

**VOLATILE ORGANIC CONTAMINATION OF GROUND WATER
AROUND UNLINED PRODUCED WATER PITS**

by

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TABLE OF CONTENTS

Abstract.....Page - 1

Introduction.....Page - 2

Hydrogeology.....Page - 6

Produced Water DisposalPage - 11

Field Methods

 A) Site Selection.....Page - 20

 B) Development of Monitor Wells

 1) Monitor Well Locations.....Page - 20

 2) Drilling Equipment.....Page - 23

 3) Monitor Well Installation.....Page - 24

 C) Decontamination Procedures.....Page - 26

 D) Water Quality Sampling

 1) Sampling Equipment.....Page - 28

 2) Field Measurements.....Page - 29

 3) Produced Water Sampling.....Page - 30

 4) Ground Water Sampling.....Page - 31

 5) Sample Identification.....Page - 32

 6) Filtration.....Page - 33

 7) Chain of Custody.....Page - 34

Results and Discussion.....Page - 39

Conclusions.....Page - 49

Appendix A - Laboratory Analyses.....Page - 52

References.....Page - 66

FIGURES

Figure 1 - Location of Study Area	Page - 7
Figure 2 - Major Aquifers of the San Juan Basin	Page - 9
Figure 3 - San Juan Basin Vulnerable Areas	Page - 16
Figure 4 - Potential Attenuation Mechanisms of Volatile Organics	Page - 18
Figure 5 - Monitor Well Locations	Page - 22
Figure 6 - Laboratory Analysis Form	Page - 36
Figure 7 - Chain of Custody Form	Page - 38

TABLES

Table 1 - 1985 New Mexico Produced Water Cumulative Summary	Page - 12
Table 2 - Major Contaminant Concentrations in Oil Field Produced Water Injected into Disposal Wells in Southeast N.M.	Page - 12
Table 3 - Major Contaminant Concentration in Oil Field Produced Water, San Juan Basin, New Mexico	Page - 13
Table 4 - New Mexico Water Quality Control Commission Standards for Water Quality	Page - 45
Table 5 - Summary of Types of Contaminated Sites Studied	Page - 46

ABSTRACT

Surface disposal of produced waters, generated at oil and natural gas production sites, in shallow ground water areas can potentially contaminate fresh ground water resources. Due to the saline nature of most produced waters, the major ground water contaminant considered in produced water disposal has, historically, been sodium, chloride and total dissolved solids (TDS). Dissolved phase volatile organics are often overlooked as an important potential contaminant contained in these same produced water waste streams.

In the natural gas fields of the San Juan Basin in northwestern New Mexico, volumes and salt content of produced waters generated are relatively small. Occasionally, the TDS of San Juan Basin produced waters are less than the TDS of local natural ground waters and, therefore, the impact of salts on ground water quality from the surface disposal of produced water can be minimal. But, these produced waters also contain high concentrations of dissolved volatile organics such as benzene, toluene, ethylbenzene and xylene. Since volatile organics are not naturally occurring in fresh ground water supplies, dissolved phase volatile organics can be excellent indicators for determining produced water encroachment on natural ground water in this area.

In 1985 the New Mexico Oil Conservation Commission prohibited large volume discharge of produced water to unlined pits in vulnerable areas with shallow ground water in the San Juan Basin. Exempted was disposal to unlined pits of up to five barrels (210 gallons) per day of produced water with a TDS of less than 10,000 milligrams per liter (mg/l) where depth to ground water exceeds ten feet. In 1987 a study funded through the New Mexico Oil Conservation Division by the United States Environmental Protection Agency using Section 106 Clean Water Act monies was performed to determine the fate of dissolved phase volatile organics at these exempt small volume produced water disposal sites.

Thirteen sites disposing of less than five barrels per day of produced water to unlined pits were extensively investigated by the N.M. Oil Conservation Division. Upgradient and downgradient monitor wells were established at each site. All monitor well samples were analyzed for aromatic and halogenated purgeable organics as well as major cations and anions. Analytical results have shown dissolved phase volatile organic contamination in excess of New Mexico Water Quality Control Commission standards at 50% of the sites investigated. Smaller amounts of volatile organic contamination were observed at another 20% of the sites.

INTRODUCTION

The production of crude oil and natural gas is usually accompanied by produced water. Produced water or brine water typically has high concentrations of sodium and chloride. But, most produced waters are also in contact with free phase petroleum hydrocarbons. These petroleum hydrocarbons contain volatile purgeable aromatic organic compounds such as benzene, toluene, ethylbenzene and xylene (BTEX). All of these volatile organic compounds are soluble, in varying amounts, in water and can be found in the dissolved phase in produced water. Varying concentrations of dissolved phase BTEX are present in produced water depending on the type of petroleum product with which it has been in contact. Produced waters in contact with highly volatile hydrocarbons, such as natural gas, will contain larger quantities of BTEX than produced water exposed to less volatile hydrocarbons.

Produced waters are separated from oil and natural gas on-site in the field at the well head. There are different types of separation equipment used to separate the three phases into individual fluid streams. The types of equipment utilized on-site depends on the nature of the fluids being generated. For three phase flow at natural gas sites in the San Juan Basin, the products are typically separated with an oil water separator and a dehydration unit.

The bulk of fluid separation occurs initially in the oil-water separator. Fluids are piped directly from the well head to the separator. As fluids enter the separator, natural gas or casing head gas (minor amounts of gas produced with crude oil) is taken off the top of the separator removing it from the oil-water mixture. The produced water is then physically separated from the natural gas condensate or crude oil and is discharged from the unit. Oil in the separator discharges to an on-site product or condensate storage tank. Additional physical separation may occur in the product storage tank if water is not entirely removed in the separator.

The dehydration unit removes smaller amounts of water entrained in the natural gas leaving the separator in the form of water vapor. Natural gas passing through the dehydrator is heated such that water vapor flashes to steam and is discharged from the unit.

Produced waters from the separator and dehydration units are disposed of as a waste fluid in the field by reinjection into the subsurface, discharge to on-site surface impoundments or they are trucked off-site to large scale commercial disposal facilities. On-site surface impoundments can be either lined or unlined. A number of pits may be found at each site depending on the number of wells at the site and the number of fluid phases being produced. There can be an individual pit

for each type of separation unit or they may all discharge to a common pit.

In the past, unlined earthen evaporation pits were the common means of disposal due to the low costs involved. These pits are easily constructed by digging a hole in the ground, adjacent to the individual separation unit, with a backhoe. These impoundments were usually built without clay or synthetic liners and were called "evaporation pits" or ponds since it was assumed that the majority of water in the pit evaporated. In the mid-1950's, a review of brine production data from southeastern New Mexico raised concern about produced water disposal practices. A comparison of typical pit size, brine volumes and evaporation rates led to the conclusion that only nine per cent of produced water evaporated under the most favorable circumstances (Nicholson and Clebsch, 1961). Recent studies of produced water pits in Utah have shown that approximately 93% of brine waters disposed of in unlined pits directly infiltrates into the surrounding soil, carrying with it much of the dissolved salt load of the pond, resulting in localized contamination of the underlying aquifers (Baker and Brendecke, 1983).

Because the salt load of most produced water is quite high, in the range of 25,000 to 50,000 TDS, the contaminants of interest in the surface disposal of produced waters have been

sodium, chloride and TDS. Over the years most states have recognized that natural ground water quality around unlined produced water pits can be locally degraded by infiltrating brine water and have taken regulatory steps to prevent ground water contamination from these sources. Many studies have shown the effects of brine contamination of natural ground water from unlined pits (Hopkins, 1970; Pettyjohn, 1973; Baker and Brendecke, 1983; Stephens and Spaulding, 1984; Murphy et. al, 1988). These studies focus on the increase in salt loading observed in ground water monitoring wells but do not consider potential aquifer degradation due to dissolved hydrocarbons which may be present in these same waters. Few studies have been performed on the fate of dissolved phase volatile organics in produced water. Only recently have investigations come to recognize the potential for serious degradation of ground water resulting from dissolved phase volatile organics in produced water disposed of in unlined pits (Eiceman, 1986; Davani et. al, 1986; Eger and Vargo, 1988).

This paper presents the results of a field study carried out by the New Mexico Oil Conservation Division to determine the impact of dissolved volatile organics in produced water on ground water quality around unlined produced water pits with small volume discharges.

HYDROGEOLOGY

The San Juan Basin, in Northwestern New Mexico (Figure 1), is a roughly circular structural and drainage basin at the eastern edge of the Colorado Plateau covering approximately 30,000 square miles of Northwestern New Mexico and Southwestern Colorado. The San Juan Basin is a broad northwest - southeast trending depression that formed during the Laramide orogeny. The basin is asymmetrical with steeply dipping tilted strata along the northeast margin; it is also deep and contains thick sequences of sedimentary rocks. The total stratigraphic record exceeds 14,000 feet (Brown and Stone, 1979). The basin contains a wide variety of land forms ranging from wide valleys and broad uplands to deep canyons, mesas and buttes. The climate is arid to semiarid with an average precipitation of approximately 8 -10 inches per year (Stone 1983). Annual class A pan evaporation rates in Farmington averaged 67.37 inches per year for the period 1948 - 1962 (Cooper and Trauger, 1967).

