ALUMINUM FILTRATION STUDY

NEW MEXICO ENVIRONMENT DEPARTMENT
SURFACE WATER QUALITY BUREAU

AUGUST 24, 2012

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Summary

According to New Mexico Water Quality Standards, aquatic life criteria for aluminum are hardness-dependent and are "...based on analysis of total recoverable aluminum in a sample that is filtered to minimize mineral phases as specified by the department" (NMED 2011).

This paper describes an investigation conducted to support the New Mexico Environment Department's specification of the filtration needed to minimize mineral phases. The approach was to collect turbid water samples and analyze both unfiltered aliquots and aliquots that were filtered using filters of pore sizes ranging from 1 – 40 µm in order to determine the pore size that minimizes mineral phase aluminum without restricting amorphous or colloidal phases. This paper also considered results from a study by ARCADIS and GEI Consultants, Inc. (ARCADIS and GEI 2011) that was done to evaluate the effects of filtration with different filter pore sizes on aluminum concentrations.

This study concluded that a filter of 10 µm pore size minimizes mineral-phase aluminum without restricting amorphous or colloidal phases. It recommends that if the turbidity of a sample is less than 30 NTU, no filtration is needed to minimize mineral phases. It also recommends that samples be filtered with capsule (disposable in-line capsule) filters, and not be filtered with paper filters that are designed for use in plate or funnel-type filter holders.

Sample Collection and Analysis

The samplers, Doug Eib and Tim Michael, Environmental Scientists with the New Mexico Environment Department Surface Water Quality Bureau, collected Rio Grande River water near the Buckman diversion (SWQB sampling station "Rio Grande at Buckman Road, 30RGrand586.5") on December 22, 2011.

For the first sample, the samplers disturbed the river sediment in order to collect a turbid sample. They collected turbid water in two 5-liter churn splitters, churned the water to maintain constant turbidity, and measured pH, specific conductance, temperature and turbidity.

The samplers removed a one liter aliquot from one of the splitters for water chemistry, total dissolved solids (TDS) and total suspended solids (TSS) analysis. Next, the samplers removed a total of 14 aliquots of 0.5 liter volume for metals analysis. Two 0.5 liter aliquots were not filtered. The remaining 0.5 liter aliquots were filtered through capsule filters of 1, 5, 10, 20 and µm pore size (two each). Also, 0.5 liter aliquots (two each) were filtered through paper filters of 5 and 40 µm pore size. Aliquots were filtered in a random order. The total was 14 aliquots of 0.5 liter volume, and one of 1.0 liter volume.

In order to obtain a more turbid second sample, the samplers disturbed the river sediment and then added sediment, mixing the sample between churn splitters to promote uniformity among the splitters. As was done for the first sample, the samplers churned the water to maintain constant turbidity, and measured the field parameters of pH, specific conductance, temperature and turbidity. Aliquots were collected from the splitters as for the first sample.

The capsule filters were manufactured by Whatman and purchased from VWR International. The capsule filters were Whatman Polycap HD disposable capsule filters with monofilament anisotropic polypropylene (MAPP) filter media. The paper filters, 5 and 40 µm size qualitative filter paper, were purchased from VWR and used in a filter holder. Filters details are indicated in Table 1.

Table 1.
Filter Description

Manufacturer	Part Number	Mfg Name	Pore Size, µm	Filtration Area, cm^2	Filter Media	Connectors
Whatman	6703-7510	Polycap 75 HD	1.0	820	Polypropylene (MAPP)	Hose Barb for 3/8 to 1/2 inch tubing
(VWR)	28137-896					
Whatman	6703-7550	Polycap 75 HD	5.0	820	Polypropylene (MAPP)	Hose Barb for 3/8 to 1/2 inch tubing
(VWR)	28137-898					
Whatman	6703-7511	Polycap 75 HD	10.0	820	Polypropylene (MAPP)	Hose Barb for 3/8 to 1/2 inch tubing
(VWR)	28137-900					
Whatman	6703-7521	Polycap 75 HD	20.0	820	Polypropylene (MAPP)	Hose Barb for 3/8 to 1/2 inch tubing
(VWR)	28137-902					
VWR	28310-128	413	5.0	700	Paper	---
VWR	28313-104	417	40.0	700	Paper	---

The New Mexico Scientific Laboratory Division analyzed the samples. Samples for metals analysis, whether filtered or not, were subjected to the same level of laboratory digestion. Table 2 indicates the list of constituents, the analytical method and the detection limits.

