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(54) **Method for determining in-situ suspended sediment properties.**

(57) The invention is directed to a method for determining in situ and in real time at least one suspended sediment property in a medium, said suspended sediment comprising a mineral and an organic fraction. Said method comprises the steps of (a) measuring light absorbance with a submersible ultraviolet-visible spectrometer, said ultraviolet-visible spectrometer being configured to analyse to analyse light absorbance at wavelengths which are comprised between 220 nm and 730 nm and of (b) correlating the light absorbance to the properties of said suspended sediment, preferentially by using the Beer-Lambert's law. Said method is remarkable in that said step (b) is performed by using one model calibrated for deriving said properties of said suspended sediment from said light absorbance.

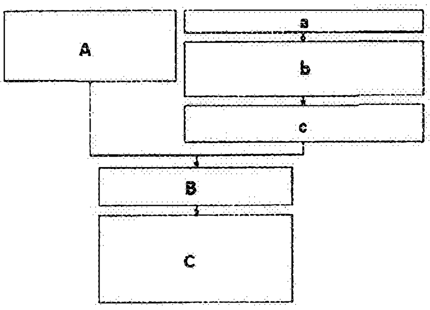

Fig. 1

№ 92827

# Method for determining *in-situ* suspended sediment properties

## Description

## Technical field

[0001] The invention is directed to a method to estimate suspended sediment properties, for example the physico-chemical composition of said suspended sediment properties.

## Background art

[0002] Suspended sediments play an important role as a vector for the transfer of nutrients and metals in fluvial systems (Horowitz A. J., Stephens V. C., *Sci. Total Environ.*, 2008, *400,* 290–314). For instance, a substantial proportion of the total phosphorus load of many rivers (Walling D.*, et al. Freshwater contamination,* 1997, *IAHS Press,* Vol. *243*; Bowes M. J., *Sci. Total Environ.,* 2003, *313*, 199–212) and >90% of the flux of the majority of trace elements (Horowitz A. J., *A primer in sediment-trace element chemistry,* 1991, 2nd ed., Lewis) are transported in association with fine particles. As a consequence, polluted sediment can lead to undesirable ecosystem conditions and water quality deterioration (Bilotta G. S. and Brazier R. E., *Water Res.,* 2008, *42,* 2849–2861). Information on suspended sediment physical and geochemical composition is thus needed in order to implement appropriate sediment control strategies and accomplish legislation requirements.

[0003] However, the need to sample suspended sediments, to sieve and to analyse the samples in the laboratory makes the determination of suspended sediment properties very demanding in terms of labour time and cost (Martínez-Carreras N. *et al.*, *J. Hydrol.*, 2010, *382*, 49-63; Walling D., *J. Soils Sediments*, 2013, *13*, 1658-1675). With the aim of reducing labour and improving the temporal resolution of suspended sediment properties estimates, spectral reflectance-based methods were developed (Martínez-Carreras N. *et al.*, *J. Soil Sediments*, 2010, *10*, 400-413). These approaches allowed analysing the suspended sediment retained in filter papers after stream water filtration. However, suspended sediment properties can exhibit significant variations within and between storm runoff events, and a robust method for measuring suspended sediment properties *in situ*, cost efficient, at high-frequency and over large periods of time is still lacking.

[0004] Instruments for monitoring suspended sediment properties *in situ* are limited to sediment physical properties (*e.g.* particle size characteristics; Walling D. *et al.*, *Water Res.*, 1993, *27*, 1413-1421). Contrarily, affordable field-deployable autoanalysers are a reality to measure stream flow chemistry. Some analysers use ion-specific electrodes, while others are based on proxy measurements. One newly available technology based on proxy data are portable ultraviolet-visible (UV-VIS) light spectrometers (220-730 nm). These spectrometers measure the light absorption spectra directly submersed in liquid media. They are often used in wastewater drainage systems for a fast and simple evaluation of wastewater quality (Brito R.S. *et al.*, *Urban Water J.*, 2014, *11*, 261-273). Recently, they have been used to estimate turbidity, DOC (dissolved organic carbon) and TOC (total organic carbon) (Avagyan A. *et al.*, *J. Hydrol.*, 2014, *517*, 435-446), and $NO_3$-N (Huebsch M. *et al.*, *Hydrol. Earth. Syst. Sci.*, 2015, *19*, 1589-1598) in stream at a temporal resolution as high as several minutes.

[0005] The hypothesis is that submersible UV-VIS spectrometers can be used to estimate suspended sediment properties in real time. This will move the field forward towards *in situ* high temporal resolution measurements of suspended sediment properties. To the inventor's knowledge, there is only one study that used a spectrometer to solely estimate suspended sediment properties (*i.e.* excluding the dissolved fraction) (Bass A. M. *et al.*, *Limnol. Oceanogr.*, 2011, *56*, 2282-2292). The authors estimated particulate organic matter (POC) at a high temporal resolution and in a catchment. Nonetheless, no calibration of the instrument was performed to predict POC directly. POC was estimated as the difference between TOC and DOC. TOC and DOC were estimated using the internal calibration procedure of the instrument.

## Summary of invention

### Technical Problem

[0006] The invention has for technical problem to provide a method for determining *in situ* suspended sediment properties which solves all the above explicated problems found in prior art techniques and explicated above. In particularly, traditional *ex situ* laboratory procedures for measuring suspended sediment physico-chemical properties are generally time-consuming and expensive. For these reasons, the analyses are normally restricted to a relatively low number of samples, which is a major drawback in the precise investigation of the suspended sediment properties.

### Technical solution

[0007] The invention is directed to a method for determining *in situ* and in real time at least one suspended sediment property in a medium, said suspended sediment comprising a mineral and an organic fraction. Said method comprises the steps of (a) analysing light absorbance with a submersible ultraviolet-visible spectrometer, said ultraviolet-visible spectrometer being configured to analyse light absorbance at wavelengths which are comprised between 220 nm and 730 nm and of (b) correlating the light absorbance to the properties of said suspended sediment, preferentially by using the Beer-Lambert's law. Said method is remarkable in that said step (b) is performed by using one model calibrated for deriving said properties of said suspended sediment from said light absorbance.

