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Graphical abstract to the paper **"Optimization of the water treatment process in an Italian winery: a case study"**

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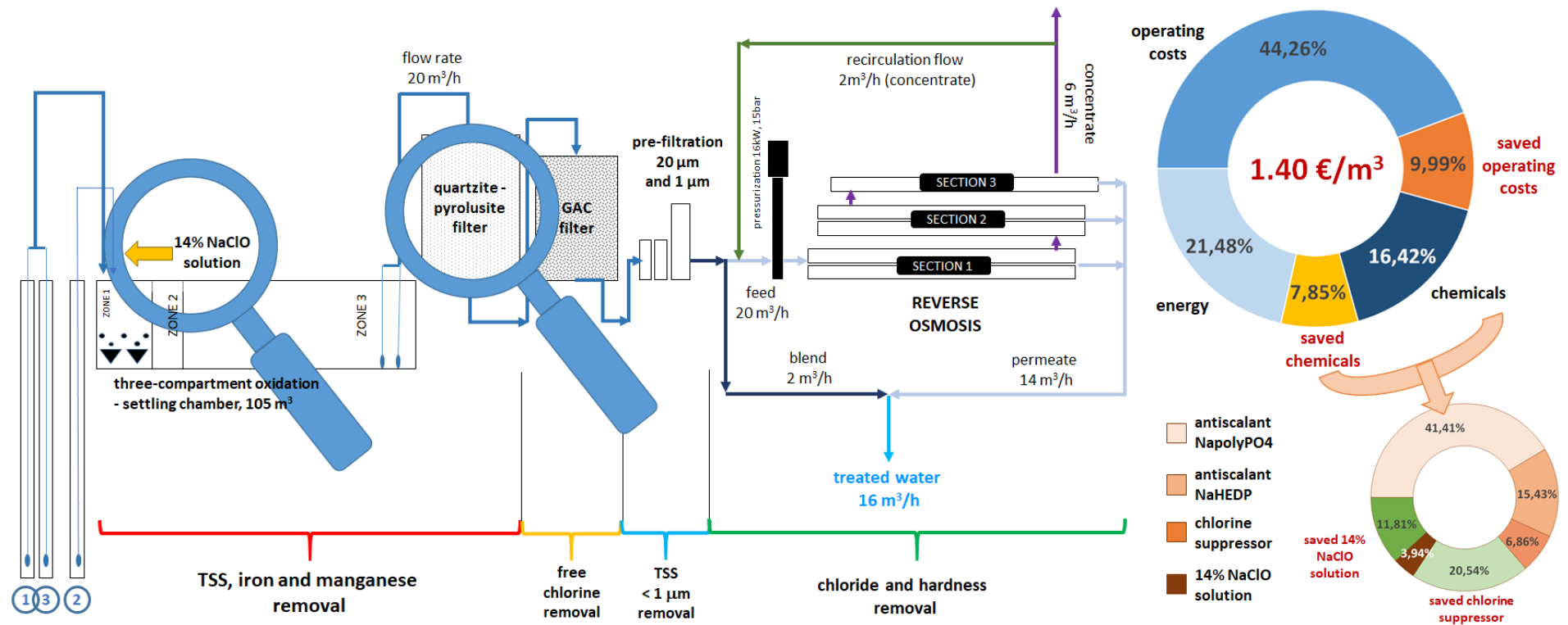
1 **Optimization of the water treatment process in an Italian winery: a case**

2 **study**

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Abstract

Water is an essential ingredient in wine production. The winery plant considered in this study, located in the Langhe area (Piedmont, NW Italy), used approx. 100,000 m^3 per year of high quality water for cleaning and sanitation operations. Water was collected from the local shallow aquifer and contained high concentrations of dissolved iron (Fe(II), 800 – 3,500 µg/L) and manganese (Mn(II), 300 – 700 µg/L). The water treatment plant (WTP) owned by the winery included a series of treatment processes (air sparging and sodium hypochlorite injection, settling, filtration on a quartzite – pyrolusite filter, removal of excess chlorine with an activated carbon filter and, finally, microfiltration and reverse osmosis, RO) that were deemed to be adequate to make the groundwater compliant with potable uses. However, a survey carried out by the authors revealed the presence of two critical issues in the WTP's management, concerning the Fe(II) and Mn(II) oxidation and removal, and the backwashing of the dual media filter. Firstly, the results of pilot tests demonstrated that the process of air sparging was sufficient for the oxidation of iron and that NaClO was not necessary for that operation. The present concentration of pure oxidant, of 21.5 mg NaClO/L, could be reduced by at least 75%, without altering the capacity of the WTP in the removal of the two metals. Secondly, a new combination of water fluxes could improve the efficiency of the dual media filter backwashing, thus allowing to simultaneously avoid the use of the RO corrosive concentrate and to minimize the use of high quality water.

In the end, a very basic cost model was used to compare the unit cost for water treatment in the current scenario and after the introduction of the two proposed solutions. Specifically, that model considered three cost items: operating costs (that included four sub-items: mortgage, maintenance, consulting and cost for non-amortizable raw materials and consumable), the costs for the purchase of the chemicals necessary for the water treatment process, and the energy costs. The results coming from the application of the cost model demonstrated that the introduction of the proposed solutions into the WTP, at no

49   additional costs, had an undeniable positive impact on the final unit cost of the treated water, that was

50   reduced by 20%.

51

52   **Keywords**: groundwater treatment; iron/manganese oxidation; dual media filtration; air sparging;

53   treatment cost; energy consumption

1. Introduction

The Langhe, a hilly area located in the Piedmont region (NW Italy), is well known for the production of wines and sparkling wines, appreciated all over the world. That area was inscribed on the UNESCO's World Heritage list in 2014. Even because of the recognized value of such an area, great efforts are necessary to enhance the environmental sustainability of the wines' production processes.

Water, other than a precious natural resource for the survival and well-being of humans and the ecosystem, is an essential ingredient in wine production. In fact, it must support grape-vine grown and fructification in the field, and cleaning and sanitation processes of bottles and pieces of equipment in the winery. Recent studies have revealed that the water footprint of wine was in the order of 800 liters of waters/ L of wine [1]. That value came from both agricultural operations and winery processes; for the latter ones, it was reported that the production of 1 liter of wine required 6 liters of water, with estimates that varied from as little as 2 liters up to 20 liters [2-3]. Consequently, even in a winery, an efficient and rationale usage of water is of primary concern to achieve a high degree of sustainability for wines' production processes.

In most cases, the water used for cleaning and sanitation processes in a winery comes from a dedicated water treatment plant (WTP), that collects raw water from the local deep or superficial water sources and makes it suitable for the winery operations. In the case of the wine factory considered in this study, the raw water came from a shallow aquifer and contained concentrations of dissolved iron, Fe(II), and manganese, Mn(II), such high as to make it unsuitable for cleaning and sanitation processes, according to the Italian regulation concerning the water intended for human consumption (D.Lgs. 31/01). In fact, the concentration ranges of iron and manganese, in the raw groundwater used by the winery, were 800 – 3,500 µg/L and 300 – 700 µg/L, respectively, with respect to the threshold values of 200 µg/L, for iron, and 50 µg/L, for manganese, fixed by D.Lgs 31/01. Iron and manganese are quite widespread in most of the Italian groundwaters [4], both in the Langhe area and outside of the Piedmont region [5-6].

