Improving Sampling Techniques for the Analysis of Lead in Groundwater: Determining Optimal Filtration Conditions

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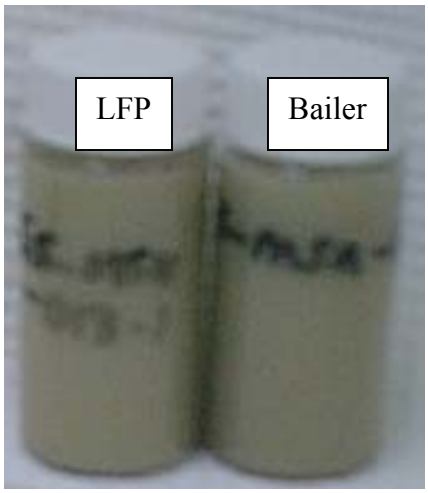
1 Introduction and Background Information

1.1 Problem Statement

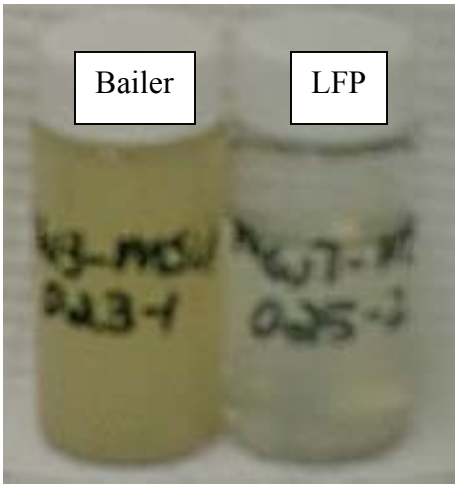
Both colloid material and particulate material can be collected during groundwater sampling, and the size range of the material overlap is 1-10 μm. Particulate material can be collected along with the groundwater sample during the sampling procedures when sediments are disturbed, elevating levels of lead due to lead naturally present in sediments. The presence of sediments in the water samples can consequently cause unnecessary site investigations. These larger sediment particles settle quickly in groundwater and are not included in the transportable lead loading.

Filtration can eliminate the particulate material (0.45-500 μm) from water samples, but also can remove naturally present colloidal material (0.01-10 μm) that should remain in the water sample as colloidal material may serve as a means for transport of contaminants in subsurface waters. A comparison of levels of lead for unfiltered and filtered (filter pore sizes 0.45 μm to 10 μm) groundwater using the low flow purge technique and bailers at several sites containing high particulate levels will be used to determine if sediment can be removed from a groundwater sample without removing the colloidal material. The goal is to develop a simple protocol for filtering water samples collected with bailers or LFP samples where sediments are present. The suitable method will minimize the introduction of soil particles, while allowing for the majority of colloidal material to remain in the groundwater sample. The technique should be as effective in removing particles as the low flow purge technique used by NJDEP, which is more costly and time consuming. Filtration will also be tested for wells were sediment derived particles are collected with the LFP.

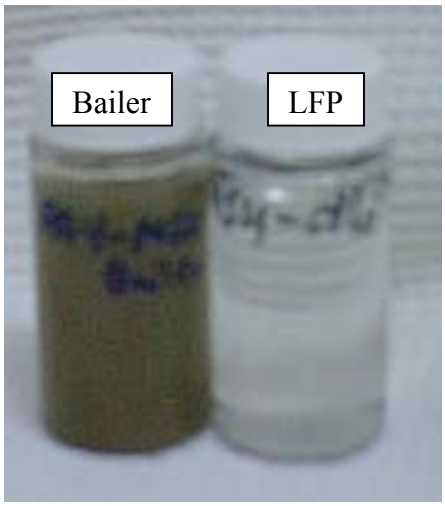
Three wells from Denzer-Schaefer site in Toms River, and two wells from Picatinny Arsenal were selected for this study due to their potential to have particles present in the groundwater. Figure 1 shows a photograph of the groundwater samples from these wells prior to filtration. The groundwater collect with the LFP at Picatinny



Well 5 S, Toms River



Well MW3, Toms River



Well 2, Picatinny Arsenal

(Well 4 not shown is similar)

Figure 1: Appearance of Groundwater Samples taken from Toms River and Picatinny Arsenal

Arsenal had very low sediment levels while the bailer samples had high sediment loadings. At Toms River, Well 10 and 5S had higher sediment loading for both the low flow purge and bailer samples, while MW3 initially had lower particle loadings taken with the LFP. These wells have different sediment loadings and particle distributions. In addition, even with the LFP the wells at Toms River still had significant particle loading. Several other wells were tested but sediment levels were too low to warrant further investigation. Although it was initially anticipated that the groundwater samples would have lead loadings above 15 ppb most filtered samples had levels < 5 ppb. Due to these low lead loadings in filtrates the filtered liquid samples were concentrated prior to analysis to ensure levels above the detection limit for ICP-AES.

The texture of sediments and color of the groundwater samples taken at the four wells indicates different contributions of soil derived particles (sand, silt, clay) with well 5S and 10 having high clay content, well MW3 silt and other suspended particles, well 2 and 4 from Picatinny Arsenal with low clay content and higher sand/silt levels. Further characterization of particle sizes above 25μm will be made outside of the objectives of this project. Initial development testing of the filtration method was completed with a grab sample taken by NJDEP staff at the Goldere site, Morristown, NJ (Coal Avenue/Center Street).

1.2 Objectives

(a) To compare levels of lead in filtered (filter pore size range 0.45 to 10 μm) and unfiltered lead contaminated groundwater samples collected at several sites in New Jersey using the low flow purge technique and bailers.

(b) To subsequently assess whether filtration (and the appropriate pore size of filter material) can be used as a low cost option for removing particulate material from groundwater samples without removing the naturally occurring colloid material.

(c) For selected wells to further characterize the lead loadings in groundwater liquid and particle phases to improve our understanding of the potential for transport of lead in subsurface waters.

2. Experimental

2.1 Analysis Methods

The initial phase of the project included evaluation of the filtration approach and modification of the SW-846 method for filtered samples. All reagents, and filters were also tested during Phase I for their purity.

2.1.1 Materials for Filtration Procedures

Filter Media.

The original list of filters included the following commercially available filters:

0.45 µm Osmonics, TefSep, Teflon, Laminated PTFE Membrane
(non-laminated not available)
0.8 µm Millipore Isopore Membrane Filters, ATTP –polycarbonate membrane
2.0 µm Millipore Isopore Membrane Filters, TTTP –polycarbonate membrane
5.0 µm Osmonics, Teflon TefSep. –Pure PTFE
10.0 µm Osmonics, Teflon TefSep. –Pure PTFE

Additional filter types used on all or selected samples during this project included

0.0 µm Osmonics, Teflon TefSep. –laminated PTFE membrane
1.2 µm Millipore Isopore Membrane Filters, RTTP –polycarbonate membrane
1.0 µm Millipore Isopore Membrane Filters, TSTP –polycarbonate membrane

Whatman 41 filters (low ash) –approximate pore size 20-25 µm
Whatman 113 filters –approximate pore size >30 µm

The final filtration method uses the following filters:

0.45 μm Osmonics, TefSep, Teflon, Laminated PTFE Membrane
(non-laminated not available)
0.8 μm Millipore Isopore Membrane Filters, ATTP –polycarbonate membrane
1.2 μm Millipore Isopore Membrane Filters, RTTP –polycarbonate membrane
2.0 μm Millipore Isopore Membrane Filters, TTTP –polycarbonate membrane
3.0 μm Millipore Isopore Membrane Filters, TSTP –polycarbonate membrane
5.0 μm Osmonics, Teflon TefSep. –Pure PTFE
10.0 μm Osmonics, Teflon TefSep. –Pure PTFE

The 1.2 μm polycarbonate membrane filter was used instead of the 1.0 μm Teflon filter as the laminated filter required pre-rinsing with methanol prior to use and the polycarbonate membrane filter could allow for removal of the particles on the filter without having to digest the filter. The Whatman 113 filter were cut to size in the laboratory and did not provide significant improvement from filtering with only Whatman 41 so this additional step was removed as sample volume was limited.

2.1.2 Reagents for Digestion

Trace Grade Nitric Acid and Hydrochloric Acid were used for all digestions. Trace grade acid blanks have been below the instrument detection levels and report similar values to the deionized water.

2.1.3 SW-846 Digestion Methods for filters and/or sediment

1. Place the filter into a Teflon beaker or Griffin beaker with the top side of the filter facing upward (showing particles collected).
2. Label the beaker with appropriate sample i.d.
3. Add 10 mL trace nitric acid and 5 mL of trace concentrated HCl.
4. Cover the beaker with a ribbed watch glass.
5. Heat the beaker on a hot plate at 90 to 95ºC to digest the sample. This step should take a minimum of 30 minutes.
6. Occasionally rinse the watch glass and sides of the beaker with deionized water.
7. Reduce the volume to approximately 5-10 mL.
8. Prepare a funnel containing a Whatman 41 filter.
9. Transfer the sample solution into a second Teflon beaker or Griffin beaker allowing the solution to pass through the funnel.
10. Rinse the beaker and funnel a minimum of three times with a solution of hot dilute nitric acid. Ensure the volume of the transferred solution remains less than approximately 80 mL.
11. Place the second beaker (with sample i.d. noted) on the hot plate at 90 to 95ºC. Cover the beaker with a ribbed watch glass. Reduce the volume to approximately 10 mL. Near the completion remove and rinse the watch glass.
12. Transfer the solution to a 100 mL volumetric flask ensuring that the beaker and funnel are rinsed 3 times with deionized water. (NO filter in funnel at this step).
13. Transfer the sample into a labeled polypropylene sample bottle.
14. Samples are stored in refrigerator at 4°C until ICP-AES analysis.

2.1.4 Recovery of Metals –Performance of Acid Digestion

Sediment samples were digested according to SW846 methods. After the filtration step a second digestion of the Whatman 41 filter paper used in filtration and remaining sediment was conducted to assess the efficiency of digestion when significant amounts of particles were present in the sample. The initial evaluation on total bailer samples showed no significant Pb levels in the second digestate. SW-846 methods does not require a second digestion.

2.1.5 Modifications to Digestion Procedure for Sediments Collected on Filters

When the sediment loadings are low (<0.01 g) or the sediment can not be easily removed from the filter, the filter and sediment are digested together. Filter media were selected to be Teflon which has low levels of Pb, or polycarbonate when Teflon filters were not available in the desired filter size range. Sediments are always removed from the large pore size filter papers, Whatman 41 or 113, prior to digestion. As sediment loadings on these filters are > 0.02 g generally a 0.01-0.015 g sample of sediment is digested. For the 10 to 3.0 μm filter papers if sediment mass is >0.02 g then sediment is removed prior to digestion.

For membrane filters, step 3 of the procedure is modified to include addition of 10 mL deionized water, 10 mL trace nitric acid, and 5 mL trace HCl. The acid concentration is reduced to prevent significant degradation of the filter, which may cause entrapment of some of the sediment particles in the filter media. The filter media (Teflon or carbonate) does not digest during the acid digestion. These filters are removed during the transferring and rinsing stages of the procedure (step 9-10).

Griffin Beakers are replaced with Teflon beakers once the sample is filtered to minimize sample loss to container walls.

2.1.6 Modification of Digestion Method for Unfiltered Samples Containing Sediment

Step 1 of the standard procedure for sediment samples is modified to

1. Pipet 2-125 mL of unfiltered sample containing sediment into a pre-weighed Griffin beaker. Weigh the beaker after transfer of the solution. Sample volume and sample mass are used to verify uniformity of sample as sediment may settle during transfer. Sample volume is optimized for each sample to ensure that the sediment in the total sample is digested. For bailer samples which have high sediment loadings the sample volume is typically 0.5-5 mL. Table 1 shows the sample volumes used for digestion of total samples.

2. The Griffin beaker is replaced with a Teflon beaker after the filtration step.

3. In Step 12, the final volume the digestate is diluted to 25 or 50 mL instead of 100 mL to concentrate the sample for ICP-AES analysis. All filtrates from the Picatinny Arsenal wells are reduced to 25 mL.

2.1.7 Standard Method for the Digestion of Liquid Phase Samples

1. Pipet 100 mL of the groundwater sample into a 250 mL Griffin beaker.
2. Label beaker with appropriate sample i.d. code.
3. Add 2 mL of trace concentrated nitric acid and 5 mL of trace concentrated HCl.
4. Cover beaker with ribbed watch glass and heat beaker on hot plate at 90 to 95ºC to reduce the volume of the sample to 5-10 mL.
5. Allow the beaker to cool.
6. Rinse the sides of the beaker and watch glass with deionized water transferring the solution to a 100 mL volumetric flask.
7. Repeat step 6 at least two more times. Ensure that the volume of the transferred solution remains below 100 mL.
8. Rinse the funnel in the volumetric flask 3 times as it is removed.
9. Dilute with deionized water to 100 mL.
10. Transfer the sample to a polypropylene sample bottle. Rinse the sample bottle 3 times with sample prior to transferring the remainder of the solution.
11. Label the sample bottle with the appropriate sample i.d. and date.

2.1.8 Modification of Digestion Procedure for Liquid Phase Samples (Filtrates and Total)

All low concentration samples are digested in Teflon beakers rather than a Griffin beaker to minimize sample loss to container walls.

For low concentration liquid samples a 100-225 mL (where available) sample is digested according to standard methods and the digestate is transferred to a 25 mL volumetric flask (rather than 100 mL with standard method).

Table 1 shows the volumes digested for unfiltered "total" samples. Generally a 5 mL volume of bailer sample and 100-225 mL volume of LFP sample is digested with acids and transferred to 50 mL (or 25 mL) volumetric flasks. Table 2-11 show the volume of sample used for digestion is 100-225 mL for filtered liquid samples. If particles are still present the digestates are filtered through Whatman 41 filters prior to transferring to a volumetric flask. For total or filtered samples containing a significant amount of particles in the filtrate the sediment digestion method is used where the acid volumes added to the sample are increased to 10 mL trace HNO_3 and 5 mL trace HCl in step 3 of the procedure. The same volume of acid is added to all filtrate samples taken from a well.

