Occurrence and fate of heavy metals in large wastewater treatment plants treating municipal and industrial wastewaters

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ABSTRACT

This paper deals with a detailed study on the occurrence and fate of heavy metals (plus As, Fe and Al) in five Italian large wastewater treatment plants treating municipal and industrial wastewaters. The study showed that some of the compounds (As, Hg and Cd) were present at trace levels, while others were dispersed in a broad range of concentrations and were sometimes under the detection limit. The occurrence followed the order Hg = As < Hg < Pb < Ni < Cu < Cr < Fe < Zn < Al. Metals were mainly present bound to particulate organic matter in municipal wastewaters while they were often present in soluble phase in industrial wastewaters. Some heavy metals, like Hg and Pb, showed clear correlations with Al and Fe, therefore the last could be used as control parameters. Metals were removed with good efficiency in the treatment works, with the order As < Cd = Cr = Zn < Pb < Hg < Ni = Al < Cu < Fe. Metals then concentrated in waste activated sludge and accumulated after sludge stabilisation because of volatile solids degradation, therefore some problems may arise with limit for agricultural application, in particular for Hg, Cd and Ni.

Key words | characterisation, correlation, industrial wastewater, metals, municipal wastewater, removal

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INTRODUCTION

The implementation of new legislation (e.g., the Water Framework Directive, Sludge Directive, Waste disposal Directive…) may have a major impact on wastewater treatment throughout Europe. In order to assess the potential treatment options required to meet new regulations a detailed understanding of the load and sources of priority substances entering wastewater treatment plants (WWTP) is necessary in order to define possible reduction measures in terms of process configuration. Further, it should be recognised that large wastewater treatment plants generally operate as treatment facilities for a large catchment area; therefore, several type of wastes, like liquid industrial wastes or solid waste in the anaerobic digestion section, enter the plant. As a consequence, a certain amount of different micropollutants, both heavy metals and organic xenobiotic compounds, undergo the wastewater treatment and are removed at different extent: heavy metals are differently adsorbed by activated sludge and removed through excess sludge wasting (Santarsiero *et al.* 1998; Chipasa 2003; Karvelas *et al.* 2003), while organic compounds undergo different removal processes: volatilisation, bioconversion (or biodegradation) and adsorption and wasting (Rogers 1996; Byrns 2001).

Since the dispersion of these compounds in the environment should be avoided because of risks for the whole ecosystem and human health (Gardea-Torresday *et al.* 1996; Karvelas *et al.* 2003), also the European Commission has classified some heavy metals as priority pollutants (see EU Water Framework Directive 2000/60/EC – Annex 10). These compounds can be

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problematic also for the activated sludge processes. Many authors (Madoni *et al.* 1999; Mowat & Bundy 2002; Juliastuti *et al.* 2003; Ren & Frymier 2005) have in fact demonstrated that heavy metals can determine inhibitory effects of both autotrophic and heterotrophic bacteria.

Understanding the behaviour of these compounds inside the activated sludge process is of fundamental importance in order to see and, possibly, predict their final fate. In this paper, which deals with some results of a global study, the presence in wastewaters and the fate after wastewater treatment of heavy metals in five different large Italian WWTPs are discussed. Although large WWTPs are only 20% of Italian plants they treat some 70% of the pollution load and represent the main barrier for pollution dispersion in water bodies. Beside the heavy metals (Cd, Cr, Cu, Pb, Hg, Ni, Zn), also As, a typical contaminant in north Italy, and Fe and Al were determined. The last are easily detected, abundant and can be conveniently used for mass balances.

MATERIALS AND METHODS

Five WWTPs were opportunely selected and monitored in order to describe a scenario as complete as possible. The criteria used for the selection of the treatment systems were the origin of wastewaters collected by the sewers system (municipal or mixed industrial/municipal) and the plant treatment capacities. Therefore, selected WWTPs treated municipal wastewater from 30 to 100% of total inflow. Table 1 summarises the main features concerning the inflows to each WWTP.

