Assessing urban soil contamination with portable XRF: model development for Cd predictions when measurements are below LOQ.

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Introduction

In Wallonia, such as in many other parts of the world, there is an increasing demand for locally-grown food. However, some urban areas face historical soil contamination and risks of transfers to the food chain.

The « Fluxmafruil » project, funded by the Walloon Region, aims at identifying locations where the development of market gardening and fruit tree growing (Fig. 1) is possible in the vicinity of Liège, one of the major towns of the region.

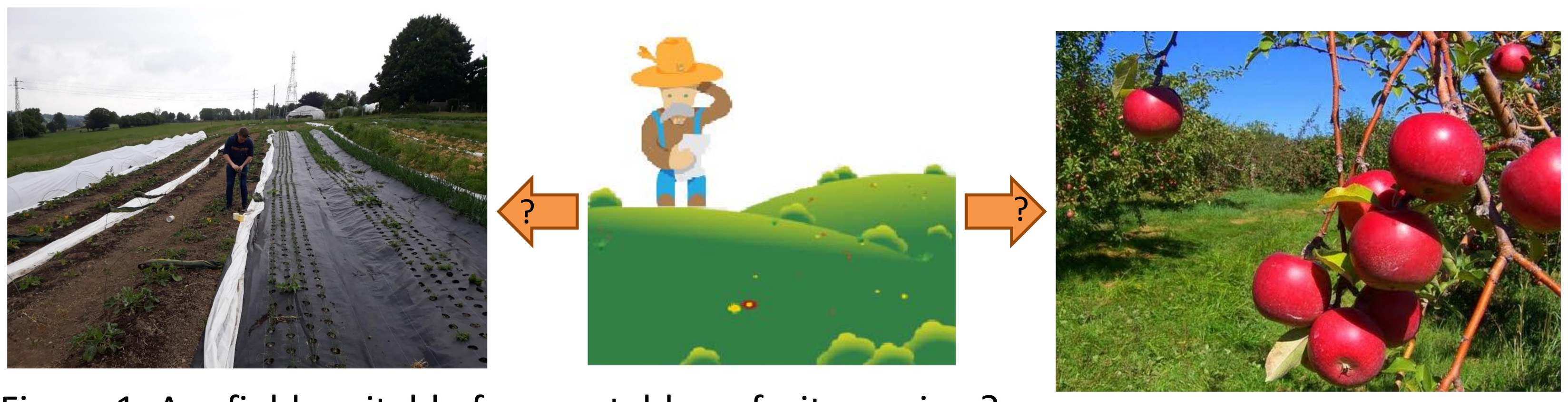


Figure 1: Are fields suitable for vegetable or fruit growing ?

Methodology

The general methodology relies on the identification of soil limitations for crop and fruit tree growing, as in classical land suitability assessment (Fig. 2).

Besides soil limitations linked to soil forming factors or land use, such as position in the relief, soil thickness, drainage or fertility, the question of contaminant content is specifically crucial in urban and sub-urban environments (Meuser, 2010; Xiao-San et al., 2012; Cichella et al.; 2020).

