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The nitrogen and phosphate forms in water of Shatt Al-Arab River in Basra/ Iraq

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Abstract

Sixty five water samples were collected from the river Shatt Al-Arab for the period of October 2011 to October 2012, the data were collected on a monthly base form five stations Qurna, Al- Sindebad, Abu Alkhaseeb, Al-Seba and Al-Fao. Some physiochemical parameters were measured as ammonia, nitrate, total Nitrogen (sum of all Nitrogen forms: $NH_4{}^{1+}$, $NO_2{}^{1-}$, $NO_3{}^{1-}$ and organic Nitrogen), phosphate (PO_4-P) Organic phosphorus and total phosphorus. The result indicate that organic form of Nitrogen is the dominant percentage, ranges from 65% to 73% and Ammonium range from 27% to 33%. The percentage of organic Phosphors form is the dominate form 84% to 98%, compared to Orthophosphurs form. This shows the presence of these parameters in high concentration thus indicate that the river suffer from organic pollution.

Key wards:Shatt Al-Arab,nitrogen forms, $NH_4{}^{1+}$, $NO_2{}^{1-}$, $NO_3{}^{1-}$ and organic Nitrogen, phosphate (PO_4-P) Organic phosphorus and total phosphorus

1- Introduction

The source of high nutrient in surface water may be the result of human activities such as industry, agriculture, cattle-breeding, waste disposal, establishment of hydroelectrically and atmospheric deposition (Alsabah 2007; Hamid and Aljorany,2011). Nitrogen and phosphorus pollution have become the main factors of surface water pollution. The total phosphorus is used for production algal biomass and total nitrogen to total phosphorus ratio used to predict algal species composition. (Maher *et al*., 2002). Organic nitrogen and organic phosphorus are used by phytoplankton and may be significant in their nutrition, but the data on organic nitrogen and phosphorus concentrations, bioavailability, and species specific abilities to use them are still limited (Palenik and Dyrhman 1998; Berman and Bronk 2003). There is positive significant correlation between Nitrate and percentage of Eutrophic species of Diatoma (Eassa 2012). Many studies have been executed on the water of Shatt Al-Arab River. Al-Sabah (2007) in his study of chemical analysis of Shatt AL-Arab river and its branches showed that the mean values of nitrate , nitrite , ammonium , soluble – P were 26.68 to 31.72 µg /l , 0.82 to 0.85 µg/l , 1.20 to 1.19 µg /l and 3.47 to 5.24 µg/l respectively. Hassan *et al.*(2011a) notes that, there were about 6.6 and 0.76 ton/year of PO_4^{3-} and NO_3^{1-} respectively added to Shatt Al-Arab River which emanating from the paper factory and Al-Hartha and Al-Najebiah Electric power stations.

The main objective of this study was to document the special and temporal variations in nutreint forms concentration in Shatt Al-Arab River.

Study area

Shatt Al-Arab river formed by confluence of Tigris and Euphrates rivers in the south of Iraq, and extends about 190 km prior to its water empties into the Arabian Gulf(Fig.1)(Saad 1980; Abdullah 1990; Hussein *et al*., 1991). There are important tributaries such as Al-Karun and Al-Sweeb flow in to the river (Abdullah 1990). It has been noted that, generally, there has been a decrease in the discharge rates over time due to the growing investment upstream in dams on the Tigris and Euphrates, as well as a decline in the discharge of the Al-Karun river in the south after redirection of its flow(Al-Mahmood et al ,2008; Al-Maliky *et al.,* 2012).

2- Materials and methods

Water samples were collected monthly during the period October 2011 to October 2012, from five stations (Qurna (ST:1) , Al-Sndebad (ST:2) ,Abu Alkasseb (ST:3), Seeba (ST:4) and Al-Fao (ST:5) (Fig.2). Water samples were taken from the surface in the middle of the River for each station using water sampler. EC and pH was conducted in the field using WTW multi-meter. The samples transferred directly to the laboratory in a cool box. Water for nutrient was analyzed as soon as possible. Distillation and titration procedure were used to determined Ammonium (NH_4^{1+}), Nitrite (NO_2^{1-}) determined by colorimetric method. Cadmium reduction method was used to determine nitrate (NO_3^{1-}). The macro-Kjeldahl was used to determine organic nitrogen (N-org). The total nitrogen(TN) were calculated from summation of ammonium and organic nitrogen the above phases. Ascorbic acid method was used to determined phosphate

(PO_4^{3-}) inorganic phosphorus and digestion on method used to determine total phosphorus(TP), organic phosphorus (P-org) calculated by subtracting inorganic from total phosphorus. All these methods describe in APHA(2005).

