

*Protecting Our Water Environment*



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***ANALYSIS OF TARGET LEVELS FOR  
40 CFR PART 503 METALS IN BIOSOLIDS***

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ANALYSIS OF TARGET LEVELS FOR 40 CFR PART 503 METALS IN BIOSOLIDS

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## INTRODUCTION

Environmental Monitoring and Research Division (EM&R) staff in collaboration with the Quality Assurance Coordinator has evaluated the target levels (TLs) for the 40 CFR Part 503 (503) metals in biosolids. TLs are self-imposed internal benchmarks for individual sludge metal concentrations which are measured at various stages of biosolids treatment. They are set significantly lower than the 503 Exceptional Quality (EQ) limits established for biosolids regulation so that they can serve as quality assurance/quality control checks and warning levels.

Currently, as part of the reporting protocol for biosolids, the District examines the following metals: arsenic, cadmium, chromium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc (503 metals). The following sludge streams are monitored: Calumet digester drawoff, Stickney digester drawoff, Stickney West Side Imhoff sludge, Stickney primary sludge, North Side gravity concentration tank sludge, Egan digester drawoff, Kirie waste activated sludge (WAS), Hanover Park digester drawoff, and Lemont WAS.

The only TLs that have been exceeded recently are those for the Hanover Park digester draw copper concentration ( $HPD_{Cu}$ ), Kirie waste activated sludge copper concentration ( $KWAS_{Cu}$ ), and Stickney Imhoff sludge lead concentration ( $SImh_{Pb}$ ) (Note: Upon sludge leaving the anaerobic digesters, it is considered biosolids, e.g. HPD).

## **OBJECTIVE**

Three specific metals and sludge streams have been examined due to frequent exceedence of their TLs:  $KWAS_{Cu}$ ,  $HPD_{Cu}$ , and  $SImh_{Pb}$ . Yearly data on sludge concentrations (1992–2007), plant metal loadings (2000–2007), and biosolids monitoring data (2000–2007) were reviewed and evaluated in order to assess the current TLs and whether changes should be made.

## RESULTS AND DISCUSSION

The current EQ limits and TLs for  $KWAS_{Cu}$ ,  $HPD_{Cu}$ , and  $SI_{mh_{Pb}}$  are summarized in [Table 1](#). Concentration data and TL exceedences for January 2003 through September 2007 are summarized in [Table 2](#). There were no EQ limit exceedences in any of the sludge streams during this period, but three specific TLs were exceeded often enough to cause concern:  $KWAS_{Cu}$ ,  $HPD_{Cu}$ , and  $SI_{mh_{Pb}}$  (14.4%, 22.5%, and 39.3% of the time, respectively). It should be noted that no significant changes in analytical procedures are known to have occurred during the study period that would affect the accuracy of these measurements.

$KWAS_{Cu}$  levels were consistently low from 2003–2007, with the exception of 2005, when a cluster of TL exceedences occurred. On the other hand, TL exceedences increased for  $HPD_{Cu}$  over the five-year period. Approximately 53.6% of the measured values were above the TL during the period of 2005–2006. This trend paralleled a general increase in average annual copper concentrations in the Hanover Park digester draw. Finally,  $SI_{mh_{Pb}}$  showed the most uniform trend of TL exceedence. With the exception of 2005, percent exceedence of the TL ranged from 33.3–54.5%. Additionally, the average  $SI_{mh_{Pb}}$  concentrations generally remained the same ([Table 2](#)).

In order to place the data in historical context, [Figure 1](#) shows the annual average concentrations of  $KWAS_{Cu}$ ,  $HPD_{Cu}$ , and  $SI_{mh_{Pb}}$  from 1992–2007.

The average annual concentration for  $KWAS_{Cu}$  was 548 mg/dry kg. Adding one standard deviation ( $\sigma$ ), 52 mg/dry kg, to the average concentration gives a  $+\sigma$  value of 600 mg/dry kg. This  $+\sigma$  value was exceeded in only two years (1992 and 2005). Based on this data, the annual average  $KWAS_{Cu}$  has varied between 488 and 600 mg/dry kg over the sixteen-year period, while the plotted trend indicates slightly decreasing concentrations.

