTS. Although this evaluation focuses on the ETPTS, the information is generally relevant to the MSPTS as well.

A main difference between treating VOCs with ZVI versus an air stripper is that the air stripper releases VOCs to the air, while the ZVI breaks down the VOC molecules in the water. If complete VOC treatment with ZVI is achieved, the primary byproducts vary but can be generalized as carbon dioxide, water, ethene, and chloride.

To simplify the evaluation, it is assumed that the air stripper removes 100 percent of the influent VOCs are stripped and released to the air. (In actuality, the goal of the ETPTS air stripper is to reduce influent VOC concentrations on a continuous basis by at least an order of magnitude. However, assuming 100 percent removal allows for a conservative comparison of air-pollutant emission.) It is assumed that, as an alternative to the air stripper, a ZVI-filled treatment cell could be added to also achieve an order-of-magnitude reduction. It is also assumed the ZVI media would need to be replaced every 5 years. (The operational history of the ETPTS has shown ZVI replacement to be required about every 4 years, on average.) Waste management assumptions include disposal of the ZVI at a licensed low-level radioactive waste (LLRW) disposal facility in Clive, Utah, as was required for the MSPTS media change-out in 2011, although actual disposition may include solid waste disposal or metal recycling of the ZVI. (Specialized disposal is required due to the historic radiological mission of the Site, even though the spent media contains extremely low levels of radionuclides.) The transportation aspect of shipping new and spent ZVI is included in the evaluation.

Considering that the life of the ZVI media is approximately 4 years, periodic media removal, disposal, and replacement are required. Post-closure groundwater treatment performance of the MSPTS and ETPTS has demonstrated that more frequent media replacement is necessary. Since closure, complete ZVI media replacement has been necessary at both the ETPTS and MSPTS. On average, since system installation, a complete ZVI media replacement has been required more frequently at the ETPTS. Over time, exposure to groundwater leads to the accumulation of iron oxides, oxyhydroxides, mineral precipitates incorporating naturally-present ions (such as calcium), and dissolved iron from the ZVI. This causes the ZVI media to clog, which triggers the need to replace the media in order to maintain effective treatment. Also, as the media clogs, the resulting decrease in available ZVI (i.e., ZVI grains fully exposed to groundwater and the VOCs dissolved in that water) causes the media to become less effective at reducing the concentrations of VOCs to consistently meet groundwater quality goals.

IS AIR STRIPPING VOCs ENVIRONMENTALLY FRIENDLY?

During the production era at the Site, VOCs (in the form of chlorinated solvents) were used in various manufacturing processes. These chemicals are or have been also widely used for diverse industrial processes such as food production, dry cleaning, and other applications, and are known to issue from landfills[4]. More commonly, VOCs are found in everyday household items, such as permanent markers and hairspray. These chemical compounds can be found in the atmosphere surrounding urban and industrial centers. Their impact on the atmosphere, in addition to their contribution to ozone depletion and greenhouse gases, is continually being researched as a significant environmental concern. Several VOCs are "stable enough to persist in the atmosphere," with atmospheric lifetimes of approximately a few days to 100 years. The atmospheric lifetime for a range of organic compounds can be difficult to determine[4]. As soon as VOCs reach the troposphere, the compounds act like a secondary greenhouse gas and can incite ozone production. It is important to evaluate the impacts of VOCs not only on their potential carcinogenicity, but also whether they represent significant contributors to ozone depletion and greenhouse gas generation.

During design consideration of the air strippers at both the MSPTS and ETPTS, the amount of VOCs released into the atmosphere was considered. Since each air stripper would be a source of air pollution emissions, an evaluation of whether the VOC release would exceed the threshold for an Air Permit Emissions Notice (APEN) in Colorado was conducted. Emissions that are below the APEN threshold are considered *de minimus*.

The Site is in a Clean Air Act non-attainment area, and an APEN is required if more than 1 ton of VOCs are released each year, or if any particular VOC is released in an amount exceeding the threshold for that chemical. In this case, the highest influent VOC concentration levels at the ETPTS were converted to kg per year (and pounds per year), based on an estimated annual total mass of VOCs flowing through the treatment system. Since the air stripper at the ETPTS will be installed in the influent manhole, VOC concentration levels from the influent system water were analyzed.

Table I shows the calculated VOC emissions for ETPTS for five main constituent chemicals: trichloroethene, tetracholoroethene, carbon tetrachloride, chloroform, and *cis*-1,2-dichloroethene. Calculations were based on the assumption of 100 percent VOC removal from the groundwater through air stripping (best-case scenario) to understand the potential emissions threshold of the system (worst-case scenario).