78 Iron and manganese in waters have been recognized as the cause of aesthetic and operating issues, such

79 as discoloration of water, staining of laundry and plumbing fixtures, metallic taste and odor, and scaling

80 of pipes [7]. Furthermore, recent studies reported that a manganese intake from water ingestion, even at

81 low levels, may lead to intellectual impairment in children [8] as well as other neurological disorders [9].

82 Ferrous iron can be oxidized quickly by oxygen under controlled conditions, particularly at alkaline pH.

83 Only occasionally, Fe(II) is complexed by natural organic matter (NOM) to the degree that oxygen is

84 unable to oxidize it in a reasonable time [10]. After oxidation, iron can be separated from water through

85 settling or granular media filtration [11].

86 Conversely, the conventional oxidation of Mn(II) through oxygen is very scarcely effective and the use

87 of free chlorine or other stronger oxidants presents a series of drawbacks: (i) free chlorine, even at pH

88 values of 8.0 or higher, required several hours of contact (and, consequently, large volume reactors) to

89 oxidize Mn(II); (ii) the oxidation efficiency of stronger oxidants, such as ozone or potassium

90 permanganate, depends on a series of factors, namely pH, temperature, initial dissolved manganese

91 concentration, contact time and presence of NOM; (iii) the presence of high concentrations of NOM

92 could cause pink water generation when potassium permanganate is used; (iv) the oxidation of Mn(II)

93 could form stabilized colloids, with a high negative charge, that are difficult to be separated by granular

94 filtration, but that could severely foul microfiltration or ultrafiltration membranes [12]. For all the above

95 listed reasons, specific treatments are required for the removal of Mn(II) from groundwater. It was

96 recognized that the combined processes of adsorption and oxidation of Mn(II) onto manganese oxide

97 (MnOx(s)) coated media, also known as "natural greensand effect" (NGE) process, was an effective and

98 economic method for Mn(II) removal. In the NGE process, Mn(II) is adsorbed onto the MnOx(s) coating

99 and then oxidized by chlorine at a neutral pH value, thus creating additional MnOx(s) [13]. The use of

100 pyrolusite as an adsorbing medium has shown a number of benefits in comparison with contactors

101 containing MnOx(s)-coated sand. In fact, pyrolusite is a natural manganese ore consisting of more than

80% MnO_2, it has high density of adsorption sites and finally, because of its specific gravity, in the order of 5, it guarantees reduced particle entrainment and adequate media separation when a dual-media granular filter (e.g. quartzite – pyrolusite) is used [14-15].

The WTP belonging to the winery considered in this study was originally designed and built with the aim of removing iron, manganese and total hardness (due to the presence of high amounts of calcium and magnesium into the groundwater), that made the collected groundwater not suitable for cleaning processes of bottles, tanks and pieces of equipment. The WTP includes the processes of oxidation with air and chlorine, settling, filtration on a granular dual-media (quartzite – pyrolusite) filter, removal of excess chlorine through adsorption on an activated carbon filter and, finally, microfiltration and reverse osmosis (RO). Even in the light of the considerations reported above, concerning the best techniques for iron and manganese removal, the combination of the operations performed in the WTP was deemed to be adequate for iron, manganese and total hardness removal. However, a survey carried out by the authors on the WTP revealed the presence of some critical issues. Those issues seemed to be mainly related to an apparent excessive amount of chemicals used for the treatment operations and to the maintenance of the main pieces of equipment of the WTP.

Consequently, several survey campaigns were carried out to collect information concerning the quality of the water at the inlet and at the outlet of the WTP, the characteristics of the pieces of equipment used in the WTP, their energy consumption, and the type and amount of chemicals used for the water treatment processes. The gathered information was used (i) to identify the critical issues connected to the water treatment process, (ii) to propose solutions for the optimization of the process and, finally, (iii) to quantify the economic impact coming from the introduction of the proposed solutions on the final unit cost of the treated water.

124   **2. Materials and Methods**

125   **2.1 Groundwater quality**

126   The winery used approx. 100,000 m^3 of water per year for operations of cleaning and sanitation of bottles,

127   tanks and pieces of equipment. The water demand of the winery was satisfied with the groundwater

128   collected from the local shallow aquifer through three wells, namely well n.1, n.2 and n.3. Well n.1 and

129   well n.3 were very close the one to the other; conversely, well n.2 was 50-m distant from wells n.1 and

130   n.3. The characteristics of the three wells are shown in Table 1.

131

132   Table 1. Characteristics of the three wells used to satisfy the water demand of the winery

Well identification	Depth (m)	Flow rate (m^3/h)
1	25.0	13.5 (*)
3	22.5	
2	22.0	10.5

133   (*) sum of the flow rates from well n.1 and well n.3

134

135   Two pipes carried the groundwater from the wells to the inlet of the WTP. One pipe conveyed the mixture

136   of the groundwater collected from wells n.1 and n.3, the other pipe conveyed the groundwater collected

137   from well n.2.

138   The winery carried out periodic sampling campaigns at the outlet of each of the two pipes to monitor the

139   quality of the water conveyed by the two pipes separately. An external certified laboratory has assessed

140   the quality of the groundwater through the analysis of the following parameters: pH, electrical

141   conductivity (EC), chloride, sulfate, nitrogen compounds (ammonium, nitrite, nitrate), earth-alkali metals

142   (calcium, magnesium) and total hardness, metals and heavy metals (Fe, Mn, As, Cd, Cr, Hg, Ni, Pb, Cu,

143   Se) and biological parameters (total coliforms, *Escherichia Coli*, enterococci).

The results of the analyses carried out on the groundwater collected from wells n.1 and n.3, and from well n.2, in the period 2015 – 2017, are detailed in Table 2. From the values of Table 2 it can be seen that iron and manganese were the most critical compounds, because their concentrations exceeded the threshold values fixed by Italian D.Lgs. 31/01 in almost all of the sampling dates. In fact, the concentrations of iron and manganese in the groundwater from wells n.1 and n.3 were 3-4 times higher than the threshold values (of 200 and 50 µg/L, respectively) and those in the groundwater from well n.2 were even 15-20 times higher. Furthermore, the quality of the groundwater collected from wells n.1 and n.3 was, on average, superior to that collected from well n.2. Specifically, the average (2015-2017) concentration of iron in well n.2 was five times higher than that found in wells n.1 and n.3 (3306 µg/L vs. 634 µg/L) and the concentration of manganese was two times higher (611 µg/L vs 322 µg/L). Finally, the concentrations of iron and manganese in the two wells in the last two years (2016-2017) were at almost constant values.

Other than iron and manganese, also chloride and total hardness deserved special attention. In fact, the average concentration of chloride was 193 mg/L, in wells n.1 and n.3, and 207 mg/L, in well n.2, respectively, while the threshold value was at 250 mg/L. The average total hardness was approx. 51 °F in wells n.1 and n.3 and of more than 60 °F in the waters of well n.2. There are no threshold values for total hardness fixed by the Italian law that regulates drinking water, but the groundwater of that site was found to be very hard, thus exceeding the upper limit of the range (15 – 50 °F) recommended for household or industrial uses.

