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PHYSICO-CHEMICAL ANALYSIS OF FERTILIZER INDUSTRY EFFLUENT AND ITS EFFECTS ON CROP PLANTS

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This study comprised physico-chemical analysis of selected fertilizer effluent, evaluation of hazardous pollutants, their effects on crop plants and remedial measures. Effluent samples of selected phosphatic and nitrogenous fertilizer industries were collected, periodically. The samples were analysed for pH, conductivity, hardness, alkalinity, dissolved solids, suspended solids, chemical oxygen demand (COD), chlorides, sulphates, sulphides, phosphates, silica, chlorine, ammonia, calcium, magnesium and iron. Trace metals like arsenic, cadmium, chromium, cobalt, copper, lead, manganese, nickel, tin and zinc were also checked. Effects of these effluents on crop plants and vegetables were observed and remedial measures for the hazardous pollutants of these effluents suggested.

Key words: Fertilizer, Effluent, Crop plants.

Introduction

Water pollution is the degradation of the quality of water that renders water unsuitable for its intended purposes.Sources of pollutants may be points sources, like industrial pipelines that discharge into a water body, or nonpoint sources such as organic chemicals applied to crops, which enter the soil and pollute the ground water. Water with a high concentration of nutrients, such as phosphorus and nitrogen, may experience damaging ecosystem effects, by lowering the dissolved oxygen in the water leading to fish kill and retard plant growth and damage to leaves and flowers as well (Daniel and Edward 1995).

With exploding population and increasing industrialization and urbanization, water pollution by agriculture, muncipal and industrial sources has become a major concern for the welfare of humanity. Water pollutants can be broadly classified into the five major categories namely organic, inorganic, suspended solids and sediments, radioactive materials and heat.

Effluent from ammonia production is highly alkaline, contains excess NH_3 from gas scrubbing and gas cleaning operation. On hydrolysis urea gives ammonia and carbon dioxide;

$$(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2$$

Effluent from phosphatic fertilizer is acidic and contains high amounts of phosphate, hexafluorosilicic acid and suspended solids. High amounts of fluorides present in phosphatic fertilizer effluent enrich the fluoride content of the receiving waters causing dental and skeletal fluorosis to humans, abnormal calcification of bones in animals and adverse effects on plants. Presence of chromium and ammonia are harmful to aquatic life (Dara 1997).

On January 11, 1994 farmers of the adjoining areas of fertilizer factories launched a complaint regarding damage of their crops and vegetables, due to the industrial wastewater. The effected areas were surveyed and the physical damage occurred to the crops and vegetable plants was observed. Following were the observations:

Crops

* Wheat (used as flour grain).
* Barley (used as food).
* Peas (seed used as vegetable).
* Spinach Coriander & Fenugreek (Leaves used as vegetable)
* Cabbage (Flower used as vegetable)
* Radish & Turnip (Roots used as vegetable)

Effect

* Tips of the leaves were turned yellowish.
* Tips of the leaves were turned yellowish.
* Flowers and fresh pods were burnt tips of the leaves and fresh plants were damaged.
* The leaves of these vegetable were shrinked become pale, tips and corners were burnt.
* Leaves damaged white flower turned black.
* Leaves of the plants were shrinked ends and corners

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became pale, veins damaged. Vegetable turned black on washing with polluted water.

The residents of the area revealed that prior to the installation of these industries, adverse effect of this water was never noticed, but after the installation of these industries, their crops were being damaged time to time. It was also noticed that some crops that were not irrigated with this water were also damaged due to the release of obnoxious materials in the ambient air (Khan and Akif 1994).

Apart from the toxic substances, which cause damage to flora and fauna and create various environmental problems, there are certain other parameters like temperature, pH, alkalinity, hardness, dissolved solids and turbidity etc., that are basically important in determining the quality of a water body. Sodium in irrigation water is toxic to plants and causes problems in soil structure excessive dissolved salts in drinking water can cause physiological effects, impalatable mineral tastes and thus necessitate further treatment of water (Krishnan 1991).

