

# Interactive Effects of Soil Properties and Manufactured Coal Ash Aggregates on Groundwater Quality

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## INTRODUCTION

Manufactured coal ash aggregates (MAs) were applied as subsoil substitute for restoration of open pits [1]. MAs are a 2:1 (w/w) solidified composite of FA and BA that are mixed in water and then air-dried. They gain strength with time due to cementitious reactions. Soil properties would greatly affect biogeochemistry of the MAs in soil systems, resulting in dissimilar characteristics of resulting water quality. It is known that the soil types can significantly affect the sorption and desorption of hydrophobic compounds [2]. Compound biodegradation can also be affected by soil characteristics [3].

The current study was conducted in a statistical design to understand interactive effects of soil properties and MAs on the resulting water quality parameters. Three levels of three factors (soil mass, MA mass, and water volume) were evaluated on water quality parameters of pH, turbidity, conductivity, and hardness. Four dissimilar natural soils (organic-rich soil, clayey soil, sandy soil, average soil) were tested.

## MATERIALS AND METHODS

### *Soil Sampling*

Organic-rich soil, sandy soil and average soil were collected from a local area (Santa Isabel, PR). Clayey soil was sampled in Isabela, PR. Soil characteristics are shown in Table 1. After being transported to the laboratory, the soils were dried at 105 °C for 24 h, and then sieved to collect soil particles smaller than 2.0 mm.

Table 1. Characteristics of soils.

Characteristics	Organic soil	Sandy soil	Clayey soil	Average soil
pH	6.5	7.9	5.1	7.4
Soil organic matter (%)	5.69	1.92	1.52	4.89
Soil texture classification	Loamy Sand	Loamy Sand	Clay Loam	Sandy Loam

### *Manufactured Aggregates*

MAs were collected from a local coal-burning power plant (AES Puerto Rico) located in Guayama, PR. The plant combusts coals in a circulating fluidized bed. Selective non-catalytic reaction, circulating dry scrubber with limestone, and electrostatic precipitator are used for reductions of nitrogen oxides, sulfur dioxide, and particulate matter, respectively, in flue gas emission. The main MAs chemical components were 51% (w/w) mixture (silica, alumina, and ferric oxides), 30% (w/w) lime, and 15% (w/w) sulfur trioxide (Figure 1).

According to the American Society for Testing and Materials (ASTM) (ASTM Standard C 618), FA can be classified in two main types: Class C and Class F. Although the ASTM classification of FA is not applicable to MAs that are a solidified composite of FA and BA, MAs can be regarded as a Class C-type CCP based on the chemical properties. However, the sulfur trioxide concentration of 14% in MAs exceeds the maximum concentration of 5% for a Class C- or F-type FA. Prior to use, they were crushed mechanically and sieved to collect the particles sizes ranging from 2.36 to 9.53 mm.

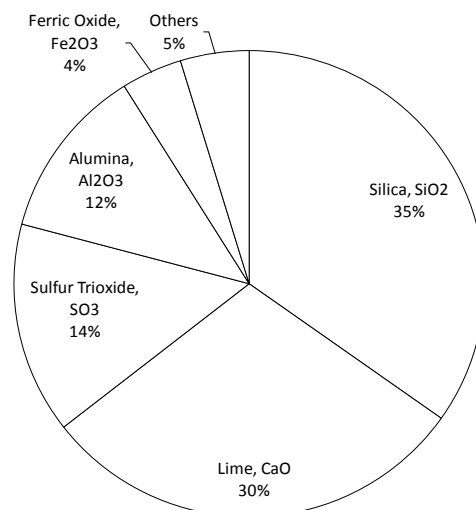


Figure 1. Metal oxide composition of the MAs (% wt).

### *Experimental Design*

Three levels of three factors (soil weight, MA weight, and water volume) were evaluated in a 3<sup>3</sup>-factorial design (Table 2) for resulting water quality parameters of pH, turbidity, conductivity, and hardness. Four dissimilar natural soils (organic-rich soil, clayey soil, sandy soil, average soil) were tested.

27 treatment reactors were run for each type of the soils (a total of 108 treatments). 9 reactors were run as controls that had three levels of MAs in combination with three levels of water volume. For each soil, 9 blank reactors were run with three levels of soil mass and water volumes (a total of 36 blanks). After 24 hrs of reaction time, liquid

portions were measured for pH, conductivity, turbidity, and hardness after filtration with 0.45  $\mu$ M membrane filters. The experiment was replicated in the same manner.