2.2 Water treatment plant description

The WTP owned by the winery was originally designed with the aim of removing those compounds, namely iron, manganese and earth-alkali metals (calcium, magnesium), that made the collected groundwater not suitable for household or industrial uses. The yearly average volume of the water treated

8

168   in the WTP was in the order of 130,000 m^3. The winery employed the treated water chiefly for the

169   washing processes of bottles, tanks and pieces of equipment. Small amounts of water were also used for

170   spirit production and for the cooling circuits; that water required advanced treatments in order to achieve

171   the quality necessary for the specific uses.

172   The scheme of the WTP is shown in Figure 1. The groundwater conveyed by the two pipes is mixed at

173   the inlet of the WTP and added with a 14% b.w. (by weight) solution of sodium hypochlorite (NaClO).

174   The NaClO solution is supplied to provide a preliminary disinfection and to facilitate the oxidation of

175   iron and manganese.

176   Subsequently, the water remains into a three-compartment chamber, with a total volume of 105 m^3,

177   located under the floor of the WTP's premise. The first compartment has a volume of approx. 20 m^3; a

178   total of 14 membrane air diffusers (Jager HD270, 270 mm diameter) are regularly distributed at 40 cm

179   from the bottom of the tank. The diffusers distribute air into the water at a volumetric flow rate of 100

180   m^3/h through a 1.5 kW blower. The air sparging should improve the oxidation of iron(II) to iron(III)

181   oxide, Fe$_2$O$_3$, and allow the subsequent removal by settling. The first compartment has a hydraulic

182   retention time (HRT) of 50 minutes at a flow rate of 24 m^3/h. The two subsequent compartments have

183   volumes of 14 m^3 and 72 m^3, respectively. These two tanks are used as settling chambers to allow iron

184   oxides be removed by settling. The average HRT of the two compartments was of 35 minutes and 3 hours

185   respectively at a flow rate of 24 m^3/h.

186   From the third compartment the water is pumped to a close, pressurized, dual media granular filter. The

187   filter has a volume of 4 m^3, 70% of which is filled with the granular media. The two media are quartzite

188   and pyrolusite. Quartzite granules are supplied in two different size ranges, that is 3-5 mm and 0.8-1.2

189   mm. Pyrolusite, a manganese oxide (MnO$_2$, $\rho = 5.06$ g/cm^3), is used to remove manganese through the

190   combination of the processes of adsorption of Mn^{2+} on the pyrolusite surfaces and subsequent oxidation

191   of the adsorbed species by chlorine [10, 16]. A granular activated carbon (GAC) filter follows the dual

media filter. The GAC filter is used to remove the residues of active chlorine (in the form of hypochlorous acid, HClO), that results from the addition of the NaClO solution, and protect the final section of the WTP, where a RO process is carried out. The GAC filter has a volume of 3 m^3 and it is filled with 800 kg of 30-8 mesh vegetal GAC. The WTP managers did not consider the GAC filter sufficient to guarantee a complete chlorine removal for the protection of the RO section. Consequently, even chlorine suppressor agents, such as sodium bisulfite (NaHSO_3), are currently used to remove residual amounts of active chlorine.

The two dual media and GAC filters are regularly backwashed, that is after the passing of 600 m^3 of water (i.e. 30 hours). The phases of the backwashing operation are detailed in Table 3.

Table 3. Phases of the backwashing operation carried out on the dual media and GAC filters

Filter	Phase 1 Air	Phase 2 RO concentrate	Phase 3 Water from the third compartment (*)
Dual media	70 m^3/h	YES	45 m^3/h
GAC	40 m^3/h	NO	25 m^3/h

(*) of the tank used for air sparging and settling

A section of pre-filtration precedes the final RO. The pre-filtration stage is composed of a first series of two 20 μm polypropylene cartridge filters and a subsequent 1 μm polypropylene cartridge filter. The RO section is made of 5 fiberglass vessels, each of them contains 3 thin-film composite, polyamide, spiral-wound membranes (RE8040-BLR). The RO section produces, on average, 14 m^3/h of permeate and 6 m^3/h of concentrate. Approximately 2/3 of the concentrate is stored in a 35 m^3 reservoir and used for the dual media filter backwashing. The remaining amount of concentrate (2 m^3/h) is recirculated back and mixed with the water that comes from the section of pre-filtration. A value of total dissolved solids

212   (TDSs) of 500 μS/cm at the outlet of the RO section is guaranteed thanks to the blending of the permeate

213   (14 m^3/h) with an amount of water (2 m^3/h) that comes from the outlet of the pre-filtration section.

214   The recirculating amount of the concentrate is added of two antiscale compounds before being mixed

215   with the water coming from the pre-filtration section. The two antiscale compounds are in the form of

216   sodium polyphosphate (25-40%) and a mixture of etidronic acid ($< 5\%$) and di-hydrogen (1-hydroxy-

217   etilden) di-sodium phosphonate ($>10\%$). The RO membrane regeneration process is carried out through

218   periodic chemical cleanings with alkali (sodium hydroxide plus surfactant) and acidic ($C_6H_8O_7$, citric

219   acid) solutions.

220   A final chlorination with NaClO guarantees the complete inactivation of pathogenic microorganisms.

221   The disinfected water is stored in a 124 m^3 reservoir for end uses or subsequent enhanced treatments.

222

223   **2.3 Water treatment plant survey**

224   Wine production is a seasonal activity, for that reason several survey campaigns were carried out on the

225   WTP in different moments of the year. Surveys were aimed at collecting information concerning the

226   quality of the water at the inlet and at the outlet of the WTP, the characteristics of the pieces of the

227   equipment of which the WTP is composed (as described in Section 2.2), their energy consumption, and

228   the type and amount of chemicals used for the water treatment processes.

229   The information acquired from the surveys was used (i) to identify the critical issues connected to the

230   water treatment process, (ii) to propose solutions for the optimization of the process and, finally, (iii) to

231   quantify the economic impact of the introduction of the proposed solutions on the final unit cost of the

232   treated water.

2.4 Tests for WTP optimization

After having identified the main WTP's critical issues, tests were executed to optimize the water treatment process. One test was carried out with the aim of assessing the amount of oxidant (14% NaClO solution) necessary for iron and manganese oxidation.

The test was performed on a sample of real water collected at the inlet of the WTP. A volume of 10 liters of the mixture of the two ground waters coming from wells 1+3 and 2 was collected in a polypropylene tank. The test was articulated in five steps: (1) analysis of the main parameters (ORP, Fe, Mn, free chlorine) of the collected water sample; (2) distribution of an air flow (50 L/h) into the water volume through porous stones for approx. 50 minutes (i.e. the air flow was consistent with the flow provided by the membrane air diffuser to the first compartment of the oxidation – settling chamber and 50 minutes was the HRT of the compartment, see Figure 2a); (3) analysis of the parameters, listed in step (1), in the water sample after the aeration treatment. The residual concentrations of iron and manganese were determined after filtration on a 0.45 μm cellulose-acetate filter (Sartorious, CA syringe filters, 25 mm Ø), in order to quantify only the concentration of the metals in the dissolved, not oxidized, form, as prescribed by Standard Methods (APHA, AWWA, WEF, 2017) [17]; (4) mixing of the water volume after the aeration with three in-sequence doses of NaClO: 4 mg/L, 10 mg/L and 40 mg/L. The contact time between water and oxidant, after the addition of each dose, was of 30 minutes; the oxidant was vigorously mixed with the water at the beginning and subsequently the water was left still; (5) analysis of the parameters listed at step (1) in the water sample after each of the contact periods for the three above-mentioned oxidant doses. As in step (3), the residual concentrations of iron and manganese were determined after filtration on a 0.45 μm cellulose-acetate filter. The test was repeated three times. Concentrations of iron, manganese and residual free chlorine were determined immediately at the end of each test step with rapid analytical kits (Reasol IPT, see Figure 2b).

