Assessment of Heavy Metals in Soil, Paddy Straw and SEM analysis of the soil for the impact of wastewater irrigation in Girudhumal Sub basin of Tamil Nadu, India.

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Abstract

The objective of the study is to determine accumulation and translocation of heavy metals from soil to paddy straw irrigated with urban sewage wastewater in peri-urban region of Girudhumal sub basin area in Madurai. The soil samples were collected in seven locations irrigated with treated and untreated wastewater and analyzed for physical properties like pH, EC, bulk density, soil type, major (N,P,K) and micro nutrients (Fe, Mn, Cu, Zn) and heavy metals Ni, Cd, Pb. SEM analysis showed that soil structure is significantly influenced by waste water irrigation. It confirms that the waste water irrigation disturbs soil structure and affecting the plant growth in long run. Pb content was higher than the prescribed safe limits in S5 and S6 location, similarly Ni also was higher than the safe limit in all the locations. Pollution Load Index values are in the range of 0.08-0.56 for all sites, and it indicated that chance of heavy metal contamination is less. The EF values show moderate enrichment to Ni and Zn, Significant enrichment for Cd and Cu, Extremely high for Pb and deficiency for Mn. All these results confirmed that there is no immediate risk of heavy metal pollution, however with respect to Pb and Ni the plant tissues are showing higher values. The transfer factor for heavy metals from soil to paddy straw is less than 0.5 for Cd and for others is more than 0.5 indicated greater chances for heavy metal

contamination.

Keywords: Heavy metals, Paddy Straw, Pollution Load Index, Enrichment Factor, Translocation Factor, SEM.

1. Introduction

Sustainable development of agriculture in India is restricted by a major factor of Water scarcity, since in India water is scarce due to the increasing growth in population, rapidly growing urbanization and industrialization, economic development. Severe water shortages are developing in many countries and water for agriculture is becoming increasingly scarce, particularly in India (Surendran *et al*., 2014, 2016 and 2017). Access to adequate water for irrigation is a matter of concern in India, to meet demand for irrigation water for agriculture (i.e. more than 80 % of water use is for agriculture), non-conventional resources are used.

Availability and disposal of huge quantity of wastewater, due to the growth of industrial sector in India, is becoming a major problem, which makes the growing economies under pressure to sort it out (Minhas and Samra, 2004; Corcoran *et al*., 2010). The technologies for treating wastewaters are often costly (Levy *et al*., 2011), whereas the optimal use of wastewaters in agriculture for irrigation makes this as a low-cost alternative to treatment and helps in preventing uncontrolled dumping of wastewaters into water bodies (Drechel *et al*., 2010). Nowadays, where ever water is scarce, wastewater is often used for irrigation / agricultural purpose. Review of literature showed that this was put into practice first in Melbourne, Australia, where sewage farms were established in 1897 (Shuval, 1990; WHO, 2006) and later being practiced in many countries such as New Zealand, China, India, Pakistan (Yang, Reichert and Abbaspour,2007; Minhas and Lal,2010)

Waste water irrigation (diluted or partially treated or raw), has both advantages and disadvantages. The benefits are conserving water and nutrients, reducing the pollution of water bodies, providing nutrients especially micronutrients and organic matter (FAO, 1992; Murtaza *et al*., 2010; Hanjra *et al*., 2012) and reliable irrigation resource in water scarce conditions which makes millions of urban and peri-urban farmers to depend on these waste water for their food security and livelihood options (Hoeks *et al*., 2002; Qadir *et al*.,2007).

On the other hand, the irrigation practices being primitive, unscientific and more of disposal oriented, these pose threat to farmer's/consumer's health and the environment through transmission of diseases from excreta related pathogens and vectors, skin irritants and irreversible accumulation of toxic chemical like heavy metals, pesticides etc. in soils and groundwater (Yadav *et al*.,2002; Rattan *et al*., 2005; Qadir *et al*., 2007, 2010; Minhas and Lal,2010; Murtaza *et al*., 2010).

However, this wastewater-based irrigation has a number of limitations, includes the pollution of groundwater, built up of heavy metals, pesticides and other pollutants in the soil and the creation of habitat for harmful microorganisms which pose threat to farmer's/consumer's health and the environment through diseases from pathogens and vectors (Mapanda *et al*., 2005; Murtaza *et al*., 2010; Qadir *et al*., 2010 and Minhas *et al*., 2015). Several studies confirmed the presence of heavy metals (Mogen Henze *et al*., 2002; Cao and Hu, 2004; Mapanda *et al*., 2005; Nan *et al*., 2002 ; Huang *et al*., 2017; Yan *et al*., 2018)) and their potential bioaccumulation, when wastewater is used for irrigation. Papaioannou *et al*. 2015 proposed a method for accumulation of heavy metals by quantification and prediction of the pollution by way of elemental interactions i.e antagonistic or synergistic. Transfer of these heavy metals, from soil ecosystem to plant, depends on the heavy metal interaction in soil (Kalavrouziotis *et al*., 2012). Heavy

Metals are highly toxic for plants phytotoxicity cause chlorosis, affects plant growth, variation of yields, reduced uptake nutrients and changes metabolism of plants (Broos *et al*.,2005; Qadir *et al*., 2000). Wastewater mixed with river water used for crop irrigation for more than a decade, have caused metal accumulation viz Cd, Pb, Ni, Zn, Cr and Co into 31 % of soil surface (Assadian *et al*., 1999). Transfer function (TF) calculation will suggest the interactions between these heavy metals in the soil and how they are getting transferred from soil to plants (Kalavrouziotis and Koukoulakis (2009) and Kalavrouziotis *et al*. (2012). These heavy metals enter the food chain and can result in a number of disorders to human health when concentrations exceed the safe limits (Martin and Griswold, 2009). The heavy metal toxicity affected the human populations by way of neurological disorders, central nervous system destruction, cancers of various body organs etc. to name a few (ATSDR, 1999). The authors have conducted studies for wastewater irrigated soil for heavy metal contamination. The alleviation policies to reduce heavy metal exposure through food are usually overlooked (Sharma *et al*., 2014).