Data were statistically analyzed using the analysis of variance (ANOVA). Significant differences were determined using a Post Hoc, Less significant difference (LSD) (set at P=0.05) and the variance was calculated for seasonal. Data were collected statistically using the software SPSS v-19.0.

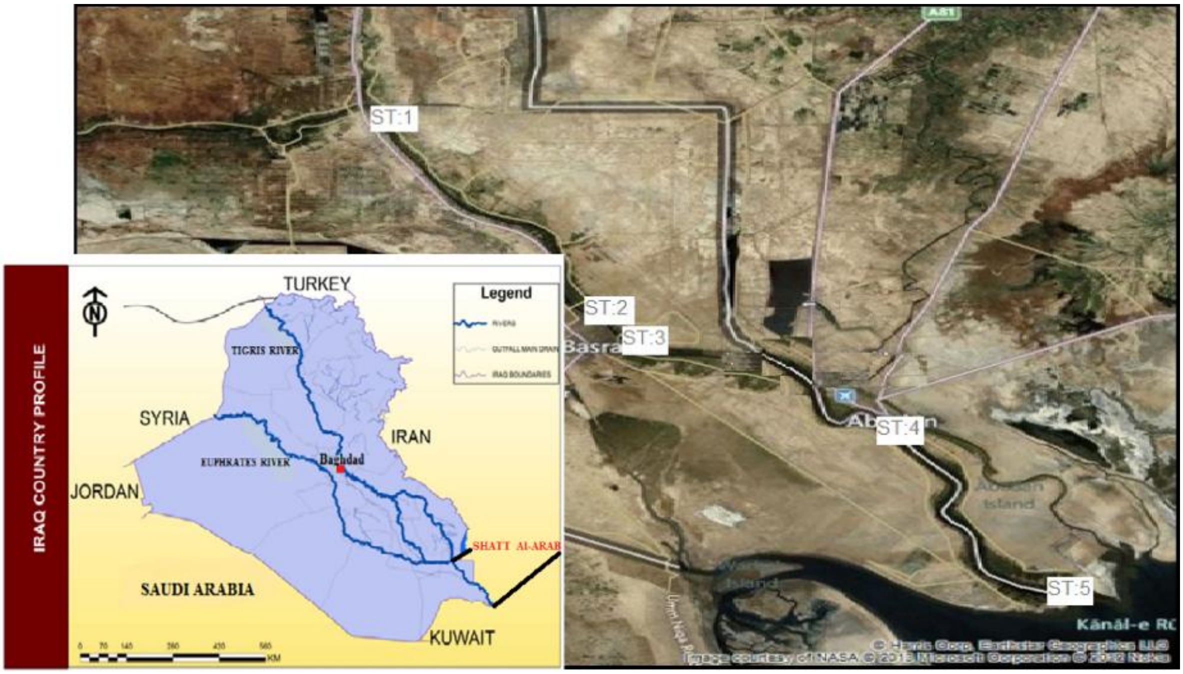

Fig. 1: Map showing the sampling stations along the Shatt Al-Arab river

3- Results and Discussions

The concentrations of total Nitrogen in the surface waters were found to be significantly different at the stations and mean concentration level ranged from 4.04mg/l in ST.1 to 5.85mg/l in ST.3 (table:1). Also amongst the seasons the mean ranged from 11.2 to 3.43 mg/l at winter 2011 and summer 2012 respectively (table:2). The highest mean of total Nitrogen concentrations were observed at St4 and St5 during in Winter, while lowest observation in Summer at St5 also (Fig. 2). The component load was the highest downstream, and decreased in upstream. The stations downstream were impacted by the most heavily populated area of Basra city. Downstream river increase in nutrient is due to a combination of anthropogenic (Hamid and Aljorany,2011; Hassan et al 2011a).

