LIFE PROJECT – ECODEFATTING
LIFE13 ENV/IT/00470

"Environmentally friendly natural products instead of chemical products in the degreasing phase of the tanning cycle"

DELIVERABLE - ACTION C.5
Report on environmental benefits of the ECODEFATTING process

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2. List of abbreviations, acronyms and symbols

Al	**al**uminum
As	**ar**senic
B	**b**oron
Ba	**ba**rium
Be	**be**ryllium
BOD	**b**iological **o**xygen **d**emand
ca.	***c***_irc_***a*** (approximately)
$Ca(OH)_2$	**ca**lcium **hydroxide**
Cd	**c**a**d**mium
Co	**co**balt
COD	**c**hemical **o**xygen **d**emand
Cr	**c**h**r**omium
Cu	***c***_ypri_***u***_m_ (copper)
E.	***E***_scherichia_
e.g.	***e***_xemplii_ ***g***_ratia_ (for example)
Fe	***fe***_rrum_ (iron)
Hg	***h***_ydrar_***g***_yrum_ (mercury)
mg	**m**illi**g**ram(s)
milli-	**10^{-3}**
Mn	**man**ganese
NaHS	**sodium h**ydro**s**ulphide
NaCl	**sodium c**h**l**oride
Na_2CO_3	**sodium carbonate**
Na_2S	**sodium s**ulphide
Na_2SO_4	**sodium sulfate**
Ni	**ni**ckel
O_2	**o**xygen
O_2/L(l)	**o**xygen per **l**iter **ratio**
P.	***P***_seudomonas_
Pb	***p***_lum_***b***_um_ (lead)
ppm	**p**arts **p**er **m**illion
Sb	***s***_ti_***b***_ium_ (antimony)
Se	**se**lenium
Tl	**t**ha**l**lium
w/w	**w**eight to **w**eight **ratio**
Zn	**z**i**n**c

3. Considerations about the defatting process

The beamhouse operations in a tannery encompass several chemical processes, to make the raw animal hides suitable for the transformation into leather. Although quite complex and far from being trivial, these operations are carried out with cheap but efficacious chemical substances, that can be summarized for 1000 Kg of raw hides to be processed, as follows:

- Na_2S, 26 Kg; NaHS, 15 Kg; Na_2CO_3, 8 Kg; $Ca(OH)_2$, 55 Kg;
- Defatting product, 7 Kg;
- Surfactants, 1.5 Kg; Chelating agents, 4 Kg;
- Amine containing products, 8 Kg;
- Organic and inorganic acids, 38 Kg;
- Enzymes, 6.3 Kg.

It is evident that the contribution of the defatting product is just about 4.1% (w/w) on the total weight of chemicals employed from the desalination till the deliming/washing stage. However, this component is fundamental for the extraction of fat from hides and, more importantly, for its emulsion within the beamhouse baths. It follows, that any defatting product contributes massively to the overall content of the polluting load of tanneries' effluents, increasing the organic fraction of it as demonstrated by the COD values.

4. Considerations about the Ecodefatting product EDF20

Product EDF20 was tested at laboratory level on sheep skin specimens, demonstrating its defatting efficacy at approximately 55% of extractable fatty material from those samples. The subsequent demonstration at semi-industrial level confirmed the laboratory results, opening up its application at pre-industrial level on 100 Kg batch of bovine and also equine hides. Therefore, the combination of chemical species to obtain the final product EDF20, resulted in their optimal synergistic cooperation, to furnish a smooth and swollen hide material free from excess fat, which is detrimental for the subsequent tanning action. These results were quite important, since the formulation of EDF20 contained a considerable reduced percentage of ethoxylated alcohols, normally present at 50% (or higher) in commercial product (**Table 4.1**).

