Ultrapure Water Testing at the Point of Use

by

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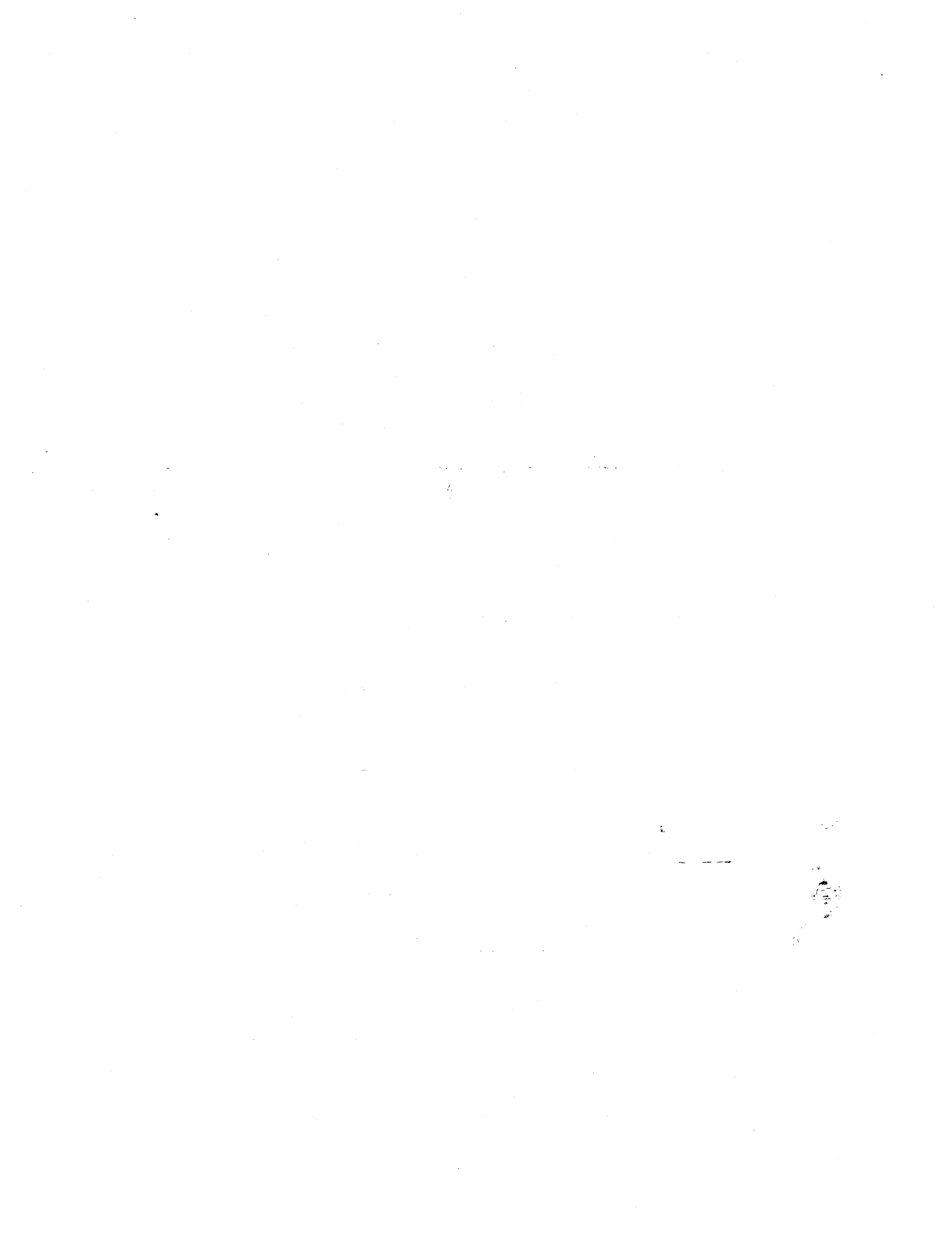

ULTRAPURE WATER TESTING AT THE POINT OF USE

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Introduction

Ultrapure water is recognized as the "bloodstream" in the manufacturing of semiconductor devices and products. Over the past decade, tremendous improvement has been made in both the making and the testing of ultrapure water. Specifications for ultrapure water at the point of distribution (final filter) have been published and adopted by the industry for years. Analytical techniques and instruments have become more and more complicated, and detection sensitivity levels were forced to go lower and lower, as the device geometry became more compact. However, most of the efforts for improving ultrapure water quality are done at the plant and compliance is checked at the final filter. Comparatively little attention has been given to the point of use (POU). The reasons are probably due to the general assumption that, except for bacteria content, water quality does not change between the final filter and POU, and to the sampling limitations at the POU. In recent years, the industry has come to realize that the quality of water changes between the final filter and wet stations due to such things as the design of equipment, chemicals used around the equipment, and other environmental factors. These realizations have resulted in a demand for more POU testing.

Techniques of Point of Use (POU) Sampling

As mentioned, one of the major limitations in POU testing today is being able to collect an uncontaminated representative sample from equipment such as a dump rinser or spin dryer. To solve the problem, a study was done using a sampling device developed for pure chemicals at the POU (Figure 1). This sampling device is composed of a polypropylene syringe-type pump which attaches to a pre-cleaned teflon sample bottle. The bottle is filled through a pre-cleaned Teflon tube. The sample itself never is exposed to either atmospheric air or the polypropylene syringe-type pump. The unit is hand-operated to create a vacuum in the bottle which causes the liquid (in this case, water) to be drawn out of the tank and into the bottle.

Since the device was tested only for chemicals where the measurement for ions and metals are at the ppb level, it was necessary to test it for ppt level testing where much of the analysis for pure water is done. Initially, the device was rinsed several times with the water to be tested, and then a sample was taken. Subsequent tests revealed the presence of sodium, zinc, magnesium and sulfate in quantities of 20 - 60 ppt that came from the sampling device. Consequently, a more stringent cleaning process had to be developed. The more stringent cleaning procedure resulted in no change in the measurements between the water that did or did not pass through the device, except possibly for TOC (see Table 1). Since there was no measurable fluoride ion found,

it is believed that the difference in TOC was caused during sample transfer to the TOC unit rather than a contaminant from the device. The increase in TOC ranged from 1 - 2 ppb. No metal contamination was found within the limits of measurement by ICP-MS (see Table 2).

Satisfying ourselves that the Pure Liquid Sampler worked for pure water sampling, a program was outlined for testing dump rinse sinks only. Since the advent of using this technique for sampling POU sinks, over 500 samples have been analyzed. However, for this particular study approximately 100 sinks were selected where both the POU and FF water could be sampled and analyzed at the same time and where our personnel could do all of the sampling. Not all 100 sinks were tested for every parameter as can be seen in the following graphs of results.

