

Comparative Analysis of Trace Elements Found in Commonly Used Vegetables Irrigated By Fresh And Waste Water in Karachi, Pakistan

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Abstract: Use of municipal waste water (both treated and untreated) has now become a common practice in urban and peri-urban areas. Mostly vegetables in urban cities like Karachi are being irrigated by sewerage water. In this study a comparison of sewage and fresh water-irrigated vegetables has been made with respect to trace metals. Among commonly used vegetables, green onion, cabbage, pumpkin, eggplant, bird's eye chili and okra were selected. Two sets of these vegetables were collected, one from local farm where irrigation was done with well water and other set of samples was collected from Malir, Karachi where irrigation was done with waste water. Samples were analyzed for heavy metals i.e. K, Na, Pb, Zn, Cu, Cd, Fe, and As by Atomic Absorption Spectroscopy. It showed that both sets of samples were found to contain metal concentrations beyond the limits set by WHO/EU. Apart from tomato, the concentration of only Cd was near the standard value for both sets. Similar results were obtained for K except for pumpkin in which the concentration for waste water irrigated samples was fairly high. Amount of Cu and Fe were moderately higher than the standard in both samples. Arsenic in all the samples was considerably high while maximum concentration was obtained for Pd against the limits. These findings suggest waste water irrigated vegetables pose high risk to human health. The concentrations of As and Pb were high in fresh water samples possibly, the well water may contain metals, therefore it is important to know the source.

Keywords: Trace metals, fresh water, wastewater, world health organization (WHO).

Introduction

Fresh water is a natural resource used extensively for agricultural, industrial and domestic purpose cause an imbalance supply and demand of fresh water in coming days. Pakistan is an agricultural country and available water used majorly for irrigation (Taj, 2018). Scarcity of fresh water shifted traditional irrigation system towards utilizations of wastewater for irrigation in water starved region, urban and peri-urban areas (Singh et al., 2010) and is also known to contribute substantial metal substance into soil (Lawal and Audu, 2011). Reuse of waste water for irrigation has many benefits like cheap replacement of fertilizers Nitrogen, Phosphorus and Potassium (NPK), economical advantage, reduction of organic load and minimum consumption of fresh water (Chary et al., 2008; Alghobar and Suresha, 2016; Alghobar and Suresha, 2017). The utilization of domestic sewage, industrial effluent and sludge for a longer period of time might contribute an increase in non-essential metals (Khan, 2008) which can disturb plant growth and accelerate the migration of heavy metals in soil including Cd, Cr, Pb and others in soluble and in combined state (Mahmood and Malik, 2014). Generally, agricultural soil possesses low level of metals but extensive use of synthetic fertilizers used for soil amendment increases the risk. Ultimately, increase in amount of heavy metals over a safe limit poses a high risk to human health in case of using vegetables irrigated with wastewater and soil containing heavy metals (Khan, 2011). Due to the absence of surface water, the dependence over groundwater has extended,

but it is costly. Therefore, one of the substitute hotspots for irrigation is waste water. Karachi is the most populated metropolis of Pakistan, having a large number of industries. Only 5 % of industrial and domestic effluent receive significant treatment out of 1.3 million L/d and rest of waste water is directly discharge into two major waste water bodies i.e. Malir and Lyari rivers which enter into Arabian sea. Both of them were seasonal rivers but now have become a drainage system due to untreated industrial and domestic discharge containing organic and inorganic pollutants creating real problem to aquatic and terrestrial environment directly or indirectly (Farooq, 2010). Lack of knowledge and increasing price of synthetic fertilizers have motivated scientists to use wastewater for irrigation. However, use of untreated wastewater has the risk of health hazards (Khan, 2014). Trace elements such as Cadmium (Cd), Chromium (Cr), Lead (Pb) are non-biodegradables having bio accumulative and bio magnification properties. Various species of plant have ability to remove variety of pollutants from soil including metals and act as phyto remediators (Balkhair and Ashraf, 2016). Excess amount of these metals could accumulate in vegetables without any visible changes in yield. Vegetables are an important ingredient of human diet that contains essential nutrients and trace elements (Asdeo and Loonker, 2011). Consumption of vegetables irrigated with heavy metals bearing wastewater could cause cardiovascular, renal, nervous and skeletal diseases in human (Akhtar, 2012). Due to these reasons, continuous monitoring of these two important water bodies Malir

