Friulian Journal of Science **25.** 2018, 77-82

# The EOX parameter in characterisation of sewage sludge in Friuli Venezia Giulia

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**Abstract.** Sewage sludge generated from wastewater treatment plants (WWTPs) has attracted greater attention because of its potential for improving soil properties and for providing important nutrient and trace element supplements that are essential for plant growth. In agricultural use of sewage sludge the pollutant risk for all sludge should be specifically evaluated due to the different characteristics of different types of sludge, which undergo different levels of treatment, as well as the extensive and variable nature of wastewater pollutant inputs. Sewage sludge generated from wastewater treatment plants in Friuli Venezia Giulia region were analysed to evaluate the extractable organic halogen (EOX) concentration. Ethyl acetate and *n*-hexane were used as extraction solvents and EOX values were determined coulometrically and compared with respect to the potential of solvents and size of WWTPs. For all sewage sludge samples, the obtained results proved ethyl acetate to be a more effective solvent in EOX-determination. It was found that sewage sludge from small WWTPs are more suitable for agricultural use due to their low concentration of EOX.

**Keywords.** EOX, Sewage sludge, Agricultural use.

**1. Introduction.** Sewage sludge refers to the sludge from urban wastewater treatment plants, to be considered as: "domestic waste water or the mixture of domestic waste water with industrial waste water and/or run-off rain water" (Directive 91/271/EEC) (Langenkamp et al. 2001). The treatment and disposal of sewage sludge is an expensive and environmentally sensitive problem. It is also a growing problem worldwide since sludge production will continue to increase as new sewage treatment plants are built

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and environmental quality standards become more stringent.

Land application of sewage sludge has proven to be a cost effective and environmentally safe disposal method, by beneficially recycling organic matter and nutrients, and improving soil quality. The characterisation of sewage sludge is extremely important prior to sludge disposal or its application to farmland as there is a risk of toxic elements accumulating in the soil.

**2. Working document on sewage sludge.** According to the European Union a "Working document on sludge", would promote the use of sewage sludge in agriculture while improving safety and harmonising quality standards. It proposes limit values on the concentrations of heavy metals and organic compounds that would restrict the use of sewage sludge in agriculture if these limits are exceeded, and provides suggestions for good practice in treatment and agricultural use. The compounds or groups of compounds recommended for regulation are AOX, LAS, DEHP, NP(E), PAH, PCB and PCDD/F.

**3. Extractable organic halogens (EOX).** Instead of the adsorbable organic halogens (AOX) concentrations found in soil, in sewage sludge the extractable organic halogens (EOX) values are used, these representing the total halogen content (Cl, Br, I) in organochlorine compounds which can be extracted by organic solvents (e.g. n-hexane, pentane, heptane) from environmental solids (sediments, organisms) or water samples (Kannan et al. 1992; Kannan et al. 1999). These compounds include not only synthetic polychlorinated biphenyls, organochlorine pesticides, polychlorinated dibenzo-p-dioxins or polychlorinated dibenzofurans and other substances, but also those produced naturally by microorganisms, flora and fauna (Asplund, Grimvall 1991; Hayer et al. 1996; Contreras Lopez 2003).

Although EOX could be a convenient parameter in the evaluation of sewage sludge quality, there isn't yet enough research on it. In the present investigation, EOX in sewage sludge samples was measured as a sum parameter of environmental pollution by synthetic organochlorine compounds which do not have to be individually assayed. For the EOX extraction two solvents were used: ethyl acetate and *n*-hexane, respectively polar and nonpolar.

**4. Sampling area.** In the present study, the sampling area covered Friuli Venezia Giulia. The sewage sludge samples were collected from different wastewater treatment plants (WWTPs) as shown in Figure 1.

**5. Analytical procedure.** All the samples were freeze-dried, sieved manually through a 2 mm mesh sieve and ground in a ball-grinder. Subsequently, one gram of each such pre-treated samples was extracted with ethyl acetate and *n*-hexane by sonification for 15 min. Most of the solvent was then evaporated from the extracts under vacuum until 10 ml remained and was refrigerated until analysis.


Figure 1. Sampling sites

**6. Instrument used.** Analyses were made using the Trace Elemental Instrument, Euroglas ECS 1000 upgraded with digital coulometer and control software (TEIS) (Fig. 2). A hundred microlitres of residual extract were poured into the instrument. At 1000°C, in an oxygen combustion atmosphere with the pyrolysis of organochlorine compounds, the release of hydrogen halides takes place. The reaction gases formed are carried by the gas stream to the titration cell after passing the absorber. The absorber is filled with concentrated sulphuric acid and its function is to remove water from the gas flow. In the titration cell there is a solution (acetic acid 70%) in which the silver ion concentration is maintained constant (approximately $10^{-7}$ M) by measuring the silver ion concentration continuously. As soon as the acid formed from the organic halogens reaches the cell, the halogen reacts with the silver ions present and precipitate as silver chloride (AgCl), silver bromide (AgBr) or silver iodide (AgI). From the integral of the current over time, the quantity of silver generated, and

