THE PARADOX OF TIN

Abstract

Italian soil must comply with the quality parameters as defined by the Environmental Framework Decree. There are 92 parameters each one with its unique contamination threshold value. If such values are exceeded then the soil is classified as "potentially contaminated" and a number of actions are imposed upon the polluter or the land owner. Similar regulatory requirements are present elsewhere in Europe and the soil quality criteria are defined based on the substances and land use. The Italian contamination threshold values were defined by the Ministerial Decree 471/99 in 1999, and in 2006 such limits were included in Legislative Decree (D.Lgs.) 152/06 with small modifications, but overlooking the error relative to Tin. This document illustrates the *Paradox of Tin*, the regulatory "error" evident to many in the environmental business, and tries to understand why, since 1999, "cautiously" Italy should be the "potentially" most contaminated country in Italy when it comes to Tin.

Tin

Tin is present in the natural environment via Cassiterite and Stannane, its most widespread minerals, and it is usually present in sedimentary deposits, like clay and limestone between 4 and 6 mg/kg; in sandstone at 1 mg/kg and in magmatic rocks between 0.5 and 3 mg/kg. In peat, Tin be present up to 300 mg/kg. Tin is a metal very much used during the prehistoric and historic periods. In the modern world is used for food packaging, wood anti-vegetative, metal alloys, welding, plastic manufacturing, aerospace industry, pesticides, ceramic and glass manufacturing, dental amalgam, magnetic superconductors, catalyzers, gas sensors and in the textile industry. In its metallic form, Tin is a very stable compound, with little toxicity, whereas in its organic forms (organotin), all man-made and not present naturally in the environment, is highly toxic and instable.