Table 2. Experimental design.

Level	Factor		
	Soil mass (g)	MA mass (g)	Water volume (mL)
	10	2	40
	15	5	60
	20	8	80

### Analysis

Soil pH (in 0.1% (w/v)  $\text{CaCl}_2$  solution) was measured with an Orion pH meter and soil organic matter was quantified by the Loss-on-Ignition [4]. Soil texture classification was done with a hydrometer analysis [5].

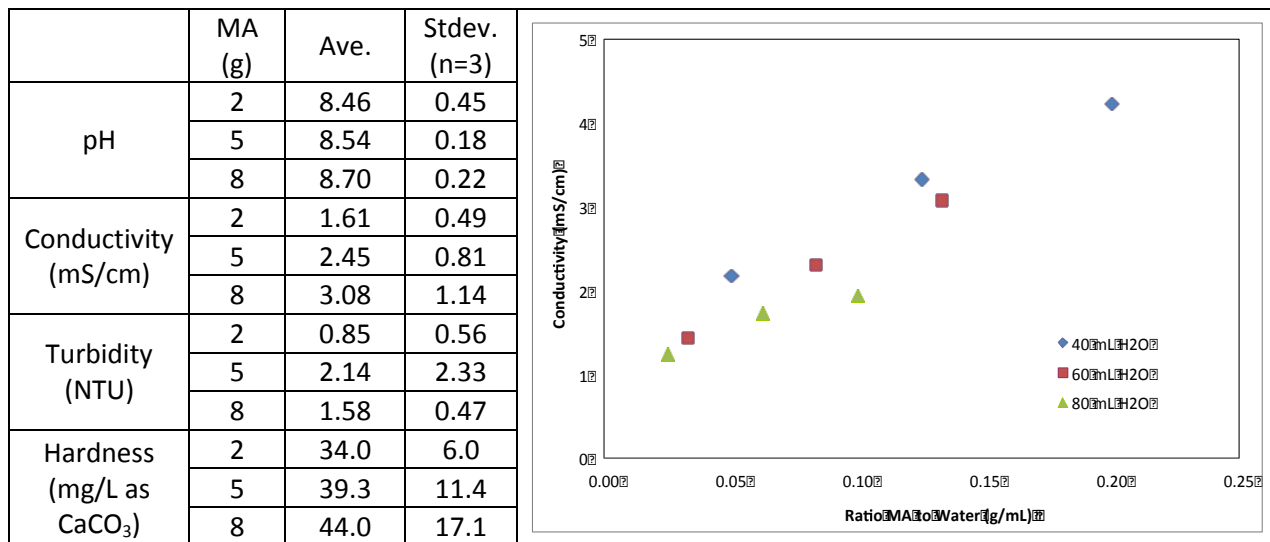
Specific conductivity and turbidity were analyzed with the Orion Specific Conductivity Meter Model 162 and the HACH 2100P Turbidity Meter. Hardness was measured with the HACH Method 8030. pH was measured with an Orion pH meter.

## RESULTS AND DISCUSSION

### Results from the MA control and soil blank reactors

Table 1 shows the water quality results from the control (MA only) reactors. The more was MA present in the reactor, the higher values of pH, conductivity, turbidity, and hardness.

Table 1. Results of water quality parameters from the MA control reactors. A subset figure is an example of conductivity values.



Soil blank reactors showed very different trend in water quality parameters (Table 2). The values of pH were in the order (highest to lowest) of organic soil, sandy soil, average soil, and clayey soil. The values of conductivity, turbidity, and hardness were generally in the order of sandy soil, average soil, organic soil, and clayey soil. However, the sandy soil had extraordinarily higher values of conductivity and turbidity than other three soils (Figure 2).

Table 2. Results of water quality parameters from the soil blank reactors.

