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Speciation And Fate Of Mercury Present In The Solid Waste And Effluent Of A Chlor-Alkali Industry Discharged Into The Environmental Segment.

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Highlights:

- The effluent and solid waste of the Chlor-alkali industry discharged into the environment contained significant amount of elemental mercury as waste and are deadly toxic to flora and fauna.
- Elemental mercury is converted to inorganic mercury, ionic and organic mercury by natural chemical transformation and methylation mediated by biological agents.
- Plants collected from the solid waste deposit site and effluent soaking pond showed higher mercury accumulation. Mercury speciation changed with depth.
- Top waste soil contained more elemental and inorganic mercury and availability of organic mercury increased with the increase depth of waste soil.
- Absorption and retention of mercury was high in roots than stem, shoot and leaf.
- The BAF value and TF1 and TF2 value significantly indicated the movement of mercury from soil to root, then to stem and from stem to leaf.

Abstract

The mercury speciation study revealed that the effluent was having more amount of metallic mercury (67.2%), less of inorganic mercury (29.4%) and least amount of organic mercury (3.4%). The mercury speciation study revealed that the solid waste present on the top soil was having more amount of metallic mercury (65.3%), less of inorganic mercury (31.6%) and least amount of organic mercury (3.1%). The bottom solid waste contained 23.6% metallic mercury, 61.5% inorganic mercury and 14.9% organic mercury. These dynamics change with each unit of time due to regular chemical transformations occurring in the environment either by oxidation or by reduction chemical reactions. The conversions of inorganic mercurial compounds in to organic mercurial chemicals in the environment were possible mostly by biological agents like resistant bacteria and phytoplankton. The old plants collected from the solid waste contaminated site contained significant amount of residual mercury in their tissues. Plants collected from the effluent stocking pond site showed lesser amount of residual mercury and the plants collected from the solid waste dumping site showed significant amount of residual mercury. Residual mercury was not found in some freshly grown plants collected from the effluent pond site. The effluent collected from the effluent canal and effluent storage tank showed significant variation. The solid waste collected from the central solid waste dumping site indicated presence of significant amount of residual mercury to the tune of 345.6±28.4µg of Hg Kg^{-1} dry wt. Mercury speciation was clearly visible in aging solid waste dumps. Organic mercury increased with the increase in depth of waste soil. Accumulation and distribution of mercury in plants depends on availability of mercury, its microenvironment and physiological activity of the plants. Significant variation in residual mercury accumulation was noted among the plants collected from the both the contaminated sites. The reasons are mostly the type of the plant, its resistance and tolerance, age of the plants, mercury absorbing capacity of the plant and its distribution.

Key words: Chlor-alkali industry, effluent, solid waste, mercury, BAF, TF.

Introduction

Mercury is available in the environment in different forms like- elemental mercury, inorganic mercury and different forms of organic mercury. Mercury at NTP is a liquid and it can volatilize once the temperature is high. Mercury can under go chemical transformation by natural processes of oxidation and reduction and can change its form / transform from inorganic to organic form by biomethylation mediated by biological agents. After death and decay of the organism's, the organic form of mercury in the plant / animal body can be available in the environment as organic form and can be absorbed by the plants and animals available in the environment. This metal can move to distances through air, if the metal is in vapour form. Being a toxic element, mercury cannot be disintegrated or degraded into harmless substances as mercury is a persistent chemical with higher half life period. But mercury can change its for from one species to another simply by chemical reaction like natural oxidation and natural reduction processes which are operating in nature like any other chemical transformation operating in nature. Status of mercury may change from one state to another states and species in its cycle in nature naturally or mediated by living organism mostly by bacteria and phytoplankton. The simplest form of elemental mercury is harmless to humans as this elemental mercury is non absorbable. The absorption of mercury from the environment, transport in the organisms body, bioaccumulation in different cells and tissues, bio-modification in the organisms body (formation of methyl mercury and dimethyl mercury, modification from absorbed elemental mercury to ionic mercury and inorganic mercury and further conversion to organic forms of mercury by methylation), retention of different forms of mercury in tissues either by reacting with cellular chemicals or infrastructural chemicals or retention in the intercellular spaces or inside the vacuoles or in the dead tissues or deposition in transporting systems, detoxification by way of conversion to unusable form and excretion from organisms body through excretory system or by simple exudation from the organisms body. Speciation of mercury also influences the movement and transport of mercury in the environmental segments. Speciation of metals is responsible for movement and transport of chemicals and distance to be travelled in the atmosphere. The movement of mercury in the atmosphere after discharge or by evaporation from contaminated soil and water bodies depend on the size and weight of the chemical, air temperature and air flow direction. The mercury in water bodies move along with water flow, direction of flow and speed of water movement in rivers & canals and high tidal influx at estuaries before joining the sea and ocean. Mercury adsorbed on dust particles and other particles and ionic (e.g. divalent) mercury compounds will settle or sediment on land and water mostly in the vicinity or in and around of the sources. The dispersion of mercury from the emission source to distances and availability of mercury in other places away from the source was probably due to movement of evaporated mercury in the atmosphere to distances. Air to soil and to vegetation exchange fluxes are an important part of global and regional, chemical and biogeochemical cycles. Much of the Hg^{++} (ionic mercury) deposited during precipitation or absorbed by plants is reduced to Hg^0 (elemental mercury). This converted mercury might get back to the atmosphere again by evaporation. Recent vegetation and soil mercury content studies suggested that vegetation elemental Hg^0 uptake dominates (50–80%) the mercury net deposition at terrestrial sites. The different forms of atmospheric Hg may be deposited on surfaces by way of wet and dry processes. These forms may be sequestered within terrestrial compartments or emitted back to the atmosphere, with the relative importance of these processes being dependent on the form of Hg, surface chemistry and most important being atmospheric temperature and prevailing environmental conditions. The evaporated mercury can also settle on the buildings, roads and on the foliar part of plants. It can also be deposited on the leaf surfaces and this mercury can also enter in to the plant body through stomata or through any other injury in the plant body. Most of the deposited mercury are generally washed during rain and the rain water washing of the foliar part of the plants can enter on to soil surface or move to distances as rain run off water joining any water body. Mercury deposition is mainly in the oxidized form (Hg^{2+}) on the land top soil or surface and its transformations are associated primarily with the oxidation–reduction potential of the environment and with the biological and chemical processes of methylation. For soils in which oxidizing conditions predominate, the Hg^{2+} and Hg_2^{2+} forms dominate and in soils with reducing conditions, Hg and sulphur compounds are mainly present. Methyl-Hg compounds are most commonly found in soils with transient conditions. Cropland is an important component of terrestrial ecosystems. It is estimated that 33% of natural-source atmospheric mercury comes from the emissions at cropland surfaces. The emission of mercury from cropland soil greatly affects the global mercury cycle. Movement and exchange of mercury in aquatic and terrestrial environments, movement of mercury from abiotic environment to biotic systems and mercury cycle in environmental segments decide the fate of mercury, availability of mercury, enrichment of mercury and cycling of mercury in the biosphere. The