2.5 Water treatment cost analysis

The cost data used for the quantification of the unit cost of the treated water were obtained from the WTP survey campaigns mentioned in Section 2.3. The cost analysis considered a period of ten months, from June 2017 to March 2018. As in previous works [18-19], the overall unit cost for the treated water was calculated by including the cost items listed in the follow:

- Amortization installments for the replacement of pieces of equipment (such as membranes for microfiltration and RO) and purchase of raw materials for filter unit filling (quartzite, pyrolusite, granular activated carbon). Amortization installments (AI) were calculated by multiplying the costs of the pieces of equipment and raw materials (TC) by the capital charge rate (CCR), as in Equation (1)

$$AI = TC \cdot CCR = TC \cdot \frac{i}{1-(1+i)^{-n}} \qquad (1)$$

The annual interest rate (i) and the operating life (n) were fixed to 5% and 3 years, respectively.

- Operating costs for maintenance, consulting, energy, raw materials and consumable (specifically for the chemicals employed in the water treatment process) [20].

13

3. Results and Discussion

3.1 Critical issues' identification
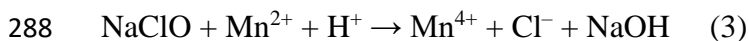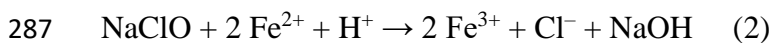
The first critical issue detected from the WTP's survey was an apparent excessive amount of NaClO solution employed for the water treatment and, specifically, for iron and manganese oxidation. In the WTP, the NaClO solution is added to the raw water immediately after the mixing of the two flows, before the water enters into the three-compartment chamber used for aeration and settling (see Section 2.2). The analysis of the cost data revealed that the amount of the 14% NaClO solution purchased from June 2017 to March 2018 was of 15,000 kg. In the same period the volume of the treated water was of 97,600 m^3, consequently, the dose of the pure oxidant distributed to the water was of 21.5 mg NaClO/L.

The theoretical amount of 14% NaClO solution necessary for iron and manganese stoichiometric oxidation was calculated for comparison. This calculation was carried out under the worst conditions, that is the presence of peak concentration values of the two metals and complete inefficiency of the air sparging for iron oxidation.

The stoichiometric reactions for Fe and Mn oxidation through chlorine are shown in Eqs. 2 and 3

$$NaClO + 2\ Fe^{2+} + H^+ \rightarrow 2\ Fe^{3+} + Cl^- + NaOH \quad (2)$$

$$NaClO + Mn^{2+} + H^+ \rightarrow Mn^{4+} + Cl^- + NaOH \quad (3)$$

Consequently, the stoichiometric chlorine doses for the oxidation of iron and manganese were of 0.67 mg NaClO/mg Fe^{2+} and 1.36 mg NaClO/mg Mn^{2+}, respectively.

The maximum concentrations of iron and manganese found in the last five years in the groundwater collected from well n.2 (the one with the lowest quality) were of 4167 µg/L for iron (detected in April 2016) and 774 µg/L for manganese (detected in April 2017). As it can be seen from Table 4, in the presence of peak concentrations, a dose of 27.46 mg/L of 14% NaClO solution was necessary for the

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oxidation of the two metals. Consequently, the theoretical amount of 14% NaClO solution to be used for

the oxidation of iron and manganese, from June 2017 to March 2018, was calculated to be equal to 2680

kg. The calculated amount, even under the worst conditions, was only approx. 18% of the amount actually

purchased and used in the WTP. At a first glance it seemed that the oxidant was indeed overdosed, with

a consequent overexploit of the GAC filter and a need of extra amounts of the chlorine suppressor agent.

Table 4. Theoretical chlorine doses for the oxidation of peak concentrations of iron and manganese

Species	MW (g/mol)	Peak concentration (µg/L)	NaClO dose (µg/L)	14% NaClO solution dose (mg/L)
Fe^{2+}	55.845	4167	2791.9	
Mn^{2+}	54.938	774	1052.6	
Total			3844.5	27.46

An overdose of NaClO could have several negative effects on the plant. The oxidant that was not

consumed for the oxidation of species in a reduced form has to be suppressed, to avoid that it comes in

contact with the membranes of microfiltration and RO. In fact, the final sections of the plant (i.e.

microfiltration and RO) cannot tolerate concentrations of free chlorine of more than 0.1 mg/L. The GAC

column is used for this precise purpose, but if the concentrations of residual free chlorine are too high,

due to an overdose of NaClO solution, the GAC is not sufficient and the low concentrations required by

the membranes can only be achieved by using chlorine suppressor substances, thus determining

additional costs for the plant.

The second critical issue concerned the process of backwashing of the dual media (quartzite and

pyrolusite) filter. At present, the filter is subjected to a backwashing process made of three subsequent

phases: with air, with the RO concentrate (countercurrent) and, finally, with the water from the third

compartment (co-current) of the aeration – settling chamber. All the exhaust water from both the second and the third phase of the backwashing is sent to the winery's WWTP.

After the identification of the above mentioned two critical issues, some solutions were studied with the aim of improving the management of the WTP and reducing the operating costs of the water treatment process.

3.2 Solutions to optimize the water treatment process

3.2.1 NaClO dosage for iron and manganese oxidation

In Section 3.1 it was observed that the amount of the 14% NaClO solution actually purchased and used for the process of oxidation of Fe and Mn in the WTP was at least five times more than the amount calculated basing on stoichiometric considerations. The oxidant dose found with the theoretical approach was subsequently verified with the aid of pilot tests carried out with real water samples collected at the inlet of the WTP. The real need of NaClO for iron oxidation had to be demonstrated, because the air distributed in the first of the three-compartment chamber was used exactly with the aim of facilitating the iron oxidation process.

The tests described in Section 2.4 were used to quantify the right amount of NaClO solution necessary to obtain the oxidation and consequent removal of iron and manganese. The average values of the parameters (ORP, Fe, Mn, free chlorine) of the water samples subjected to the tests described in Section 2.4 are listed in Table 5.

334 Table 5. Values of the parameters (ORP, Fe, Mn, free chlorine) of the water sample subjected to the pilot

335 tests

	iron (mg/L)	manganese (mg/L)	ORP (mV)	free Cl (mg/L)	total Cl (mg/L)
Initial concentrations	2	0.2	-20	< DL	< DL
After 50 min aeration	< DL	0.2	120	< DL	< DL
NaClO 14% - 4 mg/L	< DL	0.2	230	< DL	< DL
NaClO 14% - 10 mg/L	< DL	0.2	350	< DL	< DL
NaClO 14% - 40 mg/L	< DL	< DL	520	0.3	0.5
End of the 3-compartment chamber	< DL	< DL	>700	> 1.5	> 1.5

336 DL, detection limit

337

338 It can be seen that the initial concentrations of iron and manganese were in the order of 2 mg/L and 0.2

339 mg/L, respectively. The ORP of the raw water was negative, of -20 mV, in line with the values normally

340 found in a groundwater. As expected, no free chlorine was detected. After the 50-minute aeration process

341 the value of ORP increased to +120 mV. The aeration process determined an almost complete removal

342 of iron; in fact, the residual concentration of dissolved iron decreased under the detection limit (0.05

343 mg/L). This result demonstrated that the process of air sparging was sufficient for the oxidation of iron

344 and that the NaClO was not necessary for that operation. Conversely, the concentration of manganese

345 was not altered by the aeration.