Methodology. Composite samples of the polluted water were collected from different locations for chemical analysis to gauge the extent of pollution.Samples were collected periodically, twice and or thrice in a month, preserved and analysed using standard ASTM and AOAC methods. Conductivity and pH was checked by conductivity meter 4010 JENWAY (England) and pH Meter TPS model 1552, (Brisborn Australia) respectively. Spectrophotometer Model 751-G and Photometer 72 Type, China, were used for the determination of iron sodium, phosphate and silica. Alkalinity, acidity, hardness, COD, calcium, magnesium chlorides, sulphates, total dissolved solids (TDS) and total suspended solids (TSS) were checked by wet analytical methods both gravimetric and volumetric. Trace metals were determined by Atomic Absorption Spectrophotometer Hitachi 180-80 (William 1970; Vogel 1978; ASTM 1980; Vowles and Connell 1980; De 1992).

Table 1

Mixed effluent of nitrogenous fertilizer factory

	Analysis	Unit	NEQS	7.93	8.93	9.93	10.93	11.93	12.93	10.1.94	11.1.94
1.	Temperature	°C	40	33	34	29	30	30	28	22	23
2.	pH	-	6-9	8.2	8.2	6.8	7.5	7.8	8.0	9.2	9.6
3.	Conductivity	μm/cm	-	792	756	850	750	769	815	950	1400
4.	TDS	ppm	3500	275	280	375	400	385	425	275	324
5.	TSS	ppm	200	25	30	59	49	25	39	44	34
6.	T.Alkalinity	ppm	-	275	330	80	200	285	274	390	730
7.	T.Hardness	ppm	-	85	134	240	190	210	195	124	40
8.	Ammonia	ppm	40	25	34	20	25	26	15	150	250
9.	C.O.D.	ppm	150	19	10	10	12	13	18	40	35
10.	Calcium	ppm	-	20	32	67	29	19	25	36	12
11.	Magnesium	ppm	-	29	14	18	15	18	19	8	3
12.	Sodium	ppm	-	27	19	20	17	15	20	19	11
13.	Iron	ppm	2.0	-	2.0	1.5	0.8	1.0	1.2	1.5	1.2
14.	Chlorides	ppm	1000	25	18	23	29	35	44	72	30
15.	Sulphates	ppm	600	58	30	51	52	59	51	40	50
16.	Phosphates	ppm	-	0.2	0.1	0.2	0.2	0.1	0.1	0.2	0.2
17.	Silica	ppm	-	5	12	5	10	8	9	10	6
18.	Arsenic	ppm	1.0	0.01	0.01	0.01	-	0.01	0.01	-	-
19.	Cadmium	ppm	0.1	0.1	0.1	0.1	-	0.1	0.1	-	-
20.	Cobalt	ppm	-	0.71	0.5	0.56	-	0.5	0.6	-	-
21.	Copper	ppm	1.0	0.3	2.8	0.9	-	1.5	1.3	-	-
22.	Lead	ppm	0.5	3.9	0.8	0.9	-	1.5	1.0	-	-
23.	Manganese	ppm	1.5	1.1	1.3	0.9	-	0.75	0.6	-	-
24.	Nickel	ppm	1.0	0.2	0.3	0.3	-	0.25	0.2	-	-
25.	Tin	ppm	-	0.07	0.05	0.06	-	0.05	0.05	-	-
26.	Zinc	ppm	5.0	2.7	2.3	2.0	-	2.1	1.9	-	-

Results and Discussion

Industrial wastewater is contaminated with different toxic materials depending upon the nature of the industry. The analytical data of effluents being discharged from both nitrogenous and phosphatic fertilizer factories is presented in Table 1-4.

Table 1 shows the results of mixed effluents from a nitrogenous fertilizer factory. pH on Jan 10 and 11, 1994 is high (9.2-9.6) and more than National Environmental Quality Standards (NEQS) values (comparison is shown in Fig 1) Increase in pH is due to high ammonia contents 150-250 ppm against NEQS value of 40 ppm (shown in Fig 2). Presence of high quantity of ammonia is mainly due to hydrolysis of urea, being discharged from the industry. Alkalinity 730 ppm is also high which is important for aquatic life because it acts as buffer, controlling pH fluctuations. Excessive alkalinity may cause eye irritation in humans and chlorosis in plants. Lead is high throughout and beyond the NEQS limits. Lead is considered as a general protoplasmic poison that is cumulative slow-acting and subtle.

