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STUDY OF HEAVY METAL POLLUTION IN MANGROVE SEDIMENTS REFERENCE TO MARINE ENVIRONMENT ALONG THE COASTAL AREAS OF PAKISTAN

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Abstract

The aim of this paper is to measure the concentration of heavy metals (Cd, Co, Pb, Cr, Zn, Cu & Fe) in Mangrove sediments. The concentrations of heavy metals (Cd, Co, Pb, Cr, Zn, Cu & Fe) were measured in different samples of in different Mangroves sediments along the coastal areas of Pakistan and was found that concentration of heavy metals in the Mangrove sediments near to Lyari and Malir river discharge points are at much higher level than the Mangrove sediments of Port Qasim area which are not according to WHO standard and are very are very serious health hazardous. In addition to point sources, possible reasons of non point sources were also discussed.

Introduction

Pakistan is largely arid and semi-arid, receiving less than 250mm annual rainfall, with the driest regions receiving less than 125 mm of rain annually. It has a diverse landscape, with high mountain systems, fragile watershed areas, alluvial plains, coastal mangroves, and dune deserts. The flora and fauna are mainly Palaerctic and Indomalayan. Forests cover approximately 4.58 million ha (5.7 percent) in Pakistan. (Anon., 1996) Of these, 0.132 million ha (less than 3 percent) are coastal mangrove forests. Pakistan is divided into 18 habitat types (Qureshi, 1985), among them mangrove forests, which occur mainly in the Indus Delta and in a few patches westward along the Balochistan Coast (Saifullah, 1997). Karachi is situated near the coast and it is a unique city in many ways on the side of industrial development, education and multi cultures but through the rapid industrialization the quality of environment of Karachi city is getting various disturbances (Anon., 1996).

Existing estimates show that mangroves cover approximately 129,000 ha in the Indus Delta and about 3,000 ha on the Balochistan Coast in the Miani Hor, Kalmat Khor, and Gawatar Bay areas. The Indus Delta therefore supports 97% of the total mangrove forest (37% of the Delta area) while the 3 pockets on the Balochistan Coast (Rasool *et al*., 2005) support the remaining 3% (varying from 8% of the total area in Gawatar Bay to 21% in Kalmat Khor and 25% in Miani Hor).

At present by huge number of various industries are working in Karachi, which discharge their effluents of about 72 million gallons daily in addition to air pollution and are polluting the city and the continental shelf water. Automobiles, ever-increasing industrialization and urbanization are the most common source of pollution; there is an accelerating accumulation of toxic metals and gases in atmosphere, irrigation water and agricultural soils while the industrial estates of Karachi are discharging large quantities of effluents of organic matter, heavy metals, oil, greases, liquid and solid wastes into Malir and Lyari rivers, which are causing serious environmental degradation (Saifullah *et al*., 2004) to various ecosystems of the city (Fig. 1).

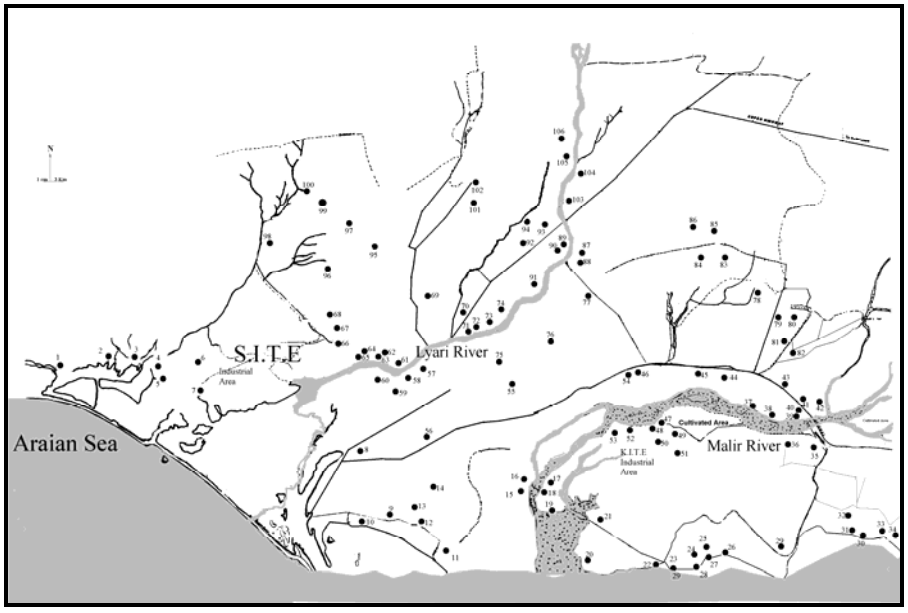

Fig. 1. Demographic distribution of the Karachi city (modified after KDA 1985).

