

SPECIATION AND REMOVAL OF TRACE ELEMENT CARRIERS IN COMBINED SEWER OVERFLOWS

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Abstract. This study is about (i) the nature of trace element carriers contained in combined sewer overflows (CSO), and (ii) the optimization of CSO coagulation with ferric chloride and WAC HB. Electron microscopy coupled with energy –dispersive X-ray spectroscopy, revealed that several sources contribute to CSO pollution: road run-off, soil run-off, and resuspension of sewer deposits. The investigation of CSO treatment indicates that good heavy removal is attained at optimal coagulant concentration defined from turbidity removal. A linear correlation between initial effluent conductivity and optimal coagulant concentration is also evidenced that enables coagulant adjustment as a function of time.

Key Words : Urban pollution, urban flush, sewer flow, coagulation, pollutant speciation.

Introduction

In urban environment, rain generally falls on impervious surfaces. Runoff is most often collected by the combined sewer system. During storm events, to avoid floods in the lower parts of the city and to protect the wastewater treatment plant, combined sewer overflows (CSO) are directly discharged in the natural environment. The impact of such discharges on the receiving natural system is nowadays a major concern in environmental protection as the amount of pollutants released from CSO within one storm event may exceed annual discharges from factories and sewage plants.

The aim of this study was (i) to investigate the nature of trace element carriers contained in CSO by TEM-EDX electron diffraction and SEM-EDX, (ii) to define optimized coagulation-flocculation conditions to remove heavy metals from CSO during storm events. This work is a part of a more extensive program granted by the “Grand Nancy Urban Community” (Elsamrani et al., 2004a,b).

Experimental section

Study Site. Samples of CSO were collected from the sewer pipe "Liberation", up-stream Boudonville detention basin. Boudonville watershed lies in the north west part of the city of Nancy (France) on the left bank of Meurthe river. The catchment area receives runoff from 246 ha of urban surfaces, both residential and commercial areas (~ 20 000 inhabitants). Samples, taken from the sewer using either a 1L chemo-sampler (Fisher Scientific) or a peristaltic pump (Delasco - flow rate = 5L/min), were collected in 10 L polyethylene jerrycans, transported to the laboratory and processed within one hour after sampling.

Trace element speciation. CSO samples were settled for 2 hours to yield a "suspended" and a "sediment" fraction which were then freeze-dried. Electron microscopy observations were performed with a Philips CM20 TEM (200 kV) coupled with an EDAX energy dispersed X-ray spectrometer (EDX), and with a S-2500 Hitachi SEM equipped with a Kevex 4850-S EDS. Trace element carriers were identified from the elemental analysis of individual particles. For TEM imaging and microanalysis, the sample was resuspended in ethanol under ultrasonication, and a drop of suspension was evaporated on a carbon-coated copper grid. Samples for SEM-EDX examination were sprinkled onto 2 cm² plates and carbon coated.

Jar-test procedure. A rapid physico-chemical characterization of CSO was first carried out with the determination of Suspended matter, effluent turbidity, pH, conductivity, total alkalinity,... Two commercial coagulants, CLARFER (ferric chloride 38%wt) and WAC HB (aluminum chlorosulfate 8.5 %wt), graciously provided by ATOCHEM, were used for the physical treatment of CSO. Coagulation-flocculation experiments were conducted in standard 1 L reactors of known energy dissipation characteristics. Stirring was maintained at 100 rpm ($G = 135 \text{ s}^{-1}$) for 20 min. The coagulated suspensions were then settled in Imhoff cones for 30 min before measuring supernatant turbidity. Heavy metal concentrations were determined by ICP-MS after filtration at $0.2 \mu\text{m}$.

Results and discussion

Trace element speciation.

Heavy metal carriers identified in sewage can be divided into two main categories : particles with an anthropic origin and neoformed mineral species. The first category includes alloys such as stainless steel (Fe, Ni, Cr) or PbSn (used for soldering in zinc works). Zeolitic minerals, iron oxyhydroxides and clay particles (kaolinite mainly) are also observed in the sewer system but do not appear to represent significant heavy metal carriers. The second category of neoformed species involves mainly sulfide species (simple Zn, Fe or Pb sulfides and double Zn-Fe and Cu-Fe sulfides) but phosphate minerals (anapaite, whitlockite, apatite,...) in which zinc atoms are substituted in the lattice are also frequently detected. The existence of such sulfides can be linked to the presence of anoxic conditions in stagnant portions of the sewer system.

Electron microscopy observations carried out on particles sampled during storm events allow to distinguish various sources of heavy metal carriers. Flushing of urban surfaces can be associated with the presence of bitumen particles and of solids derived from the corrosion and wearing of motor vehicles (barite from automobile brakes, W-Cr-Co carbide particles used as anti-corrosive metal coatings, rare earth oxides from catalytic exhaust pipes). Sulfide species are also commonly encountered and SEM microanalyses reveal that the evolution of their abundance closely follows the flow-rate dynamics. This would agree with a pattern of sediment resuspension and redeposition as flow rate changes in the combined sewer during the rain event. Contribution from soil run-off can be evidenced from the presence of clay particles as well as of weathering resistant minerals such as rare earth phosphates and zircons.

