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Differentiation of copper pollution origin: agricultural and urban sources

Différentiation de l'origine des pollutions en cuivre:
caractérisation des sources agricoles et urbaines

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RÉSUMÉ

Le cuivre est un oligo-élément indispensable à la vie mais il peut également être toxique pour l'homme à des doses élevées. Son action biocide sur les algues, les mousses et d'autres microorganismes s'exerce par contre, à des concentrations très faibles. Le cuivre n'est pas biodégradable, il peut s'accumuler et finir par atteindre des niveaux de concentrations dangereux.

Son origine dans les eaux est très diverse, outre les teneurs naturelles provenant principalement des roches et des retombées atmosphériques, son usage par l'homme provoque des rejets dans l'environnement. Ces rejets peuvent être ponctuels (usines, déversoirs d'orage, STEPes...) ou diffus, suite au lessivage par les pluies des sols, routes et toitures.

Sur le canton de Genève, 55% des stations étudiées sont polluées en cuivre c'est-à-dire qu'elles ne satisfont pas aux exigences définies par la loi (Ordonnance fédérale sur la protection des eaux, 1998). Depuis 13 ans les services cantonaux chargés de la surveillance de la qualité des eaux mesurent les polluants métalliques dans les rivières du canton. Ce suivi a permis d'obtenir suffisamment de données (plus de 3000 analyses) pour non seulement établir un diagnostic mais également identifier l'origine des contaminations. Une analyse phénoménologique de type SIG couplée à une approche statistique a permis d'identifier, localiser et caractériser les sources de pollution en cuivre des eaux du canton de Genève. Deux sources principales ont été différenciées: une source urbaine et une source agricole. La pollution en cuivre d'origine urbaine s'accompagne d'une pollution en Zn concomitante (toitures, routes...), ce qui n'est pas le cas des pollutions en cuivre d'origine agricole.

ABSTRACT

Copper is a trace element essential to life, yet, at high doses it can be toxic to humans. At very low concentrations it is biocidal on algae, mosses and other microorganisms. Copper is not biodegradable, it accumulates in the environment and eventually reach hazardous concentrations levels.

Copper origin in the waters is very diverse. In addition to natural origins, mainly from rock weathering and atmospheric deposition, its human use generates releases into the environment. These releases can be punctual (plants, sewer overflows, water treatment plants ...) or diffuse, i.e. the rain washing of land, roads and roofs for instance.

In the Geneva Canton, 55% of the sites studied are polluted by copper, i.e. they do not meet the requirements stipulated by law (Ordonnance fédérale sur la protection des eaux, 1998). For 13 years, the cantonal service in charge of water quality monitoring has been measuring metal pollution in the rivers of the district. This survey has provided sufficient data (over 3,000 measurements) not only to diagnose the contamination but also to identify its source. A phenomenological analysis (GIS-type) coupled to a statistical approach has helped identify, locate and, characterize the sources of copper pollution in the waters in the Geneva Canton. Two main sources have been identified: urban and agricultural. Copper pollution from urban origin is accompanied by concomitant Zn contamination, but not copper pollution from agricultural origin.

KEYWORDS

Aquatic environments, Copper, Characterization of pollution, Pollution sources, Water runoff

Introduction

Copper is a widely used metal employed in many fields: transportation, manufacturing, currency, transportation of electricity, construction (roofing, decoration ..) and agriculture (fungicide, herbicide).

Sources of copper in water are extensive, in addition to natural levels originating from rocks weathering and atmospheric deposition, its use by humans induces environmental releases. These releases can be punctual (factories effluents, sewages,) or diffuse (runoffs from land, roads and roofs (TDC Environmental Report, 2004).

The identification of pollution is a first step, but it is the identification of sources that will allow preventive measures and appropriate management. The issue of urban runoff impact on water systems has become salient, a great deal of attention has been given to the characterisation of the urban sources of pollution and its dynamics at national or European levels (VSA, 2002 ; Thévenot, 2006).

This work aims at developing a practical methodology to discriminate between the potential origins of copper pollution, namely agricultural and urban sources, in order to select suited management tools (adaptation of agricultural practices, treatment of roads runoffs,).