Results

Figures 2 - 14 are histograms of the accumulated results. The analysis done included TOC, bacteria, dissolved silica, optical particle count, ionic concentrations of alkalies and anions, and trace metals. The equipment used was the Anatel and/or the O.I. Corporation TOC, Millipore Culturing method at 28°C, Turner UV-vis spectrophotometer, optical microscopy using a Leitz Metaloplan microscope, Dionex dual columns ion chromatography, and an inductively coupled plasma-mass spectrometer, respectively. The x-axis represents the concentration, and the y-axis the percentage of samples that were found at that concentration level. Table III represents a summary of the quality of the water at the final filter. It is readily seen that all systems tested were producing

a high quality of pure water.

TOC (Figure 2) - As can be seen, of the 100 samples tested only 11% contained the same level of organics at the POU as at the final filter. The variation of 2 ppb contribution of organic contaminations from the sampling device was negligible when compared to the large differences in the TOC found in the POU samples. While the requirement for the 16M+ DRAM in 1991 called for TOC levels of 1 to 5 ppb[1], 89% of the water at the dump rinser did not even achieve a goal of 20 ppb.

Bacteria (Figure 3) - Bacteria has always been thought of as the most difficult to control contaminants due to its ability to multiply, especially in the "deadleg" areas. Surprisingly, among the samples tested, as many as 41% of the samples had bacteria counts similar to those found in the final filter water. This is not to say that bacteria is less of a problem since more than 50% of the samples still exceeded the final filter water's limit. Also, the bacteria counts represented only those found by a cultured count. The total bacteria counts may be much higher even though the culture counts are comparable to the final filter water.[2] However, in this series of tests using a culturing procedure, increases in bacteria did not appear to be significant.

Dissolved SiO_2 (Figure 4) - Of all the parameters tested, dissolved SiO_2 appears to be the least problem. In 94% of the samples that were tested, the concentrations were as good as the water in the

final filters. This may be due to the fact that there is little in the piping system that can add SiO_2 to the water. However, we did expect to see silica as residual from the wafers, but instead found no measurable amount in the POU water at a 3 ppb sensitivity level.

A lower detection of 0.1 ppb is currently available, but it was not used during this study. A study using the lower level analysis may give a different picture. Also, silica can exist in a colloidal form which was not measured in this study. A broader evaluation of silica at a lower concentration level may be meaningful, but to the 3 ppb level, no difference between the FF and POU water was found.

<u>Optical Particle (Figure 5)</u> - This test serves as a qualitative one only and at best is only good for determining large particle (>1.0μ) contamination in water baths. Almost all of today's semiconductor filtration systems remove particles down to 0.1 microns or better. Particles greater than 1 micron should not exist in any ultrapure water today. Their presence would indicate a gross contamination which may occur if caused by environmental contamination. Measuring particles accurately at the POU remains a testing challenge today. It was consequently surprising to find so many sinks that had a considerable quantity of particles greater than 1 micron in size. These particles did not come from the bottles or the tubing in the sampling device. This device has been used often to collect FF water samples for an optical 0.5 micron counter evaluation without detection of any significant number of particles.

Ions (Figures 6 to 14) - 62 samples were analyzed for ionic impurities. It was unexpected to find that only 25% of the samples were contaminated with sodium levels greater than 0.2 ppb. There are only a small percentage of samples contaminated with ammonium and potassium. The most abundant contaminating ion found was sulfate. More than 90% of the samples were contaminated with sulfate, 13% of which measured an increase of 10 - 100 times the sulfate found at the FF, and 6% of the samples were more than 100 times higher in concentration than the final filter water. This phenomenon coincides with the high amount of leachable sulfate measured on wafer surface.[5] Chloride was also found to be present in significant quantities. More than 70% of the samples were contaminated to some extent. Nitrate, nitrite, phosphate, and bromide were not found to be significant contaminants at the POU.

Trace Metals Only a few POU sites were tested up to the time when this paper was written. However, the data showed a slight increase in the amount of zinc, barium, magnesium and aluminum. There was not enough data collected however to do any statistical evaluation.

Conclusion

The invention of the sampler has provided a method for collecting samples at the POU. It permits monitoring for all the same parameters as the final filter except for submicron particles. Improvement and development of a sampling device for submicron

particle measurement is still needed.

As shown in the data presented, it is critical to monitor the POU, for specific contaminants but not necessarily in the same detailed way the FF water is monitored. Specifically, one needs to measure TOC, bacteria, particles, anions and possibly metals. It is important to note that this POU study was done only on dump rinsers, and is only an overview on the water quality for this particular type of equipment. Additional evaluation of other POU equipment such as spin rinser dryers, processing tools or nozzles is needed if the source and level of contamination to wafers is to be identified. The results certainly illustrate that ultrapure water quality is not just a facility's responsibility. In order to meet the demand and challenge of today's advanced semiconductor technologies, joint effort between the facility and fab personnel is needed to control and improve the quality of ultrapure water that is actually used on the wafer. This seems especially important for rinsing wafers free of anions such as chloride and sulfate.

References

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Table I

RESULTS OF SAMPLING DEVICE TESTS

	DL ppb	WATER QUALITY Without Device	With Device
TOC	5	25	27
Dissolved SiO_2	0.25	0.40	0.40
Optical Particle (Particle/L	500	<500	<500
Ions:			
F	0.1	ND*	ND
Cl	0.05	ND	ND
NO_2	0.05	ND	ND
HPO_4	0.1	ND	ND
Br	0.1	ND	ND
NO_3	0.1	ND	ND
SO_4	0.1	ND	ND
Li	0.05	ND	ND
Na	0.05	ND	ND
NH_4	0.1	ND	ND
K	0.1	ND	ND
Mg	0.05	ND	ND
Ca	0.05	ND	ND

*ND = NON DETECTED.

TABLE II

RESULTS FROM TESTING SAMPLING DEVICE FOR METALS

ELEMENT	DL ppb	ELEMENT	DL ppb	ELEMENT	DL ppb
Aluminum	0.05	Lutetium	0.01	Thulium	0.01
Antimony	0.02	Magnesium	0.02	Tin	0.02
Arsenic	0.2	Manganese	0.03	Titanium	0.05
Barium	0.01	Mercury	0.05	Tungsten	0.02
Beryllium	0.04	Molybdenum	0.05	Uranium	0.02
Bismuth	0.04	Neodymium	0.02	Vanadium	0.03
Boron	0.5	Nickel	0.05	Ytterbium	0.03
Cadmium	0.03	Niobium	0.02	Yttrium	0.02
Calcium	3	Osmium	0.02	Zinc	0.06
Cerium	0.01	Palladium	0.06	Zirconium	0.05
Cesium	0.02	Platinum	0.08		
Chromium	0.03	Potassium	5		
Cobalt	0.02	Praseodymium	0.01		
Copper	0.05	Rhenium	0.06		
Dysprosium	0.04	Rhodium	0.02		
Erbium	0.02	Rubidium	0.01		
Europium	0.02	Ruthenium	0.05		
Gadolinium	0.04	Samarium	0.04		
Gallium	0.04	Scandium	0.2		
Germanium	0.05	Selenium	7		
Gold	0.05	Silicon	50		
Hafnium	0.03	Silver	0.03		
Holmium	0.01	Sodium	0.06		
Indium	0.02	Strontium	0.01		
Iridium	0.06	Tantalium	0.02		
Iron	0.1	Tellurium	0.04		
Lanthanum	0.01	Terbium	0.02		
Lead	0.05	Thallium	0.05		
Lithium	0.03	Thorium	0.02		

DL = Detection limit.
* = Not detected above the detection limit.