and Lyari river of Karachi is required for controlling increasing concentration of heavy metals which could disturb the food chain. Unlike all previous studies cited in the work, the present paper aim to deal with problems associated with waste water irrigation in Malir, Karachi including other issues, such as the concentration of trace metals in the most common vegetables whether it's in under the limit of health standard of WHO/EU and to create awareness and issues related to waste water irrigation. Water is going to be a scare resource day by day throughout the globe just to achieve United Nation Sustainable Developments Goals (UNSDGs) including goal 3 Good Health and well-being, goal 6 clean water and sanitation and goal 12 responsible consumption and production use of recycled water for irrigation purposes will play a significant role towards natural resource consumption (UNSDGs, 2015). Therefore, the aim of this research was to assess the concentration of trace heavy metals contamination in selected vegetables irrigated with fresh and wastewater to establish the advice regarding consumption of waste water for farming vegetables and implementation of National Environmental Quality Standards (NEQS, 2000) for nearby industrial and other activities.

Materials and Methods

A. Sampling Area: Waste water irrigated vegetables were collected from Malir River whereas, freshwater irrigated samples collected from private farms sample of vegetables include tomato, eggplant, green onion, birds eye chili, okra, pumpkin and cabbage. Five samples of each vegetable were directly taken from the fields in sterilized plastic bags to minimize handling error.

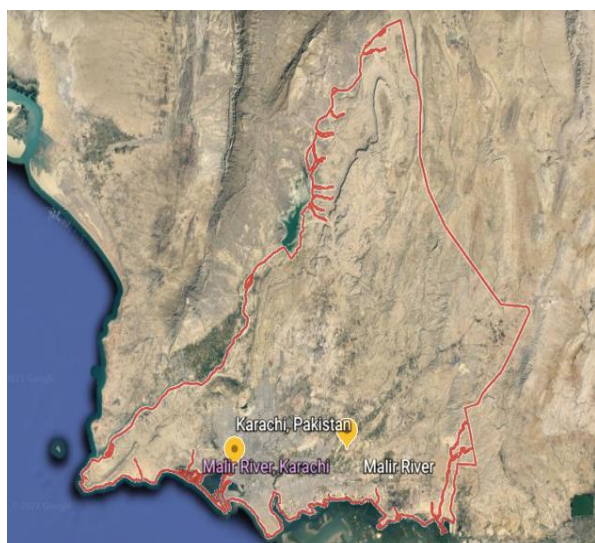


Fig. 1 Satellite image of Karachi.

B. Chemicals and reagents: Nitric acid 65 % (HNO_3) EMSURE® ISO, Hydrogen per oxide (H_2O_2), freshly prepared De-ionized water from distilled water.

Instruments: Instruments include electrical balance, magnetic starrier, hot oven, and Flame Atomic Absorption Spectrophotometer (FAAS) PE-Analyst 700

and mortar and piston. Both set of vegetables were washed thoroughly with deionized water to remove other attached solids, cut with Teflon knife and dried at 160°C by using dry oven. The vegetables were then crushed into small particles by means of mortar and piston. By using electronic balance 10g of vegetables ash was taken into a 100ml beaker and treated with 10 to 15 ml (HNO_3) nitric acid. The beaker was heated on hotplate at 120°C for digestion of organic matter. 15 ml distilled water was added into solution then filtered the solution made up to 100ml volume with deionized water. 2-3 drops of H_2O_2 was added in solution due to dark color appearance. Then each solution was analyzed for absorbance measurement by AAS using fuel flow 10L/min, Air- C_2H_2 flame with different wavelength (nm).

Table 1 European Standards of trace metals in food.