At Bin Qasim seaport, Thermal Power Plants and Pakistan Steal Mill are situated. At the side of Thermal Power Plant the sea water is being used as coolant which goes back to the beach water. The coast East of Clifton beach is sandy and extends up to Gizri Creek where Malir River drains to the sea, it also carries waste deposit. These effluents are expected to be the source of both organic and inorganic contamination in addition to the human activities on this popular beach.

Manora beach and the sites of Manora are situated on the Western side of Liayari. It is separated from Liayari river by the protruded landmass of Manora that hinders the mixing of polluted beach sediments of Liayari and Manora beach to great extend. On the Western side of Manora location, there is an apparent difference of texture and colours of sediments water as compared to Eastern Manora due to the contamination of Liayari industrial effluents. The Eastern side of this location is composed of hard steep sided sandstone and limestone .The beach on the Western side is crowded with most of the picnic points but there are no proper arrangements for the sewage discharge on this location. The effluents of industrial waste, sewage etc are poured by Liyari River on the Eastern side of Manora i.e., in between Clifton and Eastern side of Manora locations.

Sands Pit is further continuation of the beach and this side of location has relatively less polluted by sand. Apparently no other source of pollution is available except man-made activities in the form of picnic spot. In the West of Sands pit the beaches are mixed i.e. rocky and sandy of variable magnitude. This location is apparently free for many possibilities of industrial pollution except human activities on the beach and on continuation of similar conditions up to the beach of Hawks Bay

Hawks Bay is the well-known beach of Paradise Point. Karachi Nuclear Power Plant is in operation here and is accepted to be source to effect the chemical composition of beach water and sediments. It is estimated that about 300MGD of wastewater is generated in Karachi and out of which 40 MGD is treated, the rest of water waste and the treated effluents are discharge into the sea and creating harm to marine environment.

So, it has become important to estimate the heavy metal concentrations in organism which act as bioaccumulators in sediments and in overlying water in fresh water, estuarine & marine environment (Fernandaz *et al*., 1987) because many of these organisms are indicator of metal contamination. Many marine organisms are known to accumulate and concentrate metals in relatively higher level than the surrounding environment. The seaweeds are reported to concentrate heavy metals several times more than their concentration in seawater (Preston *et al*., 1972 and Yamamoto, 1972). Red and brown algae are more efficient in metal accumulation than the green algae (Fernandaz, 1995; Fernandaz & Thomas, 1995).

Mangrove ecosystem is one of the most productive coastal ecosystems of the world, which has played a crucial role in development of local communities since time immemorial. There are many mangrove species, which are useful to the rural people in meeting their day-to-day requirements of fuel wood, fodder, timber, poles and tannin (Table 1). Main activities, which resulted in destruction of mangroves were unscientific wood extraction and conversion of mangrove areas for agriculture, horticulture, aquaculture and human settlement. Mangrove ecosystem offers numerous wood and non-wood forest products (Khyber Pukhtunkhawa) for the local communities. Mangroves also provide various services to the coastal community, which are crucial for their prosperity and provide a healthy environment around them (Fig. 2).

Many Mangrove species are reported to contain very high concentration of certain heavy metals such as Fe and Mn (Untawale *et al*., 1980). The toxic effects of these metals are reduced due to the action of chelating substances present in these plants. On the other hand Mangrove sediments are considered as both a sink and source of heavy metals (Harbison, 1986) Therefore, high metal levels may be expected in Mangrove areas, and the study of metals contamination in these systems is of great relevance in pollution assessment in the tropics (Lacreda, 1987).

Table 1. Useful mangroves for rural communities.

