Molybdenum Content of Water Treatment Residuals

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ABSTRACT

Molybdenum (Mo) content of water treatment residuals (WTRs) was determined by inductively coupled plasma atomic emission spectroscopy (ICP–AES) to evaluate suitability for land application under state regulatory policies that limit Mo to 18 mg kg^{-1}. Samples of WTR were collected from 32 Pennsylvania facilities that employ aluminum salts, ferric chloride, and/or polymers for coagulation. The mean Mo content of all samples was 3.1 mg kg^{-1}, with 78% having Mo levels <5 mg kg^{-1}. The WTRs from plants using ferric chloride as a coagulant averaged 5.6 mg Mo kg^{-1}, significantly higher ($p = 0.02$) than the 1.6 mg Mo kg^{-1} for utilities using alum. Differences were related to coagulant purity: Mo content in liquid ferric chloride was 10.0 mg L^{-1} but below detection by ICP–AES for alum. The initial sample from one facility, collected from the filter backwash basin, contained 26.4 mg Mo kg^{-1}. Elevated Mo in backwash solids was attributed to filtration capture of extremely fine, Mo-enriched Al hydrous oxide particles and erosion of anthracite filter media during backwashing. Combined backwash and coagulation solids from this facility's storage lagoon averaged 6.3 mg Mo kg^{-1}, underscoring the need for consistent sampling procedures. The mean Cu to Mo ratio in these WTRs was >100, well above the minimum dietary ratio (2:1) considered protective of grazing animals.

As recently as 1971, more than 90% of water treatment plants used direct discharge into rivers and lakes for disposal of residuals produced during purification of drinking water (American Water Works Association, 1990). As environmental concerns over this practice increased, land-based disposal methods gained popularity as an alternative for WTRs. Potable water supplies and certain treatment chemicals contain potentially toxic trace elements and these constituents must be considered in managing WTRs by land application (Elliott et al., 1990). The Federal Standards for the Use or Disposal of Sewage Sludge (USEPA, 1993), codified as 40 CFR Part 503, provided national rules for recycling biosolids produced in municipal wastewater treatment. While the federal standards specifically exclude WTRs (USEPA, 1996), some states use Part 503 for regulating WTR land application.

Prior to the federal rules, state regulations typically imposed limits on heavy metals like Cd, Cu, Ni, Pb, and Zn in land-applied wastes. The inclusion of Mo in Part 503 focused attention on this element and its management in land-based waste disposal and recycling. The major issue with Mo is its potential effect on animals grazed on, or fed, forages from application sites. Relatively small concentrations of Mo in feed can induce Cu deficiency in livestock if the Cu level is below the minimum recommendation of 10 mg kg^{-1}. This Mo-induced Cu deficiency is called molybdenosis and is generally managed by insuring an adequate Cu to Mo ratio in forage and livestock feeds. The minimum dietary Cu to Mo ratio for cattle and sheep is set at 2:1 (National Research Council, 1996). In addition to monitoring the Cu to Mo ratio in the vegetation, it is important to evaluate this ratio in land-applied materials, since ruminants can consume significant soil material along with forage during grazing (Thornton and Abrahams, 1983).

The original Part 503 defined an upper limit of 18 mg Mo kg^{-1} for exceptional quality biosolids. This was based on assessment of the risk associated with ruminant animals consuming forage grown on biosolids-amended soil. This value came under attack by biosolids producers on the grounds of insufficient supportive research. Litigation followed, and the USEPA rescinded the 40 CFR Part 503 Table 3 Mo value until more field data could be gathered. However, permits issued in Pennsylvania for land application of WTRs contain a ceiling limit of 18 mg Mo kg^{-1}. Since published analyses suggest low (<5 mg kg^{-1}) Mo concentrations in WTRs (Schmitt and Hall, 1975; Elliott and Singer, 1988; Peters and Basta, 1996), sporadic reports from commercial laboratories of WTRs containing 200 to 300 mg Mo kg^{-1} were puzzling. We could find no published comprehensive study of Mo in WTRs. Therefore, our purpose was to determine Mo concentration in WTRs generated in our state and representative of utilities in the Northeast. The trace element content of WTRs is inextricably related to the purity of coagulant chemicals added during water treatment (Elliott et al., 1990), thus we surveyed utilities using both aluminum and ferric salts. The ultimate goal was to establish the level of Mo in residuals generated at coagulation–filtration water treatment plants and to interpret the findings in the context of land spreading of WTRs.

