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TEMPORAL TRENDS OF TRACE ELEMENTS IN WATERS OF THE INDUSTRIAL CANALS IN PORTO MARGHERA (VENICE, ITALY)

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Abstract

Porto Marghera is an industrial district located in the Venice Lagoon (Italy). The century-long industrial activity has left a heavy environmental burden. Data records (2004-2016) of trace metals, arsenic and suspended solids in the waters of the industrial canals of Porto Marghera were analyzed for trends. Decreasing trends were detected for Cu, Zn, Cr and Pb, as well as suspended solids. No significant trends for As and Cd were evident. A positive trend of Fe was detected in one sampling site.

Keywords: *temporal trends, trace elements, Venice Lagoon*

Introduction

Estuaries and coastal marine areas have been always interested by the presence of human activities. With the growth of the economy, estuarine and coastal areas are facing great challenges in regard to the presence of pollutants such as harmful elements (Khan et al., 2014) due to urbanization and industrialization (Cardellicchio et al., 2016), as well as agriculture activities (Petrini et al., 2014). This is also the case for the Lagoon of Venice that has been exposed for several decades to a high human pressure as a results of port, industrial and urban activities. The direct discharge from the industrial zone of Porto Marghera are largely recognized as the main source of the pollution for the Lagoon (Khan et al., 2014).

The industrial park of Porto Marghera is located on the western shore of the Venice Lagoon (548 km^2), 5 km NW of the historical centre of Venice (Italy) and spans a surface area of 20 km^2. The development of Porto Marghera started in 1919 with the construction of the first industrial district through the infilling of 5 km^2 of marshes. Main industrial activities included shipbuilding, oil refining and storage, metallurgy, processing of coke, pyrites, phosphorite and sphalerites. In 1955 was planned a further expansion of Porto Marghera into the second industrial zone where the chemical sector played a dominant role. Main industrial activities included different basic chemical products, most of which linked to the chlorine cycle. In the 1960s - 1970s Porto Marghera was recognized as one of the biggest

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industrial zones in Europe. In the last two decades many plants have closed down causing a sharp decrease in the industrial activity (Mannino et al., 2015). The activities still operating are a cracking plant, a refinery recently converted to the production of biofuel from vegetable oil and biomass, industry for cruise ships construction, a plant for the production of acetone cyanohydrin, a plant for air fractionating and industrial gas production, a glass-manufacturing company, plants for oil-seed processing. Besides these activities, an industrial and civil waste waters treatment plant, an area for collection and treatment of dredged sediments and two power plants are present.

The century-long industrial activity of Porto Marghera has left a heavy environmental burden. The contamination dates back to the beginning of activities within the industrial area where many years of uncontrolled discharge have led to a very high contamination of the canals (Bellucci et al., 2009; Bellucci et al., 2013). Many different sources and bad management choices are responsible for the contamination originating from Porto Marghera (Bellucci et al., 2013). The first district was reclaimed with sediment dredged from the Venice canals and since the late 1920s industrial waste was used for marsh land filling. The discharged waste materials used as infilling materials were originated from the distillation of coke, pyrite ashes from the production of sulfuric acid, residues from the production of phosphates from phosphorite, residues of bauxite treatment for aluminium production. Other infilling residues came from the production of glass, industries of zinc and ammonia along with sludges produced by thermoelectric plants. This practice continued until the 1970s, reaching an average thickness of 2.3-3 m above the sea level. Furthermore, in the 1960s the industrial canals South and West were excavated through those embankments of industrial waste, leaving the canal banks unprotected from erosion.

In the 1990s new environmental sensibilities and stricter environmental regulation modified the institutional framework establishing very strict limits for industrial effluents to lagoon waters and banning the discharge of several toxic, persistent and bioaccumulative contaminants. Census and controls of water discharges in the lagoon have been conducted since the second half of the 1980s (Carrer and Leardi, 2006) and a network of water quality monitoring stations in the Venice Lagoon was established in order to evaluate the chemical status of the lagoon.

In 2000 a master plan for the environmental remediation was adopted. In the 2000s the problem of canal bank erosion was faced with the beginning of the realization of a perimeter dike system.