Fuelwood	Fodder	Timber and poles	Tannin
Rhizophora mucronata	*Avicennia marina*	*Avicennia officinalis*	*Rhizophora mucronata*
Rhizophora apiculata	*Bruguiera parviflora*	*Avicennia marina*	*Rhizophora apiculata*
Avicennia officinalis	*Rhizophora apiculata*	*Sonneratia alba*	*Bruguiera gymnorrhiza*
Avicennia marina	*Acrostichum aureum*	*Sonneratia caseolaris*	*B. parviflora*
Avicennia alba		*Ceriops tagal*	*B. cylindrica*
Sonneratia alba			*Ceriops tagal*
Sonneratia caseolaris			*Kandelia candel*
Bruguiera gymnorrhiza			*Bruguiera gymnorrhiza*
Ceriops tagal			*S. alba*,
			Xylocarpus granatum

Coastal mangrove ecosystems in Pakistan have been seriously degraded over the last 50 years as a result of freshwater diversion for agriculture, industrial and urban water pollution, and over-fishing. These proximate causes are largely driven by national policies that have favored agriculture and industry over the coastal regions and that have given high priority to exports. Few studies have been carried out on regarding heavy metal pollution of Mangroves environment in Pakistan which has not been reported.

Fig. 2. Potential area for fisheries near the Coast

Materials and Methods

Sampling: The samples were collected according to the physical differences in sediments color, texture, mixing water condition and local geological conditions at different sides. The samples of mangrove sediments were taken from Sands pit, Hawks Bay, Bhullayji, Shamspir and Korangi Creek and were treated for analysis. Beach sediments were collected from the low and high tide zone of the each slope by digging one feet pit with the aluminum hand shovel to avoid surface contamination through various sources.

Materials: During performing of the experiments references to analysis, the following materials were used; HNO_3, 500 ml, Perchloric acid, Glasswares and Graphite Furnace Atomic Absorption Spectrophotometer (Perkin-Elmer, model AAnalyst 700) etc.

Preparation of samples: The colors and texture of the sediment sample were noted and then collected in polythene bags. The Mangrove sediment samples were sieved for less then 0.0625mm fraction and were selected for quantitative estimation of the elements under study. The collected sample was dried in the laboratory and accurately weighed (about 1-2 g. The weighed sample then transferred to china dish and digested by the addition of concentrated Nitric Acid, and Perchloric Acid as per required. The sample was heated to evaporate the access amount of acid, near to dryness and cooled at room temperature.

Samples analysis: After dilution upto mark by deionized water the prepared samples were subjected to analyses from each metal under study using Perkin Elmer Atomic Absorption Spectrophotometer (700) under standard conditions. The standard procedure of quantitative estimation of the element describe was adopted (Luckas, 1987; Anon., 1980 and Anon., 1983).

Quality control: The samples were collected and were dried in the laboratory for further chemical investigations. The amount of sample at range of 1-2 grams of oven dried beach sediment of < 0.0625 mm size fraction was digested in 10ml of 50% HNO_3 in 250ml beaker by gradual heating to a maximum temperature of 95°C as per accordingly. 5ml concentrated HNO_3 of analytical grade and 10 ml of Conc. $HClO_3$ was further added in the cooled solution and heated again for 30 minutes at 95°C. The solution was evaporated to about 5ml not without letting any dryness of the solution at the margin of the beaker. The solution was then diluted to 100 ml with deionized water and was run on Graphite Furnace Atomic Absorption Spectrophotometer (Perkin-Elmer, model AAnalyst 700) for the quantitative estimation of the cadmium concentration.

Data analysis: The data was analyzed through statistical standard method (Excel) by standard curves & calibration and was presented in results and discussion as per required.

Results and Discussion

In the graphical representation of heavy metal concentration in mangrove sediments samples, the vertical scale showing concentration of element in ppm and the horizontal scale represent the sites of location as shown in Figs. 3-6. The dilution factor of the element varies from 10 to100 times in the sample of the location with few exceptions. However, the concentration of Cd and Zn of location HB_1 and HB_4 were found below than the detection limit.

The graph plotted for concentration of heavy metal under study in their location have further been subdivided into sites for example location Hawks Bay which is represented by HB has further been divided into five sampling sites (HB_1, HB_2, HB_3, HB_4, HB_5 etc.) (Table 2). The division of the sites are not equal in number in all location because of local geological and geographical condition which were considered significant during collection of samples.