Extensive oil and natural gas production occurs within the San Juan Basin. Natural gas production is concentrated inside the central basin with crude oil production occurring largely along the basin margins. The basin is renown as having one of the largest accumulations of natural gas in the world. Most of these natural gas reserves are found in the basin's

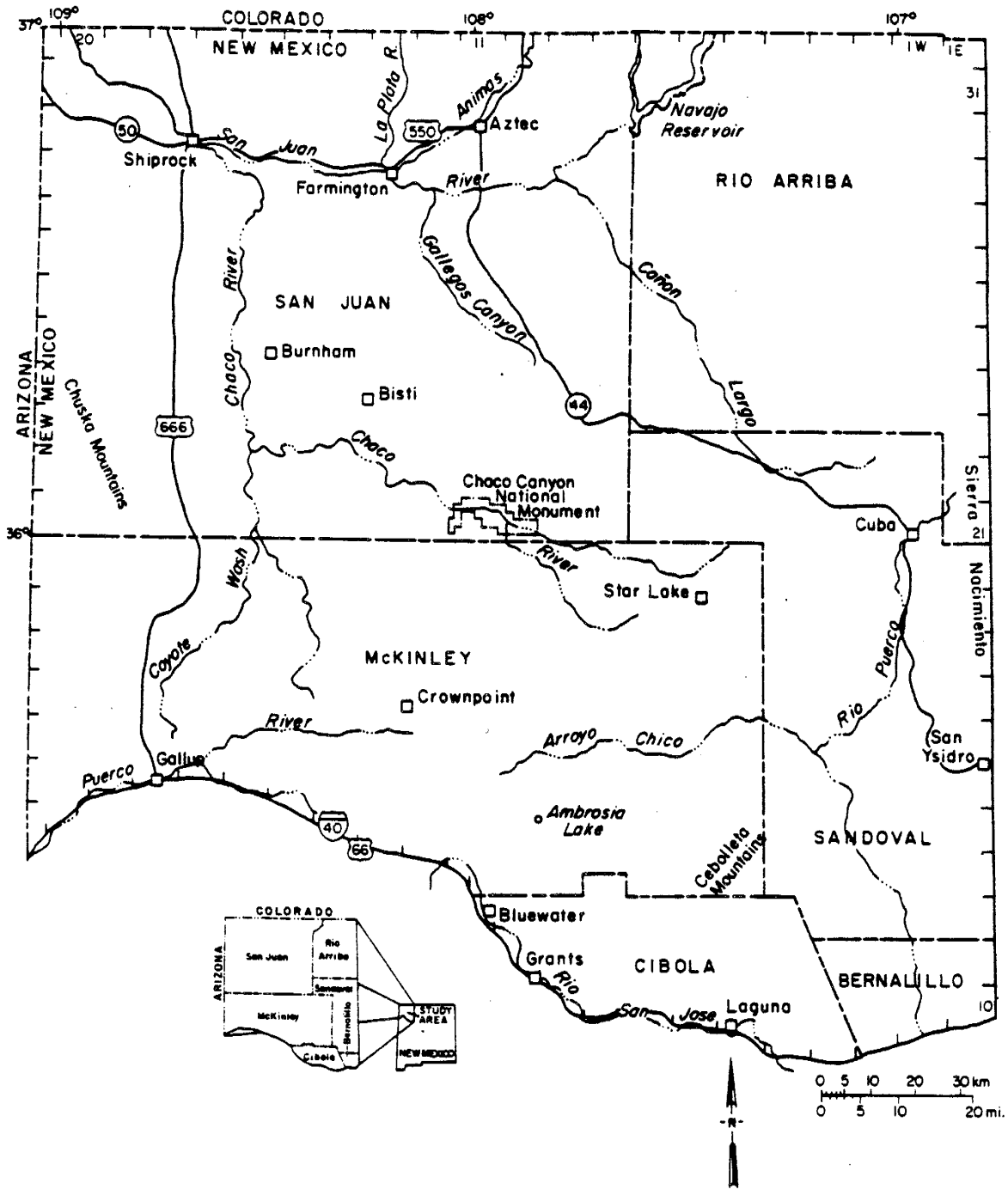


Figure 1 - Location of Study Area (Stone, 1983)

Cretaceous sedimentary sequences (McCaslin, 1987).

The San Juan Basin includes the river drainages of the San Juan, Animas and La Plata Rivers. These rivers flow through relatively wide valleys bounded by high mesas and uplands. Major aquifers (Figure 2) are contained within the Quaternary valley fill of these rivers and in sandstones of Tertiary, Cretaceous, Jurassic and Triassic age (Lyford, 1979). In addition to the major river valleys, minor aquifers are also contained within Quaternary valley fill of ephemeral canyon systems that feed the San Juan, Animas and La Plata rivers.

Much shallow ground water is contained within the valley fill of the San Juan, Animas and La Plata river systems. Alluvial sediments in the valley fill range from cobbles, gravel, sand, silt and clay to various mixtures thereof. These materials were deposited by streams in Pleistocene and Recent time (Byran, 1928). Total thicknesses of valley fill in most areas are less than 100 feet (Lyford, 1979). The thickness of the alluvium is greatest in the center of the valleys and thins toward the valley margins. Depth to water in the majority of the alluvium is less than 50 feet. Ground water in the shallow alluvial aquifers away from the river channels is a direct result of the drainage of irrigated lands, infiltration of direct precipitation or runoff and recharge from underlying and adjacent bedrock.

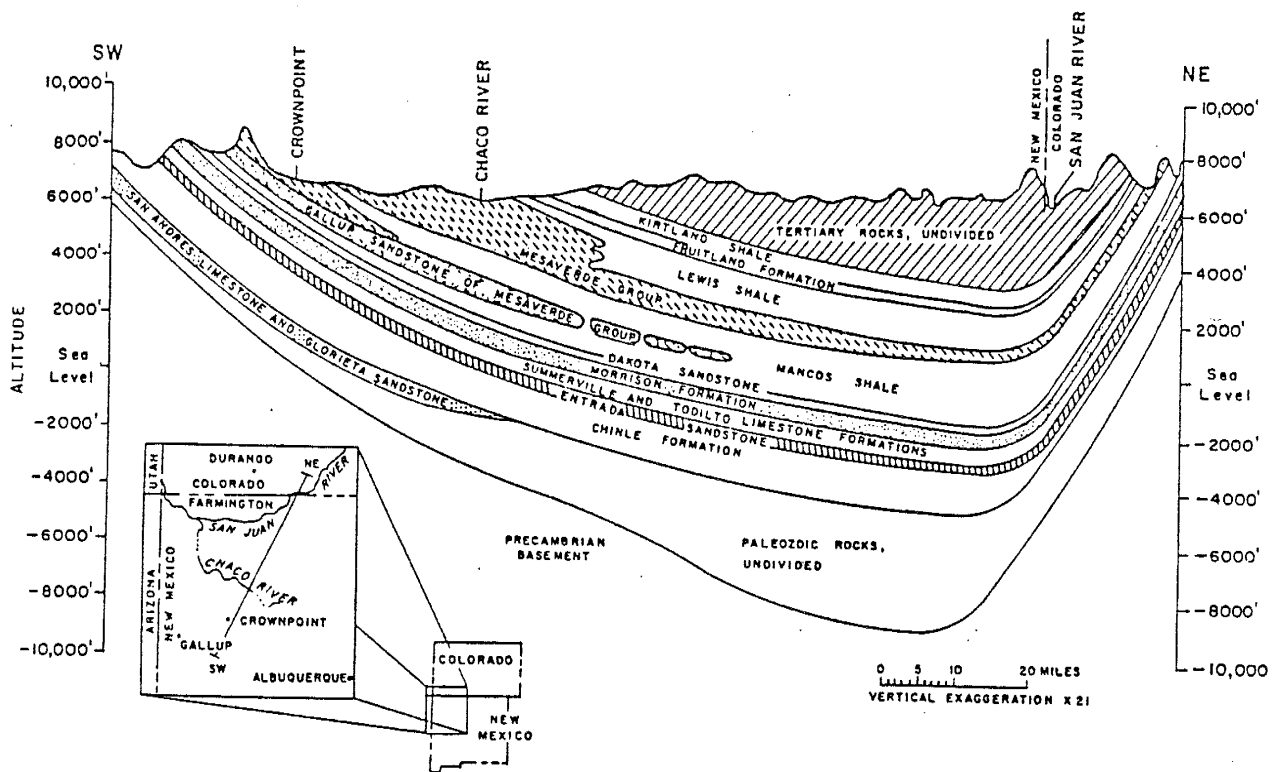


Figure 2 - Major Aquifers in the San Juan Basin (Lyford, 1979)

Although the surface water quality of San Juan River water is quite good (less than 300 mg/l TDS), the quality of ground water in the alluvium is highly variable. The average specific conductance of water from wells in the San Juan River valley fill is 2500 umhos/cm (Stone, 1983). The quality of water from the Animas River valley fill is also generally good. The average total dissolved solids content of Animas River valley fill ground water is 732 mg/l, with values ranging from 308 - 1923 mg/l (Brown and Stone, 1979).

Ground water in the sandstone aquifers generally flows down dip from the basin margins toward the San Juan River in the center of the basin. Ground water flow directions in the valley fill aquifers are influenced by the leakage from irrigation ditches and surface irrigation water infiltrating over large plots of land.

Irrigation in these river valleys occurs through the use of large scale surface irrigation ditch networks and ground water pumping. The San Juan river valley ditch systems use low TDS surface water diverted from the San Juan River below Navajo Reservoir Dam, near the Colorado border. Irrigation ditches throughout the Animas and La Plata valleys are locally fed by their respective surface waters. Because water from these rivers are already appropriated, ground water pumping is becoming increasingly used to supplement surface water

diverted into the irrigation ditch systems.

This study concentrates on petroleum production sites located over shallow water table aquifers in the Quaternary valley fill of the river drainages and their adjacent ephemeral drainage systems.

PRODUCED WATER

The production of brine water along with oil and gas is variable throughout the State of New Mexico. Table 1 is a compilation of 1985 produced water records for Northwestern and Southeastern New Mexico, the two major oil and gas producing regions in the State of New Mexico. In general, oil and gas production in Southeastern New Mexico concurrently produces large volumes of water whereas brine water volumes from the natural gas fields in the San Juan Basin are relatively low.

The general chemistry of produced waters from these two areas is also markedly different (Tables 2 and 3). Produced waters from Southeastern New Mexico characteristically have very high TDS and chloride levels. In comparison, San Juan Basin produced waters from non-Paleozoic sediments are relatively

TABLE 1 - 1985 New Mexico Produced Water Cumulative
Summaries (Boyer, 1986)

	<u>Southeast N.M.</u>	<u>Northwest N.M.</u>	<u>Statewide</u>
<u>Water Produced with Oil</u>			
Barrels Produced	304,546,026	57,805,557	362,351,583
No. of Wells	22,488	2,582	25,070
<u>Water Produced with Gas</u>			
Barrels Produced	4,981,425	916,366	5,897,791
No. of Wells	3,655	13,602	17,257
<u>Total No. Oil & Gas Wells (1985)</u>			42,327
<u>Total New Mexico Produced Water</u>			368,249,374 Bbls. 15.466 Bil. Gal.