[0008] According to a preferred embodiment, said model has been calibrated from at least one predictor variable obtained through *ex situ* physico-chemical analysis of said suspended sediment or theoretically, said step of calibration being performed at least once before and/or after said step (a), preferentially before said step (a).

[0009] According to a preferred embodiment, said model is a statistical model, preferentially a regression model.

[0010] According to a preferred embodiment, said regression model is chosen from ordinary least-square (OLS) regression, robust regression, principal component regression, partial least-squares (PLS) regression, Ridge regression, Lasso regression or non-linear regression.

[0011] According to a preferred embodiment, said at least one suspended sediment property comprises the properties of said mineral, preferentially trace elements, and/or of said organic fraction, preferentially polycyclic aromatic hydrocarbons.

[0012] According to a preferred embodiment, said at least one suspended sediment property is chosen among total phosphorus concentration, total nitrogen concentration, total carbon concentration, acid-extractable elemental concentrations of Cr, Cu, Ni, Pb and Zn, and/or any other, and/or any combination thereof.

[0013] According to a preferred embodiment, said step of analysing light absorbance with a submersible ultraviolet-visible spectrometer is performed, preferentially continuously, with an interval comprised between 1 second and 6 hours between each measurement, preferentially with an interval of 15 minutes between each measurement.

[0014] According to a preferred embodiment, said submersible ultraviolet-visible spectrometer is configured to provide one or more of light absorbance measurements, preferentially at 1 nm or 2.5 nm intervals.

[0015] According to a preferred embodiment, said submersible ultraviolet-visible spectrometer comprises at least one measuring window and at least one automatic cleaning means configured for automatically cleaning said at least one measuring window.

[0016] According to a preferred embodiment, said medium is chosen among a predetermined catchment, a waterway, a river, a stream, a wastewater drainage system, a lake, a water reservoir and/or any other.

[0017] According to a preferred embodiment, said step of calibration is repeated at least once, twice, three times, or more, before and/or after step (a), preferentially before step (a).

[0018] According to a preferred embodiment, said suspended sediments are extracted from said medium, preferentially by filtration, decantation, freeze-drying and/or wet-drying, before performing said *ex situ* physico-chemical analysis.

[0019] According to a preferred embodiment, said *ex situ* physico-chemical analysis is performed on said suspended sediments by laboratory analytical methods, preferentially by (a) loss-on-ignition studies, (b) inductively coupled plasma (ICP) spectrometry coupled with an atomic emission spectrometer (ICP-AES) and/or with a mass spectrometer (ICP-MS), and/or atomic absorption spectroscopy (AAS) after applying one or several digestion techniques to the suspended sediment sample, (c) gas chromatograph coupled with mass spectrometer, (d) combustion techniques coupled with titration, gravimetric, manometric, spectrophotometric and/or gas chromatographic techniques, (e) cold vapour atomic absorbance mercury analyser, (f) X-ray diffractometry, (g) differential thermal analysis, and/or (h) any other.

[0020] According to a preferred embodiment, said step of calibration further comprises the steps of (a) finding the optimal light absorbance wavelength to use for the model, (b) finding the optimal data transformation; and (c) finding the model coefficients.

[0021] According to a preferred embodiment, said at least one predictor variable is chosen among total phosphorus concentration, total nitrogen concentration, total carbon concentration, acid-extractable elemental concentrations of Cr, Cu, Ni, Pb and Zn, and/or any other, and/or any combination thereof.

## Advantages of the invention

[0022] The invention is particularly interesting in that the described innovative method allows the estimation of suspended sediment physico-chemical properties at high temporal resolution and for long spans of time. Furthermore to be performed directly in the medium, said method is simple, non-destructive and relatively cheap. The method of the present invention could be implemented in different environmental monitoring studies, in hydrological research and/or in water treatment plants.

Brief description of the drawings

[0023] Figure 1: Schematic representation of the method according to the invention.

[0024] Figure 2: Discharge and rainfall at the Weierbach catchment during the sampling period (December 2013 – January 2015) and suspended sediment concentration data (n=47). Precipitation data measured at the Roodt meteorological station, which is located ~3.5 km south-east from the catchment outlet.

[0025] Figure 3: Scatter plot and regression line between turbidity and suspended sediment concentration after removal of 5 light absorbance outliers (*i.e.* spectra with light absorbance values >60% or <2% for all measured wavelengths), 3 turbidity outliers (*i.e.* turbidity values>60 NTU), and after removal of five other samples that weakened the liner relationship (n=34).

[0026] Figure 4: Light absorbance spectrums of the calibration set (n=34) and adjusted coefficient of determination ($r^2$) between LOI and absorption at all measured wavelength. Adjusted $r^2$ penalizes for higher p.

[0027] Figure 5: Results obtained with different regression models. m: number of light absorbance wavelengths in the final model; Comp.: optimum number of PLS components that minimises the average standard error of prediction (SEP); $r^2$: coefficient of determination; $r^2_{adj.}$: adjusted coefficient of determination.

[0028] Figure 6: Comparison of measured and predicted LOI values using robust MM-regression. Solid line shows regression between measured and predicted LOI. Dashed line shows 1:1 line.

[0029] Figure 7: Discharge, rainfall, measured (red diamonds) and predicted LOI from light absorbance data at the Weierbach catchment for the event occurred in December 2014. Predicted LOI estimated using the robust regression calibration method. Erroneous spetroanalyser measurements associated to a dirty measuring window were discarded.

Description of an embodiment

[0030] The method of the present invention is described on figure 1.

[0031] On the block A of the schematic representation, *in situ* water light absorbance measurements are performed at high temporal resolution, for example at 15 minutes intervals. These *in situ* measurements have an interesting advantages, in time and in cost, compared to the traditional methods which required (a) to limit the collection of medium samples (*e.g.* stream water) (block a), (b) to separate the suspended sediment from the medium (*e.g.* stream water) by performing successive steps of filtration, decantation, freeze-drying and/or wet-drying (block b), and (c) to perform traditional laboratory chemical and/or physical analysis of the resulting sediment (block c).