Metals	Conc. ($\mu\text{g mL}^{-1}$)
Cadmium	0.005
Copper	0.02
Iron	0.02
Arsenic	0.01
Lead	0.01
Sodium	200
Zinc	20
Potassium	200

Results and Discussion

Seven different vegetables were cultivated in fresh and sewerage water and were analyzed for presence of eight trace metals. The results were compared with European Union (EU) standards mentioned in Table 1. As showed in Figure 2, concentration of metals in tomato irrigated from fresh and waste water compared with EU standard. According to the results showed in Table 2 and 3, concentration of Pb in both fresh and waste water irrigated tomato was approximately 350 times higher, concentrations of Fe and As were 100 times while Co was 20 times higher than the EU standards. On the other hand, concentration of Na was 80 times higher in both type of samples and Zn was 20 times lower in waste water and 50 times in fresh water as compared to EU standards while Cd was within limits. Concentration of Cu mentioned as Figure 3 was 25 and 15 times higher in waste and fresh water green onion respectively. As and Fe was 100 and 200 times higher in wastewater and 30 times in freshwater samples then EU standards, while concentration of Cd was nearly same as standard. The amount of Pb was calculated to be very high nearly 800 and 450 times greater in waste and fresh water respectively. Similarly, concentration of Fe was 200

Table 2 Detection of metal content in fresh water irrigated vegetables (n=5) by FAAS.

	Vegetables	Cu		Cd		Fe		As	
		MEAN	SD	MEAN	SD	MEAN	SD	MEAN	SD
1	Tomato	0.346	0.008	BDL	BDL	BDL	BDL	0.768	0.0807
2	Green onion	0.349	0.243	BDL	BDL	BDL	BDL	0.926	0.1441
3	Cabbage	0.328	0.0143	0.011	0.0024	1.196	0.3275	1.62	0.5743
4	Pumpkin	0.56	0.0155	0.0005	0.004	BDL	BDL	1.292	0.0236
5	Eggplant	0.465	0.008	0.0007	0.0041	1.564	0.1968	1.031	0.2237
6	Bird eye Chili	0.59	0.0076	0.002	0.0025	BDL	BDL	0.681	0.1451
7	Okra	0.522	0.0263	0.01	0.0016	0.992	0.2855	1.503	0.0574
	Vegetables	K		Na		Pb		Zn	
		MEAN	SD	MEAN	SD	MEAN	SD	MEAN	SD
1	Tomato	2.348	0.01	31.77	0.763	2.348	0.01	31.77	0.763
2	Green onion	235.5	0.01	31.46	0.707	235.5	0.01	31.46	0.707
3	Cabbage	241.4	0.05	31.9	0.253	241.4	0.05	31.9	0.253
4	Pumpkin	235.6	0.03	19.1	0.064	235.6	0.03	19.1	0.064
5	Eggplant	236.2	0.21	29.06	0.781	236.2	0.21	29.06	0.781
6	Bird eye Chili	235.5	0.03	21.66	0.097	235.5	0.03	21.66	0.097
7	Okra	240.3	0.1	30.16	0.256	240.3	0.1	30.16	0.256

Table 3 Detection of metal content in waste water irrigated vegetables (n=5) by FAAS.

	Vegetables	Cu		Cd		Fe		As	
		MEAN	SD	MEAN	SD	MEAN	SD	MEAN	SD
1	Tomato	0.41	0.0088	BDL	BDL	2.364	0.0807	0.974	0.0361
2	Green onion	0.558	0.0132	0.008	0.0047	3.731	0.3243	0.949	0.1815
3	Cabbage	0.396	0.0125	0.012	0.004	1.663	0.3069	1.79	0.1815
4	Pumpkin	0.562	0.0096	0.012	0.0018	0.654	0.1992	1.999	0.0732
5	Eggplant	0.561	0.0176	0.011	0.0023	2.242	0.1177	1.577	0.3771
6	Bird eye Chili	0.614	0.0319	0.017	0.0042	2.153	0.0685	2.029	0.3981
7	Okra	0.526	0.0124	0.011	0.0005	1.836	0.2855	1.936	0.2896
	Vegetables	K		Na		Pb		Zn	
		MEAN	SD	MEAN	SD	MEAN	SD	MEAN	SD
1	Tomato	235	0.04	37.51	1.101	3.872	0.025	0.904	0.0295
2	Green onion	239.2	0.23	58.56	5.73	7.918	0.509	1.936	0.073
3	Cabbage	241.9	0.03	33.85	0.759	11.9	0.154	0.5	0.0295
4	Pumpkin	342.7	0.05	20.35	0.259	15.72	0.443	1.328	0.086
5	Eggplant	240.7	0.06	40.57	7.962	9.709	0.526	1.205	0.0166
6	Bird eye Chili	242.2	0.04	28.22	0.308	14.76	0.274	0.758	0.0063
7	Okra	242.2	0.04	32.44	0.317	13.08	0.255	1.281	0.0376