The selected WWTPs treated wastewaters with different levels of macro-pollutants: COD ranged between 160 and 650 mg/L depending on the level of infiltration of groundwater. Table 2 shows the yearly average values.

The source of industrial wastewaters for plant A was a chemical-pharmaceutical district. However, also a beer factory is present in the catchment area of the plant, increasing the organic loading in plant A while for plant D was a large petrochemical district.

Analytical methods and sampling

Wastewater sampling was carried out over a period of 18 months. The samples were taken always in the same sections, noting the weather conditions (dry or rainy) to consider the runoff impact. In particular, a simultaneous sampling was carried out by means of two automatic samplers: the first was a vacuum sampler to collect daily composite samples; the second, properly engineered for the experimentation and equipped with an ultrafiltration membrane (ZeeWeed, Zenon, Canada), to collect the soluble fraction and the suspended particulate matter in the influent wastewater. This last device is able to filtrate 350–450 L per day of wastewater. Heavy metals were then determined both in the solid and soluble phase according to the methods established by the Environmental Protection Agency (EPA): in particular, Cd, Cr, Cu, Ni, Pb, Fe, Zn, Al were determined according to method EPA 6010B/96, As according to method EPA 7062/94 and Hg according to method EPA 7471A/94. The instrumental measurement was made with the Atomic Adsorption Spectrometer Varian SpectrAA 220 for the As and Hg samples and with the Inductively Coupled Plasma Atomic Emission Spectrometry Varian Liberty 110 for Cd, Cr, Ni, Pb, Cu, Fe, Zn and Al. The solid phase was determined with the same instruments as the liquid one, but samples were previously mineralised by a microwaves working station (CEM).

Table 1 | Characteristics of the WWTPs selected for this study

Plant	Nominal size	Influent flow, m^3/d	Municipal, %	Industrial, %
A	400,000	25,000	~30	~70
B	70,000	15,000	~100	~0
C	100,000	4,900	~100	~0
D	440,000	118,000	~63	~37
E	80,000	21,000	~94	~6

Table 2 | Conventional pollutants in the influent wastewaters (average over one year monitoring)

Plant	TSS (mg/L)	COD (mg/L)	TN (mg/L)	TP (mg/L)
A	101	371	8	1
B	129	160	13	1.2
C	262	645	37.4	5.65
D	247	346	33	5
E	327	464	47.4	6.2

RESULTS AND DISCUSSION

General characterisation

Thanks to the particular sampling procedure adopted it was possible to determine the metals content in: (a) the raw wastewater; (b) the particulate phase; (c) the soluble (liquid) phase. Table 3 reports the detection limit in total and solid phase and the frequency of occurrence of a given pollutant in the different plants for the soluble and solid samples. From data reported in Table 3 it is evident that the frequency of occurrence for Cu, Fe, Zn and Al in the solid phase was 100% while As, Pb and Cd were sometimes undetectable in both the liquid and the solid phase of samples.

Average values of metals concentrations found in raw global samples (liquid + solid) and relative variation coefficient (100 * Standard Deviation/Average) are reported in Table 4. In the same table also some literature data are reported. From the comparison appears clearly that reported concentrations of these compounds are dispersed in a broad range and results found in this study are perfectly comparable with those data. According to Rule (2006), plumbing system and pipes are the main source for metals in household wastewaters.

Considering plants treating municipal wastewater (B, C and E), it is clear that some heavy metals, like Cd and Hg, are nearly absent while some others, like Cu and Ni, although being at low levels, can show some peak of concentration. Zn is always the most abundant of heavy metals, while Fe and Al are clearly predominant and can be very high (up to mg/L) both in municipal and industrial wastewaters. As, a non metal, is generally present at low level but, because of its toxicity, should be considered with attention. However, it is important to emphasise here that, beside discharging determined by human activities also wastewaters run-off and the geochemical composition of rocks itself can play an important role in the presence of these substances.