MATERIALS AND METHODS

Treatment residuals were collected in March 1998 from lagoons or sedimentation basins at 32 water treatment plants throughout Pennsylvania. As there are no major softening plants in Pennsylvania, all facilities sampled were typical coagulation–filtration plants designed to remove turbidity, pathogens, color, taste-causing, and odor-causing compounds from the water supply and produce potable water (Fig. 1). Water treatment residuals consist primarily of the precipitated hydroxide of the coagulant [e.g., $Al(OH)_3$ for alum] along with the material removed from the raw water (sand, silt, clay, bacteria, color-forming compounds). Various other additives (chlorine, lime, polymers, filter aids, fluoride, corrosion inhibitors, activated carbon) improve process performance or finished water quality, but typically have little influence on WTR quantity or composition. Facilities provided information on coagulant usage, source water, and WTR disposal method.

Chemical Addition

Chemical Addition

Chemical Addition

To Distribution System

Raw Water Intake → Mixing Chamber → Flocculation Sedimentation → Filtration → Clear Well Storage

Sedimentation Basin Solids

Backwash Basin

Decant Discharged or Recycled to Head of Plant
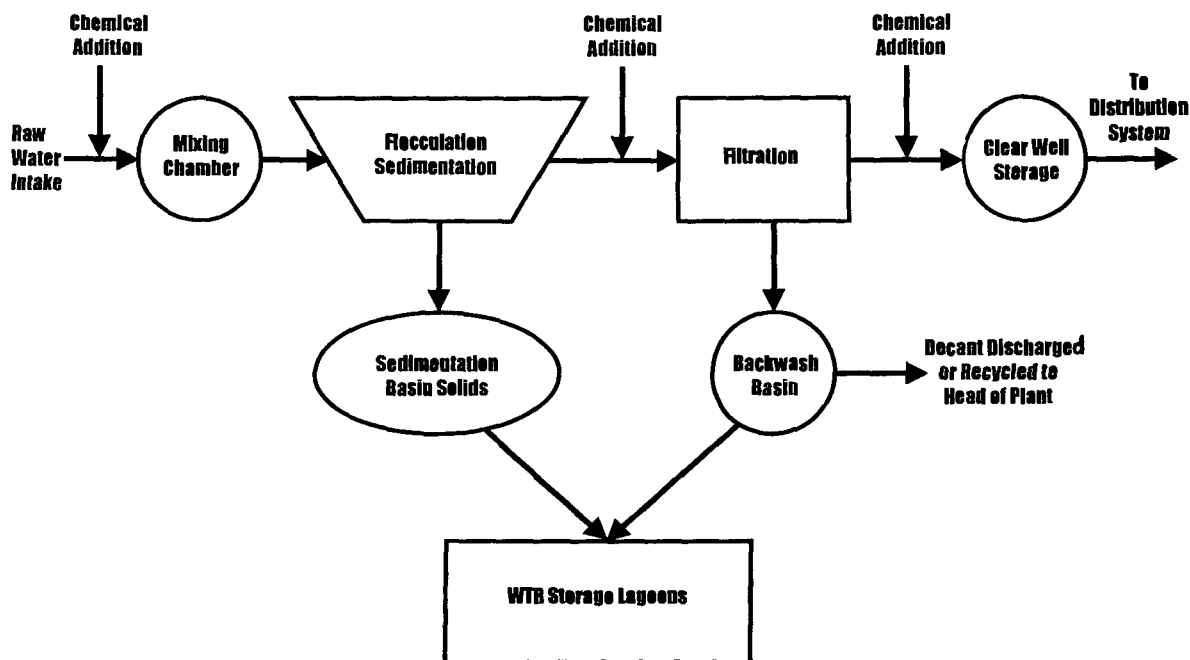
WTR Storage Lagoons

Fig. 1. Typical flow diagram for coagulation–filtration plants. This is a generalized layout and variations among individual plants are common.

Triplicate subsamples of each WTR were prepared for analysis by digestion using USEPA Method 3050. Representative subsamples were oven-dried at 105°C for 24 h and Mo concentrations reported on a dry weight basis.

Total Mo content of the digested samples was determined by ICP–AES at the 202.03 nm wavelength according to USEPA Method 6010. Molybdenum standards spiked with Al and Fe indicated that the internal correction program of the ICP–AES unit adequately accounted for interference effects at levels anticipated in solutions prepared from digested WTRs. Using these sample preparation methods, the detection limit of Mo was determined to be 0.1 mg kg^{-1} of dry WTR.