The average annual concentration for  $HPD_{Cu}$  was 853 mg/dry kg. Adding one standard deviation (111 mg/dry kg) to this average concentration gives a  $+\sigma$  value of 964 mg/dry kg. This  $+\sigma$  value was exceeded in three years (1992, 2006, and 2007). Based on this data, the annual average  $HPD_{Cu}$  has varied between 702 and 964 mg/dry kg over the sixteen-year period, while the  $HPD_{Cu}$  plotted trend indicates increasing concentrations.

The average annual concentration for  $SI_{mh_{Pb}}$  was 224 mg/dry kg. Adding one standard deviation (81 mg/dry kg) to this average concentration gives a  $+\sigma$  value of 305 mg/dry kg. This  $+\sigma$  value was exceeded in four years (1992–1995). Based on this data, the annual average  $SI_{mh_{Pb}}$  has ranged from 131 to 305 mg/dry kg over the sixteen-year period, while the  $SI_{mh_{Pb}}$  plotted trend indicates decreasing concentrations.

These trends in metals concentrations in solids should correlate with the metals loading to the plants. [Figures 2](#) through [4](#) show the metal loads to the individual plants and the metal concentrations in the studied sludge streams and biosolids.



TABLE 1: CURRENT EQ LIMITS AND TLs FOR SLUDGE STREAMS

	Kirie WAS Cu Concentration	Hanover Park Drawoff Cu Concentration	Stickney Imhoff Sludge Pb Concentration
Exceptional Quality Limit (mg/kg)	1,500	1,500	300
Target Level (mg/kg)	608	957	157

TABLE 2: ANNUAL SLUDGE METAL CONCENTRATION AND TL EXCEEDENCES  
FOR JANUARY 2003 THROUGH SEPTEMBER 2007

	2003	2004	2005	2006	2007	Total
-----Kirie WAS Cu Concentration-----						
Mean (mg/dry kg)	535	514	607	527	488	
Observations	52	52	35	12	10	161
TL Exceedences	2	5	15	1	0	23
% Exceedence	3.8	9.6	42.9	8.3	0.0	
-----Hanover Park Digester Drawoff Cu Concentration-----						
Mean (mg/dry kg)	806	775	868	1,116	979	
Observations	24	24	19	12	10	89
TL Exceedences	0	0	5	12	3	20
% Exceedence	0.0	0.0	26.3	100.0	30.0	
-----Stickney Imhoff Sludge Pb Concentration-----						
Mean (mg/dry kg)	160	161	131	156	161	
Observations	22	21	19	12	10	84
TL Exceedences	12	10	2	4	5	33
% Exceedence	54.5	47.6	10.5	33.3	50.0	

FIGURE 1: ANNUAL AVERAGE CONCENTRATIONS OF KIRIE WAS COPPER CONCENTRATION, HANOVER PARK DIGESTER DRAWOFF COPPER CONCENTRATION, AND STICKNEY IMHOFF SLUDGE LEAD CONCENTRATION FROM 1992–2007