346 As described in Section 2.4, after the step of aeration, the water sample was mixed with a dose of 4 mg/L

347 (0.56 mg NaClO/L) of the 14% NaClO solution. After a 30-min contact, it was verified that the

348 concentration of manganese was still unaltered. Only when the concentration of the 14% NaClO solution

349 was increased up to 40 mg/L, the concentration of soluble manganese was reduced to values under the

350 detection limit (0.05 mg/L). The results found in the tests were coherent with observations from the

17

literature. In fact, several lab, pilot and field tests, carried out since the 1960-s, have demonstrated that the oxidation of iron with oxygen is relatively straightforward in low-TOC, low-mineral content groundwaters [21-22]. Conversely, aeration has been found to be slow and ineffective, even at high pH values, for Mn(II) oxidation. Furthermore, even the reaction between chlorine (HOCl, the hydrolysis product of both gaseous Cl_2 and NaClO) and Mn(II) was too slow to be useful for water treatment, unless the pH was raised to values above 9. The combination of the processes of adsorption and oxidation is necessary to achieve high efficiencies in Mn(II) removal. When chlorinated water is passed through a filter containing a medium coated with MnO_2, the removal will occur by adsorption to the granular medium, and the adsorbed Mn(II) will gradually be oxidized to MnO_2 on the filter medium surface [23]. The results of the field tests demonstrated that the present amount of NaClO used for water treatment was indeed overdosed. The present concentration of pure oxidant, 21.5 mg NaClO/L, could be reduced by at least 75%, that is, lowered to 5.6 mg/L (or 40 mg/L of 14% NaClO solution), without altering the capacity of the WTP of removing iron and manganese. Furthermore, the field tests demonstrated that an efficient removal of iron could already be obtained with the sole aeration process. For this reason, in order to indeed save chlorine, the introduction of the NaClO solution into water had to be moved downstream the aeration chamber, so as to achieve the oxidation of iron effectively by using air.

It has to be underlined that the NaClO dose found in the test was in any case overestimated, because it did not take into account of the combined effect of pyrolusite adsorption and chlorine oxidation in manganese removal. The reduced utilization of the NaClO would not have only a direct effect on the cost of the water treatment (see Section 3.3), but it also had indirect effects on a better utilization of the GAC column and on the saving of chlorine suppressor substances.

3.2.2 Backwashing of the dual media filter

The analysis of the backwashing phases' sequence, the quality of the waters used for the process and the availability of water flows of several natures in the WTP suggested that changes to improve the efficiency of the backwashing process were possible. At present, after an initial air washing, the filter is backwashed firstly with the RO concentrate and, subsequently, with the water coming from the third compartment of the aeration – settling chamber.

However, according to the technical literature, the conventional sequence of the phases in a backwashing process is a first water wash, followed by an air wash and a final second water wash of the filter media [10, 24]. The first water wash aims to mainly dislodge the coarser solids accumulated in the filter media pores. Practical experience had demonstrated that backwashing of filter media grains smaller than 0.8 mm with water only is difficult [25]. Therefore, a typical backwash cycle should include a combination/sequence of air and water washing of the filtration media, where the air wash is used to create greater turbulence and enhances particle scrubbing allowing to also dislodge the finer solids and some of the bacterial film accumulated on the grains of the filtration media. Finally, the air wash is followed by another water wash, which aims to remove the solids and air accumulated in the media and to prepare the filtration bed for another filtration cycle [25].

In the context of the winery's WTP, starting the backwashing sequence with a water washing was recommended, because of the accumulation of fine particles of iron oxides into the porosity of the filter media. However, the utilization of the RO concentrate for the first water washing phase should be avoided. In fact, on the one hand, the use of the RO concentrate, instead of a filtered effluent, for the backwashing of the filter, has the positive effect of reducing the backwash volume and the energy needed to pump extra groundwater to the WTP. On the other hand, because of the corrosive nature of the RO concentrate, due to the high concentrations of alkali-earth metals and chlorides into the raw water, backwashing with the RO concentrate is definitely not recommended [25].

396   The combination of the backwashing phases and water flows shown in Figure 3 allowed to increase the

397   efficiency of the backwashing process. As in Figure 3, the water from the third compartment of the

398   aeration settling chamber is used for the second co-current water washing phase. After being used for

399   backwashing, this water is stored in a tank and used for the first countercurrent backwashing operation.

400   Only after that, it is definitely sent to the WWTP. This scheme allowed to avoid the use of the RO

401   concentrate and to minimize the use of pre-treated water (after the preliminary aeration and settling

402   treatment) for the backwashing process.

403

404   **3.3 Impact of the process improvements on the water treatment costs**

405   The volume of the raw water collected from the wells during the survey's period, that is from June 2017

406   to March 2018, was of 89,260 m^3 and the volume of finished water, that is at the outlet of the WTP and

407   ready for use, was of approx. 56,500 m^3.

408   The survey campaign on the WTP, carried out as described in Section 2.3, and the analysis of costs,

409   carried out as described in Section 2.5, returned the costs for water treatment detailed in Table 6.

Table 6. Detail of the cost items for the water treatment in the winery's WTP under the old and the new scenario (i.e. with the introduction of the proposed solutions)

			old	new
Operating costs	Amortization installments		5600 €	4480 € (-20%)
	Maintenance		31230 €	25000 € (-20%)
	Consulting		4000 €	4000 €
	Non amortizable raw materials and consumables		11300 €	9050 (-20%)
Chemicals	Antiscalant/anticorrosion (NapolyPO$_4$, 25-40%)		9660 €	9660 €
	Antiscalant/anticorrosion (NaHEDP, < 5%)		3600 €	3600 €
	Chlorine suppressor (NaHSO$_3$)		6390 €	1600 (-75%)
	14% NaClO solution		3675 €	920 (-75%)
Energy costs (Unit cost of electrical energy 0.145 €/kWh)		Energy consumption (kWh)		
	Wells	19,300	2800 €	2800 €
	Pump stations	50,000	7240 €	7240 €
	Reverse osmosis	71,400	10350 €	10350 €
	Filter backwashing	1,730	250 €	250 €

The overall cost for water treatment from June 2017 to March 2018 (10 months) was of approx. 96.1 k€, of which 54.2% were for operating costs, 24.3% were for chemicals and 21.4% for energy, as detailed in Figure 4. Considering the same period, the consequent unit cost for water treatment was of 1.70 €/m^3. This cost was approx. one half of the purchase cost of water for industrial purposes, equal to 4 €/m^3, that can be supplied by a local company for energy and water distribution [26].

The solutions for a better management of the WTP presented in Section 3.2 had inevitably positive impacts on the reduction of water treatment costs. First of all, as shown in Figure 5, the reduced dose of oxidant had a direct impact on the saving of the NaClO solution and the chlorine suppressor agent. From the results of the field tests (see Section 3.1.2), it could be estimated that the chlorine consumption could be reduced by 75% without altering the efficiency in iron and manganese oxidation. Because of the lower

423   employed dose of chlorine, also the amount of chlorine suppressor could be reduced by at least 75%. The

424   reduced dose of oxidant had also a positive impact on the lifetime of the GAC column and, consequently,

425   on the aliquot of the amortization installment laid aside for the purchase of new GAC. That saving could

426   be estimated in the order of 20% of the original amortization installment. Over long times, the cautious

427   use of reagents had a certain positive impact on the costs for maintenance and for the purchase of

428   frequently used (i.e. non amortizable) consumables [27-28]. This saving was estimated in a further 20%.