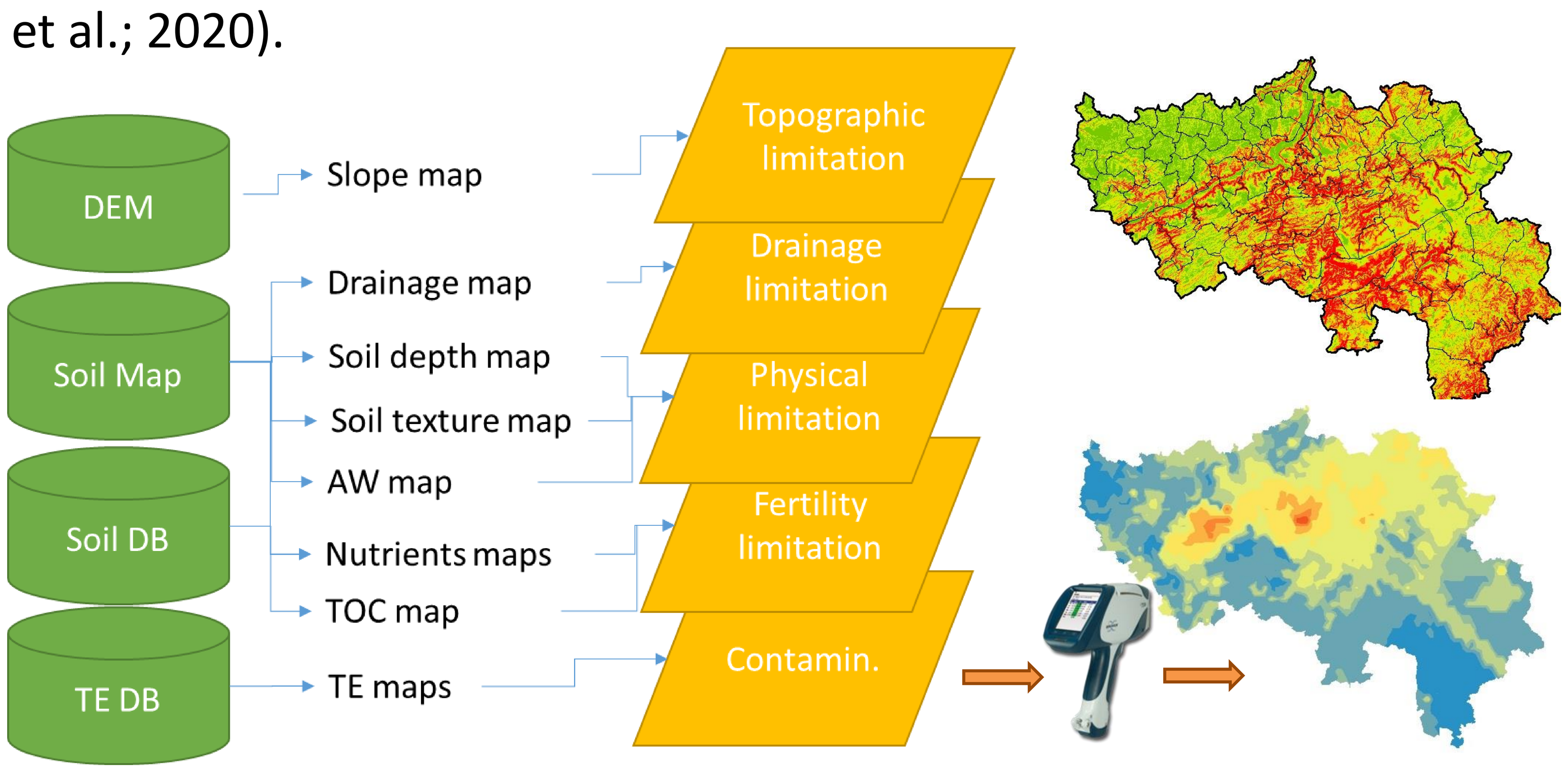


Figure 2 : Methodology for spatial assessment of soil limitations for gardening, and illustration of two maps : slopes and Trace metal contents classified

Portable X-ray fluorescence (pXRF) has been used by several authors for field of laboratory measurement of trace elements. Most have concluded to the adequacy of pXRF for rapid assessment of elements such as Pb or As, but the limits of detection of the portable devices are not compatible with the measurement of Cd content in moderately contaminated soils (Carr et al., 2007; Ravansari et al, 2020; McStay et al., 2021).

Our research intended to evaluate performances of pXRF to correlate to chemically extracted elements, specifically aqua regia content which is imposed from regulation on soil contamination. After defining a protocol of data acquisition in lab mode, we implemented a database of more than 350 samples with pseudo-total contents ranging from LOQ to tens for Cd and Hg, tens to hundreds for As, Cr, Cu, and Ni, tens to some thousands for Pb or Zn. Samples were collected from diverse types of environment including agricultural fields, kitchen gardens and brownfields.