present work was planned to study the fate and speciation of discharged mercury in the surrounds of a mercury contaminated site at Ganjam, near a chlor-alkali industry.

Materials & Methods

The industry under study:

The chlor-alkali industry M/s. Jayashree Chemicals Pvt. Ltd., is located at Ganjam, on the Bank of Rushikulya estuary about 1.5 km away from the Sea, Bay of Bengal, on the East and 30 km. North of Berhampur city on the South-Eastern side of India at 84°53'E longitude and 19°16'N latitude. The surrounding of the industry is under study, to assess the impact of mercury discharged from a chlor-alkali industry in to the environment at the contaminated site at Ganjam, Odisha.

(Satellite map of location of the industry & Photo of. the effluent pond M/S JCL, Ganjam)

(Photographs showing solid waste dumping site, effluent stocking site along with plants)

Effluent, solid waste samples were collected from different stations in plastic containers and brought to the laboratory for analysis. Plant samples were collected from solid waste dumping site and plants collected from banks of effluent pond in plastic containers in ice bags for analysis. Physico-chemical analyses of effluent and crop field soil samples of nearby crop fields were conducted periodically by following the procedure of APHA (1998), EC (1979), standardized field analysis kit and portable instruments. Dissolved oxygen was measured by modified Winkler's method. Effluent and waste soil samples were brought in glass containers and stored in cold room for use in laboratory experimental work. Measurement of mercury of the collected waste soil, effluent and plant samples were carried out by following the protocols of Wanntorp and Dyfverman (1955) and Yoshida *et al*., (1976). Effluent, solid wastes, plant samples like root, stem and leaf were digested in Bethge's apparatus in acid digestion mixture and mercury content was estimated in a Mercury Analyzer.

Bioaccumulation factor (BAF): The bioaccumulation factor (BAF) was calculated as suggested by Yoon *et al., (*2006) by using the formula as described below:

BAF= Mercury concentration in root / mercury concentration in the micro-environment. (Effluent / solid waste)

Translocation factor (TF1): The *in situ* phytoremediation capability of the plants present in and around the solid waste dumping site and effluent soaking pond was estimated by calculating the translocation factor (TF 1 and TF 2) as suggested by Gupta & Sinha (2008) by using the formula as described below:

TF1=Metal concentration in root / metal concentration in stem

TF2= Metal concentration in stem / metal concentration in shoot or leaf

The obtained data was statistically calculated to find out level of significance.

Results

The physico-chemical analysis of effluent sample and solid waste sample collected from the dumping site indicated the acute toxic nature of the toxicants (Table-1). The data is self explanatory. Significant amount of mercury was observed both in the effluent and solid waste discharged by the industry which is very high when compared to the standards fixed by the SPCB and CPCB.

Table- 1: Physico-chemical analysis of the effluent collected from a select site-SE-3 of the effluent storage tank and solid waste collected from the solid waste dumping site near the Chlor-alkali industry. Data are the mean of 5 estimations ± standard deviation.

Sl. No	Parameters	Effluent storage tank (SE3)-Y	Solid Waste from solid waste dump site (SSW-1)
1	Temperature (^oC)	29.2 ± 1.5	$28^0 \pm 2^0$ C
2	pH	9.2 ± 0.3	8.1 ± 0.3
3	Alkalinity (as $CaCO_3$)	246.2 ± 7.5 mg /l	=
4	Hardness (as $CaCO_3$)	185.9 ± 12.6 mg /L	=
5	Chlorinity	485.8 ± 18.2 mg /L	561.4±22.8mg of chloride/ Kg dry wt
6	Dissolved oxygen	1.2 ± 0.4 mg / L	=
7	BOD	7.1 ± 1.2 mg /L	=
8	COD	252.4 ± 18.6 mg /L	=
9	Suspended solids	96.5 ± 8.6 mg /L	=
10	Total nitrogen	2.6 ± 0.5 mg /L	8.6 ± 3.2 mg / Kg dry wt
11	Total phosphorus	1.28 ± 0.18 mg /L	41.4±11.4 mg / Kg dry wt
12	**Total mercury**	**4.85 ± 0.58µg / liter**	**345.6±28.4µg Kg $^{-1}$ dry wt**
13.	Texture	=	Clayish muddy
14	Colour	=	Grayish white
15	Specific gravity	=	3.1
16	Water holding capacity	=	21% by volume
17	Air content	=	11.5% by volume
18	Calcium	=	118.6 ± 12.3mg/Kg dry wt
19	Magnesium,	=	44.6 ±11.6mg / Kg dry wt
20	Sodium,	=	851.4±18.2mg/Kg dry wt
21	Potassium,	=	74.2.0±5.4mg/Kg dry wt

The fresh solid waste collected from the solid waste dumping pit in 2014-2015 from the solid waste dumps contained huge amount of mercury to the tune of 345.6±28.4µg of Hg / Kg dry weight of the solid waste. This amount of mercury was found to be much higher compared to any other solid waste collected from this locality earlier and reported earlier from any of the chlor-alkali industries of India. Significant amount of phosphate, chlorides, calcium, sodium, potassium and nitrogen content was noticed in the solid waste, which were much more than the stipulated guidelines.