Table 2.
Analytical Methods and Detection Limits

Analyte	Method	MDL, mg/L	SDL, mg/l
Aluminum	200.7	0.00226	0.05
Barium	200.7	0.00107	0.05
Calcium	200.7	0.00838	1
Copper	200.7	0.00098	0.05
Iron	200.7	0.00055	0.05
Magnesium	200.7	0.00257	1
Manganese	200.7	0.00138	0.05
Potassium	200.7	0.02068	1
Silicon	200.7	0.0034	0.05
Sodium	200.7	0.07369	1
Zinc	200.7	0.00095	0.05
Chloride	300.0		10.0
Sulfate	300.0		10.0
Alkalinity	SM2320B		10.0
Bicarbonate	SM2320B		10.0
TDS	SM2540C		25
TSS	SM2540D		9

Results

Results are tabulated in the appendix. In addition to results based on capsule filters, the appendix includes analysis of aliquots filtered through 5 and 40 µm paper filters. The 5 µm paper filters were intended to check for consistency between the capsule and the paper filters; the 40 µm filters were intended to better describe the range between 20 µm and the unfiltered samples. However, the data based on paper filters was inconsistent with that based on capsule filters and the data was considered not to be useful for this study. See additional discussion in the appendix.

The following describes results based on aliquots filtered through capsule filters. The first sample had a turbidity of 117.9 NTU and a TSS of 600 mg/L. The unfiltered aliquots had average concentrations of 8.55 mg/L aluminum and 5.5 mg/L iron. All of the aliquots filtered using 10 µm and smaller pore size filters had concentrations of aluminum and iron less than the sample detection limit (SDL) of 0.05 mg/L. The aliquots filtered through 20 µm filters had aluminum concentrations up to 0.06 mg/L, and iron concentrations of 0.08 mg/L. The aluminum concentrations in the aliquots filtered at 20 µm were less than the dissolved chronic aquatic life criteria value of 0.087 mg/L, and significantly less than the hardness-based aquatic chronic aquatic life criteria value of 1.6 mg/L.

The second sample had a turbidity of 344 NTU and a TSS of 3020 mg/L. The unfiltered aliquots had average concentrations of 26.5 mg/L aluminum and 17.5 mg/L iron. All of the aliquots filtered using 10 µm and smaller pore size filters had concentrations of aluminum less than the SDL of 0.05 mg/L, and concentrations of iron no greater than 0.06 mg/L. The aliquots filtered through a 20 µm filter had aluminum concentrations of 0.09 and 0.1 mg/L, and iron concentrations of 0.12 mg/L. The aluminum concentrations in the aliquots filtered at 20 µm were only slightly greater than the dissolved chronic aquatic life criteria value of 0.087 mg/L, and significantly less than the hardness-based aquatic chronic aquatic life criteria value of 1.6 mg/L.

As indicated in Table 2, for aluminum the method detection limit (MDL) was 0.00226 mg/L and the sample detection limit (SDL) was 0.05 mg/L. At special request, the analytical laboratory provided provisional values between the MDL and the SDL. The values are reported below:

Table 3.
Analytical Results between the MDL and the SDL

	TSS, mg/L 600				TSS, mg/L 3020			
Filter Pore Size, µm	1	5	10	20	1	5	10	20
Sample ID	2413016 2413017	2413018 2413019	2413020 2413021	2413022 2413023	2413032 2413033	2413034 2413035	2413036 2413037	2413038 2413039
Al, mg/L	0.002* -0.001*	0.030 0.016	0.029 0.037	0.043 0.060	0.014 0.043	0.022 0.021	0.032 0.036	0.096 0.091
Average Al, mg/L	0.0005*	0.023	0.033	0.0515	0.0285	0.0215	0.029	.0935

*Values less than the method detection limit

The average aluminum concentrations (with the exception of the value of 0.0005 which is below the method detection limit) are plotted in Figure 1.