Table 4.1 Composition of commercial and EDF20 products

Product	Hexylene Glycol	Alcohol iso-C10 5mEO	KEC	Lat-pip	Water
EDF20	5%	25%	20%	5%	45%
Polause-SG50	-	55%	-	-	45%

Ethoxylated alcohols have replaced the dangerous and healthy hazardous chloroparaffins and alkylphenols, but their production, although economically remunerative, may have a considerable environmental impact. Ethoxylated alcohols can use petroleum, natural gas, animal fat or plant oils as primary raw materials. The ethoxylation of alcohols with ethylene oxide is the manufacturing scheme. Ethylene oxide is obtained by the oxidation of ethylene over a silver catalyst. The ethylene chain build-up reaction occurs at a rate similar to the ethoxylation of the alcohol. As a result, the ethylene oxide chain is built up before all alcohol has been reacted, and a polydispersed mixture containing nominally eight ethylene oxides contains also significant amounts of other ethoxylates containing from 0 to 20 ethylene oxide units. In general, the emissions associated to the production of ethoxylated alcohols, involve a variety of toxic chemicals, including ethylene, ethylene oxide, ethylene glycol and methanol, commonly found in air emissions from plant sites. Even the raw alcohols result in additional chemical emissions during their production processes. The source of alcohol raw materials can either be vegetable oils or a petroleum feed stock. Most alcohols derived from vegetable oils are made by converting the fatty acids of triglycerides to their methyl esters by alcoholysis with methanol. The methyl esters are then hydrogenated to the fatty alcohols and methanol. Therefore, potential chemical releases to the environment can include methanol and methyl esters. Petroleum-based alcohols may result in the release of several hazardous air pollutants, including aldehydes, ammonia, benzene benzo(a)pyrene, biphenyl, carbon monoxide, ethyl benzene, formaldehyde, naphthalene and xylene. They also add to the volatile organic compound loading in the lower atmosphere contributing to photochemical smog, are sources of significant water pollution including oil, phenols, BOD, COD, ammonia and generate significant quantities of solid waste. Ethylene oxide is produced from ethylene, which is distilled off from either crude oil or natural gas. Potential environmental releases of chemicals from this process include ethylene oxide, benzene, ethylene and hydrocarbons.

Reducing the percentage of ethoxylated alcohols in tannery products of wide spread use such as those involved in the defatting of hides, will surely contribute to the reduction of chemical emissions and use of non-renewable natural sources. The introduction of TEC to replace 80% of the ethoxylated alcohol gap in commercial products, goes into this direction. TEC can be obtained from the massive waste of fruit and from wood waste processing, including even microbial fermentation of any sugar/cellulose based material and the gasification of recycled wood waste. Similarly, the introduction of the lactose derivative (lat-pip) in the formulation of EDF20 follows the same approach, since this component derives from lactose, which in turns is recovered from the renewable and never ending natural source, milk serum. Although the lat-pip species counts only for the 5% of the entire formulation, it is noteworthy to clear up the amount of milk serum needed for its production, when 1000 Kg of raw hides have to be processed (**Table 4.2**).

Table 4.2 Mass calculations for 1 Ton of hides to be processed

Raw hides	EDF20	Lat-pip	Lactose	Milk serum
1000 Kg	7 Kg	0.35 Kg	0.39 Kg	17 Kg

Those figures appear quite interesting, if one takes into account their projection over the annual production of leather in Italy, whose specialized companies processes approximately 400,000 Ton of hides: the amount of EDF20 required will be 2,800 Tons of defatting EDF20, leading to the use of 6,800 Tons of milk serum, which corresponds to the production of milk serum from a SME dairy company over a period of approximately 3.5 months. Obviously, that calculation is an optimistic estimate, in which EDF20 would be the only defatting agent on the market: but, it follows that the use of EDF20 appear sustainable through the recycle of a waste product such as milk serum, even when taken to the extreme boundary of its application.