Tables 5 and 6 show the concentrations found in suspended solids of the samples obtained from the membrane automatic sampler. The concentrations of heavy metals found in the wastewater, sampling followed the general order Cd < Pb < Cu < Zn < Fe < Al for both the total and solid samples. Similar relative abundances and concentration levels were reported also by other authors (Karvelas *et al.* 2003 and Chipasa 2003). Considering the specific loading (g per person per day) of heavy metals it appears clearly that, although treating municipal wastewaters, plants B, C and E showed very different values except for As, Hg and Pb.

With specific reference to the distribution of heavy metals between the soluble and solid phase in wastewaters, Figure 1 shows the different distribution for municipal and mixed wastewaters, the fractions found out in the different monitored wastewaters. Some metals (Al, Fe) are always bound to the particulate matter, while other heavy metals show a half and half distribution. Hg, Cu and Pb tend to be present in a soluble form in industrial wastewaters.

Generally, in municipal wastewater, metals are mainly associated to the suspended particulate while in industrial

Table 3 | Detection limits, and frequency of occurrence of heavy metals in liquid and solid samples

	Detection limit (d.l.)		Frequency of occurrence (f.o.)									
Metal	TP $\mu g L^{-1}$	SP mg kg SS^{-1}	A TP (%)	A SP (%)	B TP (%)	B SP (%)	C TP (%)	C SP (%)	D TP (%)	D SP (%)	E TP (%)	E SP (%)
As	<1	<2.5	20	100	50	50	0	75	75	100	29	nd
Hg	<0.2	<0.5	80	100	67	100	25	100	75	75	0	nd
Cu	<2.5	<0.5	100	100	67	100	100	100	100	100	100	nd
Pb	<2.5	<0.5	75	100	34	100	100	100	75	75	71	nd
Cd	<0.25	<0.05	20	100	0	100	50	100	50	75	29	nd
Ni	<0.5	<0.1	100	100	100	100	100	100	75	75	100	nd
Cr	<2.5	<0.5	100	100	67	100	100	100	100	75	100	nd
Zn	<50	<10	100	100	100	100	100	75	100	75	100	nd
Fe	<50	<10	100	100	100	100	100	100	100	75	100	nd
Al	<50	<10	100	100	100	50	100	100	100	100	100	nd

Table 4 | Mean and Variation Coefficient (VC) values of the heavy metals in the total sample

Metal	A Average (μg/L) ± Var.Coeff. (%)	B Average (μg/L) ± Var.Coeff. (%)	C Average (μg/L) ± Var.Coeff. (%)	D Average (μg/L) ± Var.Coeff. (%)	E Average (μg/L) ± Var.Coeff. (%)	Ref 1	Ref 2	Ref 3	Ref 4
As	8.8*	4*	n.d.	2.7 (±68%)	6 (±33%)	–	–	–	–
Hg	3.8 (±49%)	1.5 (±58%)	0.7 (±8%)	1.8 (±40%)	n.d.	0.25–5	–	–	–
Cu	32.2 (±19%)	9.9 (±56%)	9.8 (±44%)	38 (±61%)	60.9 (±39%)	5–7	70–270	79	23–61
Pb	6.5 (±29%)	8*	8.6*	2 (±60%)	10.5 (±27%)	–	30–150	39	107–493
Cd	0.4*	n.d.	8.7 (±13%)	27.8 (±62%)	0.6 (±34%)	5–10	5–70	3.3	0.6–1.3
Ni	17 (±75%)	3.5 (±31%)	16.6 (±23%)	61.7 (±4%)	21.6 (±60%)	5–25	–	–	–
Cr	26.2 (±68%)	8.1 (±11%)	56.4 (±24%)	56.4 (±37%)	59.2 (±99%)	30–85	–	40	–
Zn	254 (±42%)	348 (±31%)	1,233 (±20%)	2,411 (±29%)	227 (±37%)	–	250–800	470	550–563
Fe	696 (±20%)	515 (±29%)	361 (±10%)	531 (±30%)	2,391 (±81%)	100–250	–	480	–
Al	399 (±23%)	786 (±46%)	1,940 (±8%)	2,489 (±40%)	2,531 (±54%)	–	–	–	–