[0032] These *in situ* measurements are achieved by portable submersible ultraviolet-visible light spectrometers (configured to analyse a light with a wavelength which is comprised between 220 nm and 730 nm). They operate in the field directly submerged into the water. They measure the intensity attenuation of a light beam emitted by a lamp after contact with the medium (*e.g.* stream water) compared to the intensity attenuation when passing through a reference medium (*e.g.* distilled water). Using the Beer-Lambert's law, it is possible to relate the attenuation of the light to the properties of the medium through which the light is travelling. Specifically, the absorbance of a medium is directly proportional to (a) its thickness (*i.e.* path length), and (b) to the concentration of the attenuating species in the medium sample.

[0033] Chemometric techniques (*i.e.* the implementation of multivariate data analysis to chemistry-related data) can then be used to determine the concentration of a compound in a complex mixture. Hence, chemometrics aim at developing statistical models to optimally predict a property $y$ from several variables $x_1$, $x_2$, ...$x_n$. $y$ is the property to be estimated and $x_1$, $x_2$, ...$x_n$ are the light absorbance measurements at different wavelengths.

[0034] As suspended sediment comprises a mineral and an organic fraction, the properties of the mineral (*e.g.* trace elements) and the properties of the organic fraction (*e.g.* polycyclic aromatic hydrocarbons) might weaken the light beam of the spectrometer in a linear manner. This allows the possibility to calibrate water light absorbance values to predict the physical (*e.g.* colour) and/or the chemical properties of said suspended sediment.

[0035] On the block B of the schematic representation, a calibration step using a statistical model, in particular a regression model, is performed. This kind of step can also be achieved from theoretical data of the suspended sediment which is analysed.

[0036] The final part of the method, depicted on the block C of the schematic representation, is the determination of suspended sediment chemical or physical properties at 15 minutes time steps using the statistical model mentioned in the previous paragraph.

[0037] Said suspended sediment chemical properties that have been studied are mainly total phosphorus concentration, total nitrogen concentration, total carbon concentration, acid-extractable elemental concentrations of Cr, Cu, Ni, Pb and Zn, and/or any combination thereof.

[0038] Further details on the method of the present invention are given below.

[0039] To test the hypothesis, a spectroanalyser (scan, scan Messtechnik GmbH, Vienna) was installed at the outlet of the Weierbach catchment (0.45 km², forested, NE Luxembourg). Stream water light absorbance was measured from December 2013 to January 2015. As a proof-of-concept study, these experimental data were used to calibrate a regression model that predicts suspended sediment loss-on-ignition (LOI) from light absorbance data. LOI was selected because it can be measured in the sediment retained in filter papers after stream water filtration.

[0040] Study area

[0041] The Weierbach catchment (0.45 km², 49°49' N 5°47' E) is located in the north-western part of Luxembourg. It is mainly covered by mixed Oak-Beech deciduous forest (76% of the land cover; *Fagus sylvatica* and *Quercus petraea*) and conifers (24% land cover; *Pseudotsuga menziessii* and *Picea abies*). Geology is dominated by Devonian schists, phyllades and quartzite. Soils are shallow (<1 m) and dominated by cambisols, lithosols and colluvisols.

[0042] Material and methods

[0043] Spectrometer

[0044] The spectroanalyser probe (scan Messtechnik GmbH) was installed at the catchment outlet submersed in the stream. The sensor emits a light beam by a xenon flash lamp. After contact with the stream water, a detector measures the intensity of the beam over the UV-VIS wavelength range.

[0045] The sensor was placed at 10 cm above the ground and fixed to a metallic plate to ensure its parallel position to the stream bed during the measurements. This ensures that there is no sedimentation of particles in the measuring section and avoids adhesion of gas bubbles. Three 12 V batteries connected in parallel supplied power. This setup allowed two weeks of continuous measurements at 15 minutes intervals without maintenance.

[0046] The scan spectrometer provided measurements of light absorbance at 2.5 nm intervals, as well as turbidity, nitrate concentration, and/or dissolved organic concentration (DOC) using a global calibration developed by the company. However, local calibrations are encouraged by the manufacturer to ensure that parameters are adapted to local concentrations.

[0047] The measuring window was automatically cleaned every three hours with compressed air (scan Messtechnik GmbH), and manually cleaned at bi-weekly intervals. Nevertheless, light absorbance spectra showed unrealistic values at some periods of time, most probably due to a dirty measuring window. These unrealistic values (*i.e.* spectra with light absorbance values >60% or <2% for all measured wavelengths) were discarded. Further, spectra associated to turbidity values >60 NTU were discarded, as considered as unrealistic in the Weierbach catchment.

[0048] Stream water sampling and suspended sediment concentration measurements

[0049] Stream water samples (1-L) were collected at the outlet of the Weierbach catchment manually at fortnightly intervals from December 2013 to January 2015 (n=24). Additionally, samples were collected during a winter storm runoff event in December 2014 at 1-6 hours intervals (n=23) using automatic water samplers (ISCO 3700 FS and 6712 FS) triggered by water level.

[0050] Suspended sediment concentration was determined by filtering a known sub-sample volume (normally between 150 and 250 ml) through 1.2 µm WHATMAN GF/C glass fibre filters by means of a Millipore vacuum pump. The filters were previously dried at 105 °C for more than two hours, cooled in a desiccator, and weighted. After filtration, the filters were dried again at 105°C and reweighted. The differences between weightings provided the total amount of sediment retained in the filters. The concentration of suspended sediment was calculated by dividing the total amount of sediment retained in the filters by the volume of filtered sample.

[0051] Loss-on-ignition

[0052] The LOI method refers to the loss of matter in soils and sediments after an ashing treatment. LOI mainly involves organic matter combustion, decomposition of carbonates and removal of structural water from clay minerals. It informs about the physico-chemical composition of the sediment. LOI was used in the study because it is possible to measure it on the suspended sediment that was retained in the glass fibre filters after filtration. Filters were combusted at 550°C for 2 h in a muffle furnace. The samples were cooled in a desiccator and weighed again to obtain the weight lost-on-ignition. LOI values are presented as percentage weight loss of dry mass.