To be conservative, the VOC concentration levels were taken from October 2011 monitoring results, which included some of the highest measured concentrations at ETPTS. Table I shows that the total influent concentration levels of the VOCs mentioned above is approximately 4,125 μg/L. The volume treated by the ETPTS, like the other groundwater treatment systems fed by intercept barriers, varies from year to year due to climatic fluctuations. During 2010, the total treated volume at the ETPTS was approximately 1.6 million gallons; this volume is almost twice the treated volume at the ETPTS in 2011.

Based on these annual flow estimates, if 100 percent of the VOCs were transferred from the groundwater to the air in 2010, roughly 26.67 kg (59 pounds) of VOCs would have been released into the atmosphere. This total amount is much less than the total VOC APEN threshold necessary for an APEN in a non-attainment area in Colorado. In addition, the emission for each individual chemical is below the lowest APEN threshold for that chemical. The cumulative emissions for the chemicals in Table I is also below the lowest APEN threshold.

Table I. Estimate of VOCs Emitted Based on Total Influent Concentration Levels in October 2011 at the ETPTS, with Conversion into kg (lb) Emitted

Chemical	**Influent (μg/L)**	**kg (lb) Estimated for 2011[a]**	**kg (lb) Estimated for 2010[b]**
Trichloroethylene	3,400	11.07 (24.4)	22.1 (48.8)
Tetracholoroethylene	390	1.26 (2.79)	2.36 (5.21)
Carbon tetrachloride	180	0.59 (1.29)	1.2 (2.58)
cis-1,2-DCE	45	0.15 (0.32)	0.29 (0.65)
Chloroform	110	0.36 (0.79)	0.72 (1.58)
Totals	**4,125**	**13.4 (29.6)**	**26.67 (58.82)**

[a] 2011 calculations based on total flow of 3.26 million L (860,000 gallons)

[b] 2010 calculations based on total flow of 6.1 million L (1.6 million gallons)

Even though VOCs are precursors to ozone and greenhouse gas, the release from an air stripper on the ETPTS influent manhole would be considered to have a *de minimus* impact.

ENVIRONMENTAL ASPECTS OF PASSIVE ZVI TREATMENT

As mentioned previously, ZVI has been used to treat VOCs at the Site since its closure. The effective lifetime for a batch of media is approximately 4 years, after which time it must be removed completely from the treatment cells, packaged, and shipped offsite for proper disposal, as fresh ZVI is hauled to the Site from the manufacturer. Therefore, the process of removing the ZVI media periodically also has a significant carbon footprint, given the use of heavy equipment, the shipment of new media to the Site, and the transport of the spent media to Utah (based on MSPTS media) for disposal.

Table II provides an estimate of carbon dioxide generated during replacement of the MSPTS media in 2011. Considering the MSPTS and ETPTS are similar systems (size of treatment cells, etc.), the figures can be used to summarize the overall environmental impacts of a complete ZVI media removal at the ETPTS.

Table II. Summary of Equipment Used During the 2011 MSPTS Media Change-Out and the Amount of CO_2 Released During the Project

	Type	Liters of Fuel/Day	Total Liters of Fuel	CO_2 Emitted (kilograms)
Removal equipment[a]	Mini-excavator	151.41	4,542.49	12,083.70
	Loader	113.56	3,406.87	9,062.78
	Generator	20.82	624.59	1,661.51
Media transport to Clive, Utah	4 flatbed trucks		1,211.33	3,222.32
ZVI transport from Detroit, Michigan, to the Site	3 flatbed trucks		1,450.19	3,857.72
			TOTAL	**29,888.02**

[a] Values used for removal equipment are approximate and based off of daily construction logs written by the field team.

In particular, the total carbon emissions for the entirety of the media removal project were calculated in terms of the type of removal equipment used (in addition to frequency throughout the project), the distance to ship the new media on three flatbed trucks, and the distance to ship the spent media from the Site to a disposal facility in Utah. Environmental considerations related to actual media disposal (presence of new/additional contaminants in the facility, future of the facility, etc.) were not evaluated, nor were return trips by the vehicles or effects from manufacturing the media, the equipment

Therefore, by extension, adding a third ZVI cell to the ETPTS would result in an increase in CO_2 emissions of approximately 50 percent of the Table II total, or approximately 14,944 kg (32,945.88 pounds). The increase of emissions due to the installation of a third is solely based off the calculations of replacing the media.

The Table II estimates were based on an average of 10.15 kg (22.38 pounds)[5] of CO_2 released per gallon of diesel burned in the equipment listed above. It is evident that the mini-excavator used the most fuel and emitted the most carbon dioxide, at approximately 12,083.70 kg (26,640 pounds). Throughout the 30-day project to remove the media, approximately 29,888 kg (66,000 pounds) of carbon dioxide were released into the atmosphere.