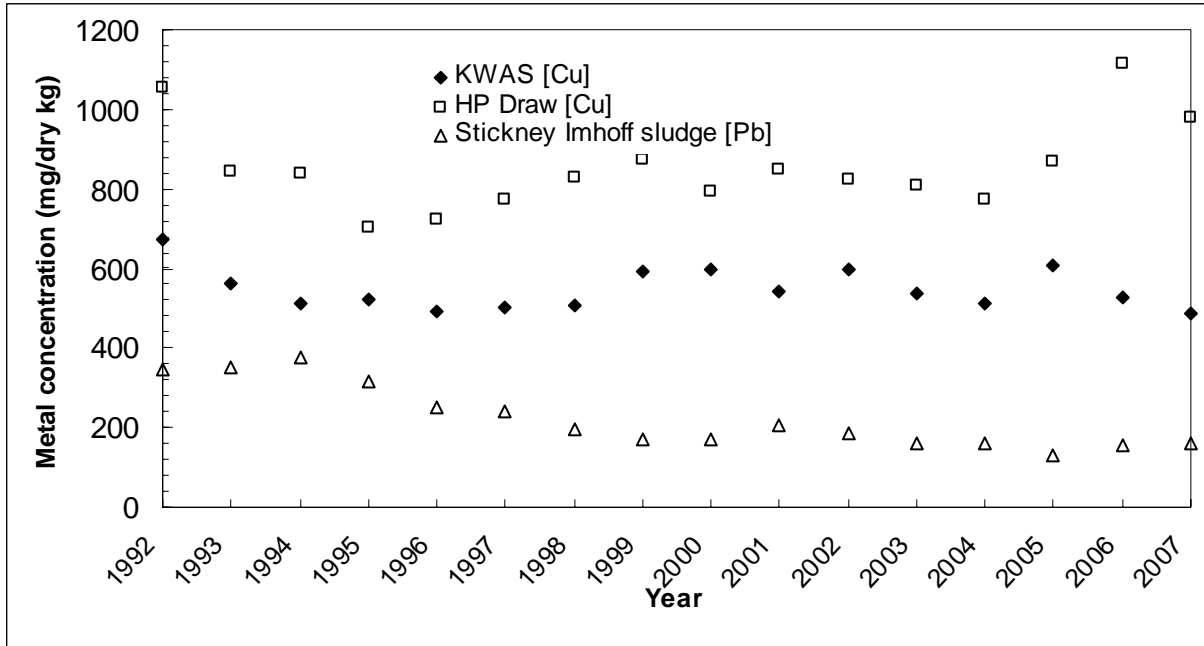


FIGURE 2: ANNUAL AVERAGES OF KIRIE INFLUENT COPPER LOADS AND COPPER CONCENTRATIONS IN SLUDGE STREAM AND BIOSOLIDS FOR 2000–2007

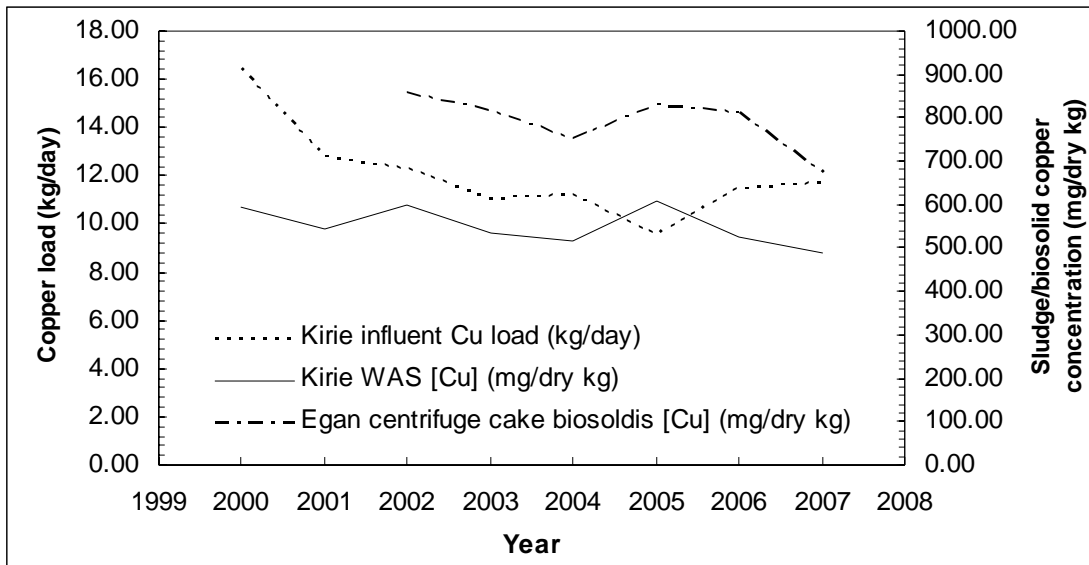


FIGURE 3: ANNUAL AVERAGES OF HANOVER PARK INFLUENT COPPER LOADS AND COPPER CONCENTRATIONS IN SLUDGE STREAM AND BIOSOLIDS FOR 2000–2007