5. Considerations about the Ecodefatting process.

Defatting products contribute less than 5% to the total mass of chemicals used in beamhouse operations: Na_2S, $NaHS$, Na_2CO_3, $Ca(OH)_2$, surfactants, chelating agents, amine containing products, organic and inorganic acids, enzymes. EDF20 has a reduced percentage of ethoxylated alcohols (25%), whose production impacts considerably on the environmental, as these are obtained from petroleum oil, natural gas, animal fat or plant oils. Their production process is responsible for the release of toxic chemicals, including ethylene, ethylene oxide, ethylene glycol and methanol, methyl esters, aldehydes, ammonia, benzene benzo(a)pyrene, biphenyl, carbon monoxide, ethyl benzene, formaldehyde, naphthalene, xylene, and hydrocarbons. In addition, all this waste is involved in the generation of photochemical smog, water pollution including oil, phenols, BOD, COD and ammonia. The reduction of the percentage of ethoxylated species will contribute to the reduction of chemical emissions and both TEC and the lactose derivative of EDF20 will sustain the role of EDF20 in this sense. EDF20 is used in the stages of soaking, liming and deliming. The demonstrations at semi-industrial and pre-industrial level show the capacity of the product, to furnish a smooth and swollen hide material free from excess fat, confirming the performance of defatting at laboratory level (about 55% of fat extracted). In the case of ovine and pig skins, the high fat content in the raw material induced to demonstrate the best amount of Ecodefatting product within the process. In particular it was found sufficient to reduce the amount of EDF20 from 6 to 4% by weight of skin to be processed, cutting down the chemical load in the effluents by *ca.* 30%. On the other hand, the good results obtained on bovine and equine hides did not induce any further demonstration about the optimization of the quantity of EDF20, since no particular difference of behaviour were noticed in all three phases of hide processing. The overall impression given by tanners is that the effluents generated by the use of the Ecodefatting product are clearer and with less suspended matter, in comparison with those obtained from the use of commercial product. Also, the extracted fat appears well emulsified. This aspect is reckoned quite important for two reason: first, the processed hides are recovered with the desired degree of smoothness and swollenness without any sticky fat chunks on the surface, that will generate fat spews even on the leather of the finished goods; secondly, the costs for effluent discharge can be reduced against some of the tariff threshold, that are linked to the content of suspended solids/matter. Although difficult to quantify, the money saving about effluent discharge may well approach 10-15% of the annual costs for waste disposal, in case the Ecodefatting products are adopted for routine productions. A significant contribution may come from cutting the expenses about the inorganic salt tariffs (e.g., Na_2SO_4 and NaCl). In this particular case, it was observed that effluents with high contents of water soluble defatting agents tend to show low values of conductivity, which is directly linked to the amount of the salts dissolved. Thus, it can be assumed that the Ecodefatting products tend to reduce the amount of salts in effluents, inducing their precipitation. This aspect is quite important from an environmental point of view, since water plant are capable to treat the organic chemical loads of tannery wastewaters, but, they may find tricky to extract common salts such as NaCl and Na_2SO_4. From the environmental point of view, tanneries' effluent are not released in the environment indiscriminately. Since the mid '80s three water treatment plants have been working in the industrial district of S. Croce sull'Arno in Italy: and the same circumstance did happen in the other main leather districts of the country (Arzignano and Solofra). Initially, water plants had only the chemical/physical treatment of effluents, but later they were upgraded with the introduction of tanks, containing activated sludge for the aerobic metabolization of the organic content of the effluents. This is also the case of Spain, where Inescop has its own wastewater plant. The demonstrated compatibility of EDF20 with the hide working procedures in the project, was confirmed by the corresponding compatibility of the effluents with the typical bioremediation schemes of a water plant. Three different approaches were chosen, covering most of the option available, to reduce the organic load of the effluents. A first demonstration at laboratory level involved the use of common bacteria strains of *E. coli* and *P. savastanoi*, that were able to achieve a 20-25% and 30-35% reduction the organic content respectively. Subsequently, a common white rot fungi species *F. trogii* was used on the effluents collected from the defatting demonstration at semi-industrial level, showing the capacity of the microorganism to increase the biodegradability of the effluents, generating an easily removable solid material already at tanneries' premises. Finally, activated sludge were demonstrated on the effluents of the defatting demonstration at pre-industrial level, where it was found a surprising opposite trend about the change of the biodegradability (expressed as BOD/COD ratio) parameter before and after treatment (**Table 5.1**).