* = only one measure over the detection limit; Ref 1, Balmer 2001; Ref 2, Chipasa 2003; Ref 3, Karvelas *et al*. 2003; Ref 4, Gromaire-Mertz *et al*. 1999.

wastewaters the presence of the soluble fraction is more important. This should be considered with attention when designing the pre-treatment steps in WWTP treating municipal or mixed wastewaters. In order to better understand the relation among the different heavy metals, also the correlation matrix for the municipal and the mixed wastewaters was calculated. Tables 7 and 8 report the correlation for municipal and mixed wastewaters.

It was assumed to exist a strong correlation (indicated in bold in the matrix) when the correlation coefficient is some 0.9 or higher. From data reported in Table 7, it is clear that Hg, Cu, Pb, Fe and Al are related directly while Cd and Cr present an inverse correlation with those compounds. Because of their abundance Fe and Al should be used as control parameters for the presence of Cu and Pb while these could be sought only once per month, reducing time and costs for analysis. Other compounds, like As, Ni and Zn, did not show any particular correlation with other metals.

When considering the data for industrial wastewaters (Table 8) the correlation is difficult to be found, probably because of different level of concentrations, type of industrial activities: the number of the correlated compounds is

Table 5 | Mean and Variation Coefficient (VC) values of the heavy metals in the solid phase of samples

Metal	A Average (mg/kgSS) (± Var.Coeff. (%))	B Average (mg/kgSS) (± Var.Coeff. (%))	C Average (mg/kgSS) (± Var.Coeff.(%))	D Average (mg/kgSS) (± Var.Coeff. (%))	E Average (mg/kgSS) (± Var.Coeff. (%))
As	7 (±6%)	5.6 (±52%)	n.d.	2.7 (±16.8)	n.d.
Hg	6.9 (±51%)	2.7 (±48%)	7.7 (±25)	1.8 (±12.2)	n.d.
Cu	1,241 (±2%)	117 (±46%)	43.9 (±13)	38 (±6.1)	213.5
Pb	67.3 (±16%)	34.8 (±25%)	n.d.	2 (±15.5)	37.7
Cd	3.7 (±4%)	1 (±74%)	13.5 (±26)	27.8 (±20.1)	0.6
Ni	124 (±7%)	15.1 (±27%)	23.4 (±20)	61.7 (±21.1)	23.3
Cr	694 (±9%)	21.9 (±39%)	23.9 (±44)	56.4 (±44.7)	95
Zn	7,326 (±56%)	780 (±48%)	19.5 (±26)	2,411 (±66.6)	395
Fe	25,103 (±14%)	4,040 (±36%)	10.4 (±22)	531 (±16.8)	6,386
Al	9,153 (±14%)	8,973 (±25%)	8.1 (±10)	2,489 (±23.7)	8,875

Table 6 | Per capita loadings of heavy metals (in brackets the % of municipal wastewater treated)

Metal		A (70%)	B (0%)	C (0%)	D (37%)	E (6%)
As	mg/PE day	1.2	4.3	n.d.	2.1	4.8
Hg	mg/PE day	2.9	1.2	0.7	1.4	n.d.
Cu	mg/PE day	10.6	8.8	9.8	29.9	48.7
Pb	mg/PE day	2.1	8.6	8.6	1.6	8.4
Cd	mg/PE day	0.1	n.d.	8.7	21.8	0.5
Ni	mg/PE day	5.6	3.8	16.6	48.6	17.3
Cr	mg/PE day	8.6	8.7	56.4	44.3	47.3
Zn	mg/PE day	83.4	373	1,233	1,896.7	181.3
Fe	mg/PE day	228.1	552.3	361.3	417.5	1,912.5
Al	mg/PE day	130.8	842.1	1,940	1,958.2	2,024.9

expected to decrease when the influent heterogeneity increases. Some relation can be found Fe and Cu, Al and Cr and Zn and Zn and Cr, while As showed an inverse correlation with Cr, Zn and Al.