1 METHODS

1.1 Sampling and analysis

In the context of water quality monitoring in the canton of Geneva, instantaneous water samples are taken on a monthly basis and analysed for dissolved metals concentrations in the laboratory.

The sampling sites are distributed along the rivers of the canton of Geneva. Samples are collected in polyethylene bottles previously washed with nitric acid (Suprapur, Merck) 10% v/v and thoroughly rinsed with MillaRo MilliQ water (Millipore). Within hours of collection, samples are filtered (0.45 µm, Millex Durapore, Millipore), acidified with nitric acid 2% v/v (Suprapur, Merck) and stored until analysis.

The analysis are performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) on a VG-PQ2 instrument in standard configuration with a Meinhard nebuliser in semi-quantitative mode.

The accuracy of the measures is estimated using a certified standard: SLRS-4 (NRC). The values of copper and zinc measured ($n = 73$) are $1.83\mu\text{g} / \text{L} \pm 0.12$ for copper and $1.10\mu\text{g} / \text{L} \pm 0.16$ for zinc, the certified values are $1.81\mu\text{g} / \text{L} \pm 0.01$ and $0.93\mu\text{g} / \text{L} \pm 0.10$, respectively. The analytical laboratory is accredited (ISO 17025).

1.2 Data interpretation

The grid in use for assessing metal pollution is divided into 5 classes according to the graduated modular approach recommended by the Confederation of Switzerland (OFEFP, 1998). On the basis of 12 annual samples one determines a quality class according to range of the 80th percentile.

STATE	Cu µg/L	Zn µg/L
Very good	<1	<2.5
Good	1-2	2.5 - 5
Medium	2-3	5- 7.5
Mediocre	3-4	7.5 - 10
Bad	>4	>10

In order to link the observed data to soil uses, we also conducted a GIS spatial analysis of type (geographical information system (ArcGIS)). In complement, we performed a hierarchical statistical analysis (2-step cluster analysis, SPSS) to estimate the significance of our results.

2 RESULTS AND DISCUSSION

2.1 Diagnosis

If we consider the results obtained between 1994 and 2007 (105 sites corresponding to 59 streams), their distribution between the 5 quality grades is presented Figure 1.

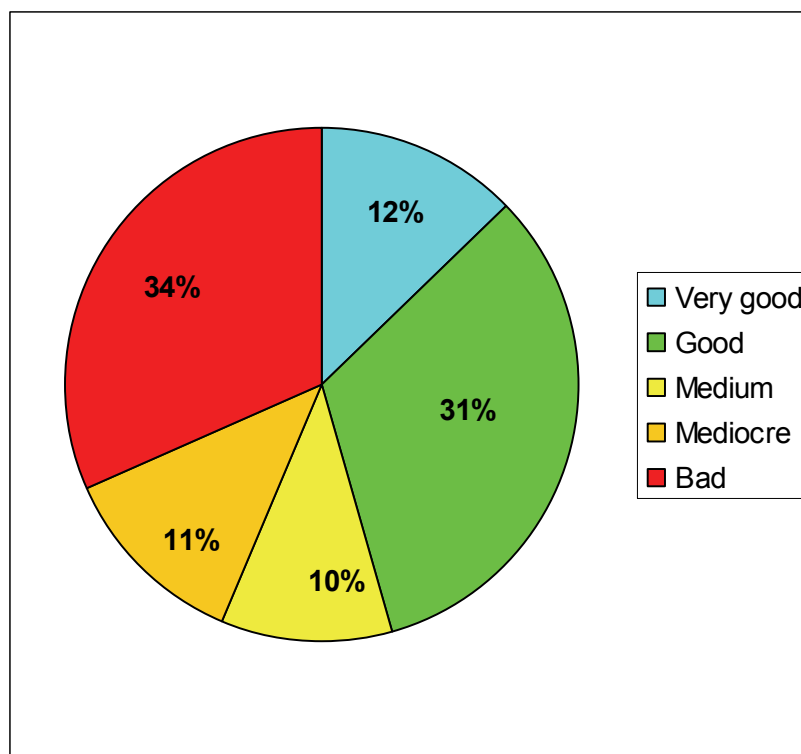


Figure 1: Distribution of sampling sites quality according to copper contamination.