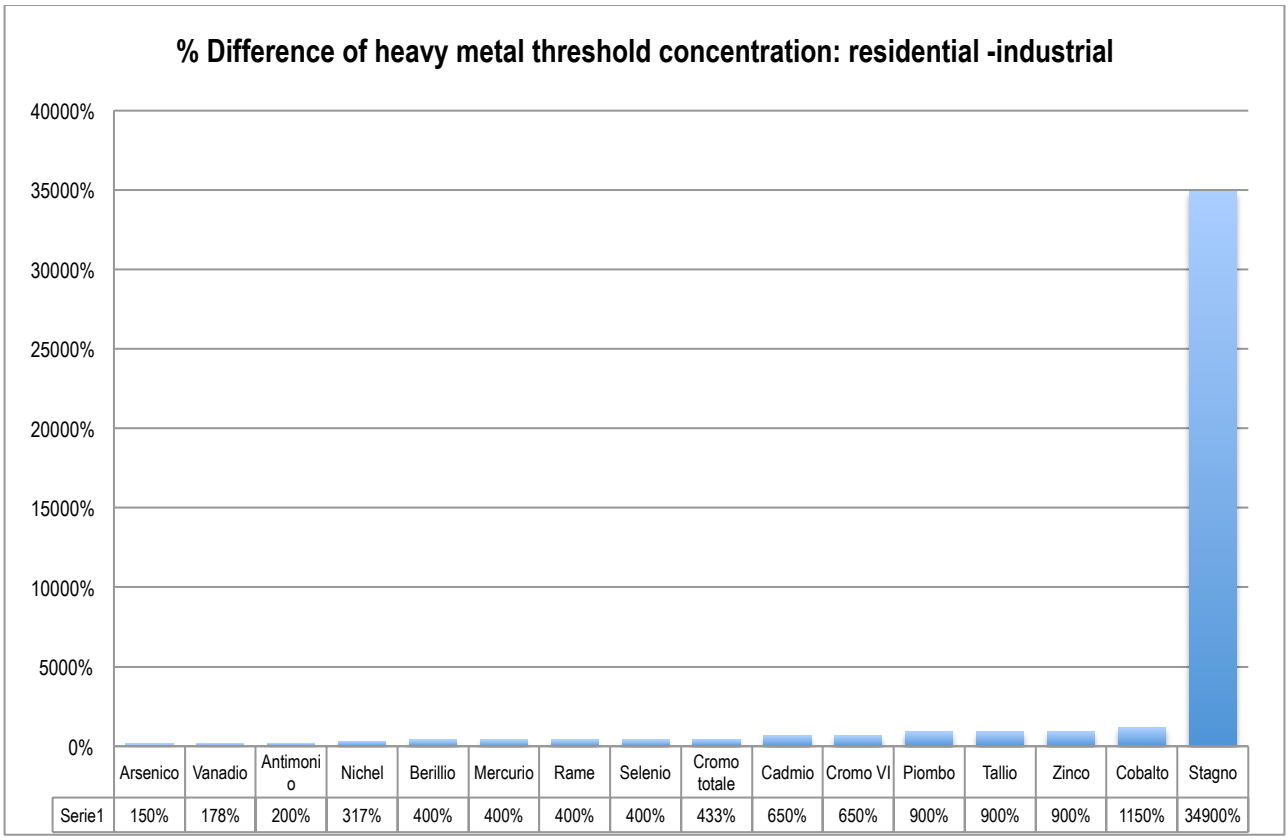
The regulation

The contamination threshold value for Tin in Italian soils has been defined, nation-wide, for the first time by the former Ministerial Decree (DM) 471/99[1], and then by the current Environmental Framework Decree (D.Lgs. 152/06). Both decrees did not modify the contamination threshold value (CSC) for Tin, set at **1 mg/kg** for residential-recreative land use and at **350 mg/kg** for the commercial-industrial land use[2].

Parameters	Residential	Industrial	% Difference between A and B
Arsenic	20	50	150%
Vanadium	90	250	178%
Antimonium	10	30	200%
Nickel	120	500	317%
Beryllium	2	10	400%
Mercury	1	5	400%
Copper	120	600	400%
Selenium	3	15	400%
Total Chromium	150	800	433%

Cadmium	2	15	650%
Chromium VI	2	15	650%
Lead	100	1000	900%
Thallium	1	10	900%
Zinc	150	1500	900%
Cobalt	20	250	1150%
Tin	1	350	34900%

The table shows the relevant difference between the "residential" and the "industrial" concentration for Tin, unique among the metals included in the Decree: the percentage difference between the recreational/private/residential and commercial/industrial according to the formula ((B-A)/B)) x 100 shows the **unjustified anomaly of almost 35,000 percent for Tin between columns A and B**. This anomaly is known to those in the environmental business and best pictured in the graph below:



The reason for this anomaly has not been clarified yet, also considering that Tin, compared against the other heavy metals is not certainly the most "dangerous" one. The 1 mg/kg threshold value anomaly for Tin in residential/recreational land use has been discussed in various occasions by the environmental professionals in Italy, including the Italian Environmental Agency (ARPA), as presented in the coming sections of this document.

EMILIA ROMAGNA

ARPA Emilia Romagna[1] – excerpt from the Proceedings of the "Characterization and Remediation of Contaminated Sites Congress. Ravenna, 20 September 2002" – "…. *following are some observations from the meetings between ARPA and ANPA (National Association of Public Administrations), relative to the implementation of D.M 471/99:* ***the 1 ppm limit for Tin in soil for residential land use is too***

limiting when compared against the natural occurring values (where concentrations often exceed 1 ppm)". Also, already in the Emilia Romagna region Regional Decree (DGR) no. 1183, dated 24 April 1996, providing the Technical Guidelines for contaminated sites remediation, Attachment 4 included soil quality standards obtained comparing the quality standards at the time available from other regulations with the natural background values received from the Provincial Health Agencies. Attachment 4 of DGR 1183 indicated the following limit for Tin in soil: **50 mg/kg (agricultural/residential land use)**, and 300 mg/kg (industrial land use).

PIEDMONT

In 2006 ARPA Piedmont[2], within the environmental monitoring of agrarian-chemical data of organic and inorganic contamination, soil biological quality, indicates that: "*Tin deserves a separate discussion, **inserted in the tables as an element, but in reality dangerous only if present as organotin compounds***". Table 16.4 of the document provides the content of 8 metals examined in Piedmont soils between 2001 and 2005: **of 86 data examined Tin is present with an average concentration of 10.98 mg/kg** (the 10th percentile is equal to **4.95 mg/kg** and the 90th percentile is equal to **20 mg/kg**). The document also clarifies that the Piedmont Regional Law no. 42/2000 provides a threshold value for Tin of **50 mg/kg** for agricultural land use soils. ARPA Piedmont states that: "A separate discussion is necessary for Tin where **the national regulation has a 1 mg/kg threshold value for residential land use; such value is not justified from the metal toxicity standpoint, but seems more likely to derive from an erroneous definition of the toxic compound**, that should have been indicated as organotin compounds and not the Tin molecule. **It is not surprising then, the constant exceeding of the 1 mg/kg threshold value. This should not be cause of concern**, also because the average and almost all of the values identified are well below the Regional threshold limit [50 mg/kg]". In addition, the Regional Council Decree no. 1005-4351 dated 8 March 1995 provided Guidelines for the cleanup of contaminated sites and indicated soil quality standards based on land use: the threshold value for Tin is at **50 mg/kg (residential-agricultural land use)**, and at 300 mg/kg (industrial land use).