Table 1: the mean concentration of nutrient in study stations

Stations		ST.1	ST.2	ST.3	ST.4	ST.5	LSD (P=0.05)
PH		7.76	7.63	7.95	7.9	7.81	NS
EC	mS /cm	2.38	2.35	4.52	14.39	32.56	0.84
Tem.	ºC	26.95	29.95	22.69	29.07	23.36	NS
TN	mg/l	4.08	5.02	5.85	5.21	5.49	0.79
NH_4^{1+}		1.31	1.96	2.27	2.03	2	NS
N-org		3.59	3.85	4.16	3.78	4.31	0.48
TP		12.8	10.64	15.95	13.05	9.11	NS
PO_4^{3-}		9.49	4.21	10.36	3.77	6.13	NS
P-org		8.6	9.63	8.38	11.47	5.16	NS
NO_2^{1-}	μg/l	3.91	5.27	9.89	5.4	7.67	NS
NO_3^{1-}		21.61	18.62	28.1	26.5	24.61	0.27
TN:TP		0.32	0.47	0.37	0.4	0.6	
inorg N:Norg		0.37	0.52	0.55	0.55	0.47	
PO_4:P-org		1.1	0.44	1.24	0.33	1.19	

Table 2: the mean concentration of nutrient during the study season

Season		Winter	2011	Autumn	Spring	Summer	Winter	LSD (P=0.05)
PH		7.95		7.53	7.88	7.83	8.1	NS
EC	mS /cm	12.14		21.35	7.39	17.73	8.16	1.03
Tem.	ºC	15.05		28.36	25.5	29.49	15.2	1.13
TN	mg/l	11.2		3.78	4.44	3.43	6.83	1.05
NH_4^{1+}		4.73		1.35	1.45	0.98	1.86	0.07
N-org		7.13		2.33	3.8	2.45	5.21	0.43
TP		-		2.82	20.47	4.11	10.44	NS
PO_4^{3-}		3.33		0.35'?	11.76	2.48	-	0.02
P-org		-		2.57	12.55	3.56	-	NS
NO_2^{1-}	μg/l	8.81		3.52	8.94	4.61	6.97	NS
NO_3^{1-}		28.72		9.2	30.18	21.98	24.86	8.33
TN:TP				1.34	0.22	0.83	0.65	
inorg N:Norg		0.67		0.59	0.39	0.41	0.36	
PO4:P-org				0.14	0.94	0.7		

Nitrogen forms

The statistical analyses show a significant difference in ammonium ion (NH_4^{1+}) concentration with season(table 2) but not with stations (table 1) which may be explained by the high variation between stations as showing in Fig (3). The concentration of ammonium was highest in winter (4.73 mg/l) in St5 which is the downstream station.The reason for such difference may be due to the cold temperature which might have decreased the growth of bacteria that needs Ammonium as source for protein synthesis and subsequent production of biomass thus reduce the NH_4^{1+} consumption (Chang et al 2006). Also the lack of dissolved oxygen in water causes a reduction of ammonia transformation as a result of the low activity of bacteria analyzed and converted to nitrate.

Fig (4 and 5) show the variation of Nitrite (NO_2^{1-}) and Nitrate (NO_3^{1-}) ions. The highest mean concentration of NO_2^{1-} appears in the St3 during winter 2011 and 2012 (17.5 and 10.41 µg/l) respectively . Typically the lowest mean concentration appear in summer. The height mean of NO_3^{1-} appeared at St3 in Spring (47.71 µg/l). The lowest mean concentration appeared in the autumn, there is no significant difference among stations or seasons (table:1 and 2). Bacteria such as *Nitrobacter, Nitrococcus*, and *Nitrospira* uses the Nitrite ion for nutrient. The nitrite ion is thus converted to another Nitrogen-bearing compound nitrate ion, which is in a small reasonable quantities is non-toxic but will pose a problems with algae (e.g., Algae Bloom) (Yang et al 2008).

The reason for increasing nitrate levels in the Shatt al-Arab attributed to rainfall that dissolve compounds of nitrogen from land and thus move through the branches and channels to Shatt al-Arab, in addition to that, these channels receive water drainage from their surrounding areas which is rich with nitrate fertilizer(Al-Sabah, 2007; Lomoljo, 2009).

Tables (1 and 2) show a significant variation in organic nitrogen concentration among stations and seasons. The concentration increases from up to downstream river (3.59-4.31 mg/l in ST.1 and ST.5 respectively) and increase in the cold weather about 2-3 times compared to hot weather (7.13-2.33 mg/l in winter 2011 and autumn2012 respectively).