Table 1: Sample Volumes Used for analysis, digestion final volume, and Pb Total (ppb)

Sample ID	Well	Sampling Method	Sample Volume for Analysis (mL)	Digestion Final Volume (mL)	Pb Total (ppb)
5S-MSU-002-10	5S	BAILER	0.5	50	397.1
5S-MSU-013-9	5S	LFP	0.5	50	987.0
MW3-MSU-023-3	MW3	BAILER	125	25	48.8
MW3-MSU-025-1	MW3	LFP	125	25	10.5
PA2-MSU-002	2	BAILER	4.9914	50	734.4
PA2-MSU-006	2	LFP	225.36	25	2.4
PA4-MSU-010	4	BAILER	5.0064	25	1109.8
PA4-MSU-014	4	LFP	224.96	25	3.0
PA2-MSU-004	2	BAILER-ACIDIFIED	4.9799	50	1180.6
PA2-MSU-008	2	LFP-ACIDIFIED	225.69	25	2.0
PA4-MSU-012	4	BAILER-ACIDIFIED	4.9784	50	1453.8
PA4-MSU-016	4	LFP-ACIDIFIED	225.57	25	2.2

Table 2: Digestion Volume, and Final Dilution Volume for Filtrates Taken from Bailer Sample, Well 5S, Sample 5S-MSU-002-10

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total					397.12
25	8934.94	31.60	100.1	25	115.58
10	2937.00	15.99	50.50	25	62.97
5	87.87	458.89	50.08	25	49.17
2	2447.45	35.28	50.07	25	6.48
1.2	91.22	349.01	50.03	25	3.42
0.8	0.00	278.29	75.04	25	3.04
0.45	0.00	186.34	75.08	25	2.80

Table 3: Digestion Volume, and Final Dilution Volume for Filtrates Taken from LFP Sample, Well 5S, Sample 5S-MSU-013-9

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			0.64	50	987.04
30	6281.60	40.59	0.51	50	453.95
25	8796.99	99.21	0.51	25	222.55
10	2235.02	12.89	1.97	25	166.32
5	297.01	43.04	4.97	25	130.87
3	2429.99	50.13	75.02	25	9.95
2	22.78	171.01	100.21	25	6.17
1.2	50.96	209.83	68.84	25	6.46
0.8	2.29	185.11	94.92	25	6.47
0.45	0.045	89.13	78.52	25	6.44

Table 4: Digestion Volume, and Final Dilution Volume for Filtrates Taken from Bailer Sample, Well MW3, Sample MW3-MSU-023-2/4 (MW3-MSU-023-3)

Pore Size (µm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			129.93 (125)	25	42.46 (48.83)
25	601.58	(132.13)	103.75 (100.31)	25	20.36 (23.78)
10	599.57	(345.48)	139.65 (100.24)	25	19.33 (20.75)
5	15.36	(344.49)	75.10	25	19.59
3	339.57	68.48	155.82	25	3.33
2	0.49	126.06	171.27	25	1.30
1.2	2.05	601.63	171.84	25	0.47
0.8	0.75	416.74	203.73	25	0.43
0.45	1.61	210.90	188.22	25	0.40

Table 5: Digestion Volume, and Final Dilution Volume for Filtrates Taken from LFP Sample, Well MW3, Sample MW3-MSU-025-2 (MW3-MSU-025-1)

Pore Size (µm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			129.41	25	11.47
25	139.64	(94.39)	125.00	25	9.50
10	50.22	(56.96)	97.95	25	9.21
5	4.65	(349.93)	125.69 (97.96)	25	2.34 (2.62)
3	17.41	292.60	135.14	25	1.70
2	2.56	220.12	161.15	25	1.54
1.2	8.25	479.66	180.41	25	0.63
0.8	1.81	296.03	137.93	25	0.47
0.45	5.30	149.57	147.64	25	0.44

Table 6: Digestion Volume, and Final Dilution Volume for Filtrates Taken from Bailer Acidified Sample, Well 2, Sample PA2-MSU-004

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			4.9799	25	1180.6

Table 7: Digestion Volume, and Final Dilution Volume for Filtrates Taken from LFP Acidified Sample, Well 2, Sample PA2-MSU-008

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			225.69	25	2.0
25	0.65	1925.24	225.56	25	1.3
10	1.32	1644.26	202.29	25	1.5
5	0.03	1418.81	204.12	25	1.5
3	0.07	1010.75	207.81	25	1.9
2	0.001	782.96	208.55	25	2.0
1.2	0.12	555.47	203.74	25	2.4
0.8	0.01	333.04	149.42	25	3.3
0.45	0.13	167.93	151.31	25	2.5

Table 8: Digestion Volume, and Final Dilution Volume for Filtrates Taken from Bailer Sample, Well 2, Sample PA2-MSU-002

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			4.9650	25	734.4
25	4251.02	98.78	204.23	25	0.4
10	3.54	401.49	200.21	25	0.2
5	0.22	1453.90	203.64	25	0.1
3	1.02	1237.63	207.31	25	0.1
2	0.04	992.98	219.12	25	0.1
1.2	0.86	820.10	207.30	25	0.1
0.8	0.12	754.03	226.50	25	0.1
0.45	0.25	507.40	221.38	25	0.1

Table 9: Digestion Volume, and Final Dilution Volume for Filtrates Taken from LFP Sample, Well 2, Sample PA2-MSU-006

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			225.36	25	2.4
25	4.31	540.33	202.49	25	0.3
10	0.21	830.55	213.55	25	0.4
5	0.05	817.31	204.14	25	0.2
3	1.13	905.71	202.00	25	0.3
2	0.02	932.14	187.86	25	0.4
1.2	0.08	586.49	200.01	25	0.4
0.8	0.04	384.20	192.74	25	0.4
0.45	0.13	189.47	187.23	25	0.3

Table 10: Digestion Volume, and Final Dilution Volume for Filtrates Taken from Bailer Sample, Well 4, Sample PA4-MSU-010

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			5.0064	25	1109.8
25	6466.83	67.70	209.56	25	3.1
10	1.89	499.06	204.79	25	1.7
5	0.51	1501.96	202.69	25	1.6
3	1.39	1295.69	210.70	25	1.1
2	0.20	1080.81	210.41	25	1.1
1.2	0.36	854.09	219.46	25	1.2
0.8	0.08	418.97	203.61	25	2.6
0.45	0.03	212.92	211.13	25	1.5

Table 11: Digestion Volume, and Final Dilution Volume for Filtrates Taken from LFP Sample, Well 4, Sample PA4-MSU-014

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			224.96	25	3.0
25	10.48	848.37	200.31	25	0.8
10	2.54	266.09	176.81	25	0.6
5	0.27	1286.13	173.61	25	0.5
3	1.69	524.41	174.98	25	0.8
2	0.50	887.33	193.27	25	0.8
1.2	0.28	678.04	185.36	25	1.5
0.8	0.12	477.36	226.50	25	1.4
0.45	0.53	212.88	210.88	25	1.1

Table 12: Digestion Volume, and Final Dilution Volume for Filtrates Taken from Bailer Acidified Sample Well 4, Sample PA4-MSU-012

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			4.9784	25	1453.8

Table 13: Digestion Volume, and Final Dilution Volume for Filtrates Taken from LFP Acidified Sample, Well 4, Sample PA4-MSU-016

Pore Size (μm)	Sediment Loading (mg/L)	Volume Used for Determination of Sediment Loading (mL)	Volume Used for Filtrate Digestion (mL)	Final Volume of Digestate (mL)	Pb Filtrate (ppb)
Total			225.57	25	2.2
25	9.40	1645.27	201.83	25	2.2
10	0.33	830.98	202.56	25	2.6
5	0.23	1071.19	205.75	25	2.3
3	2.73	862.92	198.62	25	2.2
2	0.17	662.07	193.41	25	2.5
1.2	0.30	466.38	152.82	25	2.5
0.8	0.32	310.84	145.23	25	2.7
0.45	0.36	163.24	161.54	25	3.1

2.2 Filtration Approach for Groundwater Samples

Two methods for filtering samples were tested on the grab sample taken from Goldere site, Morristown, NJ. Figure 2 shows that in Approach A 10-25 mL of sample is filtered and after filtration the volume of sample filtered and the amount of sediment collected on the filter are determined. As the sediment levels of the total sample were high (67-86 g/L) the filtration for all pore size ranges was slow. To ensure better quantification of sediment loadings the volume of sample filtered was low (<50 mL). Reducing the volume of sample filtered reduced problems associated with particles collecting on the filtration apparatus in addition to the filter media. As the volume of sample filtered is small this process needed to be repeated numerous times to have sufficient sample filtered for determination of lead concentration in the filtrate. Due to the high sediment loadings it is also difficult to distinguish differences in lead levels on filters of different pore sizes that can be attributed to presence of colloidal material as the major portion of particle mass collected on filters is from soil derived particles.

Figure 3 shows the sequential filtration approach that was used for analysis of samples taken from Toms River and Picatinny Arsenal. With this approach the entire volume of sample (1-2 L) is filtered through the largest pore size (20-25 μm). The filtering flask, filtration apparatus components, and filter paper are weighed before and after filtration. A small volume is used for determination of the amount of sediment in the groundwater when particle loadings are high. For samples with low turbidity a larger volume of 1-2 L is filtered for sediment loadings. From the sediment mass and groundwater sample volume filtered, the sediment loading can be determined. Tables 2 to 11 show sample volumes used for the determination of sediment loading in the groundwater sample. The first filtration step typically requires 20-30 filters per 1 L solution due to the high particle loadings particularly for bailer samples. After the first few steps, filtration is generally quicker with the entire 1-2 L filtered through one filter.

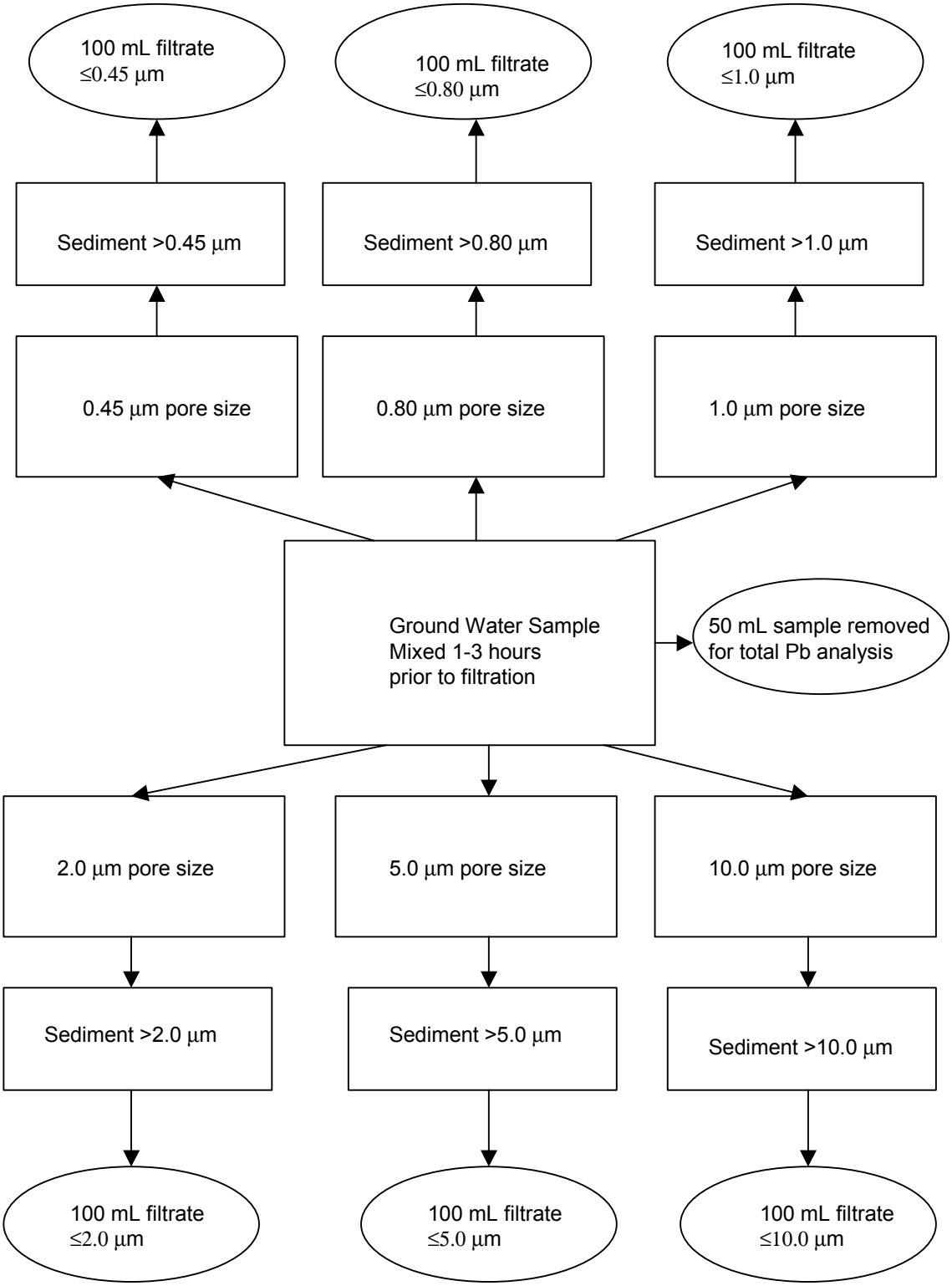
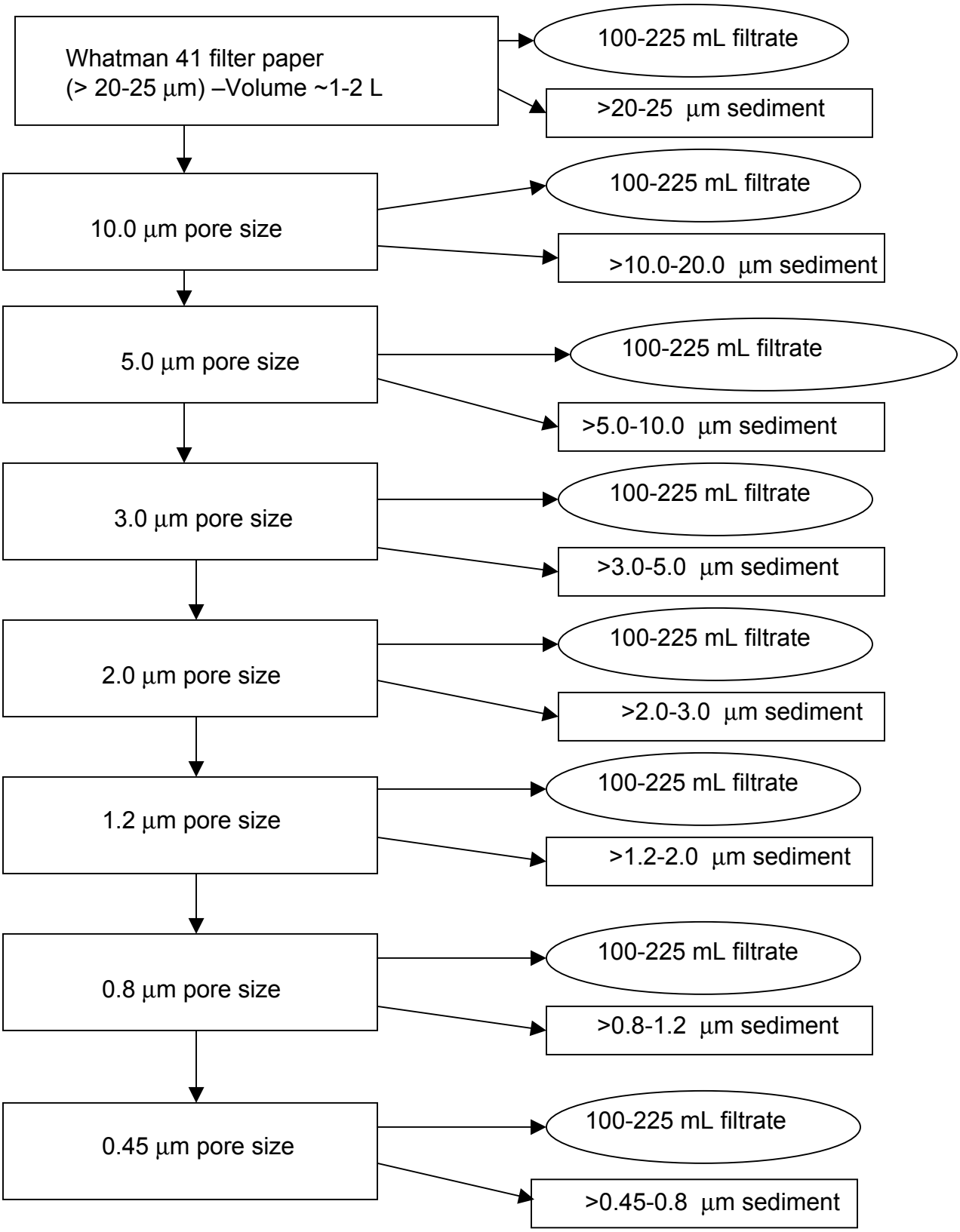


Figure 2: Filtration Approach A

Figure 3: Sequential Filtration



The sequential filtration approach involves filtering the entire 1-2 L sample through the Whatman 41 filter media. Typically a 100-200 mL aliquot of the filtrate is removed for lead analysis. A 0.01 – 0.015 g sample of the dried sediment on the filter media is also digested. After the first filtration step, the filtrate from step 1 is then filtered through sequentially smaller pore size ranges. First through 10.0 µm, then 5.0 µm, then 3.0 µm (newly added to the procedure), then 2.0 µm, then 1.0 (now replaced with 1.2 µm to allow for a change in filter media type), then 0.80 µm, and lastly 0.45 µm. During each filtration step the volume of solution filtered and the mass of sediment collected on the filter are determined. Typical a 100-225 mL aliquot of the solution is removed from the filtrate at each filtration stage for acid digestion of liquid phase + particles in the sample.