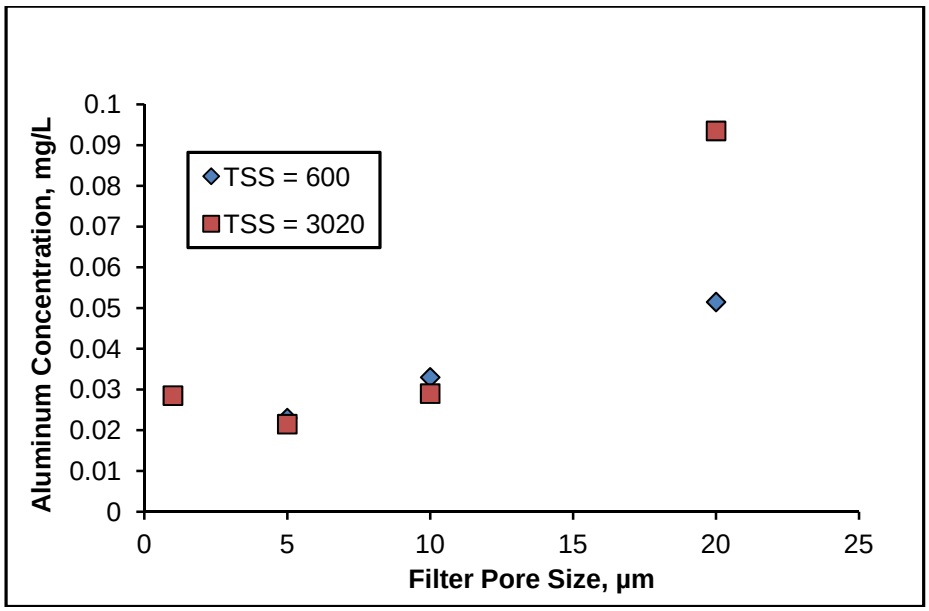

Figure 1.
Aluminum Concentration (TSS = 600 and 3030 mg/L) vs. Filter Pore Size

Although the pore size of the unfiltered samples is not known, Table 4 and Figure 2 (plotting the unfiltered samples as 100 µm pore size) can be generated.

Table 4.
Analytical Results including Unfiltered Values

Filter Pore Size, µm	At TSS = 600 mg/L Al, mg/L	At TSS = 3020 mg/L Al, mg/l
1	0.0005	0.0285
5	0.023	0.0215
10	0.033	0.029
20	0.0515	0.0935
Unfiltered	8.55	26.5