TUSCANY

Tuscany Region soil quality criteria were provided within the Remediation Guidelines included in the Tuscany Remediation Plan approved by the Tuscany Regional council in April 1993 and recalled in Regional Law no. 29 dated 12 May 1993. The criteria did not include a threshold value list, using for this purpose the first version of the Piedmont Region compound list. For this reason, in the Tuscany Regional Law, Tin threshold value was **50 mg/kg (residential-agricultural land use)**, and 300 mg/kg (industrial land use). Therefore, the implementation of the national decree, first with former DM 471/1999 and then with D.Lgs. 152/2006, reduced the Tim threshold value from 50 mg/kg to 1 mg/kg in Tuscany as well, causing the "potential" pollution of the largest part of Regional soils.

CAMPANIA

ARPAC Campania [3] - Operative Unit for Contaminated Sites and Remediation, National Priority Sites (SIN) and University of Naples AMRA, show that the natural background values for Tin from locations external to the SIN sites are: "*5 mg/kg (backfill-type soil) and 3 mg/kg (deep soil, sands and pumices)*". The ARPAC data relative to the Acerra Municipality characterization are based upon 264[4] samples examined for Tin, of which only seventeen (17) were below the national regulatory 1 mg/kg threshold value (CSC). The number of regulatory compliant samples would only be 0.06 percent of the total examined samples; within the same investigation campaign **such anomalous percentage has not been reported for any of the other 12 heavy metals assessed**. The data commentary from ARPAC within this assessment study allowed ARPAC Technical Director to state[5]: "*As far as Tin is concerned, the whole territory shows a homogeneous distribution of the threshold exceeding that could be related to the natural composition of soils in the area. In fact, the Acerrana Plain is a reclaimed swamp zone, characterized by peat deposits, justifying the high concentration of Tin present.* ***It should be also pointed out that, as several time discussed during technical meetings among the environmental agencies network, the national threshold value for Tin for residential and park land use*** *[1mg/kg]* ***is likely to be too conservative considering the limited toxicity of this element***".

VENETO

ARPAV Veneto [5] - Soil Protection, Treviso Provincial Department: Metals and Metalloids Background Values in Veneto Soils: "*…. Considering the D.Lgs. 152/06 threshold values for parks and residential land use (Column A) as reference, only Tin presents higher median and mean average, while other elements present their 95th percentile values above the regulatory threshold value."* …. "***The metal that more often exceeds D.Lgs. 152/06 Column A threshold values is Tin, whose almost every shallow sample*** *(96%) and over 80% of the deeper samples is above the threshold value; on the contrary there is no excess of Colum B threshold value (commercial and industrial land use)*". Further on the document clarifies that: "*A separate consideration is required for* ***Tin*** *presenting background values above the threshold limit in all the Veneto physiographic and sedimentary units,* ***with highest values 7 times higher the threshold limit*** *in the Brenta River basin.* ***As far as the Tin threshold limit value in D.Lgs. 152/06 for park and residential land use is concerned, the incongruity respect the natural background value in Veneto soil is evident****.* In the addendum document to the project presented on 5 August 2002 to the Technical Secretariat for the Programmatic Agreement on Porto Marghera chemical area, and relative to the natural background values for soil inland of Venice, ARPAV, Province of Venice and Municipality of Venice proposed the background value for Tin at **6.5 mg/kg**[6].