RESULTS AND DISCUSSION

For the 32 facilities, alum was the most common coagulant chemical (56% of plants), followed by ferric chloride (28%), polyaluminum chloride (PAC) (9%), and polymers only (6%). Of the plants surveyed, nearly 70% employ land application for WTR disposal, with the remaining facilities roughly equally divided between landfilling and discharge to sanitary sewers. This is not typical nationally. A 1991 survey of 612 utilities serving populations of >50 000 (Kawczyinski and Achterman, 1991) revealed the following prevalence of WTR disposal methods: land application (19.6%), landfilling (39.7%), discharge to sanitary sewers (17.7%), direct stream discharge (14.5%) and other practices such as lagooning (9.4%).

Many states have no regulations specifically for WTRs, while others regulate such materials under biosolids or solid waste rules. The preference for land application in Pennsylvania reflects intentional cooperation between the water treatment industry and state regulatory agency. The state, however, decided to use 40 CFR Part 503 Table 3 values, developed for sewage sludges, as compositional limits for WTRs to be land applied and began issuing permits prior to the rescinding of the

Mo level by the USEPA. The 18 mg Mo kg^{-1} limit continues to be used for land application of WTRs.

Total Mo concentrations of the WTRs are presented in Table 1. The average Mo concentration for all plants was 3.1 mg kg^{-1}, well below the 18 mg Mo kg^{-1} regulatory limit. The initial sample collected at one plant of the 32 surveyed had an Mo level exceeding this limit. This facility was targeted for additional study and is discussed below.

Trace elements in WTRs originate from either the raw water source or chemicals added during the treatment process. Stream and river sediments reflect the trace element content of the surrounding geological material and, in fact, sediment surveys are a standard tool in mineral exploration. Thus, Mo in WTRs can contain elevated Mo levels due to the parent geological material or industrial activities in the watershed.

To shed light on the Mo compositional variations in WTRs, we investigated the possible presence of Mo-rich geological material or significant industrial uses of Mo in Pennsylvania. Pennsylvania has no major deposits of Mo, and soils of the eastern United States typically contain less than 3 mg Mo kg^{-1} (Kubota, 1977). A map showing the regional distribution of Mo deposits indicates that the Appalachian province, running from Alabama to Maine, crosses the southeastern corner of Pennsylvania (Kubota, 1977). However, in this province, Mo tends to occur in small isolated veins. We were surprised to find that wulfenite (PbMoO$_4$) was mined in the southeastern corner of Pennsylvania. However, these localized subsurface pockets of high geochemical abundance seem inconsequential in this study. The three treatment plants from within this geological province had WTR Mo concentrations of 2.6, 2.6, and 0.9 mg kg^{-1}. Kubota (1977) reported that there are no instances of naturally occurring molybdenosis in grazing animals in Pennsylvania.

Table 1. Molybdenum concentration in water treatment residual (WTR) samples.

Coagulant type	Number	Mean	Range
		— mg kg^{-1} dry wt. —	
All samples	32	3.1	BD†–12.4
Alum	18	1.6	BD–4.5
Ferric chloride	9	5.6	0.7–12.4
Polyaluminum chloride	3	3.6	2.1–6.3
Other (e.g., polymers only)	2	5.2	4.8, 5.5

† BD = below detection.

While Mo levels in WTRs are not readily explicable in terms of variations in geochemical abundance, trace elements in WTRs are sometimes linked to the purity of the water treatment chemicals. For most facilities, the inorganic salts added for coagulation are the highest dosage chemicals and, therefore, most likely to affect WTR composition. In this study, 84% of the plants use either alum or ferric chloride as the primary inorganic coagulant chemical. These two coagulants can have very different contaminant levels as reflected in the composition of WTRs. For example, Elliott et al. (1990) attributed elevated Ni and Cr levels in certain WTRs to high levels of these elements in ferric chloride coagulant produced from steel industry waste pickle liquor.

To investigate the role of coagulant type in WTR Mo content, we divided the data based on whether the primary coagulant was alum or ferric chloride (Table 1). The average Mo content in WTRs from plants using ferric chloride (5.6 mg kg^{-1}) was significantly higher ($p = 0.015$) than for those using alum (1.6 mg kg^{-1}). The greatest Mo level detected in any alum WTR (4.5 mg kg^{-1}) was below the *average* Mo concentration for the group of ferric chloride WTRs.