It should be noted that 56% of the stations do not meet the requirement of the Federal regulation for the protection of waters. This is not up to the goal and implies the identification and characterisation of sources in order to implement corrective measures.

Metallic fingerprints have been extensively used to characterise sources contribution to contamination. Some approaches rely on normalisation (Masson et al., 2006), other consider individual or metal groups as tracers (Gounou et al, 2006).

In order to differentiate sources of copper pollution one must identify and characterise them (Thevenot et al. 2007). The main suspected sources are the urban area (roofs, fairway metal and urban settings, and the agricultural zone (particularly vineyards and orchards). Concerning the urban source, one can assume that copper will be accompanied by other metals. Several studies (Gromaire-Mertz et al., 1999; Turer et al. 2001; Hengren et al., 2005; Robert-Sainte et al., 2009) show simultaneous contamination by copper and zinc in urban runoff. In agricultural zones, especially vineyards and orchards, Cu is extensively used as a fungicide (Célarin et al., 1989; Natali, 1994). We then made the hypothesis that the extend of Zn contamination could be used to discriminate between Cu sources.

Zn contamination in our sampling sites is presented Figure 2. Zn distribution between quality classes is very contrasted compared to Cu with "only" 29% of stations not meeting legal the requirements. The dissimilarity between copper and zinc distributions is consequential and shows that zinc contamination in the canton is relatively less problematic than copper contamination. Nevertheless, the distinction between Cu and Zn distributions is compatible with our hypothesis.

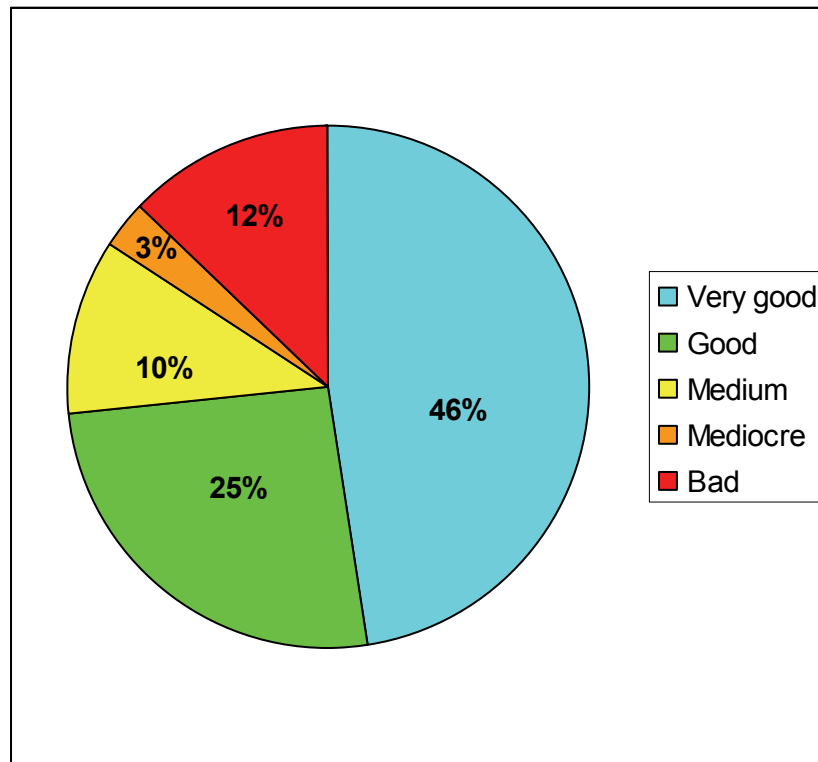


Figure 2: Distribution of sampling sites quality according to zinc contamination.

2.2 Spatial analysis

In order to determine whether there are common sources of copper and zinc (which would confirm the hypothesis of a "cogeneration" in urban areas) and in order to locate them, we will consider the relationship between contamination of copper and zinc in different areas. Our approach consisted in representing the spatial distribution of our combined results according to Cu and Zn concentrations (80th centile of 12 measurements) in regards of soil use (Figure 3).