	Soil (g)	Organic soil		Sandy Soil		Clayey soil		Average soil	
		Ave.	Stdev. (n=3)	Ave.	Stdev. (n=3)	Ave.	Stdev. (n=3)	Ave.	Stdev. (n=3)
pH	10	7.11	0.13	7.21	0.10	7.13	0.03	6.98	0.06
	15	7.22	0.07	7.16	0.06	6.86	0.09	6.97	0.05
	20	7.26	0.07	7.13	0.04	6.66	0.27	6.96	0.07
Conductivity (mS/cm)	10	0.51	0.17	1.43	0.53	0.14	0.04	0.36	0.11
	15	0.48	0.10	1.66	0.64	0.16	0.04	0.49	0.13
	20	0.68	0.24	2.04	0.73	0.19	0.04	0.60	0.15
Turbidity (NTU)	10	7.55	2.53	26.5	14.2	2.26	1.01	10.08	5.32
	15	9.58	4.74	27.7	11.7	1.91	0.75	6.16	3.66
	20	7.67	0.49	24.3	15.7	3.27	1.49	6.93	1.39
Hardness (mg/L as CaCO <sub>3</sub> )	10	12.7	7.0	19.3	4.6	6.0	2.0	9.3	2.3
	15	12.7	4.6	15.3	6.4	3.3	2.3	8.0	0.0
	20	16.0	7.6	19.2	6.4	4.8	4.2	10.8	1.2

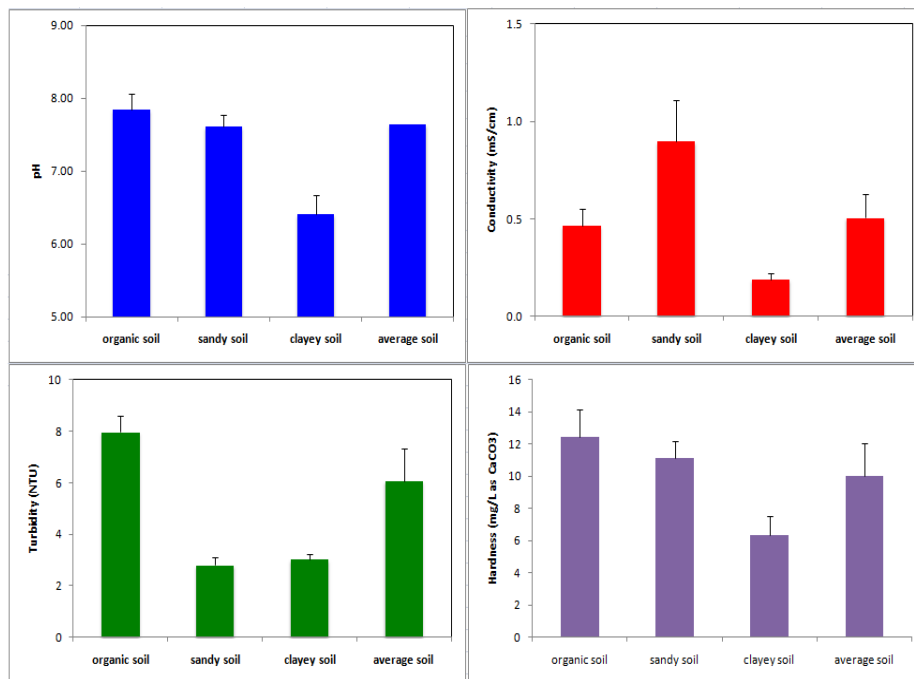


Figure 2. Trend of water quality parameters from the soil blank reactors. Data are the average values with the standard deviations (n=9).

### Results from the treatment reactors

In general, the addition of more MA to the soil did not increase the values of pH, due probably to buffering capacity of the soils (Figure 3). The values of pH after addition of MAs to the organic soil and clayey soil were in the range of 6.0 to 6.5. The sandy soil showed a pH value in the range of 6.5 to 7.5, whereas clayey soil showed in the range of 6.5 to 7.0. This trend generally corresponded to the pH values from the soil blank reactors (Figure 2).