By keeping the above factors, it is most important to monitor soil health where wastewater irrigation being carried out in order to prevent the entry of heavy metals into food chain. Girudhumal river total length is 84 km, which flows in urban and peri urban stretch of Madurai for the first 24 km, carries urban sewage, solid waste, small scale industries wastes water ends with nearby peri urban irrigation tanks. Due to shortage of water for agriculture, this water is directly used for irrigation without prior treatment. Paddy crop (Oryza Sativa) is mainly cultivated on commercial scale using this untreated waste water for the past three decades around 800 acres during rainy seasons. There is no information on heavy metals in soil and paddy crop in these areas. This study is aimed to assess the pollution indices and translocation of heavy metals from soil to paddy straw and assessing the physical structure of the soil using Scanning Electron Microscope (SEM) analysis on the impacts of long term waste water irrigation.

2. Materials and methods

2.1. Study area

This study area selected was in the urban reach of Girudhumal river (with a length of 28 km) of Madurai city of Tamil Nadu, Southern part of India and situated at $9^0 25^{'}$ N to $78^0 25^{'}$E as shown in Figure 1. It receives all the domestic sewage, solid waste, rice mill, bleaching and small-scale industries wastes in and around Madurai region. Moreover, the city drainage of Avaniyapuram Channel, Chinthamani Channel, Anuppanadi Channel, Panaiyur Channel and Sotathatti channel are joining into river. This river water is retained in large and small tanks and diverted to irrigation canals to be used by farmers for agricultural purposes and nearly 800 acres land get benefit for the past three decades. The predominant soil texture is clayey, loam and clay loam soils. This soil layers are in general fertile and suitable for growing many crops and paddy is the predominant crop in that area for both Rabi and Kharif period. The other crops cultivated are groundnut, banana, vegetables viz., Chilly and Greens. Urban and Peri urban reach of this area receives 806 mm of average annual rainfall, temperature varies from 15^0 to 41^0 C and relative humidity varies from 45 to 85 % and high in NE monsoon (Water Year, 2007).

2.2. Soil sampling locations

Seven sites were selected as shown in Figure 1 for collection of soil and paddy straw samples namely Thuvariman (9.9585^0N, 78.0524^0E)(S1) as controlled site irrigation with bore well water remaining six places are irrigated with treated and untreated wastewater namely Avaniyapuram (9.8771^0N, 78.1137^0E)(S2), Kaluvankulam (9.9252^0N, 78.119^0E)(S3), Chinthamani(9.892^0N, 78.1413^{0}E)(S4),Samanatham(9.866^{0}N, 78.147^{0}E)(S5), Sottathatti(9.8616^{0}N, 78.1671^{0}E)(S6) and Virathanoor (9.8142^{0}N, 78.1771^{0}E)(S7). Sampling in all the stations were taken in the year of October, 2015.

2.3. Soil and paddy straw sample collection

Soil and paddy straw samples were collected in October 2015 at the time of farmers harvested the crops. Straw from 10-20 paddy clumps were collected randomly from seven selected sites with same physiological age and identical size. All the samples were oven dried at 65^0 for 24 hours and samples are dried, pulverized in wiley mill and stored in polythene bags for analysis. In order to analyze the influence of soil properties on agronomic performance, and to assess the impact of waste water irrigation, representative soil samples were taken from each field at post-harvest stage. Samples were taken from the cultivated soil layer (upper 20 cm), using a single auger and combining 12 samples evenly distributed over the field to one composite sample. The samples were air dried, crushed, and gravel and other particles of more than 2 mm were removed with a sieve. The samples were analysed in the soil laboratory, for the parameters listed below.

2.4. Analytical procedures adopted

The pH of soil was determined using Elico pH meter and EC was determined using a conductivity bridge (Jackson, 1973). The bulk density was determined by gravimetrically by Keen-Raczkowski brass cup. The Organic Carbon content of soil was estimated by chromic acid wet digestion method (Walkely and Black, 1934). The available Nitrogen by Macrojeldahl method (Piper, 1966), Phosphorus by Vandomolybdate method and Potassium by Flame photometric method in HCL extract (Stanford and English, 1949). For heavy metal extraction, 1g of dried sample of soil or paddy straw was digested in 15 ml of HNO_3,H_2SO_4 and $HCLO_4$

mixture (5:1:1) at 80^0C until a transparent solution was obtained (Allen *et al*.,1986). These transparent solutions were then filtered through Whatman number 42 filter paper and diluted to 50 ml with distilled water. The concentration of heavy metal Ni, Cd, Pb, Cu, Fe, Zn of soil and paddy straw samples were analyzed by atomic absorption spectroscopy (AAS, AA250-VARIAN). The AAS value of blank (without sample) of each metal was deducted from the sample value for final calculations (Singh *et al*.,2010). The characteristics of soil structure analyzed by Phillips X2-30 Scanning Electronic Microscope (SEM) with a 3.5 nm of resolution. Glass was properly cleaned and blank determination was used to correct the reading of instruments. The results were found to be + or – 2 % of the certified values.

