Purpose of Study:
There is a lot of concern about how clean the fruits are that are coming from outside the United States. The U.S. EPA regulates what pesticides are used domestically but how much do we monitor the chemicals being used on imported products? I will evaluate which fruits are free of pesticides, imported fruits or locally grown ones.

Hypothesis:
If we detect more pesticides in imported fruit, then locally grown fruit is a better choice.

Materials:
Assorted Fruits: local and imported, organic and non-organic
Blender
Chemicals – water, acetonitrile, acetic acid, pesticide standards
API 4000 Mass spectrometer
QuEChERS kit
Volumetric flasks and beakers
Pipettes
Analytical balance
Centrifuge
Autosampler vials
Gloves
Lab coat
Eye protection

Procedure:
1. Cut up fruits and place in individual marked containers.
2. Place containers in freezer overnight
3. Blend each fruit sample and place back in container (wash blender between each sample) – Figure 5
4. Weigh out 15g of each homogenized fruit and place in a 50mL conical tube. Record the weight of each sample - Figure 6
5. Make a standard solution of 1% acetic acid in acetonitrile (v/v)
6. Add 15mL of the standard solution to each vial and add 375ul of pesticide internal standard
7. Add a Q-ep packet from the QuEChERS kit to each vial following the instructions in the kit.
8. Shake each vial by hand for 1 minute.
9. Spin down each vial in a centrifuge for 1 minute at >1,500 rcf
10. Remove 1.5mL from each vial and add a Q-ep dSPE packet from the QuEChERS kit to each vial following the instructions in the kit – Figure 7
11. Shake each vial by hand for 30 seconds
12. Spin down each vial in a centrifuge for 1 minute at >1,500 rcf
13. Transfer 200ul of supernatant to each auto sampler vial and label
14. Add 800uL of mobile phase A to each vial (5x Dilution)
15. Place vials into mass spectrometer
16. Calibrate instrument using standards in the table below
17. Run 10ppb standard 5 times for quality control
18. Analyze calibration curves and data using quantitation software

Calibration and Quality Controls:
1. First make 1000ppb pesticide solution:
2. Take 10uL of stock 10ppm of pesticide mix and add 990uL of mobile phase A to make a 1000ppb standard.
3. Dilute the 1000ppb standard down to 5, 10, 20 and 50 ppb using the table below:

Results:
Table 1 contains the list of samples analyzed by LC/MS/MS. Figure 1 and Table 2 contain calibration and QC results for a subset of the pesticide standards. Calibration curves all have an R value between .998 and .999 which means they are a good fit. The QC results for the 10ppb standard are also good. The accuracies, which are a measure of how close the calculated value of the standard is to the actual value, are all between 81% and 105%. The Percent Coefficient of Variation (CV) should be less than 10%, and this was observed.

Figure 2 is a representative LC/MS/MS chromatogram. The different color lines represent each of the ~180 pesticides that were analyzed.

Graph 1 illustrates the positive pesticide results. Seven of the fruit samples contained detectible amounts of pesticides. Pesticides were pretty evenly distributed between the local and imported fruits. The US Grapes contained several detectible pesticides whereas the Grapes from Chile and Peru did not. The dirtiest sample appears to be the Organic Pear from the US! It contains several non-organic pesticides including Thiabendazole (Figure 3) which is a fungicide.

Graph 2 illustrates a comparison between the organic US cherries and the cherries from Chile. The organic cherries are truly organic since only chemicals that are approved as organic were detected. The most significant result for the Chile cherries was the level of Tebuconazole (Figure 4) reported! Tebuconazole is typically used as a turf herbicide, especially on golf courses. Even though it is thought to have mild toxicity and moderate carcinogenicity it is still an approved pesticide and the level detected is below the maximum allowable limit.

Graph 3 is a comparison of US grown organic pears and a Korean pear. As stated earlier the US pear is relatively dirty. It does contain the organic Spinosyn A and D pesticides but also contains several hits for non-organic pesticides - all are below the maximum allowable limit. In this example it is better to eat an imported pear!

Conclusions:
In summary, in this study we found out that organic is not always truly organic as in the case of the organic pear from the US. The organic cherries from the US, on the other hand, only contained approved organic chemicals. None of the fruits from Mexico contained significant pesticides. The US grapes were also dirtier than the imported varieties. The issue seems to be whether a fruit is truly organic, and doesn’t matter so much that the fruit is imported. Maybe we need to closer follow our own import regulations?

Application:
This project will help people reliably define what are good sources of truly organic fruit.

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