In this paper concentration levels and temporal trends of iron, zinc, chromium, lead, copper, cadmium, arsenic in the waters of the industrial canals of Porto Marghera are discussed. Total suspended solids (TSSs) have been also included in the study. Adsorption onto suspended particulate matter is an important process controlling dissolved metal concentrations, bioavailability, and toxicity to biota, and both the fate and transportation of trace metals. Contaminant fate and transportation in the Venice Lagoon have been investigated in Sommerfreund et al. (2010) which demonstrated that contaminants in the water column, most of which are in the particulate phase, circulate throughout the lagoon by advective transport in the water column.

Materials and methods

Study area

The monitoring of concentration levels of arsenic and trace metals in the water column of the Venice Lagoon is performed every three months by measuring the concentration of the dissolved fraction in 23 sampling sites whereas TSSs is measured monthly. In the present study we focused on three sampling sites located in the industrial canals of Porto Marghera monitored between 2006 and 2016. The sampling sites were (figure 1): D located in the Northern industrial canal (45°27'24.5" N, 12°15'37.8" E), E located in the Western industrial canal (45°27'23.6" N, 12°14'4.8" E) and F located in the S.Leonardo-Marghera canal (45°25'6.5" N, 12°15'34.4" E).
Furthermore, the measurements from 2004 to 2016 of the water quality at four industrial inlets, which is regularly controlled by measuring total concentrations of As, metals and TSSs, in order to be able to estimate the difference between waters before and after their utilization in industrial processes, were included in this study. The industrial inlets were (figure 1): A010 of the refinery located on the Vittorio Emanuele III canal (45°27'17.6" N, 12°16'0.7" E), A005 of the power plant located on the Western industrial canal (45°26'54.0" N, 12°15'19.2" E), A006 of the chemical plants located on the Southern industrial canal (45°26'17.0" N, 12°14'50.7" E) and A002 of the power plant located on the Southern industrial canal (45°26'9.8" N, 12°14'57.4" E).

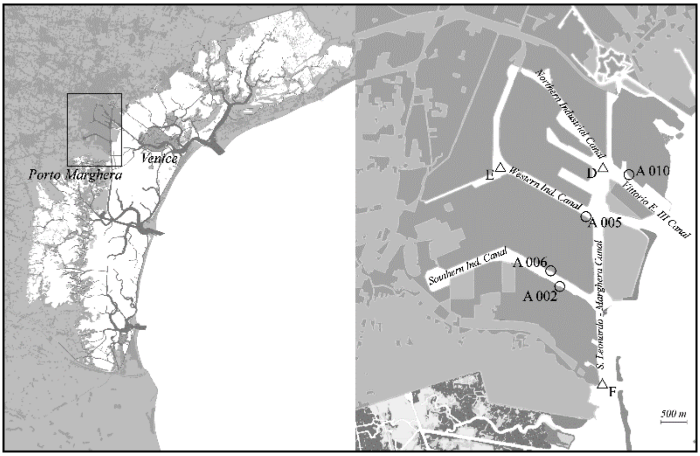

Figure 1
Study area with the position of the inlets ○ and the sampling sites of water column △

Field sampling and laboratory analysis

The determination of dissolved metals requires rigorous quality protocols to prevent systematic errors due to contamination during sampling and handling steps

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(USEPA 1669 1996). Hence, all polyethylene bottles and vials used were leached in washing solutions. All handling and preparation steps were carried out in HEPA filtered Class 100 laminar flow clean room. The samples of the water column were collected using precleaned 250 mL bottles. The capped bottles were fastened to the end of a 2 m long pole and submerged at the depth of 0.5 m selected for the sampling. A second pole permits to remove and fasten again the cap allowing to collect the sample. The samples were filtered in the clean room by using 0.45 μm pore size filters and then acidified with ultrapure nitric acid. The samples collected at the inlet points were mineralized by means of microwave assisted acid digestion (Speedwave4, Berghof) (USEPA 3015A 2007). Concentrations of elements were measured by inductively coupled plasma mass spectrometry (ELAN DRC II, Perkin Elmer) according to method USEPA 6020B 2014. TSSs were measured by means of a gravimetric procedure (APAT CNR IRSA 2090B 2003). The detection limits of the dissolved fractions of Fe, Zn, Cr, Pb, Cd, Cu and As were respectively: 1, 1, 0.1, 0.1, 0.02, 1 and 0.2 μg/L. The detection limits of the total fractions were respectively: 30, 10, 0.5, 0.5, 0.1, 1 and 0.2 μg/L.