Table III

Final filter water analyzed at time of sample collection of the dump rinsers.

	Concentration Range in PPB
TOC	5 -20
Dissolved SiO_2	<3 - 3
Optical Particle (Particles/L)	<500 - 500
Bacteria (Colonies/100 mL)	<1 - 5
Ions:	
Cl	<0.05 - 0.1
NO_2	<0.05 - 0.1
Br	<0.1 - 0.1
HPO_4	<0.1 - 0.1
NO_3	<0.1 - 0.1
SO_4	<0.1 - 0.1
Na	<0.05 - 0.2
NH_4	<0.1 - 0.1
K	<0.1 - 0.1

Trace metals: all below detection limits (see table I).

Pure Liquid Sampler *

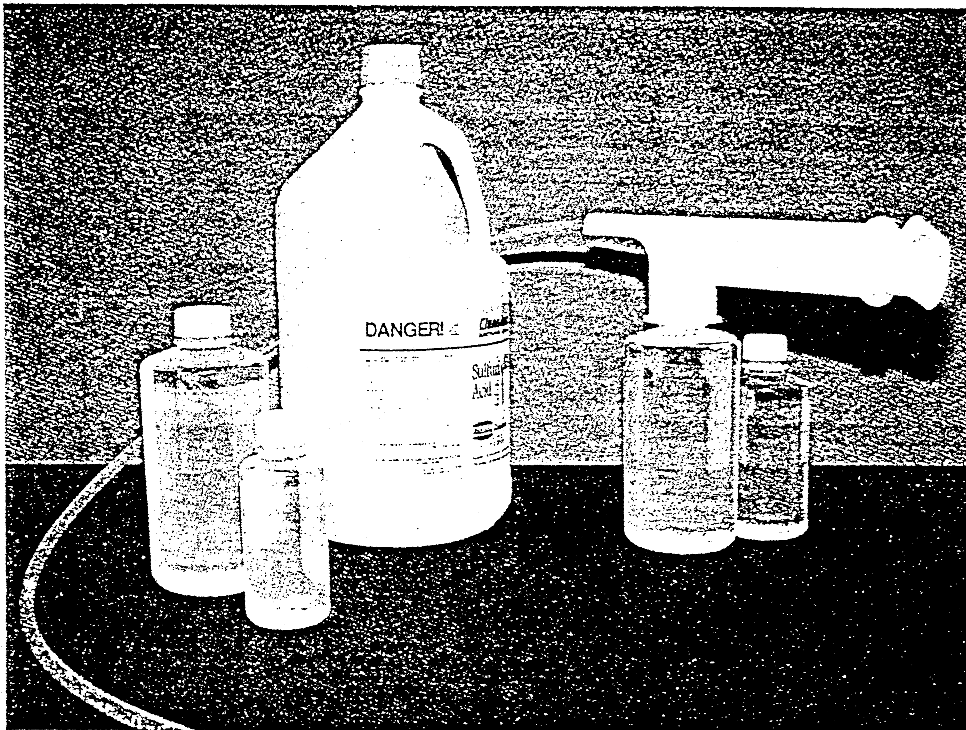

Fig. 1

* Invented and patented by Balazs Analytical Laboratory

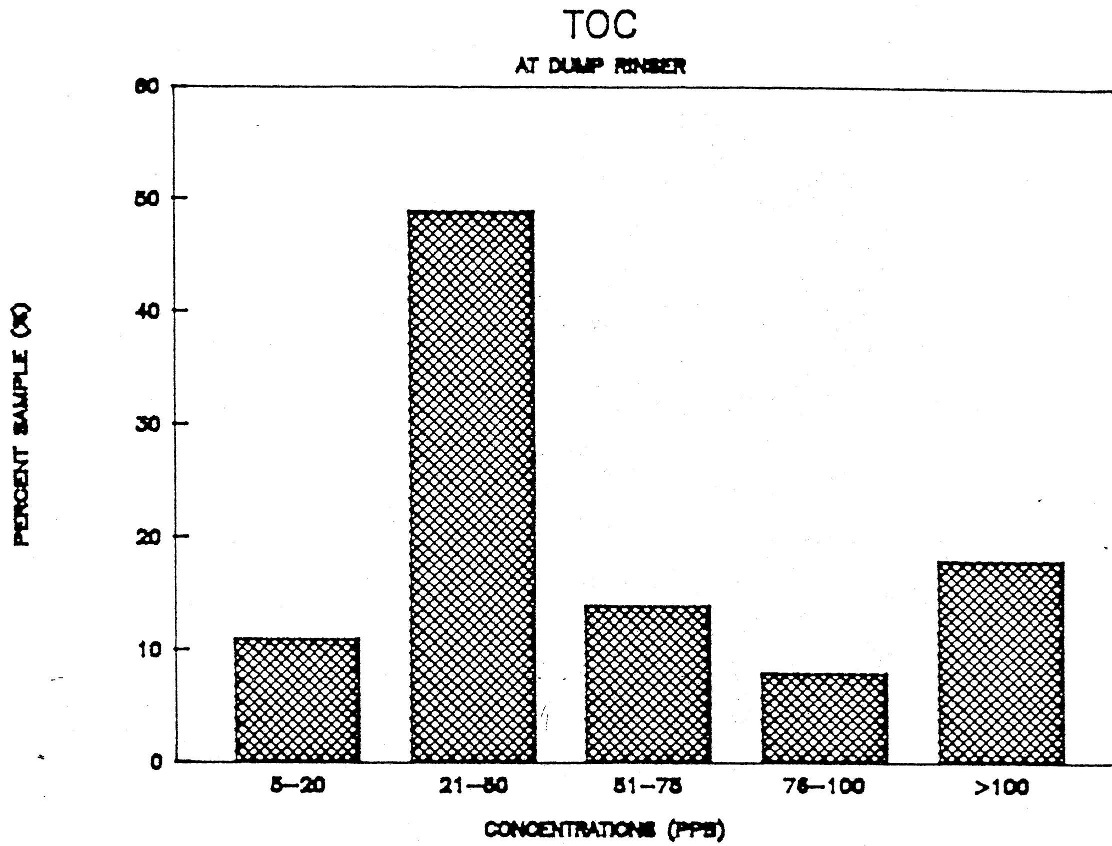