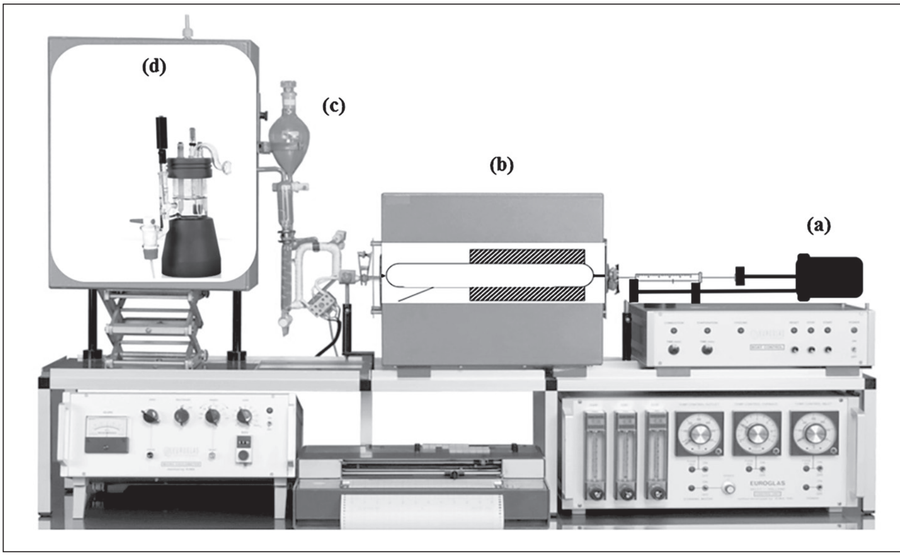


Figure 2. Schematic of the injection part (a), thermal extraction (b), trapping apparatus (c) and titration cell (d) in Euroglas ECS 1000.

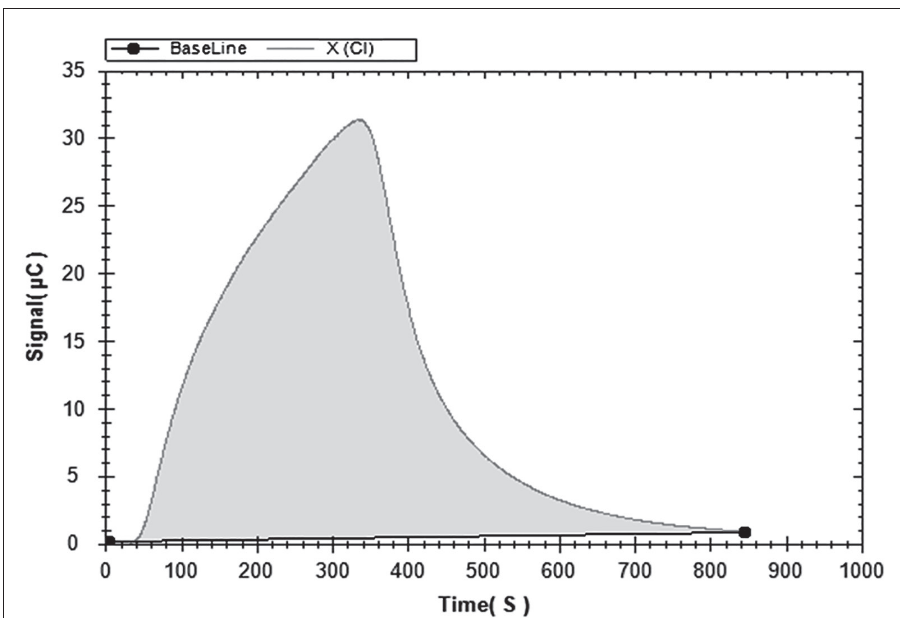


Figure 3. Single peak from ECS 1000 for 580 mg Cl/kg DM.

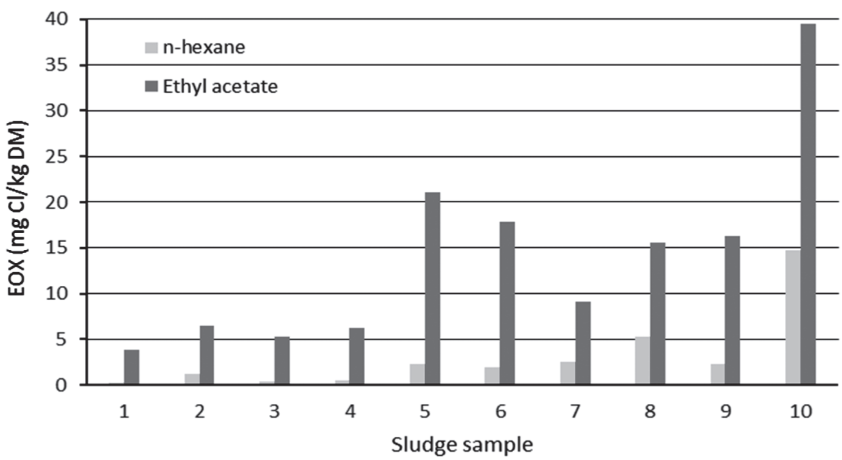


Figure 4. Concentrations of EOX measured in sludge samples from WWTPs (Goi et al. 2006).

Table 1. EOX (mg Cl/kg DM) extracted with ethyl acetate and *n*-hexane in samples collected from sewage sludge of different WWTPs.

| *Solvents* | *Sampling Sites* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| EOX by ethyl acetate | 26.9 | 5.1 | 11.7 | 2.7 | 6.8 | 4.3 | 1.23 | 21.01 |
| EOX by *n*-hexane | 5.6 | 0.93 | 3.4 | 0.5 | 1.02 | 0.72 | 0.33 | 2.55 |

thus the quantity of halogen introduced, can be calculated as chloride or as halogen molecules (Fig. 3).

**7. Results and discussion.** Comparing the two different solvents, ethyl acetate and *n*-hexane, the former was found to be a very effective extractant for the determination of extractable organic halogens (EOX) from contaminated sewage sludge (Tab. 1). Reemtsma and Jekel (1996) and Goi et al. (2006) obtained the same results (Fig. 4).

Considering current European regulations, the sewage sludge studied in this research on the EOX parameter is suitable for agricultural use. Our results were consistent with those shown in Goi et al. (2006), namely that a decrease in the size of WWTP leads to a decrease in EOX concentrations.

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