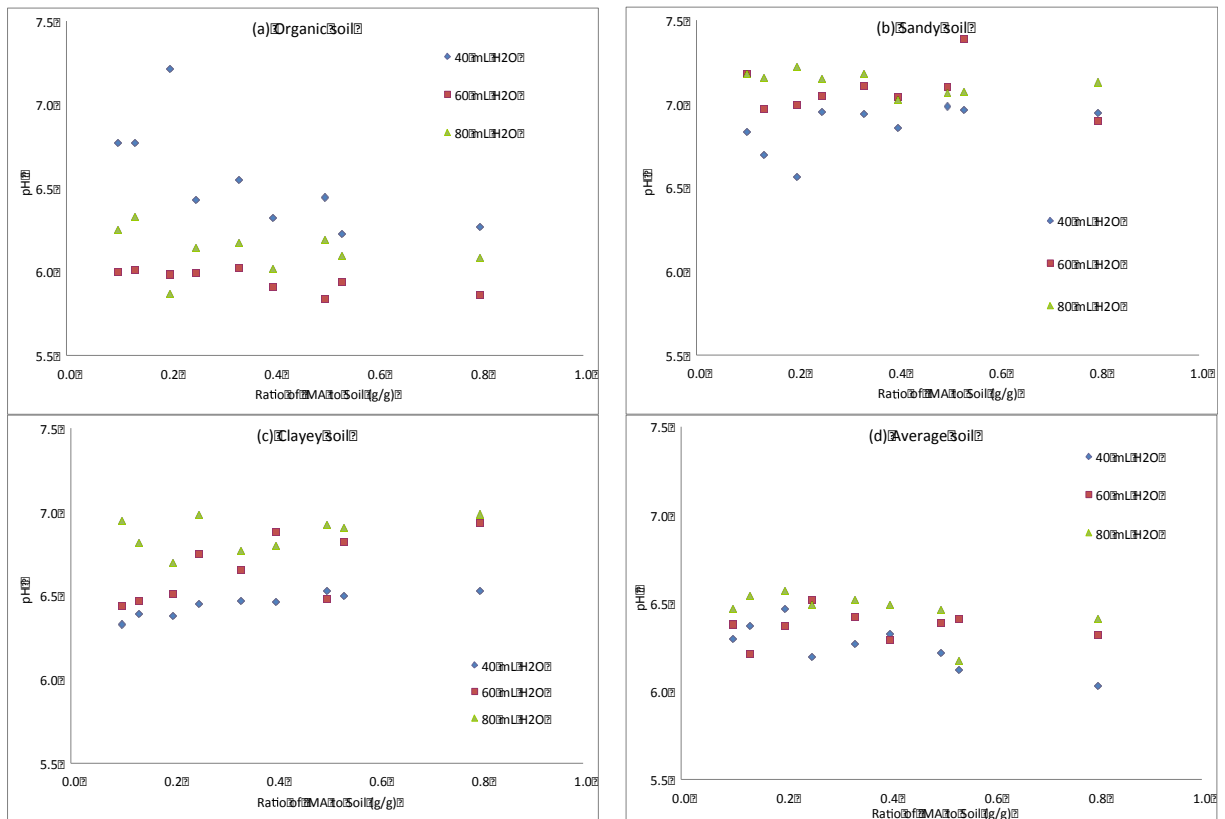


Figure 3. Trend of average pH values (n=3) from the treatment reactors.

Conductivity values from the treatment reactors were generally increased with an increased ratio of MAs to the soils. The greater was the water volume, the lower the conductivity values, due probably to the dilution effect by water. The values were in the range of one to four mS/cm for the organic soil, sandy soil, and average soil, whereas the clayey soil had the conductivity lower than three mS/cm.

Among four soil systems, the organic soil showed the lowest turbidity values, generally having the turbidity lower than three NTU (Figure 4). The trend of turbidity was very similar between the clayey soil and average soil, with the values ranging from two to seven NTU. Much fluctuated turbidity was observed from the sandy soil reactor. Considering low turbidity from the MA control reactor ranging 0.85 to 2.14 NTU (Table 1), the soils seemed responsible for such high turbidity values observed in the treatment reactors (Table 2 and Figure 2).