Table-2: Showing mercury speciation in the contaminated environment and leaching / infiltration of mercury to different depths of the soil stratum. (SE-Site Effluent; SSW-Site solid waste, EC-Effluent canal)

Mercury speciation at different sites of study				
Sl. No.	Site No.	Site of study	Percentage of type of mercury concentration (%)	
			Inorganic	Organic
1	SE1	Effluent canal (EC)	<98.4	>1.0
2	SE2	EC on way to storage pond	<96.5	>2.5
3	SE3	Effluent storage pond	<89.4	>9.4
4	SW4	SW deposit site, Surface	<95.8	>5.1
5	SW5	SW deposit site,1ft depth	<91.2	>8.4
6	SW6	SW deposit site,3ft depth	<90.1	>9.6
7	SW7	SW deposit site,5ft depth	<85.2	>14.5
8	SW8	SW deposit site,7ft depth	<62.5	>34.2

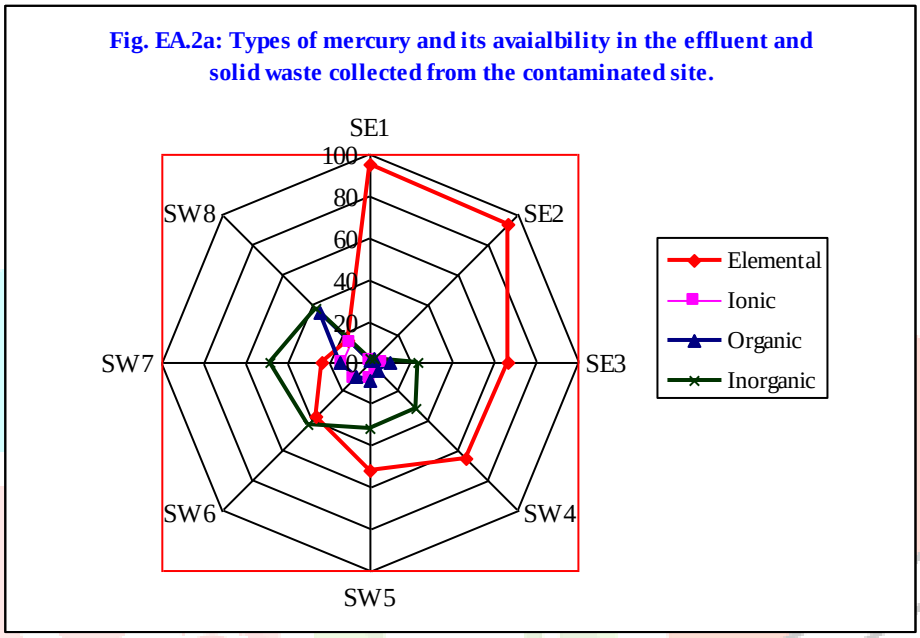
The mercury speciation study revealed that the effluent collected from the effluent canal (SE1) was having more amounts of inorganic mercury (less than 98.4%) and less of organic mercury (little more than 1%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-2). The mercury speciation study revealed that the effluent collected from the effluent canal (SE2) nearer to the effluent storage tank was having more amount of inorganic mercury (less than 96.5%) and less of organic mercury (little more than 2.5%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-2). The mercury speciation study revealed that the effluent collected from the effluent storage pond (SE3) was having more amounts of inorganic mercury (less than 89.4%) and less of organic mercury (little more than 9.4%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-2). The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW4) on the surface was having more amounts of inorganic mercury (less than 95.8%) and less of organic mercury (little more than 5.1%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury. The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW5) at one foot depth was having more amount of inorganic mercury (less than 91.2%) and less of organic mercury (little more than 8.4%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury. The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW6) at three feet depth was having more amounts of inorganic mercury (less than 90.1%) and less of organic mercury (little more than 9.6%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury. The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW7) at five feet depth was having more amounts of inorganic mercury (less than 85.2%) and less of organic mercury (little more than 14.5%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury. The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW8) at seven feet depth was having more amounts of inorganic mercury (less than 62.5%) and less of organic mercury (little more than 34.2%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-2). The estimated data indicated that the amounts of inorganic mercury decreased with the depth and organic mercury increased with depth indicated that more and more of inorganic mercury was converted to organic mercury with the increase in depth of the solid waste dumping site. The organic mercury content increased from the effluent canal point to effluent storage point. The increase in inorganic mercury content was probably due to higher rate of methylation of inorganic mercury to organic mercury by microorganisms and was strongly dependent on effluent retention time. The effluent of the storage pond was having 9.4% of organic mercury and 89.4% inorganic mercury. The conversion of elemental mercury to other forms of mercury was probably due to natural oxidation / reduction occurring in nature. The data clearly indicated that with the increase in retention time the organic mercury conversion increased showing a positive correlation and the amount of inorganic mercury decreased showing a negative correlation.

Table-3: Showing mercury speciation in the contaminated environment and leaching / infiltration of mercury to different depths of the soil stratum. (SE-Site Effluent; SW-Site solid waste, EC-Effluent canal).