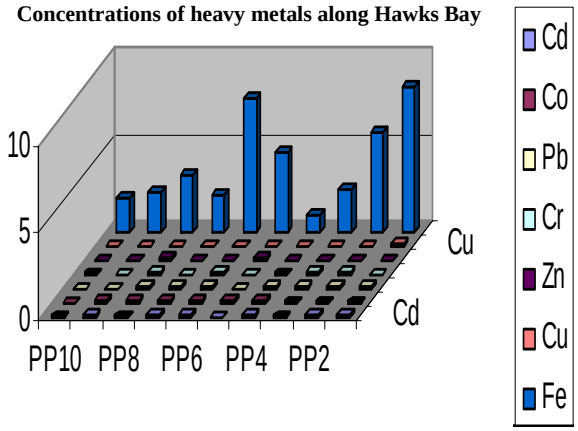

Fig. 3. Concentrations of heavy metals along Hawks Bay.

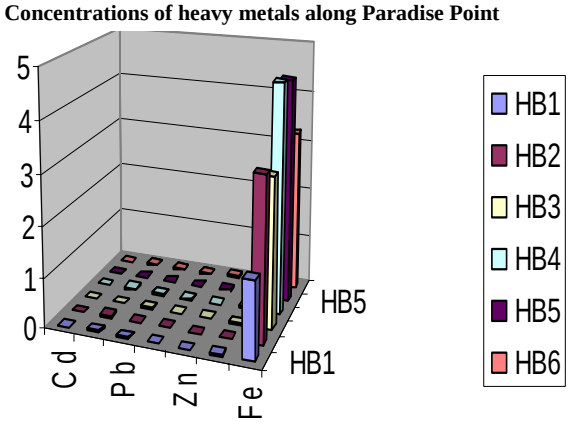

Fig. 5. Concentrations of heavy Metals along Paradise Point .

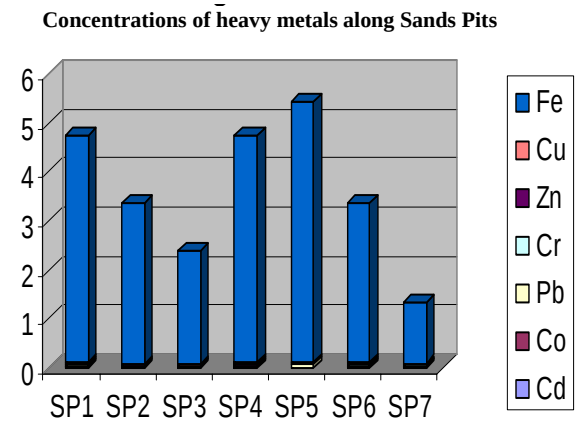

Fig. 4. Concentrations of heavy Metals along Sands Pits.

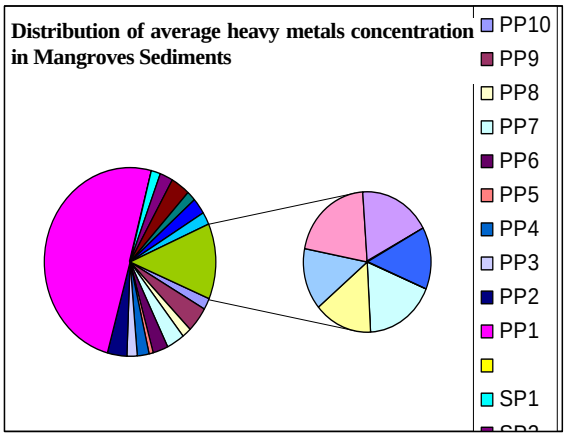

Fig. 6. Distribution of average heavy Metals Concentration in Mangroves Sediments

Table 2. (Sites and abbreviation).

