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U.S. Environmental Protection Agency
Emergency Response Section (H-8-3)
75 Hawthorne Street
San Francisco, CA 94105

TAT#: 099009-T-001
TDD#: T099108-001
PAN#: EAZ0419-SAA

Attention: William E. Lewis, Deputy Project Officer

Subject: **Middle Mountain Silvex Site, Alpine, Arizona**

On August 1, 1991, U.S. Environmental Protection Agency (EPA) On-Scene Coordinator (OSC) Robert Mandel tasked the Technical Assistance Team (TAT) to assist him in conducting a site assessment at the Middle Mountain Silvex Site, located in the Apache-Sitgreaves National Forest near Alpine, Arizona (Figure 1). A site visit was made on August 20th to determine the suitability of the site for a removal action and to gather information for the possible development of a field analytical method.

1.0 Background

Information obtained from the Arizona Department of Environmental Quality (ADEQ) and the U.S. Forest Service (USFS) indicated that ten 55-gallon drums and three to five 5-gallon containers were buried at the site by the USFS in 1970. The drums were placed on their sides and covered with soil; in the process, the drums were ruptured. It was not known whether the drums have retained any of their original liquid.

The USFS hired a consultant to perform a site investigation in the summer of 1990. During that study a backhoe was used to excavate the drum burial area. The drums were discovered at three feet below the surface. A total of five 55-gallon drums and four five-gallon cans were uncovered. Further excavation was not performed because the drum contents spilled when they were disturbed. Previous analytical results from soil samples showed the maximum levels of 2,4,5-TP (Silvex) to be 510 mg/kg. The maximum levels of 2,4-D and 2,4,5-T in the soil were 160 mg/kg and 4.0 mg/kg respectively. After replacing soil over the drums, the USFS contractor covered the site with plastic and clean topsoil. They then seeded the burial area with native grasses. A fence eight feet high was constructed around the perimeter of the burial area to prohibit elk, deer and cattle from disturbing the area.

2.0 Chemical Contaminants

USFS records show that they employed three chlorinated phenoxy herbicides during the 1960's: 2,4-D (2,4-dichlorophenoxyacetic acid); 2,4,5-T (2,4,5-trichlorophenoxyacetic acid); and 2,4,5-TP (2-(2,4,5-trichlorophenoxy)propionic acid--also known as Silvex). Most of these compounds were purchased as various ester formulations including isooctyl, mixed propylene glycol, and butyl esters. There are records of purchases from Dow Chemical Company (Kuron and Esteron 99), Monsanto (Crop Guard), American Chemical Company (Weedone), Chipman (Rhodin), and Thompson-Hayward (Ded Weed). There is no way to know which of the above products are buried at the Middle Mountain site. These contaminants are all restricted use, post-emergence herbicides which contain minute amounts of dioxins and furans as impurities. The investigation conducted during the summer of 1990 did not target dioxins; therefore, the concentration of dioxin on-site is unknown. Dioxins and furans are assumed to be present because they are a well-documented impurity peculiar to the manufacture of these chlorinated phenoxy herbicides. TAT, at the request of OSC Mandel, will not specifically address dioxins and furans with respect to analytical work performed for the site.

Both the acid and the ester forms of these herbicides are only slightly soluble in water, and so were often applied as mixtures diluted with oil products, such as diesel. TAT anticipates that a combination of diluted and pure products are buried at the site.

2.1 Environmental Fate

Although these compounds can be highly mobile in sandy soils, their leachability is balanced by biodegradation. Biodegradation to non-toxic products is reported to occur at a fairly rapid rate, with the acids degrading faster than the esters or amines. For example, the persistence of 2,4,5-T acid in soil is reportedly 14-300 days, but usually does not exceed one full growing season regardless of application rate (Toxnet Database). Silvex biodegrades with average half-lives of 12-17 days when applied to the soil. These time periods, however, refer to compounds diluted for surface application. The situation is undoubtedly much different for spilled material which has not been exposed to sunlight and air. The harsh winters in the Apache-Sitgreaves forest will also have retarded the biodegradation rate. In addition, degradation occurs much more slowly if the herbicides are released to water.