2.5. Pollution load index (PLI)

To calculates the soil pollution severity, Pollution Load Index is used (Tomlison *et al*.,1980; Harikumar *et al*.,2009) were derived the equation for PLI, is based on the concentration factors of each metals. The PLI of the place are calculated by obtaining the n-root from the nCFs that were obtained for all the metals which is given in equation 1 as follows,

CF = C metal/ C background value,

$$PLI = n < \sqrt{\ }(CF1xCF2xCF3x \ldots\ldots CFn)\text{-----------} (1)$$

Where CF = Contamination Factor, n= no. of metals

C metal = Metal Concentration in Polluted Sediments.

C background Value = Background value of the metal

The PLI value >1 is polluted, whereas <1 indicates no pollution.

Turekian and Wedepohl (1961), were considered the World Average concentration of Cu(45µg/g), Ni(68 µg/g), Mn (900µg/g), Pb(20µg/g) and Cd(0.3µg/g) reported as the background value.

2.6. Enrichment factor

The Enrichment Factor (EF) was calculated to drive the degree of soil contamination and heavy metal accumulation in soil and in plants growing on contaminated site with respect to soil and plants growing on uncontaminated soil (Kisku, Barman and Bhargava, 2000). When EF<2 it may be deficiency to mineral enrichment, EF=2-5 it is moderate enrichment, EF=5-20 it is significant enrichment, EF=20-40 it is very high enrichment, EF>40 it is extremely high enrichment.

2.7. Translocation factor

Translocation factor from soil to crop or mobilization ratio (Barman *et al*.,2000; Gupta *et al*.,2008 and Cui *et al*.,2004) was calculated to examine the relative translocation of metals from soil to other parts of the plants

3. Results and discussion

3.1. Physico-chemical properties of soil

The soil texture was found to be generally clay loam soil. The soil pH values ranged from 7.93-8.8. The Control site S1 (Thuvariman, Bore water irrigation), have lower pH values than other wastewater irrigation sites (Table 1**).** The EC values ranges from 136-770 dS/cm and Organic Carbon (OC) values lies 0.42-.82% in all sites, lower values noticed in bore water irrigation site (S1) than wastewater irrigation areas (S2,S3,S4,S5,S6 and S7). Long-term sewage irrigation may cause can increase the OM content of irrigated soils. Similarly, EC values, sites S1,S3

(Kaluvankulam), and S7(Virathanoor) are the harmless to salinity effect and S2 (Avaniyapuram), S4(Chinthamani), S5(Samanatham) and S6 (Sottathatti) are have higher values cause salinity effect and limit to yield for crops. The surface soil was (0-20 cm) was richer in nutrients, availability of N,P,K in soils improved with sewage water irrigated sites, S6 have higher accumulated more nutrients than other sites. The N,P,K values ranges from 112-434 kg/ha, 22-150 kg/ha and 229-948 kg/ha respectively. The N values are <280 kg/ha for low values for all sites than S6 (Sottathatti) compared with standard limit values, P values > 22 kg/ha for all sites compared with standards and K for all sites >280 kg/ha higher in values than standards values. It is observed that P and K values are higher in all the sites, because of long time wastewater irrigation practices in all the sites. This was similar to the earlier reports of Jat *et al*., (2016), in which they had the opinion that saving of nitrogen depend upon the accumulated organic carbon contents in soils as a result of sewage irrigation. However, in this study it is too early to decide that, farmers can go for skipping / reducing the quantity of fertilizers and we suggest to go in for fertilizers as recommended for normal water irrigated soils as recommended by agricultural universities. The micronutrients Fe, Mn, Zn and Cu had registered higher values in all the locations compared to control, except S7 location and ranges from 2.4-27.95 mg/kg, 0.22-16.57 mg/kg, 0.42-19.14 mg/kg and 1.5-61.64 mg/kg respectively. This confirms that waste water irrigation increases the micronutrient levels in soils to sufficient level and which may induce toxicity in near future if continue to irrigate using untreated waste water.

3.2. Heavy metal concentration in soil

The concentration of heavy metals presents in the soil is given in Table 2. The control site S1(bore water irrigation and other sites S2, S3, S4, S5, S6 and S7 (Untreated and treated domestic sewage irrigation) mean concentration of heavy metals trends revealed that Cu(18.95) is the dominant one followed by Mn(14.15), Ni(5.6), Zn(4.89), Pb(2.29), Cd(0.70). The present concentrations of metals for compared with permissible limits of Indian Standards (Awasthi, 2000) and also international safe limits. However, the heavy metal present in control site is lower limit than other sites.