Fig. 2

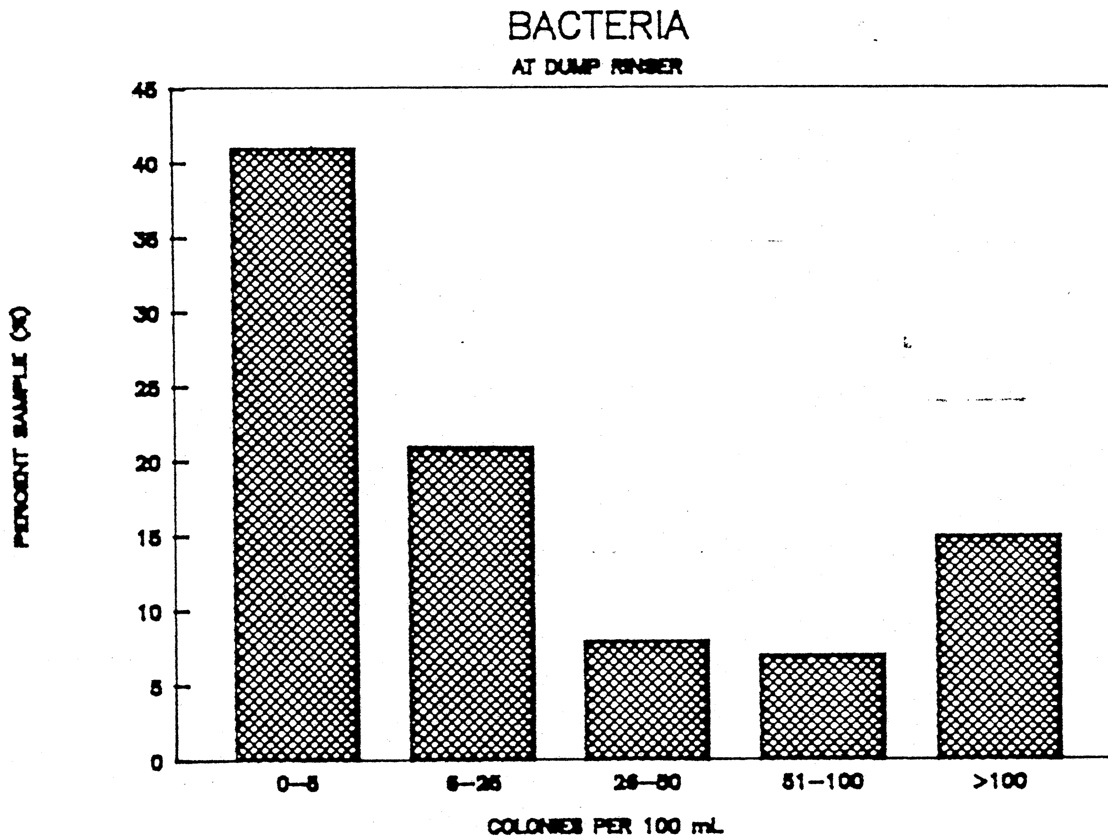

Fig. 3

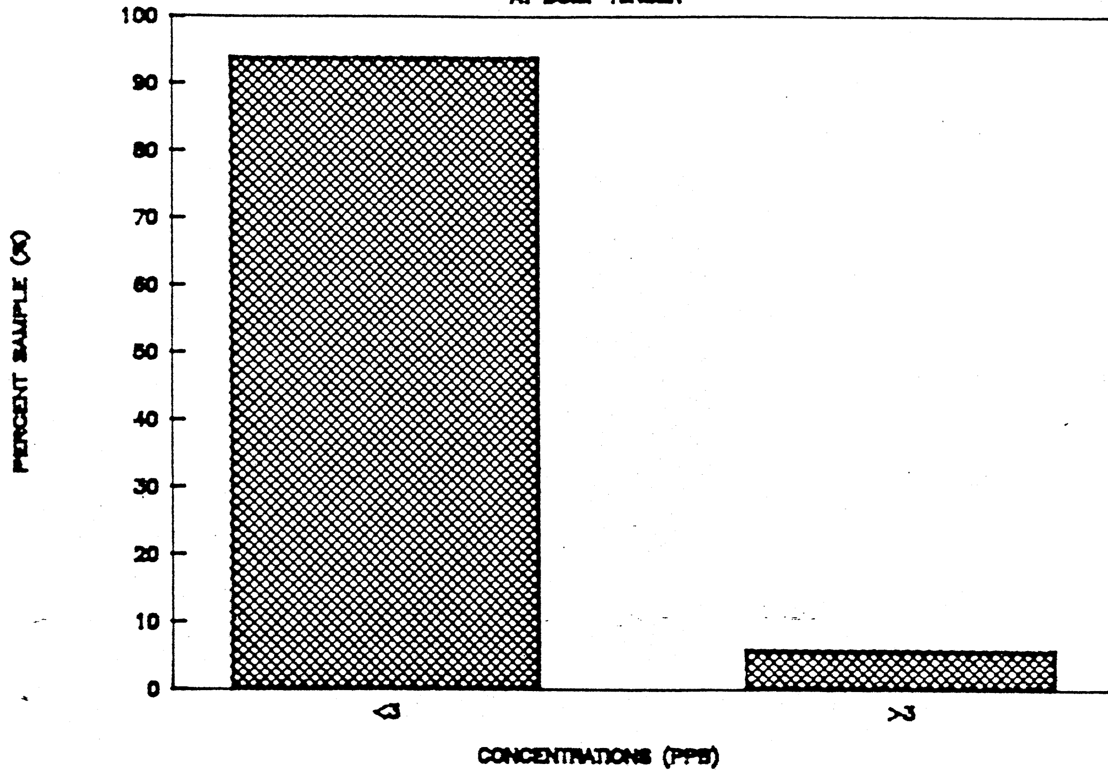

Fig. 4

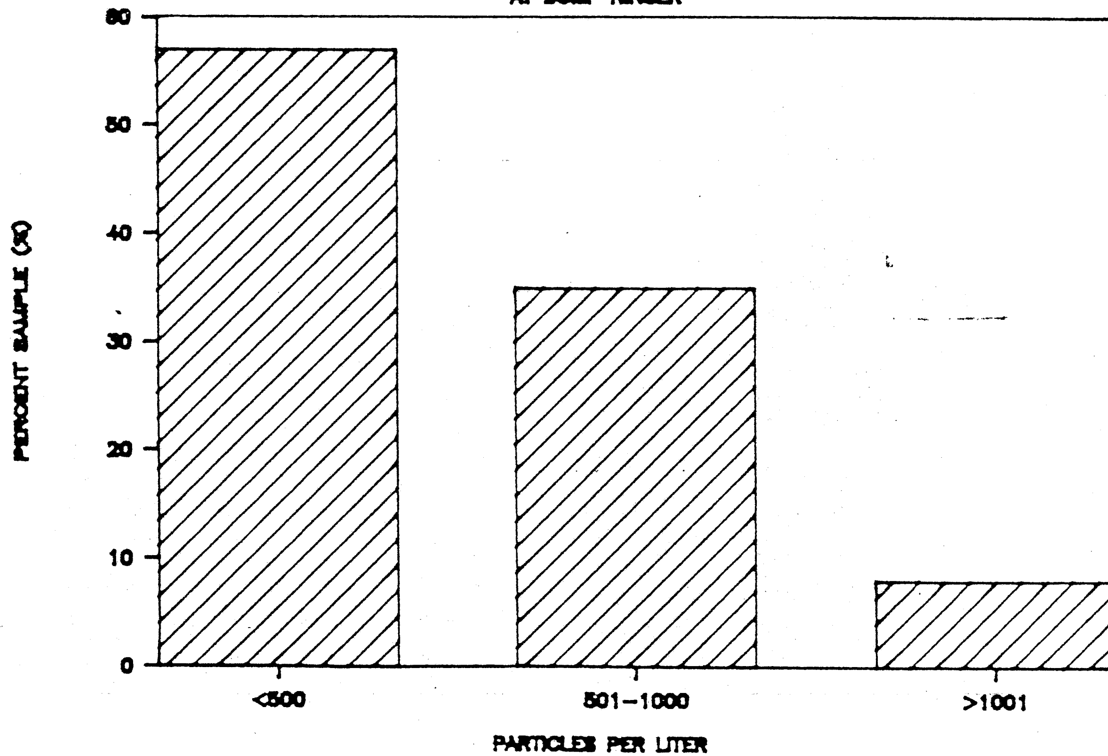

Fig. 5

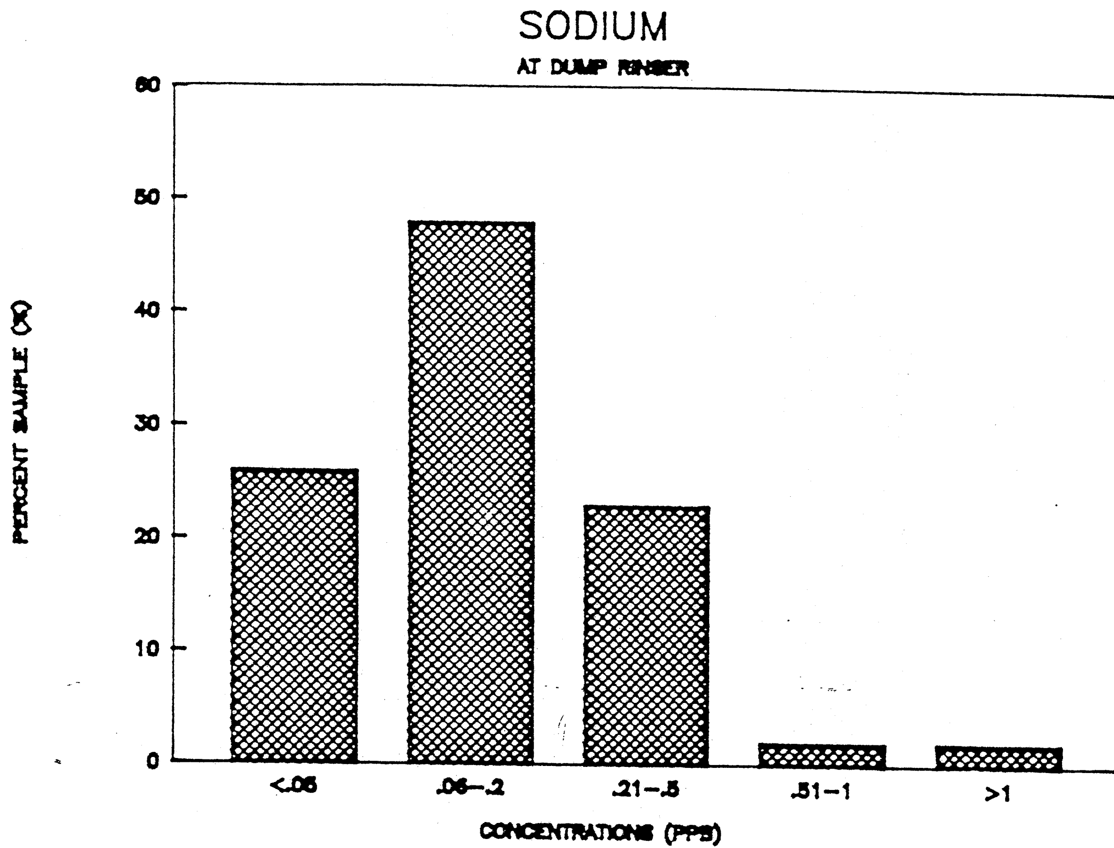

Fig. 6

