SECTION 3: ANALYSIS OF OHIO BRINE CONTAMINANT DATA AND RECOMMENDATIONS

A primary goal of this report has been to compare analyses of chemical constituents in brine with existing regulatory status of these chemical parameters. From this exercise, a subset of brine chemicals which pose relatively greater environmental risks could be identified. Sections 1 and 2 describe the health impacts, environmental behaviors, and water quality standards for inorganic and organic brine contaminants, respectively.

Two reports were supplied for characterization of brine-related contaminants:

1. "Analysis for Aromatic Hydrocarbons in Oil Field Brines: A Preliminary Report," (1984) by the Michigan Department of Natural Resources, Geological Survey Division, Oil Field Brine Sampling Committee. Referred to as MI Report in this text.
2. "Preliminary Analyses of Ohio Oilfield Produced Brines for Selected Heavy Metals and Aromatic Hydrocarbons," (1986) by D.R.Christ and G.Hudak of the Ohio Department of Natural Resources, Division of Oil and Gas, Underground Injection Control Section. Referred to as ODNR Report in this text.

In this section data are extracted from these reports and evaluated for the potential risks posed by selected brine constituents. This portion of the report has been subdivided in two units: general evaluation; and prioritization of contaminants with potential adverse impact on water quality.

I. <u>General Evaluation.</u>

This general evaluation examines the ODNR Report and MI Report for their ability to answer the question, "Do these samples and chemical analyses of brine constitiuents represent the actual or potential chemical risks to surface and groundwater supplies?" Two foci of attention are investigated: sampling strategy; and analytical procedures.

A. Sampling Strategy.

Brines can be expected to vary in chemical quality independent of human interaction over a geographical area (county to county basis); between geological formations; and even within geological formation. Such variation is demonstrated across all chemical parameters in the MI and ODNR Reports. In addition, the MI Report indicates that even within a single geological formation at the same geographic site, samples collected at subsequent dates may not correlate well with previous samples (MI Report: Reed City Formation; Crimmins #4; Montcalm County).

Significant for evaluating the Ohio brine disposal problem is the fact that no attempt was made to include all wells suppling brines for road spreading operations. Both the ODNR and MI Reports indicated that the limited samples numbers precluded the ability to make statistically significant comparisons between the individual formations and individual contaminant constituents.

Such natural variability in chemical quality can be enhanced by sampling procedures under human control. This possibility can become much more significant for organic contaminants than for inorganic contaminants. Benzene, ethylbenzene, toluene, xylenes, polynuclear aromatic hydrocarbons, phenolic compounds and other organics are subject to complex interactions with the environment and each other, thereby rendering predictions of fate more tenuous. In particular, volatilization, adsorption onto humic and fulvic soil constituents, chemical alteration (hydrolysis and oxidation) and biological alteration (hydrolysis, oxidation and conjugation) can radically alter the apparent concentration in a sample, thereby masking the true environmental concentration. The physico-chemical properties of six organics are presented in summary reports appended in section 2.

At a particular site, concentrations of organics are likely to vary widely according to where the sample was collected. The ODNR Report presented data on benzene concentrations in twenty five samples. For the highest concentration samples (5000 ug/l or greater), four of the five samples were collected directly from wellheads. For the six lowest concentration samples (300 ug/l or less), none were collected from a wellhead.

A parsimonious hypothesis on benzene in brine would be that compared to wellhead levels its concentration would decrease during surface tank or concrete vault storage. This rate of decrease would vary directly as functions of: duration of storage; surface area of brine contact with an atmosphere; volume of surface atmosphere; depth of brine storage volume; rate of aeration or mixing of storage tank; storage temperature; presence of acclimated microbial populations which can utilize benzene as a source of organic nutrients in storage facility. Such hypotheses may not be appropriate for other organics. Phenolic compounds have relatively low volatility; chemical and biological alterations during surface storage can convert benzene and xylene into phenol and dimethylphenol, respectively, thereby potentially increasing concentrations of these during storage.

Similar influences on measured concentrations can be extrapolated from the macro-storage situation of bulk brine volumes to the micro-storage situation of brine samples collected for chemical analyses. While specific sampling protocols are not presented for each report, the ODNR Report considers the importance of: collection vial material composition; storage temperature; aeration during filling; and completely filling the vial with brine. Despite efforts to insure sample homogeneity, a thin film of oil was observed on four wellhead samples. While the ODNR considered this as contamination, no evaluation was presented to assess why these wellhead samples would not be considered representative of a disposal brine.

B. Analytical Procedures.

The analytical procedures employed in any environmental survey projects need to be evaluated with a high degree of scientific scrutiny in order to insure that the concentration values reported for a sample accurately and precisely reflect the actual concentration of the chemical parameter measured.

For both the ODNR and the MI Reports, detailed procedures for the chemical analyses were not reported.