Mercury speciation at different sites of study					
Site No.	Site of study	Percentage of type of mercury concentration			
		Elemental	Ionic	Organic	Inorganic
SE1	Effluent canal	>95.4	>1.0	>1.0	>2.0
SE2	Effluent canal on way to storage pond	>93.6	>0.8	>2.5	>2.9
SE3	Effluent storage pond	>66.2	>6.2	>9.4	>23.2
SW4	SW deposit site, Surface	>65.3	>3.4	>5.1	>30.6
SW5	SW deposit site,1ft depth	>52.1	>7.6	>8.4	>31.9
SW6	SW deposit site, 3ft depth	>36.4	>11.7	>9.6	>42.3
SW7	SW deposit site, 5ft depth	>23.3	>13.2	>14.5	>48.3
SW8	SW deposit site, 7ft depth	>14.8	>13.5	>34.2	>36.4

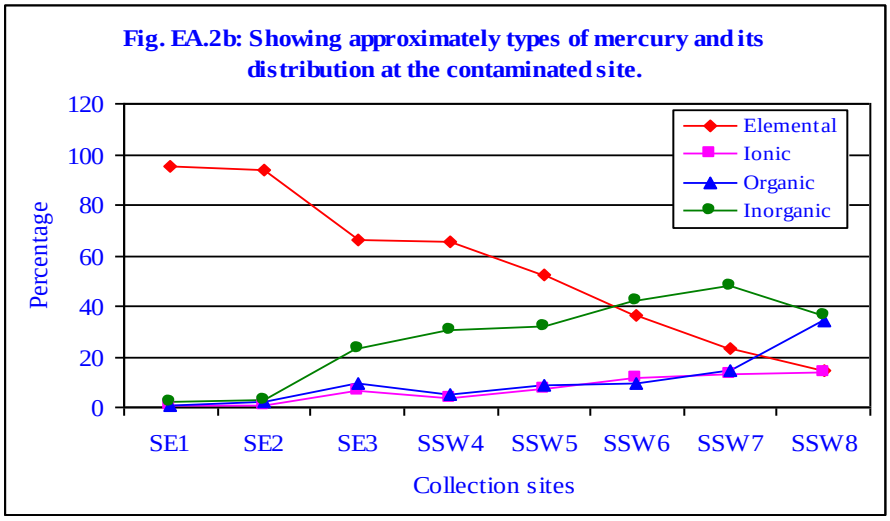
The mercury speciation study revealed that the effluent collected from the effluent canal (SE1) was having more amounts of inorganic mercury (less than 98.4%), out of which 95.4% was elemental, more than 1% ionic , more than 2% inorganic and little more than 1% of organic mercury (Table-3 and Fig. EA.2a). The mercury speciation study revealed that the effluent collected from the effluent canal (SE2) nearer to the effluent storage tank was having more amount of inorganic mercury (less than 96.5%) out of which 93.6% was elemental, more than 0.8% ionic, more than 2.9% inorganic and little more than 2.5% of organic mercury (Table-3 & Fig. EA.- 2a & b). The mercury speciation study revealed that the effluent collected from the effluent storage pond (SE3) was having more amounts of inorganic mercury (less than 89.4%) and less of organic mercury (little more than 9.4%) out of which 66.2% was elemental, more than 6.2% ionic, more than 23.2% inorganic and little more than 9.4% of organic mercury. The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-E.A2 & Fig.EA.-2a & b). The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW4) on the surface was having more amounts of inorganic mercury (less than 95.8%) and less of organic mercury (little more than 5.1%) out of which 65.3% was elemental, more than 3.4% ionic, more than 30.6% inorganic and little more than 5.1% of organic mercury. The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-3 & Fig.EA.- 2a & b).

Fig. EA.2a: Types of mercury and its avaialbility in the effluent and solid waste collected from the contaminated site.



The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW5) at one foot depth was having more amount of inorganic mercury (less than 91.2%) and less of organic mercury (little more than 8.4%) out of which 52.1% was elemental, more than 7.6% ionic, more than 31.9% inorganic and little more than 8.4% of organic mercury. The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-3 & Fig. EA.- 2a & b).

Fig. EA.2b: Showing approximately types of mercury and its distribution at the contaminated site.



The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW6) at three feet depth was having more amounts of inorganic mercury (less than 90.1%) and less of organic mercury (little more than 9.6%) out of which 36.4% was elemental, more than 11.7% ionic, more than 42.3% inorganic and little more than 9.6% of organic mercury. The inorganic mercury estimated was the

combined value of elemental mercury and inorganic mercury. The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW7) at five feet depth was having more amounts of inorganic mercury (less than 85.2%) and less of organic mercury (little more than 14.5%) out of which 23.3% was elemental, more than 13.2% ionic, more than 48.3% inorganic and little more than 14.5% of organic mercury. The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-3 & Fig. EA.- 2a & b). The mercury speciation study revealed that the effluent collected from the solid waste deposit site (SW8) at seven feet depth was having more amount of inorganic mercury (less than 62.5%) and less of organic mercury (little more than 34.2%) out of which 14.8% was elemental, more than 13.5% ionic, more than 36.1% inorganic and little more than 34.2% of organic mercury. The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury (Table-3 & Fig.EA.- 2a & b). The quantity of elemental mercury decreased with depth and ionic mercury also increased with depth of the solid waste dump. The organic mercury also increased with the depth of the solid waste dumping site indicating high rate of conversion mediated by natural oxidation and reduction and also biological agents. The analyzed data indicated that the amounts of inorganic mercury increased with the depth where as the elemental mercury content decreased owing to natural or biological conversions and organic mercury increased with depth indicated that more and more of inorganic mercury was converted to organic mercury with the increase in depth of the solid waste dumping site. In the effluent canal less of ionic mercury and organic mercury was observed. Most of the mercury was present in the elemental form and least of organic mercury, ionic mercury and inorganic mercury. The organic mercury content increased from the effluent canal point to effluent storage point. The increase in inorganic mercury content was probably due to higher rate of methylation of inorganic mercury to organic mercury by microorganisms and was strongly dependent on effluent retention time. The effluent of the storage pond was having 9.4% of organic mercury and 89.4% inorganic mercury. The conversion of elemental mercury to other forms of mercury was probably due to natural oxidation / reduction occurring in nature. The data clearly indicated that with the increase in retention time the organic mercury conversion increased showing a positive correlation and the amount of inorganic mercury decreased showing a negative correlation.