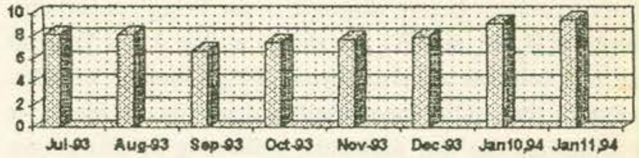

Fig 1. pH of effluent from nitrogenous fertilizer industry.

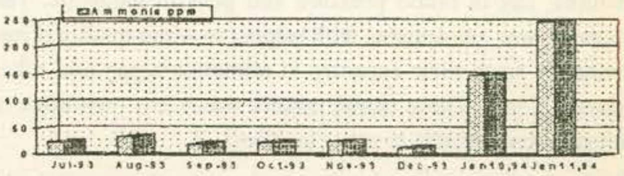

Fig 2. NH_3 ppm in effluent of nitrogenous fertilizer Industry.

Table 2 shows the analytical results of phosphatic fertilizer effluents. pH is highly acidic 1.0-3.1 (Fig 3), TDS, TSS and silica values are also high. Abnormal conditions indicate that

Table 2

Mixed effluent of phosphatic fertilizer factory

	Analysis	Unit	NEQS	7.93	8.93	9.93	10.93	11.93	12.93	10.1.94	11.1.94
1.	Temperature	°C	40	35	32	30	30	29	28	20	19
2.	pH		6-9	3.1	2.2	1.0	2.1	2.2	2.5	2.1	2.2
3.	Conductivity	µm/cm	-	6450	3130	12600	3900	5150	3445	12900	13000
4.	TDS	ppm	3500	2750	1347	908	1050	1170	995	3750	4364
5.	TSS	ppm	200	256	1015	342	290	315	256	315	295
6.	T.Acidity	ppm	-	1205	1020	2190	1350	1495	1015	950	980
7.	T.Hardness	ppm	-	1080	1900	3400	2500	1850	2100	1500	1250
8.	C.O.D.	ppm	150	15	15	62.4	51	49	37.5	40	35
9.	Calcium	ppm	-	801	835	961	850	795	656	515	460
10.	Magnesium	ppm	-	25	28	243	151	170	159	140	127
11.	Sodium	ppm	-	19	21	59	35	31	19	21	15
12.	Iron	ppm	2.0	1.5	1.9	2.1	1.5	2.0	1.5	2.0	12
13.	Chlorides	ppm	1000	850	200	175	250	191	200	700	1225
14.	H_2SiF_6	ppm	20	1225	2500	3475	2711	3100	1975	3715	3500
15.	Sulphates	ppm	600	96	75	121	115	200	174	295	230
16.	Sulphides	ppm	1.0	0.9	0.8	1.9	1.7	0.95	0.8	1.7	0.95
17.	Phosphates	ppm	-	200	400	500	495	417	551	475	380
18.	Silica	ppm	-	150	40	9600	1050	750	395	415	375
19.	Arsenic	ppm	0.1	0.01	0.01	0.01	-	0.01	0.01	-	0.01
20.	Cadmium	ppm	0.1	-	0.1	0.1	-	0.1	0.1	-	0.1
21.	Cobalt	ppm	-	0.15	0.1	0.1	-	0.2	1.5	-	2.1
22.	Copper	ppm	1.0	2.1	3.6	2.5	-	2.0	1.5	-	2.1
23.	Lead	ppm	0.5	4.3	1.2	1.1	-	3.7	1.5	-	3.1
24.	Manganese	ppm	1.5	0.9	0.7	0.5	-	0.2	0.7	-	0.5
25.	Nickel	ppm	1.0	1.9	0.8	0.9	-	1.0	0.7	-	0.5
26.	Zinc	ppm	5.0	6.7	4.5	4.0	-	4.9	5.1	-	4.5

waste treatment before disposal is not being carried out. Values of H_2SiF_6 and PO_4 are shown in (Fig 4 and 5). Lead and zinc contents are also beyond NEQS limits. Corrosive nature of the acidic water itself is dangerous to plants; it decolourizes the leaf pigments, yellowing by this action decrease the productivity. Fluorides cause respiratory failures, fall in blood pressure and general paralysis. The concern over phosphates with respect to water quality arises primarily from their capacity to stimulate algae and other aquatic plants. These plants require much less quantities of phosphorous relative to other nutrients.