Problems were mentioned with specific chemical analyses in both reports. For example, the MI Report considered that the presence of aliphatic (long-chain) hydrocarbons interfered with the measurement of benzene in two samples. Such compounds may also have interfered with the analyses of polynuclear aromatic hydrocarbons and phenolic compounds. Aliphatic hydrocarbons were quantified and identified in two Ohio samples, but no indication of interference ith benzene quantification was discussed.

Similarly, the MI Report discusses the problem of high chloride concentrations in brine causing higher detection limits for particular inorganic constituents (Al, Ba, Ti, and V). The ODNR Report also discusses the high detection limits for barium due to chloride interference. The detection limits for inorganic contaminants are not presented in the ODNR Report, yet some presented result appear confusing. For example, in Table 2 (ODNR Report) for barium the detection limit for samples #6 through #17 is less than 3 milligrams per liter (mg/l), yet for sample #18 the measured value is 2 mg/l. For the same data set, samples #19 through #27 seem to have a much lower limit of detection (less than 0.2 mg/l). In an appended table to the 1986 report barium values for eleven samples are recorded as less than 100 mg/l.

Recommended procedures for these parameters should include in addition to the target samples, quality control samples such as field blanks, duplicates and spiked matrices.

Integrating the potential problems inherent with the sampling strategies and the analytical difficulties of chemical identification and quantification in brines, it can be concluded that the data presented in the two reports represent neither a best nor a worst case scenario for estimating potential risks posed by brine contaminants.

II. <u>Prioritization of Brine Contaminants.</u>

After understanding and accepting the caveats about the extrapolation of the MI and ODNR reports to represent 'typical' disposal brines, it is possible to examine the data in conjunction with the standards reported in the previous sections. Dividing measured concentrations by the water quality standards for that individual chemical parameter can generate dilution factors. The dilution factor represents the number of equal volumes of clean, contaminant-free drinking water which would be necessary to dilute the brine sample to drinking water quality for that chemical parameter.

The average concentrations for selected brine contaminants reported or calculated from the available data in the MI and ODNR Reports are presented in Table 3.

Table 3. Average Concentrations of Selected Contaminant in Brines and Dilutions Necessary to Achieve Drinking Water Quality Standards.

Chemical (Locality)	Average Concentration (ug/l)	Standard* (ug/l)	Dilution Factor+
Benzene (MI)	1131	0.67	1688
Benzene (OH)	2000	0.67	2985
Cl (Mi)	177,000,000	250,000	708
Cl (OH)	172,730,000	250,000	691
Cr (OH)	1591	50	32
Cr (MI)	Below Detection for Most Samples		
Mn (OH)	41,118	50	822
Mn (MI)	Not Examined in Most Samples		
Na (Mi)	56,800,000	20,000	2840
Na (OH)	68,909,000	20,000	3445
Ni (OH)	1373	150	9
Ni (MI)	Below Detection for Most Samples		
Pb (MI)	531	50	11
Pb (OH)	3000	50	60
Zn (OH)	1482	5000	0.3
Zn (MI)	Below Detection for Most Samples		

Average concentration values derived from:

"Analysis for Aromatic Hydrocarbons in Oil Field Brines: A Preliminary Report," (1984) by the Michigan Department of Natural Resources, Geological Survey Division, Oil Field Brine Sampling Committee.

"Preliminary Analyses of Ohio Oilfield Produced Brines for Selected Heavy Metals and Aromatic Hydrocarbons," (1986) by D.R.Christ and G.Hudak of the Ohio Department of Natural Resources, Division of Oil and Gas, Underground Injection Control Section.

* Standards can represent primary federal drinking water standards, secondary standards, or state standards.

+ Dilution Factor = volume of contaminant-free water required to dilute a unit volume of brine contaminated water sample to achieve drinking water quality.

Primary drinking water standards, secondary standards, or health guidance levels are also recorded, and the appropriate dilution factors are calculated and tabularized. Table 3 demonstrates that dilution of average sodium levels in either Michigan or Ohio brines to recommended drinking levels will also result in dilution of all other chemical parameters to their recommended safe drinking water levels. Benzene and chloride average dilution factors approached the sodium in terms of relative magnitude of environmental risk.

The maximum concentrations of selected contaminants in brines from the Michigan and Ohio Reports were tabulated along with the water quality recommendations for each parameter. Dilution factors for these maximum contaminant levels were calculated and are presented in Table 4. In this table, benzene was demonstrated to be the contaminant requiring the highest dilution volume (10,000 to almost 15,000) to achieve recommended drinking water quality. Another way of considering such an impact would be that 1000 gallons of this high benzene-contaminated Ohio brine evenly dispersed in 14 million gallons of groundwater would render that groundwater not recommended for human consumption.