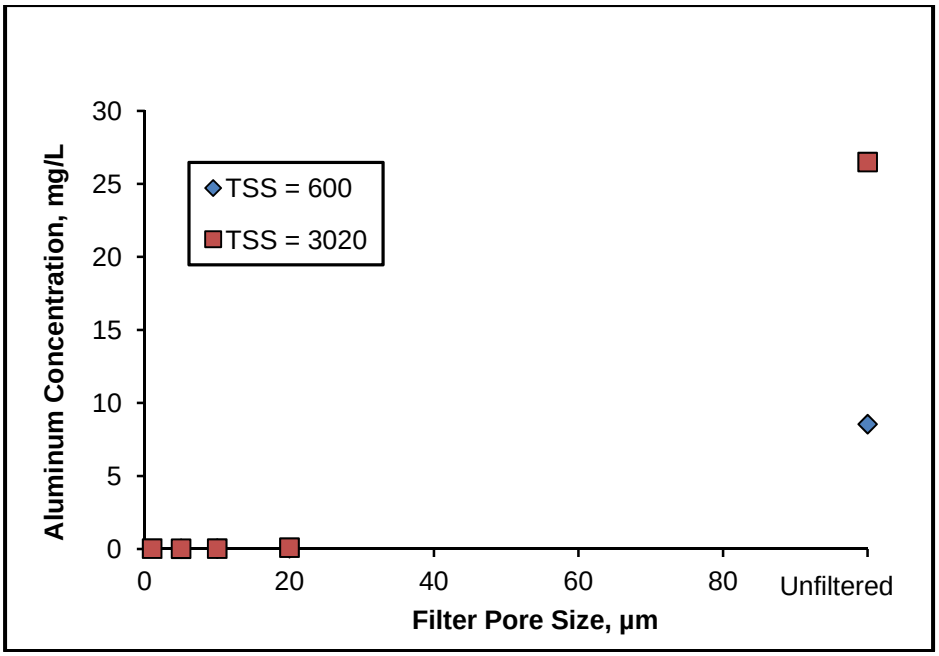

Figure 2.
Aluminum Concentration vs. Filter Pore Size

The results shown in Tables 3 and 4 indicate an increase in aluminum concentration with increasing filter pore size. However, in comparison to the concentrations of minerals in the unfiltered samples, even at 20 µm the evidence for the breakthrough of aluminum and iron minerals is limited.

A filter designed to exclude particles 10 µm and larger is not designed to allow particles up to 10 µm to pass through. The size of particles that pass through a 10 µm filter is smaller than 10 µm, and based on this data, not of the mineral phase. It is worth noting that particles in the 10 µm range are considered fine silt, and clay is considered to be 4 µm and smaller (Wentworth 1922). A filter with pore size smaller than 10 µm (such as 5 µm) could be expected to exclude a portion of clay-size materials, some of which may be colloidal.

Filtration Requirements and Turbidity

It is not necessary to filter samples that do not have a mineral phase. Practically, field turbidity measurements can be used to determine if there is a mineral phase that requires filtration. In order to determine the level of turbidity that is required before filtering is necessary, some 60 data points from the San Juan River 2010 Water Quality Survey were examined. The data included turbidity, aluminum, and hardness measurements. Turbidity ranged from 0 to 634 NTU; aluminum ranged from 0.06 to 25 mg/L and hardness ranged from 100 to 700 NTU. A portion of the data that was reviewed is shown in Figure 3. Based on the evaluation and as indicated in the figure, waters with turbidity less than 30 NTU are unlikely to have sufficient concentrations of aluminum to exceed hardness-based criteria, even without filtration.

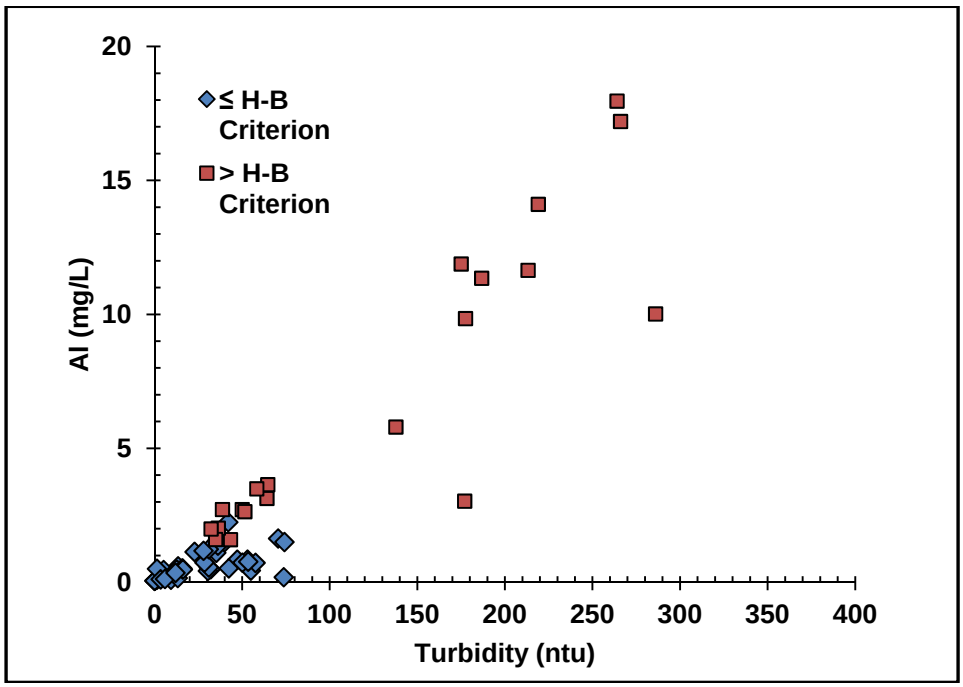

Figure 3.
Aluminum Concentration vs. Turbidity
Data from San Juan River Study, 2010