TABLE 2 - Major Contaminant Concentrations (mg/l) in Oil
Field Produced Water Injected into Disposal
Wells in Southeast New Mexico (Boyer, 1986)

<u>Parameter</u> ¹	<u>Range</u>	<u>Arithmetic Mean</u>	<u>Standard Deviation</u>	<u>Geometric Mean</u> ²	<u>Median</u>	<u>No. Samples</u>
Chloride	498- 198,000	71,227	46,882	49,754	56,750	123
Sulfate	0-5,500	1,533	1,124	1,083	1,300	119
TDS ³	2,060- 320,495	110,086	69,921	81,212	92,924	98
pH ⁴	4.2 - 8.7	6.4	0.7	6.4	6.5	110
Iron	0 - 1,396	122.3	315.1	9.2	11.1	68

¹Analyses from salt water disposal applications on file with N.M. Oil Conservation Division, Santa Fe. All values milligrams per liter except pH. All values total values; not field filtered. State ground water standards: chloride 250 mg/l; sulfate 600 mg/l; TDS 1,000 mg/l; pH 6 to 9; iron 1.0 mg/l.

²Log geometric mean = $\sum \log x_i / N$.

³Total Dissolved Solids.

⁴Values are pH units as reported on laboratory analysis form.

TABLE 3 - Major Contaminant Concentration (mg/l) in Oil
Field Produced Water, San Juan Basin,
New Mexico (Boyer, 1986).

<u>Parameter</u> ¹	<u>Range</u>	<u>Arithmetic Mean</u>	<u>Standard Deviation</u>	<u>Geometric</u> ² <u>Mean</u>	<u>Median</u>	<u>No. Samples</u>
Dakota Sandstone						
Chloride	0-41,814	6,917	10,262	1,062	939	34
Sulfate	0-5,416	1,248	1,639	245	395	33
TDS ³	48-68,386	13,802	16,914	5,173	3,819	33
pH ⁴	6.3-9.7	8.2	0.8	8.2	8.4	23
Iron	0-3,712	182.0	737.0	7.1	18	25
Mesaverde Group ⁵						
Chloride	3-18,716	4,801	5,688	1,372	2,010	18
Sulfate	0-2,941	419	875	16	13	18
TDS ³	50-36,427	12,588	9,932	5,809	1,303	18
pH ⁴	7.2-9.0	8.1	0.6	8.1	8.3	11
Iron	0-47	16.0	17.0	3.5	12	13

¹Analyses from salt water disposal injection applications and N.M. Oil Conservation Division sampling. All values milligrams per liter except pH. All values total values; not field filtered. State ground water standards: chloride 250 mg/l; sulfate 600 mg/l; TDS 1,000 mg/l; pH 6 to 9; iron 1.0 mg/l.

²Log geometric mean = $\sum \log x_i / N$.

³Total Dissolved Solids.

⁴Values are pH units as reported on laboratory analyses forms.

⁵Includes Point Lookout Sandstone and Menefee Formation.

low in TDS and chlorides, except water produced from coal gas formations. Occasionally the TDS of San Juan Basin produced waters are lower than natural ground waters thereby leaving dissolved phase hydrocarbons as the only potential ground water contaminants.

The difference between disposal volumes and compositional makeup of produced waters from these two regions of the state resulted in different regulatory approaches toward unlined pits for each area. In 1958, concern over the disposal of brine water in unlined pits resulted in a prohibition on surface disposal of large volumes of produced water in some areas of Southeastern New Mexico. This prohibition was expanded in 1969 by New Mexico Oil Conservation Commission Order No. 3221 to include all surface disposal throughout the southeast with some exceptions for small volumes (less than one barrel per day) and for areas without protectable fresh water. Because of lower produced water volumes with relatively low TDS and a lack of known petroleum related contamination incidents, no regulations were proposed, at that time, for surface disposal in the San Juan Basin.

Although dissolved phase hydrocarbons are present in produced water waste streams, little was understood, until recently, of their health effects. Among the organic compounds known to cause health effects are benzene, toluene, ethylbenzene and

xylenes. In addition to the toxic effects of these contaminants, benzene is a known human carcinogen.

Concern over the presence of dissolved hydrocarbons in produced water resulted in hearings before the New Mexico Oil Conservation Commission in 1985 regarding the prudence of surface disposal of these wastes and led to the definition of the San Juan Basin "Vulnerable Areas". The "Vulnerable Areas", as defined in New Mexico Oil Conservation Commission Order No. R-7940, are all areas within 100 vertical feet of the San Juan, Animas and La Plata river channels and within other known shallow ground water areas (Figure 3). These are designated areas which are susceptible to contamination from surface disposal of produced water. Even though these areas were recognized as sensitive to ground water contamination, there was disagreement during the hearings over the need for a total ban on produced water disposal to unlined pits in these areas. The oil and gas industry argued in testimony presented at the hearings that numerous attenuation mechanisms would act at the surface and in the near surface to degrade the dissolved phase volatiles of small volume discharges. In addition, it was also argued that there was currently no knowledge of ground water contamination resulting from present produced water disposal practices in the San Juan Basin. This put the New Mexico Oil Conservation Commission in the difficult position of needing proof that small volume produced

water discharges presented a threat to ground water before preventing their discharge. As a result surface discharges of produced waters to unlined pits in the "Vulnerable Areas" were only banned for volumes of five barrels per day (210 gallons per day) or greater. Lacking proof of ground water contamination around unlined produced water disposal pits in the San Juan Basin and due to the low TDS of most San Juan Basin produced waters, low volume, low TDS discharges were exempted in locations where ground water was at depths in excess of ten feet.

The ten foot depth criteria was imposed under the assumption that attenuation mechanisms at the surface and in the vadoze zone would act to degrade small volumes of dissolved phase volatile organics before they reached the underlying ground water. Figure 4 shows various potential surface and subsurface attenuation mechanisms of dissolved phase volatile organics. Surface attenuation mechanisms include volatilization and photolysis. Discharge from the separator usually occurs under high temperature and pressure. The turbulent nature of the discharge as it leaves the separator causes many of the volatiles to flash into the atmosphere. Volatilization and photolysis will also occur as the discharged fluids lie impounded on the surface. The rate of volatilization and photolysis can be greatly decreased by the presence of any paraffins, from separator upsets, floating on

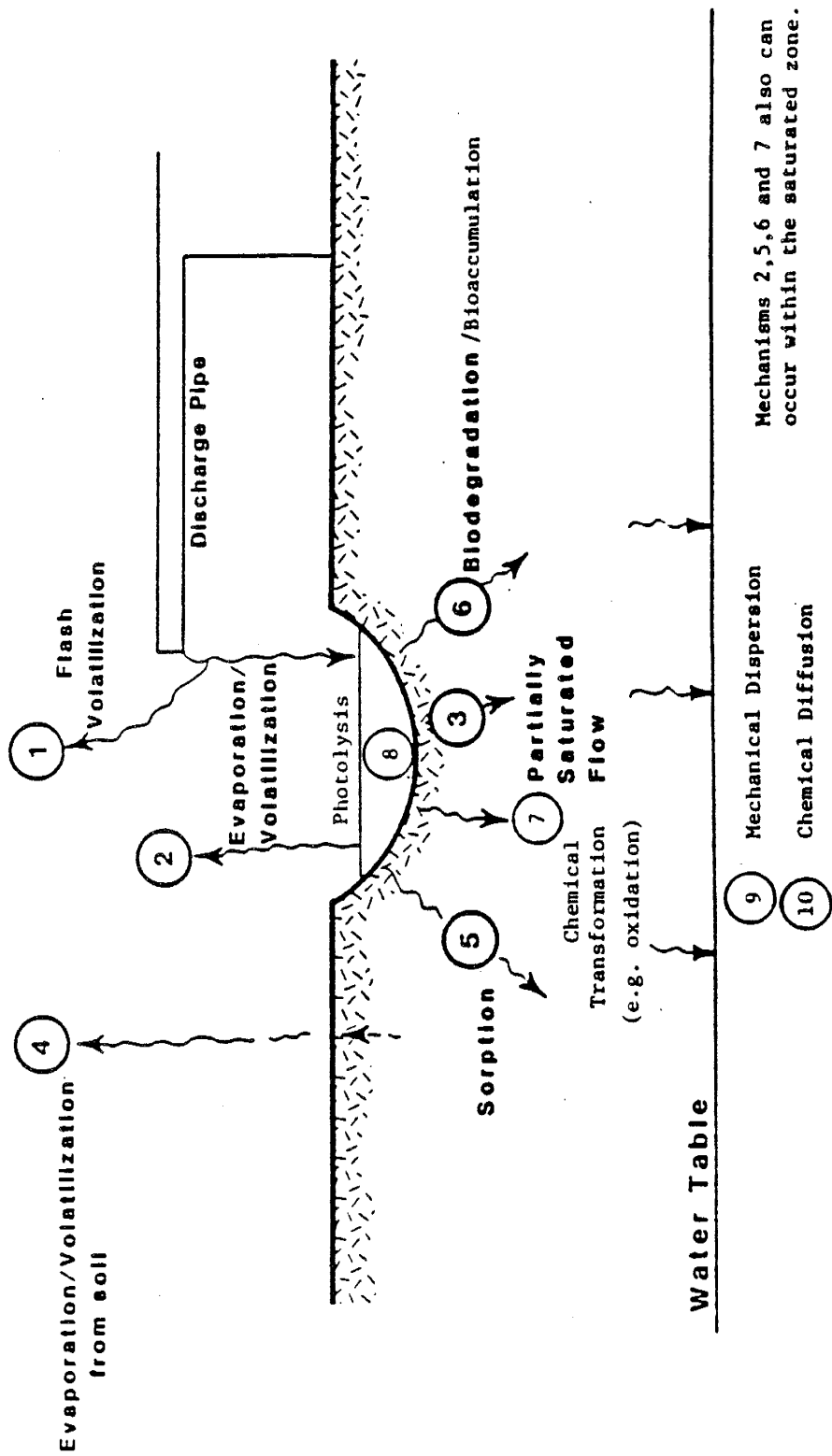


Figure 4 - Potential Attenuation Mechanisms of Volatile Organics (McQuillan, 1986).

the surface which will reduce the amount of surface area exposed to the atmosphere. As the produced water infiltrates the soil surrounding the pit by partially saturated flow, additional attenuation mechanisms can act on the volatile organics in the migrating flow. These mechanisms include volatilization into soil gas, sorption, biodegradation, and chemical transformation in oxidizing or reducing zones. These same vadoze zone attenuation mechanisms, as well as mechanical dispersion and chemical diffusion, can also act on dissolved phase volatiles that make it to the water table.