Statistical analysis

Records were statistically analyzed to identify the trends in time series data (Chandler et al., 2011). Mann–Kendall trend (MKT) test (Kendall, 1975) and Sen's slope were applied. Mann-Kendall is a non-parametric test commonly employed to detect monotonic trends in series of environmental data in particular with water quality multiple data sets that depart from normal distribution and with censored or values smaller than detection limit (Hirsch et al., 1991, Yue et al., 2002, Mozejko, 2012). The null hypothesis, H_0, is that the data come from a population with independent realizations and are identically distributed. The alternative hypothesis is that the data follow a monotonic trend. A step trend procedure was applied on the data of inlets using the nonparametric Mann-Whitney-Wilcoxon Rank Sum test. The end of the realization of the perimeter dike was used to divide the records into "before" and "after" periods. Correlations between total metal concentrations and TSSs were tested using Kendall Rank Correlation. Statistical significance for all tests was set at 0.05. Concentrations lower than detection limits were set at half of the limit.

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Results and discussion

Box-and-whisker plots of data for each variable grouped by sampling sites were depicted in figure 2. The box-and-whisker plot depicts the distribution of data around the median; the lower and upper hinges correspond to the first and third quartiles (the 25th and 75th percentiles); the lower and upper whiskers extend from the hinges respectively to the lowest and highest value that is within 1.5 fold the inter-quartile range; data beyond the end of the whiskers are plotted as points.

Results of Mann-Kendall test as τ value, significance of trend (p), and trend slope estimate (TSE) are shown, for each sampling site, in table 1 and 2 for inlets and water column respectively. Some records showed a significant trend but an estimated slope equal to zero. This discrepancy is probably the consequence of ties in the record due to the presence of values lower than the detection limit.