The masses of sediment collected on filters obtained will then relate to sediment > 20-25 µm, 10-20 µm, 5-10 µm, 3-5 µm, 3-2 µm, 1.2-2 µm, 0.8-1.2 µm, 0.45-0.80 µm. This approach may require digestion of sediment with filter media as masses collected are expected to be small for lower pore size ranges. The use of membrane filters is sometimes preferred as the sediment can be more easily removed than from the Teflon laminated filters. However for low sediment masses, filter and the collected sediment are digested together to avoid loss of available sample. Gravimetric analysis of filter and filter + sediment masses are to ±0.003 mg using a Mettler MT-5 microbalance.

2.3 Inductively Coupled Plasma-Atomic Emission Spectrometry(ICP-AES)

2.3.1 Calibration/ Interference Check/Continuing Calibration Standards

For the analysis of sediment samples with high levels of lead or total lead in a sample when sediment is present a high calibration range is used when lead levels are > 30 ppb. Lead calibration curve is run with the following standards prepared in 2% HNO_3: 30 ppb, 60 ppb, 100 ppb, 150 ppb, 200 ppb, 300 ppb, and 400 ppb. After the calibration curve is run interference check 1 at 60 ppb, interference check 2 at 150 ppb, and continuing calibration curve verification standard at 180 ppb, and 2% HNO_3 solution are run to check for drift in calibration curve, interferences, and background lead levels.

Many of the filtrate and total samples from the current sampling have levels of lead below 30 ppb and as low as 1 ppb. A calibration curve is run with the following standards in 2% trace HNO_3: 0 ppb, 2 ppb, 4 ppb, 5 ppb, 6 ppb, 8 ppb, 10 ppb, 20 ppb, 50 ppb. The calibration curve verification (CCV) checks are completed every 4 samples with 0 ppb, 3 ppb, 15 ppb, and 30 ppb standards. Interference checks are performed along with the CCV standards at 5 and 20 ppb Pb. For samples with levels of lead suspected to be near 2 ppb a larger volume of sample is digested with acids and then concentrated to 25 mL volume.

The Picatinny Arsenal total samples collected with the LFP have a volume of 200-225 mL used for digestion followed by reduction and transfer to a 25 mL volumetric flask. This is a modification from the standard SW846 method of a 100 mL sample digested, reduced, and transferred to a 100 mL volumetric flask. The standard procedure would not allow for accurate quantification of the levels of lead in the samples which is near the ICP-AES detection limit of 2-3 ppb Pb. In order to distinguish small differences in filtrate levels as many of the filtrates from the difference pore sizes from a well sample are analyzed on the same day whenever possible. Samples are in ~2% HNO_3 and refrigerated prior to analysis.

2.2 Sampling

2.2.1 Groundwater Samples from Denzer-Schaefer Site, Toms River, NJ

Groundwater samples were collected with bailers and the low flow purge technique from two of the five wells (well 10 and 5S) at Denzer-Schaefer site, Toms River, NJ on January 10, 2001. On April 4, 2001 additional bailer and low flow purge samples were taken from well 5S and well MW3. As with the January 10,2001 sampling at well 5S the LFP sample contained high levels of sediment similar to those taken previously and that observed for the bailer as shown in Figure 1. Well 5S was selected as it has a history of having higher lead concentrations than the other wells. Well MW3 had lower levels of sediment in the low flow purge sample with lower turbidity than the bailer sample. The MW3 sample did not appear to have the high clay sediment loading as observed with the other wells. Visually a difference in sediment levels between the bailer and LFP could be observed for well MW3 (see Figure 1).

Samples collected during the January 10,2001 sampling at Toms River are listed in Table 14 and 15. Samples collected during the April 4, 2001 sampling at Toms River at noted below in Table 16 and 17.

Table 14: Samples Collected from Well 10, Denzer-Schaefer Site

Sample ID (well-analysis location-sample number)	Sampling Method	Sample Size	Purpose
10-MSU-003 – (1 to 9)	Bailer	1 L samples (1-9)	Filtration method
10-UD-004-1	Bailer	40 L	U of Delaware
10-UD-004-2 to 10-UD-004-5	Subset of 10-UD-004-1	250 mL or 1 L	For comparison analysis at MSU
10-MSU-008-(1 to 10)	Bailer	250 mL	Duplicate analysis as necessary
10-UD-009-1	Low Flow Purge	26 L	U of Delaware
10-UD-009-(2 to 5)	Subset of 10-UD-009-1	250 mL	For comparison analysis at MSU
10-MSU-010-(1 to 9)	Low Flow Purge	1 L (1 to 9)	Filtration Method
10-MSU-011-(1 to 9)	Low Flow Purge	250 mL (1 to 9)	Duplicate analysis as required

Table 15: Samples taken from Well 5S, Denzer-Schaefer Site

Sample ID (well-analysis location-sample number)	Sampling Method	Sample Size	Purpose
5S-UD-005-1	Bailer	26 L	U of Delaware
5S-UD-005-(2 to 4)	Subset of 5S-UD-005-1	250 mL	For comparison analysis at MSU
5S-MSU-002- (1-10)	Bailer	1 L	Filtration Method
5S-MSU-006-(1 to 11)	Bailer	250 mL	Duplication analysis as necessary
5S-MSU-007-(1 to 9)	Bailer	250 mL	Acidified at site with 1.5 trace HNO_3 for comparison to samples 5S-MSU-006
5S-UD-012-(1 to 10)	Low Flow Purge	1 L (1 to 10)	U of Delaware
5S-MSU-013-(1 to 9)	Low Flow Purge	1 L (1 to 9)	Filtration Method
5S-MSU-014-(1 to 10)	Low Flow Purge	250 mL (1 to 10)	Duplication analysis as required

Table 16: Samples Collected at Well 5S, Denzer-Schaefer, April 2001

Sample ID (well-analysis location-sample number)	Sampling Method	Sample Size	Purpose
5S-UD-019-1 to 3	Low Flow Purge	1 –1 L, 2 and 3 –20L	U of Delaware
5S-UD-019-1B to 3B	Low Flow Purge	Subset of 5S-UD-019	For comparison analysis as necessary at MSU
5S-MSU-020-1 to 6	Bailer	1 L	Filtration Method
5S-UD-021-1 to 3	Bailer	20 L	U of Delaware
5S-UD-021-2B	Bailer	Subset 1 L of 5S-UD-021-2	For comparison analysis as necessary

Table 17: Samples Collected from Well MW3, Denzer-Schaefer Site

Sample ID (well-analysis location-sample number)	Sampling Method	Sample Size	Purpose
MW3-MSU-025-1 to 2	Low Flow Purge	1 L	Filtration Method –note LFP samples first sample lowest sediment levels
MW3-UD-024-1	Low Flow Purge	20 L	U of Delaware
MW3-UD-024-1B	Low Flow Purge	1 L subset of MW3-UD-024-1	For comparison as necessary
MW3-022-1 to 3	Bailer	1 and 2 –20L, 3 –10 L	U of Delaware
MW3-UD-022-2B	Bailer	1 L subset of MW3-UD-022-2	For comparison as necessary
MW3-MSU-023-1 to 4	Bailer	1 L	Filtration method

2.2.2 Groundwater Samples from Picatinny Arsenal, NJ

Groundwater samples were collected with bailers and the low flow purge technique from two wells (Well 2 and 4 –subsequently noted as PA2 and PA4) at the Picatinny Arsenal site, NJ on June 21, 2001. Low flow purge samples were collected following the samples collected by the contractor. Bailer samples were collected after the low flow purge samples. Low flow purge samples have low turbidity, are clear and colorless with some larger particles visible in samples that settle quickly. The bailer samples had significantly higher sediment loadings and were a cloudy brown color (see Figure 1). Wells selected were based on recommendations from Joe Marchesani, NJ DEP. Some samples were acidified at the site with HNO_3 ~ 6 mL per 1 L volume. Other samples were not acidified as potentially the acid could digest particles in solution and affect the filtration results. A comparison of the results with LFP and LFP-acidified sampling protocols will be made.

Table 18 and 19 list the samples collected from this project from well 2 and well 4.

Table 18: Samples Collected from Well 2, Picatinny Arsenal

Sample ID (well-analysis location-sample number)	Sampling Method	Sample Size	Purpose
PA2-MSU-001 PA2-MSU-003	Bailer Bailer Acidified	1 L 1 L	Initial screening of lead levels –appropriate digestion volumes
PA2-MSU-002 PA2-MSU-004	Bailer Bailer-Acidified	2 L amber	Filtration method
PA2-MSU-005 PA2-MSU-007	Low Flow Purge Low Flow Purge –acidified	1 L	Initial screening of lead levels –appropriate digestion volumes
PA2-MSU-006 PA2-MSU-008	Low Flow Purge Low Flow Purge –acidified	2 L amber	Filtration Method

Table 19: Samples Collected from Well 4, Picatinny Arsenal

Sample ID (well-analysis location-sample number)	Sampling Method	Sample Size	Purpose
PA4-MSU-009 PA4-MSU-011	Bailer Bailer Acidified	1 L 1 L	Initial screening of lead levels –appropriate digestion volumes
PA4-MSU-010 PA4-MSU-012	Bailer Bailer-Acidified	2 L amber	Filtration method
PA4-MSU-013 PA4-MSU-015	Low Flow Purge Low Flow Purge –acidified	1 L	Initial screening of lead levels –appropriate digestion volumes
PA4-MSU-014 PA4-MSU-016	Low Flow Purge Low Flow Purge –acidified	2 L amber	Filtration Method

Table 20: Well Samples Used for Lead Analysis

Well	Site	Sampling Method	Sample I.D. (s)
5S	Toms River	Bailer	5S-MSU-002-10
5S	Toms River	LFP	5S-MSU-013-9
MW3	Toms River	Bailer	MW3-MSU-023-3 (2/4)
MW3	Toms River	LFP	MW3-MSU-025-1 (2)
2	Picatinny Arsenal	Bailer	PA2-MSU-002
2	Picatinny Arsenal	Bailer-Acidified	PA2-MSU-004
2	Picatinny Arsenal	LFP	PA2-MSU-006
2	Picatinny Arsenal	LFP-Acidified	PA2-MSU-008
4	Picatinny Arsenal	Bailer	PA4-MSU-010
4	Picatinny Arsenal	Bailer-Acidified	PA4-MSU-012
4	Picatinny Arsenal	LFP	PA4-MSU-014
4	Picatinny Arsenal	LFP-Acidified	PA4-MSU-016

3. Results

3.1 Toms River, Denzer-Schaefer Site

The filtration approach was examined on samples taken with bailer and LFP from two wells from the Denzer-Schaefer site in Toms River. Well 5S is characterized by high sediment loadings for both the sample taken with bailers and the LFP with sediment loading of >25 μm particles of 8378 mg/L and 8797 mg/L, respectively. Figure 1 shows that groundwater taken from well 5S (and also well 10) are grayish in color and expected to have clay derived soil particles. Well MW3 differs from the other wells at Denzer Schaefer site in that a groundwater sample with much lower particle content is obtained with the LFP. Sample sediment levels for particles > 25 μm are 139.6 mg/L for the LFP sample and ~600 mg/L for the bailer sample. The appearance of these particles in samples from well MW3 is significantly different with groundwater having a yellowish color for bailers to slight white haziness in the LFP sample (see Figure 1).

Figure 4 shows that the sediment loading in the bailer sample taken from well 5S are highest for particle diameters >20-25 μm at ~8378 mg/L and significant collection of particles for the 10-20 μm filtrate and 2.0 μm filtrate at ~2000-3000 mg/L. Only a small fraction of particles are removed on the 5 μm filter. At the time of this analysis the Whatman 113 and 3.0 μm filter was not included in the filtration process. The grayish color from the presence of particles expected to be clay is not removed until the 2.0 μm filtrate as observed in filtrates shown in Figure 5. Particles collected on filters 2.0 μm and above are all suspected of containing sediments derived from clay sediment derived particles.

Figure 6 shows the sediment loadings in the groundwater sample taken with the LFP from well 5S have similar particle distribution to the bailer sample. Highest for particle diameters >20-25 μm at ~8800 mg/L and significant collection of particles for the 10-20 μm filtrate and 2.0 μm filtrate at ~2000-2500 mg/L. The addition

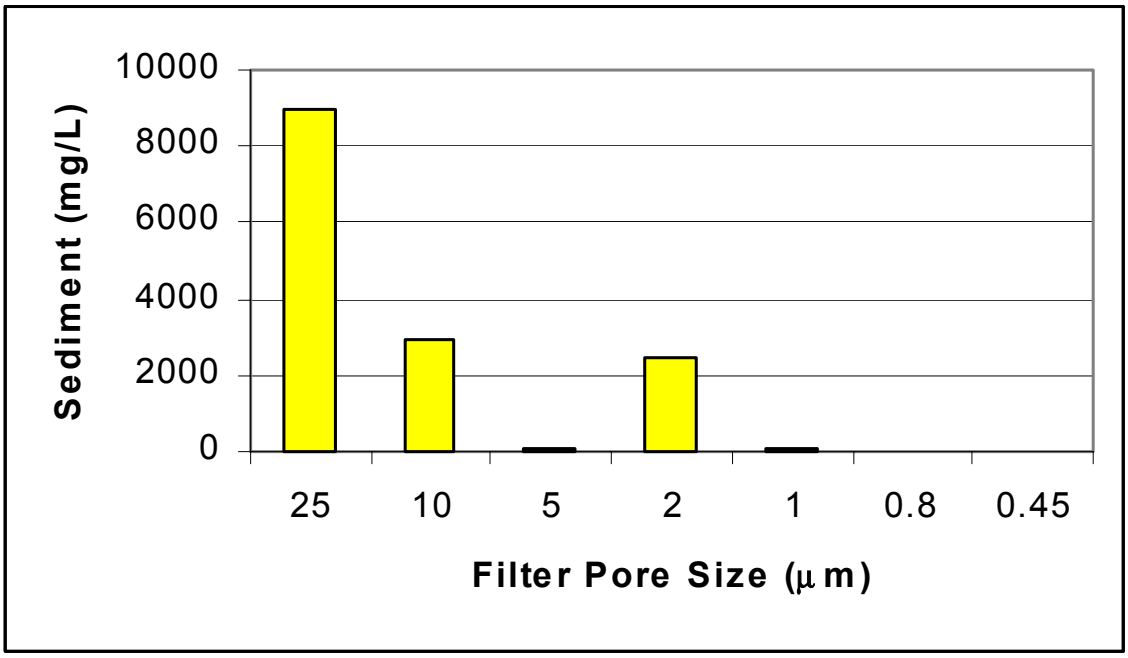


Figure 4: Sediment Levels in Filtrates from Groundwater Sample 5S-MSU-002-10, Bailer Sample from Well 5S, Denzer-Schaefer, Toms River.