We observed 4 types of situations:

- both Cu and Zn satisfy the requirements (43 stations out of 101, i.e. 42% of cases, blue dots)
- neither Cu nor Zn satisfy the requirements (24 stations out of 101, i.e. 24% of cases, red dots)
- Cu does not meet the requirement but the Zn does (31 stations out of 101, i.e. 31% of cases, orange dots)
- Cu meets the requirement but Zn does not (3 stations out of 101, i.e. 3% of cases, khaki dots)

The areas meeting the requirements for both Cu and Zn lie on "large" systems, in areas less anthropised as the headwater or the left bank of the Rhone at the exit of the canton - an area mostly occupied by forests.

It appears that some rivers are particularly affected by both Cu and Zn contamination. Most of them are located in urban areas, downstream STPs, industrial zones, and/or in the downstream part of the watercourse. Only 1 stations deviates from this rule, in these case the contamination results from a local contamination (special agricultural activity as identified in Seymaz Report, 2008).

The stations that do not meet the requirements for Cu but do for Zn are located in agricultural area, especially vineyards.

Three sites do not meet the requirements for Zn but do for Cu. Two of them are located downstream a site with cooling towers using a Zn based product, the case of the third site remains unexplained.

This confirms our basic assumption, that in case of urban inputs (roofs, channels, etc.) copper pollution is accompanied by a discharge of zinc ; whereas pollution from agricultural source is characterized by high concentrations of copper and relatively low concentrations of zinc. Then, the simultaneous consideration of 2 contaminants permits to differentiate their sources.