Regarding prediction of Cd content from pXRF, as no direct measurement could be quantified by the apparatus, we hypothesized that a predictive model could be build from correlations between Cd content and other soil properties. We therefore investigated different kinds of regression : single linear, multiple linear or CART-regression with the other inorganic elements and the origin of the samples.

Main results

Table 1: Detection limits given by the manufacturer in (mg.kg^{-1})

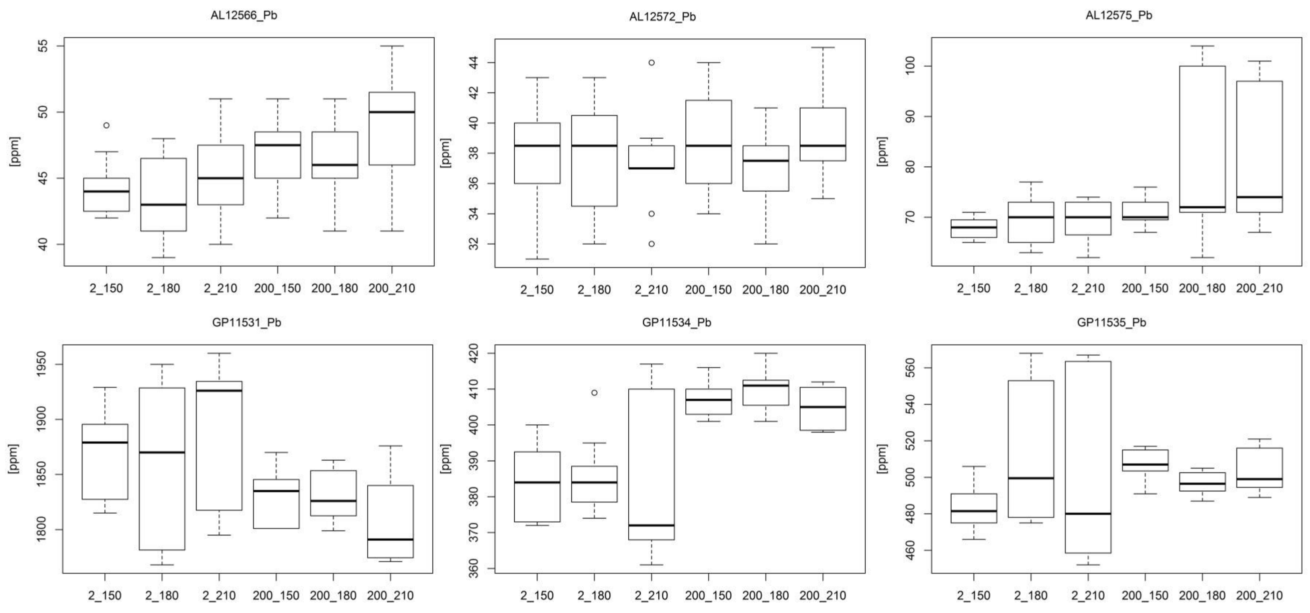
Al	Fe	Mn	As	Cd	Co	Cr	Cu	Hg	Mo
960	13	18	3	19	5	19	5	6	6
Ni	Pb	Zn	Ag	Sb	Se	Sn	P	Ca	K
5	11	3	10	30	3	20	90	37	31

Titan S1 Bruker

Numerous tests have been performed on a collection of soil samples from the lab library in order to evaluate the performance of the pXRF in the lab configuration mode, prior to acquisition of new samples on the field.

Study of the effect of measurement conditions : example for Pb

Figure 3



13 samples along a gradient of TE content, 2 grinding sizes (2mm & 0.2mm), 3 lengths of measurement (150, 180, 210 sec) x 12 repetitions → high variability