Table 5.1 COD and BOD are in mg O_2/l

Effluent	Product	Before treatment			After treatment		
		COD	BOD	BOD/COD	COD	BOD	BOD/COD
Bovine	EDF20	1360	562	0.41	573	115	0.20
	SG50	1466	665	0.45	337	80	0.24
Equine	EDF20	1441	542	0.38	567	129	0.23
	SG50	1794	649	0.36	573	137	0.24

A rationale to those results was found in the absence of any pre- or post-treatment phase of the effluents (sedimentation, flocculation, oxidation of sulfides and biological generation of nitrates) that integrate the treatment of wastewaters with activated sludge. In particular, those effluents were too rich in sulfide/hydrosulfide salts, that are by far the exclusive reducing agents. to convert raw hides into a malleable, soft and mechanical resistant material. It is known that the oxidation of sulfides upstream is fundamental to achieve the efficient purification of wastewaters, since sulfides are responsible for the deterioration of the purification process, inducing poor oxygenation and the generation of toxic waste. The next treatment of the supernatants with active carbon (0.2 g / 50 ml of sample) confirmed the good work done by the activated sludge, since the value of the COD dropped below the threshold limit of the instrument (ca. 50 mg/l O_2) for the effluents from both bovine and equine hide processing. In the case of effluents from the defatting of calf-hides the COD was remarkably reduced by 98% of the original value.

Table 5.2 COD of effluents after contact with carbon

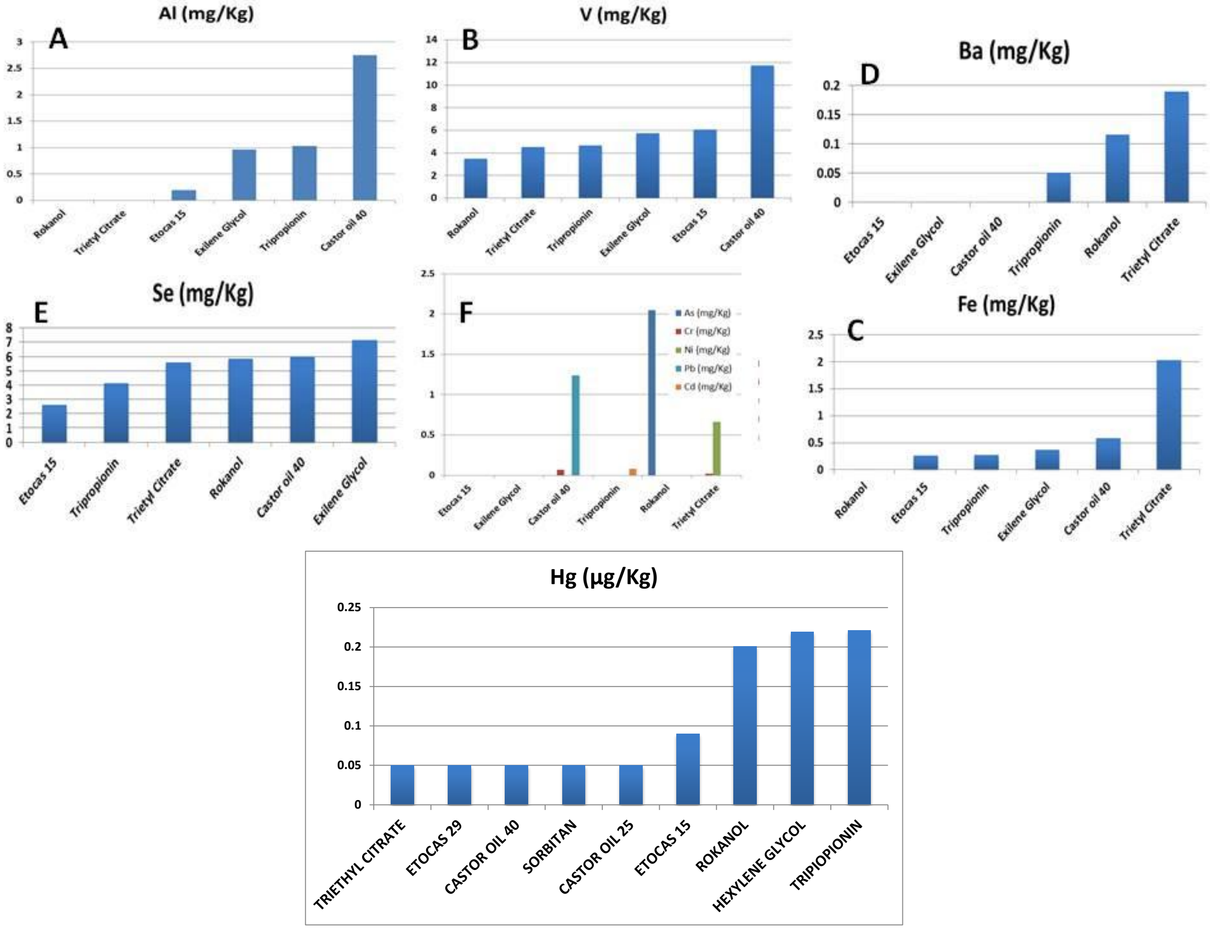
Effluent	Product	COD	
		After sludge	After carbon
Bovine	EDF20	573	< 50
	SG50	337	< 50
Equine	EDF20	567	< 50
	SG50	573	< 50