From September 1986 through January of 1988 the U.S. Environmental Protection Agency, under Section 106 of the Clean Water Act, provided grants to the N.M. Oil Conservation Division for ground water investigations related to the production of oil and natural gas. These grants enabled the N.M. Oil Conservation Division to conduct investigations into ground water quality around these exempt low volume unlined produced water pits in the San Juan Basin's "Vulnerable Areas". The purpose of the study was to determine if the depth criteria provides adequate protection of natural ground water from the dissolved organic load in produced water and the magnitude of any impacts on ground water quality. This paper presents the results of the N.M. Oil Conservation Division's unlined produced water pit study.

FIELD METHODS

A) SITE SELECTION

The object of the site selection process was to locate unlined produced water pits receiving discharges of less than five barrels per day in the San Juan Basin's shallow ground water areas. Potential study sites were identified using San Juan Basin R-7940 produced water pit registration forms and 1986/87 C-111 oil and natural gas production records on file with the N. M. Oil Conservation Division. A preliminary field evaluation was then performed at each potential site. The preliminary evaluation documented the feasibility of hand augering, equipment locations, types of pits on site, subsurface stratigraphy and any observations about potential alternate sources of contamination.

B) DEVELOPMENT OF MONITOR WELLS

1) MONITOR WELL LOCATIONS

Each site selected, which met the study criteria, was targeted for a characterization of the quality of produced water along with the ground water quality surrounding the produced water pits. Four holes were augered, depending on site conditions, around each produced water pit in order to determine the

geology, hydrology and water quality of the site. Each auger hole was completed as a temporary monitor well. After each site field investigation was completed, well casings and screens were removed from the ground for use at the next site.

Figure 5 is a sketch of where the auger holes were typically located. The orientation of the auger holes was such that one hole was upgradient and three holes downgradient of the pit. The direction of the hydraulic gradient was not exactly known so orientation of the auger holes depended on assuming that the direction of the gradient was approximately the same as the slope of the land surface. Along the irrigated lands of the San Juan, land slopes toward the river from the valley sides resulting in flow perpendicular to the river. In the tributary canyons the land slopes down the reach of the canyons resulting in a hydraulic gradient sub-parallel to the canyon length. The upgradient hole was located at least 50 feet from the upgradient pit. The purpose of the 50 foot minimum was to ensure that ground water unaffected by fluids in the pit could be sampled to determine natural ground water chemistry. At some of the sites the upgradient hole was located much greater than 50 feet from the pit because of equipment on location such as storage tanks and plumbing from the well head. The remaining three holes were located downgradient from the pit at a distance such that they sampled ground water only and did not intercept infiltrating pit

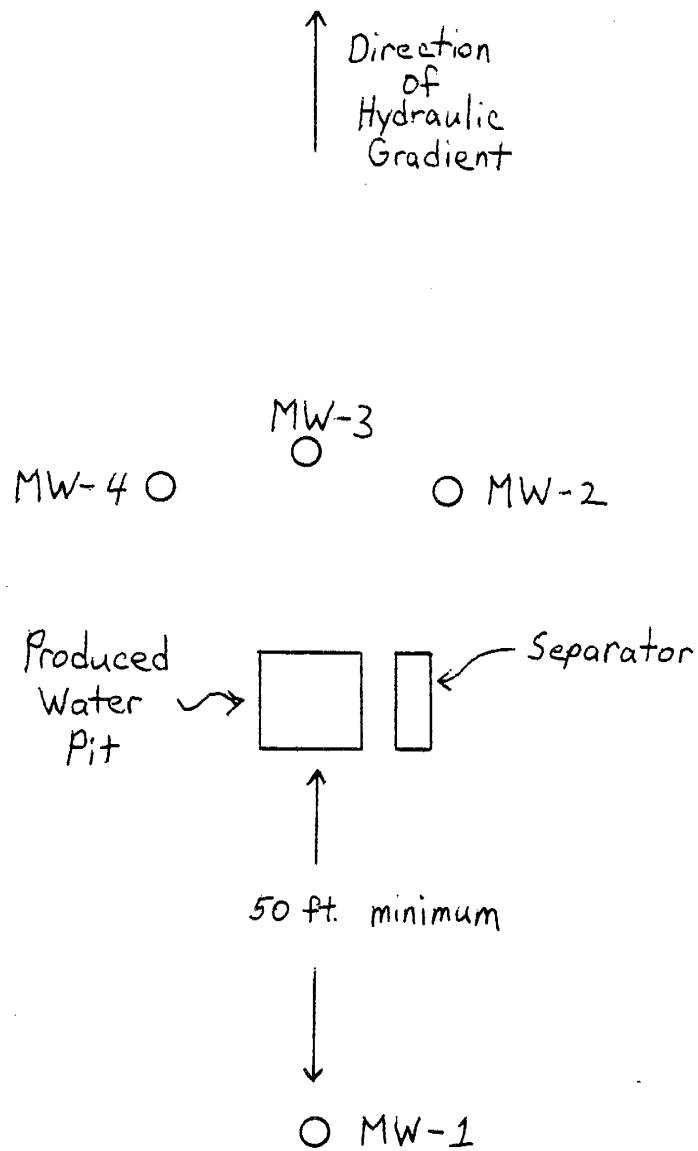


Figure 5 - Sketch of Typical Monitor Well Locations

fluids.

2) DRILLING EQUIPMENT

An AMS four inch diameter sand and gravel hand auger was used for soil borings during all of the initial site characterizations. The auger consists of a six inch long steel bucket with opposing cupped auger blades. The auger bucket threads into five-foot lengths of pipe topped with a T-handle. The auger is screwed into the ground until the bucket is full of soil, removed from the hole and emptied. After the auger bucket is advanced the full five-foot length of pipe, another five-foot length is threaded on and the bucket is advanced another five feet. This process is continued until the desired depth is reached. This type of auger is only able to access ground water at depths of 25 feet or less, eliminating many sites from consideration. The auger also has considerable trouble penetrating large gravels and cobbles common throughout the San Juan and Animas River valleys.

Monitor wells were installed using the same hand augering equipment at 11 of the sites. Two of the sites had monitor wells installed with a hollow stem auger drill rig. One was installed during a company investigation of ground water

contamination and details of the make of equipment used is not available. At the other site, a Mobile B-53 drill rig, loaned to N. M. Oil Conservation Division by the New Mexico Environmental Improvement Division, was used to access ground water deeper than 25 feet. The Mobile B-53, manufactured by the Mobile Drilling Co., is a custom auger drill rig, with a 20 foot collapsible hydraulic mast mounted on a Ford F-600 truck body. The rig uses five foot, square threaded, eight inch diameter augers with a four inch internal diameter hollow stem. The B-53 is equipped with an auxiliary hoist for lifting casing into the hole and a wireline downhole hammer for split spoon sampling of soils.

3) MONITOR WELL INSTALLATION

Two inch internal diameter Timco Triloc PVC monitor well casing and screens was used in the installation of all temporary monitor wells. Timco Triloc PVC casing has male and female threaded ends which screw together so that the shoulders of the PVC are flush with each other. Threaded end caps are used to seal the bottoms of the screens. The casing and screens were obtained in five foot lengths so that they could easily be threaded together by hand. A 0.10 inch slot screen was selected to serve as a multipurpose screen size for any type of sediment encountered. However, this screen can

present problems when very fine grained sediments are encountered.

Temporary hand augered monitor wells were installed using the following procedure:

- (a) The hand augering equipment, PVC well casing and PVC well screen were thoroughly decontaminated with the procedure described later.

- (b) Using the 4-inch hand auger, a hole was bored approximately three feet below the water table, the maximum depth that can be augered below the water table and still be able to lift the auger bucket out of the hole. Records were kept in the field book of all changes in sediment type, color of sediments, soil moisture and any odors present. The bore hole usually collapsed once the water table was reached.

To alleviate problems in installing well casing in these collapsed holes, the bore hole was continually reamed out below the water table with successive augerings. This provided a soft, disturbed soil area at the bottom of the hole into which PVC well screen and casing could easily be emplaced.

(c) The PVC casing and screen was placed in the hole and pushed the last three feet into the disturbed sediments below the water table which formed a natural gravel pack. The bottom five feet of PVC was slotted well screen to provide for entry of ground water.

d) When field work at the site was completed, all of the casing and screen was pulled from the ground and the holes were backfilled with soil.

Monitor wells drilled with the Mobile B-53 were installed using the same technique described above so that casing and screens could be easily removed upon completion of sampling.

C) DECONTAMINATION PROCEDURES

The importance of proper decontamination procedures cannot be over-emphasized when sampling for dissolved phase volatile organics to an accuracy of a few micrograms per liter or parts per billion (ppb). Equipment which comes in contact with soils or water must be kept meticulously clean to avoid cross contamination.

All drilling equipment, well casing, screens and sampling equipment was decontaminated using a four step process. First the equipment was washed inside and out with a Liguinox laboratory soap solution. Laboratory brushes were used to get to hard-to-reach places inside the bailers, casing, screens and augers. Stiff hand brushes were used to clean sediments out of the slots of the well screens. After the soap wash all of the equipment was rinsed with deionized water. When deionized water supplies were low, City of Farmington water was substituted for deionized water and the deionized water was saved for the final rinse. Equipment was then given a rinse with a laboratory reagent alcohol mixture to remove any remaining organics followed by a final rinse with deionized water.