The highest and lowest mean concentrations of organic nitrogen (N-org) observed at St5 at Winter 2011 (11.76 mg/l) and in St4 in Autumn (1.51mg/l) respectively (Fig 6). Organic form is the dominant form percentage ranged from 65%-73% while the ammonium percentage ranged from 33% to 27%. These result indicate that there is a low transformation of organic compounds into inorganic forms along the river. The mean ratio of inorganic nitrogen to organic nitrogen increased from 1.19 in St1 to 1.46 in St3. Self-purification or transformation of organic nitrogen to mineral forms in the upstream is more evident than in the downstream . The decomposition of organic matter by bacterial activities can produce nutrients and organic substances, which may promote algal bloom breaking out. It may be related to the decomposition of bacterial biomass, which can promote effective circulation of nutrients when alga bloom and eutrophication occur under lower concentrations of nutrients(Yang et al 2008).

Phosphorus

Tables 1 and 2 shows that the concentrations of total phosphorus at ST3 was highest (15.95 mg/l) whereas at ST5 was the lowest (9.11mg/l). Seasonally the highest concentration that was absorbed in Spring (20.47 mg/l) and the lowest in the Autumn(2.82 mg/l) and there is no significant difference among stations or seasons (Fig7.).

The mean concentration of orthophosphates were the highest at St3 in the Spring (18.76 mg/l) , decreased in the middle part of Shatt Al-Arab river and increased again at St5 in the Spring too. The load of phosphates increased along the River course, but the largest increase occurred in the lower part of the river (Fig8). Fig.9 shows the variation in the concentration of organic phosphorus thus the highest variation is at ST3 and ST4.

The ratio of phosphate to total phosphorus was 1.35 at St1 and 2.60 at St4. The process of transformation of organic phosphorus into inorganic phosphorus (self-purification) was very low in the lower part of the river. Shatt Al-Arab River is impacted by agriculture and untreated waste (sewage) water disposal especially at downstream stations Hussein(2001). According to Hamid and Aljorany (2011) Phosphorus delivered into rivers through point and diffuses sources.

The high concentration of phosphate at St3 could be caused by the discharge of large amounts of sewage in the upper part of the river and the internal canals flow, The above results are consistent with Eassa(2012) in addition to that water at Fao station was greatly influencd by saline water of Arabian Gulf (Hassan et al 2011b) . The decrease of phosphate at St4 could be explained by processes such as dilution,

sedimentation, polymerization, etc. there is heigh variation in Spring at all station compared to other seasons. The ratio of organic phosphors to total phosphors range from 1.35 to 2.60 at stations St1 and St4 respectively. The percentage organic phosphorus form is the dominant one (98-84%) compared with orthophosphorus form.

The ration of TN:TP ranged from 0.15 to 1.8 (table 1 and2) that's the phosphorus controlling of the eutrophication that is caused by the autotrophy algae blooming. These results are not consistent with Eassa (2012) which Indicated that inorganic nitrogen is the major control factors for the phytoplankton. The calculation of the TN was based on the summation of NO_2^{1-} and NO_3^{1-} only and TP equal to PO_4^{3-} metal (only) nitrates and nitrites only and not to the estimated total nitrogen, contrary to the method used in this project.

Conclusion

There are significant variance within different seasons and stations in concentration of some nitrogen or phosphorus forms. The process of transformation of organic forms into inorganic (self-purification) was very low at all parts of the river in particular in the downstream. According to the ratio of TN:TP the phosphorus is controlling the eutrophication.

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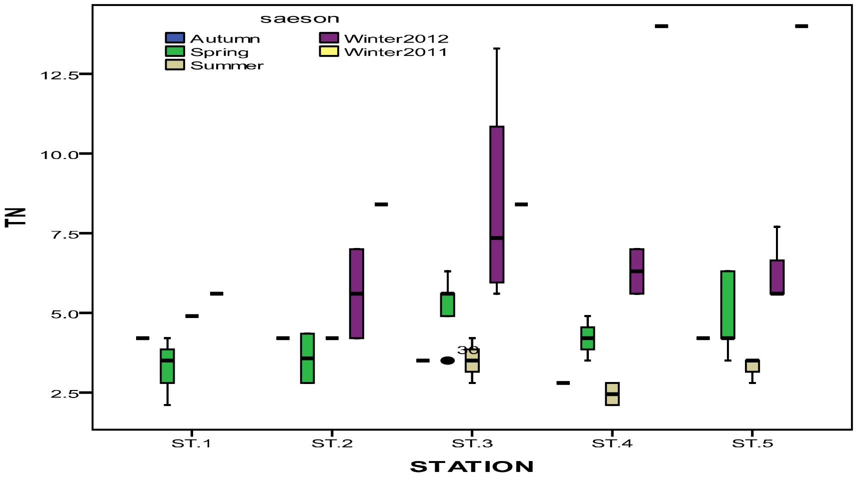


Fig 2: the variance of TN in station during seasons(mini.,maxi.,mean,S.D.)