The important role of the coagulant in the Mo composition of the resulting residuals was confirmed by chemical analysis of the coagulants alone. Liquid ferric chloride supplied to the water treatment industry contained 10.0 mg Mo L^{-1} whereas the Mo content of aluminum sulfate was below the detection limit (6 μg Mo L^{-1}). The presence of detectable Mo in ferric chloride was not surprising, since it is often processed as steel industry pickle liquor. A predominant industrial use of Mo is to impart high tensile strength and corrosion resistance to steel. The water treatment industry has adopted purity requirements, called the *Water Chemicals Codex*, for chemicals used in drinking water treatment (Committee on Water Treatment Chemicals, 1982). This codex specifies maximum levels of Ag, As, Cd, Cr, Pb, Hg, and Se in treatment chemicals, but Mo is not addressed. Thus, there is no formal mechanism for monitoring or limiting the effect of Mo in treatment chemicals on WTR composition.

The small number of samples from facilities using PAC or polymers alone (Table 1) limits the inferences that can be drawn regarding Mo concentrations in the associated WTRs. However, the initial WTR sample from the Clarion, PA facility, which uses PAC, contained 26.4 mg Mo kg^{-1}, more than twice the Mo content in any other WTR sampled. This warranted further investigation. A split sample from Clarion, sent to a commercial laboratory, reportedly contained 39 mg Mo kg^{-1}. Based on either analysis, this WTR could not be

land applied in Pennsylvania. Although WTRs generated at the plant are currently discharged periodically from lagoons into a sanitary sewer system, land application is being considered for future use.

The Clarion facility is a conventional sedimentation–filtration plant with a design capacity of 5680 m^3 d^{-1} (1.5 million gallons d^{-1}). The plant consists of a mixing tank, two flocculation–sedimentation basins, two multimedia (anthracite, sand, gravel) filters, and a clear-water storage. The Clarion River is the sole source of water to the plant and is regarded as an abundant, high-quality supply. The river drains a 2330 km^2 (900 mi^2) watershed that is largely forested or agricultural. The geological material consists primarily of gray acidic shales and coarse-textured sandstones with interbedded coal seams. This area of the state has been extensively strip-mined for coal.

Initial attempts to explain the high Mo in the original Clarion sample focused on the purity of treatment chemicals and the level of Mo in the river sediments. Besides PAC, other chemicals are used at this plant for pH control, corrosion inhibition, removal of taste and odors, fluoride addition, disinfection, and filter performance enhancement. All chemicals, except gaseous chlorine, were analyzed for Mo. The PAC had 0.48 mg Mo L^{-1} and the other chemicals had similarly small or nondetectable Mo levels. The low dosing rates of these sources cannot account for elevated Mo in the WTRs. Two river sediment samples collected at the water supply intake point had an average Mo content of 7.6 mg kg^{-1}. This value is higher than either the typical background Mo level of 1 to 3 mg kg^{-1} in soils (Jones et al., 1990) or the <2 mg Mo kg^{-1} reported for stream sediments in areas where the source rock is gray shales and sandstones (Thomson et al., 1972). However, the elevated sediment Mo levels cannot alone explain the high Mo (26.4 mg kg^{-1}) of the original sample.

The original sample was collected from the backwash basin (see Fig. 1). At this plant, the filter backwashing stream is decanted and the liquid is discharged to the river. The settled solids are pumped to an earthen storage lagoon where they are combined with slurry containing solids from the sedimentation basins. Thus, the original sample collected from the backwash basin was not representative of the residuals from the lagoon that would be land applied. Three samples taken from the storage lagoon had a mean Mo content of 6.3 mg kg^{-1} (SD = 1.13). This value is somewhat higher than the mean Mo level for all samples, but it probably reflects the relatively high Mo content of the river sediments.

Although the WTRs from the Clarion facility storage lagoon could be applied under the existing regulations, explanation for the elevated Mo in the backwash solids was sought. Samples were collected during a routine backwashing event. The initial solids washed from the filter were sampled as well as a sample of the media at the end of the backwashing cycle. Prior to digestion, this latter sample was rinsed several times with distilled water in an attempt to obtain clean filter media. The solids initially washed from the filter had an Mo content of 44.2 mg kg^{-1} (SD = 0.8, n = 2) and the filter media particles contained 22.8 mg Mo kg^{-1} (SD = 0.9, n = 2).

Two phenomena are proposed to explain the high Mo in backwash solids. First, the aluminum hydroxide particles formed in the flocculation process are extremely effective in scavenging oxyanions (e.g., MoO_4^{2-}) from solution. The finest particles accumulate the greatest concentrations of Mo (Runnells et al., 1977) and largely escape gravity sedimentation. Thus they are removed during filtration. Second, the multimedia filter at this plant consists of anthracite coal over graded sand. Coal can contain elevated levels of Mo relative to soils and sediments (Kaakinen, 1977), although generally not as high as our media sample, which was probably incompletely washed of sorbed materials. Erosion of media particles occurs during backwashing and anthracite particles also may have contributed to elevated Mo in the backwash sample.