The alcohol mixture was made by mixing a laboratory reagent alcohol, containing 90% ethyl alcohol, 5% methyl alcohol and 5% iso-propyl alcohol, with deionized water in a ratio of 25% reagent alcohol to 75% deionized water. Deionized water was obtained from a Millipore, Milli-RO4 deionizer in the N.M. EID Ground Water Laboratory in Santa Fe N.M. and transported to the site in five gallon Nalgene containers. Lawn and garden sprayer bottles were used to mix and apply all of the washing solutions. The sprayers have a hand pump to pressurize the contents of the bottle so that a high pressure wash stream can be directed at the equipment to be cleaned.

D) WATER QUALITY SAMPLING

1) Sampling Equipment

The high temperature, high pressure discharge of produced water exiting the separator and the steepness of pit walls did not allow produced water samples to be taken directly without a special collection device.

Pit and separator samples were obtained with a homemade sampler consisting of a one quart glass Mason canning jar clamped onto the end of a handle made from a five foot length of PVC. Before each use, the Mason jar, clamp and parts of the pipe handle in contact with fluids were thoroughly decontaminated. The jar was then clamped onto the plastic pipe handle for sampling. With this arrangement the Mason jar could be used to dip fluids from the pit or to hold in front of the discharge line leaving the separator.

Monitor wells were sampled with a Timco one and a half inch outer diameter PVC bailer. The bailer is four feet long and unscrews into one foot sections for easy cleaning. The lower section of the bailer is equipped with a teflon ball and rubber washer check valve to prevent loss of sample volume.

New 100% cotton rope was used to lower the bailers into the monitor wells. A fresh piece of rope was tied to the bailer

when sampling different monitor wells to prevent the cross contamination of wells and samples.

2) Field Measurements

Certain properties of produced water and ground water, such as specific conductivity, temperature and pH, are closely related to the environment of the water and are likely to be altered by sampling and storage. Meaningful data on these parameters can only be obtained in the field. The specific conductance of a water sample is a measurement of it's ability to carry an electrical current and is dependent on temperature of the sample. Specific conductivity measures ionized salts in solution and gives an idea of the concentration of TDS in the water. Once a sample is in a container, its specific conductivity may change with time as a result of precipitation of minerals in solution and therefore it is essential to obtain an accurate determination in the field. A Yellow Springs Instrument Company Model 33 specific conductivity meter was used for all measurements. It is battery operated, equipped with an integral conductance cell and temperature probe. The instrument is red-lined prior to each use. The probe is then suspended in a 1000 milliliter beaker with so that approximately one inch of water is on all sides of the

probe. The probe is gently moved around in the sample until a steady reading of specific conductivity is obtained. The specific conductivity is then read directly from the instrument in micromhos per centimeter at a specific centigrade temperature. To avoid cross contamination the probe was rinsed with laboratory reagent alcohol and deionized water between samples.

The pH was determined using colorimetric pH paper strips. This type of paper only measured pH to the nearest 0.5 pH but is adequate to show pH major changes.

3) Produced Water Sampling

Depending on the availability of fluids, produced waters were sampled from ponded pit fluids or from the discharge pipe leaving the separator. Occasionally, the pit had small amounts of oil and paraffins from separator upsets floating on the surface. Special care was taken not to let these products into the sampling jar so that only the dissolved fraction could be sampled. Produced waters were then transferred to the appropriate container. Aromatic and halogenated purgeable volatile organics were collected in two 40 milliliter glass vials with teflon lined rubber septum caps. The vials are filled to overflowing then capped so that

no bubbles or air space remains in the capped vial. General chemistry samples were collected in one gallon plastic Cubitainers which were filtered later in the day. No filtering was performed in the field due to the lack of electricity.

4) Ground Water Sampling

Ground water from the monitor wells was sampled using the following procedure:

- (1) Thoroughly decontaminate the PVC bailer using the previously discussed procedure.
- (2) Purge a minimum of three well volumes from the monitor well so that a representative aquifer sample can be taken which will not reflect stagnant water in the well casing. This was especially important for samples taken for organic analyses since samples were sometimes taken 24 hours after the wells had been completed. In this amount of time significant aerobic volatilization can occur making the analytic results unreliable.
- (3) Collect samples using the PVC bailer and place into

individual sample containers. Samples were taken from each well for aromatic and halogenated volatile organic analysis and general ground water chemistry.

5) Sample Identification

Sampling points were identified by an detailed and accurate description of its location. Each Cubitainer or glass vial was identified by attaching an inscribed tag or label, or by writing with a waterproof pen directly on the plastic Cubitainer. A record was kept in the field book of every sample collected. Information about the sample recorded in the field book included: geographic location of the site to the nearest quarter section, well name, exact location of sampling site and point of collection, date and time of collection and rate of discharge if the sample was taken from a discharge point.

Each sample was numbered with a unique ten digit number which represented the time and date of collection. The first two digits represent the year , third and fourth digits the month, fifth and sixth digits the day and the last four digits the time of day in military time. For example a sample numbered 8706091300 would represent a sample taken at 1:00pm on June 9, 1987. Cubitainers and glass vials were numbered with this

code along with sampling location, well name, and the name of the person collecting the sample.

6) Filtration

Because of suspended solids in the ground water from the monitor wells, General Chemistry samples for measurement of dissolved inorganic constituents in the water had to be filtered. A Geotech Geopump 2 systolic filter pump with a tripod filter stand was used to filter all samples. The system works by pumping the water collected through a Micro Filtration Systems 0.45 micrometer average pore diameter membrane filter placed in the filter stand. If the sample had a lot of suspended material it was necessary to use a cloth prefilter to remove the bulk of the solids so that the water could pass the 0.45 millimeter membrane filter. The first 200 milliliters of filtrate was discarded in order to rinse the filter and filtration apparatus of any contaminating substances. The remaining filtrate was collected in one liter plastic Cubitainers. Extremely turbid samples which would not pass the cloth prefilters or limited samples from low yield wells were not filtered.

Deteriorated samples negate all the efforts and costs expended in obtaining quality samples. In general, the shorter the

time that elapses between collection of the sample and it's analysis, the more reliable will be the analytical results. Preservation methods such as chilling of the sample or the use of preservatives can allow the sample to stand for a period of time before analysis. All samples were continuously stored in a 32 F ice bath in coolers from the time they were sampled until they were delivered to the laboratory.

7) Chain of Custody

After collection and identification, the samples were maintained under strict chain of custody procedures. Due to the importance of the samples as potential legal evidence, the possession of the samples was traceable from the time the samples were collected until the samples were delivered to the laboratory. To document sample possession, the following chain of custody procedures were followed:

Sample Custody

A sample is under custody if:

- 1) it is in the sampler's actual possession; or
- 2) it is in the samplers view after being in his or her physical possession
- 3) it was in the sampler's physical possession and

then the sampler locked it in a secure area or vehicle to prevent tampering

Field Custody Considerations

- 1) Evidence Tape was used to preserve the integrity of the sample. The seal was attached in such a manner that it is necessary to break the seal in order to open the sample container.
- 2) The field sampler was personally responsible for the care and custody of the samples until they are transferred or properly dispatched to the laboratory.

Transfer of Custody and Shipment

- 1) Samples were accompanied by a laboratory analysis form (Figure 6) which has a section to document chain of custody. When transferring the samples, the individuals relinquishing and receiving must sign, date and note the time and location of transfer on the analysis form. This laboratory analysis form records transfer of samples from the sampler to any other person including final transfer to a laboratory.



SCIENTIFIC LABORATORY DIVISION

700 Camino de Salud NE
Albuquerque, NM 87106 841-2570

REPORT TO: _____ S.L.D. No. OR- _____
_____ DATE REC. _____
_____ PRIORITY _____
_____ PHONE(S): _____

COLLECTION CITY: _____; COUNTY: _____
COLLECTION DATE/TIME CODE: (Year-Month-Day-Hour-Minute) [][] [][] [][] [][] [][] [][] [][] [][] [][] [][]
LOCATION CODE: (Township-Range-Section-Tracts) [][] [][] + [][] [][] + [][] [][] + [][] [][] (10N06E24S4E)
USER CODE: [][] [][] [][] [][] SUBMITTER: _____ CODE: [][] [][] [][] [][]
SAMPLE TYPE: WATER [], SOIL [], FOOD [], OTHER: _____

This form accompanies _____ Septum Vials, _____ Glass Jugs, and/or _____
Samples were preserved as follows:
 NP: No Preservation; Sample stored at room temperature.
 P-ice: Sample stored in an ice bath (Not Frozen).
 P-Na₂S₂O₃: Sample Preserved with Sodium Thiosulfate to remove chlorine residual.

ANALYSES REQUESTED: Please check the appropriate box(es) below to indicate the type of analytical screens required. Whenever possible list specific compounds suspected or required.

<u>PURGEABLE SCREENS</u>		<u>EXTRACTABLE SCREENS</u>	
<input type="checkbox"/> (733) Aliphatic Headspace (1-3 Carbons)		<input type="checkbox"/> (731) Aliphatic Hydrocarbons	
<input type="checkbox"/> (734) Aromatic & Halogenated Purgeables		<input type="checkbox"/> (735) Base/Neutral Extractables	
<input type="checkbox"/> (765) Mass Spectrometer Purgeables		<input type="checkbox"/> (758) Herbicides, Chlorophenoxy acid	
<input type="checkbox"/> (766) Trihalomethanes		<input type="checkbox"/> (759) Herbicides, Triazines	
<input type="checkbox"/> _____	Other Specific Compounds or Classes	<input type="checkbox"/> (760) Organochlorine Pesticides	
<input type="checkbox"/> _____		<input type="checkbox"/> (761) Organophosphate Pesticides	
<input type="checkbox"/> _____		<input type="checkbox"/> (767) Polychlorinated Biphenyls (PCB's)	
<input type="checkbox"/> _____		<input type="checkbox"/> (764) Polynuclear Aromatic Hydrocarbons	
<input type="checkbox"/> _____		<input type="checkbox"/> (762) SDWA Pesticides & Herbicides	

Remarks: _____

FIELD DATA:
pH= _____; Conductivity= _____ umho/cm at _____ °C; Chlorine Residual= _____ mg/l
Dissolved Oxygen= _____ mg/l; Alkalinity= _____ mg/l; Flow Rate _____ / _____
Depth to water _____ ft.; Depth of well _____ ft.; Perforation Interval _____ - _____ ft.; Casing: _____
Sampling Location, Methods and Remarks (i.e. odors, etc.)