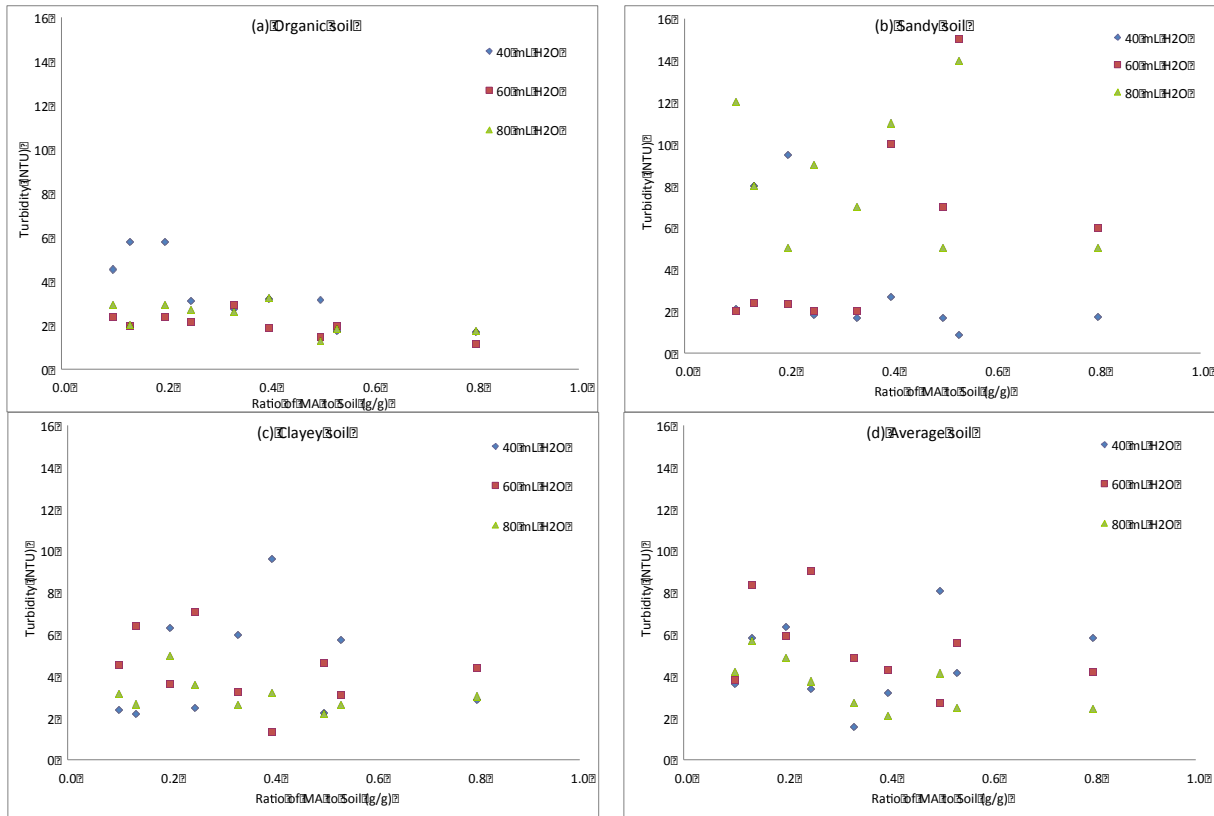


Figure 4. Trend of average turbidity (n=3) from the treatment reactors.

In general, the greater was ratio of MAs to the soils, the higher the hardness concentration. Also, a higher hardness was found with a less volume of water at given ratio of MAs to the soils. This would be attributed to dilution effect by water, just like the conductivity concentrations. Judged by the values obtained from the MA control reactors (Table 1) and the soil blank reactors (Table 2 and Figure 2), hardness concentrations in the treatment reactors were additive from the MAs and soils.

### Statistical analysis

The Minitab statistical program was used to assess the main effects of three factors in the 3<sup>3</sup>-factorial design. For pH (Figure 5), the factors of water volume and soil mass produced a decreasing trend in the organic soil, whereas they produced an increasing trend in the sandy, clayey, and average soils. MA mass did not show any main effects for all soils.

For conductivity (Figure 6), water volume and soil mass showed proportionally decreasing and increasing trends, respectively, regardless of the soil types. MA mass did not produce much differences in conductivity values for all soils. Turbidity values varied in a very dissimilar manner among four soils. The trend of hardness was somewhat similar to that of conductivity.