Given the need to expand the sampling program for brine disposal problems, yet mindful of funding limitations for chemical analyses, I would recommend that:

1. Inorganic analyses be prioritized to focus sodium (Na) and chloride (Cl). These chemicals represent by weight the most important brine contaminants. Analytical techniques for detecting and quantifying these parameters in the range of 10% of the secondary standards or health guidance levels would provide a powerful tool for estimating brine disposal impact upon drinking water supplies.
2. Organic analyses be prioritized to focus initially upon benzene. Measurable quantities of benzene were found in all Michigan Oilfield brines and other brine samples. Benzene was detected in all Ohio brine samples. Benzene poses high risks as a toxic substance, therefore drinking water quality recommendations are very restrictive.
3. Benzene analytical procedures in brine needs to be thoroughly examined and rigorously defined to insure that the sampling protocol is a high contaminant potential sample. Limits of benzene detection in various matrices need to be evaluated for brine samples and for dilution series.
4. The recommended water quality standards for polynuclear aromatic hydrocarbons and phenolic compounds warrents investigation of these compound classes for identification and quantification in brines. Analytical procedures similar to those devised for benzene analysis need to be developed. With answers to these analytical questions, polynuclear aromatic hydrocarbons and phenolic compounds may need to be added to benzene as standards monitoring parameters in brine disposal problems.

Table 4. Maximum Concentrations of Selected Contaminants in Brines and Dilutions Necessary to Achieve Drinking Water Quality Standards.

Chemical (Locality)	Maximum Concentration (ug/l)	Standard* (ug/l)	Dilution Factor+
Benzene (MI)	6,900	0.67	10299
Benzene (OH)	10,000	0.67	14925
Ethylbenzene (MI)	470	1360	0.4
Alkylbenzene (OH)	2190	1360	1.6
Toluene (MI)	3300	343	9.6
Toluene (OH)	29,000	343	84.5
Xylenes (MI)	1400	620	2.3
Xylenes (OH)	3440	620	5.5
Cl (MI)	207,000,000	250,000	828
Cl (OH)	180,000,000	250,000	720
Cr (MI)	650	50	13
Cr (OH)	2200	50	44
Mn (MI)	15,000	50	300
Mn (OH)	69,000	50	1380
Na (MI)	96,000,000	20,000	4800
Na (OH)	79,000,000	20,000	3950
Ni (MI)	700	150	4.7
Ni (OH)	1900	150	12.7
Pb (MI)	800	50	40
Pb (OH)	7000	50	140
Zn (MI)	6000	5000	1.2
Zn (OH)	2200	5000	0.4

Maximum concentration values derived from:

"Analysis for Aromatic Hydrocarbons in Oil Field Brines: A Preliminary Report," (1984) by the Michigan Department of Natural Resources, Geological Survey Division, Oil Field Brine Sampling Committee.

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4438 Mobile Dr. #314
Columbus, OH 43220
November 17, 1986

Julie Weatherington-Rice
Ohio Oil and Gas Commission Committee
298 W. New England Ave.
Worthington, OH 43085

Dear Julie,

Enclosed please find a copy of my analysis of Ohio brine contaminants and their potential impact. My report is divided into three sections:

1. Summary evaluation of water quality standards for inorganic elements and compounds in Ohio brines.
   Available summarized data concerning individual elements, for which standards have been promulgated, are appended. Data are derived from the Wisconsin Department of Health and Social Services (1985), "Public Health Related Groundwater Standards - Summary of Scientific Support Documentation for NR 140.10."

2. Summary evaluation of water quality standards for organic compounds in Ohio brines (benzene, ethylbenzene, toluene, and xylenes).
   Available summarized data for these are appended. Data are derived from the Wisconsin Department of Health and Social Services (1985 & 1986), and from the Harry G. Armstrong Aerospace Medical Research Laboratory at Wright-Patterson Air Force Base, Ohio (1985), "The Installation Restoration Program (IRP) Toxicology Guide."
   Polynuclear aromatic hydrocarbons and phenolic compounds are major classes of organic chemicals which were examined in several Michigan brine samples, and they can be expected to occur in Ohio brines. Therefore, I have added the IRP summary environmental toxicology data for naphthalene and dimethylphenol, which contain generic information on standards for polynuclear aromatics and phenolic compounds respectively.

3. Analysis of the Ohio brine contaminant data with suggestions for prioritization of chemicals with human health concerns.
   Two brine contaminant reports from the Ohio Department of Natural Resources (1986) and the Michigan Department of Natural Resources (1984) are evaluated and criticized. Average and maximum concentrations of selected contaminants are rated according to their suggested standards for potential risk in surface and groundwater contamination.

I beleive that the enclosed report is self explanatory, and that it fulfills the tasks as outlined in my original estimate for this project. Should there be any need for clarification or additional information, please do not hesitate to contact me. Three working days were expended for this report and my charge to the commission is $1200.

Sincerely,

Gerald V. Poje

Gerald V. Poje, Ph.D.
614-459-4250

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