I certify that the results in this block accurately reflect the results of my field analyses, observations and activities.(signature collector): _____ Method of Shipment to the Lab: _____

CHAIN OF CUSTODY
I certify that this sample was transferred from _____ to _____
at (location) _____ on _____ / _____ / _____ and that
the statements in this block are correct. Evidentiary Seals: Not Sealed OR Seals Intact: Yes No
Signatures _____

Figure 6 - Laboratory Analysis Form

- 2) The person relinquishing the samples requested the signature of a representative of the appropriate party acknowledging receipt of the sample on a chain of custody master sheet (Figure 7).

- 3) All shipments were accompanied by the chain of custody form showing identification of the contents. The original laboratory forms and chain of custody master sheet accompanied the sample shipment until custody was relinquished to the laboratory. The master sheet was then returned to be retained by the sampler.

Laboratory Custody

Responsibility for the samples was transferred to the laboratory the moment the samples were accepted by the laboratory receiving station. The receiving station is then responsible for distributing the samples to the performing laboratory area. The supervisor of the performing area then takes custody of the samples according to the laboratories own chain of custody rules and is responsible for their distribution and storage.

RESULTS AND DISCUSSION

Approximately 200 unlined produced water disposal pits were evaluated for inclusion in the San Juan Basin produced water study. Numerous difficulties were encountered when carrying out the preliminary site evaluations. Inaccuracies in reporting depth to ground water on the N.M. Oil Conservation Division R-7940 pit registration forms was a common problem because many companies used United States Geological Survey topographic quadrangle maps to estimate ground water depths for each well site based on the elevation of the site above the elevation of adjacent rivers. But, such estimates were not entirely accurate. As a result many sites visited during the preliminary evaluations encountered ground water at depths of much less than ten feet or at depths greater than 25 feet, the limit of hand augering and could not be used in the study. In addition, other sites could not be investigated due to the presence of large gravel and cobbles or because the site was inaccurately listed and had no unlined produced water pits.

Of the 200 sites evaluated, 13 had ground water that was accessible with the available equipment and had small volume produced water discharges of less than five barrels per day. Information at two of these sites was gathered during joint company/OCD investigations. Observations for the 13 sites studied are summarized in Appendix A.

Three sites had steel tanks installed in place of the unlined pits in the three month period between the preliminary site evaluation and installation of the monitor wells. An additional two sites had produced water pits replaced by steel tanks prior to the preliminary site evaluations. These five sites were considered to represent ground water conditions related to prior disposal of produced water in unlined pits.

A variety of alluvial sediments were encountered during installation of the monitor wells. Sediments consisted of alternating layers of sands, silts and clays of varying thickness. Approximately half the sites had wells completed in medium to coarse sands. The remaining wells were completed in silty to sandy clays with the exception of the Valdez A#1E. At the Valdez A#1E, dense clays were encountered which were difficult to penetrate with the hand auger.

Depth to ground water at the sites was also variable. At six of the sites ground water depths ranged from 10 to 15 feet. Two additional sites had depths to ground water between five to 10 feet and the remaining sites had ground water at depths ranging from 15 - 32 feet.

Background water quality

The background chemistry of the ground water (Appendix A) from the upgradient monitor wells is characterized by high sulfate, low chloride waters due to the abundance of gypsum in the sedimentary deposits of the San Juan Basin. The TDS of these waters varied from 444 to 7802 mg/l. The chloride concentrations of these natural ground waters rarely exceeded 100 mg/l. Ground water from two tributary canyons adjacent to two of the sites studied, Largo Canyon and Carrizo Canyon, also exhibited the same general water chemistry as that of the valley fill at sites studied along the San Juan River.

No volatile organics were present in the upgradient wells at 10 of the 13 sites. Three well sites, the Sullivan Frame A#1E, Grambling A#3A and Tapp Comm 5 (Appendix A) had BTEX levels near the laboratory detection limits in the upgradient wells. The origin of these organics can not be conclusively determined with the available information. All three sites have oil and gas production facilities with unlined produced water pits located upgradient from them. The low level organics seen upgradient at these sites could be due to upgradient oil and gas production disposal practices or old buried reserve pits, the locations of which are not known. It should be noted that BTEX levels in monitor wells downgradient from these three produced water pits were higher

than those found in the upgradient wells.

Produced water

Tables containing the reported discharge volume, depth to ground water and water quality analyses for each site can be found in Appendix A. Company reported discharges of produced water ranged from a low of 0.05 barrels per day to a high of three barrels per day. Ten sites studied had unlined pits receiving discharges of one barrel per day or less. The daily discharge volumes reported by companies are calculated based on the total volume discharged over a one month period which is determined by a counter on the separator. The volumes discharged could not be independently verified in the field since various wells were shut in due to the slack natural gas market and had no discharge, or because no discharges occurred during the time of the investigations.

Of the 13 sites, only eight had produced water available for sampling and analysis. Four of the eight sampled had no fluids in the pits and were sampled at the discharge pipe off of the separator by an operator tripping the separator's discharge mechanism. Only pit fluids were available for sampling at three of the eight locations. The other five sites could not be sampled because they had neither pit fluids

nor produced water in the separator or because the wells were shut in.

Samples from the pits or separators commonly contained both a hydrocarbon and water phase. With the exception of one site, all of the produced water sampled was high in dissolved phase volatile organics (Appendix A). The exception was the Sullivan Frame A#1E which had no ethylbenzene and very low benzene, toluene and xylene concentrations. These low values are most likely the result of volatilization since the well was shut-in four months prior to sampling and the produced water had been in an open tank for this entire period. The attenuation of volatile organics as a direct result of flash volatilization was also observed at the one site, Valdez A#1E (Appendix A), from which both the separator and pit was sampled. Here there was approximately a four-fold decrease between the concentrations of volatile organics in produced water exiting the separator and produced water contained in the pit.

Chloride and TDS concentrations of the produced waters at four of the eight sites sampled were relatively low. Produced waters at Gallegos Canyon Unit F#162, Tapp Comm 5, Grambling A#3A, and Gerk B#1M were lower in TDS than the natural ground waters, but, chloride concentrations of the produced waters were still higher than natural ground waters. According to

the New Mexico Water Quality Control Commission standards for ground water quality (Table 4), the produced waters discharged at the Tapp Comm 5 and the Gallegos Canyon Unit F#162, with total dissolved solids of 382 and 320 respectively, are so low in total dissolved solids as to be in the range of TDS of fresh water supplies. The other four sites had produced waters with total dissolved solids in excess of 10,000 mg/l, two of which, the Marquis Eaton A#1E and Sullivan Frame A#1E, have produced water with chloride levels exceeding 10,000 mg/l.

Downgradient water chemistry

Table 5 provides a brief summary of the number of sites contaminated by salts and dissolved phase hydrocarbons. Although chloride and TDS concentrations of ground water occasionally increased downgradient from the produced water pits, nine of the 13 sites studied show only minimal effects of chloride and TDS contamination. Whereas the encroachment of fluids discharged to produced water pits upon natural ground water was not readily apparent at these nine sites using historical contaminant markers, chloride and TDS, ground water was significantly impacted by volatile organic compounds from produced water pits at five sites. Four of these five sites with minimal downgradient ground water degradation from

Aluminum (Al)	5.0	mg/l
Arsenic (As)	0.1	mg/l
Barium (Ba)	1.0	mg/l
Benzene	0.01	mg/l
Benzo-a-pyrene	0.00007	mg/l
Boron (B)	0.75	mg/l
Cadmium (Cd)	0.01	mg/l
Carbon Tetrachloride	0.01	mg/l
Chloride (Cl)	250.0	mg/l
Chloroform	0.1	mg/l
Chromium (Cr)	0.05	mg/l
Cobalt (Co)	0.05	mg/l
Cooper (Cu)	1.0	mg/l
Cyanide (Cn)	0.2	mg/l
Ethylbenzene	0.75	mg/l
Ethylene dibromide (EDB)	0.0001	mg/l
Fluoride (F)	1.6	mg/l
Iron (Fe)	1.0	mg/l
Lead (Pb)	0.05	mg/l
Manganese (Mn)	0.2	mg/l
Total Mercury (Hg)	0.002	mg/l
Methylene chloride	0.1	mg/l
Molybdenum (Mo)	1.0	mg/l
Nickel (Ni)	0.2	mg/l
Nitrate (NO as N)	10.0	mg/l
PAHs: total naphthalene plus monomethylnaphthalenes	0.03	mg/l
pH	between 6 and 9	
Phenols	0.005	mg/l
Polychlorinated biphenyls (PCB's)	0.001	mg/l
Radioactivity: Combined Radium-226 and Radium-228	30.0	pCi/l
Selenium (Se)	0.05	mg/l
Silver (Ag)	0.05	mg/l
Sulfate (SO)	600.0	mg/l
Toluene	0.75	mg/l
Total Dissolved Solids (TDS)	1000	mg/l
Uranium (U)	5.0	mg/l
Vinyl chloride	0.001	mg/l
Total xylene	0.62	mg/l
Zinc (Zn)	10.0	mg/l
1,1 - dichloroethane	0.025	mg/l
1,2 - dichloroethane (EDC)	0.01	mg/l
1,1 - dichloroethylene (1,1-DCE)	0.005	mg/l
1,1,2,2 - tetrachloroethane	0.01	mg/l
1,1,2,2 - tetrachloroethylene (PCE)	0.02	mg/l
1,1,1 - trichloroethane	0.06	mg/l
1,1,2 - trichloroethane	0.01	mg/l
1,1,2 - trichloroethylene (TCE)	0.1	mg/l

Table 4 - State of New Mexico Water Quality Standards (New Mexico Water Quality Control Commission, 1989)

	HYDROCARBON IMPACT	NO HYDROCARBON IMPACT
SALT IMPACT	4	0
MINIMAL SALT IMPACT	5	4

Table 5 - Summary of Types of Contaminated Sites Studied.

chloride or TDS had BTEX in ground water at levels greatly in excess of New Mexico Water Quality Control Commission ground water quality standards. One of these sites, the Grambling A#3A, had floating product on the water table which was identified as a high quality natural gas condensate. The product on the water table at this site is probably the result of a past oil-water separator upset to the pit or a spill from the adjacent condensate storage tank as virtually no product was observed in the produced water pit.