429   The overall cost for water treatment, on a period of ten months, would then reduce from 96.1 k€ to 79.0

430   k€. Consequently, the unit cost for water treatment would lower from 1.70 €/m^3 to 1.40 €/m^3, with a

431   saving of approx. 20%. Furthermore, the reduced utilization of chemicals will make the WTP able to

432   produce the same volumes of water with the same quality but with a higher environmental sustainability.

433   Finally, it had to be considered that the quality of the groundwater used to satisfy the winery requirements

434   was not homogeneous. Water collected from wells n.1 and n.3 had a better quality than that collected

435   from well n.2. Field tests will have to be carried out to verify if the productivity of wells n.1 and n.3

436   could be increased, without affecting the characteristics of the groundwater, so as to definitely avoid the

437   utilization of well n.2. That intervention would make possible to further reduce the use of chemicals for

438   the groundwater treatment.

439

440   **4. Conclusions**

441   The treatment processes performed in the WTP owned by the winery were deemed to be adequate to

442   make the groundwater usable for cleaning operations. However, a survey carried out by the authors

443   revealed the presence of two critical issues in the WTP's management, concerning the Fe(II) and Mn(II)

444   oxidation and removal, and the backwashing of the dual media filter, respectively.

445   For what concerns Fe(II) and Mn(II) oxidation and removal, the results of pilot tests demonstrated that:

446 • the sole process of air sparging was sufficient for the oxidation of iron and the injection of the

447   14% NaClO solution was not necessary for that operation;

448 • the amount of NaClO returned by the survey and presently used for the water treatment was

449   indeed overdosed. The consequent concentration of pure oxidant, 21.5 mg NaClO/L, could be

450   reduced by at least 75%, that is, lowered to 5.6 mg/L (or 40 mg/L of 14% NaClO solution),

451   without altering the capacity of the WTP of removing iron and manganese;

452 • because an efficient removal of iron could be obtained already with the sole aeration process, in

453   order to indeed save chlorine, the introduction of the NaClO solution into water had to be moved

454   downstream the aeration chamber, so as to achieve the oxidation of iron effectively by using air.

455 With reference to the second critical issue, a new combination of water fluxes could improve the

456 efficiency of the dual media filter backwashing. The new backwashing scheme should include a first

457 countercurrent backwashing process with the water coming from the second backwashing step, and a

458 second co-current washing phase with the water from the third compartment of the aeration settling

459 chamber. This new fluxes'combination allowed to simultaneously avoid the use of the RO corrosive

460 concentrate and to minimize the use of high quality water.

461 The introduction of these solutions into the WTP had an undeniable positive impact on the final unit cost

462 of the treated water, that decreased from 1.70 €/m^3 to 1.40 €/m^3. Meanwhile, the reduced utilization of

463 chemicals will make the WTP able to produce water with the same quality but in a more environmentally

464 friendly way.

465

23

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well n.1 +
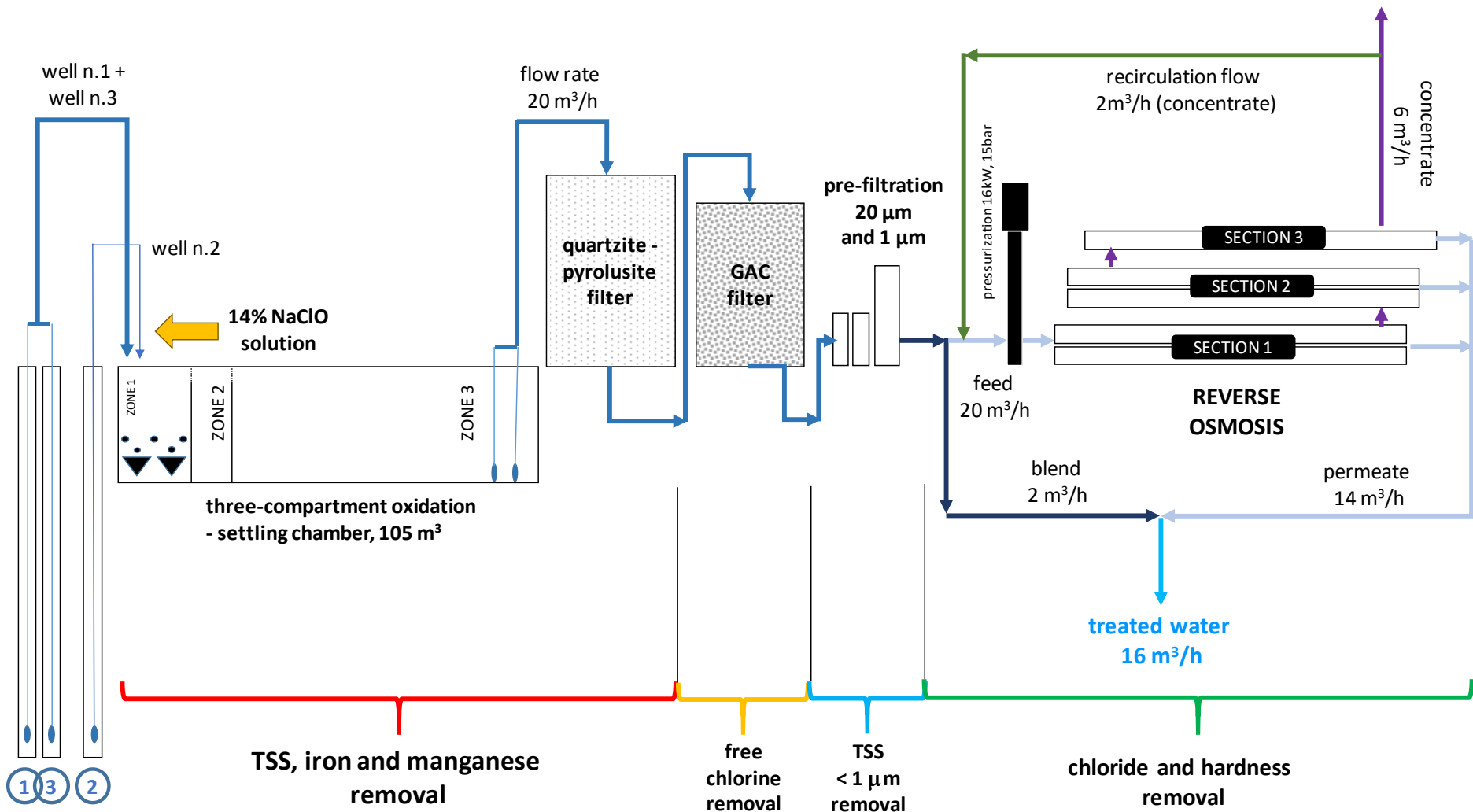well n.3

well n.2

flow rate
20 m³/h

recirculation flow
2m³/h (concentrate)