2.2 Aquatic Toxicity

The compounds are harmful to aquatic life in fairly low concentrations. However, the streams in the vicinity of the site are intermittent. The following Median Tolerance Limit (TLM) values were obtained for the compounds using fresh water and bluegill trout. (The Median Tolerance Limit is the concentration at which 50% of the test population exhibit adverse effects, including death). The test period was 24 hours for 2,4,5-T and 48 hours for 2,4-D and 2,4,5-TP.

Compound	TLM (mg/L)
2,4-D	375
2,4,5-T	11
2,4,5-TP	2.4

These values illustrate that 2,4,5-TP is by far the most toxic of the compounds. None of the compounds in question bioaccumulate.

3.0 Site Activities

At 0800 hours on August 20, 1991, OSC Mandel and TAT members B. Pester and A. Frankel met the following people at the Apache-Sitgreaves National Forest Supervisor's Office: Dean Berkey, Walt Brooks, Gary Christianson, and Steve McCloskey of the USFS; and Tim Steele and Mike Leach of the ADEQ. OSC Mandel presented the USFS with a preliminary plan for a removal action. Enforcement of this plan would mitigate the environmental threat posed by the site by pumping any remaining liquids into new drums, decontaminating the old drums, and discarding them as scrap metal. The contaminated soil would either be excavated into fabric bags and stored with the drums of liquid or bioremediation of the soil would be attempted. The logistics of a removal action in such a remote location were also discussed.

After stopping at the Alpine Ranger Station, the group proceeded to the site. The goals of the site visit included collection of contaminated soils samples to aid in the development of a field analytical method as well as planning for the logistics of a removal action.

3.1 Collection of Contaminated Soil Samples

TAT used a shovel to dig below the plastic liner in hopes of uncovering contaminated soils in and around the buried drums. From previous reports it was not clear where in the fenced area drums were buried (see attached photodocumentation, Appendix A). Digging began at Hole A (Figure 2). Once the hole was three to four feet below the surface (this excludes the clean fill dirt and the plastic liner) it became evident that the soil was undisturbed and uncontaminated. Five samples were taken from this pit to be used as representative clean soil samples.

A second hole was dug near the middle of the fenced area (Figure 2). Two perpendicular pits were excavated; the deepest part of Hole B was four feet below the surface. At this depth TAT encountered altered clays, indicating that the soil was possibly contaminated. Several samples were taken of this altered clay to be used in development of a field analytical method. After collection of the samples, the two holes were refilled with soil and covered with plastic to reduce the possibility of rainwater permeating the contaminated soil.

4.0 Development of a Field Analytical Method

At the request of OSC Mandel, TAT investigated the utility of thin-layer chromatography (TLC) as a field screening method for the contaminants present on-site. TLC is a two-phase separation process which utilizes a solid support (either glass or plastic) coated with fine-grained particles (usually silica gel). The liquid phase consists of a suitable solvent which will move up the TLC plate by capillary action. The compounds of interest are dissolved in a solvent, applied to the plate in small spots using a micropipet, and the bottom edge of the plate is immersed in the solvent. The compounds of interest are partitioned between the solid and liquid phases as they move up the plate based upon their polarity, the polarity of the solvent, and the affinity of the compounds for the solid phase (silica gel) as compared to the affinity for the mobile phase (solvent). Visualization of the compounds can be accomplished in a variety of ways; in this case, by ultraviolet light.

4.1 Separation of 2,4-D and 2,4,5-TP

The free acid forms of 2,4-D and 2,4,5-TP were dissolved in methylene chloride in order to spot the compounds on the TLC plate. For determination of the appropriate TLC solvent system to be used as the mobile phase, several combinations of methylene chloride and methanol were used. Even with the addition of acid to the solvent system, separation of the compounds was not clean. This is because the two compounds only differ by one chlorine atom and one methyl group; therefore, it is not surprising that the TLC spots appear at roughly the same place on the TLC plate. This fact eliminates the feasibility of using the free acid form of these chlorinated phenoxy herbicides in a field TLC method based.