This fact involves that a predictive model is not applicable to these systems where it is desirable the deep knowledge of the industries present in the catchments area.

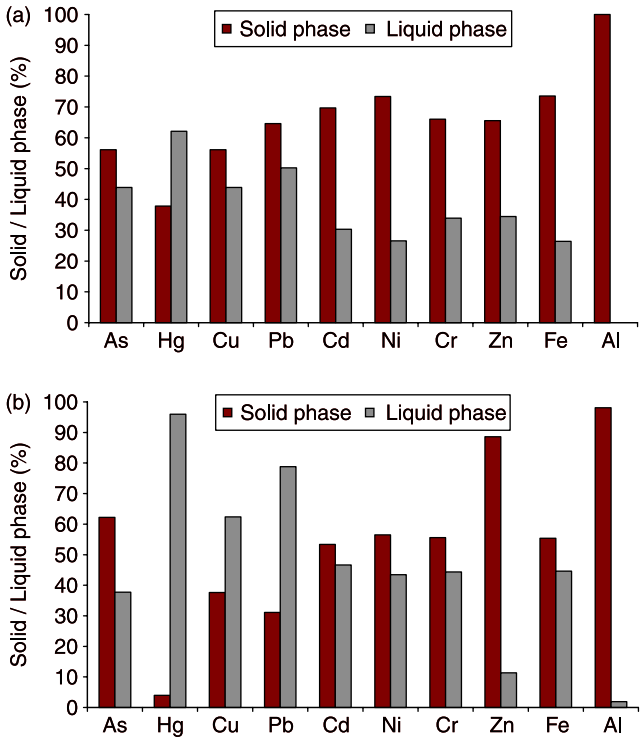

Figure 1 | Solid/liquid partition of the metals in (a) almost municipal and (b) mixed municipal/industrial wastewaters.

With specific reference to the removal efficiency of these micropollutants, the process configuration can play an important role. All the WWTPs studied have conventional pre-treatments at the beginning of the processes, then plants A and E have also primary sedimentation tanks; four of the five plants monitored have conventional activated sludge processes (CASP) followed by secondary sedimentation tanks and one (plant C) has a membrane biological reactor (MBR) where the biological process is controlled according to the Alternate Cycles logic. In order to evaluate the fate and the removal efficiency of metal compounds, strategic samples have been collected always using the same described methods (effluent of the plants and waste sludges). Table 9 shows the effluent concentrations found in this research and the corresponding removal efficiencies. These are then compared with literature data. According to data reported in Table 9 it sounds that heavy metals are, generally, removed with a good efficiency and in complete agreement with previous experiences (Chipasa 2003; Karvelas *et al.* 2003; Kurniawan *et al.* 2006). In particular, the removal efficiency follows the order: As < Cr = Zn < Pb < Hg < Ni = Al < Cu < Fe in good agreement with literature data. Concentrations were often under the detection limit thus not detectable (n.d. in the table). Plant C, which was equipped with an ultrafiltration membrane instead of clarification, showed the best performance in metals removal because of its capability to produce an effluent virtually free from suspended solids (Fatone *et al.* 2005). Further, the activated sludge in the reactor is at greater concentrations, increasing the biosorption capability of the system. As a consequence removal efficiency in membrane bioreactor is greater than the one observed in conventional activated sludge processes. This is true in particular for Al, Fe, Zn, Cu, Hg and Cr removal.