This is a limited analysis; specifically, the data is from a small number of samples, collected in one region, in one sampling season. However, given the practical need to limit costs in part by filtering only when necessary, 30 NTU appears to be a reasonable choice to make regarding the required level of turbidity before filtering. This study concludes that filtration to minimize mineral phases is not required if the turbidity is less than 30 NTU. If unfiltered water is measured to have aluminum concentrations greater than hardness-based criteria, in order to verify a criteria exceedence additional samples can be collected in the field and filtered through a 10 µm filter.

References

ARCADIS U.S., Inc., and GEI Consultants, Inc. 2011. *Aluminum Sample Pre-Filtration Study of the Red River*. Prepared for Chevron Mining Inc., Questa, New Mexico; August 30.

NMED. 2011. 20.6.4 *Water Quality Standards for Interstate and Intrastate Surface Waters*. Effective January 14, 2011.

Wentworth, C.K. 1922. *A Scale of Grade and Class Terms for Clastic Sediments*. J. Geology V. 30, 377-392. Found at http://en.wikipedia.org/wiki/File:Wentworth-Grain-Size-Chart.pdf, July 9. 2012.

Appendix

Table A1. Results (Capsule Filters)

Units are mg/L unless otherwise indicated

	Sample ID	2413029	2413014 2413015	Various	2413022	2413023
Field Meas	Filtration (Capsule)		Unfiltered	1 - 10 µm	20 µm (1)	20 µm (2)
	pH	8.1				
	SC (µS/cm)	283				
	Turbidity (NTU)	117.9				
Lab Meas and Gen Chem	pH	8.03				
	SC (µS/cm)	203				
	TSS	600				
	TDS	186				
	Cl	<10.0				
	SO_4	34.5				
	Alkalinity	97.2				
	HCO_3	119				
	Calculated H (1 µm)	114				
	H-based Al Chronic (Total)	1.6				
	Al Chronic (Dissolved)	0.087				
Lab Metals Results (Replicates Averaged)	Aluminum		8.55	<0.05	<0.05	0.06
	Barium		0.23	0.06	0.06	0.06
	Calcium		51	34	34	32
	Iron		5.5	<0.05	0.08	0.08
	Magnesium		10	7	7	6
	Manganese		0.36	0.1	0.11	.1
	Potassium		5	3	3	3
	Silicon		31	11	11	11
	Sodium		20	18	17	17

	Sample ID	2413045	2413030 2413031	Various	2413038	2413039
Field Meas	Filtration (Capsule)		Unfiltered	1 - 10 µm	20 µm (1)	20 µm (2)
	pH	8.21				
	SC (µS/cm)	283				
	Turbidity (NTU)	344				
Lab Meas and Gen Chem	pH	8.03				
	SC (µS/cm)	217				
	TSS	3020				
	TDS	188				
	Cl	<10.0				
	SO_4	34.9				
	Alkalinity	103				
	HCO_3	125				
	Calculated H (1 µm)	111				
	H-based Al Chronic	1.6				
	Al Chronic	0.087				
Lab Metals Results (Replicates Averaged	Aluminum		26.5	<0.05	0.1	0.09
	Barium		0.61	0.06	0.07	0.07
	Calcium		96.5	33	33	32
	Iron		17.5	<0.05 to 0.06	0.12	0.12
	Magnesium		17	7	7	6
	Manganese		1.2	0.23	0.25	.25
	Potassium		10	3	3	3
	Silicon		64.5	11	11	11
	Sodium		19.5	17	17	17

Table A2. Results (Paper Filters)