concentrate
6 m³/h

14% NaClO
solution

ZONE 1 ZONE 2 ZONE 3

quartzite -
pyrolusite
filter

GAC
filter

pre-filtration
20 μm
and 1 μm

pressurization 16kW, 15bar

SECTION 3

SECTION 2

SECTION 1

REVERSE
OSMOSIS

feed
20 m³/h

three-compartment oxidation
- settling chamber, 105 m³

blend
2 m³/h

permeate
14 m³/h

treated water
16 m³/h

1 3 2

TSS, iron and manganese
removal

free
chlorine
removal

TSS
< 1 μm
removal

chloride and hardness
removal

Figure 1. Scheme of the WTP

Figure 2. Apparatus for the aeration test (a) and for the rapid analysis of iron (b)
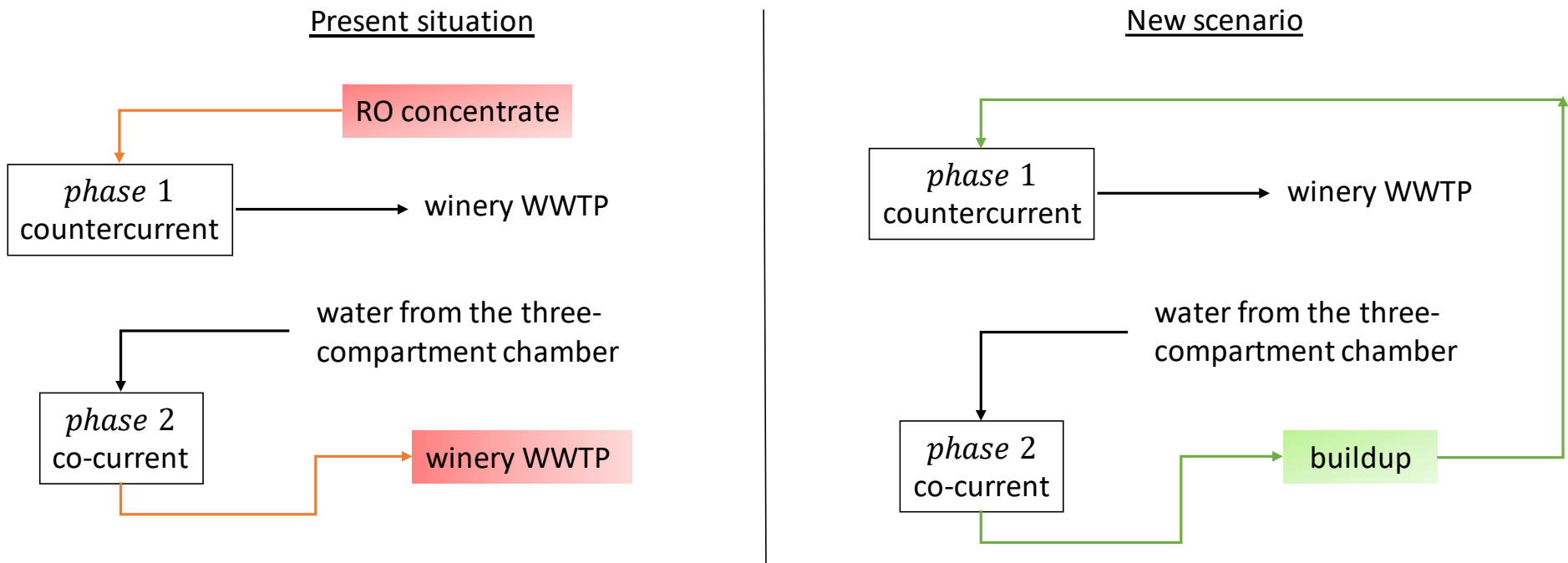
Figure 3. Combination of the backwashing phases and water flows in the present and in an optimized situation
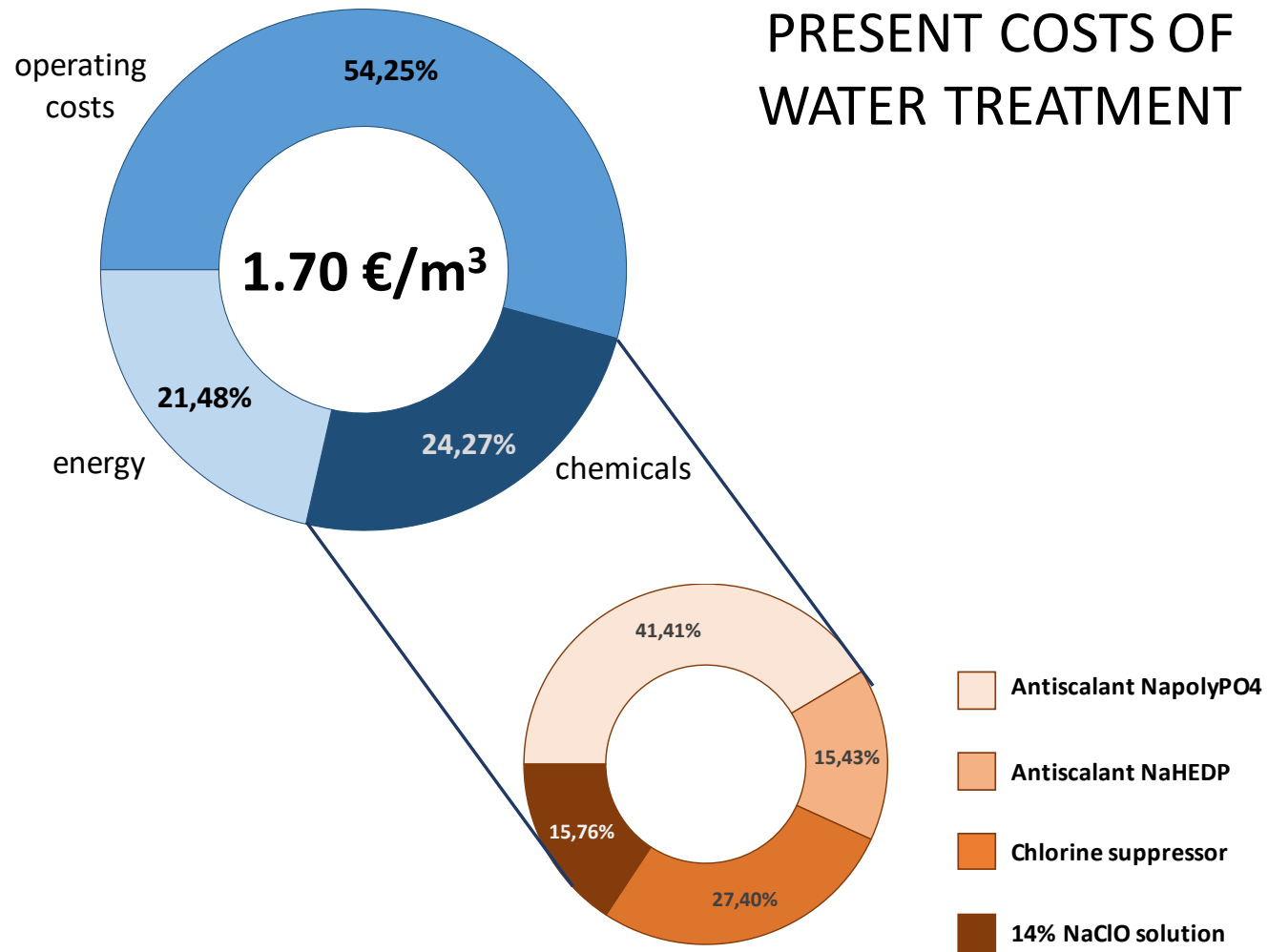
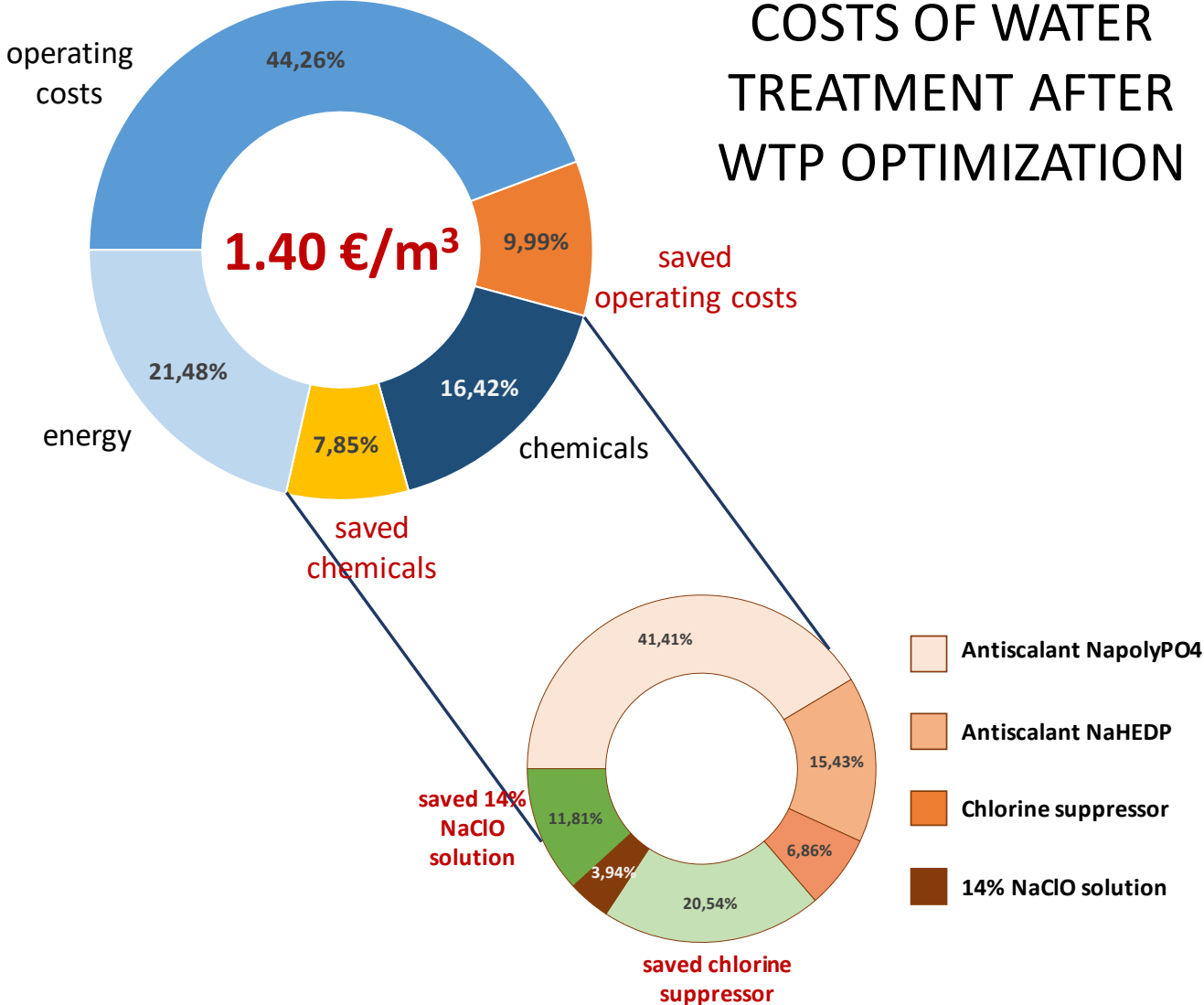Figure 4. Detail of the water treatment costs in the present situation