[0053] Calibration of light absorbance measurements with percentage weight loss-on-ignition

[0054] A regression model was calibrated to predict LOI from light absorbance values by finding (i) the optimal light absorbance wavelength(s) to use for the model, (ii) the optimal data transformation, and (ii) the model coefficients. The light absorbance spectra measured were selected at the same time of or at the time closest to the time manual samples were collected. Assuming a univariate model, according to equation 1.

[0055] $y = X \bullet b + e$ (Eq. 1)

[0056] In equation 1, y is the variable to be modelled, the matrix X contains the predictor variable, the regression coefficients are collected in the vector b and e is the residual vector. An estimate for the spread of the error distribution is the standard error of prediction (SEP), *i.e.* the standard deviation of the residuals, according to equation 2.

[0057] $$SEP = \sqrt{\frac{1}{z-1}\sum_{i=1}^{z}(e_i - \bar{e})^2} \qquad \text{(Eq. 2)}$$

wherein $\bar{e}$ is the arithmetic mean of the residuals (or bias). SEP is measured in units of y and can be used to compare the performance of different methods.

[0058] With the objective of modelling LOI by one or several light absorbance values, the prediction performance of different linear regression models was estimated with one or several variables (*i.e.* light absorbance at different wavelengths). Three different regression methods were tested: (1) ordinary least-square (OLS), (2) MM-robust, and (3) partial least-squares (PLS) regressions. In robust statistics, another function than the sum of all squared residuals is minimized, with the objective to diminish the influence of outliers. In PLS regression, instead of minimizing only the explained variance of the predictor variables, PLS components take into account the dependent variables by maximizing, for example, the covariance between the scores of the predictor and modelled variables. This means that PLS components are relevant for the predication of the modelled variable, not for the modelling of the predictors. Several pre-processing techniques were tested but not used as any significant improvement in the predictions was observed (results not shown). Models with multiple variables are fitted to mean-centered data. Moreover, as the LOI data set was rather small, a resampling strategy was used rather than splitting the samples in several sets (*i.e.* training, validation and test sets) for calibration.

[0059] R for statistical analysis (R Core Team, 2013) was used. The R package 'chemometrics' implemented by Varmuza and Filzmoser (2009) and its associated vignette (Garcia 200 and Filzmoser, 2015) were used.

[0060] Results

[0061] Suspended sediment concentration and loss-on-ignition measurements

[0062] Figure 2 depicts that the fortnightly sampling covered various flow stages. The maximum sampled suspended sediment concentration during the observation period was 124 mg/L. This coincided with the maximum catchment discharge during the study period (80 L/s). Suspended sediment concentration (SSC) positively linearly correlated to loss-on-ignition (LOI; $n=47$, $r^2=0.85$, $p<0.01$). LOI measured values ranged from 1.9 to 9.6%.

[0063] Calibration of light absorbance measurements with percentage weight loss-on-ignition

The performance of a sample set was studied to calibrate the relationship between LOI and light absorbance. This sample set resulted from the exploration of the relationship between suspended sediment concentration and turbidity (figure 3). A scatter plot and a regression line between turbidity and suspended sediment concentration, after removal of 5 light absorbance outliers (*i.e.* spectra with light absorbance values >60% or <2% for all measured wavelengths), 3 turbidity outliers (*i.e.* turbidity values >60 NTU), and after removal of five other samples that weakened the liner relationship ($n=34$) are shown.

[0064] Ordinary least-square regression between LOI and light absorbance was performed at all measured wavelengths (220-735 nm). Measured absorption spectrum for the calibration set and adjusted $r^2$ results are shown in figure 4. Results show that wavelengths in the visible part of the spectra (*i.e.* 400-735 nm) have a higher correlation to LOI (up to 0.86 adjusted $r^2$ for the calibration set, at 710 nm), compared to the ultraviolet range (*i.e.* 100-400 nm). The standard error of prediction (SEP) for calibration set was 0.52% (see figure 5).

[0065] The resulting coefficients of determinations for the MM-robust regression between LOI and light absorbance at all measured wavelengths (220-735 nm) were lower for calibration set to those obtained using OLS regression (maximum of 0.77 at 710 nm, see figure 5). However, the SEP was lower (*i.e.* 0.48% at 237 nm). Figure 6 shows the scatterplot between measured and predicted LOI values (from light absorbance at 710 nm) using MM-robust regression for the calibration set.

[0066] The partial least-squares regression method with repeated double cross-validations (100 predictions for each measured LOI) resulted in higher average SEP value (0.95% for the calibration set) and lower coefficients of determination (0.77 for calibration set) than with the other two methods (see figure 5). Moreover, the 100 predictions of LOI for each measured value presented relatively high dispersions (data not shown), resulting in relatively high uncertainty ranges.

[0067] Prediction of percentage weight loss-on-ignition from light absorbance measurements

[0068] MM-regression was used to predict LOI from light absorbance at 710 nm as the predicted error of prediction was lower than with the other methods (see figure 5). Figure 7 shows measured and predicted LOI from light absorbance data collected at 15-min intervals at the Weierbach catchment for the storm runoff event occurred in December 2014.

[0069] Stream flow response during the event was double peaked. Specifically, several small stream flow peaks occurred and their timing was coincident with the rainfall inputs. Later on, a larger and delayed peak occurred. Higher suspended sediment LOI percentages were measured during the relatively low discharge peak occurred the 11 December and during the rising limb of the hydrograph (*i.e.*, 12 and 13 December). During the long falling limb (*i.e.* from 14 to 18 December) LOI percentages decreased to pre-event values.

[0070] Discussion on predicting LOI from light absorbance data

[0071] Several calibration methods were tested to predict LOI from light absorbance (*i.e.* obtained *in-situ*) and relatively good correlation were found between predicted values (*i.e.* obtained *ex-situ*) and measured values (*i.e.* obtained *in-situ*) (see figure 5).

[0072] When using MM-regression for calibration, a good agreement between predicted and measured LOI was observed (figure 7). This could be expected as measured samples were included in the calibration set due to the low number of available measurement. The predictive model did not predict LOI values lower than 2.7% (figure 6). This might be due to the low concentration of sediment in stream water when such a low LOI values occurred. Consequently, this sediment might have a very low impact on the light absorbance measurements.