Table-4: Showing residual mercury concentration in plant parts (root, stem and leaf) collected from the contaminated sites and mercury concentration in soil collected from the surrounding roots of the plants.

Mercury concentration at different sites of study and residual mercury in different plants parts.					
Sl Site No.	Site of study	µg of mercury / liter (Effluent); µg of mercury / g dry weight soil / sediment / grazed plant / plant part collected from different sites of study at the contaminated site. Data mean of 5samples ± standard deviation.			
		Soil base	Root part	Stem part	Plant leaf
E1	Effluent canal (EC)	38.65±3.36	6.33±1.14	2.95±0.85	2.35±0.98
E2	EC on way to storage pond	36.98±2.82	5.61±2.85	4.89±2.14	3.37±1.85
E3	Effluent storage pond	23.88±2.46	5.85±3.33	4.85±3.66	3.95±0.66
SW4	SW deposit site, Surface	216.8±32.4	9.86±2.11	8.12±2.24	5.56±2.54
SW5	SW deposit site,1ft depth	138.5±12.8	8.98±3.84	9.18±0.88	5.52±1.32
SW6	SW deposit site,3ft depth	78.5±28.4	6.69±1.18	6.95±4.11	5.42±2.47
SW7	SW deposit site,5ft depth	35.2±11.4	4.65±2.27	2.64±2.28	7.25±2.14
SW8	SW deposit site,7ft depth	9.5±6.8	3.95±2.88	2.88±1.08	6.99±3.86

These dynamics change with each unit of time due to regular chemical transformations occurring in the environment due to simple chemical transformation in the environment either by oxidation or by reduction, chemical reactions and mostly by biological agents like resistant bacteria and phytoplankton. It was also reported that fish and other biological agents can also transform mercury from one type to the other type once absorbed by them. Mercury can enter into the body either in the inorganic form or organic form but not in the form of metallic mercury.

Table-4 Showed the residual mercury concentration in plant parts (root, stem and leaf) collected from the contaminated sites and mercury concentration in soil collected from the surrounding roots of the plants. The plants collected from both the sides of the effluent canal showed significant amount of residual mercury. The sediment collected from the effluent canal periphery contained significant amount of total mercury. The amount of total mercury present was 38.65±3.36µg of mercury / g dry weight soil / sediment. The plant root collected from the same zone contained 6.33±1.14µg of mercury / g dry weight plant part; the

plant stem portion collected from the same plant contained 2.95±0.85µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 2.35±0.98µg of mercury / g dry weight plant part. The plants collected from both the sides of the effluent canal on the way to storage pond showed significant amount of residual mercury. The sediment collected from the effluent canal periphery contained significant amount of total mercury. The amount of total mercury present was 36.98±2.82µg of mercury / g dry weight soil / sediment. The plant root collected from the same zone contained 5.61±2.85µg of mercury / g dry weight plant part; the plant stem portion collected from the same plant contained 4.89±2.14µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 3.37±1.85µg of mercury / g dry weight plant part. The plants collected from the sides of the effluent storage pond showed significant amount of residual mercury. The sediment collected from the effluent canal periphery contained significant amount of total mercury. The amount of total mercury present was 23.88±2.46µg of mercury / g dry weight soil / sediment. The plant root collected from the same zone contained 5.85±3.33µg of mercury / g dry weight plant part; the plant stem portion collected from the same plant contained 4.85±3.66µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 3.95±0.66µg of mercury / g dry weight plant leaf. The plants collected from the solid waste dump site showed significant amount of residual mercury. The solid waste collected from the surface of the solid waste dumping site contained significant amount of total mercury. The amount of total mercury present was 316.8±32.4µg of mercury / g dry weight of the solid waste collected from the surface of the solid waste dump. The plant root collected from the same zone contained 9.86±2.11µg of mercury / g dry weight of the plant part; the plant stem portion collected from the same plant contained 8.12±2.24µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 5.56±2.54µg of mercury / g dry weight plant leaf (Table-4). The plants collected from the solid waste dump site showed significant amount of residual mercury. The solid waste collected from one foot depth of the solid waste dumping site contained significant amount of total mercury. The amount of total mercury present was 138.5±12.8µg of mercury / g dry weight of the solid waste collected from one foot depth of the solid waste dump. The plant root collected from the same zone contained 8.98±3.84µg of mercury / g dry weight of the plant part; the plant stem portion collected from the same plant contained 9.18±0.88µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 5.52±1.32µg of mercury / g dry weight plant leaf. The plants collected from the solid waste dump site showed significant amount of residual mercury. The solid waste collected from three feet depth of the solid waste dumping site contained significant amount of total mercury. The amount of total mercury present was 78.5±28.4µg of mercury / g dry weight of the solid waste collected from three feet depth of the solid waste dump. The plant root collected from the same zone contained 6.69±1.18µg of mercury / g dry weight of the plant part; the plant stem portion collected from the same plant contained 6.95±4.11µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 5.42±2.47µg of mercury / g dry weight plant leaf (Table-4). The plants collected from the solid waste dump site showed significant amount of residual mercury. The solid waste collected from five feet depth of the solid waste dumping site contained significant amount of total mercury. The amount of total mercury present was 35.2±11.4µg of mercury / g dry weight of the solid waste collected from five feet depth of the solid waste dump. The plant root collected from the same zone contained 4.65±2.27µg of mercury / g dry weight of the plant part; the plant stem portion collected from the same plant contained 2.64±2.28µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 7.25±2.14µg of mercury / g dry weight plant leaf. The solid waste collected from seven feet depth of the solid waste dumping site contained significant amount of total mercury. The amount of total mercury present was 9.5±6.8µg of mercury / g dry weight of the solid waste collected from seven feet depth of the solid waste dump. The plant root collected from the same zone contained 3.95±2.88µg of mercury / g dry weight of the plant part; the plant stem portion collected from the same plant contained 2.88±1.08µg of mercury / g dry weight plant part and the plant leaf collected from the same plant contained 6.99±3.86µg of mercury / g dry weight plant leaf (Table-4). From the data of Table-4, it was very much clear that the plants present in and around the effluent canal and solid waste dumping site absorbed mercury and accumulated in different plant parts by translocation of mercury after absorption by the roots from the surrounding effluent or solid waste present. The amount of mercury concentration decreased with the increase in depth of the solid waste dumping site. The amount of mercury absorbed and accumulated by root was the highest when compared to the stem and leaf part. The mercury absorption decreased with the increase in distance and decrease in mercury concentration in the sediments. The data also indicated that the residual mercury absorption and retention depends on the amount of mercury present in a particular site. The amount of residual mercury present in the stem of the exposed plants increased with the increase in absorption by the roots and the amount of mercury present in the environment. The amount of residual mercury present in the stem was the amount of mercury absorbed by the root and translocated to the stem part from where the mercury gets