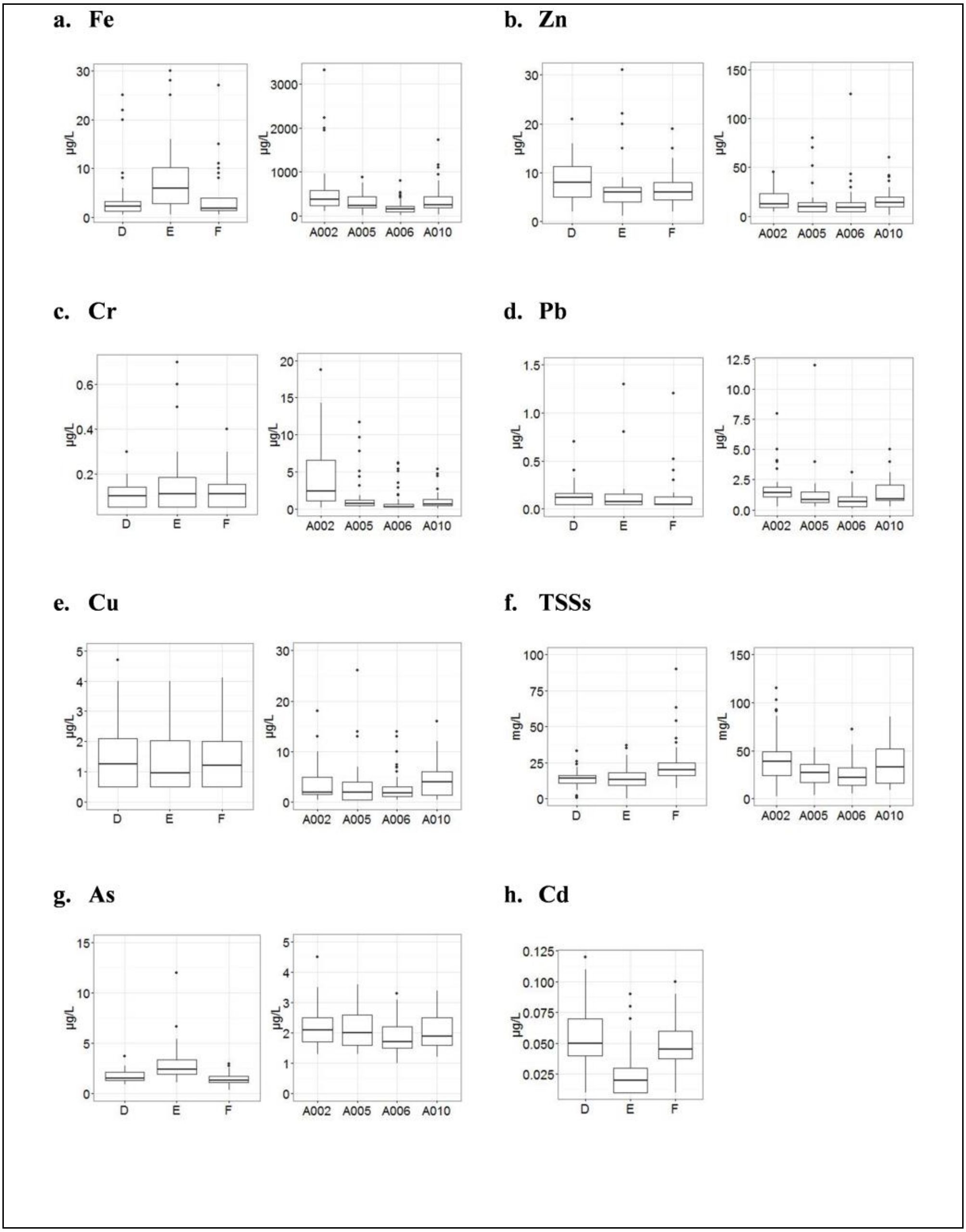

Figure 2. *Box-and-whisker plots*

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Table 1. *Results of Mann-Kendall test on inlets records*

		As	Cr	Cu	Fe	Pb	Zn	TSS
A010	τ	0.011	-0.175	-0.501	0.024	-0.202	-0.194	-0.467
	p	0.92	0.099	<0.01	0.83	0.057	0.068	<0.01
	TSE	0.00	-0.013	-0.18	0.52	-0.015	-0.22	-1.12
A005	τ	0.001	-0.018	-0.52	-0.16	-0.47	-0.15	-0.53
	p	1.00	0.10	<0.01	0.15	<0.01	0.19	<0.01
	TSE	0.00	-0.013	-0.13	-3.61	-0.031	-0.091	-0.88
A006	τ	-0.046	-0.25	-0.48	-0.072	-0.34	-0.18	-0.55
	p	0.49	<0.01	<0.01	0.28	<0.01	<0.01	<0.01
	TSE	0.00	0.00	-0.037	-0.30	-0.007	0.00	-0.29
A002	τ	0.033	0.12	-0.30	0.27	-0.060	0.087	-0.20
	p	0.77	0.28	<0.01	0.013	0.59	0.43	0.080
	TSE	0.00	0.045	-0.077	9.09	-0.006	0.061	-0.56

Table 2. *Results of Mann-Kendall test on water column records*

		As	Cd	Cr	Cu	Fe	Pb	Zn	TSS
D	τ	-0.094	0.003	-0.24	-0.42	0.14	-0.23	-0.14	-0.41
	p	0.38	0.98	0.033	<0.01	0.19	0.041	0.19	<0.01
	TSE	0.005	0.00	0.00	-0.041	0.026	0.00	-0.067	-0.11
E	τ	-0.17	0.064	-0.34	-0.36	0.012	-0.25	-0.34	-0.30
	p	0.11	0.58	0.003	<0.01	0.92	0.031	<0.01	<0.01
	TSE	-0.017	0.00	-0.002	-0.022	0.00	0.00	-0.11	-0.11
F	τ	-0.18	0.007	-0.19	-0.48	0.17	-0.34	-0.26	-0.29
	p	0.098	0.96	0.082	<0.01	0.11	<0.01	0.016	<0.01
	TSE	-0.009	0.00	0.00	-0.045	0.026	0.00	-0.091	-0.14

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Concentrations of total Fe measured at the inlets were two order of magnitude greater than values of dissolved Fe in the water column (figure 2a) confirming that most of the Fe is adsorbed on the suspended solids. Higher concentrations of dissolved Fe were found at sampling site E located in the Western industrial canal. Hypothesis of no trend in Fe cannot be rejected in any of the records with the exception of total Fe in A002 record (southern bank of Southern industrial canal) where the Mann-Kendall test showed a significant positive trend.