3.3. SEM analysis

The soil samples were scanned at various magnification modes to collect general information about morphological characteristics. From Figure 2, it is observed that, site S1 (Thuvariman) soil sample image, appear rather rough and the particles are well aggregated and finer (10 μm) grains are loosely aggregated on the surface. With respect to the site S2(Avaniyapuram) untreated wastewater irrigated soil, SEM image showed that the most of the material consists of grains greater than 10 μm in diameter, coarse grains and are mostly of quartz (usually well-rounded), or more angular in shape. It also confirms that particles have porous and cracking structure. The site S3 (Kaluvankulam), irrigated with treated and untreated wastewater, the soil image from SEM analysis revealed that loose aggregate of fine grains and the surface of grains to be thickly coated in platy to poorly crystalline and the very bright grains with rough surfaces. The next site S4 (Chinthamani), using untreated wastewater for irrigation, SEM image showed that the soil samples are small, flaky or platy coatings on larger grains are probably clay. The loose aggregates of small grains are noticed in the surface. Many of the finer (<10 μm) grains are loosely aggregated into larger particles. In the case of S5 (Samanatham) using untreated wastewater for agriculture purposes, the SEM image illustrated that the flocculated arrangement of loosely packed grains. Shapes of soil particles were found to be angular with non-uniformed shapes. The surfaces were rough with sharp corners. Distribution of grain size of soil was within a range of 10 to 200 μm with clearly defined porosity. SEM image of the site S6 (Sottathatti), showed that the microstructure is more porous where pore spaces are relatively large. The surface of soil structure consists of thin plate like morphology. As shown in Figure 2, structure of soil consisted of many sheet-like particles. The flaky and plate-like particles could be identified as minerals. Soils that have flaky shape are likely to have high compressibility. The site S7 (Virathanoor), SEM image illustrated that, the soil structure aggregates is clearly visible in the image. Those aggregates have three-dimensional structure are very different in shape, size, stability and interior structure. The aggregate structure has a strong influence on soil strength. This SEM image analysis clearly interprets the waste water irrigation continuously disturbs the soil structure. It confirms that fact that plants growing in structurally degraded soils are often constrained by water-logging and poor aeration when the soil is wet and by high strength, rather than by the availability of water, as the soil dries. Excessive contamination of these heavy metals may also have an adverse effect on soil structure, causing a decline in soil permeability, and therefore in a soil's ability to further accept and treat wastewater. Hence these soil properties need to be considered before applying the quantity of Waste water for irrigation.

3.4. Heavy metal concentrations in paddy straw

The heavy metal concentrations for paddy straw are presented in Table 3. The concentration (mg/kg, dry wt.) of heavy metal in control site (S1) was found in the order of Zn (192)>Cu(54)>Mn(35)>Ni(1.52)>Pb(0.04)>Cd(0.01), whereas other sites heavy metal mean concentrations level was found in the order of Zn(154.29)> Cu(63.86) > Mn (49.43) > Ni (3.30) >Pb(1.71)>Cd(0.29) respectively. The Cd mean values for both soil (0.7 mg/kg) and paddy straw (0.29 mg/kg) respectively, there is no significance difference were found for both soil and paddy straw.

Irrigation through untreated waste water increased the concentration of heavy metals in paddy plants. The concentrations of all the heavy metals showed spatial variations, which may be ascribed to the variations in heavy metal sources and the quantity of heavy metals discharged through the sewage and effluents in irrigation water. Absorption and accumulation of heavy metals in plant tissue depend upon many factors, which include temperature, moisture, organic matter, pH, and nutrient availability. Soil properties influencing heavy metal availability varied significantly between the sites. In the case of S5 and S6, Pb content was higher than the prescribed safe limits, similarly Ni also was higher than the safe limit in all the locations. In the case of Cd it is well within the Indian standards in all the locations. The consumption of Ni and Pb contaminated portion of paddy by people / live stock may pose serious health hazards in long run (Sharma *et al*., 2006, 2007). Interesting thing to observe is that the contamination levels were higher than permissible limits in the plant tissue, at the same sites where soil samples comply with established safe standards. Cd was easily absorbed by plants and transported to different parts of plants and no beneficial effects to plants (Jarvis, 1976). The Zn, Cu and Mn concentrations values were higher in paddy straw than in soil. These metals are required for various activities and plays important roles in growth of the plant and photosynthesis (Tripathi *et al*., 1997). The heavy metals like Ni and Pb are required continuous monitoring and suitable measures are needed before these poses serious problems. Crop growth parameters and yield attributes are also significantly influenced by the waste water irrigation (Data not shown). Average yield obtained for Paddy from different sites are presented in Table 4. Data showed that the waste water irrigation significantly influenced the yield when compared to bore well irrigation water. Slight reduction in yield is due to the excess EC, Sodium content and alkaline pH, which might have influenced the uptake of other nutrients. Even though the waste water may contain appreciable quantity of plant essential nutrients, organic carbon, the other factors such as Na, TDS, Heavy metals and EC needs to be taken care of, otherwise it will have a negative impact on the crop yield in the long run. Post harvest soils samples were analyzed for the impact of waste water irrigation. Salient results are discussed: Soil pH values vary from 7.1 to 9.4 in all these sites; EC values ranges from 0.2 to 2.1 dS/m; Organic Carbon varied from 0.to1.8 % and as expected continuous irrigation had a significant effect over soil properties when compared with the fresh water irrigated area.

3.5. Pollution load index

The calculated PLI values varied from 0.08(S1)- 0.56(S6)and are presented in Figure 3. The lowest values was identified at control site (S1, Bore water irrigation) and higher values are observed at S6 (Sottathati) site, whereas untreated wastewater is used for irrigation, other values are S2 (0.1), S3(0.13), S4(0.17), S5(0.223) and S7(0.1) respectively.

3.6. Enrichment factor

The enrichment factor (EF) in all sites for heavy metals were found in the descending order of Pb (53.2) > Cu (10.64) >Cd (6.5) Zn (3.16) >Ni (3.16) >Mn (0.79) respectively and are presented in Table 5. **S**ignificant difference in EF values were observed among all the heavy metals. The values of EF was greater than 1, indicates that chances of accumulation of metals in plant species where wastewater used for irrigation (Kisku *et al*., 2000). Among six metals estimated, the maximum EF was found to be Pb for soil Ni, Zn are moderate enrichment, Cd and Cu are significant enrichment, Mn is deficiency to mineral enrichment respectively.

