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Monitoring metal ions present in the effluent discharged from a surface treatment plant: Analytical results

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ABSTRACT

Precise data concerning the metals occurring in industrial discharge water from the surface treatment sector as well as their qualitative and quantitative fluctuations have to our knowledge never been reported. In the present study, we monitored 28 metals in the effluent from a surface treatment plant every week for about a year. The effluent studied was taken at the outlet of a depollution plant that removed a large proportion of the metals as insoluble forms. We report and discuss the analytical results obtained on a total of 49 samples. The results, expressed both as concentrations and as fluxes, showed high levels of polymetallic contamination of the effluent. Of the 28 metals tested for, 13 were detected and 6 (Co, Cr, Fe, Mn, Ni, and Zn) were systematically present at quantifiable levels. Our findings also indicated how Cr, Fe, Ni and Zn levels were strongly dependent on certain conditions prevailing at the inlet of the wastewater treatment unit. Even though the levels of each metal were under the regulatory limits when taken individually, overall pollution from metals was far from negligible, with a calculated total of 264 kg of metals being discharged each year.

1. Introduction

The current European policy on water results from the Water Framework Directive (WFD) of 2000 [1], which establishes guidelines for the protection of surface water, underground water and coastal water in Europe. The main objective of the WFD is to maintain or restore the quality of water in Europe with the aim of reaching good chemical and ecological conditions, before a deadline set for 2015, by controlling the effects brought about by human activity [2–4]. The WFD of 2000 was adapted to the different European member states, and was followed up by other directives, notably that of 2006 concerning dangerous substances (Directive 2006/11/EC). In France, the WFD was incorporated into French legislation by a law passed on 21 April 2004 [4]. Among the numerous actions that took place following this law, was the campaign known as "Monitoring and Reduction of Substances present in Water" (or in French: "Recherche et réduction des substances présentes dans l'eau"; circular dated 7 May 2007). As part of this national campaign, a list was set up of the substances to be monitored in the aim of reducing their presence or suppressing them completely. There were two categories of unwanted substances: priority substances (PS) presenting a significant risk for the environment, and dangerous priority substances (DPS) considered to be persistent, highly toxic or to lead to bioaccumulation [2,4]. The selection of priority substances can either be based on individual substances or families of substances (metals, chlorobenzenes, anilines, alkylphenols, etc), or on the basis of the industrial site or sector (agro-food industry, chemicals industry, etc). In France, 50 substances are concerned and

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have been divided into four main categories (DPS list, PS list, list I and list II) each with their own national objectives of reduction and/or elimination. Of these 50 substances, 41 (13 DPS + 20 PS + 8 S) give information on the chemical state of the water, and certain metal ions and their derivatives, such as the DPS Hg and Cd (objective of 50% reduction by 2015 and total elimination from discharge water by 2021–2028) and the PSs Ni and Pb (objective: 30% reduction by 2015). Eight major metals, namely As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn, are a particular focus of attention in that they are used in the calculation of an indicator known as the metox index (for toxic metals) which is used to quantify certain toxic forms of pollution. It is an officially recognized index developed by the French Water Authority, a public organization involved in actions to counter pollution, and is used to calculate the taxes that certain high-risk installations (those susceptible of becoming a serious threat, causing pollution or other treats to the environment) must then pay to the Water Authority.

The human origins of the metals present in the environment are diverse [4]. They arise either from localized urban or industrial discharges or from dispersed sources such as transport or spreading on agricultural land. Many industries are concerned by the issue of metal release [5–8]. We can mention waste incineration, fossil fuel power plants, the timber industry, wine production, the plastics industry, paper or cardboard pulp manufacturers, the glass industry, surface-finishing installations and the steel industry. The presence of metals in wastewater can be accounted for either by their direct use during various industrial processes or by their presence in chemical reagents and/or related materials commonly used in the various activities of the factories producing the effluent. Since the end of the 1970s, industry, and particularly the surface treatment or surface-finishing sector (ST sector) that is widespread across France and the whole of Europe, has made a serious effort to limit its impact on aquatic environments [7,8]. In spite of the considerable improvements made in decontamination, this sector of industry still has a poor image [9–11]. Even though industrial wastewater respects current legislation, the effluent from ST plants, which is decontaminated using physical and chemical approaches, still contains a non-negligible load of metals that can be a cause for concern [12–14]. The metals make their way to the rivers, either by direct discharge or indirectly passing first by municipal wastewater treatment plants.

As far as we are aware, no studies have been devoted to determining the precise levels of the metals contained in ST effluent and its variability both quantitative and qualitative. It is in this context that we monitored 28 metals in the discharge from a surface-finishing plant. The discharge was taken at the outlet of a decontamination setup based on a process to render the metals insoluble. The present study reports and discusses the analytical results of a one-year follow up. The values are expressed both as concentrations and as total fluxes, to facilitate comparison with the limits laid down by the law.

2. Experimental

2.1. Industrial site

The study was carried out in collaboration with Galvanoplast (Les Aynans, France), a company specialised in chemical surface treatment of parts mainly for the automotive and building industries. During the different stages of treatment of the parts (mainly galvanization and flake coating) several metal species are released in the process water. This wastewater can be more dilute as in rinsing water, or more concentrated as in the bath solutions varying the load of pollutants released. Spent process water, i.e. rinse water and baths of the same type are stored together making 4 broad categories of effluent depending on their chemical composition: acido-basic effluent, chromic effluent, Zn and Ni effluent and concentrated acid effluent. These effluents, which are mainly polluted with Zn, Ni and Cr(VI), are the main issues to be dealt with by the industry. They are sent to a precipitation decontamination plant working with a continuous process. Only two categories of wastewater receive specific pre-treatment: chromic effluent undergoes a dechromatation step (reduction of Cr(VI) to Cr(III) by sodium bisulphite) and Zn–Ni baths are decomplexed by treatment with hypochlorite (bleach). The effluents are then known as pre-treated and decomplexed effluents. Note that chromic decomplexation effluent (containing mainly Cr(III) and Co) and decomplexed effluent (containing mainly Zn, Ni, and F) are not sent to the main treatment part at the same time, at least a day is left between processing these two types of effluent. All the water is then treated by metal sulphide precipitation and the resulting purified water, termed discharge water, is directed straight into the river.

2.2. Industrial discharge

To carry out our monitoring programme, every week we sampled the discharge characteristic of a day's work. Overall, the metal composition of 49 effluent samples was determined over a 1-year period. To respect the standards laid down by the local authorities (Table 1), the ST plant is required to carry out regular analyses of its discharge: levels of Cr(VI), Ni and Zn must be tested daily and three other metals, Cr(III), Cu and Fe, weekly. Each of the aliquots for analysis came from a sample characteristic of a day's work in the plant. The results for these 6 metals are expressed as mean daily concentration (MDC in $mg{\cdot}L^{-1}$) and as maximum daily flux (MDF in $g{\cdot}day^{-1}$) calculated knowing that the flow of purified water at the discharge outlet is 192 m^3 per day.

2.3. Assaying the metals

The metals (Ag, Al, As, Ba, Cd, Co, Cu, Cr, Cr(VI), Fe, Hg, Li, Mn, Mo, Ni, Pb, Pd, Pt, Sb, Se, Sn, Sr, Te, Tl, Ti, V, W, and Zn) were assayed by a certified laboratory following a standard protocol using an ICP-AES instrument [13]. The results are expressed in $\mu g{\cdot}L^{-1}$. The pH was measured using a portable pH meter (model 3110 WTW, Alès, France) and