Use of the ester forms of 2,4-D and 2,4,5-TP as TLC analytes presents several prohibitive problems. Although there are records pertaining to herbicides purchased by the USFS during the 1960's, there is no way to know which compounds have been buried at the Middle Mountain site. Determination of which esters are present would require non-routine GC/MS analysis. The time and materials necessary to determine which esters are present and to develop a suitable TLC method are not cost effective, considering the small size of the site. Additionally, sample standards are unavailable for the proprietary formulations of these long-banned herbicides.

4.2 Extraction of the Soil Samples

An integral part of the development of a field TLC method is finding a suitable soil extraction method. Methylene chloride and acetone were both used as extraction solvents. The methylene chloride extract showed no UV-active material when spotted on a TLC plate. The acetone extract was UV-active but did not reveal any of the free acid form of 2,4-D or 2,4,5-TP when the extract was spotted and run with standard solutions of the two herbicides in a methylene chloride/methanol mixture. The acetone extract was then analyzed using a less polar solvent (hexane) and a more polar solvent (methanol). The UV-active spot did not move from the baseline in either case. This indicated that the compounds dissolved in the extract of contaminated soil did not contain either free acid or ester forms of the herbicides. If the esters had been present, they would have moved up the TLC plate with a slightly less polar solvent than that of the free acid compounds.

4.3 Evaluation of a Commercial Field Kit

TAT investigated a commercial test kit for 2,4-D and 2,4,5-TP available from Millipore Corporation. The kit uses antibodies specific to 2,4-D and 2,4,5-TP acids to detect the herbicides. The field kit is used as a "yes/no" indicator of the presence or absence of the herbicides. However, the detection limit of the kit is in the parts per billion range, which is too low for this application. This problem could be circumvented were it not for the fact that the kit detects the free acid and methyl ester forms of the compounds. Although these compounds may be present on-site, they are certainly not the sole species. Any quantification using only the methyl ester and free acids would be grossly inaccurate with respect to total herbicide concentration in the soil.

5.0 RCRA Hazardous Waste Classification

The compounds present at the Middle Mountain Silvex Site are included in two parts of the RCRA regulations. The salts and esters of 2,4-D are classified as discarded chemical products [40 CFR 261.33 (f)]. Their corresponding EPA Hazardous Waste Number is U240. The salts and esters of 2,4,5-T and 2,4,5-TP are included in the listed wastes from non-specific sources (40 CFR 261.31). These compounds, derived from trichlorophenol, have been given the EPA Hazardous Waste number F027.

6.0 Disposal Options

The fact that chlorinated phenoxy herbicides manufactured during the 1960's contained dioxins and furans impacts the disposal options for these wastes. There are currently no facilities in the United States which will accept dioxin-containing wastes for incineration. Consequently, the USFS will need to construct a permanent facility at the site for long-term storage or they will need to pay a third party for storage service. This second option may be problematic due to prohibitions placed upon transporting dioxin-containing wastes.

7.0 Conclusion and Recommendations

Although TAT has no conclusive evidence from this site visit concerning the presence of contaminated material, information gathered from various sources indicates the existence of buried drums of chlorinated phenoxy herbicides. The USFS admits having buried the drums and have readily supplied herbicide purchase records. In addition, the site investigation performed in the summer of 1990 uncovered several drums, some with remaining liquid. The altered clay soil TAT encountered during this site visit also suggest contaminated soil.

Conversations with the USFS revealed the site may be a habitat for sensitive species such as Cooper's Hawk, Northern Goshawk, and the Pine Grosbeak. The burial area also lies near a watering hole frequented by elk , deer and cattle. The presence of buried, ruptured drums of listed hazardous wastes in an ecologically sensitive area presents a threat to the environment and constitutes grounds for a removal action.

Considering the degradation rates of the herbicides in question when exposed to light and air, removal of the drums and any remaining liquid will likely remove the immediate threat. A portion of the contaminated soil should also be removed to prevent leaching of the compounds to a nearby watering hole frequented by elk and cattle.

The results of the TLC study conducted for this project indicate that a field analytical method to monitor excavation progress is not feasible in this case. However, stringent cleanup levels may not be necessary if natural degradation of residual herbicides in the soil is pursued as part of the removal action.