S. No.	Sites	Abbreviations
1.	PP1	Paradise point one
2.	PP2	Paradise point two
3.	PP3	Paradise point three
3.	PP4	Paradise point four
4.	PP5	Paradise point five
5.	PP6	Paradise point six
6.	PP7	Paradise point seven
7.	PP8	Paradise point eight
8.	PP9	Paradise point nine
9.	PP10	Paradise point ten
10.	HB1	Hawks bay one
11.	HB2	Hawks bay two
12.	HB3	Hawks bay three
13.	HB4	Hawks bay four
14.	HB5	Hawks bay five
15.	HB6	Hawks bay six
16.	SP1	Sands pit one
17.	SP2	Sands pit two
18.	SP3	Sands pit three
19.	SP4	Sands pit four
20.	SP5	Sands pit five
21.	SP6	Sands pit six
22.	SP7	Sands pit seven

The concentration of Cd in Mangrove sediments samples of the location under study show positive degree of correspondence in general, although the degree of concentration increased by the factor of 10. In the case of samples on location of Paradise Point, there is a general increasing in concentration of Cd from site PP_1 to PP_{10}. It is remarkable to note that the concentration of Cd at site PP_{10} is highest (0.11ppm) for which the possible reason can be attributed to the presence of Karachi Nuclear Power Plant which discharge its pollutant in to the sites PP_{10} area. The second highest concentration of Cd was found at site PP_2 due to the discharges of the organic pollutant by boats and ships of Naval base and Naval ships activities. The minimum concentration of Cd (0.002 ppm) was found at site pp_6 which shows the dilution effect of the discharges of organic pollutant by boats and ships of Naval base and Naval ships (Table 3).

The Cd in the sample of location Hawks Bay on the Eastern site of Paradise Point shows the less concentration and similar pattern in sediments samples , the highest concentration (0.006ppm) of Cd were found at the site HB_2 this is so most probably due to the sewage discharge of the local population . No systemic variation in the concentration of Cd was noted in sediments samples but the increasing of concentration in the sample of HB_2 is quite prominent which show the effect of effluents

drained at site PP_{10} of paradise point. In Sand Pit location the concentration of Cd in Mangrove sediments was noted less as compared to location in the West which is due to wave direction in the closed hoar like structure in this part. The highest concentration of Cd (0.008ppm) at site Sand Pit $_3$ may be attributed to the effect of Liyari River pollutant in the East of this location.

Table 3. Mean concentration (ppm) of heavy metals in the mangrove sediments along Karachi coastal area.

	Cd	Co	Pb	Cr	Zn	Cu	Fe
PP10	0.004	0.009	0.01	0.023	0.015	0.011	1.96
PP9	0.01	0.045	0.01	0.005	0.01	0.009	2.23
PP8	0.004	0.012	0.023	0.085	0.1	0.013	3.22
PP7	0.007	0.032	0.022	0.011	0.01	0.022	2.15
PP6	0.006	0.042	0.045	0.032	0.015	0.016	7.62
PP5	0.002	0.022	0.01	0.009	0.042	0.01	4.54
PP4	0.005	0.021	0.021	0.025	0.016	0.014	0.95
PP3	0.004	0.011	0.032	0.054	0.014	0.025	2.36
PP2	0.008	0.01	0.023	0.032	0.011	0.026	5.64
PP1	0.11	0.01	0.022	0.004	0.02	0.04	8.32
SP1	0.004	0.025	0.045	0.008	0.033	0.01	4.62
SP2	0.005	0.011	0.033	0.004	0.032	0.007	3.26
SP3	0.008	0.023	0.021	0.0011	0	0.023	2.33
SP4	0.004	0.011	0.011	0.016	0.031	0.031	4.65
SP5	0.006	0.01	0.08	0.01	0.009	0.011	5.31
SP6	0.005	0.009	0.032	0.031	0.016	0.031	3.23
SP7	0.005	0.01	0.026	0.022	0.012	0.023	1.23
HB1	0.004	0.045	0.015	0.026	0	0.014	1.54
HB2	0.004	0.041	0.009	0.012	0.012	0.009	3.23
HB3	0.006	0.009	0.01	0.015	0.01	0.009	2.98
HB4	0.005	0.04	0.01	0.01	0.01	0.041	4.56
HB5	0	0.011	0.008	0.01	0.022	0.01	4.47
HB6	0.004	0.023	0.032	0.011	0.065	0.02	3.25

Cobalt concentration in the Mangrove sediments shows a lower average concentration in most of the site of the location and average value of Co concentration in the Mangrove Sediments ranges between 0.009 to 0.015ppm. However, the impact of pouring pollutant at different site of location under study are sensitively indicated. At location Paradise Point near to Karachi Nuclear Power Plant at site PP_2 due to where high concentration of Co was observed as compared to the adjacent location in the West. The minimum concentration of Co in the Mangrove Sediments (0.009ppm) was noted at site PP_{10} which is located at Western site of PP_{10} and under least influence of the pollutant or effluent of Nuclear Power Plant at the coast.