[0073] During the studied storm runoff event (figure 7), the increase in LOI values during the rising limb of the hydrograph might be associated to a remobilization of suspended sediments enriched in organic matter from the stream and/or near stream areas.

Revendications

1. Méthode pour détermination *in situ* et en temps réel d'au moins une propriété de sédiment en suspension dans un milieu, ledit sédiment en suspension comprenant un minéral et une fraction organique,
   ledit procédé comprenant les étapes
   a) d'analyse de l'absorbance de lumière avec un spectromètre ultraviolet-visible submersible, ledit spectromètre ultraviolet-visible étant configuré pour analyser l'absorbance de la lumière aux longueurs d'onde qui sont comprises entre 220 nm et 730 nm, et
   b) de corrélation de l'absorbance de lumière aux propriétés dudit sédiment en suspension, de préférence en utilisant la loi de Beer-Lambert,
   caractérisée en ce que
   ladite étape (b) est effectuée en utilisant un modèle calibré pour dériver lesdites propriétés dudit sédiment en suspension à partir de ladite absorbance de la lumière.

2. Méthode selon la revendication 1, caractérisée en ce que ledit modèle a été calibré à partir d'au moins une variable prédictive obtenue par *ex situ* analyse physico-chimique dudit sédiment en suspension ou théoriquement, ladite étape de calibrage étant effectuée au moins une fois avant et / ou après ladite étape (a), de préférence avant ladite étape (a).

3. Méthode selon l'une quelconque des revendications 1-2, caractérisée en ce que ledit modèle est un modèle statistique, de préférence un modèle de régression.

4. Méthode selon la revendication 3, caractérisée en ce que ledit modèle de régression est choisi parmi la régression des moindres carrés ordinaires, la régression robuste, la régression sur un composant principal, la régression des moindres carrés partiels, la régression de Ridge, la régression Lasso ou la régression non-linéaire.

5. Méthode selon l'une quelconque des revendications 1-4, caractérisée en ce que ladite au moins une propriété de sédiment en suspension comprend les propriétés dudit minéral, de préférence des éléments en trace, et/ou de ladite fraction organique, de préférence des hydrocarbures aromatiques polycycliques.

6. Méthode selon l'une quelconque des revendications 1-5, caractérisée en ce que au moins une propriété de sédiments en suspension est choisie parmi la concentration totale en phosphore, la concentration totale en azote, la concentration totale en carbone, la concentration extractible à l'acide du Cr, Cu, Ni, Pb et Zn, et/ou tout autre, et/ou toute combinaison de ceux-ci.

7. Méthode selon l'une quelconque des revendications 1-6, caractérisée en ce que ladite étape d'analyse de l'absorbance de lumière avec un spectromètre ultraviolet-visible submersible est effectuée, de préférence en continu, avec un intervalle compris entre 1 seconde et 6 heures entre chaque mesure, préférentiellement avec un intervalle de 15 minutes entre chaque mesure.

8. Méthode selon l'une quelconque des revendications 1-7, caractérisée en ce que ledit spectromètre ultraviolet-visible submersible est configuré pour fournir une ou plusieurs des mesures d'absorbance de lumière, de préférence à 1 nm ou à 2,5 nm d'intervalles.

9. Méthode selon l'une quelconque des revendications 1-8, caractérisée en ce que ledit spectromètre ultraviolet-visible submersible comprend au moins une fenêtre de mesure et au moins un moyen de nettoyage automatique configuré pour automatiquement nettoyer ladite au moins une fenêtre de mesure.

10. Méthode selon l'une quelconque des revendications 1-9, caractérisée en ce que ledit milieu est choisi parmi un bassin prédéterminé, une voie d'eau, une rivière, un cours d'eau, un système d'évacuation des eaux usées, un lac, un réservoir d'eau et/ou de tout autre.

11. Méthode selon l'une quelconque des revendications 1-10, caractérisée en ce que ladite étape de calibration est répétée au moins une fois, deux fois, trois fois, ou plus, avant et/ou après l'étape (a), de préférence avant l'étape (a).

12. Méthode selon l'une quelconque des revendications 2-11, caractérisée en ce que les sédiments en suspension sont extraits à partir dudit milieu, de préférence par filtration, décantation, lyophilisation et/ou séchage humide, avant d'effectuer ladite analyse physico-chimique *ex situ*.

13. Méthode selon l'une quelconque des revendications 2-12, caractérisée en ce que ladite analyse physico-chimique *ex situ* est effectuée sur lesdits sédiments en suspension par des méthodes d'analyse de laboratoire, de préférence par
    a. des études de perte par combustion,
    b. spectrométrie plasma à couplage inductif, ICP, couplée avec un spectromètre d'émission atomique, ICP-AES, et/ou avec un spectromètre de masse, ICP-MS, et/ou par spectroscopie d'absorption atomique, AAS, après l'application d'une ou plusieurs techniques de digestion à l'échantillon de sédiment en suspension,
    c. chromatographie en phase gazeuse couplée à un spectromètre de masse,
    d. des techniques de combustion couplées avec des techniques de titrage, gravimétrique, manométrique, spectrophotométrique et/ou chromatographique en phase gazeuse,
    e. analyse de la vapeur froide par absorbance atomique de mercure,
    f. diffractométrie aux rayons X,
    g. analyse thermique différentielle, et/ou
    h. tout autre.

14. Méthode selon l'une quelconque des revendications 2-13, caractérisée en ce que ladite étape de calibration comprend en outre les étapes consistant à
    a. trouver l'absorbance optimale de lumière timale à utiliser pour le modèle,

b. trouver la transformation optimale des données; et

c. trouver les coefficients du modèle.

15. Méthode selon l'une quelconque des revendications 2-14, caractérisée en ce que ladite au moins une variable prédictive est choisie parmi la concentration totale en phosphore, la concentration totale en azote, la concentration totale en carbone, la concentration extractible à l'acide du Cr, Cu, Ni, Pb et Zn, et/ou tout autre, et/ou toute combinaison de ceux-ci.