If you have any questions regarding this report, please do not hesitate to call this office.

Respectfully submitted,

Beverly Pester
Technical Assistance Team Member

cc: File
Robert Mandel, OSC

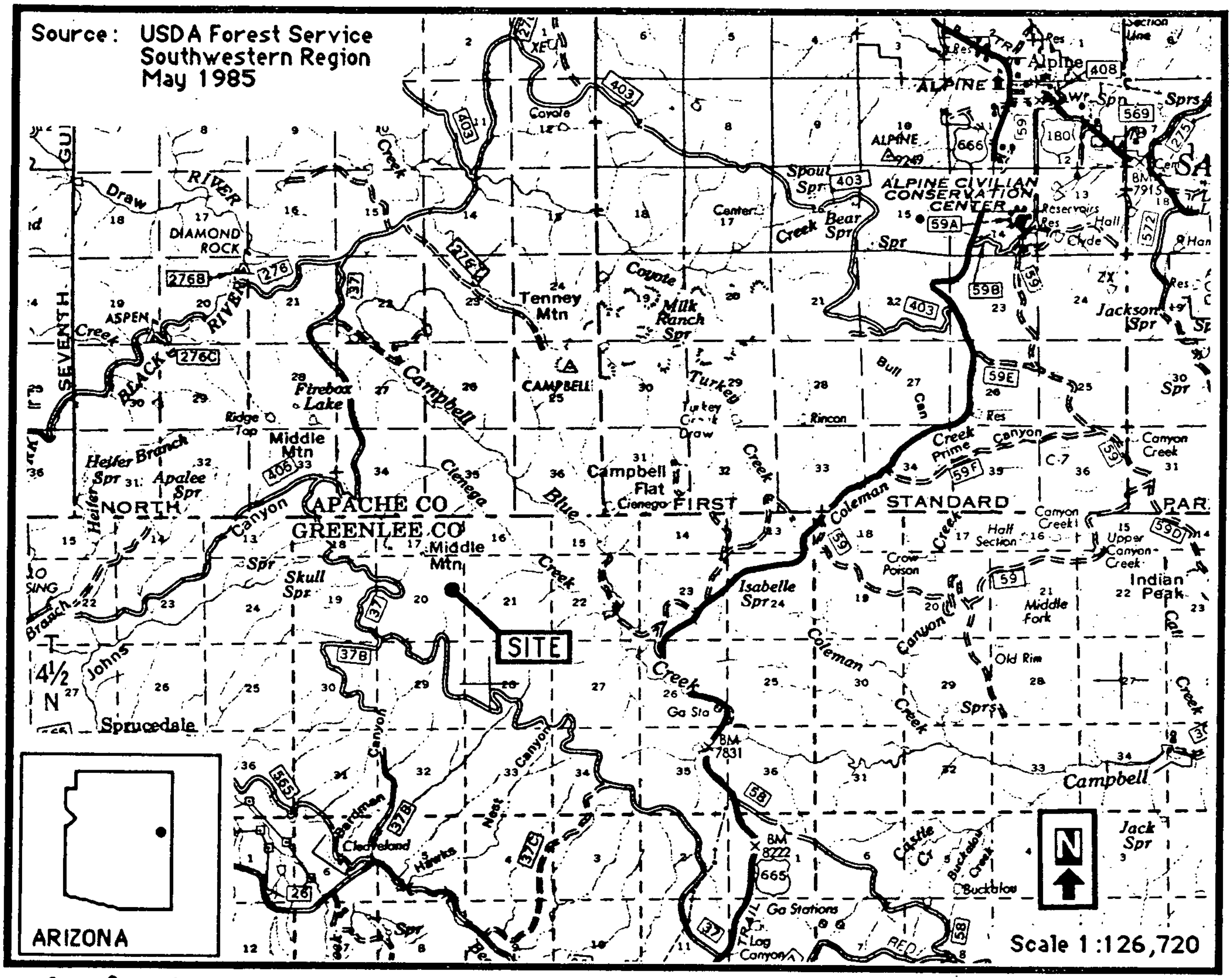

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FIGURE 1
Middle Mountain Silvex Site Location Map