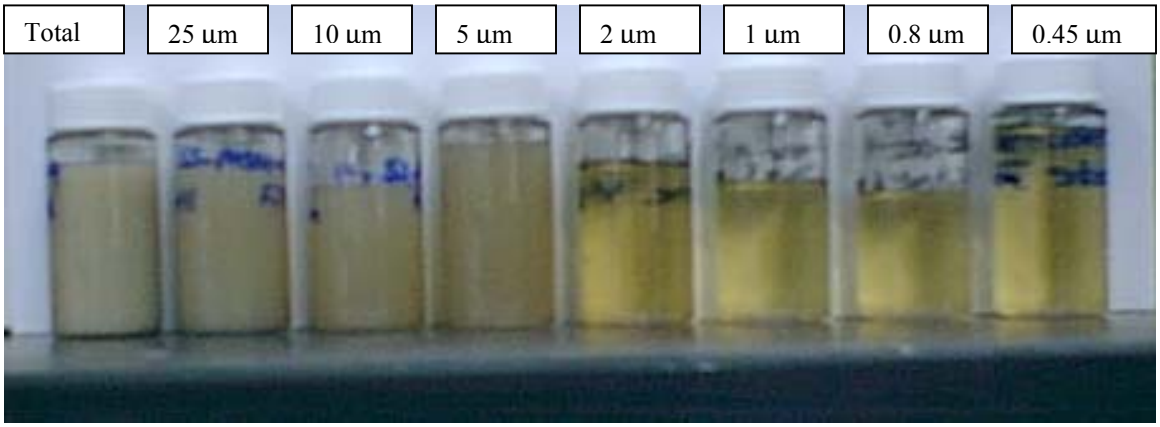
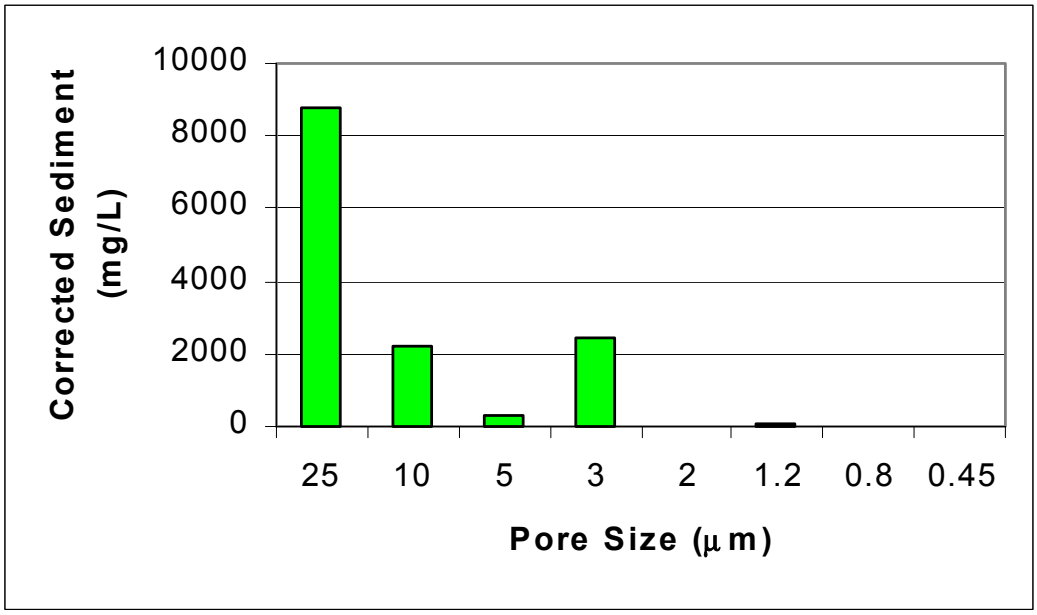


Figure 5: Filtrates from Groundwater Sample 5S-MSU-002-10, Bailer Sample from Well 5S, Denzer-Schaefer, Toms River.



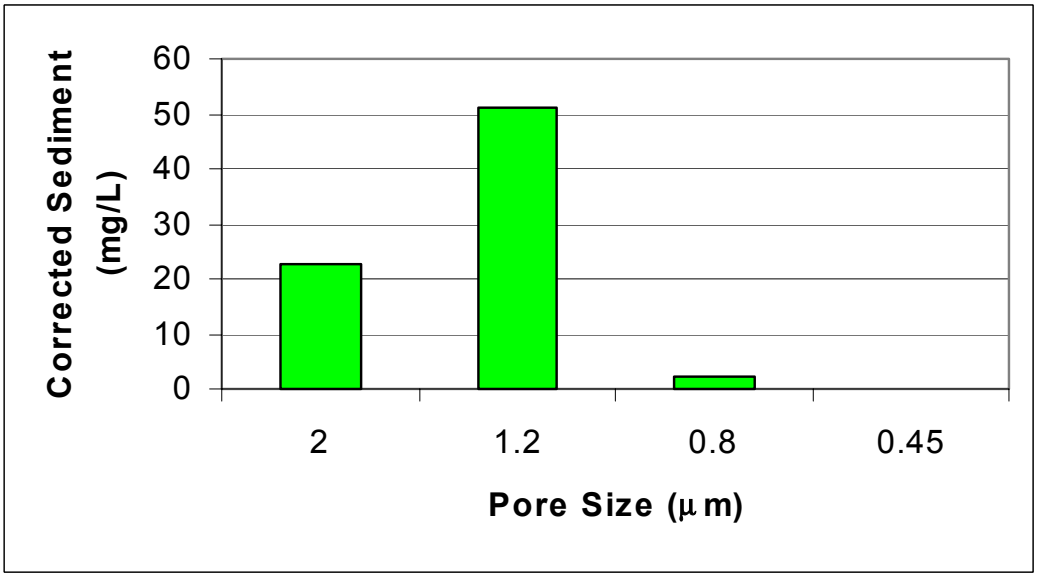


Figure 6: Sediment Levels in Filtrates from Groundwater Sample 5S-MSU-013-9 Low Flow Purge (LFP) Sample from Well 5S, Denzer-Schaefer, Toms River.

of the 3.0 μm filter shows that most of the sediment mass can be removed with this filter rather than the 2.0 μm filter. Figure 7 shows that the clay derived particles are removed with a 3.0 μm filter. Particles removed on 2.0 μm filters and smaller pore sizes are brownish in color. This brownish film was also observed on the 1 μm filter of the bailer sample.

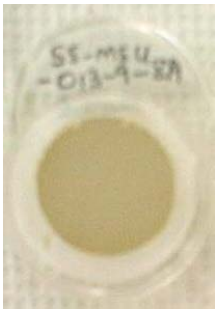
Figure 8 shows the lead levels in the filtrates of the bailer sample taken from well 5S. Very high lead levels are observed (397 ppb) when the sample is not filtered due to the high sediment loading in this sample. The actual level of lead observed may vary from sample to sample with small differences in sediment loadings as the sediments contain the major portion of the lead. Figure 9 shows that the groundwater sample taken with the LFP from well 5S also had high lead loadings (987 ppb) with slightly higher sediment loadings than the bailer sample (see Table 2 and 3). Levels of lead in the filtrates of the groundwater sample taken with the bailer at well 5S decrease dramatically until the 2 μm filtrate. For the 5.0 μm filtrates and above the presence of clay can be observed by the gray color of the filtrates. Filtration through the 2.0 μm filter removes the remaining particles that are expected to be clay particles and the filtrate color is a clear yellow color. The 1.0 μm filtrate has sediment levels < 100 mg/L as compared to the 25 μm filtrate with sediment levels ~8900 mg/L.

Figure 9 shows that the lead levels in the filtrates of the groundwater sample taken with the LFP also decrease dramatically with lower sediment levels until the 3.0 μm filtrate which has lead levels < 10 ppb as compared to ~990 ppb in unfiltered sample. The addition of the 3.0 μm filter to the filtration method allowed for the removal of clay particles at 3.0 μm as compared to 2.0 μm observed for the bailer sample. Figure 7 shows that at 2.0 μm colloidal material is being removed from the solution as apparent in the brownish-yellow film collected on the 2.0 μm. This would suggest that for the bailer sample some colloidal material in addition to clay derived particles are removed at 2.0 μm.

Whatman 113 Whatman 41

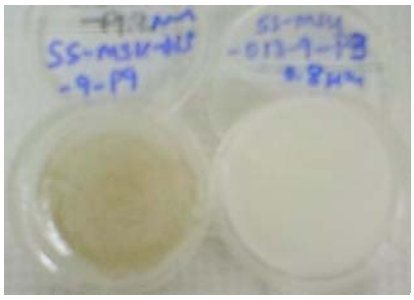
10 µm filter

5 µm filter



3 µm filter

2.0 µm filter



1.2 µm filter 0.8 µm filter

Figure 7: Particles Collected on Filters from Groundwater Sample
5S-MSU-013-9 Low Flow Purge (LFP) Filtrates, Well 5S, Denzer-Schaefer, Toms River.

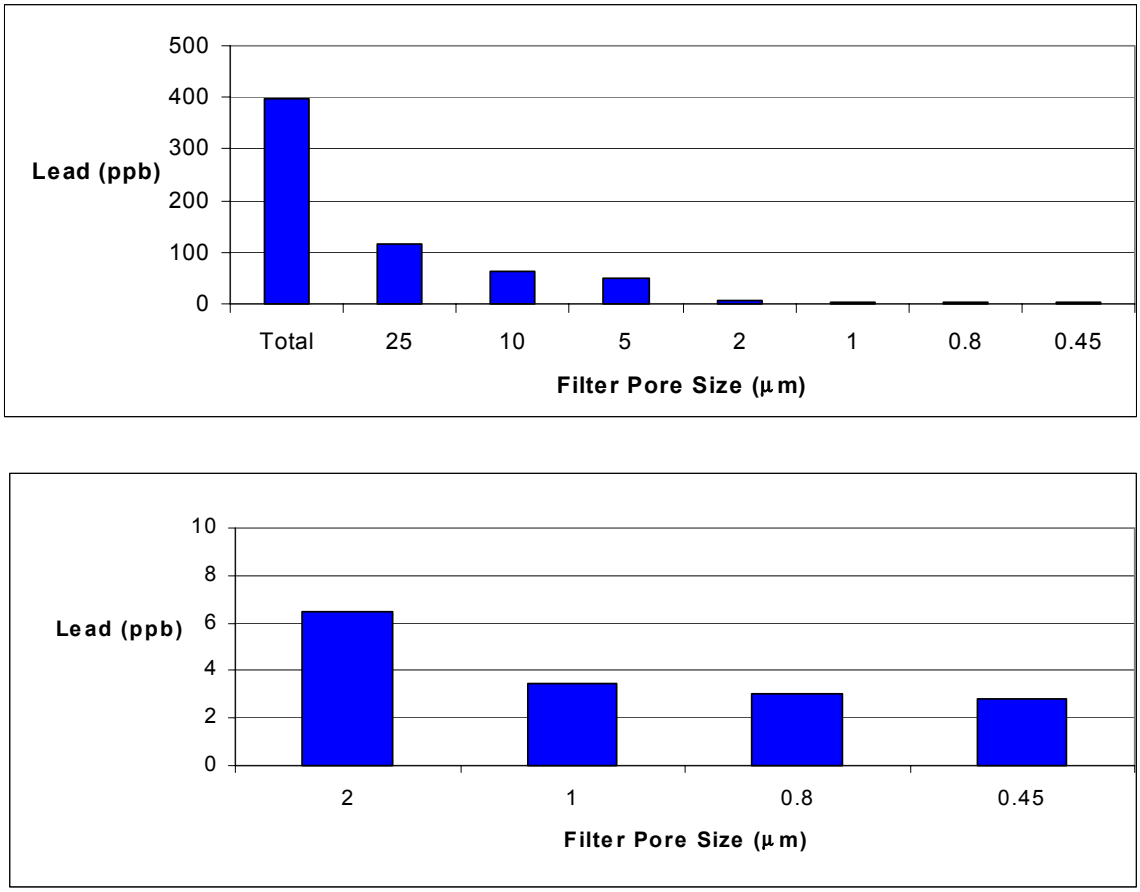


Figure 8: Lead Filtrate Concentrations for a Bailer Sample taken from Well 5S, Denzer-Schaefer, Toms River.

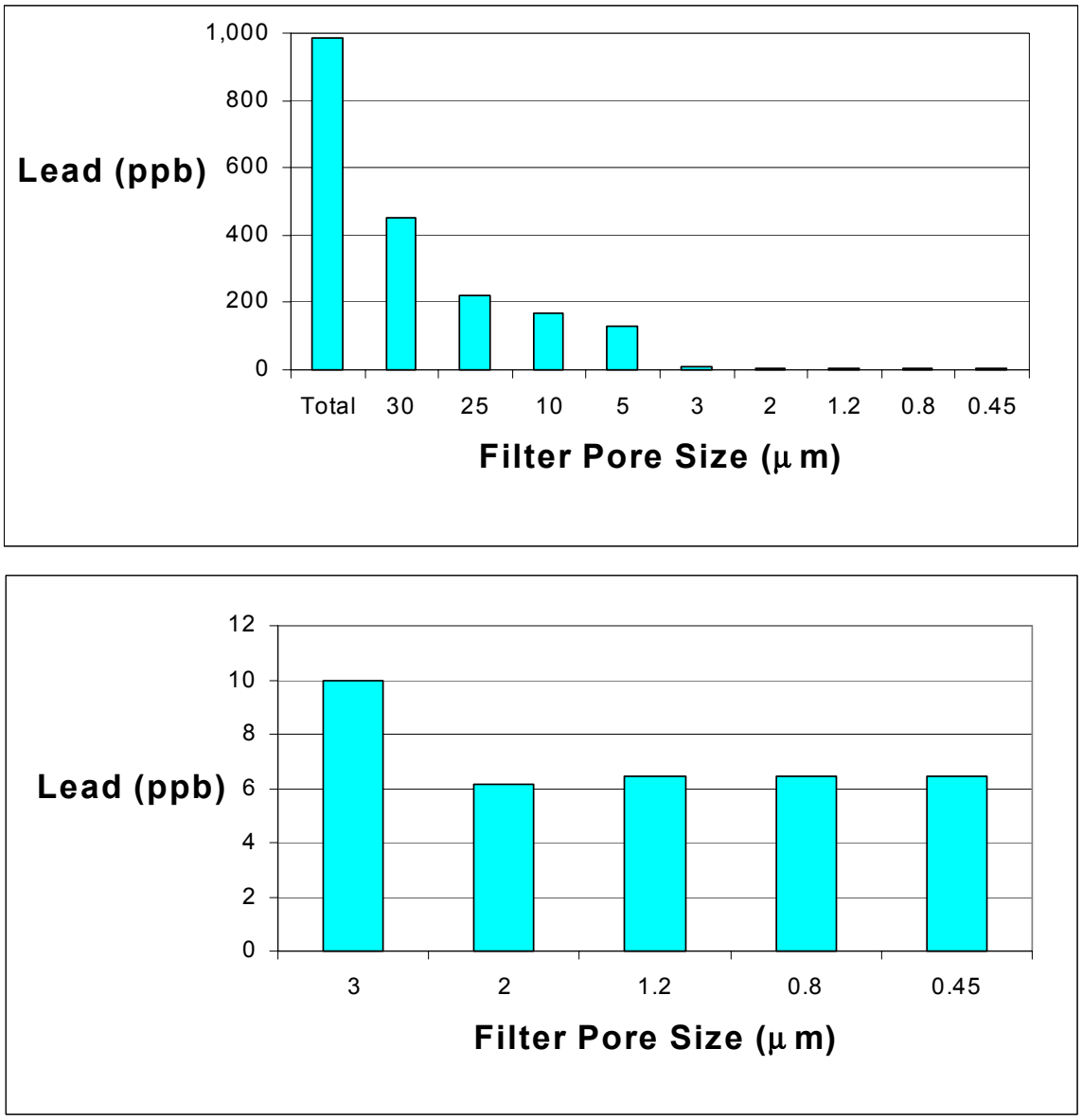


Figure 9: Lead Filtrate Concentrations for a LFP Sample taken from Well 5S, Denzer-Schaefer, Toms River.

Figure 10 shows the concentrations of lead in the bailer sample taken from well 5S. Lead levels per mass of sediment remain constant for sediments collected on 25 to 2 μm filters which can be attributed to the major particles removed with these pore sizes being clay derived particles. At 1.0 μm a higher amount of lead per mass sediment is removed as shown in Figure 10. This is attributed to the removal of colloid material with the 1.0 μm filter. Below 1.0 μm too small of a mass of particles is removed during filtration to determine levels of lead above detectable levels. Figure 11 shows that although the amount of lead per mass of particles is high on the 1.0 μm filter the actual concentration of lead associated with these particles is low due to the small particle mass. For the larger filter pore size ranges most of the lead is associated with the clay-derived particles. When sediment is present the filtrate levels will largely be influenced by the amount of sediment present leading to differences in filtrate lead levels 3.0 μm and above. The additional filtration step at 3.0 μm appears to be necessary to remove the clay derived particles from the colloidal material. The 1.2 and 0.8 μm filters also show the presence of a brownish to light yellow film of particles.