Clearly, removed metals accumulated in activated sludge. Table 10 reports the average concentrations of metals in waste activated sludge.

Metals in sludge accumulated depending on their concentration in the influent; therefore, As, Cd, Hg showed very little concentrations in waste activated sludge, both for WWTPs treating municipal and mixed wastewaters, while Zn, Fe and Al were present in terms of gram per kg.

Waste activated sludge underwent stabilisation by means of anaerobic digestion in all the five WWTPs. Table 11 shows the levels of heavy metals in sludge after the sludge treatment.

Table 7 | Correlation matrix for municipal wastewaters

	As	Hg	Cu	Pb	Cd	Ni	Cr	Zn	Fe	Al
As	**1**									
Hg	0.452	**1**								
Cu	0.321	**0.987**	**1**							
Pb	0.209	**0.961**	**0.982**	**1**						
Cd	−0.415	**−0.976**	**−0.982**	**−0.942**	**1**					
Ni	−0.406	0.087	0.175	0.240	−0.055	**1**				
Cr	−0.471	**−0.889**	**−0.890**	**−0.814**	**0.947**	0.175	**1**			
Zn	−0.676	−0.676	−0.640	−0.523	0.769	0.459	**0.887**	**1**		
Fe	0.024	**0.898**	**0.940**	**0.975**	**−0.884**	0.234	−0.766	−0.430	**1**	
Al	−0.026	**0.879**	**0.931**	**0.969**	**−0.863**	0.340	−0.724	−0.368	**0.993**	**1**

Table 8 | Correlation matrix for mixed (municipal + industrial) wastewaters

	As	Hg	Cu	Pb	Cd	Ni	Cr	Zn	Fe	Al
As	**1**									
Hg	0.379	**1**								
Cu	−0.230	0.052	**1**							
Pb	0.529	0.002	−0.267	**1**						
Cd	−0.566	0.116	0.498	−0.525	**1**					
Ni	−0.559	−0.124	0.248	−0.321	0.767	**1**				
Cr	**−0.857**	−0.566	0.333	−0.664	0.471	0.378	**1**			
Zn	**−0.852**	−0.396	0.636	−0.545	0.634	0.590	**0.817**	**1**		
Fe	−0.385	−0.322	**0.851**	−0.415	0.310	0.202	0.592	0.772	**1**	
Al	**−0.922**	−0.412	0.417	−0.620	0.676	0.720	**0.840**	**0.953**	0.584	**1**

Table 9 | Mean concentration in the effluent (Avg) effluent samples and removal efficiencies (RE)

	A (70%)		B (0%)		C (0%)		D (37%)		E (6%)		Typical
Metal	**Avg (μg/L)**	**RE (%)**	**Avg (μg/L)**	**RE (%)**	**Avg (μg/L)**	**RE (%)**	**Avg (μg/L)**	**RE (%)**	**Avg (μg/L)**	**RE (%)**	**Removals***
As	2.7	60	2.0	60	n.d.	n.d.	1.6	40	4.9	18	
Hg	2	86	0.6	86	0.7	92	1.35	33	n.d.	n.d.	57–92
Cu	20.8	99	13.5	85	5.59	90	15.2	73	15.6	74	54–82
Pb	2.5	78	9.5	77	4.4	74	16.4	73	4.95	53	68–100
Cd	0.25	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	94	n.d.	n.d.	25–74
Ni	11.7	78	3.9	78	2.41	72	7.15	74	1.93	91	43–95
Cr	8.6	57	6.9	57	2.70	72	14.0	63	19.8	67	68–85
Zn	223	90	82.8	93	63	83	325	39	164	28	87–88
Fe	251	89	283	90	130	89	533	78	320	87	67–90
Al	328	44	413	94	209	89	557	78	512	80	70–80

*Chipasa (2003), Karvelas (2003) and Kurniawan *et al.* (2006).