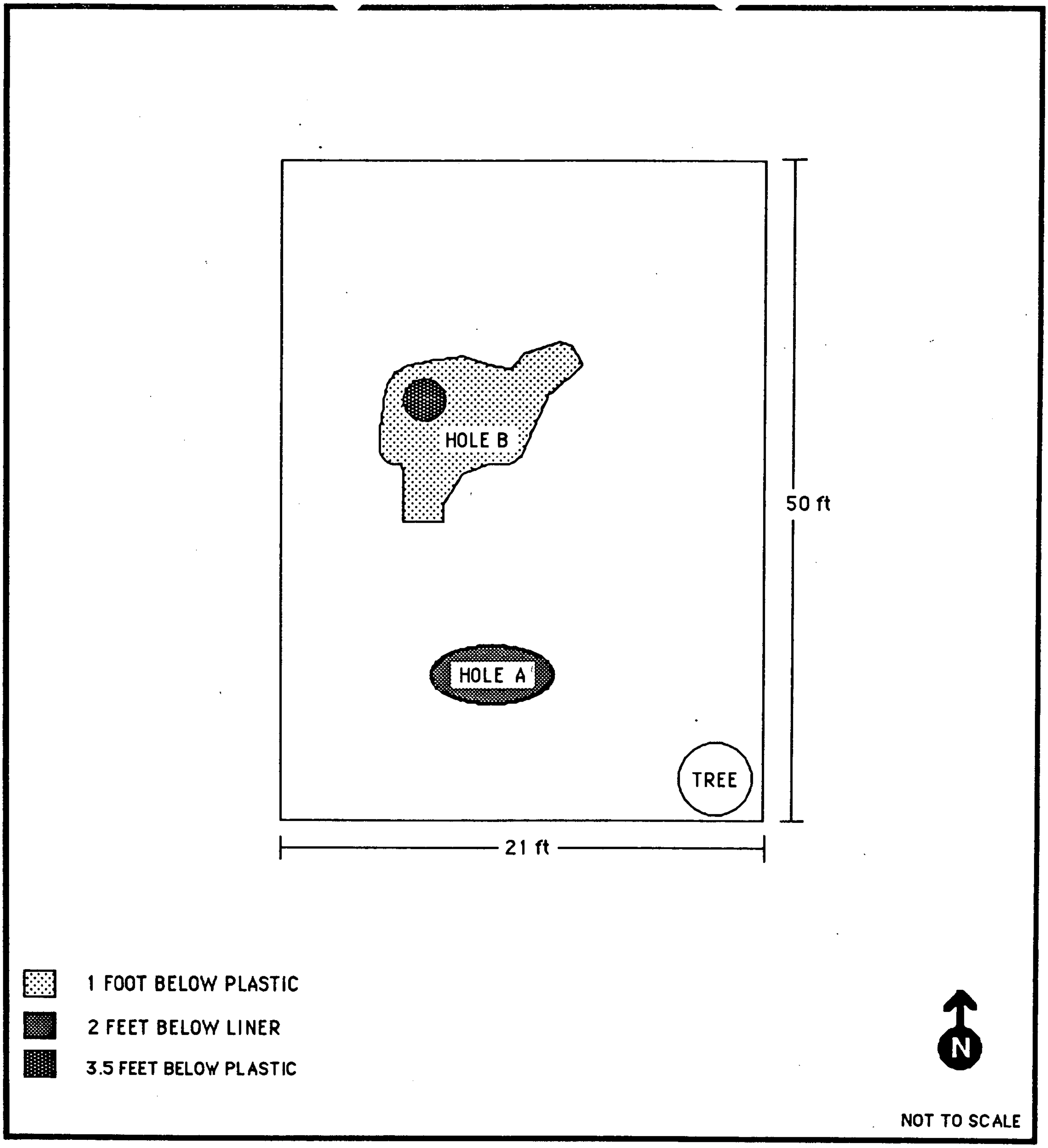

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Figure 2

Middle Mountain Silvex - Site Map
Alpine, Arizona

APPENDIX A

Photodocumentation

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Technical Assistance Team

Middel Mountain Silvex Site - Alpine, Arizona
PAN: EAZ0419-SAA TDD: T099108-001
Photographer: B.Pester Date: 08/20/91