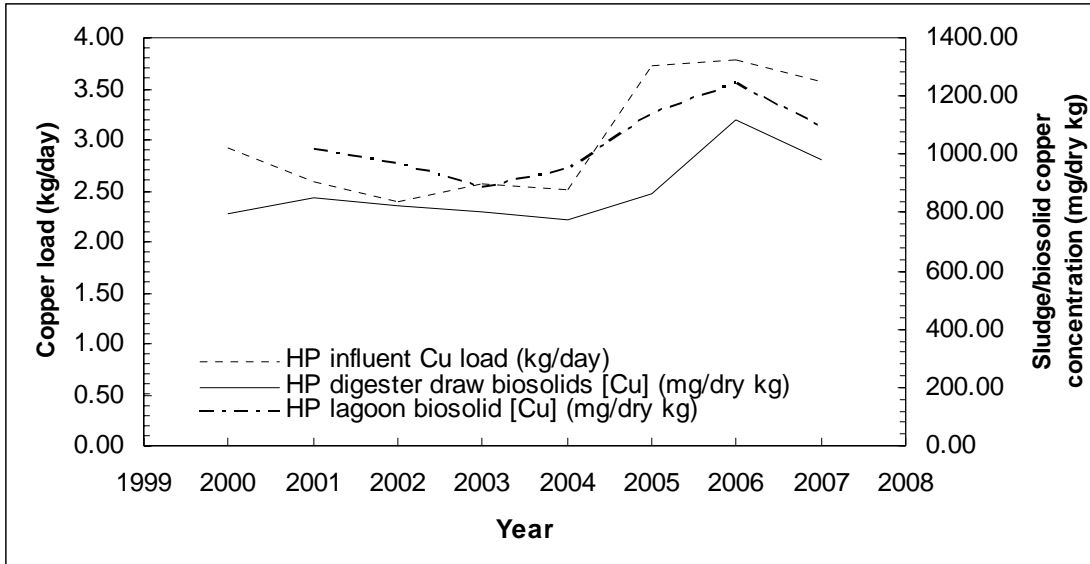
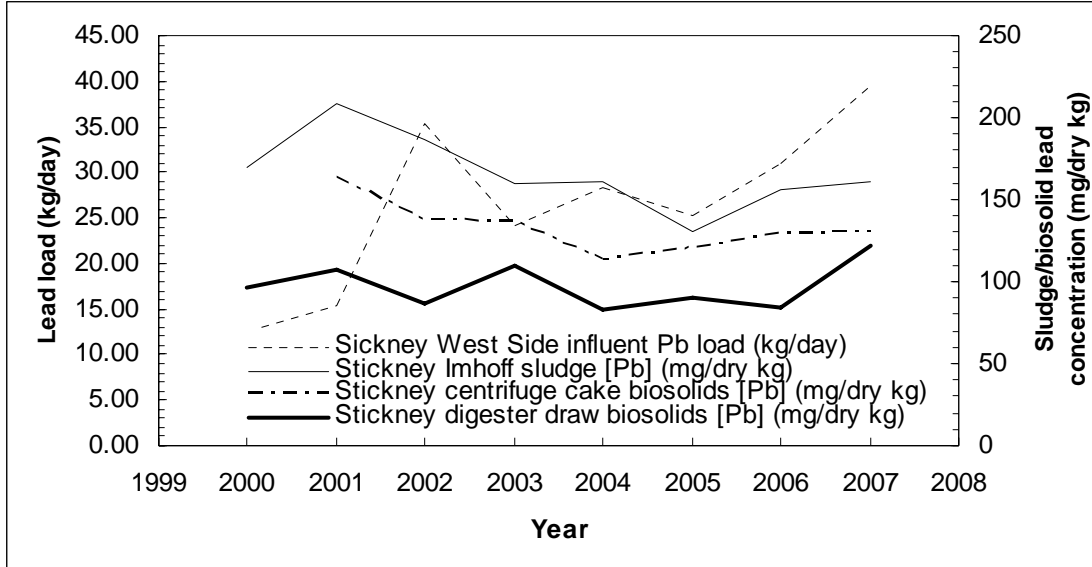


FIGURE 4: ANNUAL AVERAGES OF STICKNEY INFLUENT LEAD LOADS AND LEAD CONCENTRATIONS IN SLUDGE STREAM AND BIOSOLIDS FOR 2000–2007



The influent loading of copper to the Kirie WRP ( $KI_{Cu}$ ) has decreased and essentially plateaued during the period of 2000–2007 (Figure 2). As metals preferentially partition into the solid sludge stream, a similar trend is expected for the sludge concentrations. This is observed with respect to the  $KWAS_{Cu}$  trend line, and generally to the final biosolids product at Egan ( $EB_{Cu}$ ).