Units are mg/L unless otherwise indicated

	Sample ID	2413029	2413024	2413025	2413026	2413027
Field Meas	Filtration (Paper)		5 µm(1)	5 µm(2)	40 µm(1)	40 µm(2)
	pH	8.1				
	SC (µS/cm)	283				
	Turbidity (NTU)	117.9				
Lab Meas and Gen Chem	pH	8.03				
	SC (µS/cm)	203				
	TSS	600				
	TDS	186				
	Cl	<10.0				
	SO_4	34.5				
	Alkalinity	97.2				
	HCO_3	119				
	Calculated H (1 µm)	114				
	H-based Al Chronic	1.6				
	Al Chronic	0.087				
Lab Metals Results (Replicates Averaged)	Aluminum		0.25	0.16	0.41	0.67
	Barium		0.06	0.06	0.06	0.07
	Calcium		33	34	34	34
	Iron		0.21	0.16	0.32	0.49
	Magnesium		7	7	7	7
	Manganese		0.11	.11	.12	.13
	Potassium		3	3	3	3
	Silicon		11	12	12	12
	Sodium		18	19	19	17

	Sample ID	2413045	2413040	2413041	2413042	2413043
Field Meas	Filtration (Paper)		5 µm(1)	5 µm(2)	40 µm(1)	40 µm(2)
	pH	8.21				
	SC (µS/cm)	283				
	Turbidity (NTU)	344				
Lab Meas and Gen Chem	pH	8.03				
	SC (µS/cm)	217				
	TSS	3020				
	TDS	188				
	Cl	<10.0				
	SO_4	34.9				
	Alkalinity	103				
	HCO_3	125				
	Calculated H (1 µm)	111				
	H-based Al Chronic	1.6				
	Al Chronic	0.087				
Lab Metals Results (Replicates Averaged	Aluminum		0.57	0.73	0.95	0.86
	Barium		0.07	0.07	0.08	0.07
	Calcium		34	34	35	35
	Iron		0.42	0.53	.65	.6
	Magnesium		7	7	7	7
	Manganese		0.25	0.24	0.28	.27
	Potassium		3	3	3	3
	Silicon		12	13	14	13
	Sodium		17	17	18	18

Capsule and Paper Filters

Aluminum results using paper filters were not consistent with results from capsule filters, see Table A3. At 5 µm, results from paper filters indicated four to eleven times greater aluminum concentrations than those with capsule filters; results with 40 µm paper filters were nine to ten times greater than from 20 µm capsule filters. Results of iron analyses were similar.

Because of the inconsistency of the results in comparison to capsule filters, and because 0.45 µm pore size capsule filters are commonly used in collecting samples for dissolved metal, samples for aluminum and other metal determinations should be filtered through capsule filters, and not filtered through paper filters designed for or used in plate or funnel-type filter holders.

Table A3.
Comparison of Aluminum Results, Capsule to Paper Filters

	TSS = 600			TSS = 3020		
Filter Pore Size, µm	5	20	40	5	20	40
Capsule Filter, Al mg/L	<0.05	≤0.06	---	<0.05	0.095	---
Paper Filter, Al mg/L	0.21	---	0.54	0.65	---	0.91

Results from ARCADIS 2011

The Aluminum Sample Pre-Filtration Study of the Red River (ARCADIS 2011) filtered Red River water samples through capsule filters of 0.45, 1, and 5 µm pore size.

Table A4.
ARCADIS 2011 Aluminum Results
Aluminum Concentration, mg/L

Filter Pore Size, µm	TSS = 0	TSS = 2	TSS = 5	TSS = 330	TSS = 510
0.45	0.2	0.18	0.18	0.094	0.04
1	0.19	0.17	0.16	0.1	0.034
5	0.31	0.32	0.3	0.22	0.074
unfiltered	0.64	0.64	0.61	3.1	45

Although the aluminum concentration increased with 5 µm filters, based on the unfiltered samples, the evidence for mineral breakthrough compared to the unfiltered samples is limited. If a 5 µm filter excludes particles larger 5 µm as it is designed to, the size of particles permitted is smaller than 5 µm, and in the range of clay material (Wentworth 1922).

Figure A1.
Aluminum Concentration (TSS = 0 to 510 mg/L) vs. Filter Pore Size