Comparatively, the ETPTS air stripper is estimated to release about 27 kg (59 pounds) per year of VOCs into the atmosphere. Even though ZVI media removal is needed approximately every 4 years on average (since closure), the amount of greenhouse gas emissions during media removal is substantially higher than VOCs released by an air stripper over the same period.

SUSTAINABILITY EVALUATION OF USING SOLAR POWER

Aforementioned, during closure of the Site, all of the line power was removed and since, solar photovoltaic power has been used in its place for monitoring and groundwater treatment purposes. It is important to evaluate the sustainability aspect of using photovoltaic power to operate the air stripper at ETPTS, as opposed to the emissions that could have been released if line power was utilized to power the air stripper instead.

The air stripper at ETPTS operates off of a 6 kilowatt hour solar photovoltaic system. The Grundfos pump used for the air stripper requires 360 watts per hour, and the fan to ventilate the manhole and enhance the treatment requires an additional 20 watts per hour. Cumulatively, the air stripper system requires 380 watts per hour or 3,328.8 kilowatts per year. On average, power plants release 1.5 pounds of CO_2 per kilowatt hour[5]. Therefore, if a power plant (combination of fossil fuels) powered the air stripper at ETPTS, 2.5 tons of CO_2 would be released each year. Considering that the solar power prevents a significant amount of CO_2 from being released into the atmosphere, it can be reiterated that the solar photovoltaic air stripper is a sustainable technology. It must be noted, however, that the environmental effects of manufacturing and maintaining the solar components (e.g., panels, batteries, racking: replacing batteries; and so on) are not included in this evaluation.

COST COMPARISON BETWEEN TECHNOLOGIES

In terms of environmental impact, the air stripper is calculated to be a greener technology. It produces fewer emissions than the ZVI media does, and it uses PV power. A cost comparison is also of interest.

A complete ZVI media removal has been needed approximately every 4 years at the ETPTS; since Site closure in 2005, this frequency also applies at MSPTS. This process entails mobilizing heavy equipment, excavating and jackhammering out the spent ZVI, packaging the media, and shipping it to a proper disposal facility. It is important to note that the spent media in the treatment cells has been oxidized; therefore, it can be extremely difficult to remove from the cells. The excavation process takes patience and time, and requires significant manual labor, all of which contributes to the cost. Altogether, the typical media replacement, based on the MSPTS replacement activity performed in 2011, costs approximately $130,000. This cost does not include the maintenance of the media that is necessary between media replacements while the system is in operation. Figures 4 and 5 show the 2011 MSPTS media removal.

Figure 4. Removing spent MSPTS ZVI media.

Figure 5. One of the 19 Super Sacks of spent MSPTS ZVI media being moved to a staging area for subsequent transport and disposal.

An air stripper is a simple water treatment concept, but because of the need for PV power, it has high initial cost. The installation of an air stripper system does require minimal groundwork for trenching for electrical wiring, but otherwise, it requires little use of heavy equipment. The cost for the ETPTS air stripper (installation in late 2012) encompasses the solar panels, electrical and telemetry equipment, plumbing, and labor to install the system. The design of the system entails building an air stripper in the influent manhole at the ETPTS, using a pump with a flow rate of approximately 60.6 L (16 gallons) per minute. The required solar array is projected to have a peak of around 6 kilowatts, and the system will be in operation 24 hours a day. The estimated cost of this system is approximately $100,000, including the cost of the air stripper components. This one-time installation cost does not include any recurring maintenance costs, the major component of which is expected to be battery replacement, which will likely be necessary once every 10 years, at a projected cost estimate of approximately $40,000. (Note that the batteries are recyclable.)

Also, the amount of staff resources and the time needed for routine maintenance that the MSPTS prototype air strippers require have been comparable to those of the ZVI media treatment; therefore, labor would be the same.

The cost to install a third ZVI cell, including necessary changes to the existing system's plumbing, would be similar to the costs for the PV system. The two technologies are comparable in cost regarding installation, but the cost of the ZVI media (plus disposal and labor associated with its replacement) recurs approximately every 4 years. Comparatively, the air stripper is a one-time expenditure (apart from maintenance) that costs approximately 25 percent less than the periodic ZVI media replacement, even including periodic battery and pump replacements.

CONCLUSIONS

The current air stripper design at the MSPTS and ETPTS is an effective, sustainable, and cost-effective treatment enhancement to the existing ZVI treatment components, and is favorable in comparison to the addition of a third ZVI cell. If the air stripper in the influent manhole at the ETPTS is effective at treating for VOCs at the highest concentration, it might also prove feasible to replace some or all of the ZVI treatment capacity at the MSPTS and ETPTS. These two groundwater treatment systems would then be media-free, which would eliminate the need for periodic media removal, replacement, and maintenance.

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