Similarly,  $HPD_{Cu}$  and the HP biosolids copper concentrations ( $HPB_u$ ) parallel the copper influent loading for Hanover Park ( $HPI_{Cu}$ ) (Figure 3). There was a slight decrease in the three trend lines from 2000–2004, followed by a significant increase in the three trend lines from 2004–2006, followed by a decrease in the three trend lines in 2007.

$SI_{mh_{Pb}}$  does not parallel the West Side influent Pb loading ( $SWSI_{Pb}$ ) (Figure 4).  $SWSI_{Pb}$  increases from 2000–2007, but  $SI_{mh_{Pb}}$  generally decreases during this time period. Reasons for the stable or decreasing  $SI_{mh_{Pb}}$  concentrations relative to the incoming West side lead load are as follows:

1. The monitoring frequency of West Side influent and Imhoff sludge is different.  $SWSI_{Pb}$  is measured daily whereas  $SI_{mh_{Pb}}$  is measured approximately once a month. With the thirtyfold disparity in the number of observations, it is difficult to compare the two trend lines. However, the  $SI_{mh_{Pb}}$  trend line does parallel the decreasing Stickney centrifuge cake biosolids lead concentrations ( $SB_{Pb}$ ). This trend is also corroborated by the Stickney digester draw lead concentrations.
2. An investigation of sources of lead in Stickney WRP sludges was performed and summarized in the 1996 R&D Annual Report (Report No. 97-9). The major sources of lead were found to be municipal water service, industrial discharge, and TARP pumpback discharge with significant contributions from first flush events after a rainfall. In this report, it was noted that operation of the Imhoff tanks was modified to more closely resemble primary settling tanks to lower lead content of the Imhoff sludge. The detention time of the wastewater entering the Imhoff tanks was reduced significantly. For example, the average detention time for the three Imhoff batteries in 1991 and 2005 was 4.6 and 2.3 hours, respectively.

From 2000 to 2007, incoming Stickney West Side influent had an average pH of 7.3. This basic condition of influent indicates that most of the incoming lead would be observed as a precipitate or sorbed onto solid particles (particulate lead). This is reflected in the average total and soluble lead concentrations in the influent over this time period, 0.02 mg/L and 0.005 mg/L, respectively. Only 23% of the incoming lead is measured as a soluble species and cannot account for the lead passing through to the aeration batteries. In order to bypass settling, the particulate lead must be associated with suspended, non-settable particles. As the detention time is reduced in the Imhoff tanks, coarser particles and therefore particulate lead are able to flow through the Imhoff without settling into the sludge blanket.

This is corroborated by the fact that similar to lead, cadmium, nickel, and zinc were observed to have increasing loads from 2000 to 2007 but showed little to no change in their respective concentrations in the Imhoff sludge.



## SUMMARY

Three sludge streams and metal concentrations were evaluated over the period of 1992–2007, with an increased emphasis on the most recent years (2000–2007). The dynamics of the three sludge streams should mimic that of the metal loadings to the individual plants. This held true for Kirie and Hanover Park with decreasing  $KWAS_{Cu}$  and  $KI_{Cu}$  measurements observed from 2000–2007. Both  $HPD_{Cu}$  and  $HPI_{Cu}$  measurements observed over the same time period decreased from 2000–2004, increased from 2004–2006, and decreased in 2007. However,  $SWSI_{Pb}$  was observed to increase while  $SI_{mhPb}$  decreased during 2000–2007. Reasons for this may be due to differences in monitoring frequency between  $SWSI_{Pb}$  and  $SI_{mhPb}$  and changes in Imhoff tank operation.

In addition, trends in sludge stream concentrations should also parallel the biosolids concentrations from the plants. As expected, both  $KWAS_{Cu}$  and  $EB_{Cu}$  decreased from 2000–2007, as did  $SI_{mhPb}$  and  $SB_{Pb}$ .  $HPD_{Cu}$  generally decreased during the period of 2000 to 2004, increased from 2004 to 2006, and decreased in 2007;  $HPB_{Cu}$  paralleled these trends.

Biosolids sampling and analysis occurs much more frequently than the studied sludge streams (17–79 times per year).  $EB_{Cu}$  and  $SB_{Pb}$  have generally decreased over the study period (2000–2007). However, Hanover Park biosolids copper concentrations have elevated in recent years due to increased copper loadings to the plant. However, there have been no exceedences of the EQ limits by the biosolids for any plant.