PUGLIA

On 19 March 2008, ARPA Puglia [7] published a Risk Assessment Study according to the D.Lgs. 152/06 requirements, relative to the Brindisi industrial area. The study indicates that: "***Tin*** *deserves deeper*

considerations. The problems relative to Tin are represented by the threshold value proposed in Attachment 5 to Title V of Part IV of D.Lgs. 152/06 for soil and subsoil. ***The technical agencies involved highlighted that such value are very stringent for park and residential land use (1 mg/kg)****. Such value makes quite difficult to implement adequate remedial actions achieving the 1 mg/kg value and* ***it also causes the fact that the most part of the sites assessed are classified as contaminated****".* The same Study the following considerations are also reported: "*The acceptability/remediation limits precursory to DM 471/99 and taken from foreign countries, in particular The Netherlands, United Kingdom and Canada, on remediation indicate threshold values of* ***50 mg/kg of dry matter for residential/park land use and of 300 mg/kg of dry matter for industrial land use****";* also: "*the limit imposed on Tin in DM 18 February 1984* [Discipline on tin-foiled container welded with lead-tin alloy and other food product containers], *is quite higher compared to what indicated in D.Lgs 152/06.* […] *In fact, Attachment III-C of the 1984 DM is highlighted that in order to be considered apt for use as food container,* ***the concentration of Tin should not exceed 150 mg/kg with a 30 percent tolerance****; EC Regulation no. 242/2004 dated 12 February 2004 relative to the presence of inorganic Tin in foodstuff, established the maximum concentration of inorganic Tin in canned food beverages* ***from a minimum of 50 mg/kg*** *for foodstuff for infants and toddlers* ***up to 200 mg/kg*** *for canned food different from beverages. Also mineral Tin, even if ingested in massive quantities never originated chronic intoxication because it is not absorbed; internationally, threshold values in soil and subsoil are higher or Tin is not even considered as a parameter to monitor (NN)*.

Source	Residential	Industrial
Italy (D.Lgs. 152/2006)	1 mg/kg	350 mg/kg
US EPA (PRGs 1996)	4,600 mg/kg	10,000 mg/kg
Canada	5 mg/kg (agricultural land use cleanup level) 50 mg/kg (residential – park land use cleanup level)	5 mg/kg (investigation level) 300 mg/kg (cleanup level)
The Netherlands	NN (not foreseen)	NN (not foreseen)
Switzerland	NN (not foreseen)	NN (not foreseen)
Germania	NN (not foreseen)	NN (not foreseen)
Svezia	NN (non prevista)	NN (non prevista)
Inghilterra	NN (non prevista)	NN (non prevista)

The limit adopted by D.Lgs. 152/06 is reasonable applicable to organotin compounds, much more toxic than metallic Tin toward the environment and human health".

LOMBARDY

ARPA Lombardia[8] – Within the presentation relative to the Guidelines for Excavated Soil Material, the Manager of the operative section of ARPA Laboratory in Brescia indicates that: "*APAT created a Task Force called "Contaminated Sites Methodologies" made of ARPA, APPA and Territory and Soil National Thematic Center. Up to today, the Task Force engaged to highlight, investigate and evaluate the problems relative to the implementation of DM 471/99 both on the in-situ technical controls aspects*

(sampling, characterization, background values), and on the laboratory technical control aspects (analytical methods, data validation); in addition, other questions were debated ***such as the lack of threshold values concentration for some site-specific substances, the impossibility to technically implement some regulatory threshold values****, the technical interpretation of the Decree*. It also defines one of the problems investigated by the Task Force: "***Tin: the residential/park threshold value adopted (1 mg/kg)****, likely referred to the organotin compounds and not to metallic Tin,* ***is extremely restrictive and cannot be compared against the natural background values identified at national level****".* In addition, the Regional Decree no. 6/17252 dated 1 August 1996 – Contaminated Sites Remediation – indicating the soil quality standards for contaminated sites remediation in Lombardy and published on the Regional Gazette no. 41, 2nd Special Supplement, part 2 dated 10 October 1996, did not even included Tin as a heavy metal compound deserving a threshold value.

LIGURIA

The Liguria Region issued Regional Decree no. 3811 dated 3 October 1997 and Regional Law no. 17 dated 15 May 1997 [Approval of Technical Guidelines for Brownfield Remediation], whose Table 4 provides the soil quality standards based on land planning use. The following limits are provided for Tin: **50 mg/kg (for residential/agricultural land use)**, and 300 mg/kg (industrial land use).

European Commission, General Directorate Joint Research Centre - Ispra (VA)

In 2007, the European Commission, General Directorate Joint Research Centre, Institute for the Environment and Sustainability (*Istituto per l'Ambiente e la Sostenibilità*) of Ispra, Varese, Italy, in its document "Derivation methods of soil screening values in Europe" [EUR 22805-EN, 306 pp.] presenting a revision and evaluation of national procedures for their harmonization, within Paragraph 4.6 [9] already signaled the Italian anomaly relative to Tin, and for the other metals, as shown in the table below, where among various European countries regulating this metal at residential land use, only Italy provides such low threshold value of 1 mg/kg.