At Hawks Bay no significant change in Co concentration or its pattern of distribution in Sediments which is due to lime stones in the beach at this location which resist further eroding of coastal area by opening of the pollutants. The location Sands pit situated at east of Hawks Bay shows the highest Co concentration. Generally an increasing in the level of Co contents was noted in the different sites of location .This is most probably due to the effluents which are opining into the Liyari River located at the eastern site of Sands pit_3.

The lead concentration in the Mangrove Sediments sample of the location paradise point indicate inconsistent pattern due to the location of Nuclear Power Plant is situated ,so that is why the highest content of lead is evident in sediments samples. The highest content of Pb was found in the sample of the site PP_5. It appears that the impact of long shore current from East to West and the waste water of Nuclear Power Plant are the main factor caused higher concentration of Pb in Mangrove Sediments of this location. The Sediment samples of Hawks Bay represented by (HB_1, HB_2, HB_3, HB_4, HB_5, HB_6) show a prominent impact of Pb pollution in this location no obvious source of pollution can be assigned except that the beaches is crowded every day. The low concentration in the Mangrove Sediments in this location is most probably the effect of long shore current from East to West and human activities at the beach. The location Sands pit is further extension East toward of HB location where Pakistan Naval Base is situated. The concentration of Pb in sediments is most probably due to the effluents pour into the sea by Liyari River situated at the Eastern site of location.

Chromium concentration in the Mangrove sediments in the location under study shows a wide variation in its concentration (PP_8 0.054ppm to SP_1 0.004ppm) which reflects the degree of contamination from industrial and urban sources.

The Zinc concentration in the Mangrove sediments of the area under study also shows wide variation among the location .The effect of sources of pollutants from the land through river and sewage drainage, very clearly show the concentration of Zn in the samples of different sites of location under study. The highest concentration of Zn (0.1ppm) noted in Mangrove sediment sample at PP_3 due to the effluents of Nuclear Power Plant pouring into the sea and their redistribution in the East and West the lowest content of Zn was found at HB_1 and SP_3 which are the Eastern sites of location sites of location Paradise Point.

Generally Cu concentration in the Mangrove Sediments of location understudy shows the erratic changes in the Cu content .The highest and the lowest concentration of Cu among the location was found at the Sands pit location SP_4(0.031ppm) to SP_1(0.007ppm).The main source of Cu containing effluents is the waste of electrical based industries where the maximum electrical based industries are situated in the vicinity of Liyari River. So, untreated effluent are directly pour into the sea through Liyari River. Most probably the highest concentration of Cu at this location is attributed due to the said sources.

Iron being relatively common with 20 years residence time exhibits erratic concentration in sediments sample collected from the location under study. The occurrence of variable concentration of Fe in sediments sample clearly reflects to the geochemical control in term of turbidity, vegetation and wave action for its redistribution from main sources to the adjacent location. The main sources of Fe are mostly probably from the industries situated in the coastal region .The pollutant of industries are directly poured into the stream from where it mixed with the sea water. The low residence time in oxidizing environment favors the rapid precipitations of iron. The highest concentration of Fe (8.32ppm) was found in the location of Paradise point PP_{10} and lowest concentration (0.95ppm) was noted in the same location but different site PP_3.

Conclusion

In conclusion, the location under study is influenced by variable degrees of natural and manmade pollution in respect to urbanization, and industrialization and by geological and lithologicl condition of the coastal areas. A significant reduction in the river water supply and increased marine water pollution in the Indus Delta as well as overharvesting of mangroves by the local communities, sedimentation, and coastal erosion are generally considered to be the proximate causes of this loss. Another threat is emerging in the form of overharvesting of fish resources, largely provoked by increased pressure for exports with little or no consideration for the existing environmental laws and regulations. Policies and decisions made at the national and international levels have determined these proximate causes. Therefore, it is suggested that the government organizations and non- governmental organizations should take seriously actions for the environmental pollution of Mangroves along the coast of Karachi. Because mangroves can be sources of valuable products like black tea, mosquitocides, gallotannins, microbial fertilizers, antiviral drugs, and UV-screen compounds.

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