times higher in wastewater irrigated green onion. It is clearly seen in Figure 4 that concentration of Cu was 30 times higher in both samples. As was 200 times and Fe being 100 times higher in waste and 30 times in fresh water resources than standards. Concentration of Pb was very high nearly 1400 times in wastewater and 500 times higher in fresh water irrigated chilli. Concentration of Zn and Na were found to be lower than the EU limits in both fresh and waste water samples. While Cd and K was nearly similar to the standards in both samples respectively. Similar results were obtained for pumpkin with only minor differences in Figure 5. Concentration of Pb was very high around 1500 times greater in wastewater samples and 600 fold higher in fresh water samples as compared to the EU standards. Concentration of Cu and As were 100 and 25 times higher in both samples. While Na and Zn were present at a lower concentration in fresh and waste water samples with respect to EU standards. On the other hand, Cd concentration was nearly similar to the standard values in both fresh and waste water while concentration of Fe was calculated to be 30 times greater in wastewater irrigated pumpkin only. Both fresh and wastewater cultivated brinjal samples shown Figure 6 were also contaminated considerably having

concentration of Cu 30 times higher than standards value. As was 150 and 100 times higher in waste and fresh water samples than the standard value respectively. Concentration of Zn and Na were low compared to the standards in both samples. Amount of Pb was found to be very high in both fresh and waste water samples approximately 700 -900 times greater than the standard limit respectively. Likewise, Concentration of Cu, As and Fe were 100 times higher in fresh and wastewater samples of cabbage while Cd and k were nearly present in similar quantity as set by EU standard as showed in Figure 7. Concentration of Zn and Na were found to be low in both samples while concentration of Pb was significantly high nearly 1000 times higher than the EU standard limit in both samples. Similarly, in Figure 8. It is clearly seen that Cu, As and Fe were present in slightly higher concentration in both fresh and wastewater samples of Okra while concentration of K and Cd were found to be similar to the EU standards value. Concentration of Zn and Na were lower than the limits and concentration of Pb was very high approximately 1300 and 850 times higher in waste and fresh water samples of okra respectively. The calculated concentration of the selected trace elements showed similar trend in all the fresh and waste water

irrigated samples. Concentration of Cu, As and Fe were slightly higher compared to the standard value. However, the contamination of trace elements was found to be several times higher than the EU standards in both type of samples. Concentration of Pb was highest in both fresh and waste water irrigated vegetables. Cd and K were similar in concentration while Zn and Na were lower than the limits set by EU in both.

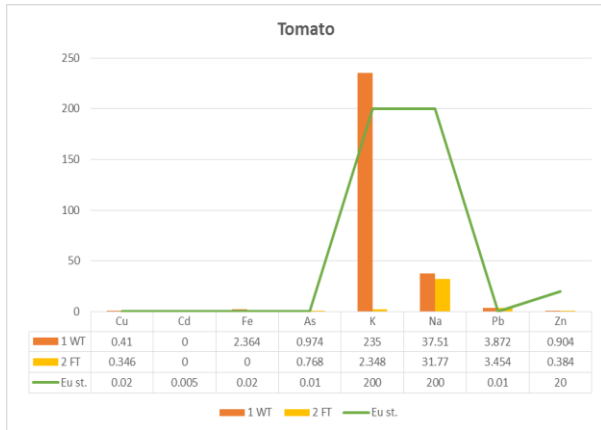


Fig. 2 Comparison of conc. of metal in tomato irrigated from fresh and waste water with EU standard.

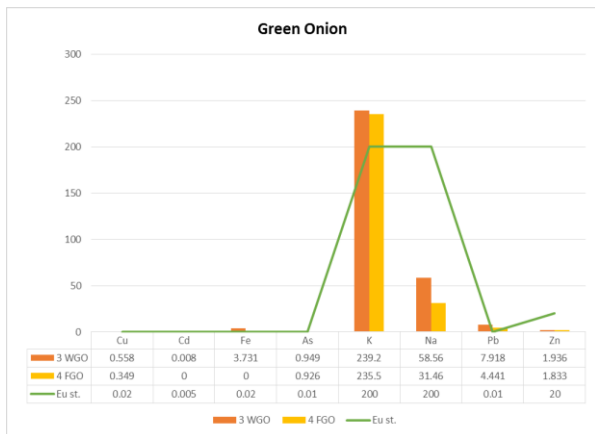


Fig. 3: Comparison of conc. of metal in Green Onion irrigated from fresh and waste water with EU standard.