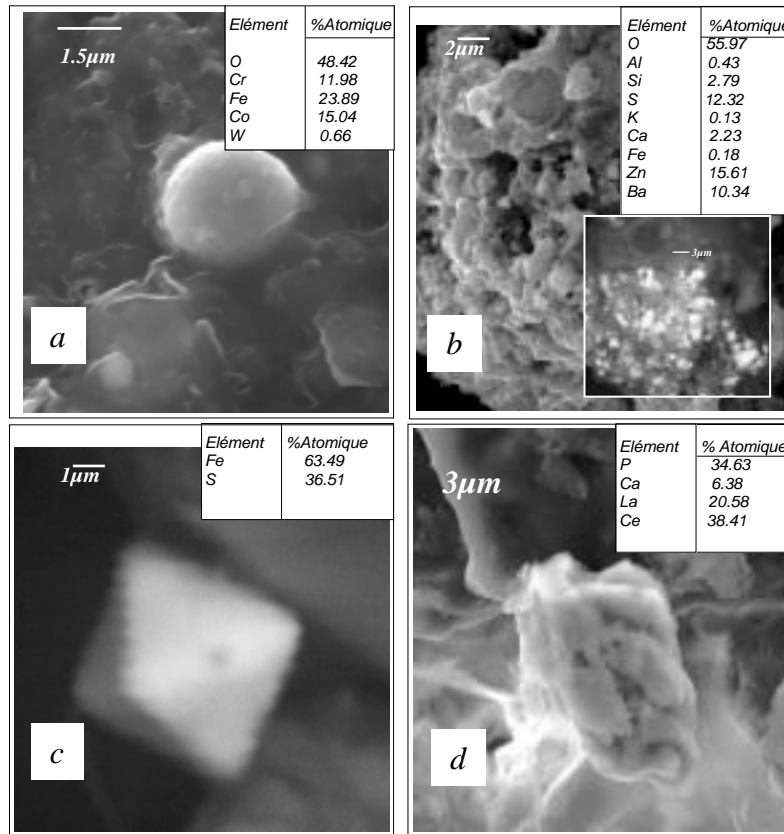


Figure 1. Typical examples of particles of anthropic origin, neoformed minerals, natural particles illustrating runoff of soils (d), urban surfaces (a), and sewer deposits (b,c).

Coagulation-flocculation experiments.

Jar tests show that the optimal coagulant concentration (OCC) defined from residual turbidity measurements corresponds to the dosage required for an efficient removal of heavy metals in combined sewer overflows. Detailed investigations indicate that trace elements in the dissolved fraction are removed before the OCC is reached. This suggests that dissolved heavy metals are trapped within coagulant species formed upon hydrolysis of CLARFER and WAC HB. Heavy metal associated with solid particles are eliminated simultaneously with the turbidity (Zn, Cu, and Pb). An exception to this rule can be found for Cr which is removed at coagulant concentrations higher than the OCC due to its association with dissolved organic matter and iron oxihydroxides.

In any case, a satisfactory elimination of heavy metals can be achieved for coagulant concentrations close to the OCC determined from turbidity removal. However, as the physicochemical characteristics of combined sewer overflows constantly evolves with time, defining the OCC can be a rather difficult task. Indeed, an OCC at a given time can provoke restabilization a few minutes later. It is therefore important to try to provide the operators with an easily determinable parameter allowing an on-line adjustment of coagulant dosage. As shown in figure 2, OCC loosely depends on effluent turbidity and suspended matter whereas total alkalinity is linearly correlated with OCC.

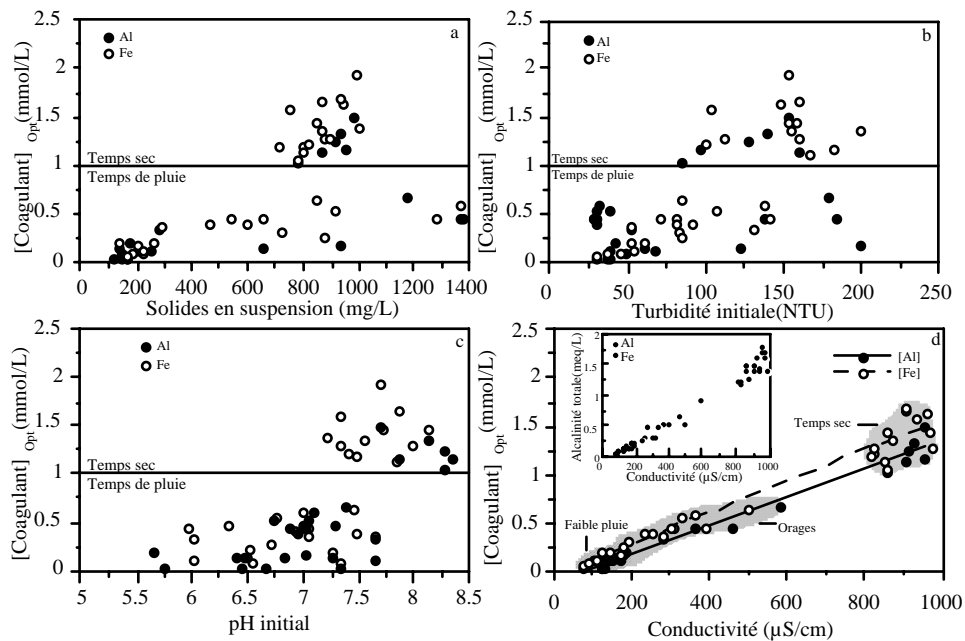


Figure 2. Evolution of the OCC in Clarfer and WAC-HB as a function of (a) suspended matter, (b) effluent turbidity, (c) pH (d) conductivity, during dry weather and storm events.

Acknowledgments: The financial support provided by Grand Nancy Urban Community is gratefully acknowledged. The authors wish to express their sincere thanks to Patrice Robaine and his staff for technical support.

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