Table 3 represents mixed samples of nitrogenous and phosphatic fertilizer factories after mixing with natural stream (nullah) water. Acidic and alkaline effluents were neutralized by mixing both the nitrogenous and phosphatic effluents. pH of mixed effluent is in the range of 7-8. Further improvement was observed after mixing with stream water. TDS, TSS, H_2SiF_6, PO_4 and Silica contents are decreased mainly due to dilution factor, but variation is not much due to less quantity of water in stream.

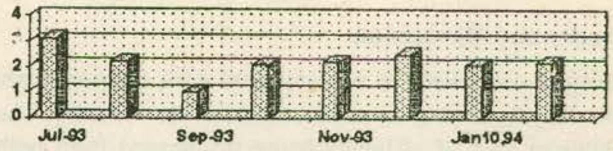

Fig 3. pH of effluent from phosphatic fertilizer industry.

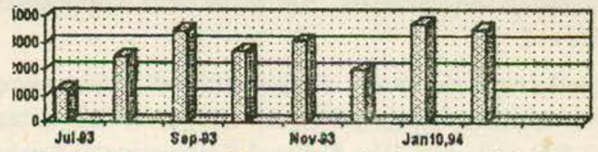

Fig 4. $HSiO_6$ ppm in effluent of phosphatic fertilizer industry.

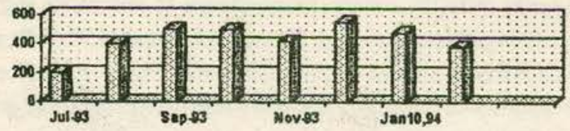

Fig 5. PO_4 ppm in effluent of phosphatic fertilizer industry.

Table 4 represents samples of mixed effluent from both fertilizers mixed with stream water collected from a distance of 1000 meters. the results are almost within normal NEQS limits, due to mixing of these effluents with other sources of water joining the stream.

Table 3

Effluent of phosphatic & nitrogenous fertilizer mixed with stream

	Analysis	Units	NEQS	Sep 93	Dec 93	10.1.94	11.1.94	2.94
1.	Temperature	°C	40	31	28	14	13.5	12
2.	pH		6-9	2.5	2.6	2.5	2.5	2.8
3.	Conductivity	µm/cm	-	1370	3050	4500	5400	4820
4.	TDS	ppm	3500	2250	915	450	435	1792
5.	TSS	ppm	200	2102	150	150	130	91
6.	T Acidity	ppm	-	1205	2100	1050	1045	650
7.	T Hardness	ppm	-	580	1950	1700	1680	720
8.	COD	ppm	150	38.2	35	25	20	50
9.	Calcium	ppm	-	160	550	580	572	202
10.	Magnesium	ppm	-	44	145	71	60	52
11.	Sodium	ppm	-	25	19	18	17	19
12.	Iron	ppm	2.0	2.0	1.5	2.0	2.0	1.5
13.	Chlorides	ppm	1000	22	140	450	460	140
14.	H_2SiF_6	ppm	20	850	540	480	456	560
15.	Sulphates	ppm	600	48	150	35	20	120
16.	Sulphides	ppm	1.0	0.5	0.2	0.1	0.1	0.2
17.	Phosphates	ppm	-	300	545	450	415	120
18.	Silica	ppm	-	10	400	250	225	140
19.	Arsenic	ppm	1.0	0.01	0.01	-	0.01	-
20.	Cadmium	ppm	0.1	0.3	0.2	-	0.1	-
21.	Cobalt	ppm	-	0.15	0.1	-	0.1	-
22.	Copper	ppm	1.0	2.0	1.5	-	1.0	-
23.	Lead	ppm	0.5	0.6	0.5	-	0.4	-
24.	Nickel	ppm	1.0	1.1	0.9	-	0.5	-
25.	Zinc	ppm	5.0	6.0	4.8	-	3.5	-