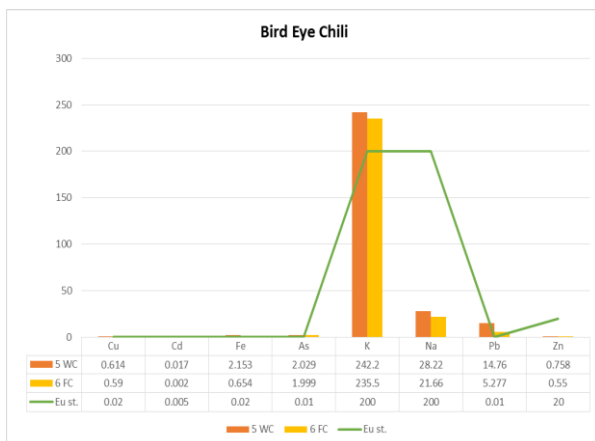


Fig. 4 Comparison of conc. of metal in Bird eye chili irrigated from fresh and waste water with EU standard.

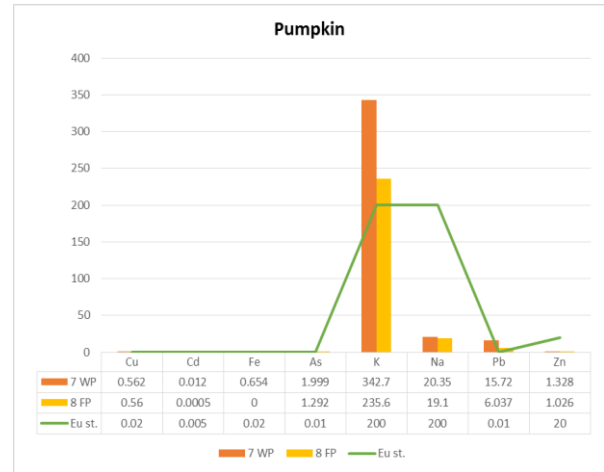


Fig. 5 Comparison of conc. of metal in Pumpkin irrigated from fresh and waste water with EU standards.

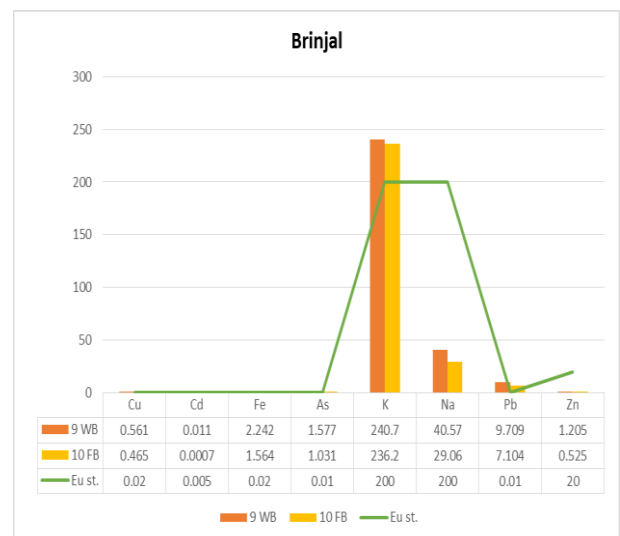


Fig. 6 Comparison of conc. of metal in eggplant irrigated from fresh and waste water with EU standards.