Figure 5. Detail of the water treatment costs in a future situation, after the WTP optimization

Table 2. Results of the analyses carried out on the groundwater collected from wells n.1 and n.3, and from well n.2, in the period 2015 – 2017

Parameter	Threshold value D.Lgs. 31/01	well n.1 + well n.3						well n.2					
		21/04/15	26/10/15	01/04/16	13/12/16	04/04/17	10/10/17	21/04/15	26/10/15	01/04/16	13/12/16	04/04/17	10/10/17
pH	6.5 – 9.5	6.8	6.6	6.7	7.0	6.8	7.0	6.7	6.5	6.7	7.0	6.7	6.8
Electrical conductivity (µS/cm at 20°C)	2500	1299	1312	1370	1311	1317	1304	1431	1399	1494	1478	1512	1520
Chloride, Cl$^-$ (mg/L)	250	172	197	198	208	196	184	178	187	197	231	228	221
Sulfate, SO$_4^=$ (mg/L)	250	95.9	74	68,3	65,9	71,2	141	145	128	139	152	143	118
Calcium, Ca (mg/L)	-	171	169	155	147	147	152	214	212	184	150	152	158
Magnesium, Mg (mg/L)	-	26.5	24.8	27.5	28.4	27.5	46.7	26.2	24.1	18.7	55.9	54.4	67.3
Total hardness (°F)	15 - 50 (*)	**53.6**	**52.4**	50.0	45.7	48.0	**57.2**	**64.4**	**62.8**	**53.6**	**60.4**	**60.4**	**67.2**
Nitrate, NO$_3^-$ (mg/L)	50	4.2	<1	1.3	5.2	4.3	<1	7.8	<1	<1	3.6	<1	<1
Nitrite, NO$_2^-$ (mg/L)	0.5	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ammonium, NH$_4^+$ (mg/L)	0.5	0.08	0.04	0.21	0.37	0.08	<0.05	0.11	0.10	0.32	0.45	0.14	<0.05
Iron, Fe (µg/L)	200	118	**354**	**929**	**709**	**927**	**765**	**452**	**3688**	**4167**	**4155**	**4101**	**3272**
Manganese, Mn (µg/L)	50	**291**	**282**	**320**	**325**	**411**	**305**	**500**	**548**	**625**	**664**	**774**	**557**
Arsenic, As (µg/L)	10	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	0.4	<0.1	<0.1	<0.1	<0.1
Cadmium, Cd (µg/L)	5	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Chromium, Cr tot (µg/L)	50	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Mercury, Hg (µg/L)	1	<0.2	0.3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Nichel, Ni (µg/L)	20	9.9	8.6	5.0	6.5	5.7	5.3	2.9	3.7	1.6	2.7	1.5	2.0
Lead, Pb (µg/L)	10	<1	<1	<1	<1	<1	<1	<1	<1	<1	1,6	<1	<1
Copper, Cu (µg/L)	1000	<1	<1	<1	<1	<1	<1	<1	2	<1	<1	<1	<1
Selenium, Se (ug/L)	10	<1	<1	<1	<1	<1	<1	1,2	1,2	<1	<1	<1	<1
Escherichia Coli (CFU/100 ml)	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Coliforms (CFU/100 ml)	0	0	**20**	0	0	0	0	0	**13**	0	0	0	0

(*) recommended values