3.7. Translocation factor

The ability of heavy metal species to transfer from the soil into plant roots is referred to as transfer factor (TF). The concentrations of metals in this study area were within the normal standards. The TF of the heavy metals from soil to paddy straw in the study area are presented in Figure 4. The TF values are in order from Zn(31.5) >Mn (3.49) >Cu (3.36) >Ni (0.653) >Pb(0.75)>Cd(0.40) respectively. The high toxic element concentrations indicate that some degree of heavy metal contamination occurred in the crops. According to study conducted by Sajjad et.al.,2009, if the transfer factor coefficient of heavy metal is greater than 0.50, the plant will have a greater chances of heavy metals contamination by anthropogenic activities. This indicates that the values of Ni, Pb and Cd concentrations of heavy metals in the plant are low but, there is a chance for it to be contaminated with Zn, Cu and Mn by further anthropogenic activities. In, world populations, most affected heavy metal toxicity are pregnant women and children (Boon and Soltanpour, 1992), central nervous system destruction, body organs cancers and disorders of neurological are some of the common report for heavy metal poisoning (ASTDR, 2000), hence enough mitigation measures need to be adopted in these areas.

In nutshell, the issue is that the contamination levels were higher than permissible limits in the plant tissue for some heavy metals at the site where even soil samples showed the value of heavy metals within the prescribed limits. This study suggests that imperative consideration is required to focus on regular monitoring and pollution control mainly to ensure food for human consumption and regularize the use of sewage for irrigation. This indicates, enough caution should be given to farmers for the use of waste water for irrigation. This has important implications for policy and programmes should be aimed at monitoring and controlling the level of heavy metal concentrations in irrigation water sources. Policies and programs need to be adapted so that local edaphic conditions and agricultural practices are taken into account, and appropriate local measures developed for ameliorating heavy metal uptake by crops for a given set of local conditions. These measures need to be regularly reviewed to take into account factors such as the accumulation of heavy metals in the topsoil over time.

4. Conclusions

In the present study, soil and plant samples were collected from peri-urban region of Girudhumal sub basin area in Madurai district, Tamil Nadu, India irrigated with urban sewage wastewater. The results showed that the value of pH for both soil and paddy straw are within the permissible limits. EC values forS1 and S7 are within permissible limit than other sites; possess salinity affect to soil and in long run will affect soil quality (soil fertility& structure) and limit the yield crops. The OC values are low in S1, medium in S2 site and high in other five sites, this may be due to use of long time wastewater irrigation. The nutrients values in all the sites showed that, N values are observed moderate in all sites, whereas P and K values are more than the permissible limit prescribed by Indian Standards. However, this accumulation of nutrients in the soil due to decades of untreated wastewater irrigation is a boon for agricultural production, since these nutrients are essential for plant growth, hence farmers can save money by reducing the quantity of P and K fertilizers. The micro nutrients Fe, Mn, Zn and Cu are also within standards limit. From the SEM images, it is observed that Control site (bore water irrigation) shows clear morphological characteristics of soil, particle are well graded and other wastewater irrigation sites shows soil particles are flaky and plate-like particles could be identified as minerals and the surface of grains to be thickly coated in platy to poorly crystalline. This structural deformation will result in poor growth of plants. The heavy metals Ni, Pb and Cd were assessed for both soil and paddy straw to determine the status of pollution load in the soil. The Pollution Load Index (PLI)values indicated that all the values are within 1, and there is a less chance of metal pollution in the soil. The EF values for metals, Ni(3.16) and Zn(3.61) are shows moderate to enrichment, Cd (6.5) and Cu (10.64) shows significant enrichment, Pb(53.2) is extremely high and Mn(1.79) deficiency to mineral Enrichment. The transfer factor of heavy metals from soil to paddy straw are less than 0.5 for Cd, indicates less intake by the plant and other metals are greater than 0.5 suggesting the possibility of heavy metal contamination. Long time wastewater irrigation more than decades impacts on soil quality and in turn may reduce value of land and periodic monitoring of soil quality levels are needed for effective irrigation management.