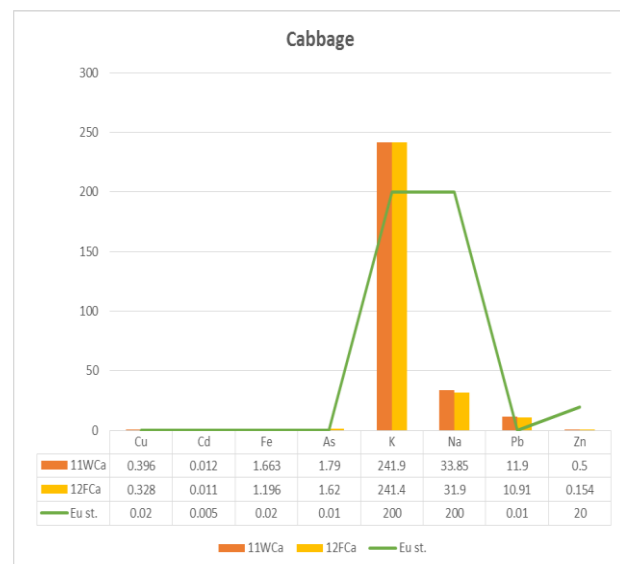


Fig. 7 Comparison of conc. of metal in cabbage irrigated from fresh and waste water with EU standards.

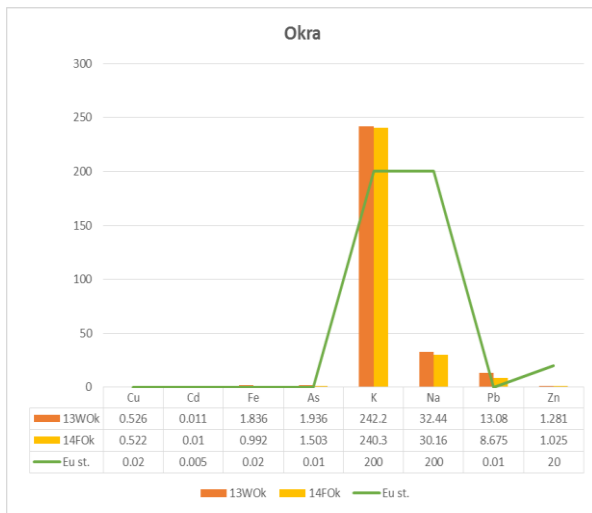


Fig. 8 Comparison of conc. of metal in okra irrigated from fresh and waste water with EU standards.

Conclusion

It is concluded that, all the above eight selected vegetables have some of the nutrients in common and every individual has its unique health benefits, nutritional value in diets and almost all of them are involved to cure some harmful diseases. Agricultural activities with wastewater caused an ample buildup of metals in soil according to studies by (Jan et al., 2010). In the present study, result showed bioavailability of heavy metals in waste water irrigated and fresh water irrigated vegetables although, concentration was above permissible limits of WHO/EU in both. The source of trace metals in fresh water irrigated vegetables may be soil and source of water used for irrigation. A similar study conducted at Rawalpindi (Mustaq & Khan., 2010) which reported clay soil have higher potential to absorb maximum amount of trace metals due to high surface area whereas, soil with coarse texture possess poor absorption capacity. Karachi the most urbanized and industrializes city of Pakistan discharged 500MGD (Million gallon per day) industrial effluent and domestic wastewater into major rivers (Malir and Lyari). The result of this study indicates a substantial buildup of trace metals in vegetables irrigated with the waste water and thus justify the restrictions of the use of irrigation was due to transfer of high toxic element into food network. The reason of high concentration of Pb is that it can easily takes up by leafy vegetables and foliar absorption of metal from leaves surface. Results has shown that waste water irrigation practices that are done in Karachi is dangerous to human health and environment, as the raw sewage water is used for irrigation. According to studies conducted by Shuaibu et al., 2013 in Nigeria, Africa and Yogananda et al., 2015 in Banglore, India, the absorption capacity of

metals depends on size, weight and nature of vegetables as leafy vegetables grown in metals contaminated soil accumulate more metals than others. Vegetables are the main source of food for human and animals and their monitoring must continue because are supposed to environmental pollution bio-indicators. Consumption of foodstuff with elevated levels of heavy metals may lead to high level of accumulation in the body causing different disease like thalassemia, dermatitis, brain and kidney damage and cancer (Khan et al., 2014). Recycled Waste water, undoubtedly is a good choice to overcome food shortages and water scarcity, but this water should be treated with maintaining standards. Overall, our study recommended that the alternate source of water for irrigation must be explore, proper treatment of industrial and domestic wastewater is mandatory before utilization in agriculture practices at the same time soil contamination could be treated by phytoremediation. The serious actions should be taken to stop likewise irrigation practices after the detail examination and studies.

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