Samples of ground water taken from the monitor wells at the remaining four sites showing minimal downgradient effects from chloride or TDS did not have any detectable concentrations of dissolved phase purgeable aromatic hydrocarbons. Possible reasons include attenuation of the volatile organics at the surface and in the vadoze zone, lack of separator discharges from producing wells which were shut in or incorrect location of monitor wells at sites as a result of the unlined pits being replaced by steel tanks. For example, though operating, the Heath Gas Comm G#1 well did not discharge during three site visits, including two full day investigations. Another well, the Marquis Eaton A#1E, had its pit replaced by a tank between the time of the initial site visit and the detailed investigation several months later. The pit was covered and its exact location was uncertain at the time of the return visit.

The four remaining sites, the Gallegos Canyon Unit #153E, Sullivan Frame A#1E, Riddle F LS#3A and Abrams L#1 have ground water downgradient from the pits contaminated with both salts and dissolved phase volatile organics. BTEX levels at these sites exceed state ground water quality standards except at the Sullivan Frame A#1E. Traces of free floating product were also present at one downgradient well on the Gallegos Canyon Unit #153E site, again probably due to oil-water separator upsets. It is interesting to note that all of sites that had downgradient ground water contaminated by TDS and chloride also had BTEX contaminated ground water.

All volumes of produced water fluids discharged to unlined pits appear to be significant when looking at infiltration of dissolved phase organics. BTEX was discovered in ground water downgradient of produced water pits with reported discharges as low as 0.05 barrels per day. Eight pits received discharges of less than one barrel per day. Of these eight, six sites showed BTEX contaminants in downgradient ground water at levels greater than New Mexico Water Quality Control Commission water quality standards.

Contamination of ground water by dissolved phase volatile organics was observed to occur at about all types of ground water depths studied. High concentrations of dissolved BTEX was present in ground water downgradient of all sites with

depths to water between 5-10 feet. Varying levels of BTEX contaminated ground water were also discovered at 66% of the sites with depths to ground water between 10-15 feet and at 60% of the sites with ground water depths ranging from 15-35 feet. One site, the Gallegos Canyon Unit F#162, with a vadoze zone thickness of 20 feet had high concentrations of dissolved BTEX contamination of ground water downgradient from the pit with a produced water discharge as low as 0.10 barrels per day.

CONCLUSIONS

In the San Juan Basin, localized contamination of shallow water table aquifers by dissolved phase volatile organics is occurring as a result of surface disposal of produced water fluids in unlined pits. These studies have shown that even small volume discharges of relatively low TDS produced water to unlined pits results in the deterioration of shallow natural ground water quality by purgeable aromatic hydrocarbons. Although numerous mechanisms exist at each site for the attenuation of volatile organics, significant BTEX contamination of ground water is still occurring.

Small volumes of produced water infiltrating through unlined

pits resulted in ground water contaminated with varying levels of dissolved phase purgeable aromatic hydrocarbons and/or salts at 70 percent of the sites studied. The analytic results show benzene, toluene, ethylbenzene and xylene in excess of New Mexico Water Quality Control Commission water quality standards at over 50 percent of the sites. Benzene, toluene, ethylbenzene and xylene alone was responsible for contaminated ground water at approximately 40 percent of the sites.

In addition to documenting the potential for ground water contamination from small volume discharges to unlined produced water pits, this study illustrates one of the problems facing regulatory agencies when developing ground water protection regulations. In order to enact regulations to prevent potential ground water contamination from an industries preexisting disposal practices, the burden of proof lies with the regulatory agency and not with the affected industry. This leaves the regulatory agency in the position of having to provide evidence that a disposal practice is currently contaminating ground water or can be reasonably foreseen to be a threat to ground water before preventing it. In contrast, if an industry is required to apply to a regulatory agency for a discharge permit, the industry would be asked to prove that the discharge would have no detrimental effect on underlying ground water thereby shifting the burden of proof

to the affected industry. Therefore, in the absence of a specific regulation an industry could be allowed to continue disposal practices that are potentially damaging to ground water until the disposal practice actually contaminates ground water.

In New Mexico, regulatory steps have been taken over the years to minimize ground water degradation from the surface disposal of large volumes of produced water. As a result of this study, it is apparent that additional measures need to be taken to further reduce the potential for contamination of ground water by unlined pits receiving small discharges of fluids in areas of shallow vulnerable ground water. This can be accomplished by replacing all existing unlined pits in shallow ground water areas with lined pits or tanks, or by connecting existing oil and gas well separators into injection well systems. Alternately, for unlined pits located in these areas, a monitoring well network should be installed and sampled periodically by the operators for aromatic and halogenated purgeable organics as well as historical contaminants such as TDS and chloride. Such a system would at least provide for the early detection of produced water encroachment on natural ground water.

APPENDIX A

ABRAMS L #1

PARAMETER	SEPARATOR	PRODUCED WATER			DOWNGRADIENT			
		PIT	HOLE 1	HOLE 2	HOLE 3	HOLE 4		
Discharge *(bbl/day)	3.0							
DTW **(ft.)		16						
Detection Limit - organics (ppb)			1	1	2	2		2
Benzene (ppb)	NS	NS	ND	ND	ND	ND	90	
Toluene (ppb)	NS	NS	ND	ND	ND	ND	ND	
Ethylbenzene (ppb)	NS	NS	ND	ND	ND	ND	ND	
Total xylenes (ppb)	NS	NS	ND	ND	ND	ND	65	
Chloride (mg/l)	NS	NS	8.9	859	6450	10530		
Sulfate (mg/l)	NS	NS	269	1520	1500	175		
TDS (mg/l)	NS	NS	1972	3853	13128	20942		

* - As Reported on San Juan Basin Vulnerable Area pit registration forms
 ** - Relative to ground surface at pit location
 ND - Not Detected
 NS - No Sample Available
 TDS - Total Dissolved Solids

BRUCE SULLIVAN COMM B #1

PARAMETER	SEPARATOR	PRODUCED WATER PIT	UPGRADIENT		DOWNGRADIENT		
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	
Discharge *(bbl/day)	0.06						
DTW **(ft.)		18					
Detection Limit - organics (ppb)			1	1	1	1	1
Benzene (ppb)	NS	NS	ND	ND	ND	ND	ND
Toluene (ppb)	NS	NS	ND	ND	ND	ND	ND
Ethylbenzene (ppb)	NS	NS	ND	ND	ND	ND	ND
Total xylenes (ppb)	NS	NS	ND	ND	ND	ND	ND
Chloride (mg/l)	NS	NS	L5	11.2	9	L5	L5
Sulfate (mg/l)	NS	NS	123	200	190	166	166
TDS (mg/l)	NS	NS	568	736	704	662	662

* - Volume average from 1986 production records

** - Relative to ground surface at pit location

L - Less than

ND - Not Detected

NS - No Sample Available

TDS - Total Dissolved Solids

GALLEGOS CANYON UNIT F #162

PARAMETER	SEPARATOR	PRODUCED WATER		UPGRADIENT		DOWNGRADIENT		FIELD	
		PIT	PIT	HOLE 1	HOLE 2	HOLE 3	HOLE 4	HOLE 4	BLANK
Discharge *(bbl/day)	0.10								
DTW **(ft.)		20							
Detection Limit - organics (ppb)	100	NS	10	10	10	10	10	1	1
Benzene (ppb)	27700	NS	ND	10600	11000	145	ND	ND	ND
Toluene (ppb)	27100	NS	ND	27	14	180	ND	ND	ND
Ethylbenzene (ppb)	670	NS	ND	925	1160	39	ND	ND	ND
Total xylenes (ppb)	6200	NS	ND	8090	10850	386	ND	ND	ND
Chloride (mg/l)	62.5	NS	L5	8.9	11	6.1	NA	NA	NA
Sulfate (mg/l)	L5	NS	115	5.0	4.8	70	NA	NA	NA
TDS (mg/l)	320	NS	444	654	688	488	NA	NA	NA

* - As reported on San Juan Vulnerable Area pit registration forms
 ** - Relative to ground surface at pit location
 L - Less than
 NA - Not Analyzed
 ND - Not Detected
 NS - No Sample Available
 TDS - Total Dissolved Solids

GALLEGOS CANYON UNIT #153 E

PARAMETER	SEPARATOR	PRODUCED WATER PIT	UPGRADIENT			DOWNGRADIENT							
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	HOLE 5	HOLE 6	HOLE 7				
Discharge *(bbl/day)	0.05												
DTW **(ft.)		9											
Detection Limit - organics (ppb)			1	100	100	2	4	1	2				
Benzene (ppb)	NS	NS	ND	14000	2400	ND	ND	ND	ND	ND	ND	ND	ND
Toluene (ppb)	NS	NS	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene (ppb)	NS	NS	ND	280	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total xylenes (ppb)	NS	NS	ND	4590	4060	ND	ND	ND	ND	ND	ND	ND	ND
Chloride (mg/l)	NS	NS	108	1336	1202	106	269	117	670				
Sulfate (mg/l)	NS	NS	3572	3488	12146	3041	4157	3104	29853				
TDS (mg/l)	NS	NS	5860	8218	11178	4788	7290	4726	44726				

* - As Reported on San Juan Basin Vulnerable Area pit registration forms

** - Relative to ground surface at pit location

NA - Not Analyzed

ND - Not Detected

NS - No Sample Available

TDS - Total Dissolved Solids

GERK B #1M

PARAMETER	SEPARATOR	PRODUCED WATER PIT	UPGRADIENT			DOWNGRADIENT			FIELD
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	HOLE 4	BLANK	
Discharge *(bbl/day)	0.26								
DTW *(ft.)		15							
Detection Limit - organics (ppb)	50		1	1	1	1	1	1	1
Benzene (ppb)	13900	NS	ND	ND	ND	ND	ND	ND	ND
Toluene (ppb)	14850	NS	ND	ND	ND	ND	ND	ND	ND
Ethylbenzene (ppb)	450	NS	ND	ND	ND	ND	ND	ND	ND
Total xylenes (ppb)	6215	NS	ND	ND	ND	ND	ND	ND	ND
Chloride (mg/l)	435	NS	23	NS	NS	19.5	36.3	NA	NA
Sulfate (mg/l)	L5	NS	1710	NS	NS	1705	1790	NA	NA
TDS (mg/l)	960	NS	3260	NS	NS	2666	2796	NA	NA