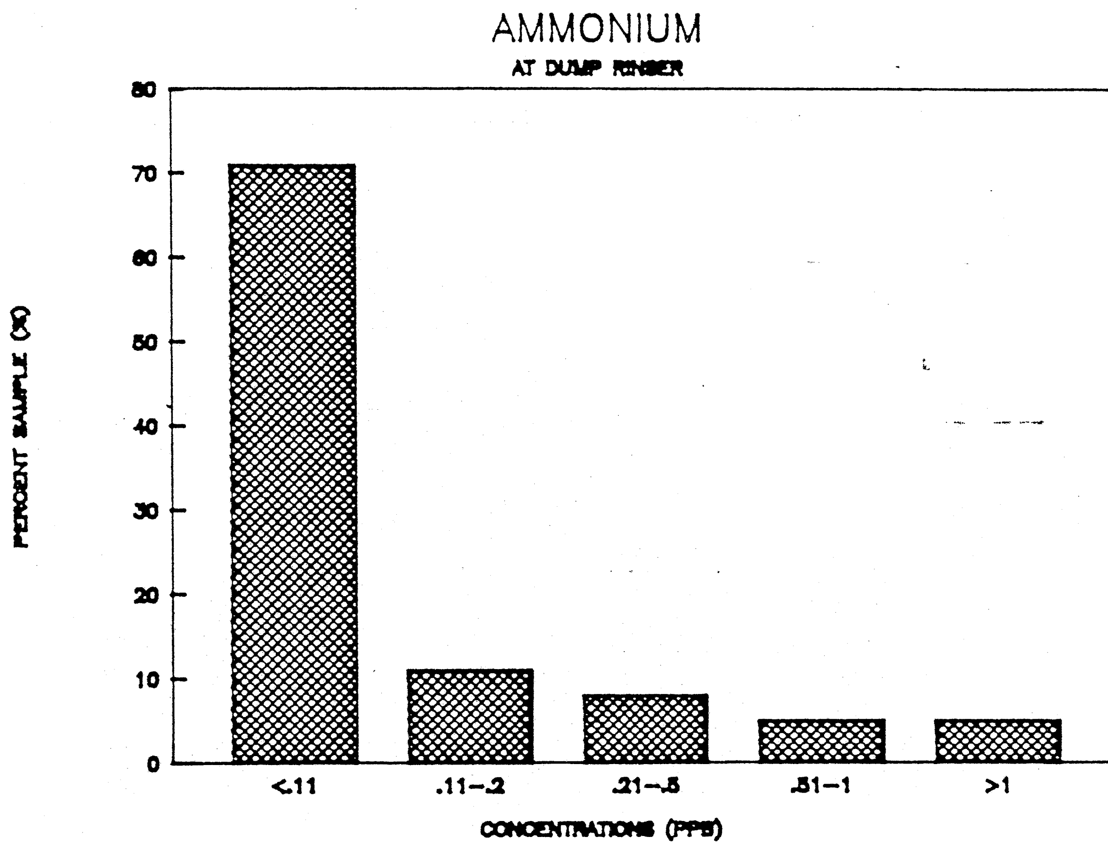

Fig. 7

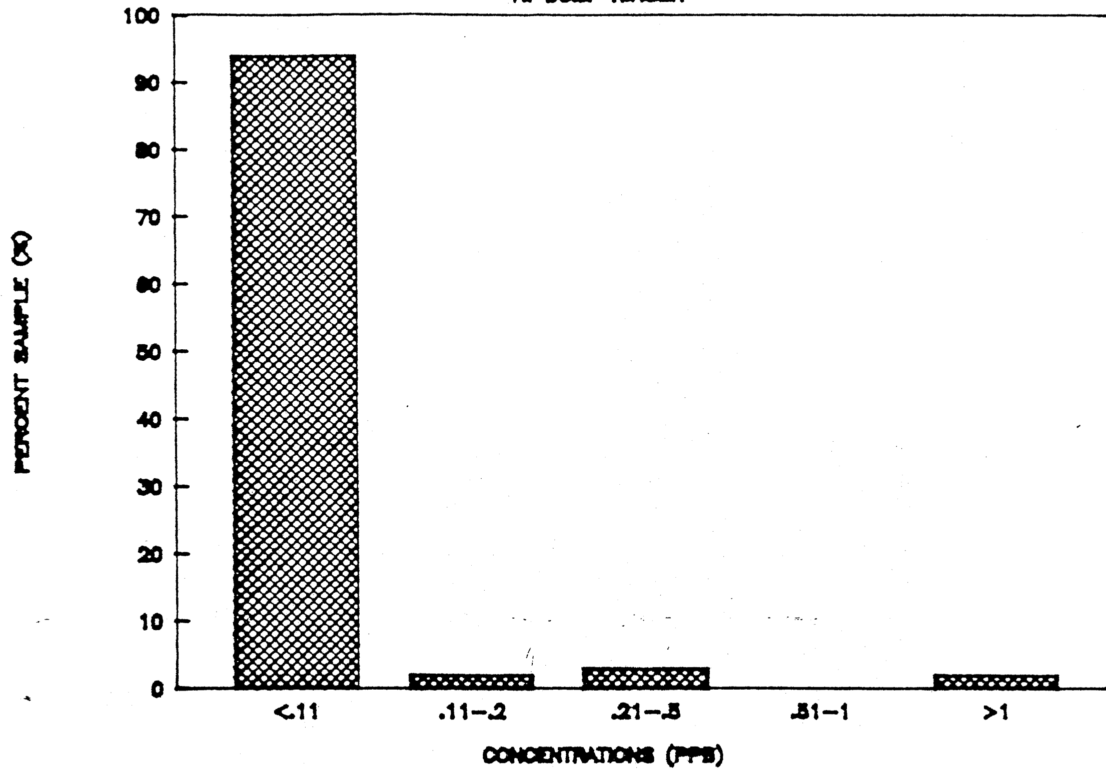

Fig. 8

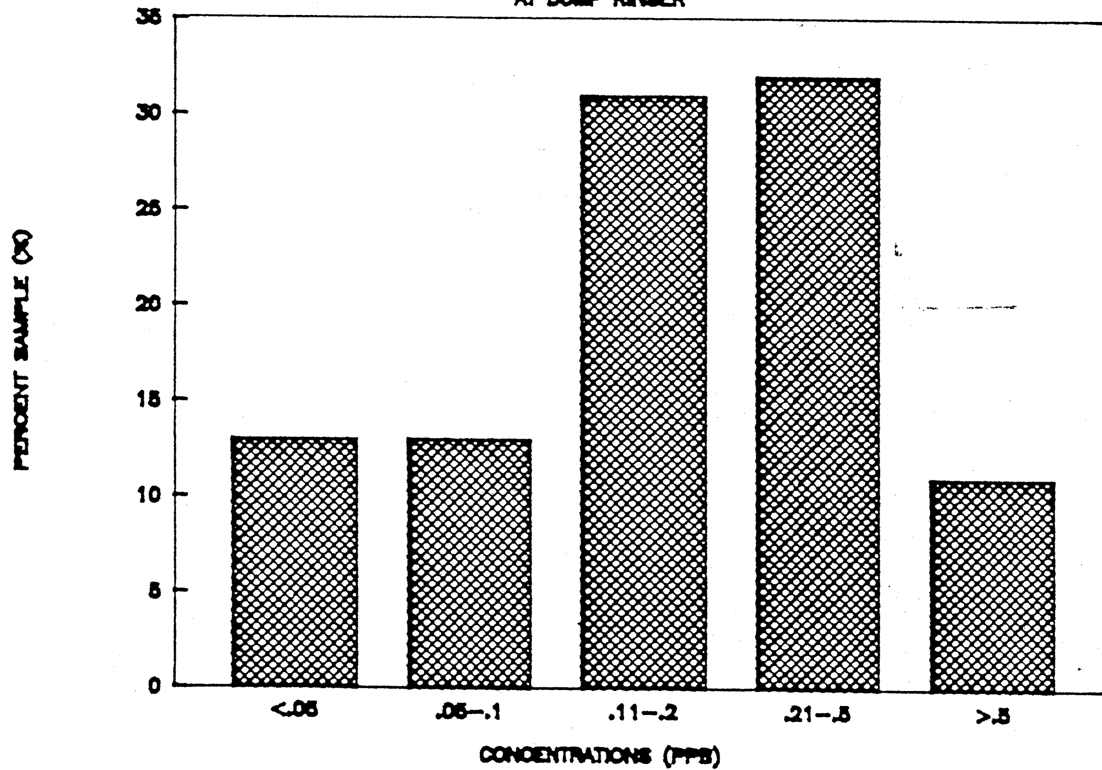

Fig. 9

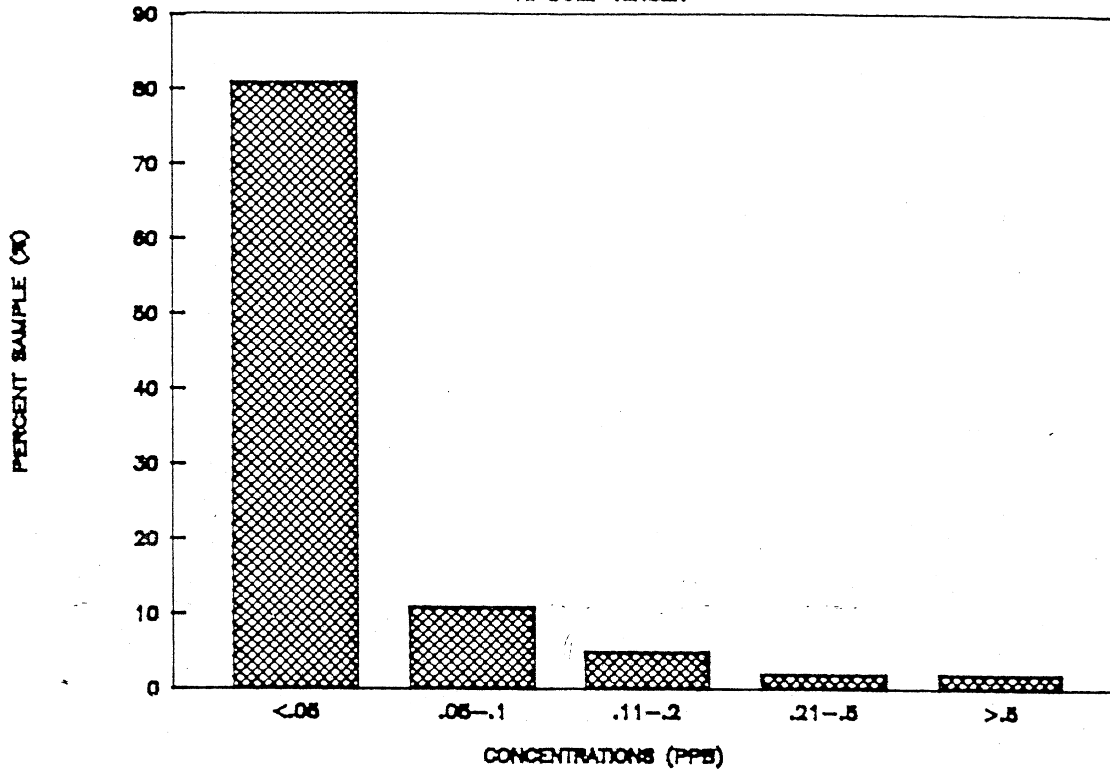

Fig. 10