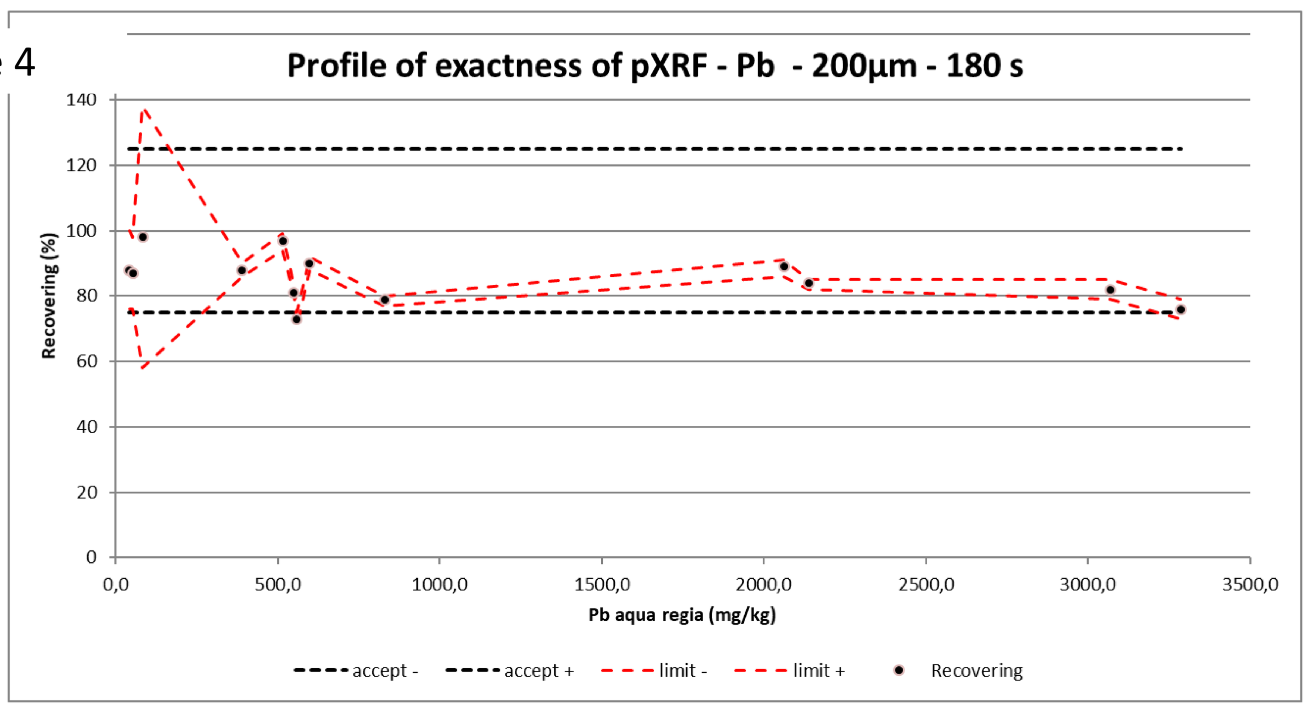
Determination of the LOQs

Spike (ppm)	Cd	Co	Cr	Cu	Ni	Pb	Zn	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	0	0	0	0	0	0	0	< LOD	0,0	24,5	4,7	< LOD	< LOD	10,7
2	2	5	10	5	10	10	10	< LOD	0,0	51,5	8,7	6,5	11,3	13,3
3	5	10	20	10	20	20	20	< LOD	0,0	40,0	15,7	20,3	19,0	26,3
4	10	20	30	20	30	30	30	< LOD	0,0	68,0	23,3	26,3	24,0	33,3
5	20	30	40	30	40	40	40	< LOD	0,0	79,7	33,3	36,3	37,0	48,3
6	50	40	50	50	50	50	50	17,5	0,0	72,0	42,7	37,0	35,3	44,0

Quartz spiked with known quantities of TE, 3 repetitions, 180 sec → bad performance for Cd, Co

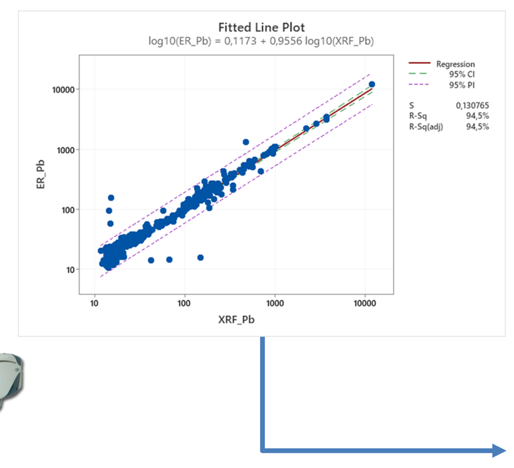
Determination of accuracy profiles versus aqua regia contents

Figure 4



Profiles of exactness allow determination of the ranges of measurement for every elements.