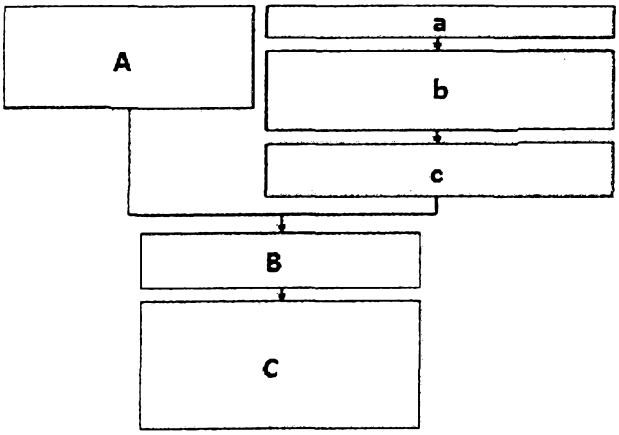

Fig. 1

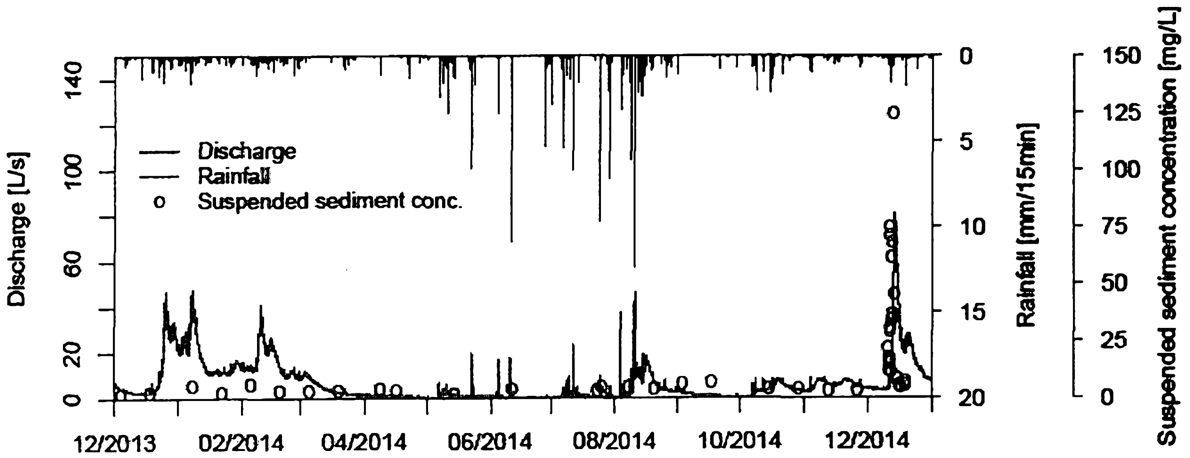

Fig. 2

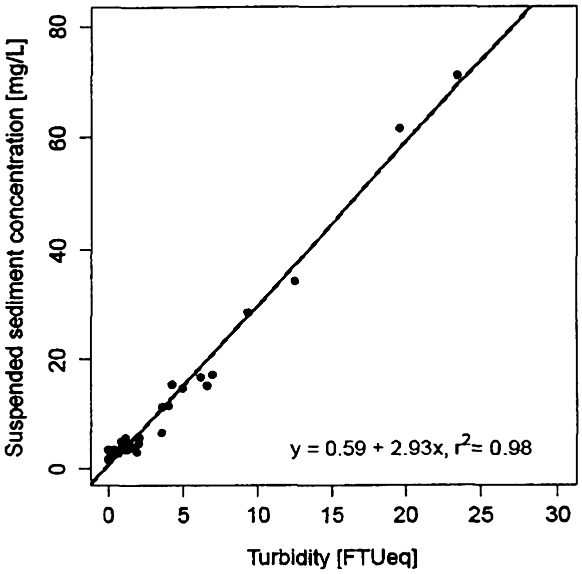

Fig. 3

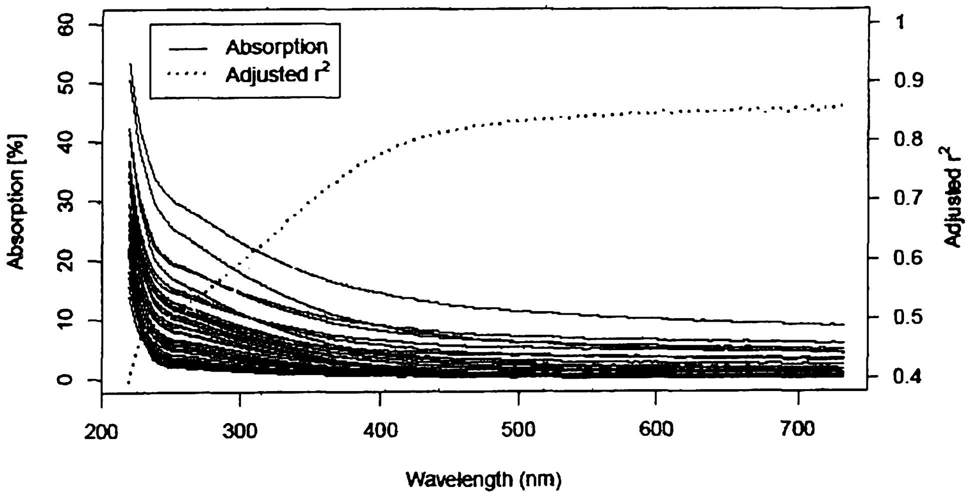

Fig. 4

| Method (n=34) | m | Comp. | $r^2$ | $r^2_{adj}$ | SEP |
|---|---|---|---|---|---|
| Ordinary last square regression (OLS) | 1 (710 nm) | - | 0.86 | 0.86 | 0.52 |
| Robust regression (RR) | 1 (710 nm) | - | 0.77 | 0.76 | 0.48 |
| Partial least-squares regression (PLS)[1] | 207 | 2 | 0.77 | 0.75 | 0.95[2] |

*[1]Light absorbance data was centred and the NIPALS algorithm was used. [2]Average SEP from repeated double cross-validation using 4 segments and 100 repetitions.*