Since the critical parameter for molybdenosis is the Cu to Mo ratio in the animal's diet, Cu content in WTRs was also evaluated. Two WTRs had very high Cu (4.6 and 10.4 g kg^{-1}), probably reflecting the use of $CuSO_4$ as an algicide in impounding reservoirs. Excluding these two values, the mean Cu content for the remaining 30 WTRs was 145 mg kg^{-1}. A previous study reported an average Cu content for eight WTRs of 171 mg kg^{-1} (Elliott et al., 1990).

Because crop uptake coefficients can vary widely between elements, the Cu to Mo ratio in the WTR may bear little relationship to the ratio in forages grown on WTR-amended soils. Yet the ratio in WTRs is of interest because it may disproportionately change the total soil levels of Cu and Mo, and because animals consume soil along with forage during grazing. Excluding two samples with extremely high Cu and one sample with nondetectable Mo, the mean Cu to Mo ratio for 29 WTRs was 122 (range 7–1300), well above the critical value of 2:1 cited for animal diets. Thus, although some WTR might increase the soil Mo, Cu levels will be increased to an even greater extent.

CONCLUSIONS

Residuals produced at 32 water treatment plants throughout Pennsylvania had an average Mo content of 3.1 mg kg^{-1}. Facilities that employ the most common coagulant, alum, averaged only 1.6 mg Mo kg^{-1}. These latter levels are not dramatically different than background Mo content for U.S. soils, reported to average from 1 to 1.3 mg Mo kg^{-1} (Jones et al., 1990). Treatment plants using ferric chloride as a primary coagulant had higher Mo levels (mean = 5.6 mg kg^{-1}) in their WTRs. Ferric chloride used in water treatment is often reprocessed pickle liquor from the steel industry. Higher WTR Mo levels can also reflect elevated Mo in the sediments from raw water supplies in watersheds affected by industrial emissions or containing geological material high in Mo.

Compared with biosolids that are routinely applied to soils, WTRs have lower average and narrower ranges of Mo contents. A national survey found the range of Mo in sewage sludges to be 2 to 68 mg kg^{-1}, with a median value of 11 mg Mo kg^{-1} (Kuchenrither and McMillan, 1990). Biosolids sampled in Pennsylvania

from 1993–97 had a median of 9 mg Mo kg^{-1} (Stehouwer and Wolf, 1999). The Mo content of Pennsylvania WTRs (3.1 mg kg^{-1}) should not limit their application if the original Part 503 Table 3 value of 18 mg Mo kg^{-1} is used as an upper limit of acceptability. Even a conservative Mo loading limit of 1 kg ha^{-1} (McBride, 1998) would allow application of about 330 Mg ha^{-1} (150 U.S. tons acre^{-1}) for WTRs with the median Mo concentration in this study.

We speculate that sporadic reports from commercial laboratories of very high Mo levels (200–300 mg kg^{-1}) in WTRs are in error as a result of inadequately accounting for Al and Fe matrix interferences in Mo analysis. Moreover, caution is warranted regarding where samples are collected at a treatment plant. Filtration backwash solids may be an unreliable indicator of the quality of the composite WTRs that are destined for land spreading or ultimate disposal.

The role of Mo in land-applied materials relative to molybdenosis in grazing livestock is extremely complex and probably inadequately described by the original risk assessment algorithm used to develop the Part 503 regulations (O'Connor and McDowell, 1999). Although guidelines are usually based on total Mo and Cu levels in diets, the relative bioavailability of these elements is crucial. Sulfur can also induce hypocuprosis in cattle by decreasing Cu bioavailability, and this cannot be ignored when investigating molybdenosis. While a thorough understanding of molybdenosis seems illusive, several lines of reasoning suggest that Mo in land-applied WTRs poses little threat to ruminants. First, the total Mo levels are not dramatically different than typical background soil levels. Because WTRs are inherently high in Al or Fe hydrous oxides that strongly bind Mo, the availability of Mo is expected to be low. The Cu to Mo ratio in WTR is typically much higher than the minimum critical 2:1 values suggested for livestock diets. Thus, surface spreading of WTRs will normally add more Cu than Mo to the soil. Finally, the typically acid conditions of soils in the region would be expected to differentially favor Cu uptake by crops over Mo.

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