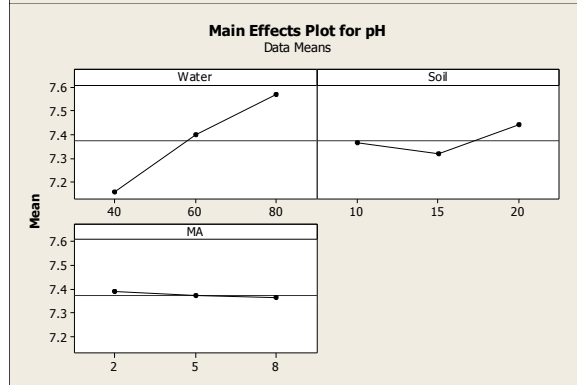
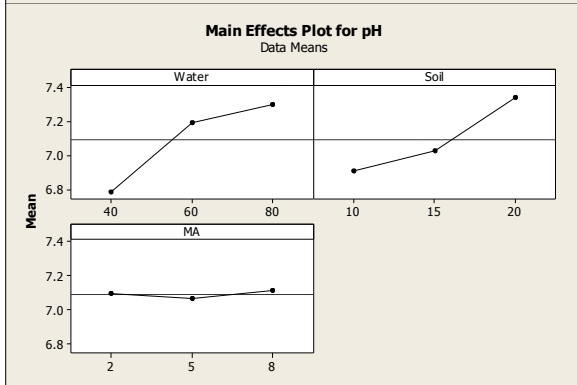
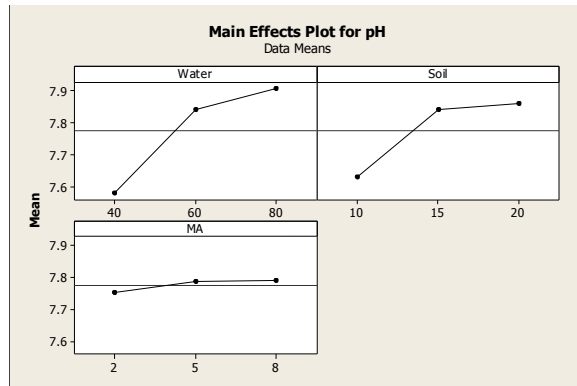
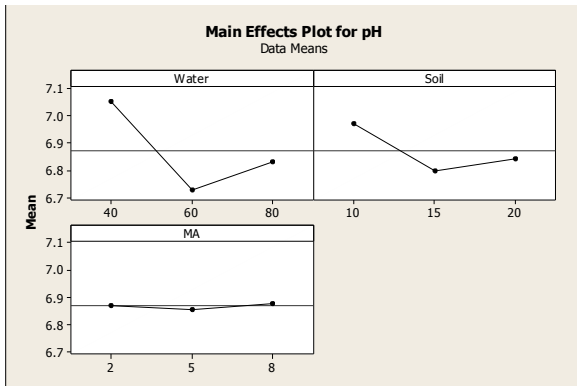


Figure 5. Main effect plots for pH values.

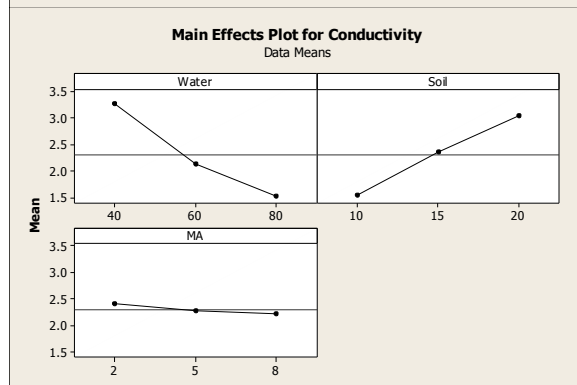
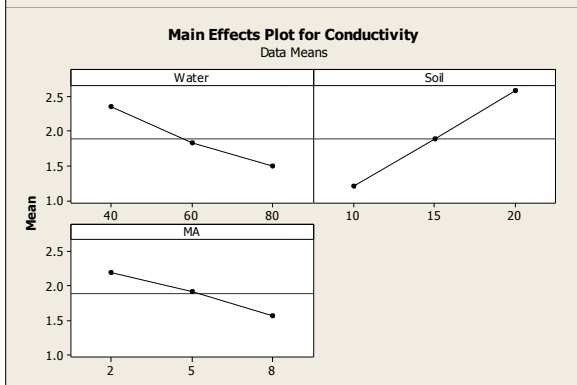
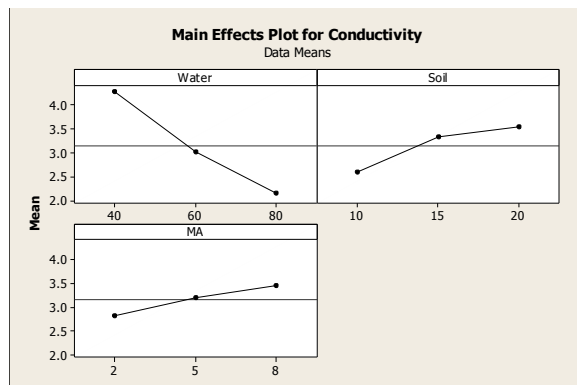
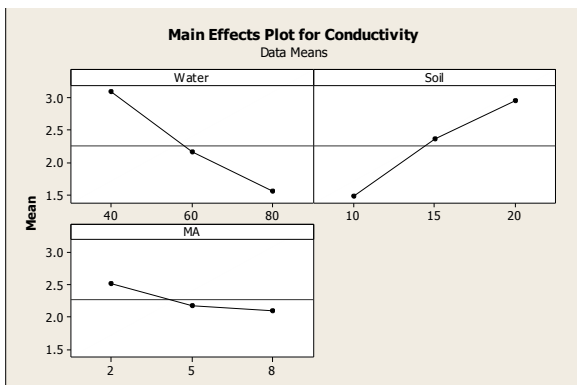