Fig. 5

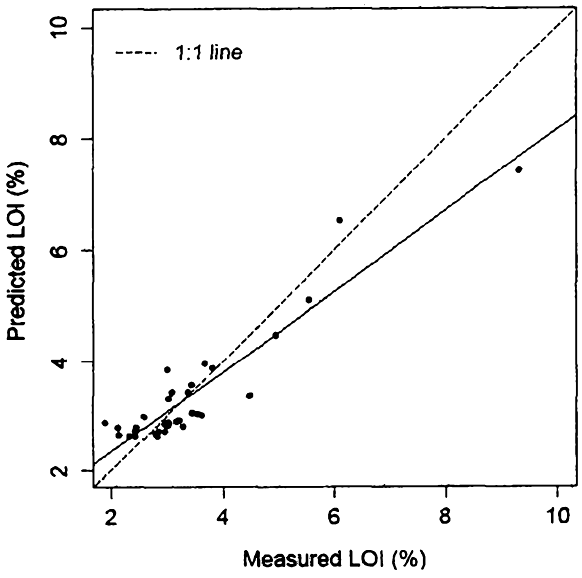

Fig. 6

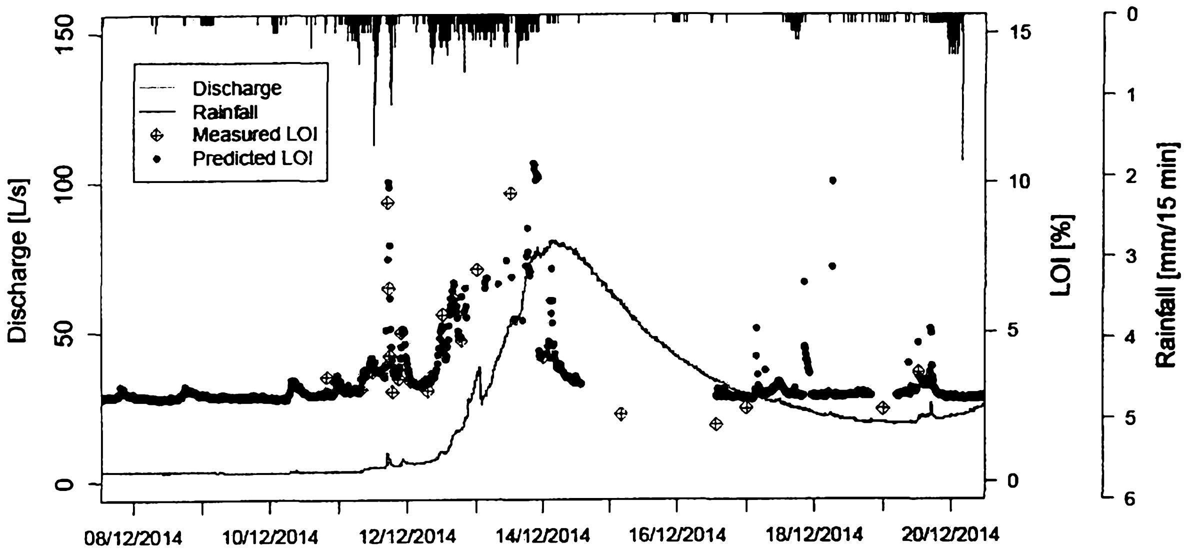
Discharge
Rainfall
Measured LOI
Predicted LOI
Discharge [L/s]
0
50
100
150
LOI [%]
0
5
10
15
Rainfall [mm/15 min]
0
1
2
3
4
5
6
08/12/2014
10/12/2014
12/12/2014
14/12/2014
16/12/2014
18/12/2014
20/12/2014

Fig. 7

Abstract

The invention is directed to a method for determining *in situ* and in real time at least one suspended sediment property in a medium, said suspended sediment comprising a mineral and an organic fraction. Said method comprises the steps of (a) measuring light absorbance with a submersible ultraviolet-visible spectrometer, said ultraviolet-visible spectrometer being configured to analyse to analyse light absorbance at wavelengths which are comprised between 220 nm and 730 nm and of (b) correlating the light absorbance to the properties of said suspended sediment, preferentially by using the Beer-Lambert's law. Said method is remarkable in that said step (b) is performed by using one model calibrated for deriving said properties of said suspended sediment from said light absorbance.

Fig.: 1

LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Économie
et du Commerce extérieur

**National Application Number**

LO 1184
LU 92827

# SEARCH REPORT

in accordance with Article 35.1 a)
of the Luxembourg law on patents
dated 20 July 1992

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim |
|---|---|---|
| X | ADRIAN M. BASS ET AL: "Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment", LIMNOLOGY AND OCEANOGRAPHY., vol. 56, no. 6, 1 November 2011 (2011-11-01), pages 2282-2292, XP055281807, US ISSN: 0024-3590, DOI: 10.4319/lo.2011.56.6.2282 * page 2284, last paragraph - page 2285, paragraph 1; figures 2, 4 * | 1-15 |
| X | G LANGERGRABER ET AL: "A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater", WATER SCIENCE & TECHNOLOGY, vol. 47, no. 2, 31 January 2003 (2003-01-31), page 63, XP055282214, GB ISSN: 0273-1223 * the whole document * | 1-10,<br>13-15 |
| A | ALLEN G BURTON JR. ET AL: "A sediment ecotoxicity assessment platform for in situ measures of chemistry, bioaccumulation and toxicity. Part 1: System description and proof of concept", ENVIRONMENTAL POLLUTION, vol. 162, 1 December 2011 (2011-12-01), pages 449-456, XP055282330, * pages 449-451 * | 1-15 |

CLASSIFICATION OF THE APPLICATION (IPC)

INV.
G01N21/31
G01N21/33

TECHNICAL FIELDS SEARCHED (IPC)

G01N

The present search report has been drawn up for all claims

| | Date of completion of the search | Examiner |
|---|---|---|
| | 21 June 2016 | Huenges, Alexandra |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

LE GOUVERNEMENT
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Ministère de l'Économie
et du Commerce extérieur

# WRITTEN OPINION

| | | | |
|---|---|---|---|
| File No.<br>LO1184 | Filing date *(day/month/year)*<br>14.09.2015 | Priority date *(day/month/year)* | Application No.<br>LU92827 |