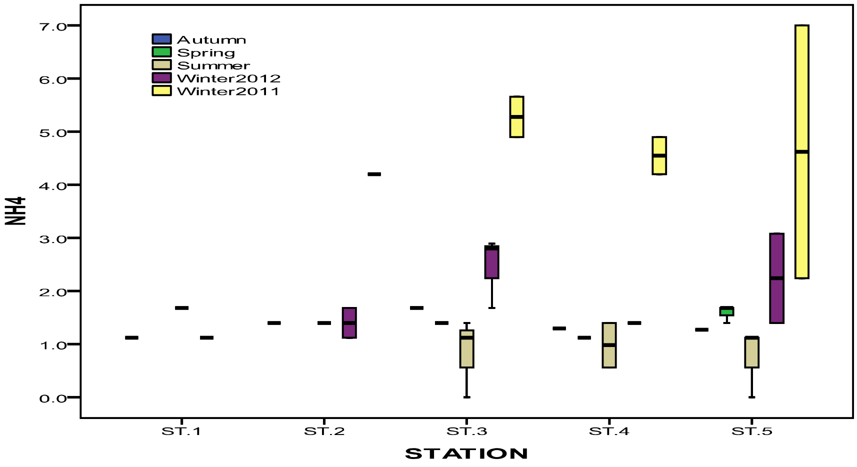


Fig 3: the variance of NH41+ in station during seasons(mini.,maxi.,mean,S.D.)

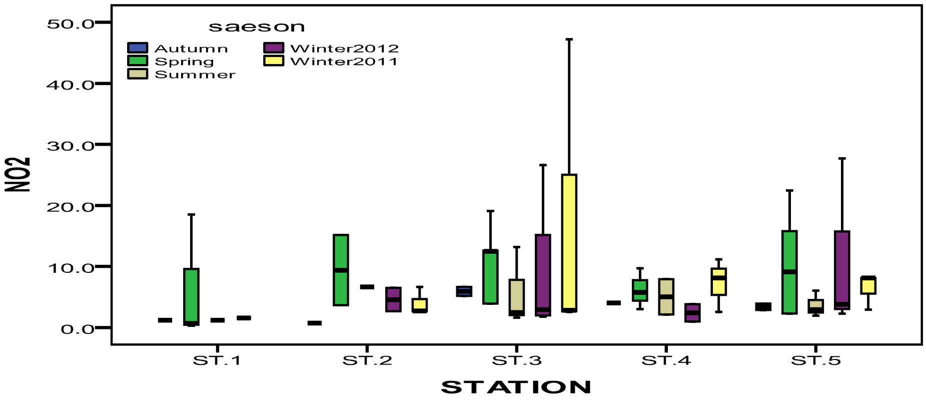


Fig 4: the variance of NO_2^{1-} in stations during seasons (mini.,maxi.,mean,S.D.)

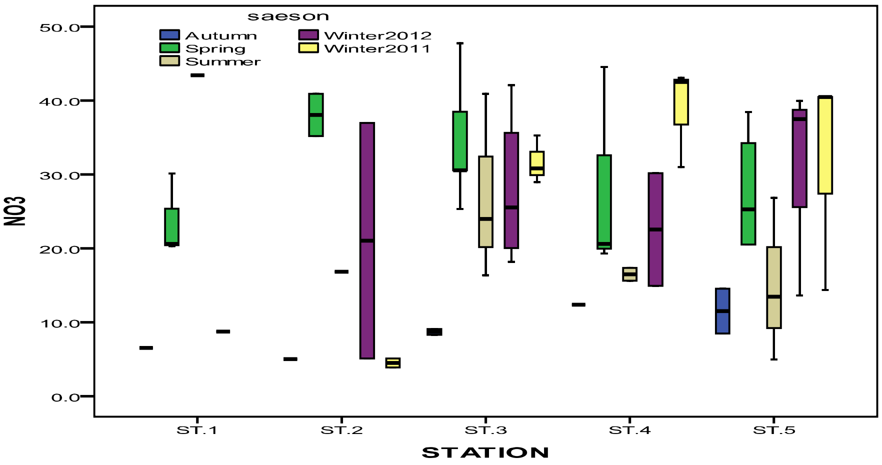
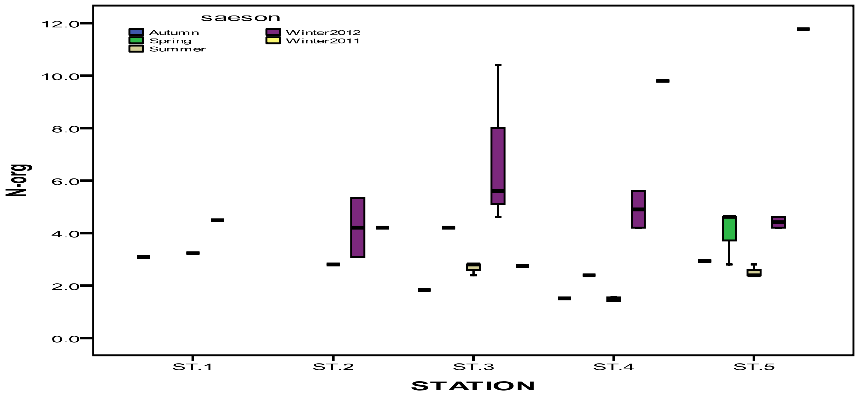
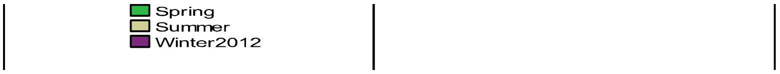