translocated to the leaf part. It was observed that the residual mercury concentration increased in the leaf part of the contamination exposed plant collected from the sides of the effluent canal and effluent storage pond. The residual mercury availability on the solid waste dumping site surface area was high. The mercury concentration decreased with the increase in depth of the solid waste dumping site. Most of the mercury available in the deeper layers was due to leaching of mercury or percolation of mercury from the surface to the bottom enriching the bottom. This was the only cause of contaminating the ground water. The residual mercury concentration decreased in the root with the increase in depth of the collection of root site showing a negative correlation. The amount of residual mercury concentration of stem part decreased with the increase in depth of the solid waste dumping site. The roots collected from the deeper layers showed accumulation of mercury which gets transported to all other parts of the plant body. The residual mercury availability in leaves increased with the increase in depth of the waste. Availability of higher values in the leaves was due to translocation of mercury from roots to the leaf via the stems. Decrease in residual mercury concentration was mostly due to translocation of mercury to the foliar parts after absorption by the roots. Table-5 showed the bioaccumulation factor of mercury in plants. The bioaccumulation factor analysis is an important tool to explain the extent of mercury toxicity of the area. The bioaccumulation factor can be calculated by taking the mercury concentration of the soil and mercury absorbed by the root. The translocation factor was calculated from the residual mercury absorbed by the roots and mercury concentration present in the stems. The data of table-5 was considered for calculation of translocation factor at two stages. The second phase of translocation occurs generally from stem part to the leaf part and the third type of translocation consequently occurs from the leaf part to the reproductive part like flowers & fruits and finally to the seeds. In the present study flowers, fruits and seeds were not tested and hence the translocation factor could not be collected to reach to a logistic conclusion. The bioaccumulation factor of plants collected from site SE1, SE2, SE3, SW4, SW5, SW6, SW7 and SW8 were 0.163, 0.151, 0.244, 0.031, 0.064, 0.085, 0.132 and 0.415 respectively. Maximum bioaccumulation factor was observed at site SE3 in the effluent location. Interestingly highest bioaccumulation factor was observed at seven feet depth of the solid waste dump where the BAF was 0.415. The bioaccumulation factor increased with the increase in depth of the solid waste and is directly related to mercury concentration at that particular site.

Table-5: Showing changes in bioaccumulation factor (BAF) and Translocation factor (TF) of the plants at solid waste exposed site. The calculation is based on the data of table-A-2. Data calculated from the mean of the samples.

Sl Site No	Site of study	Factor analysis		
		BAF (Root) (Root / Soil)	TF1 (Stem) Root / Stem	TF2 (Leaf) Stem / Leaf
SE1	Effluent canal (EC)	0.163	2.145	1.255
SE2	EC on way to storage pond	0.151	1.147	1.451
SE3	Effluent storage pond	0.244	1.206	1.227
SW4	SW deposit site, Surface	0.031	1.214	1.460
SW5	SW deposit site,1ft depth	0.064	0.978	1.663
SW6	SW deposit site,3ft depth	0.085	0.962	1.282
SW7	SW deposit site,5ft depth	0.132	1.761	0.364
SW8	SW deposit site,7ft depth	0.415	1.371	0.412

The bioaccumulation factor depends on the physiological status of the plant available at the contaminated site of study and rate of absorption of the plant through barriers. The translocation factor was calculated from the amount of mercury absorbed by the root and the amount of mercury translocated from root to the stem part. The translocation factor1 (TF1) was the transfer value of mercury from root to stem. No significant trend was noticed pertaining to the availability of mercury in root and the rate of translocation from root to stem. At SE1, the TF1 was 2.145; at SE2 the TF1 was 1.147 and at SE3 the TF1 value was 1.206 with out following any trend in the same species. In the site where solid waste was deposited, plants absorbed significant amount of mercury but could not transfer all the absorbed mercury into the whole plant body. This might be due to some barrier acting for non transfer of the chemical to the foliar part of the plant. The TF1 factor at site SW4 was 1.214, SW5 - 0.978, SW6 - 0.962, SW7–1.761 and SW8 was 1.371. The exposed plants showed lower value of translocation of mercury from root to stem except in case of SW8 the TF1 value was more and significant. The translocation factor-2 (TF2) was the transfer value of mercury from stem to leaf. No significant trend was noticed pertaining to the availability of mercury in stem and the rate of translocation from stem to leaf. At SE1, the TF2 was 1.255; at SE2 the TF2 was 1.451 and at SE3 the TF2 value was 1.227 with out following any trend in the same species. The TF2 factor at site SW4 was 1.460, SW5 – 1.663, SW6 – 1.282, SW7 – 0.364 and SW8 was 0.412. The exposed plants showed lower

value of translocation of mercury from stem to leaf except in case of SW7 the TF2 value was less compared to TF2 value SW5 and significant (Table-5). The BAF value and TF1 and TF2 value significantly indicated the movement of mercury from soil to root, then to stem and from stem to leaf. These two factors were responsible for the movement and retention of mercury in different plant parts and the mercury burden of the exposed plant.