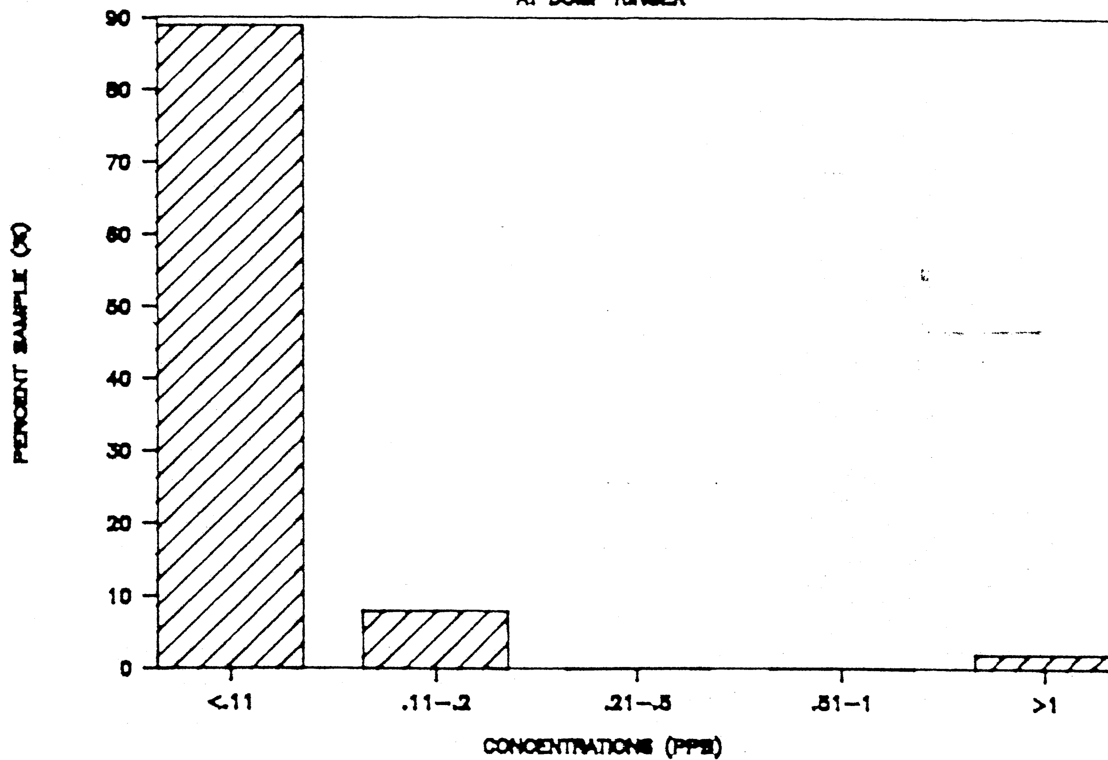

Fig. 11

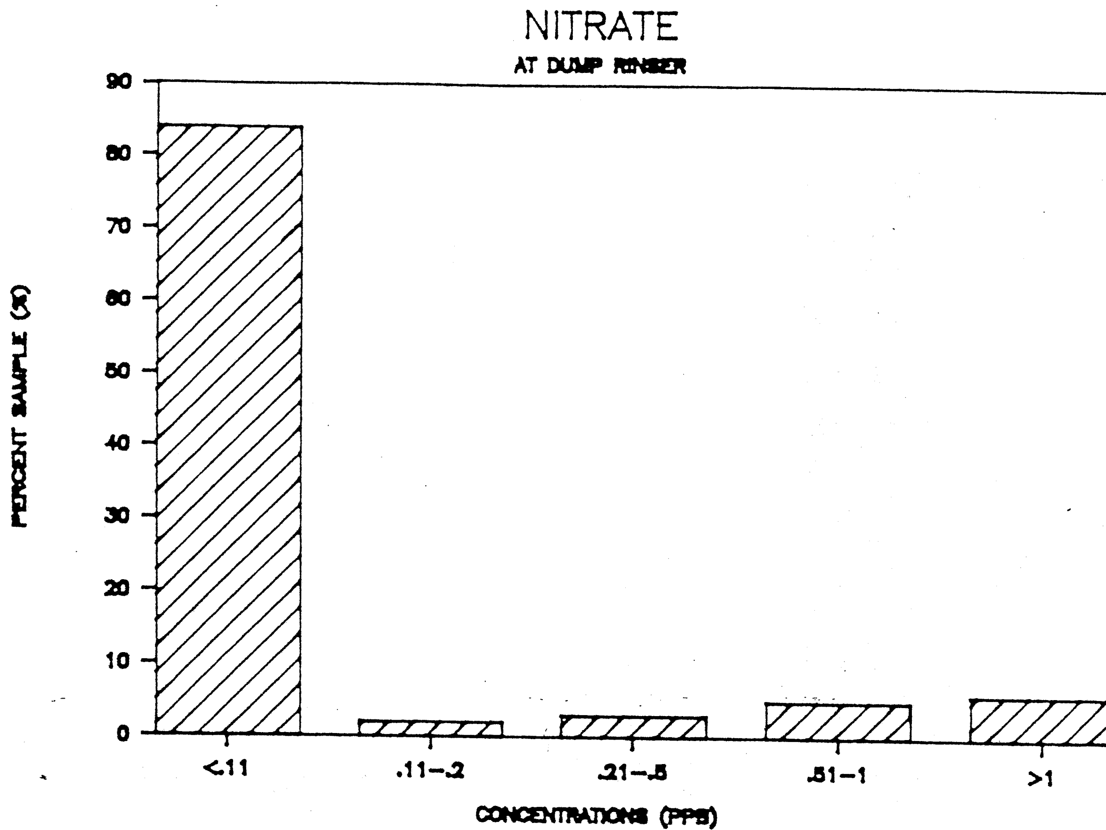

Fig. 12

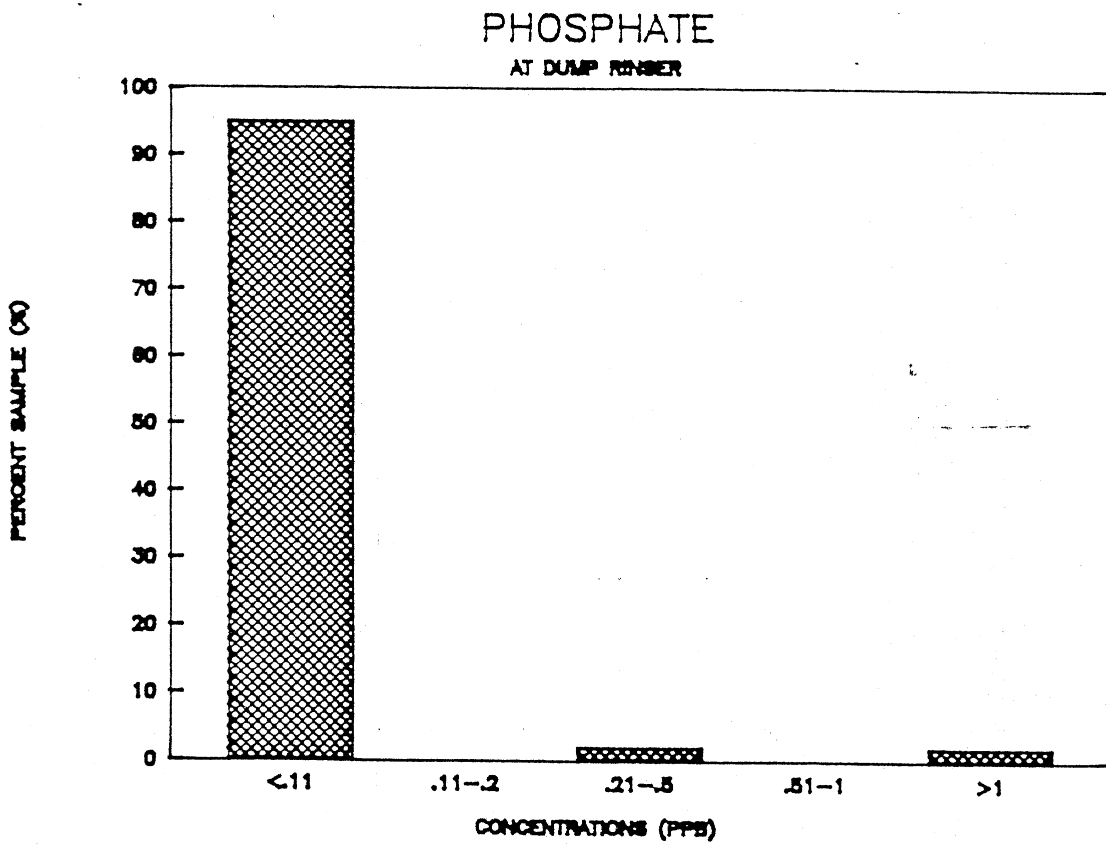

Fig. 13

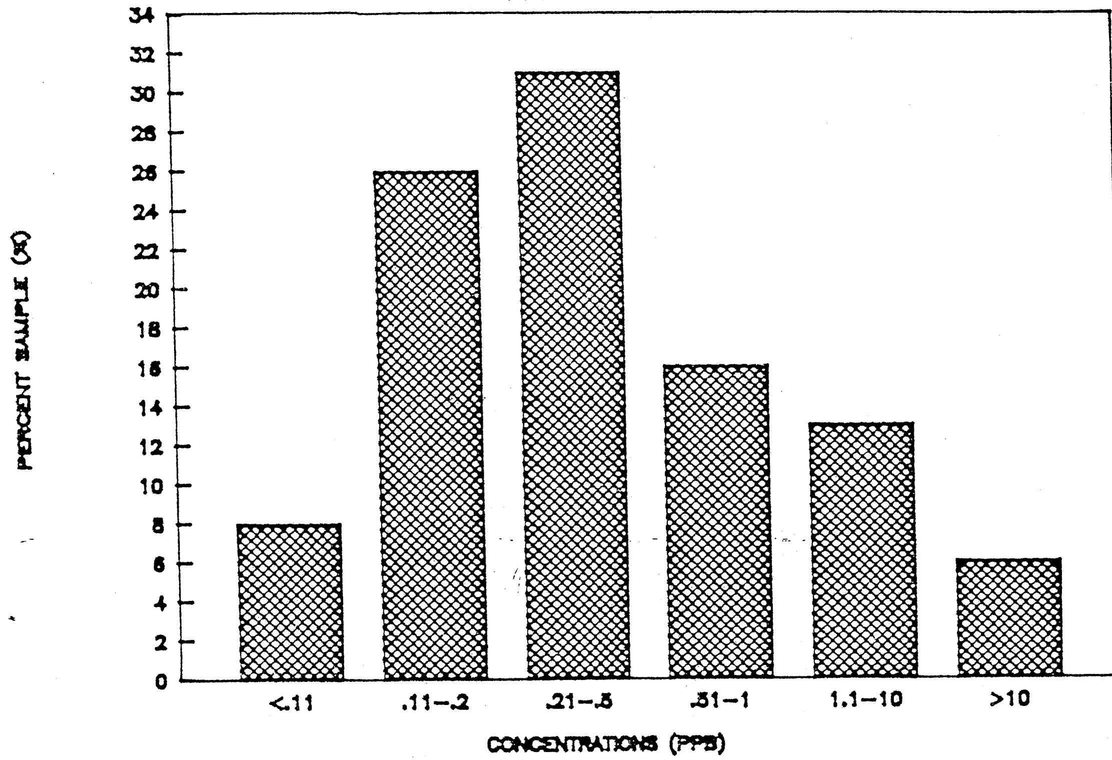

Fig. 14