The groundwater samples taken from Well MW3 at the Denzer-Schaefer site, Toms River had a different appearance than other wells (Well 5S, 10) as seen in Figure 1. Initially the samples were filtered through stages 25 to 10 μm, however upon storage prior to the next filtration step pink/white crystals precipitated out of solution as shown in Figure 12. No lead was found to be associated with these crystals, however their origin is unknown. As the precipitation of these crystals interferes with the sediment loading determination the filtration approach was repeated with another sample. It was also noted that the 1 L volume would be insufficient for all the filtration steps as 150-200 mL filtrate samples was required for digestion to ensure levels of lead above the ICP-AES detection limit of 2-3 ppb. Bailer 1 L samples MW3-MSU-023-2 and MW3-MSU-023-4 were combined to provide a 2 L sample (MW3-MSU-023-2/4) for the filtration procedure. For the low flow purge sample, 1 L samples MW3-MSU-025-2 and MW3-UD-024-1B were combined to provide a 2 L sample (referred to as MW3-MSU-025-2). For these samples the filtration approach is completed as quickly as possible and no precipitation of crystals was observed during the short storage time between filtration steps.

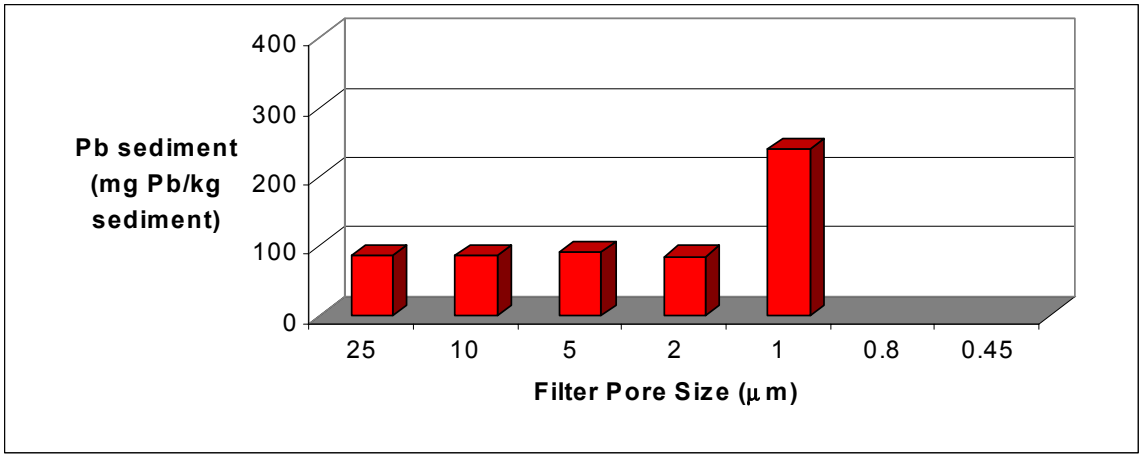


Figure 10: Levels of Lead in the Sediment in Particles Removed from the Bailer Sample Taken from Well 5S During Filtration for Pore Sizes Ranges 25 to 0.45 µm.

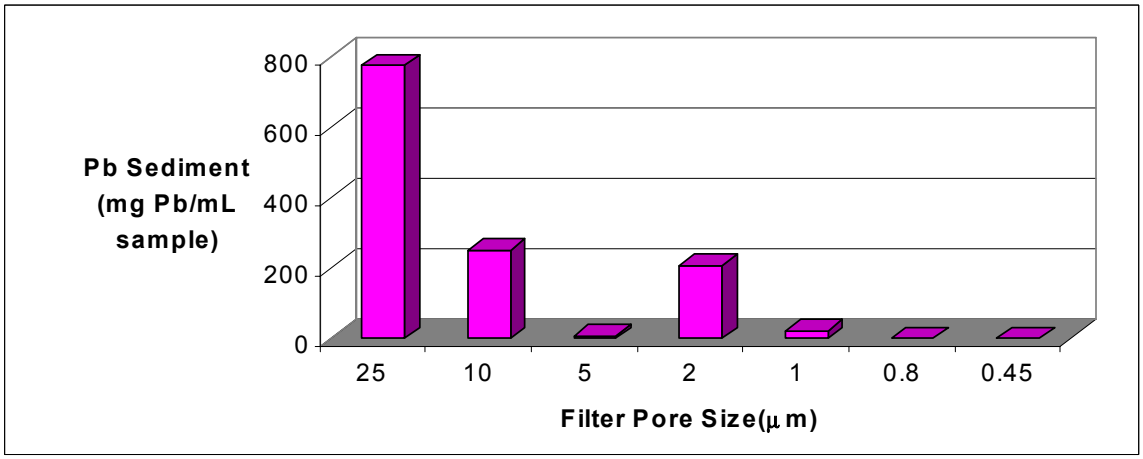
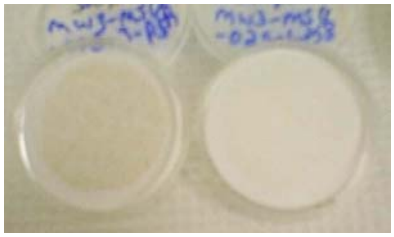


Figure 11: Levels of Lead in the Bailer Sample from Well 5S Associated with Sediments Removed During Filtration for Pore Sizes Ranges 25 to 0.45 µm.

Crystals formed upon storage of filtrates

Bailer LFP
Whatman 41

Bailer LFP
10 µm



Bailer LFP
5 µm

Figure 12: Filter Samples Collected During Initial Filtration of Samples From Well MW3

Figure 13 shows the sediment loadings in the filtrates of the low flow purge sample taken from well MW3 are significantly lower than well 5S with sediment levels for particles > 25 μm of 139.6 mg/L and < 20 mg/L for 5 μm and below filter pore size ranges. It appears that most of the sediment in the low flow purge sample is observed on the 25, 10 and 3.0 μm pore size filter as shown in Figure 14. Figure 14 shows that the low flow purge groundwater sediments are yellow brown in appearance differing from the gray clay like particles observed in well 5S and 10 at Toms River. The particles collected on filters with pore size 2.0 μm and below still have a yellowish appearance, including the 0.45 μm filter.

Figures 13 and 14 shows that the bailer sample taken from well MW3 had higher sediment loadings than the low flow purge sample (~600 mg/L at 25 and 10 μm filters) but the major portion of particles were removed by filtration through 25, 10, and 3.0 μm pore size filters. The 3.0 μm filter still had yellowish/brown particles collected, while sediments collected on smaller pore size filters had the typical yellowish color as observed for particles collected with the LFP sample. Figure 13 also shows that the samples filtered through 25, 10 and 3.0 μm pore size filters had the highest sediment loadings of the bailer sample (> 300 mg/L).

Figure 15 shows a comparison of the lead levels in filtrates from the bailer and LFP samples taken at well MW3 at the Denzer-Schaefer site. The groundwater sample taken with the LFP has relatively constant lead levels of ~10 ppb for total, 25 and 10 μm filtrates. The bailer sample shows significantly higher lead levels of 50-20 ppb for total and filtrates of pore size ranges 25-5 μm. For the bailer sample there is a significant decrease in lead levels after filtration through the 3.0 μm filter where sediments collected on the 3.0 μm filter had a brownish-yellow appearance. Below 3.0 μm only a small particle mass is removed with filtration and the filtrate levels remain between 1.5-0.4 ppb. All filtrates for both the bailer and LFP samples taken from well MW3 are clear below 3.0 μm as shown in Figure 16 and 17. The data available suggest that filter pore

sizes 3.0 μm and above remove predominately sediments. Filters with pore sizes 2.0 μm and below will remove some of the colloidal material from the groundwater samples.

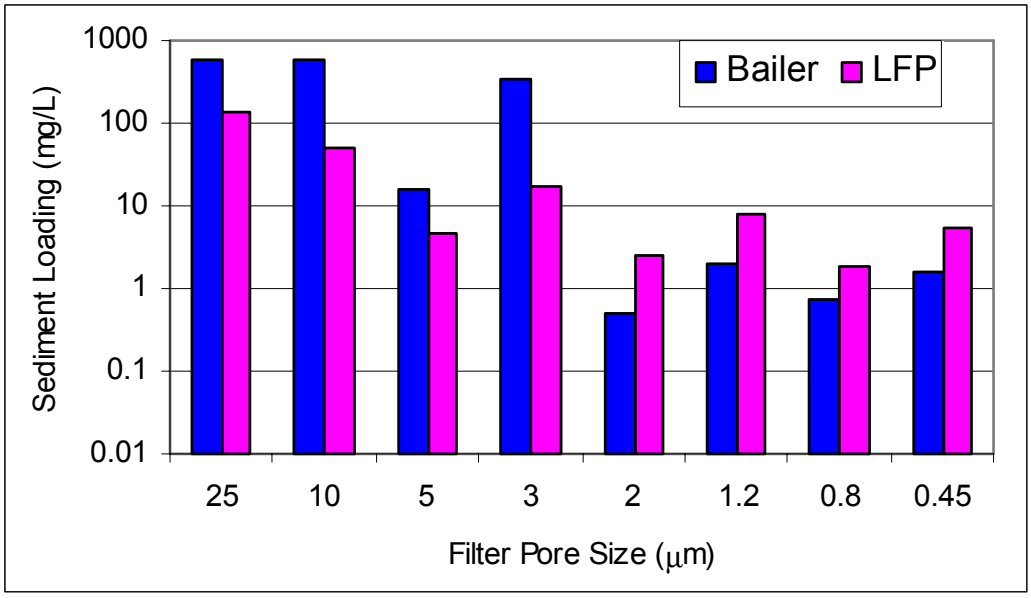


Figure 13: Sediment Levels in Filtrates from Bailer and Low Flow Purge Samples Taken from from Well MW3, Denzer-Schaefer, Toms River.

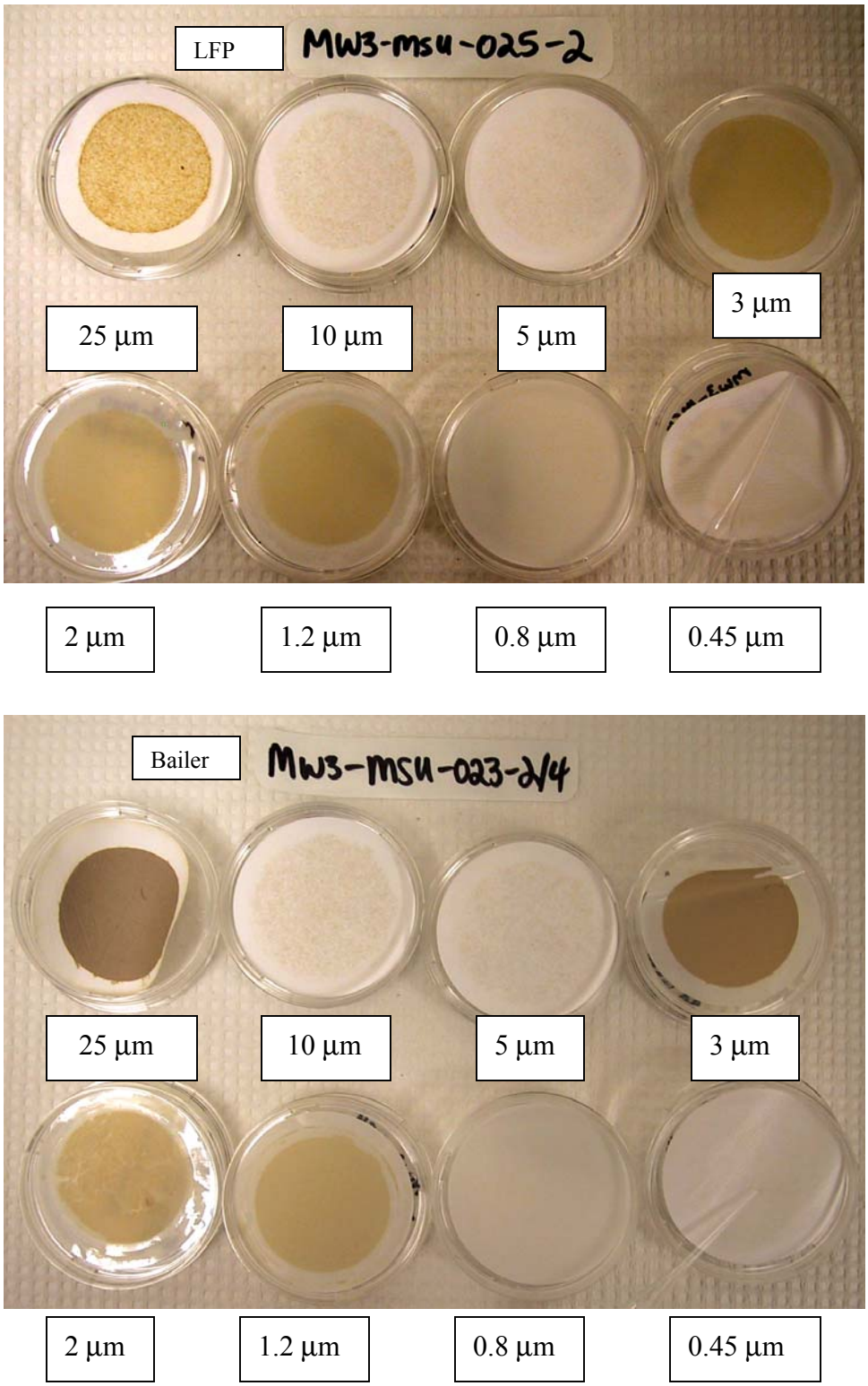


Figure 14. Sediment Levels in Filtrates from the Low Flow Purge (MW3-MSU-025-2) and Bailer (MW3-MSU-023-2/4) Samples Taken from Groundwater Sample from Well MW3, Denzer-Schaefer, Toms River.

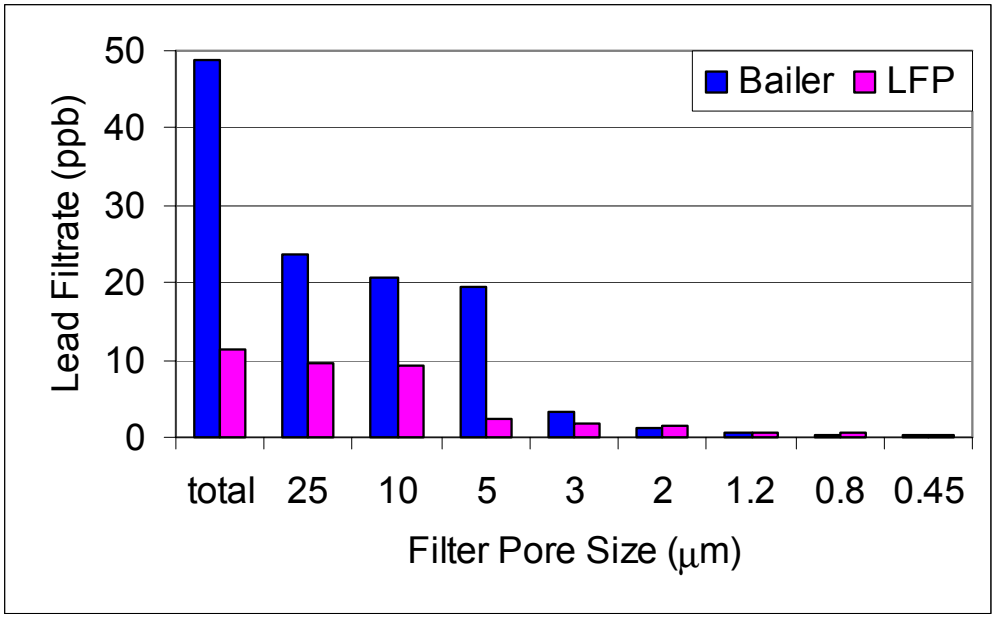
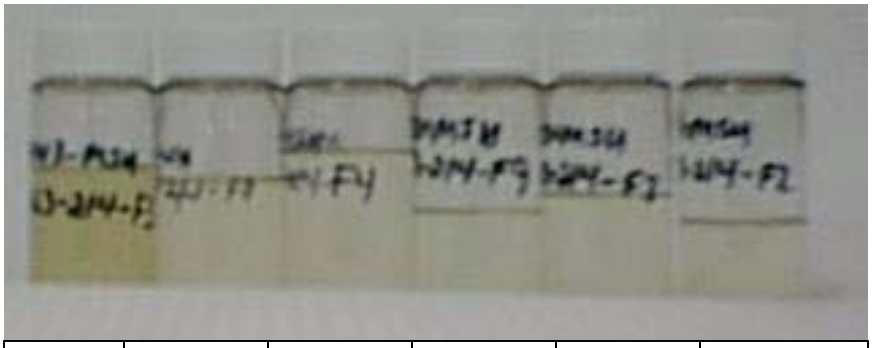


Figure 15: Levels of Lead in Filtrates from the Bailer and Low Flow Purge Pump (LFP) Sample Collected at Well MW3.