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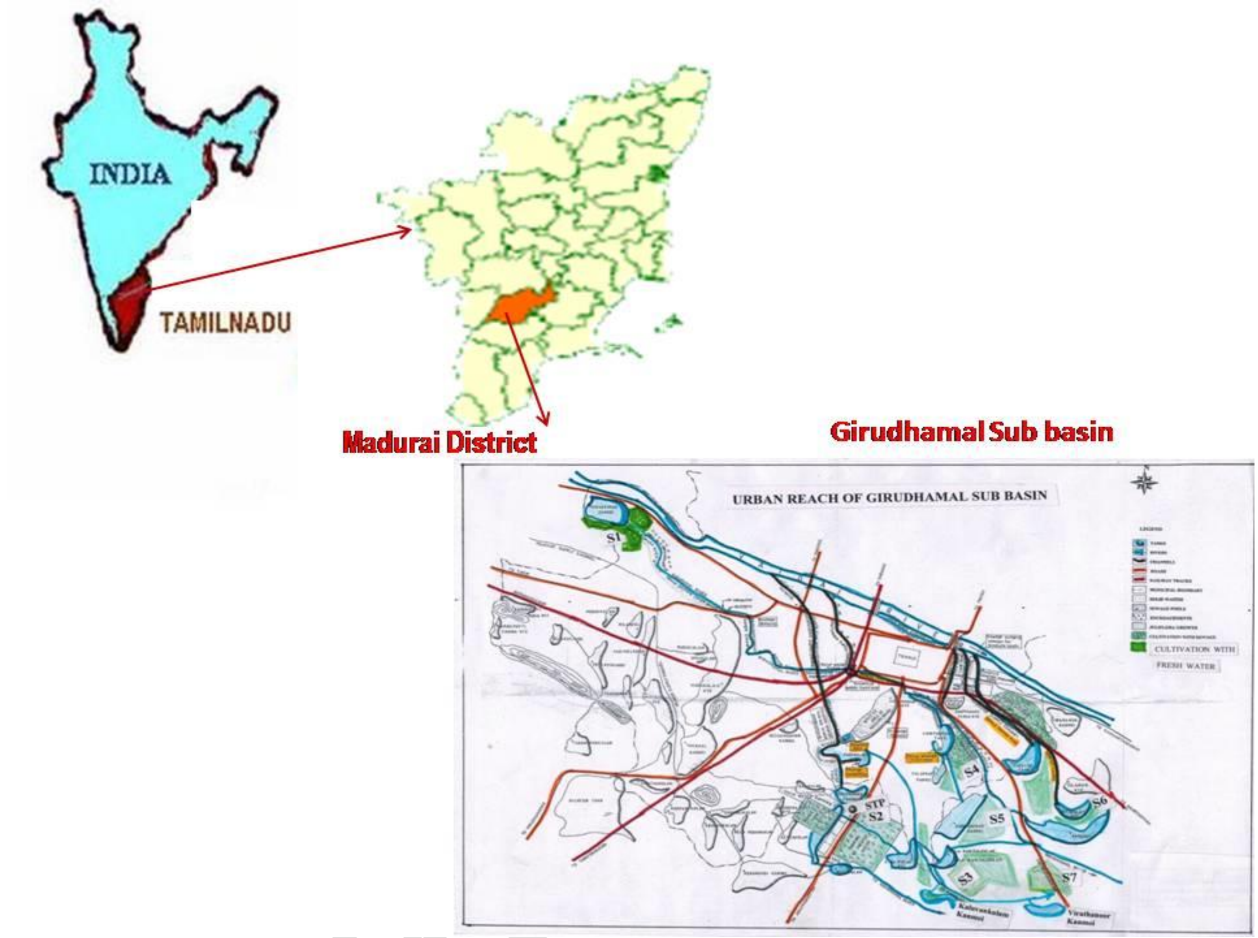
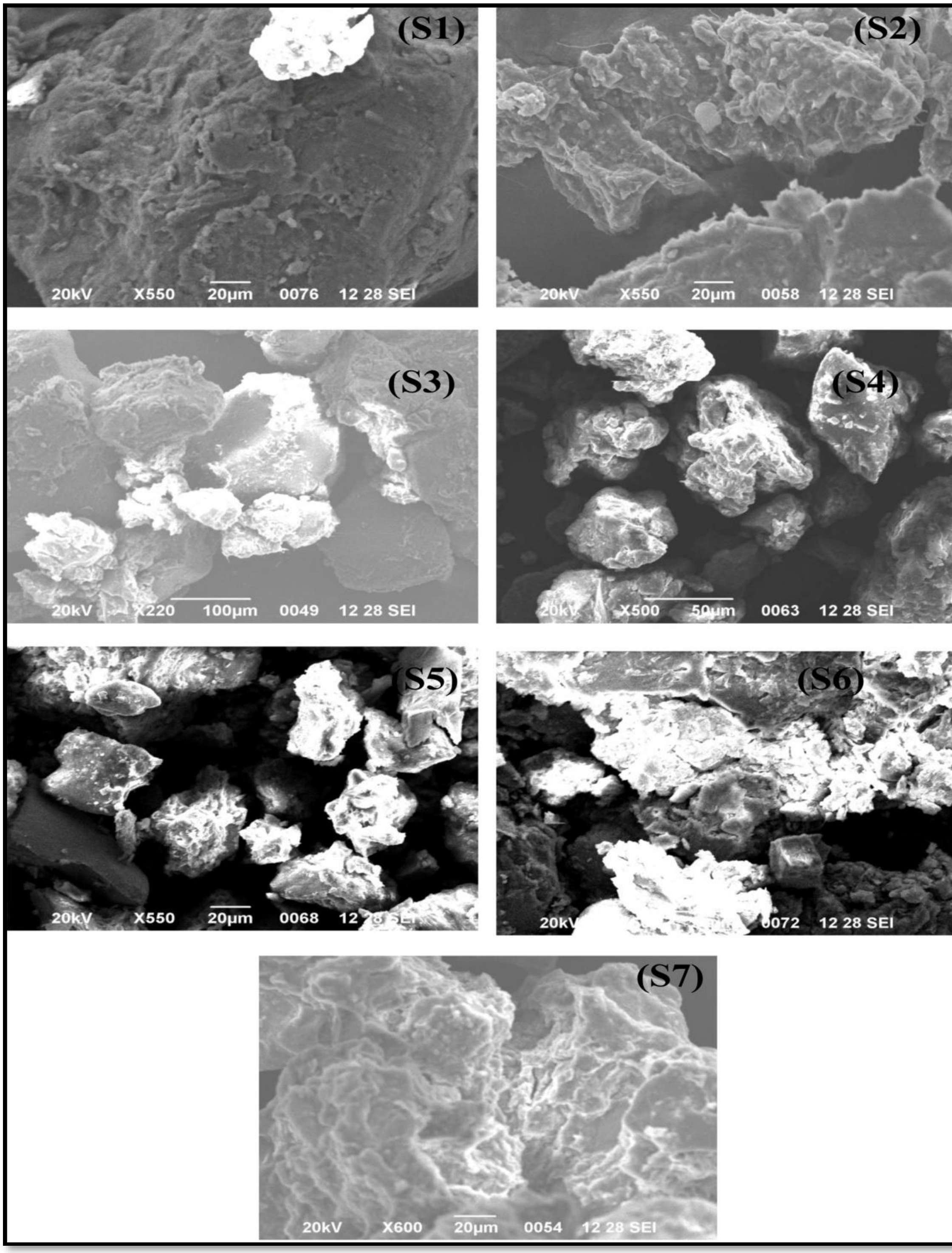