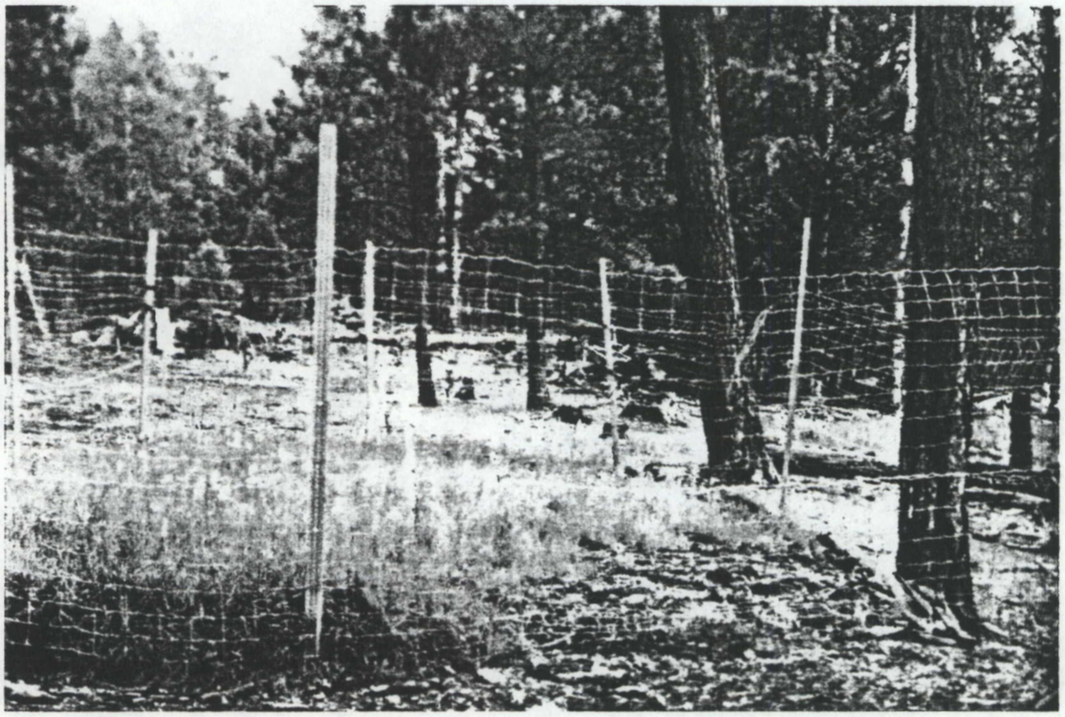

Photo 1: View of the site

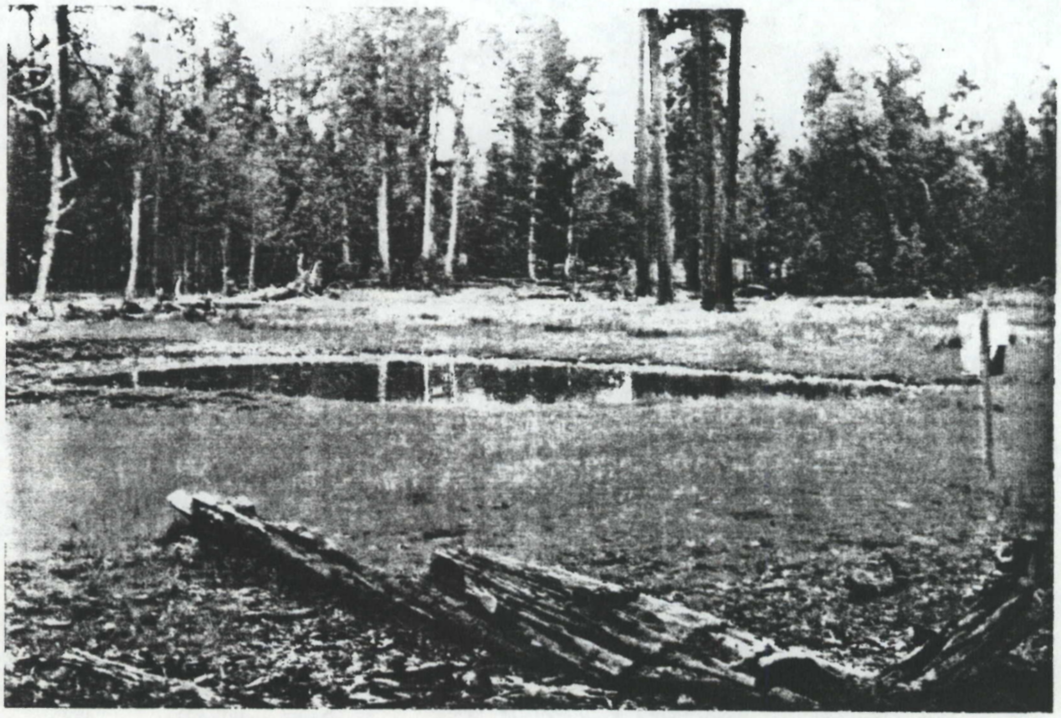

Photo 2: Watering hole to the east of the site

Middle Mountain Silvex Site - Alpine, Arizona