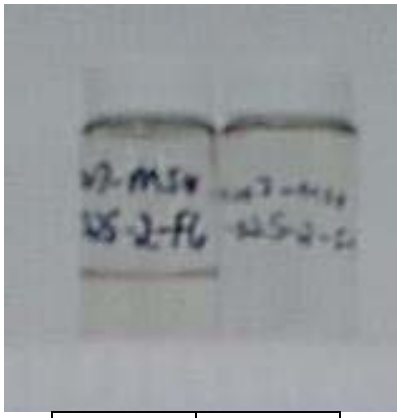
Bailer

LFP

Figure 16: Filtrates from the Initial 1 L Groundwater Samples from Well MW3, Denzer-Schaefer, Toms River.



Bailer	5 µm	3.0 µm	2.0 µm	1.2 µm	0.8 µm	0.45 µm



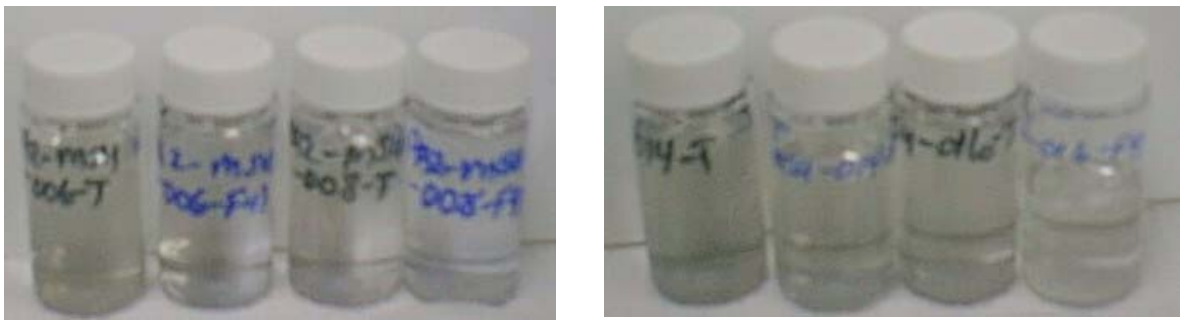
LFP	10 µm	5 µm

Figure 17: Filtrates from the 2 L Groundwater Samples from Well MW3, Denzer-Schaefer, Toms River. Bailer (MW3-MSU-023-2/4) and LFP (MW3-MSU-025-2)

3.2 Picatinny Arsenal Sampling Results

The groundwater samples taken with the low flow purge pump (LFP) are clear and colorless with a small number of larger particles with a sand-like appearance observed when the sample is shaken as shown in Figure 18. Filtration of the low flow purge samples shows that there are particles present in all samples with particle diameter >20-25 μm although significantly less (5-10 mg/L) than observed at the Denzer-Schaefer site (well 5S ~8800 mg/L and MW3 ~140 mg/L). Figure 19 shows that at well 2 the LFP (1 L) sample that was not acidified has a higher particle loading than the acidified LFP sample with the filter showing that the particles collected have a deep medium brown color as compared to the faint grayish granular color of particles collected from the LFP sample that was acidified. The addition of acid appears to cause dissolution of some large particles in the groundwater well 2 LFP sample. The sediment loadings collected on the Whatman 41 filter (25 μm pore size) were similar for the 1 L and 2 L samples filtered with 5.2 mg/L and 4.3 mg/L for the LFP sample and 0.65 mg/L and 0.65 mg/L for the acidified samples, respectively.

The 2 L samples were used for collection of filtrates of different pore size ranges. Figure 20 shows the particles collected on the filters from filtration of the LFP sample at well 2 from Picatinny Arsenal. Most of the sediment mass is removed with filtration through the Whatman 41 filter (25 μm filter pore size) with sediment levels of the 2 L sample (4.3 mg/L) and 0.65 mg/L for the LFP and LFP-acidified sample, respectively. Figure 21 shows that very little particle mass is removed with the other filter pore sizes with the 3.0 μm filter removing the second largest portion of particles (filtrate filtered was 1.1 mg/L for LFP sample). The LFP groundwater sample that was acidified at the site had much lower sediment loadings with 25 and 10 μm filtrates having levels of 1-1.3 mg/L while the other filtrates had < 0.13 mg/L particles. This suggests that the addition of acids to groundwater samples taken at well 2 caused dissolution of some of the particles in the groundwater sample prior to filtration particularly in the 25 and 3.0 μm range. A larger sediment loading was observed on the 10 μm filter that may account for some of the loss from the 25 μm filter.



Total <20-25µm Total <20-25µm Total <20-25µm Total <20-25µm

Well 2 LFP Well 2 LFP Acidified Well 4 LFP Well 4 LFP Acidified

Figure 18: Low Flow Purge Samples and Filtrates of Whatman 41 Filtration from Well 2 and 4 at Picatinny Arsenal, NJ.

Whatman 41 Filters Whatman 41 filters

Well 2 LFP Well 2 LFP Acidified Well 4 LFP Well 4 LFP Acidified

Sediment Loadings Sediment Loadings

5.2 mg/L 0.65 mg/L 10.5 mg/L 9.4 mg/L

Figure 19: Sediments Collected on Whatman 41 filters from Groundwater Samples taken with the LFP at Well 2 and 4 at Picatinny Arsenal, NJ.

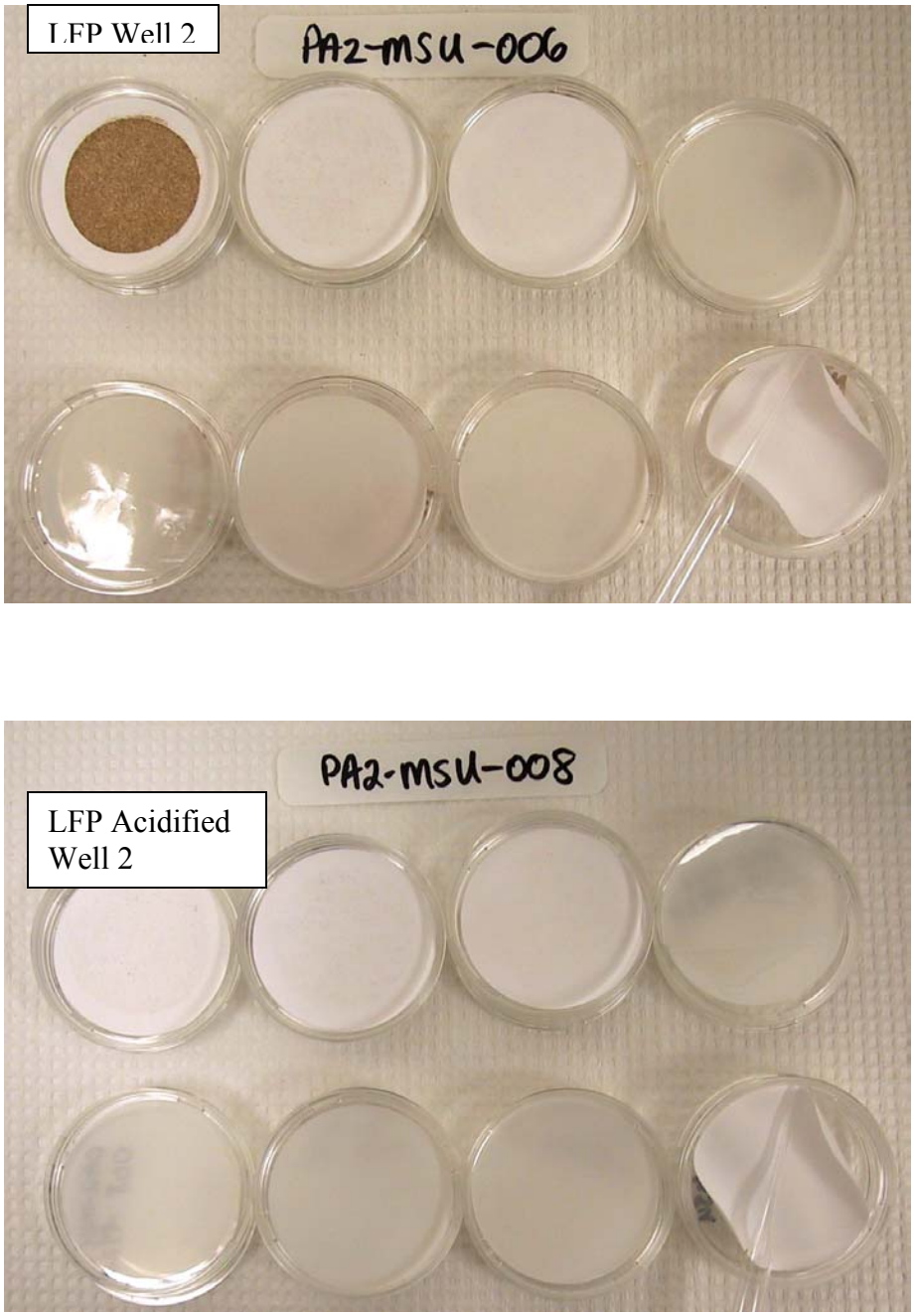


Figure 20. Filters from Filtration of Groundwater Samples Collected with the Low Flow Purge Pump (LFP) at Well 2, Picatinny Arsenal, NJ. In Each Photo Top Row: (Left to Right) Filter Pore Sizes: 25, 10, 5, and 3.0 µm; and Bottom Row (Left to Right) 2.0, 1.2, 0.8, and 0.45 µm.

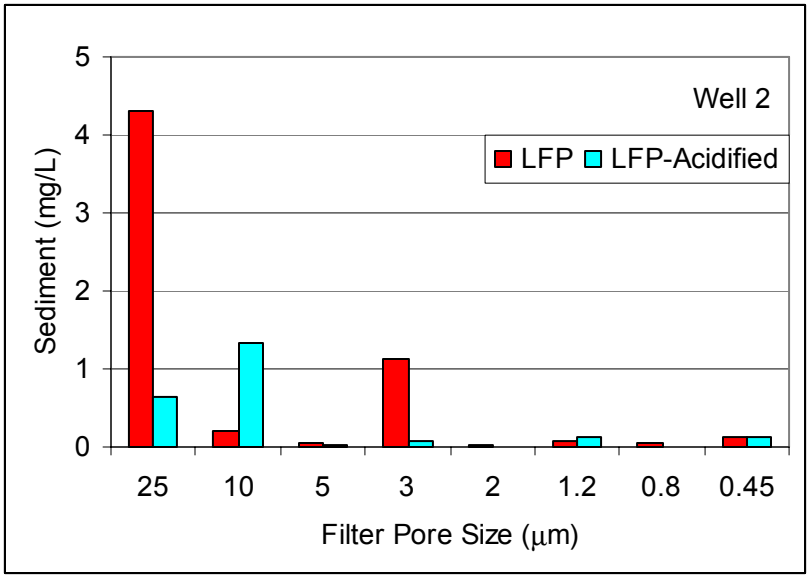


Figure 21. Sediment Levels of Filtrates from Low Flow Purge Samples Collected At Well 2, Picatinny Arsenal, NJ.

A groundwater sample was also collected at Picatinny Arsenal from well 4 during the same time period with the LFP. Figure 22 shows the particle collection from filtration of the 2 L LFP and LFP-acidified sample can be seen on the 25, 10, 3.0 μm filters. Particle concentrations are ~10 mg/L for the acidified and unacidified groundwater sample filtered with the 25 μm filter. These sediment loadings are slightly greater than observed at well 2 at Picatinny Arsenal (5 mg/L). The 3.0 μm filter also removed significant particles from the LFP sample at well 4 with 1.7-2.7 mg/L sediment as shown in Figure 23. Smaller filter pore sizes only removed very small amounts of sediment typically < 0.5 mg/L. The groundwater sample that was acidified had similar particle concentrations as the LFP groundwater sample that was not acidified at the sampling site suggesting that there was little digestion of particles (except for the 10 μm pore size) caused by adding acid to groundwater samples taken from well 4. This differs from the observations of well 2 which may be partially attributed to the different type of particles observed on the Whatman 41 filters (coarser grain). Well 4 showed the grayish-brown granular particle collection for the LFP and LFP-acidified sample. Sediment masses determined for the Whatman 41 filter for the 1 L and 2 L samples were the same (10.5 mg/L LFP and 9.4 mg/L LFP-acidified). Because of the large granular nature of these particles and quick settlement it is difficult to get a uniform collection of these particles for the total sample analysis. In the 2 L total samples all samples were checked to ensure that some larger particles were transferred when obtaining the aliquot for digestion.

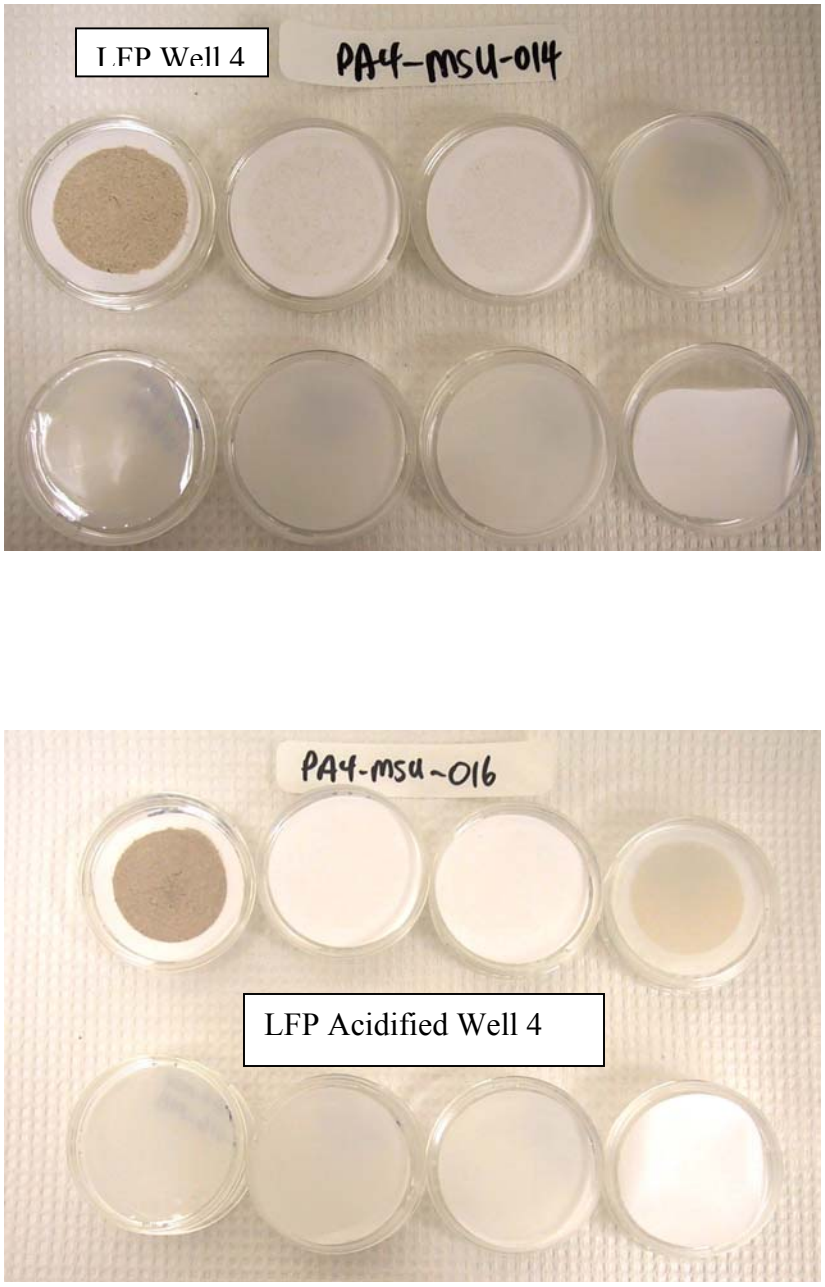


Figure 22. Filters from Filtration of Groundwater Samples Collected with the Low Flow Purge Pump (LFP) at Well 4, Picatinny Arsenal, NJ. In Each Photo Top Row: (Left to Right) Filter Pore Sizes: 25, 10, 5, and 3.0 µm; and Bottom Row (Left to Right) 2.0, 1.2, 0.8, and 0.45 µm.