Figure 1. Study Area



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519 **Figure 2.** SEM Morphological image for different sites in the study area

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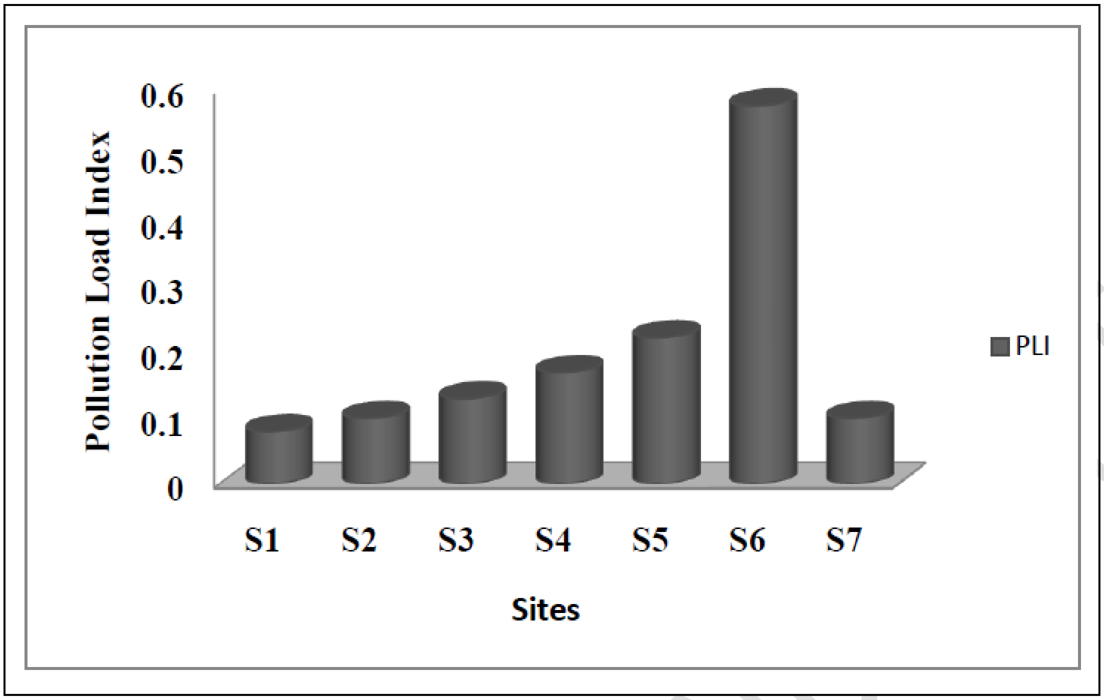

Figure 3. Pollution Load Index in the study area.

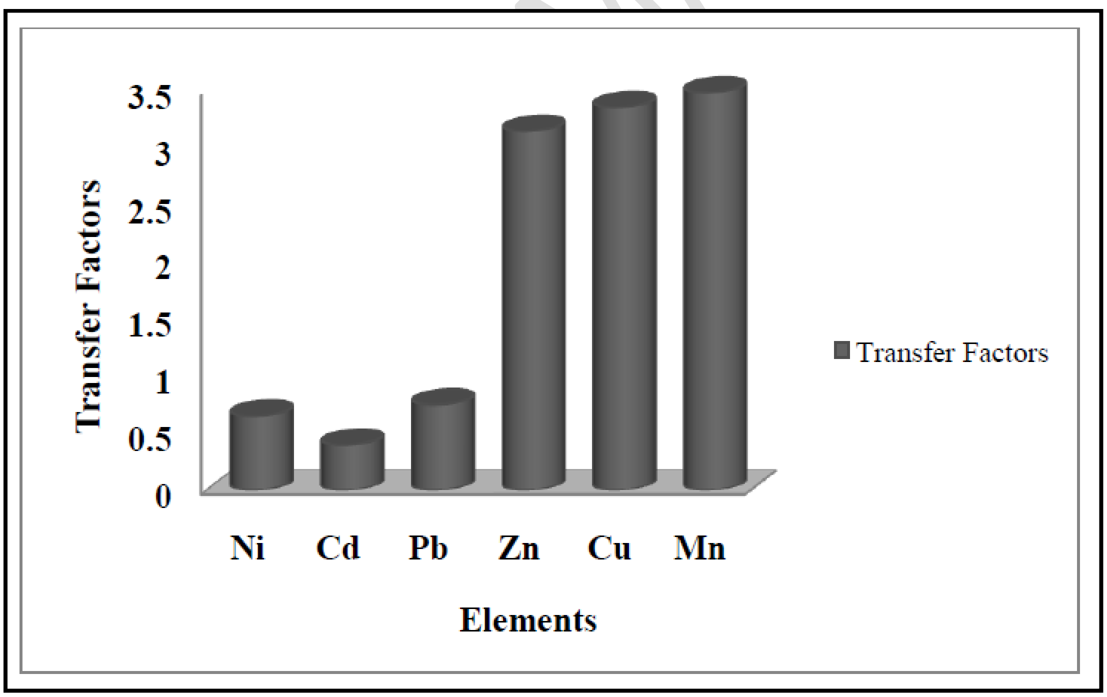

Figure 4. Transfer Factors of Heavy metals from Soil to paddy Straw

525 **Table 1. Physico-chemical properties of soil irrigated with treated untreated and Bore water irrigation**