International Patent Classification (IPC)
INV. G01N21/31 G01N21/33

Applicant
Luxembourg Institute of Science and Technology (LIST)

This report contains indications relating to the following items:

☒ Box No. I Basis of the opinion
☐ Box No. II Priority
☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐ Box No. IV Lack of unity of invention
☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐ Box No. VI Certain documents cited
☐ Box No. VII Certain defects in the application
☐ Box No. VIII Certain observations on the application

Examiner
Huenges, Alexandra

Application No.
LU92827

# WRITTEN OPINION

## Box No. I Basis of the opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

## Box No. V Reasoned statement with regard to novelty, inventive step and industrial applicability; citations and explanations supporting such statement

1. Statement

| | | | |
|---|---|---|---|
| Novelty | Yes: | Claims | |
| | No: | Claims | 1-15 |
| Inventive step | Yes: | Claims | |
| | No: | Claims | 1-15 |
| Industrial applicability | Yes: | Claims | 1-15 |
| | No: | Claims | |

2. Citations and explanations

**see separate sheet**

## Re Item V

### Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

| | |
|---|---|
| D1 | Adrian M. Bass ET AL: "Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment",<br>LIMNOLOGY AND OCEANOGRAPHY.,<br>vol. 56, no. 6, 1 November 2011 (2011-11-01), pages 2282-2292, XP055281807,<br>US<br>ISSN: 0024-3590, DOI: 10.4319/lo.2011.56.6.2282 |
| D2 | G Langergraber ET AL: "A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater",<br>Water Science & Technology,<br>vol. 47, no. 2, 31 January 2003 (2003-01-31), page 63, XP055282214,<br>GB<br>ISSN: 0273-1223 |

1. Lack of novelty of claim 1

The present application does not meet the criteria of patentability, because the subject-matter of claim 1 is not new. It will be shown in the following that each of documents D1 and D2 anticipate the subject-matter of claim 1.

Document D1 discloses the following features of claim 1:

method for determining in situ and in real time at least one suspended sediment property in a medium

(see the abstract of D1, last sentence: "... a field-portable instrument for DOC and POC...", where POC stands for particulate organic carbon),

said suspended sediment comprising a mineral and an organic fraction

(a mineral fraction is implicitly disclosed with particulate matter in water and turbidity measurements, see D1, page 2284, left-hand column, last paragraph - right-hand column, second sentence)

said method comprising the following steps

a) analysing light absorbance with a submersible ultraviolet-visible spectrometer, said ultraviolet-visible spectrometer being configured to analyse light absorbance at wavelengths which are comprised between 220 nm and 730 nm,

(see D1, page 2284, left-hand column, last paragraph - right-hand column, second sentence),

and

b) correlating the light absorbance to the properties of said suspended sediment, preferentially by using the Beer-Lambert's law

(see D1, page 2284, right-hand column, second sentence and third paragraph: dissolved organic carbon (DOC) and total organic carbon (TOC) is determined from absorption spectra of water; the difference between total organic carbon (TOC) and dissolved organic carbon (DOC) yields particulate organic carbon (POC) which represents a property of suspended sediment in water)

whereby

said step (b) is performed by using one model calibrated for deriving said properties of said suspended sediment from said light absorbance

(see D1, page 2284, right-hand column, last paragraph - page 2285, left-hand column, first paragraph. D1 uses a model (see equation (2) on page 2285 of D1) which is calibrated ("... DOC and POC data from the spectrolyser were calibrated with the following equations based on our manual sample data set) for deriving a property of the sediment (here the value $POC_{actual}$) from said light absorbance (the light absorbance allows to determine $POC_{spec}$). The fact that $POC_{spec}$ is not obtained directly from the light absorbance but through the difference between TOC and DOC is not relevant. The characterizing portion of claim 1 is formulated such that document D1 can be read onto it.)

The subject-matter of claim 1 is anticipated by document D1. Claim 1 is therefore not novel.

Likewise document D2 anticipates the subject-matter of claim 1, see the abstract of D2 disclosing the measurement of UV/Vis spectra and a calibration model in order to determine total suspended solids (TSS).

2. Lack of novelty of dependent claims 2-15

Dependent claims 2-15 do not appear to contain any additional features which meet the requirements of novelty.

**claim 2**: see D1, page 2284, right-hand column, fourth paragraph ("For DOC and POC calibration samples, 1 liter of sample water was filtered through 0.45 - µm polycarbonate filters. Filter papers were weighed before, and again after filtration and drying (50°C for ≥ 2 h)...") and see D2, page 29, third paragraph ("... The local calibration is based on reference grab samples analysed for the parameters of interest...")

**claims 3 and 4**: see D1, figure 2 and see D2, page 27, last paragraph

**claim 5**: see D1, page 2284, right-hand column, fourth paragraph ("POC was calculated ..." where POC is the abbreviation for particulate organic matter, i.e. a property of the organic fraction of the sediment) and see the abstract of D2 ("TSS" stands for total suspended solids and represents a property of both the mineral and organic fraction.)

**claim 6**: documents D1 and D2 disclose "any other" suspended sediment property

**claim 7**: see D1, page 2284, left-hand column, last paragraph ("... in-situ at 15 min intervals using a Sc::an spectrolyser...") and see D2, page 30, last paragraph ("... The first two month were used for calibration (28 data sets) and the last two month for validation (24 data sets).")

**claim 8**: see D1, page 2284, right-hand column, first paragraph ("... over the entire absorption spectrum of water (200-750nm)...") and see D2, page 29, first paragraph.

**claim 9**: see D2, page 25, first paragraph, last sentence ("The spectrometer is equipped with an auto-cleaning system.")

**claim 10**: see the titles of D1 and D2

**claim 11**: see figure 4 of D1

**claim 12**: see D1, page 2284, fourth paragraph and last paragraph.

**claim 13**: "any other" ex-situ physico-chemical analysis is disclosed in D1 and D2

**claim 14**: see D2, page 27, first and last paragraph.

**claim 15**: "any other" predictor variable is disclosed in D1 and D2.