Box-and-whisker plots of Zn are shown in figure 2b. Two values measured at A005 and A006 inlets (250 and 740 μg/L respectively) were omitted to reduce compression. Half of the measures at A006 (northern bank of Southern industrial canal) were smaller than the detection limit. A significant trend of total Zn was detected in A006 record but the estimated slope was equal to zero. The Mann-Kendall τ was negative and indicated a significant decreasing trend (p-value<0.05) in dissolved Zn at two of the three sampling sites of water column (sites E and F).

Total Cr at the inlets was an order of magnitude higher than values of dissolved Cr in the water columns (figure 2c). Higher concentrations of total Cr were found at A002 inlet (southern bank of Southern industrial canal). Three values greater than 20 μg/L measured at A002 inlet (37, 27 and 70 μg/L respectively) were omitted from box-and-whiskers plot to reduce compression. A high number of measures inferior to detection limit were found in A006 record inlet. Hypothesis of no trend in total Cr cannot be rejected in any of the inlet records with the exception of total

Cr in A006 record for which the estimated slope was equal to zero. A small but significant trend (p-value<0.05) of dissolved Cr was detected at Western industrial canal (site E). The decreasing trend of dissolved Cr at Northern industrial canal (site D) was significant but a TSE equal to zero was estimated.
Total Pb at the inlets was an order of magnitude higher than dissolved Pb (figure 2d). While a monotonic decrease was detected at A005 and A006 (Western and Southern industrial canals respectively) inlets, a TSE equal to zero was estimated in any of the water column records.
Total Cu was threefold higher than dissolved Cu (figure 2e). Decreasing trends were detected both for total and dissolved Cu in the industrial canals of Porto Marghera. There were no notable differences between Cu concentrations in the various sites monitored in the industrial canals.
Total Cd measured at inlets was almost always lower than detection limit and box-and-whiskers were not depicted. Half of the measures of dissolved Cd at Western industrial canal sampling site (E) were lower than the detection limit and almost always less than 0.05 μg/L (figure 2h). Higher concentrations were measured at Northern industrial canal and S.Leonardo-Marghera sampling sites (D and F) with median values close to 0.05 μg/L. The MKT showed no significant trend in dissolved Cd for any records.
Concentrations of total As measured at the inlets were similar to dissolved As in the water column, confirming that As is not adsorbed on the suspended solids (figure 2g). Higher concentrations of dissolved As were measured at Western industrial canal sampling site (E). The MKT showed no significant trend both for total and dissolved As at any sampling sites.
Box-and-whisker plots of TSSs are shown in figure 2f. One value measured at A010 inlets (280 mg/L) was omitted from box-and-whiskers plot to reduce compression. TSSs showed a significant decreasing trend both in the water column and at the inlets with the exception of A002 inlet record (southern bank of Southern industrial canal) for which the hypothesis of no trend cannot be rejected (p-value 0.08).
Results of Kendall Rank Correlation test between total concentrations and TSSs as τ value and significance of correlation (p) are shown in table 3. While As didn't show correlation at any inlets, a significant Kendall Rank Correlation between total metals and TSSs was detected in particular for Fe, Cu and Pb (p-value<0.05).

		As	**Cr**	**Cu**	**Fe**	**Pb**	**Zn**
A010	τ	0.21	0.44	0.52	0.49	0.62	0.48
	p	0.064	<0.01	<0.01	<0.01	<0.01	<0.01
A005	τ	0.081	0.21	0.44	0.26	0.56	0.18
	p	0.50	0.071	<0.01	0.024	<0.01	0.13
A006	τ	0.11	0.32	0.41	0.15	0.36	0.20
	p	0.12	<0.01	<0.01	0.031	<0.01	<0.01
A002	τ	0.20	0.29	0.48	0.42	0.60	0.45
	p	0.098	0.013	<0.01	<0.01	<0.01	<0.01

Table 3
Results of Kendall Rank Correlation test between total concentrations and TSS

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Results of Mann-Whitney-Wilcoxon Rank Sum test as significance of difference (p) are shown in table 4.