These results highlighted the importance of wastewaters pre-treatment before entering into the tanks containing activated sludge, which was demonstrated to adapt to the new defatting agent.

6. Consideration about the content of heavy metals in defatting effluents

The introduction of analyses, to determine the content of heavy metals both in the products used to formulate the Ecodefatting agents and in the effluents obtained from any of the demonstration actions, was suggested by the results obtained in project Life ENV/IT/000352 “Bionad”. In that project an astonishing content of Hg metal equal to 0.6 ppm was found in a commercial dye, supposed to be free from Hg. Therefore, extensive metal analyses was carried out, revealing that commercial dyes have a quite high amount of heavy metals (expressed as total content) that may pose serious issue for the healthy profile of the leather goods used by consumer. The analyses of Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Se, Tl, V and Zn were carried out in semi quantitative fashion, recording quite low values. In some cases most of the metals were even below the detection limit. Even more important was the low content of mercury, which was only 5% of the 1 ppm threshold limit (**Figure 6.1**).

Figure 6.1
Metal content in products for defatting formulations



Metal content in effluents from defatting at semi-industrial level

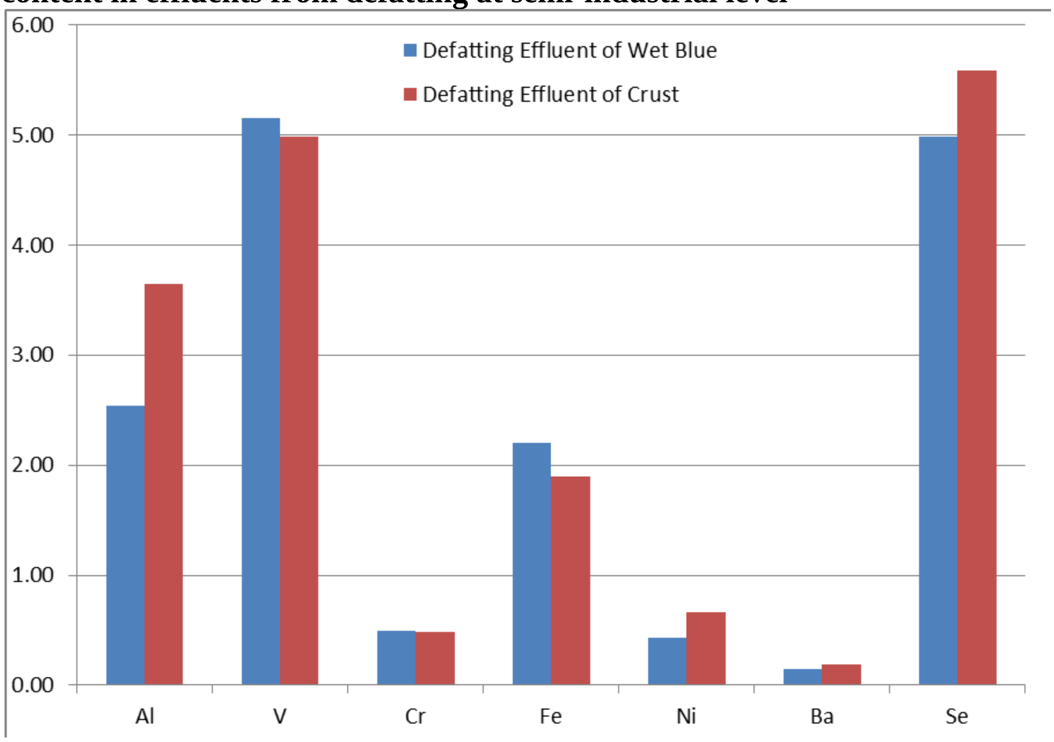
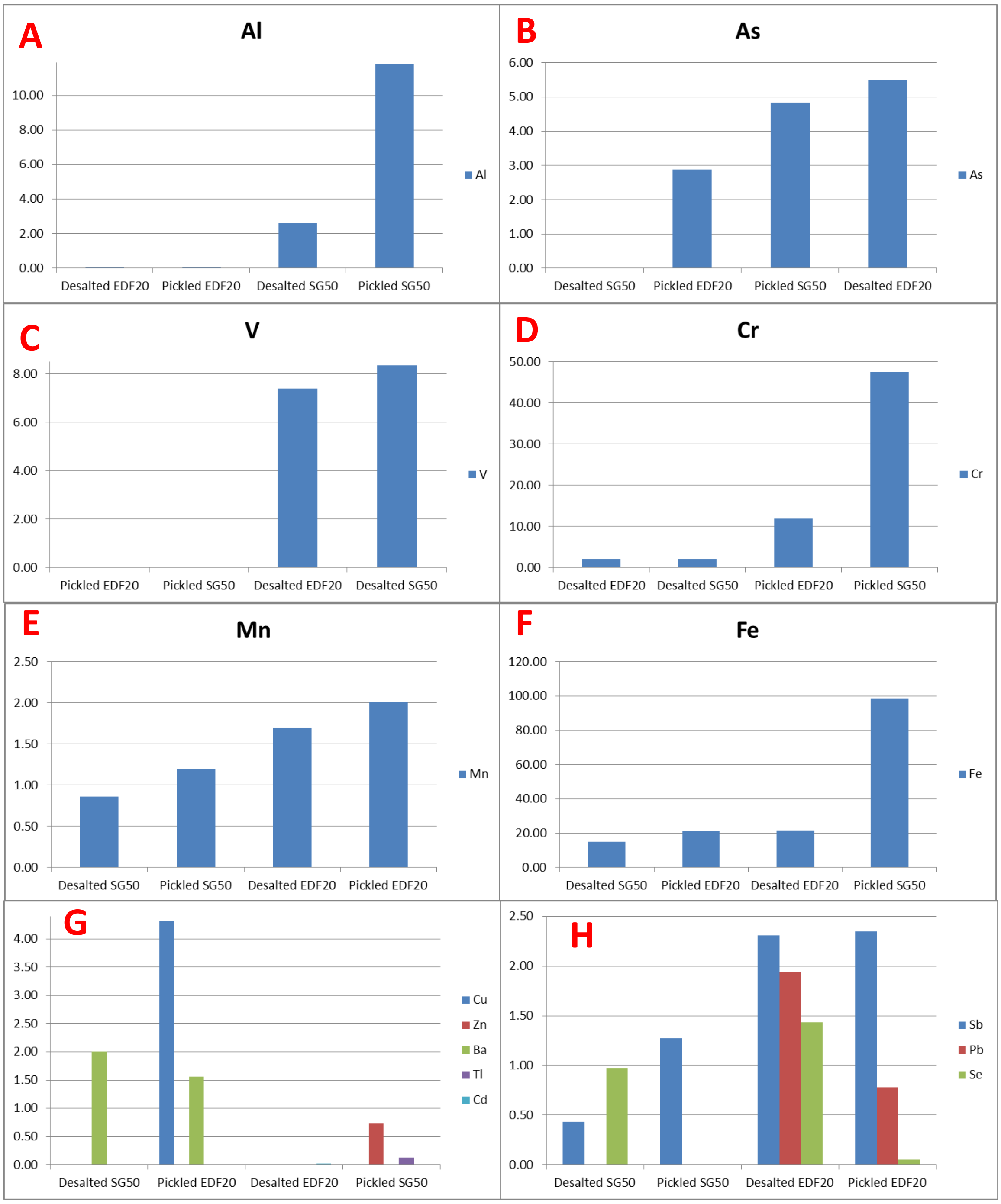