Discussion

The effluent is toxic and showed significant affects on all types of plants tested. The mercury speciation study revealed that the effluent collected from the effluent canal (SE1) was having more amounts of inorganic mercury (less than 98.4%) and less of organic mercury (little more than 1%). The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury. The mercury speciation study revealed that the effluent collected from the effluent canal (SE2) nearer to the effluent storage tank was having more amount of inorganic mercury (less than 96.5%) and less of organic mercury (little more than 2.5%). Speciation study revealed that with the increase in depth the elemental mercury decreased and inorganic mercury increased followed by more of organic mercury at the bottom. The inorganic mercury estimated was the combined value of elemental mercury and inorganic mercury. The estimated data indicated that the amounts of inorganic mercury decreased with the depth and organic mercury increased with depth indicated that more and more of inorganic mercury was converted to organic mercury with the increase in depth of the solid waste dumping site. The organic mercury content increased from the effluent canal point to effluent storage point. The increase in inorganic mercury content was probably due to higher rate of methylation of inorganic mercury to organic mercury by microorganisms and was strongly dependent on effluent retention time. The effluent of the storage pond was having 9.4% of organic mercury and 89.4% inorganic mercury. The conversion of elemental mercury to other forms of mercury was probably due to natural oxidation / reduction occurring in nature. The data clearly indicated that with the increase in retention time the organic mercury conversion increased showing a positive correlation and the amount of inorganic mercury decreased showing a negative correlation. Mercury can enter into the body either in the inorganic form or organic form but not in the form of metallic mercury. The quantity of elemental mercury decreased with depth and ionic mercury also increased with depth of the solid waste dump. The organic mercury also increased with the depth of the solid waste dumping site indicating high rate of conversion mediated by natural oxidation and reduction and also biological agents. The analyzed data indicated that the amounts of inorganic mercury increased with the depth where as the elemental mercury content decreased owing to natural or biological conversions and organic mercury increased with depth indicated that more and more of inorganic mercury was converted to organic mercury with the increase in depth of the solid waste dumping site. In the effluent canal less of ionic mercury and organic mercury was observed. Most of the mercury was present in the elemental form and least of organic mercury, ionic mercury and inorganic mercury. The organic mercury content increased from the effluent canal point to effluent storage point. The increase in inorganic mercury content was probably due to higher rate of methylation of inorganic mercury to organic mercury by microorganisms and was strongly dependent on effluent retention time. From the data, it was very much clear that the plants present in and around the effluent canal and solid waste dumping site absorbed mercury and accumulated in different plant parts by translocation of mercury after absorption by the roots from the surrounding effluent or solid waste present. The amount residual accumulation was highly significant and warrants attention. The amount of mercury present in the sediment collected from the effluent canal at different sites indicated that higher amount of mercury was deposited immediately after the effluent was discharged into the canal and the residual mercury concentration of the sediment decreased with the distance. The amount of mercury present on the surface of the solid waste dumping site was the maximum compared to deeper layers of the waste dumping site. The amount of mercury concentration decreased with the increase in depth of the solid waste dumping site. The amount of mercury absorbed and accumulated by root was the highest when compared to the stem and leaf part. The mercury absorption decreased with the increase in distance and decrease in mercury concentration in the sediments. The data also indicated that the residual mercury absorption and retention depends on the amount of mercury present in a particular site. The amount of residual mercury present in the stem of the exposed plants increased with the increase in absorption by the roots and the amount of mercury present in the environment. The amount of residual mercury present in the stem was the amount of mercury absorbed by the root and translocated to the stem part from where the mercury gets translocated to the leaf part. It was observed that the residual mercury concentration increased in the leaf part of the contamination exposed plant collected from the sides of the effluent canal and effluent storage pond. The residual mercury availability on the solid waste dumping site surface area was high. The mercury concentration decreased with the increase in depth of the solid waste dumping site. Most of the mercury