Table 4.6. Screening values for potentially unacceptable risk (residential soil-use) for metals and metalloids (mg/kg d.w.).

Legend: Austria (AUT); Belgium Flanders (BE(F)); Belgium Bruxelles (BE(B)), Belgium Walloon (BE(W)); Czech Republic (CZE); Finland (FIN); Italy (ITA); Lithuania (LTU); Netherlands (NLD); Poland (POL); Slovakia (SVK); United Kingdom (UK); Denmark (DNK)

	AUT	BE(F)*	BE(B)	BE(W)	CZE	FIN	ITA	LTU	NLD	POL	SVK	UK	DNK
As	50	110	110	300	70	50	20	10	55	22.5	50	20	20
Ba					1000			600	625	285	2000		
Be					20		2	10	30		30		
Cd	10	6	6	30	20	10	2	3	12	5.5	20	2	5
Co					300	100	20	30	240	45	300		
Cr	250		300	520	500	200	150	100	380	170	800	130	1000
Cu	600	400	400	290	600	150	120	100	190	100	500		1000
Hg	10	15	15	56	10	2	1	1.5	10	4	10	8	3
Pb	500	700	700	700	300	200	100	100	530	150	600	450	400
Mo					100			5	200	25	200		
Ni	140	470	470	300	250	100	120	75	210	75	500		30
Sb	5				40	10	10	10	15				
Se							3	5	100		20	35	
Sn					300		1	10	900	40	300		
Te									600				
Tl	10						1		15				
V					450	150	90	150	250		500		
Zn		1000	1000	710	2500	250	150	300	720	325	3000		1000

**For new contaminants only*

In the ISPRA document the table is commented as follows: "*From the table it is possible to conclude that the maximum and minimum threshold values for residential land use often differ by almost one order of magnitude (antimony, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, vanadium). None of the metals shows a variance much lower than one order of magnitude between the max and min values. A relatively high variance (between 1 and 2 order of magnitude) between the max and min values for the residential land use risk, is present for arsenic, mercury, molybdenum and selenium (5-13 items). With Tin, the difference between the max and min values is in the 900 factor range (6 items). From the table it is possible to say that there is no clear tendency relative to the residential land use threshold values for metals exists, in terms of relatively high or relatively low values, for specific countries.* ***One exception to this is Italy, where the residential land use threshold values are relatively low for many metals****."*

Highest Health Institute (*Istituto Superiore della Sanità* - ISS) and National Workers' Safety Institute (INAIL)

ISS and INAIL are the main Italian technical-scientific supporting agencies in defining the toxicological and carcinogenic parameters of the substances listed in the soil quality criteria Tables within Attachment 5 to D.Lgs. 152/2006. The "ISS-INAIL" database, updated to November 2012[10] includes the following reference dose for ingestion (RdF Ing.) concentration for ingestion of the metals listed in decreasing order of hazardousness.

Parameter	RfD Ing. [mg/kg-day]
Tetraethyle lead	1.00E-07
Thallium	1.00E-05
Metallic Arsenic	3.00E-04
Cobalt	3.00E-04
Tributyl Tin	3.00E-04
Antimony	4.00E-04
Cadmium	5.00E-04
Cyanides (not compl.)	6.00E-04
Vanadium	1.80E-03
Beryllium	2.00E-03
Chromium VI	3.00E-03
Lead Compounds[i]	3.50E-03
Selenium	5.00E-03
Nickel	2.00E-02
Copper	4.00E-02
Fluorides	6.00E-02
Zinc	3.00E-01
Tin	6.00E-01
Total Chromium (III) [ii]	1.5

From a human health perspective, **Tin is among the "least dangerous"** metals, just after Zinc, but its threshold value concentration for residential land use is defined by the law as being 150 times lower than the Zinc one (1 mg/kg < 150 mg/kg). Comparing the RfD with a hazardous metal like Thallium, the values are 5 order of magnitude lower than those of Tin (1.00E-05 < 6.00E-01); to better understand the singularity of this anomaly the percentage difference between the RfD concentrations of the two metals according the formula ((RfD Ing. Tin – RfD Thallium) / RfD Ing. Thallium)) x 100 must be considered. It results a difference of about **6,000,000%**, that is percentage-wise, Tin is six million times less hazardous than Thallium, but the regulation these two metals have the same threshold value in soils: 1 mg/kg (Table A).