Figure 6.1
Metal content in effluents from defatting at pre-industrial level



7. Conclusions

The Ecodefatting project achieved the goal to demonstrate a new formulation for removing fat from animal hides, replacing old fashioned chloroparaffins and alkyl phenols without posing any environmental issue. In addition, the project went even beyond its technical goal, since it was possible to reduce even the content of ethoxylated species, currently used to formulate commercial defatting products. This has important environmental implications, due to the industrial process behind the production of ethoxylated species: that are much more safe in terms of human exposure, but have an important impact in terms of chemical emissions for the environment. The introduction of alternative species, derived from natural substances such as lactose in a defatting formulation, led to the achievement of three main objectives: the good defatting performance demonstrated on different hides on pilot scales, the sustainability of the production of the new formulation and the reduction of chemical emission. In this case, the project gave clear evidence about the complete uselessness of chlorinated defatting agents, or even to embark on any kind of chemical elaboration of the lactose derivatives shown in the project, to insert any chlorine related functional group. This has the immediate consequence of removing totally any chlorine related waste from the effluents. Ecodefatting showed also the possibility to reduce the content of ethoxylated species, currently used to formulate commercial defatting products. Alternative species from natural substances led to the achievement of good defatting on different hides. This was connected to the sustainability of the EDF20 production and the reduction of chemical emission. This latter aspect was also analysed in an Life Cycle Assessment study, where the production of the lactose derived species was examined in details, due to the proposed chemistry. It came out that some of the processes, adopted to produce the compound present in EDF20, may even bring a positive contribution to the reduction of chemical emission. In other cases the development of the scale-up should focus on drafting work protocols for production campaigns able to reduce further the chemical emissions, that were estimated only at laboratory scale: the working time, the management of resources and the operative working scale can be optimized to approach 20-30% energy saving, comparing to standard processes for the production of ethoxylated alcohols.

The good adaptability of the new product to the standard tanneries' procedures allowed to demonstrate the hide defatting in on pilot scales, that were representative of routine production operations. The quality of the leather was good as well as that of the effluents since they appeared as fluid emulsions easily dischargeable down the dedicated industrial sewers. It was possible to demonstrated the purification of the effluents, mimicking most of the current methodologies of water treatment plants. Only the specific chemical treatments were not demonstrated: but this was not contemplated within the general objectives of the projects. The general trend of the analyses for heavy metals in the effluents highlighted the presence of only few metals and in some cases far below the legal limits required both for drinking water and for the water to industrial use. In some cases, Fe and Cr were detected as the most abundant metals, as the result of work processes carried out with metal based equipment *(i.e.*, steel) releasing inevitably traces of those elements. It was quite reassuring that the products of Ecodefatting did not have any role in the introduction of heavy metals during the development of hide processing. Therefore, the metal analyses of the effluents confirmed its important role as indirect environmental monitoring tool, which may acquire even more precious importance, monitoring the heavy metals directly on the hide matter. In this case, any abnormal presence of metals may well be a spot alert about the environment in which animals had grown: especially those confined into stables or shed premises of dubious housekeeping.