PAN: EAZ0419-SAA TDD: T099108-001
Photographer: B. Pester Date: 08/20/91

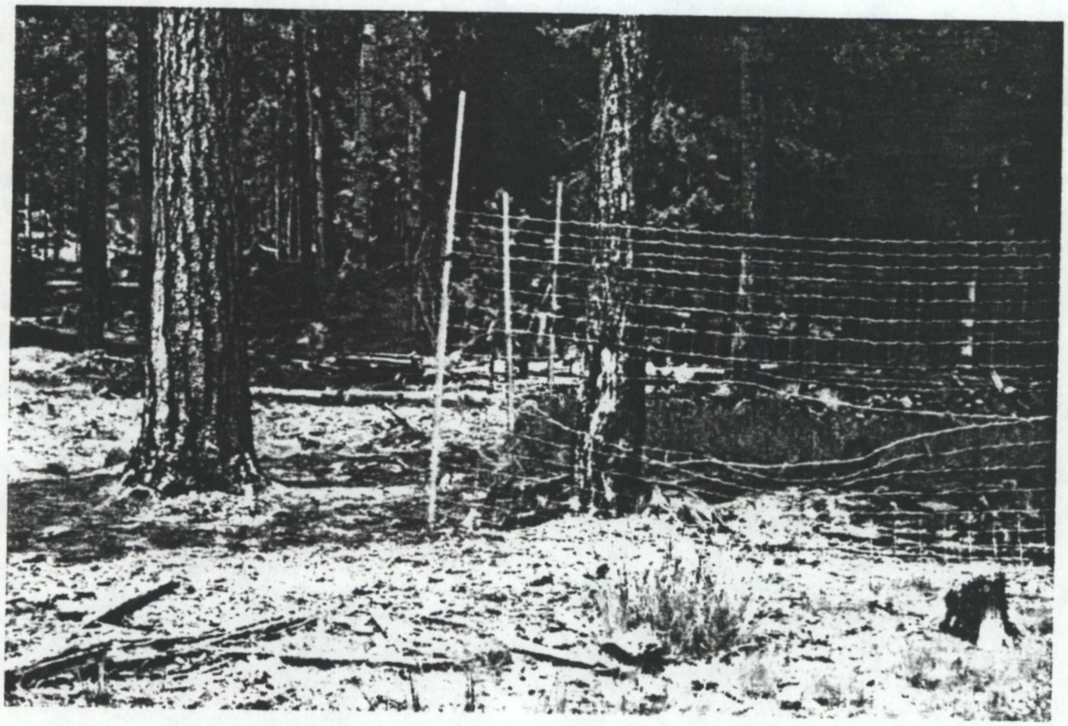

Photo 3: View of Hole A

Photo 4: View of Hole B.