In addition, for Tin the ISS-INAIL database does not provide any reference concentration for the inhalation RfD and RfC (*reference concentration*): these are parameters absent also for other substances void of significant risk. Not-negligible concentrations of RfD Inhal. and RfC are instead assigned to other, "more hazardous" metals, such as Nickel: RfD Inhal. (2.57E-05 mg/kg/day) and RfC (9.00E-05 mg/kg/day): but in this case as well the threshold value assigned to Nickel for residential use soil is, inexplicably, 120 time higher than Tin's threshold value: 120 mg/kg > 1 mg/kg. In the most important Italian's toxicological data bank, updated by ISS and INAIL, the parameter Tin is not considered the "most dangerous" metal, but instead is properly differentiated from the organotin compounds (for example, Tributhyl Tin).

i Not included in EC Regulation 1262/08

ii Only Chromium III if Chromium VI can be excluded

End Remarks

It is now several years that the correction of the mere error for Tin, included as item 13 within Table 1A of Attachment 5 to Title V, Part IV of D.Lgs. 152/06 is expected. The singularity of 1 mg/kg limit assigned to Tin for residential land use determines – by law – that all Italian soils are "potentially contaminated" by Tin. Also, this anomaly is not limited to residential land use soils, but it affects also the agricultural land use soils because, lacking the dedicated regulation for agricultural areas indicated at point 15 of Article 17 of former DM 471/1999 and by Article 241 of D.Lgs. 152/06 (so far not issued by the Ministries of Environment, Production and Forestry Policy), the local Administrations are forced to spread the 1 mg/kg limit error to agricultural lands, transforming Italy in the European country potentially more contaminated by Tin. The technical and legal debate deriving from the residential limits implementation to agricultural soils implies long legal proceedings and opposing court rulings[11]. Therefore the technical confrontation could only be wide because it involves the sensitive agriculture sector and the Italian agricultural land value itself, but while waiting for a better regulatory evolution, would it be possible to just correct the "error" after 14 years?

[1] http://www.arpa.emr.it/cms3/documenti/_cerca_doc/siti%20contaminati/ra/ra_conv_atti_siti02camicibis.pdf (ultima visita Giu 2013)
[2] http://www.arpa.piemonte.it/upload/dl/Rapporto_Stato_Ambiente/Rapporto_Stato_Ambiente_2006/cap_16_Suolo.pdf (ultima visita Giu 2013)
[3] http://www.amracenter.com/doc/news/AMRA_Vito_25-02-10.pdf (ultima visita Giu 2013)
[4] http://www.arpacampania.it/files/docs/2008%20marzo_metalli_264_campioni_Acerra.pdf (ultima visita Giu 2013)
[5] http://www.arpa.veneto.it/suolo/docs/documenti/Valori_di_fondo_di_metalli_e_metalloidi_suoli_Veneto.pdf e http://www.regione.veneto.it/NR/rdonlyres/E24522A7-6FDF-432F-B7F4-BCDA728E0D41/0/Addendum_test_cessione.pdf (ultima visita Giu 2013)
[6] http://www.arpa.veneto.it/dapve/docs/rel16_addendum_metalli_suolo_venezia.PDF (ultima visita Giu 2013)
[7] http://www.google.it/url?sa=t&rct=j&q=stagno%20limite%20residenziali&source=web&cd=10&ved=0CFcQFjAJ&url=http%3A%2F%2Fwww.arpa.puglia.it%2Fc%2Fdocument_library%2Fget_file%3Fuuid%3Dd1b67db8-6a5d-4488-b59c-7398034ab0b3%26groupId%3D13879&ei=6-yjTpfHHsXc4QTYsZHUBA&usg=AFQjCNFNznaxqnzzj7rgTgab8mq7r0n77g (ultima visita Giu 2013)
[8] http://www.ancebrescia.it/articoli/_3Presentazione_dott_Gramegna_ARPA.pdf (ultima visita Giu 2013)
[9] http://eusoils.jrc.ec.europa.eu/esdb_archive/eusoils_docs/other/EUR22805.pdf (ultima visita Giu 2013)
[10] http://www.iss.it/iasa/?lang=1&tipo=40 e http://www.iss.it/binary/iasa/cont/Doc_supporto_banca_dati_ISS_INAIL.pdf (ultima visita Giu 2013)