available in the deeper layers was due to leaching of mercury or percolation of mercury from the surface to the bottom enriching the bottom. This was the only cause of contaminating the ground water. The residual mercury concentration decreased in the root with the increase in depth of the collection of root site showing a negative correlation. The amount of residual mercury concentration of stem part decreased with the increase in depth of the solid waste dumping site. The roots collected from the deeper layers showed accumulation of mercury which gets transported to all other parts of the plant body. The residual mercury availability in leaves increased with the increase in depth of the waste. Availability of higher values in the leaves was due to translocation of mercury from roots to the leaf via the stems. Decrease in residual mercury concentration was mostly due to translocation of mercury to the foliar parts after absorption by the roots. It was also reported that fish and other biological agents can also transform mercury from one type to the other type once absorbed by them. Mercury can enter into the body either in the inorganic form or organic form but not in the form of metallic mercury. The data clearly indicated that with the increase in retention time the organic mercury conversion increased showing a positive correlation and the amount of inorganic mercury decreased showing a negative correlation. The conversion of elemental mercury to inorganic mercury and then to organic mercury was due to the microorganisms particularly bacteria, temperature and retention time and in addition natural oxidation and reduction of chemicals and interaction of other environmental chemicals. These dynamics change with each unit of time due to regular chemical transformations occurring in the environment due to simple chemical transformation in the environment either by oxidation or by reduction, chemical reactions and mostly by biological agents like resistant bacteria and phytoplankton. It was also reported that fish and other biological agents can also transform mercury from one type to the other type once absorbed by them. Mercury can enter into the body either in the inorganic form or organic form but not in the form of metallic mercury. The plants collected from both the sides of the effluent canal showed significant amount of residual mercury. The sediment collected from the effluent canal periphery contained significant amount of total mercury. The plants collected from the sides of the effluent storage pond showed significant amount of residual mercury. The amount residual accumulation was highly significant and warrants attention. The amount of mercury present in the sediment collected from the effluent canal at different sites indicated that higher amount of mercury was deposited immediately after the effluent was discharged into the canal and the residual mercury concentration of the sediment decreased with the distance. The amount of mercury present on the surface of the solid waste dumping site was the maximum compared to deeper layers of the waste dumping site. The amount of mercury concentration decreased with the increase in depth of the solid waste dumping site. The amount of mercury absorbed and accumulated by root was the highest when compared to the stem and leaf part. The mercury absorption decreased with the increase in distance and decrease in mercury concentration in the sediments. The data also indicated that the residual mercury absorption and retention depends on the amount of mercury present in a particular site. The amount of residual mercury present in the stem of the exposed plants increased with the increase in absorption by the roots and the amount of mercury present in the environment. The amount of residual mercury present in the stem was the amount of mercury absorbed by the root and translocated to the stem part from where the mercury gets translocated to the leaf part. It was observed that the residual mercury concentration increased in the leaf part of the contamination exposed plant collected from the sides of the effluent canal and effluent storage pond. The residual mercury availability on the solid waste dumping site surface area was high. The mercury concentration decreased with the increase in depth of the solid waste dumping site. Most of the mercury available in the deeper layers was due to leaching of mercury or percolation of mercury from the surface to the bottom enriching the bottom. This was the only cause of contaminating the ground water. The residual mercury concentration decreased in the root with the increase in depth of the collection of root site showing a negative correlation. The amount of residual mercury concentration of stem part decreased with the increase in depth of the solid waste dumping site. The roots collected from the deeper layers showed accumulation of mercury which gets transported to all other parts of the plant body. The residual mercury availability in leaves increased with the increase in depth of the waste. Availability of higher values in the leaves was due to translocation of mercury from roots to the leaf via the stems. Decrease in residual mercury concentration was mostly due to translocation of mercury to the foliar parts after absorption by the roots. The bioaccumulation factor analysis is an important tool to explain the extent of mercury toxicity of the area. The bioaccumulation factor can be calculated by taking the mercury concentration of the soil and mercury absorbed by the root. The translocation factor was calculated from the residual mercury absorbed by the roots and mercury concentration present in the stems. The second phase of translocation occurs generally from stem part to the leaf part and the third type of translocation consequently occurs from the leaf part to the reproductive part like flowers & fruits and finally to the seeds. In the present study flowers, fruits and seeds were not tested and hence the translocation factor could not be collected to reach to a logistic conclusion. The BAF value

and TF1 and TF2 value significantly indicated the movement of mercury from soil to root, then to stem and from stem to leaf. These two factors were responsible for the movement and retention of mercury in different plant parts and the mercury burden of the exposed plant. Plants collected from the contaminated site having less impact on the pigment content by the wastes and effluent can be considered for plantation of the said plants in the contaminated site, as it seems they are resistant and can survive although those plants have accumulated significant amount of mercury. Both the effluent and the solid waste collected from the contaminated site contained significant amount of mercury.

Mercury can be accumulated and biomagnified at all levels of aquatic food chains (Mason *et al*., 1995), and high levels of mercury have been detected in fish, especially in the organic form. Wu and Wang (2012) studied the accumulation, sub-cellular distribution and toxicity of inorganic mercury and methyl mercury in marine phytoplankton. Mercury exerts its toxicity by binding with sulphydryl groups and producing oxidative stress. Mercury might be getting attached -SH groups, glutathiones and form a complex, thereby inhibiting chlorophyll biosynthesis in exposed plants. A significant volume of information is available on the pollution of the surrounding biota due to the discharges of gaseous exhausts, solid wastes and effluents discharged from chlor-alkali industries (Suckcharoen & Nourteva, 1982; and Shaw *et al*., 1986). The waste discharge from a caustic soda factory significantly impacted the surrounding environment as reported by Wiener *et al*., (2012) in the past. Glass *et al*., (1986) reported the dispersion of mercury and consequent contamination of Lake Superior region and Sorensen *et al*., (1990) reported in eight northern Minnesota lakes. It is time to save the existing flora & fauna at the contaminated sites, river and estuary. Due to change in technology, now no more mercury is available but the dumped mercury as solid waste needs attention. The industry people instead of recycling mercury removing all the top soil up to the depth of 10feet and shifting to some other place and use these solid wastes for construction of roads. Now the problem is the new dumping sites, where mercury gets exposed and chances of evaporation of mercury and leaching of mercury to neighboring areas can not be ruled out. Non availability of mercury in the area might be due to change in technology or washing of all discharged mercury into Bay of Bengal or a major portion of discharged mercury was recovered by following recycling technology. A total review of the whole work done in our laboratory suggested that these effluents and solid wastes of the industry can be treated by biological methods to obtain a heavy metal free waste water which can be used in the agriculture.

Conclusion:

The conversion of elemental mercury to inorganic mercury and then to organic mercury was due to the microorganisms particularly bacteria, temperature and retention time and in addition natural oxidation and reduction of chemicals and interaction of other environmental chemicals. These dynamics change with each unit of time due to regular chemical transformations occurring in the environment due to chemical transformation in the environment either by oxidation or by reduction, chemical reactions and methylation mostly by biological agents like bacteria and phytoplankton. It was also reported that fish and other biological agents can also transform mercury from one type to the other type once absorbed by them. Mercury can enter into the body either in the inorganic form or ionic form or organic form but not in the form of metallic mercury.

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Declarations

AUTHOR CONTRIBUTION STATEMENT

Prof. A.K. Panigrahi: Conceptualization, planning and execution of the project, field visit, original draft preparation, supervision, reviewing and editing. Research work conducted by scholar – J. Prusti- samples of solid waste, effluent & plant collection and analysis. Prusti contributed reagents, glassware, field related work, manuscript preparation, calculation and finalization of data.

CONFLICT OF INTEREST STATEMENT

The authors declare that they have no conflicts of interest.

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