Table 4 *Results of Mann-Whitney-Wilcoxon Rank Sum test*

		As	**Cr**	**Cu**	**Fe**	**Pb**	**Zn**
A010	**p**	0.37	0.058	<0.01	0.21	<0.01	0.010
A005	**p**	0.90	0.56	<0.01	0.21	<0.01	0.58
A002	**p**	0.86	0.35	<0.01	0.055	0.37	0.92

The end of the realization of the perimeter dike was used to divide the inlets records into “before” and “after” periods. The realization of the perimeter dike at Vittorio Emanuele III canal was concluded in 2012. The Mann-Whitney-Wilcoxon Rank Sum test showed a significant difference between the period before 2012 and the period after 2012 concerning total concentrations of Zn, Pb and Cu at the inlet A010 record. A significant difference was found for total Pb and total Cu at the A005 inlet located in the Western canal where the perimeter dike had been concluded in 2007. At the A002 inlet located in the Southern canal, where the perimeter dike had been concluded in 2009, a significant difference was detected only for Cu. The perimeter dike for the northern bank of Southern canal was realized before the year 2004.

Heavy metals in coastal areas are closely associated with local economic development (Wang et al., 2013). However, the analysis of trends on long time series have demonstrated that the adoption of environmental regulation with the aim of reducing emissions and changes in human activities could lead to noticeable decrease of the levels of harmful elements in estuarine and coastal marine areas affected by heavy anthropic pressure, even if a time lag exists between the moment that a reduction in the emission of a given pollutant is realized and the decrease of its concentration in the receiving aquatic environment (Gao et al., 2013).

Conclusions

The industrial district of Porto Marghera has recently undergone major transformation such as the implementation of treatment plants, the realization of perimeter dikes on the canal banks and the closing of some facilities. Nevertheless, the contamination of sediments and runoff from canal banks, where the perimeter dike is still not completed or is deteriorated, is of concern.

The time series analysis of suspended solids, arsenic and heavy metals collected in the last decade allows to draw a picture of no trends or decreasing trends. Decreasing trends were detected for Cu, Zn, Cr and Pb, as well as suspended solids. It is noteworthy to point out the positive trend of Fe detected at the inlet located at the southern bank of the Southern industrial canal.

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TENDANCES TEMPORELLES DES TRACES D'ÉLÉMENTS DANS LES EAUX DES CANAUX INDUSTRIELS À PORTO MARGHERA (VENISE, ITALIE)

Resumé

Porto Marghera est un quartier industriel situé dans la lagune de Venise (Italie). L'activité industrielle séculaire a laissé un lourd fardeau environnemental. Les enregistrements de données (2004-2016) des traces de métaux, d'arsenic et de solides en suspension dans les eaux des canaux industriels de Porto Marghera ont été analysés pour connaître les tendances. Des tendances décroissantes ont été détectées pour le Cu, le Zn, le Cr et le Pb, ainsi que pour les solides en suspension. Aucune tendance significative pour As et Cd n'était évidente. Une tendance positive de Fe a été détectée dans un site d'échantillonnage.

Mots-clés: *tendances temporelles, traces d'éléments, lagune de Venise*

ANDAMENTI TEMPORALI DEGLI ELEMENTI IN TRACCE NELLE ACQUE DEI CANALI INDUSTRIALI DI PORTO MARGHERA (VENEZIA, ITALIA)

Riassunto

Porto Marghera è un distretto industriale situato nella laguna di Venezia (Italia) la cui attività industriale lunga un secolo ha lasciato una pesante eredità ambientale. Le serie storiche (2004-2016) delle concentrazioni di metalli in tracce, arsenico e solidi sospesi nelle acque dei canali di Porto Marghera sono state studiate per valutare la presenza di andamenti temporali. Sono stati osservati andamenti decrescenti per Cu, Zn, Cr, Pb e solidi sospesi mentre per As e Cd non sono stati osservati andamenti significativi. In un sito di campionamento è stato riscontrato un andamento crescente per il Fe.

Parole chiave: *andamenti temporali, elementi in tracce, laguna di Venezia*