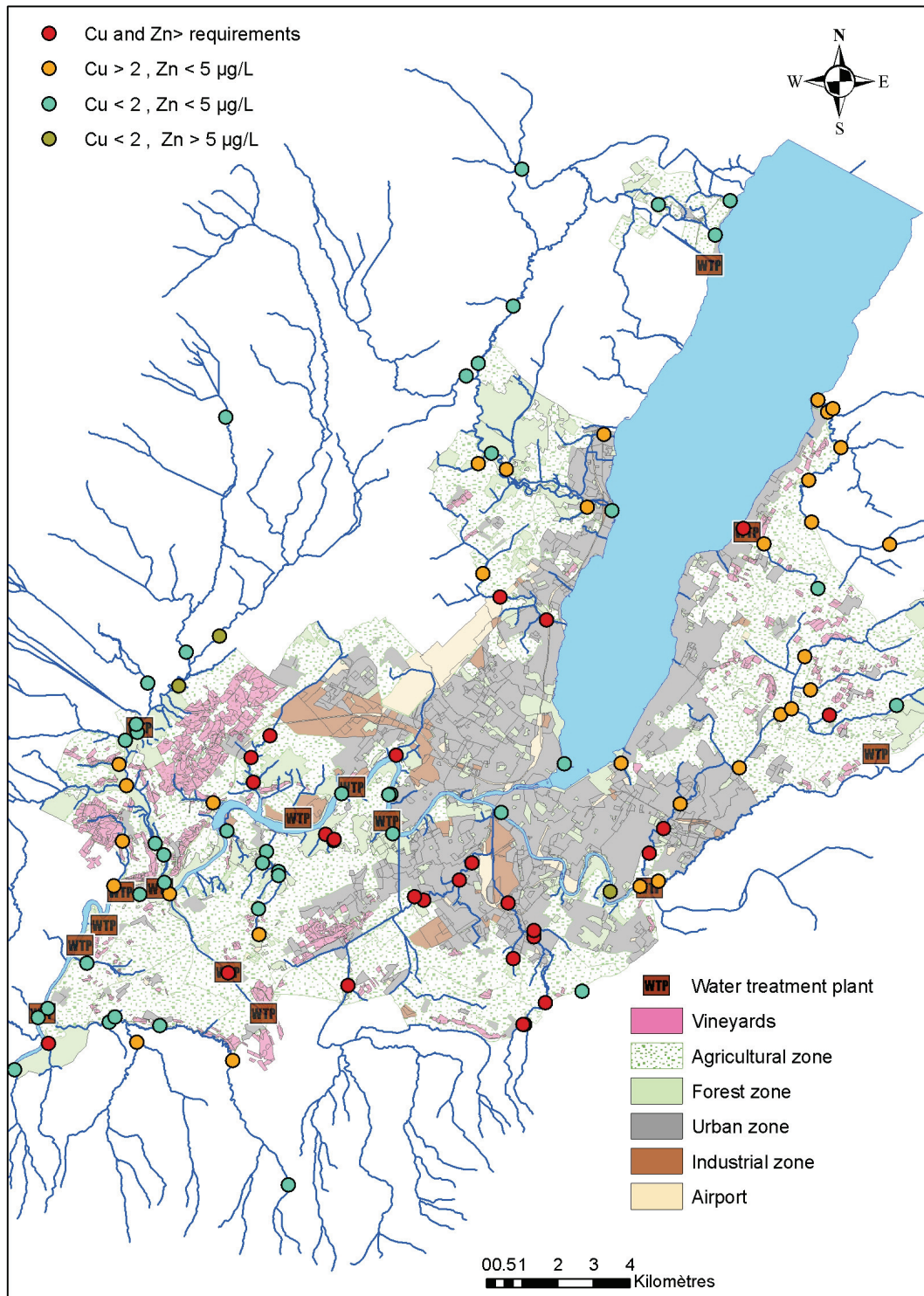


Figure 3: Combined copper and zinc contamination with regard to soil occupation.

2.3 Statistical analysis

To validate our approach, we conducted a hierarchical analysis (2-step cluster analysis, SPSS). This analysis is commonly used to identify groups in a set of data.

To this end, we considered monthly results individually (i.e. 3117 samples), rather than the diagnosis of each station (80th percentile of 12 samples a year) presented before. This method is more detailed than the previous, each analysis being considered individually.

	Urban and industrial zones		Agricultural zones		Other	
	Frequency	%	Frequency	%	Frequency	%
High Cu and Zn	977	93.9	0	0	0	0
Very High Cu and Zn t	64	6.1	6	0.9	4	0.3
High Cu low Zn	0	0	663	99.1	0	0
Low Cu and Zn	0	0	0	0	1384	99.7
Total	1041	100	669	100	1388	100

Table 1: Frequency hierarchical table.

The 2-step cluster analysis highlighted 4 groups:

- a group in which Cu and Zn concentrations are high (averaging $3.78 \mu\text{g/L} \pm 3.81$ and $6.02 \mu\text{g/L} \pm 5.2$ respectively),
- a group in which Cu and Zn concentrations are very high (averaging $28 \mu\text{g/L} \pm 42$ and $45 \mu\text{g/L} \pm 41$ respectively),
- a group in which Cu concentrations are high and Zn concentrations are low (averaging $3.6 \mu\text{g/L} \pm 3.3$ and $2.5 \mu\text{g/L} \pm 2.9$ respectively),
- a group in which concentrations of Cu and Zn are low (averaging $1.3 \mu\text{g/L} \pm 1.8$ and $2.1 \mu\text{g/L} \pm 2.0$ respectively).

Sites contaminated with zinc not with copper are not highlighted because they are not statistically significant as a group in reason of their scarcity (130/3098).

The analysis also permitted to match groups to land use (Table 3) . Their distributions perfectly fits the areas identified by mapping. The 10 cases in which concentrations of copper and zinc are very high outside agricultural areas may correspond to accidental pollution.

These results substantiate and refine the ones obtained with classification map.

The stations contaminated by both Cu and Zn are separated in 2 groups, namely high Cu and Zn and very high Cu and Zn. This graduation does not improves the determination of the sources but highlights the severity of damage.

3 CONCLUSIONS

The extend of copper pollution in rivers of Geneva District has been evidenced. A phenomenological approach combining GIS-analysis and statistical analysis has helped identify, locate and characterize sources of copper pollution.

Two main sources have been recognized : one urban the other agricultural. Copper pollution from urban origin is accompanied by Zn contamination. This is not the case of copper pollution originating from agricultural practices.

This approach can help to determine the origins of chronic pollution in order to implement appropriated measures of correction:

- in urban zones, it is necessary to strictly apply the recommendations for the qualitative treatment of runoff waters (VSA, 2002; STORM VSA, 2007),
- in agricultural areas a reasoned approach for using copper based products has to be developed. National plans are underway to find tracks in order to reduce the impact of agricultural practices on river water quality. However, memory effect from historical contributions could well delay an improvement of water quality (Célarin et al . 1989).

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