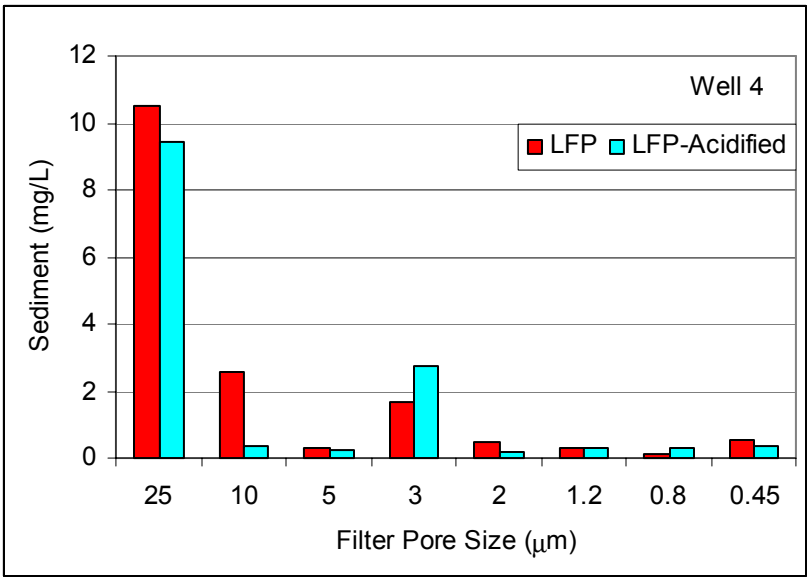


Figure 23. Sediment Levels of Filtrates from Low Flow Purge Samples Collected At Well 4, Picatinny Arsenal, NJ.

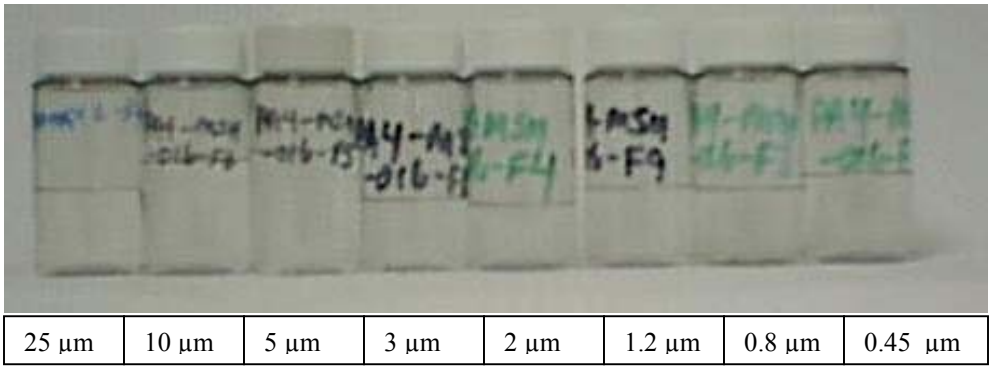


Figure 24. Filtrates from Low Flow Purge Acidified Sample PA4-MSU-016, Well 4, Picatinny Arsenal, NJ.

The groundwater samples collected with bailers have a very high sediment loading and have brown colored filtrates after mixing as shown in Figure 25. Figure 25 shows that the particles in the liquid particularly for the acidified samples quick settle out of solution to give a clear colorless filtrates. The bailer samples that were not acidified at the site show much slower settlement of particles out of solution with a yellow-brownish color visible for several hours after mixing suggesting that there is a range in particle diameters in addition to the larger dark brown soil-derived particles. The addition of acid to well water samples at Toms River also resulted in immediate coagulation of particles and for this reason it was decided not to add acid to preserve samples at the Toms River site as it may alter the filtration results.

The 2 L sample was used to obtain samples of particles collected on filters of different pore size ranges from 25 to 0.45 μm. Figure 26 shows that the largest portion of particles removed from the bailer sample at well 2 was with the 25 μm filter with significant amounts of particles also collected on the 10, 5, and 3.0 μm filters. Figure 27 shows that after the filtration through the 25 μm filter the filtrates are clear and colorless as compared to the original sample. Figure 28 shows that the sediment levels drop from ~4300 mg/L at the 25 μm stage to < 1 mg/L for the remaining filtration stages. There are also higher sediment loadings for the 10 and 5.0 μm filters collected with the bailer sample than with the groundwater sample collected with a low flow purge pump (Figures 28 and 29). The 3.0 μm filter removes ~1 mg/L similar to that observed for the groundwater sample collected with the low flow purge pump. This would suggest that the major difference in the groundwater samples collected with the bailer and LFP is collection of a large portion of particles >5 μm with the bailer (more predominate for > 10 μm pore size).

The bailer sample collected at well 4 shows similar particle distribution to the well 2 bailer sample with high particle loadings on the 25 μm filter as seen in Figures 29 and 30. Particle loadings decrease to ~ 1 mg/L for the 10-3.0 μm pore size ranges and <0.5 mg/L for smaller pore size ranges. There is a much greater loading of particles observed for

Bailer Bailer Acidified Bailer Bailer Acidified

Well 2 Well 4

after settlement for 2 hours

Well 2 Well 4

Bailer Bailer Acidified Bailer Bailer Acidified

Figure 25: Bailer Total Samples Taken from Well 2 and 4, Picatinny Arsenal, NJ

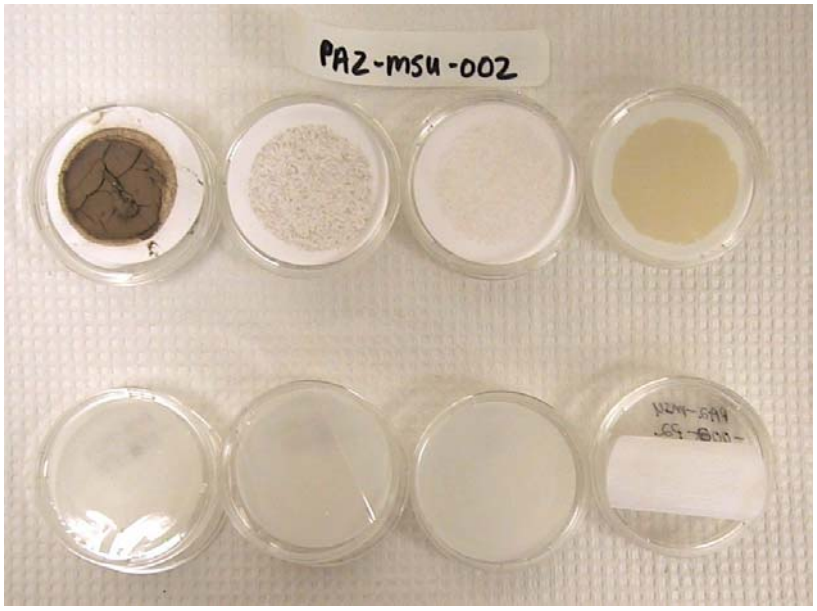


Figure 26. Filters from a Bailer at Well 2, Picatinny Arsenal, NJ. In Each Photo Top Row: (Left to Right) Filter Pore Sizes: 25, 10, 5, and 3.0 µm; and Bottom Row (Left to Right) 2.0, 1.2, 0.8, and 0.45 µm.

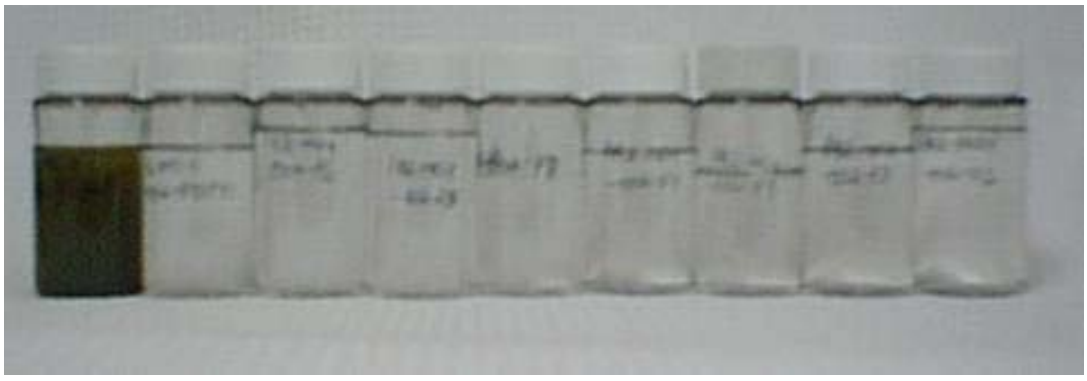


Figure 27. Filtrates from Bailer Sample PA2-MSU-002, Well 2, Picatinny Arsenal, NJ.

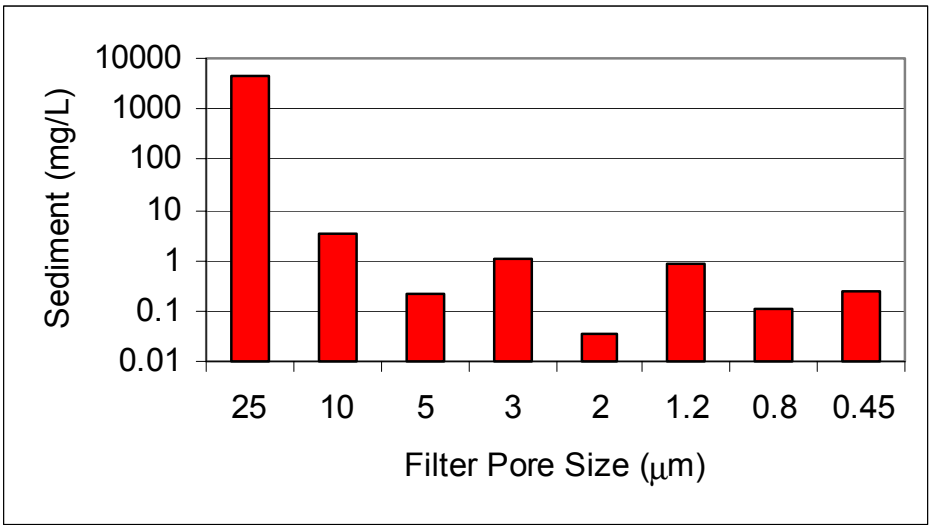


Figure 28. Sediment Loadings in Filtrates from Bailer Sample PA2-MSU-002 from well 2 at Picatinny Arsenal, NJ.

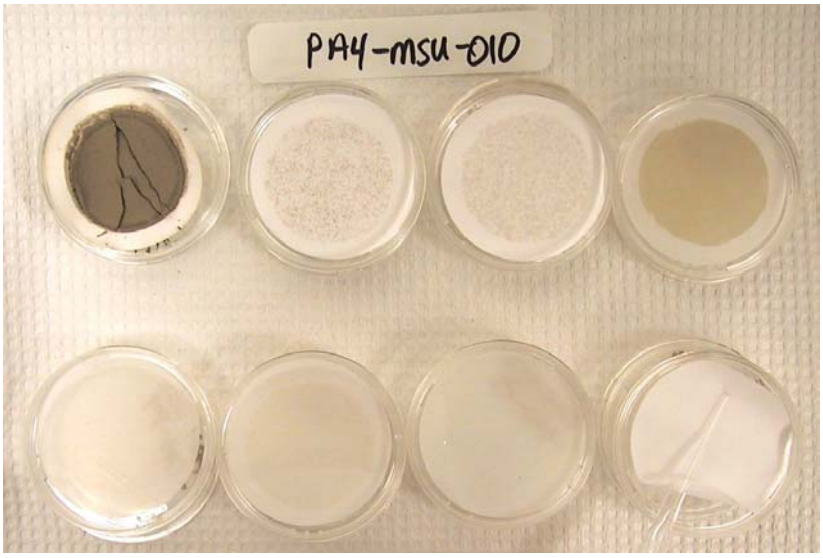


Figure 29. Filters from a Bailer at Well 4, Picatinny Arsenal, NJ. In Each Photo Top Row: (Left to Right) Filter Pore Sizes: 25, 10, 5, and 3.0 μm; and Bottom Row (Left to Right) 2.0, 1.2, 0.8, and 0.45 μm.

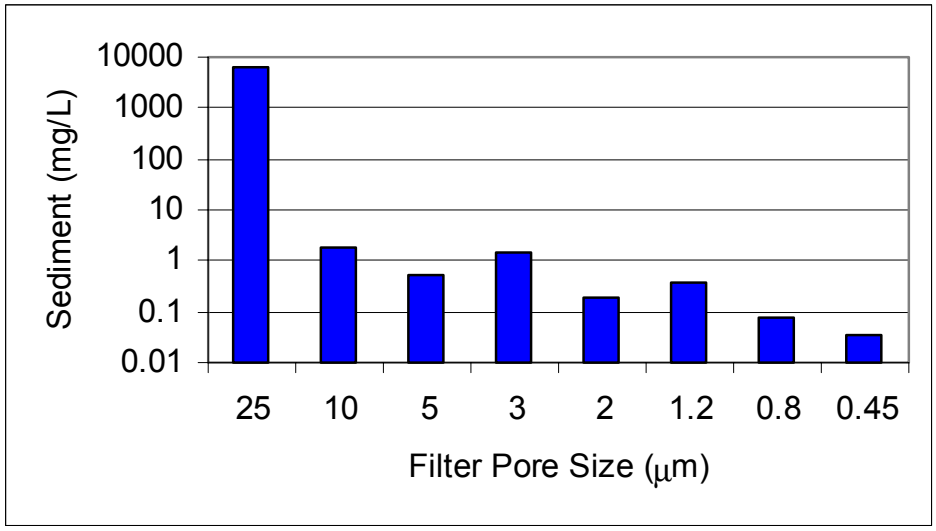


Figure 30. Sediment Loadings in Filtrates from Bailer Sample PA4-MSU-010 from Well 4 at Picatinny Arsenal, NJ.

the 25 μm filter (~6500 mg/L) for the bailer sample as compared to the groundwater sample collected with the low flow purge pump (10.5 mg/L). The use of bailers has significantly increased the amount of particles with size range > 25 μm.