Figure 6. Main effect plots for conductivity.

Table 3 shows the results from the statistical comparisons of the data. For pH, conductivity and hardness, the main factors, water volume and soil mass, produced statistically differences ( $p < 0.05$ ) in all of the soils tested, except for the organic and average soils where pH was not significantly different ( $p > 0.05$ ) with the main factor, soil mass. The main factor, MAs mass, produced statistical differences only for conductivity in organic, sandy, and clayey soils and only for hardness in clayey soil. The main factor, soil mass, only produced significantly different turbidity in organic and average soils. Statistically different interactive effects between the two factors of water volume and soil mass were found for pH in sandy soil, conductivity in organic and average soils, and hardness in sandy and clayey soils. No interactive effects between the MA mass and the other factor were significant.

Table 3. Significant differences ( $p < 0.05$ , in yellow) in water quality parameters.

pH				
Factor	Organic soil	Sandy soil	Clayey soil	Average soil
A	0.004	0.000	0.000	0.000
B	0.142	0.001	0.003	0.326
C	0.972	0.791	0.926	0.951
A*B	0.807	0.001	0.042	0.595
A*C	0.748	0.869	0.792	0.988
B*C	0.996	0.726	0.930	0.973
A*B*C	0.998	0.980	0.953	1.000

Conductivity				
Factor	Organic soil	Sandy soil	Clayey soil	Average soil
A	0.000	0.000	0.000	0.000
B	0.000	0.000	0.010	0.000
C	0.000	0.005	0.011	0.578
A*B	0.001	0.065	0.126	0.000
A*C	0.552	0.928	0.587	0.827
B*C	0.563	0.267	0.909	0.584
A*B*C	0.592	0.881	0.987	0.947

Turbidity				
Factor	Organic soil	Sandy soil	Clayey soil	Average soil
A	0.107	0.084	0.786	0.313
B	0.000	0.337	0.48	0.027
C	0.124	0.83	0.616	0.781
A*B	0.243	0.36	0.578	0.75
A*C	0.818	0.665	0.929	0.207
B*C	0.668	0.771	0.678	0.102
A*B*C	0.65	0.944	0.609	0.765

Hardness				
Factor	Organic soil	Sandy soil	Clayey soil	Average soil
A	0.000	0.000	0.000	0.000
B	0.000	0.000	0.000	0.000
C	0.233	0.202	0.002	0.620
A*B	0.775	0.004	0.021	0.167
A*C	0.376	0.440	0.214	0.223
B*C	0.566	0.904	0.359	0.839
A*B*C	0.466	0.506	0.838	0.978

## CONCLUSIONS

The followings can be concluded based on the experimental results and statistical analysis:

- Generally, soil mass and water volume produced the dominant main and interactive effects on water quality parameters of pH, conductivity, turbidity, and hardness.;
- MA mass only produced a significant main effect on conductivity, but did not produce any interactive effects with the other factors on water quality parameters.;

- In conjunction with water volume they contact with, soils are themselves the dominant factor influencing resulting water quality.

Therefore, it is construed that MAs application as a subsoil substitute would not produce negative impacts on water quality in terms of pH, conductivity, turbidity, and hardness. However, it is warranted to run a toxicological analysis for the resulting water to ensure the findings of the current study.

## ACKNOWLEDGMENTS

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