* - As Reported on San Juan Basin Vulnerable Area pit registration forms

** - Relative to ground surface at pit location

L - Less than

NA - Not Analyzed

ND - Not Detected

NS - No Sample Available

TDS - Total Dissolved Solids

GRAMBLING A #3A

PARAMETER	SEPARATOR	PRODUCED WATER PIT	UPGRADIENT		DOWNGRADIENT			FIELD	
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	BLANK		
Discharge *(bbl/day)	0.21								
DTW **(ft.)		15							
Detection Limit - organics (ppb)	NS	50	1	100	200	1	1	1	
Benzene (ppb)	NS	11600	2	12400	2400	1820		ND	
Toluene (ppb)	NS	18200	3	25900	10620	3		ND	
Ethylbenzene (ppb)	NS	465	2	1950	1100	34		ND	
Total xylenes (ppb)	NS	5090	7	23030	13900	189		ND	
Chloride (mg/l)	NS	1290	22	221	23.5	NS		L5	
Sulfate (mg/l)	NS	198	2800	2575	2750	NS		L5	
TDS (mg/l)	NS	3146	4630	5184	4807	NS		146	

* - Average Volume Determined From 1986 Production Records

** - Relative to ground surface at pit location

L - Less than

ND - Not Detected

NS - No Sample Available

TDS - Total Dissolved Solids

HEATH GAS COMM C #1

PARAMETER	SEPARATOR		PRODUCED WATER		UPGRADIENT		DOWNGRADIENT	
	SEPARATOR	SEPARATOR	PIT	PIT	HOLE 1	HOLE 1	HOLE 2	HOLE 2
<u>Discharge *(bbl/day)</u>	1.0 (Well operating but no discharges observed during 3 site visits)							
DTW **(ft.)			20					
Detection Limit - organics (ppb)					1	1	1	1
Benzene (ppb)	NS	NS	NS	NS	ND	ND	ND	ND
Toluene (ppb)	NS	NS	NS	NS	ND	ND	ND	ND
Ethylbenzene (ppb)	NS	NS	NS	NS	ND	ND	ND	ND
Total xylenes (ppb)	NS	NS	NS	NS	ND	ND	ND	ND
Chloride (mg/l)	NS	NS	NS	NS	47	47	24.7	24.7
Sulfate (mg/l)	NS	NS	NS	NS	1240	1240	921	921
TDS (mg/l)	NS	NS	NS	NS	2232	2232	1750	1750

* - As Reported on San Juan Basin Vulnerable Area pit registration forms
 ** - Relative to ground surface at pit location
 ND - Not Detected
 NS - No Sample Available
 TDS - Total Dissolved Solids

MARQUIS EATON A #1E

PARAMETER	SEPARATOR	PRODUCED WATER TANK	UPGRADIENT		DOWNGRADIENT			FIELD BLANK
			HOLE 1	HOLE 2	HOLE 3	HOLE 4		
Discharge *(bbl/day)	1.5							
DTW **(ft.)		13						
Detection Limit - organics (ppb)		10	1	1	1	1	1	1
Benzene (ppb)	NS	4200	ND	ND	ND	ND	ND	ND
Toluene (ppb)	NS	4870	ND	ND	ND	ND	ND	ND
Ethylbenzene (ppb)	NS	220	ND	ND	ND	ND	ND	ND
Total xylenes (ppb)	NS	2205	ND	ND	ND	ND	ND	ND
Chloride (mg/l)	NS	13900	443	916	475	347	NA	NA
Sulfate (mg/l)	NS	L10	3430	3270	4400	3450	NA	NA
TDS (mg/l)	NS	27100	6536	6794	7906	6806	NA	NA

* - Volume average determined from 1986 production records.

** - Relative to ground surface at pit location

L - Less than

NA - Not Analyzed

ND - Not Detected

NS - No Sample Available

TDS - Total Dissolved Solids

RIDDLE F LS #3A

PARAMETER	SEPARATOR	PRODUCED WATER PIT	UPGRADIENT UPGRADIENT			DOWNGRADIENT			BLOW-DOWN PIT	LARGO WASH
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	HOLE 5			
Discharge *(bbl/day)	0.64									
DTW **(ft.)		14.3								
Detection Limit - organics (ppb)	25		1	10	1	1	1	1	1	1
Benzene (ppb)	14150	NS	ND	278	ND	ND	ND	ND	3	ND
Toluene (ppb)	9375	NS	ND	ND	ND	ND	ND	ND	5	ND
Ethylbenzene (ppb)	115	NS	ND	209	ND	ND	ND	ND	TR	ND
Total xylenes (ppb)	1295	NS	ND	ND	ND	ND	ND	ND	2	ND
Chloride (mg/l)	6925	NS	19.8	2400	1225	32.5	1295	4.6	5.4	
Sulfide (mg/l)	95	NS	4925	1690	4850	3525	6775	3020	1955	
TDS (mg/l)	13926	NS	7802	7828	8478	5770	11100	4902	3370	

* - Volume Average From 1986 Production Records
 ** - Relative to ground surface at pit location
 ND - Not Detected
 NS - No Sample Available
 TDS - Total Dissolved Solids
 TR - Trace (detected at a level below detection limit)

SULLIVAN FRAME A #1 E

PARAMETER	SEPARATOR	PRODUCED WATER TANK	UPGRADIENT		DOWNGRAIENT			
			HOLE 1	HOLE 2	HOLE 3	HOLE 4		
Discharge *(bbl/day)	2.0							
DTW **(ft.)		13.5						
Detection Limit - organics (ppb)		5	1	1	1	1	1	1
Benzene (ppb)	NS	15	3	4	ND	ND	ND	ND
Toluene (ppb)	NS	21	2	ND	ND	ND	ND	ND
Ethylbenzene (ppb)	NS	ND	TR	13	ND	ND	ND	ND
Total xylenes (ppb)	NS	37	1	59	ND	ND	ND	ND
Chloride (mg/l)	NS	14400	4	1480	173	15		
Sulfate (mg/l)	NS	L20	227	620	1300	748		
TDS (mg/l)	NS	25878	832	4192	2764	1684		

* - As reported on San Juan Vulnerable Area pit registration forms

** - Relative to ground surface at pit location

L - Less than

ND - Not Detected

NS - No Sample Available

TDS - Total Dissolved Solids

TR - Trace (detected at a level below detection limit)

TAPP COMM 5

PARAMETER	SEPAKATOR	PRODUCED WATER		UPGRADIENT		DOWNGRADIENT		FIELD	CARRIZO
		PIT		HOLE 1		HOLE 2	HOLE 3		
Discharge *(bb1/day)	1.0								
DTW **(ft.)		31.5							
Detection Limit - organics (ppb)	50		1	5	5	5	5	1	5
Benzene (ppb)	28000	NS	ND	ND	ND	ND	ND	ND	ND
Toluene (ppb)	96000	NS	4	10	14	14	14	TR	TR
Ethylbenzene (ppb)	1900	NS	ND	ND	ND	ND	ND	ND	ND
Total xylenes (ppb)	29500	NS	ND	ND	ND	TR	TR	ND	ND
Chloride (mg/l)	136	NS	L5	L5	L5	L5	L5	L5	23
Sulfate (mg/l)	2.7	NS	1805	1720	1870	1870	1870	94	3550
TDS (mg/l)	382	NS	2996	2888	2770	2770	302	302	6220

* - As reported on San Juan Basin Vulnerable Area pit registration forms

** - Relative to ground surface at pit location

L - Less than

ND - Not Detected

NS - No Sample Available

TR - Trace (detected level below stated detection limit)

TDS - Total Dissolved Solids

VALDEZ A #1

PARAMETER	SEPARATOR	PRODUCED WATER TANK	UPGRADIENT			DOWNGRADIENT									
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	HOLE 5	HOLE 6							
Discharge *(bbl/day)	N 0.5														
DTW **(ft.)		6													
Detection Limit - organics (ppb)			5	5	5	2.5	10	5							
Benzene (ppb)	NS	NS	ND	270	310	ND	290	18							
Toluene (ppb)	NS	NS	ND	ND	ND	ND	ND	ND							
Ethylbenzene (ppb)	NS	NS	ND	160	25	ND	1000	ND							
Total xylenenes (ppb)	NS	NS	ND	2340	880	ND	18300	392							
Chloride (mg/l)	NS	NS	L5	14	NS	NS	NS	NS							
Sulfate (mg/l)	NS	NS	117	120	NS	NS	NS	NS							
TDS (mg/l)	NS	NS	466	506	NS	NS	NS	NS							

* - Volume Average From 1988 Production Records
 ** - Relative to ground surface at pit location
 L - Less than
 ND - Not Detected
 NS - Not Sample Available
 TDS - Total Dissolved Solids

VALDEZ A #1E

PARAMETER	SEPARATOR	PRODUCED WATER TANK	UPGRADIENT		DOWNGRADIENT		
			HOLE 1	HOLE 2	HOLE 3	HOLE 4	
Discharge *(bbl/day)	0.45						
DTW **(ft.)		13					
Detection Limit - organics (ppb)	100	50	1	1	1	1	1
Benzene (ppb)	26300	6350	ND	ND	ND	ND	2400
Toluene (ppb)	62900	21800	ND	ND	ND	ND	7200
Ethylbenzene (ppb)	2400	425	ND	ND	ND	ND	920
Total xylenes (ppb)	26800	5850	ND	ND	ND	ND	7750
Chloride (mg/l)	NS	5950	75.6	6.15	21.5	6.15	695
Sulfate (mg/l)	NS	42	2525	1445	1463	1463	605
TDS (mg/l)	NS	10918	4098	2556	2634	2556	2572

* - Average volume determined from 1986 production records

** - Relative to ground surface at pit location

ND - Not Detected

NS - No Sampled Available

TDS - Total Dissolved Solids

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