Prediction of aqua regia contents based on correlation with pXRF



TE	Mean error		Absolute mean error		RMSE	
	mg/kg	%	mg/kg	%	mg/kg	%
As	2,7	11%	5,1	21%	21,9	91%
Cr	0,8	2%	7,4	20%	11,2	30%
Cu	0,9	2%	7,3	14%	18,4	35%
Mo	0,04	3%	0,92	59%	1,18	76%
Ni	0,0	0%	2,7	9%	3,9	14%
Pb	12,1	6%	26,5	13%	122,2	60%
Zn	20,6	5%	48,4	12%	141,0	35%

Acceptable prediction for As, Cr, Cu, Mo, Ni, Pb and Zn

Prediction of aqua regia Cd contents based on correlation with other TE

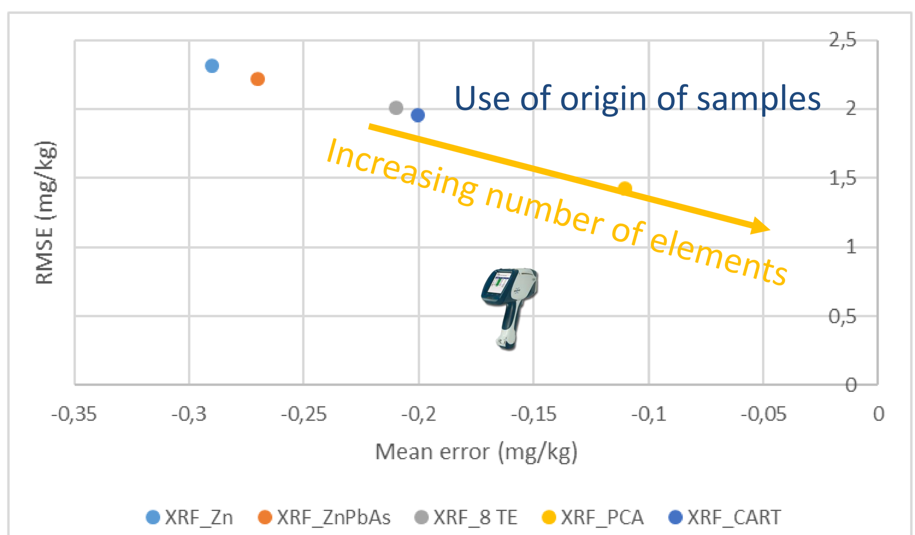


Figure 5 : Comparison of regression models for Cd prediction

Prediction of Cd is possible but still needs improvement

References

Carr R. et al. (2007). Identification and mapping of heavy metal pollution in soils of a sports ground in Galway City, Ireland, using a portable XRF analyser and GIS. *Environ Geochem Health*.

Cichella D. et al. (2020) Urban soil contamination in Salerno (Italy): Concentrations and patterns of major, minor, trace and ultra-trace elements in soils. *J. geochem. Explor*. 213, 106519.

Mc Stay et al (2022). Nutrient and toxic elements in soils and plants across 10 urban community gardens: Comparing pXRF and ICP-based soil measurements. *J. Env. Qual.,* 51(3), 439-450

Meuser H. (2010). Contaminated urban soils. *Envir. Pollution* 18.

Ravansari, R. et al. (2020). Portable X-ray fluorescence for environmental assessment of soils: Not just a point and shoot method. *Environ Intern*, 134, 105250.

Xiao-San L. et al. (2012). Trace metal contamination in urban soils of China. *Sci Tot Envir* 421–422, 17–30.