Fig 5: the variance of NO_3^{1-} in stations during seasons (mini.,maxi.,mean,S.D.)





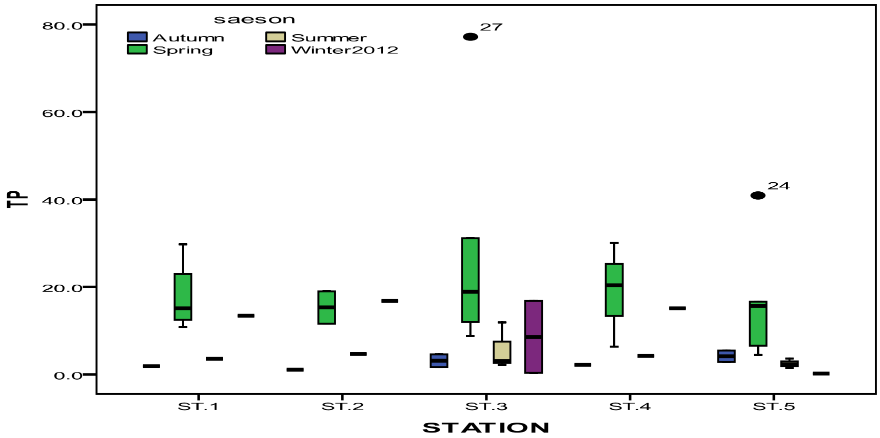


Fig 8: the variance of PO_4^{3-} in stations during seasons (mini.,maxi.,mean,S.D.)

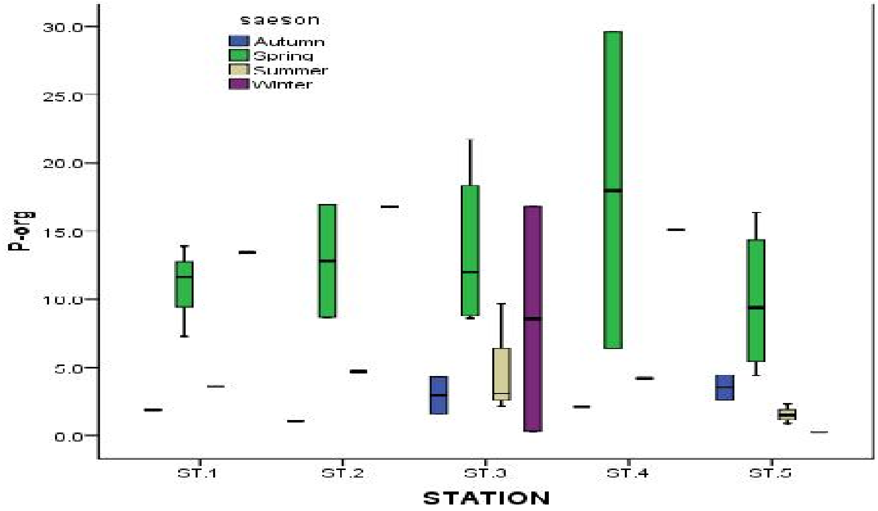


Fig 9: the variance of P-ORG in stations during seasons (mini.,maxi.,mean,S.D.)