Table 10 | Average concentrations in waste activated sludge samples and variation coefficient (VC)

Metal		A	B	C	D	E
As	mg/kgSS	3*	7*	n.d.	15 ± (42%)	4 ± (35%)
Hg	mg/kgSS	3 ± (52%)	5 ± (96%)	n.d.	35.9*	2 ± (81%)
Cu	mg/kgSS	192 ± (12%)	165 ± (18%)	264*	239 ± (61%)	348 ± (8%)
Pb	mg/kgSS	46 ± (6%)	72 ± (30%)	78*	135 ± (50%)	61 ± (18%)
Cd	mg/kgSS	1 ± (7.5%)	1 ± (57%)	1*	3 ± (50%)	1 ± (49%)
Ni	mg/kgSS	35 ± (8%)	31 ± (40%)	34*	35 ± (67%)	107 ± (45%)
Cr	mg/kgSS	560 ± (9%)	46 ± (56%)	17*	118 ± (56%)	525*
Zn	mg/kgSS	840 ± (4%)	1,408 ± (74%)	716*	2,341 ± (98%)	433 ± (27%)
Fe	mg/kgSS	11,833 ± (6%)	6,267 ± (74)	4,399*	14,511 ± (93%)	9,335 ± (39%)
Al	mg/kgSS	14,069 ± (4%)	13,047 ± (13%)	11,065*	26,447 ± (15%)	15,605 ± (27%)

*Only one sample greater than the detection limit.

Table 11 | Metals contents in the sewage sludge after the anaerobic digestion

Metal		B	C	D	Land Application*	Land Application*
As	mg/kgSS	–	12	40.4	–	–
Hg	mg/kgSS	–	5.1	3.2	16–25	5
Cu	mg/kgSS	196	317	38.9	1,000–1,750	800
Pb	mg/kgSS	56	64.5	3.1	750–1,200	500
Cd	mg/kgSS	1	1.6	6.8	20–40	5
Ni	mg/kgSS	36	25.5	201.2	300–400	200
Cr	mg/kgSS	40	30	310.2	–	800
Zn	mg/kgSS	8,900	946	8,385	2,500–4,000	2,000
Fe	mg/kgSS	1,264	5,980	881	–	–
Al	mg/kgSS	22,362	13,360	28,035	–	–

*EU Directive 86/278/EEC and to the limits expected by 2015.

Because of the anaerobic treatment with consequent reduction of sludge due to transformation of volatile solids into biogas, metals accumulated and concentrations are greater than those found in waste activated sludge (compare Tables 10 and 11).

In the same table also the limits for application in agriculture, according both to the EU Directive 86/278/EEC and to the limits expected by 2015. Considering these limits some problem could eventually arise at 2015 for Hg, Cd, Ni and Zn.

CONCLUSIONS

A detailed characterisation of the metals influent to a selected number of municipal and municipal/industrial Italian wastewater treatment plants was carried out. The following conclusions can be derived from the study:

- most of the heavy metals were present in municipal wastewaters at trace levels except for Zn;
- the occurrence of metals was Hg = As < Hg < Pb < Ni < Cu < Cr < Fe < Zn < Al for both liquid and solid samples;
- metals were mainly present bound to particulate matter in municipal wastewaters while they were present in soluble phase in industrial wastewaters;
- when the source of the pollution is mainly urban, the concentration of metals into the suspended particulate (expressed as $mgkgSS^{-1}$) was almost constant. Otherwise, it is very variable when industrial wastewaters are mixed to the municipals;

- good correlations between the concentrations of different metals are possible only when considering municipal wastewaters. In this case, Hg and Pb were strongly related to Al and Fe, so the last could be used for checking the presence of the two heavy metals;
- metals were effectively removed by WWTPs. Removal efficiency followed the order As < Cr = Zn < Pb < Hg < Ni = Al < Cu < Fe and was in good agreement with literature;
- metals accumulated in waste activated sludge and, after stabilisation, some problems can arise for Hg, Cd and Ni.

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