### **$KWAS_{Cu}$**

With the decreasing trend of copper loading to Kirie and  $KWAS_{Cu}$ , TL exceedences are expected to decrease for  $KWAS_{Cu}$ . Additionally,  $EB_{Cu}$  is likewise decreasing. As such, there is no reason to decrease the TL of 608 mg/dry kg. EM&R recommends that the  $KWAS_{Cu}$  TL should remain at 608 mg/dry kg.

### **$HPD_{Cu}$**

With the increasing trend in plant loading of copper to Hanover Park and  $HPD_{Cu}$ , TL exceedences of  $HPD_{Cu}$  are expected to increase. The current  $HPD_{Cu}$  TL limit is 957 mg/dry kg. This TL is approximately 64% of the EQ limit (1,500 mg/dry kg). Adding two standard deviations ( $\sigma = 154$  mg/dry kg) to the 2003–2007 average  $HPD_{Cu}$  of 872 mg/dry kg gives a value of 1,180 mg/dry kg (78.7% of the EQ limit). If the TL was adjusted to this value, the number of exceedences from 2003–2007 would go down from 20 to 4.

It is not expected that increasing the current TL to 1,180 mg/dry kg would cause a violation in the Hanover Park biosolids. Therefore, EM&R recommends that the  $HPD_{Cu}$  TL be raised to 1,180 mg/dry kg. Nevertheless, it is imperative that both  $HPD_{Cu}$  and  $HPB_{Cu}$  be monitored closely over the next five years to ensure that concentrations are indeed stabilizing or decreasing.

Copper loadings to the plant increased significantly in the Summer of 2005 and have remained elevated indicating possible new sources of copper.  $HPD_{Cu}$  and  $HPB_{Cu}$  have followed suit. However, 2006-2007 values indicate all three streams copper concentrations have leveled off. Because the Hanover Park plant copper load has increased recently, EM&R strongly recommends that the Industrial Waste Division (IWD) should evaluate current plant loadings to determine the nature and source of the elevated copper concentrations.

### **$SI_{mh_{Pb}}$**

Finally,  $SI_{mh_{Pb}}$  trends do not follow  $SWSI_{Pb}$ . While  $SWSI_{Pb}$  has increased over the last seven years,  $SI_{mh_{Pb}}$  has decreased. This is the opposite of what is expected as both  $SI_{mh_{Pb}}$  and  $SWSI_{Pb}$  trends should parallel each other. Monitoring frequency between  $SWSI_{Pb}$  and  $SI_{mh_{Pb}}$  and changes in Imhoff tank operation may provide insight into these incongruous trends.

Currently, the TL (157 mg/dry kg) is 52% of the EQ limit (300 mg/dry kg). Adding a standard deviation ( $\sigma = 26$  mg/dry kg) to the 2003–2007 average  $SWSI_{Pb}$  of 153 mg/dry kg gives a value of 179 mg/dry kg (59% of the EQ limit). If the TL were adjusted to this value, the number of exceedences from 2003–2007 would go down from 32 to 12.

Additionally,  $SB_{Pb}$  has continued to decrease over this time period. Therefore, there is little concern that an EQ limit exceedence would occur in the Stickney biosolids at the higher TL. EM&R recommends that the TL be adjusted to 180 mg/dry kg. However, as the West Side plant lead load has increased recently, EM&R strongly recommends that IWD should evaluate current plant loadings to determine the nature and source of the elevated lead concentrations.

## RECOMMENDATIONS

EM&R recommends that the  $HPD_{Cu}$  TL be raised from 957 mg/dry kg to 1,180 mg/dry kg, the  $KWAS_{Cu}$  TL remain the same at 608 mg/dry kg, and the  $SI_{m_{Pb}}$  TL be raised from 157 mg/dry kg to 179 mg/dry kg. All other TLs were retained at their current values.

Due to the recent increases in copper loading at Hanover Park and lead loading at the Stickney West Side headworks which directly affect the above sludge concentrations, it is strongly recommended that IWD investigate the sources and reasons for these current trends. Continued increases in the metal loads will eventually raise biosolids concentrations to levels that violate the 503 EQ limits, thus disallowing biosolids land application.