The total lead concentration from the 2 L groundwater sample collected with the low flow purge pump at well 2 are 2.4 ppb for the LFP and LFP-acidified sample, respectively. This is similar to that observed for the 1 L samples (2.3 and 2.4 ppb). Upon filtration through the Whatman 41 filter (25 μm pore size) the concentration of the filtrate decreases to a minimum as shown in Figure 31. The concentrations of the filtrates are relatively constant for 25-0.45 μm with LFP sample at 0.2-0.4 ppb and the LFP-acidified sample at generally 1.3-2.5 ppb. The LFP sample acidified immediately after sampling appear to have slightly higher lead concentrations. This may be caused by the addition of acid to the sample at the site immediately following sampling or to the dissolution of some of the particles present in the sample when the acid was present. The LFP sample at well 2 clearly showed a low particle loading for the 25 and 3.0 μm filters (see Figure 20). Lead concentrations in filtrates (within the error of the analysis) are relatively constant as a function of pore size after the 25 μm filtration. This would suggest that the small amount of particles removed with filtration below 25 μm filter pore size are not significantly contributing to the lead concentrations of the sample.

The bailer sample at well 2 was shown to have significantly higher loadings of particles primarily > 25 μm and Figure 30 shows that for both the bailer and bailer-acidified sample the lead concentrations are very high (734 and 1180 ppb, respectively) as compared to the LFP samples (2-2.4 ppb). Filtration with the Whatman 41 filter (25μm) removes the major portion of the particles and the lead concentrations decrease to 0.45 ppb similar to that observed for the LFP sample at well 2. The removal of particles with the 10 μm filter may account for a small decrease in lead concentrations of the filtrates. The levels for the 10-0.45 filtrates are low 0.1-0.15 ppb. These levels are also slightly lower than observed for the LFP sample, however the sample concentrations are very low making the analysis more difficult. The difference in total lead concentration of the

bailer and bailer-acidified sample is attributed to different sediment loadings as it has been seen previously that bailer sample sediment loadings are variable between samples taken from the same well. The filtration of the bailer-acidified samples were not completed.

The 2 L groundwater samples collected with the low flow purge pump at well 4 show a similar trend to well 2 with total concentrations of 2.9 and 2.2 ppb Pb for the LFP and LFP-acidified samples, respectively. These total lead concentrations are also similar to that observed previously for the 1 L samples at well 4 (2.1 and 2.7 ppb). Figure 31 shows that the filtrates of the LFP sample at well 4 show a small decrease in concentration with filtration through 25 μm pore size then relatively constant lead concentrations at ~0.7 – 1.5 ppb. The LFP acidified sample did not show a decrease in lead concentration with filtration with levels at ~2-3 ppb. The higher levels in this sample may be due to the acid that was added to the sample at the site or dissolution of some particles by the acid. However it should be noted that the well 4 sample had similar particle loadings at 25 μm with ~ 10 mg/L so it is not likely a result of dissolution of these larger particles.

The bailer sample at well 4 was also shown to have significantly higher loadings of particles particularly > 25 μm and Figure 32 shows that for both the bailer and bailer-acidified sample the total lead concentrations are very high (~1110 and 1450 ppb, respectively) as compared to the LFP samples (2-2.4 ppb). Filtration with the Whatman 41 filter (25μm) removes the major portion of the particles (see Figure 29) and the lead concentrations decrease to 3.2 ppb. Subsequent removal of particles with the 10 μm filter may account for a small decrease in lead concentrations of the filtrates to 1-2 ppb range. Filtration with filters of pore size range 5-0.45 μm does not cause significant reductions in lead levels (1-2 ppb) similar to that observed for the LFP sample. As seen with well 2 the difference in total lead concentration of the bailer and bailer-acidified sample at well 4 is attributed to different sediment loadings as it has been seen previously that bailer sample sediment loadings are variable between samples taken from the same well.

Duplicate digestions of the same sample show similar lead loadings for the total bailer sample suggesting complete digestion of the sample.

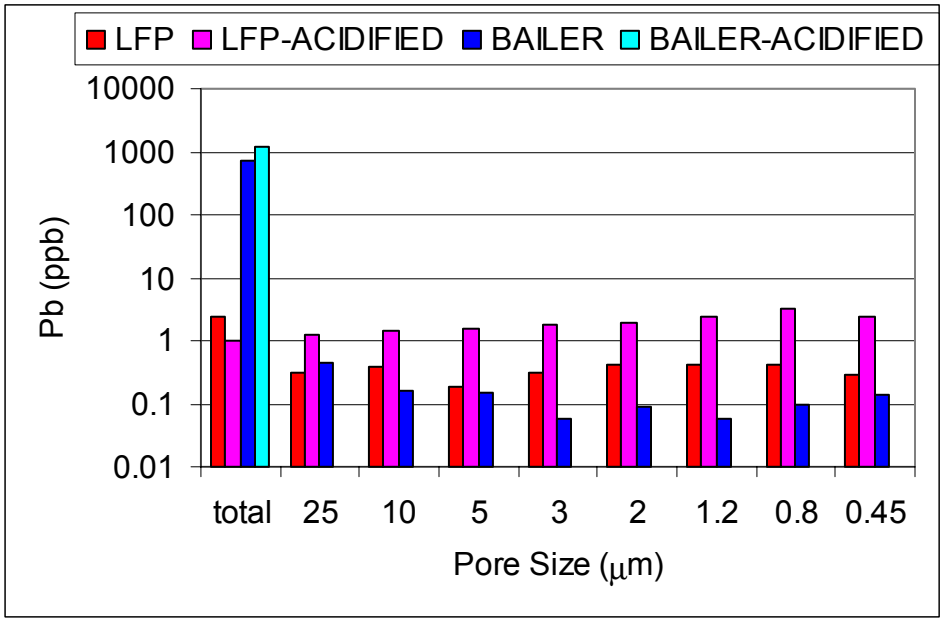


Figure 31. Lead Concentrations in Filtrations of Groundwater Samples Collected at Well 2, Picatinny Arsenal, NJ.

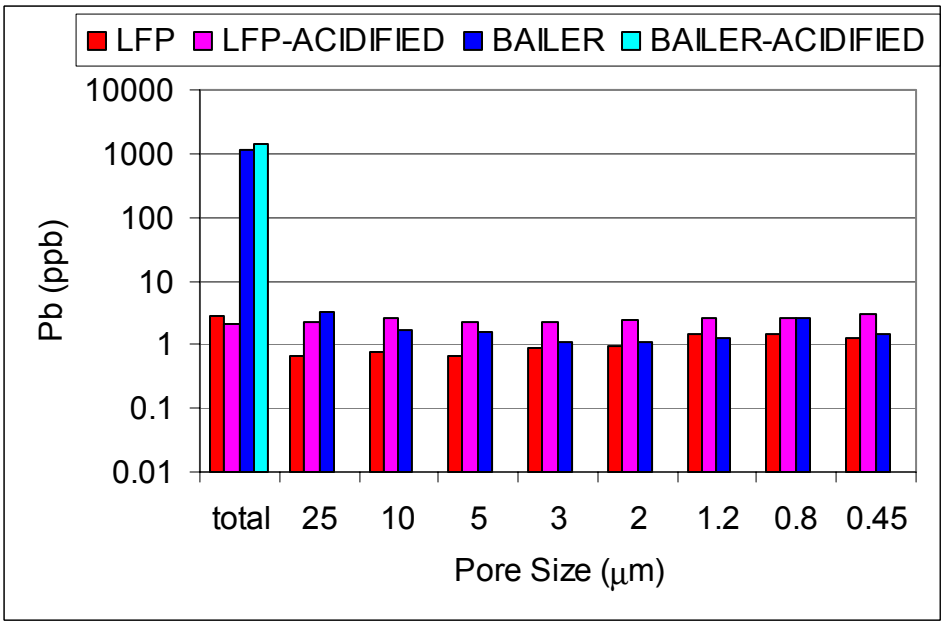


Figure 32. Lead Concentrations in Filtrations of Groundwater Samples Collected at Well 4, Picatinny Arsenal, NJ.

4. Overall Progress (Relative to Scope of Work Schedule)

Groundwater samples were collected with a low flow purge pump and bailers from wells 5S, 10, and MW3 at the Denzer-Schaefer site. Well 5S and MW3 were selected for further analysis due to differences in types and sediment levels in groundwater samples. The groundwater samples that were analyzed were not acidified at the site due to potential digestion of particles in solution prior to filtration. Groundwater samples were also collected with the low flow purge pump and bailers from Well 2 and 4 at the Picatinny Arsenal Well. One set of groundwater samples were acidified at the site. Comparison of acidified and unacidified samples were completed for the low flow purge samples from both wells. Filtrates of seven different pore size ranges (25, 10, 5, 3, 2, 1.2, 0.8, and 0.45 μm) were analyzed for lead from these samples. Sediment levels in the bailer sample from well 5S were also examined to determine differences in lead levels of particles as a function of size.

5. Conclusions

The filtration approach was used on groundwater samples collected from several wells using bailers and the LFP that had different particle loadings and type of particles. Wells 2 and 4 at Picatinny Arsenal are typical wells were the groundwater sample collected with the low flow purge pump is visually a clear colorless solution with only small number of particles present predominately > 25 μm (4.3-10.5 mg/L). The bailer sample from these wells differed significantly with very high particle loadings (4300-6500 mg/L) and visually the appearance of brown sediment in solution (Figure 1).

The filtration approach showed that the larger particles observed in samples collected with the low flow purge pump were removed with filtration through Whatman 41 filter (25 μm) with lead concentrations from total sample decreasing from 2.4 to 0.3 ppb and 3.0 to 0.8 ppb for wells 2 and 4, respectively. Within the error of the filtration approach no significant decreases in lead concentrations were observed with the smaller pore size ranges. Filtration of the bailer sample showed that the major portion of the sediment could be removed with filter pore size 25 μm with lead levels decreasing from 734.4 to 0.4 ppb and 1109.8 to 3.1 ppb for wells 2 and 4, respectively. A smaller decrease in lead concentration could be observed by filtration with a 10 μm filter due to removal of sediment (1.9-3.5 mg/L). Further filtration did not result in decreased lead levels in the filtrates. Filtration of the bailer sample through 25 μm pore size filter would remove most of the larger particles in solution and provide levels of lead closer to that observed with the samples collected with the low flow purge pump. Filtration through 10 μm filter provides further removal of remaining sediment particles in the bailer sample and similar levels to that observed for the LFP. Figure 27 shows that the groundwater samples collected with bailers after filtration through 25 μm pore size filter have a clear colorless appearance as observed for samples collected with the low flow purge pump (Figure 24).

Comparison of the acidified and unacidified samples collected with the low flow purge pump from wells 2 and 4 at Picatinny Arsenal showed that there is some potential for dissolution of particles prior to filtration when sediment samples are acidified at the site.

This was more apparent at well 2 where the total sample had similar levels of lead (2-2.4 ppb). The levels of lead are relatively constant with filtration for the acidified sample with only a small decrease with filtration through 25 μm filter. For the unacidified LFP sample at well 2 removal of sediment with filtration through 25 μm filter (4.3 mg/L as compared to 0.65 mg/L in acidified sample) resulted in a larger decrease in lead concentration from 2.4 ppb to 0.3 ppb. The remaining filtrates all had lower lead levels 0.2-0.4 ppb than the acidified sample. As total lead levels in the sample were similar (2 and 2.4 ppb) it is unlikely that this is due to presence of lead in the acid that was added but rather due to digestion of some of the particles in solution prior to filtration for the acidified groundwater sample. Higher levels of lead were also observed in all filtrates of the acidified sample from well 4 (~2.2-2.7 ppb) as compared to the sample that was not acidified which had 0.6-1.5 ppb lead after filtration through 25 μm or small pore size filters (Table 11). At this well there was little difference in sediments filtered with 25 μm filter (10.5 and 9.4 mg/L for LFP and LFP-acidified respectively), however there was a smaller sediment loading in the 10 μm pore size range (2.5 compared to 0.3 mg/L).

Groundwater samples collected from well MW3 at Denzer-Schaefer site in Toms River were characterized by the presence of some particles in solution even with samples collected with the low flow purge pump. These particles were yellowish in color and not typical of soil clay derived particles as seen at well 5S and 10. Sediment loadings were higher for the sample collected with the bailer (602 mg/L as compared to 140 mg/L for LFP with 25 μm pore size filtration). The groundwater sample collected with the low flow purge pump shows removal of particles and significant decreases in lead concentrations for filtration to 5.0 μm pore size. Filtration with 3.0 μm removes additional particles (17.4 mg/L) with a small decrease in lead concentrations. Filtration through smaller pore size ranges causes a smaller change in lead concentrations 1.5-0.4 ppb for 2 to 0.45 μm pore size filters. The bailer sample also showed significant decreases in lead concentration with filtration through 25 to 3.0 μm filter pore sizes. A much larger particle mass is removed for the bailer sample (340 mg/L as compared to 17.4 mg/L for LFP sample) suggesting that significant amounts of sediments are removed with filtration through 3.0 μm filter. The groundwater samples collected with both the

bailer and LFP contain sediments suspected to be 3.0 μm and larger. Below 3.0 μm the decrease in lead levels is expected to be due to loss of colloidal material with similar trends observed in lead concentration for both the bailer and LFP sample (Table 4 and 5).

Wells 5S and 10 have high sediment loadings for groundwater samples taken with both the bailer and LFP (>8900 mg/L). The groundwater sample collected with the low flow purge pump actually had higher sediment loadings than the bailer sample for > 25 μm. Other sediment levels were similar for the different pore size ranges. Filtration of the sample collected with the low flow purge pump showed that the addition of the 3.0 μm filtration step could remove the clay-derived particles with grayish appearance from the colloidal material (yellow-brown appearance) as shown in Figure 7. Lead levels decreased from 987 ppb for the unfiltered LFP sample to ~10 ppb for the 3.0 μm filtrate. The presence of any soil derived particles (as seen by the gray coloration on filters) caused levels to dramatically increase from lead naturally present in soil particles. A small decrease in lead levels from 10 to 6 ppb was observed with filtration through 2.0 μm filtration as attributed to the removal of colloidal material from the solution. The bailer sample showed a similar trend with lead levels decreasing dramatically as particle loadings in solution decreased. At the time of the analysis the 3.0 μm filter was not used in the filtration approach so that all the sediment particles were not removed until the 2.0 μm set. An additional sample of 5.0 μm filtrate of a bailer sample from well 5S will be filtered through 3 and 2 μm steps in the next few weeks to confirm that the 3.0 μm filter can be used to successfully remove the sediment derived particles. Analysis of the sediments from the bailer sample did show that there was a significant difference in lead per sediment mass for the soil derived particles obtained on 25, 10, 5, and 2 μm filters as compared to the 1.0 μm filter (Figure 10). Most filter samples at the smaller pore size ranges do not have enough mass to get a quantitative measurement of the lead associated with the colloidal particles. The results however show that filtration through a 3.0 μm filter provides a means of removing fine sediment particles from groundwater samples at well 5S. Similar results would be expected for well 10 at Denzer-Schaefer site.

6.0 Recommended Future Activities

The activities conducted under the work plan showed that filtration of groundwater samples is a valuable technique that can be used to investigate wells with high particle loadings when either particles are collected when using a low flow purge pump or when there are concerns about the potential for transport of lead on particles in solution. The results indicate for wells such as wells 2 and 4 at Picatinny Arsenal that filtration of a bailer sample through 25 μm (or 10 μm) filter can remove the majority of the larger particles in solution giving lead concentrations similar to that observed for groundwater samples collected with the low flow purge pump. The characterization of the particle mass as a function of particle size should be completed for the larger particle size ranges >25 μm at these two wells to determine the source of the particles observed in bailer samples and the amount of lead associated with these particles

In addition many of the groundwater samples collected for this study after filtration had very low levels of lead making the analysis and interpretation more difficult. Other wells at Picatinny Arsenal with higher lead loadings could be examined (along with particle distribution) to improve the understanding of the flow of particles in the groundwater. These higher lead loadings would also provide an opportunity to study potential small losses in lead from removal of colloidal material for the smaller particle size ranges. In future a 4 L sample should be used whenever possible to provide a large enough volume for filtration and collection of particles on filters. With the larger amount of particles collected on filters the sediment levels of lead in the smaller particle size ranges could be examined in more detail. The filter samples from this study could be used to obtain an estimate of the lead levels but only the larger pore size filter has a significant mass of particle collection.