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Sampling sites	pH	EC (dS/cm)	Bulk Density (g/m3)	Oganic Carbon (%)	Soil Texture	Available (kg/ha)			Fe (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Cu (mg/kg)	Available Sulphur (kg/ha)	Irrigation
						N	P	K						
S1	7.93	270	1.25	0.42	Loam	218	32	779	2.41	8.41	1.51	2.09	6.9	Bore Well Water
S2	8.72	666	1.25	0.56	Clay Loam	104	37	503	3.47	15.46	1.28	3.86	32.9	Untreated Sewage
S3	8.80	290	1.26	0.8	Sandy	230	150	229	35.51	16.57	1.38	1.5	11.4	Treated and Untreated Sewage
S4	8.11	770	1.33	0.78	Clay Loam	210	38	872	11.17	10.58	7.37	48.31	4.3	Untreated Sewage
S5	8.55	660	1.25	0.82	Clay	162	22	948	12.19	15.14	2.65	11.24	3.3	Untreated Sewage
S6	8.11	770	1.33	0.75	Clay	434	60	903	27.95	15.6	19.14	61.64	14.6	Untreated Sewage
S7	8.37	1.36	1.11	0.82	Clay	112	120	631	2.4	0.22	0.42	1.61	12.5	Treated and Untreated Sewage

Table 2. Heavy Metal Concentration in soil

Places	**Sites**	**Ni**	**Cd**	**Pb**	**Zn**	**Cu**	**Mn**
Thuvariman	S1	1.77	0.12	0.05	1.51	2.09	8.41
Avaniyapuram	S2	5.26	0.1	1.15	1.28	3.86	15.46
Kaluvankulam	S3	3.38	0.31	1.25	1.38	1.5	16.57
Chinthamani	S4	5.36	0.82	0.16	7.37	48.31	10.58
Samanatham	S5	3.83	1.86	3.99	2.65	11.24	15.14
Sottathatti	S6	11.47	0.81	8.89	19.14	61.64	15.6
Virathanoor	S7	4.32	0.85	0.52	0.92	4.03	17.32
Mean		**5.06**	**0.70**	**2.29**	**4.89**	**18.95**	**14.15**
Median		**4.32**	**0.81**	**1.15**	**1.51**	**4.03**	**15.46**
SD		**3.08**	**0.61**	**3.20**	**6.67**	**25.11**	**3.33**
Indian Standard (Awasthi,2000)		75-150	3-6	250-500	300-600	137-270	-
WHO/EU standards (EU 2002)		75	3.0	300	300	140	-

Table 3. Heavy metal Concentration in Paddy Straw

Places	**Sites**	**Ni**	**Cd**	**Pb**	**Zn**	**Cu**	**Mn**
Thuvariman	S1	1.52	0.01	0.04	192	54	35
Avaniyapuram	S2	4.30	0.08	1.02	110	45	67
Kaluvankulam	S3	2.82	0.02	1.12	179	37	72
Chinthamani	S4	4.83	0.56	0.10	93	177	35
Samanatham	S5	2.75	1.30	**2.90**	241	55	50
Sottathatti	S6	4.50	0.01	**6.56**	158	42	20
Virathanoor	S7	2.41	0.02	0.24	107	37	67
Mean		3.30	0.29	1.71	154.29	63.86	49.43
Median		2.82	0.02	1.02	158	45	50
SD		1.24	0.49	2.36	54.04	50.42	20.04
Indian Standard (Awasthi,2000)		1.5	1.5	2.5	50	30	-
WHO/FAO, 2007		-	0.2	5.0	60	40	-

Table 4. Effect of waste water irrigation on crop yield

Places	**Sites**	**Cropped area (ha)**	**Types of Crops**	**Seasons (Kharif, Rabi)**	**Paddy Mean Yield (kg/ha)**
Thuvariman	S1	48	Paddy, Banana, Coconut	Both the seasons	9500[a]
Avaniyapuram	S2	44	Paddy, Fodder Grass	Both the seasons	8750[c]
Kaluvankulam	S3	72	Paddy	Rabi	9000[b]
Chinthamani	S4	32	Paddy	Rabi	8750[c]
Samanatham	S5	72	Paddy, Banana	Rabi	9000[b]
Sottathatti	S6	48	Paddy	Rabi	9000[b]
Virathanoor	S7	71	Paddy	Rabi	8750[c]

Alphabets a to c indicates the significant difference at $p<0.01$

Table 5. The Enrichment Factor for Heavy Metals in Soil

Metals	**Enrichment Factors**	
Ni	3.16	Moderate Enrichment
Cd	6.5	Significant Enrichment
Pb	53.2	Extremely high Enrichment
Zn	3.61	Moderate Enrichment
Cu	10.64	Significant Enrichment
Mn	1.79	Deficiency to mineral Enrichment