Table 4
Mixed effluent of fertilizer with natural stream (Soka) 1000 m away

	Analysis	Units	NEQS	Sep 93	Dec 93	10.1.94	11.1.94	2.94
1.	Temperature	°C	40	28	26	16	16	15
2.	pH		6-9	7.3	7.3	7.4	7.3	8.2
3.	Conductivity	µm/cm	-	1090	1000	1050	1100	1390
4.	TDS	ppm	3500	850	975	750	887	568
5.	TSS	ppm	200	75	110	120	110	200
6.	T Alkalinity	ppm	-	105	100	120	110	200
7.	T Hardness	ppm	-	395	350	395	428	200
8.	Ammonia	ppm	40	1.7	1.5	2.0	2.2	2.8
9.	COD	ppm	150	39	25	20	16	44
10.	Calcium	ppm	-	75	65	95	110	64
11.	Magnesium	ppm	-	32	31	35	36	34
12.	Sodium	ppm	-	24	22	21	24	25
13.	Iron	ppm	2.0	2.0	1.5	1.0	1.0	2.0
14.	Chlorides	ppm	1000	22	140	450	460	140
15.	H_2SiF_6	ppm	20	5	6	8	4	3
16.	Sulphates	ppm	600	41	40	45	40	80
17.	Phosphates	ppm	-	78	75	80	120	20
18.	Silica	ppm	-	28	25	30	28	30
19.	Arsenic	ppm	1.0	0.01	0.01	-	0.01	-
20.	Cadmium	ppm	0.1	0.1	0.1	-	0.1	-
21.	Cobalt	ppm	-	0.2	0.21	-	0.2	-
22.	Copper	ppm	1.0	2.5	0.4	-	0.5	-
23.	Lead	ppm	0.5	0.4	0.3	-	0.2	-
24.	Nickel	ppm	1.0	0.5	0.4	-	0.5	-
25.	Zinc	ppm	5.0	1.0	0.9	-	1.2	-

Table 5
Comparative analysis of effluent from different locations around fertilizer factories

Samples collected on January 10, 1993

	Analysis	Unit	NEQS	1	2	3	4	5	6	7	8
1.	Temperature	°C	40	22	18	20	20	14	17	16	16
2.	pH	-	6-9	9.2	9.2	2.1	2.1	2.5	4	7.4	7.4
3.	Conductivity	µm/cm	-	950	1265	12900	12500	4500	1990	1050	1060
4.	TDS	ppm	3500	275	300	3750	3700	450	750	750	750
5.	TSS	ppm	200	44	35	315	300	150	75	120	40
6.	T Alk/T Aci	ppm	-	390	1065	950	3705	1050	125	120	115
7.	T Hardness	ppm	-	124	142	1500	1450	1700	390	395	400
8.	Ammonia	ppm	40	150	100	-	-	45	15	2	2.2
9.	COD	ppm	150	40	10	40	37	25	20	20	25
10.	Calcium	ppm	-	36	40	515	500	550	100	95	96
11.	Magnesium	ppm	-	8	11	140	135	71	29	35	38
12.	Sodium	ppm	-	19	21	21	51	18	15	21	22
13.	Iron	ppm	2.0	1.4	1.6	2	1.8	2	1.2	1	1.5
14.	Chlorides	ppm	1000	72	54	700	695	450	135	450	67

(Table 5 cont'd...)

(Table 5 continue)

15.	H_2SiF_6	ppm	20	0	0	3715	100	480	370	8	2
16.	Sulphates	ppm	1000	40	45	295	285	35	19	45	42
17.	Sulphides	ppm	1.0	0	0	1.7	0.35	0.1	0.1	0.1	0.1
18	Phosphates	ppm	-	0.2	0.2	475	450	450	35	80	75
19.	Silica	ppm	-	10	6	415	140	250	40	30	21
20.	Arsenic	ppm	1.0								
21.	Cadimum	ppm	0.1								
22.	Cobalt	ppm	-								
23.	Copper	ppm	1.0								
24.	Lead	ppm	0.5								
25.	Manganese	ppm	1.5								
26.	Nickel	ppm	1.0								
27.	Tin	ppm	-								
28.	Zinc	ppm	5.0								

Samples collected on January 11, 1993

.	Analysis	Unit	1	2	3	4	5	6	7	8
1.	Temperature	°C	23	19	19	19	13.5	16	16	16
2.	pH		9.6	9.3	2.2	2.2	2.5	3.7	7.3	7.3
3.	Conductivity	µm/cm	1400	1195	13000	12500	5400	2000	1100	1150
4.	TDS	ppm	324	350	4364	4500	435	355	887	868
5.	TSS	ppm	34	38	295	350	130	45	110	12
6.	T Alk/T Aci	ppm	730	1015	980	3490	1045	135	110	110
7.	T Hardness	ppm	40	150	1250	1170	1680	410	428	456
8.	Ammonia	ppm	250	115	0	0	10	5	2.2	2.5
9.	COD	ppm	35	12	35	38	20	15	16	20
10.	Calcium	ppm	12	40	460	515	572	118	110	118
11.	Magnesium	ppm	3	12	127	130	60	28	36	39
12.	Sodium	ppm	11	20	15	29	17	14	24	24
13.	Iron	ppm	1.2	1.7	12	1.5	2	1	1	1
14.	Chlorides	ppm	30	59	1225	975	460	130	460	60
15.	H_2SiF_6	ppm	0	0	3500	90	456	345	4	8
16.	Sulphates	ppm	50	51	230	225	20	20	40	40
17.	Sulphides	ppm	0	0	0.95	0.5	0.1	0.1	0.1	0.1
18	Phosphates	ppm	0.2	0.2	380	415	415	50	120	120
19.	Silica	ppm	10	11	375	395	225	16	28	25
20.	Arsenic	ppm		0.01	0.01	0.01	0.01	0.1	0.01	0.1
21.	Cadimum	ppm		0.1	0.1	0.1	0.1	0.15	0.1	0.1
22.	Cobalt	ppm		0	0.1	0.1	0.1	0.1	0.2	0.2
23.	Copper	ppm		1.5	2.1	2	1	0.5	0.5	1
24.	Lead	ppm		0.5	3.1	2.9	0.4	0.2	0.2	0.2
25.	Manganese	ppm		0.7	0.5	0.75	0	0	0	0
26.	Nickel	ppm		0.7	0.5	0.5	0.5	0.2	0.5	0.4
27.	Tin	ppm		0.04	0	0	0	0	0	0
28.	Zinc	ppm		2.1	4.5	4.5	3.5	1.5	1.2	1

1. Mixed effluent of nitrogenous fertilizer factory; 2. Mixed effluent of nitrogenous fertilizer factory (500 meter away); 3. Mixed effluent of phosphatic fertilizer factory; 4. Mixed effluent of phosphatic fertilizer factory (500 meter away); 5. Effluent of nitrogenous & phosphatic fertilizer mixed with stream; 6. Mixed effluent of fertilizer with stream (500 meter away); 7. Mixed effluent of fertilizer with stream (1000 meter away); 8. Mixed effluent of fertilizer with (2000 meter away).

Table 6
Neutralization of phosphatic and nitrogenous effluent (500 ml each)

	Analysis	Units	NEQS	Phosphatic	Urea	Mixed
1.	pH	-	6-9	1.85	9.8	6.57
2.	Acidity	ppm	-	3550	Nil	29
3.	Alkalinity	ppm	-	Nil	260	Nil
4.	Ammonia	ppm	40	Nil	208	35
5.	H_2SiF_6	ppm	10 as F	11781	Nil	5211

Table 5 shows the samples of different locations collected on and before the accident day (10 Jan 1994) pH is very high 9.6 in case of nitrogenous fertilizer with high ammonia upto 250 ppm, increasing the alkalinity also. While pH is very low upto 1.1 in the effluent of phosphatic fertilizer. The condition improved when alkaline water of nitrogenous fertilizer factory was mixed with acidic water of phosphatic fertilizer. Further improvement was observed with the increase in distance as the effluents move away and mixed with other waters.

Conclusion

The complexity of water pollution in surface and ground water is due to several processes occuring simultaneously in nature, like variation in the flow rate of water effluent, nature of effluent, chain of reactions, reaction products, biological activities and the extent of water quantity modification with time. According to investigation carried out to determine the cause of high concentration of ammonia it was found that there was some leakage in the ammonia compressor of the urea fertilizer factory which was controlled by showering water on it. The ammonical water was discharged without any treatment, which caused this damage. Two most likely sites of absorption of pollutants are the roots and leaves. Leaves are normally sensitive and are directly effected by the vapours and gaseous pollutants.

After the incident study was carriedout, in which effluents of both the fertilizer factories were mixed in different ratios and analyse (Table 6). It was observed that its neutralization was very successful. A proposal was submitted to the management to arrange for mixing of the effluents before discharge to the nearby natural stream. Similar neutralization shall also be effective for mixing of acidic and alkaline effluents of different factories or industries presently discharging their effluents independently and causing damage to the environment as well as flora and fauna.

Attempts should be made to study and examine the system as a whole and not in isolation, and then develop a workable model to preserve and maintain water in its best quality.

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